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6th Global Innovations Symposium: Trends in Materials and Manufacturing Technologies for Transportation Industries: Novel Processes I

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), MPMD-Powder Materials Committee, MPMD-Shaping and Forming Committee, MPMD-Solidification Committee, MPMD-Surface Engineering Committee, MPMD/EPD-Process Modeling Analysis & Control Committee

Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John E. Carsley, General Motors Corp, Warren, MI USA; Hamish L. Fraser, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210-1179 USA; John E. Smugeresky, Sandia National Laboratories, Department 8724, Livermore, CA 94551-0969 USA

Wednesday AM Room: 2009
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Paul R. Dawson, Cornell University, Sibley Sch. Mech. Aeros. Engrg., Ithaca, NY 14853 USA; Paul Krajewski, General Motors, Matls. & Processes Lab., Warren, MI 48090 USA

8:30 AM Invited
Adaptation of Automotive Technologies for the Production of General Aviation Aircraft: *Mahmoud Y. Demeri*[1]; [1]FormSys Inc., 40180 Woodside Dr. S., Northville, MI 48167-3427 USA

NASA has initiated a number of substantial efforts over the last decade to impact personal transportation for the future. A number of national consortia for aviation mobility and various programs in the General Aviation (GA) arena such as the Advanced General Aviation Technologies Experiment (AGATE), the General Aviation Propulsion (GAP) and the Small Aviation Transportation System (SATS) have been developed to address the ideas of virtual highways in the skies. Success for this concept depends on the ability of the aerospace industry to produce a highly affordable personal aircraft that is comfortable, safe and easy to fly. This presentation reviews and assesses advanced automotive materials and innovative manufacturing technologies for possible adaptation to the production of affordable and lightweight fuselage for the MI-SATS program. Automotive technologies are reviewed in view of the functional requirements for autobody structures and aircraft fuselage.

8:55 AM Invited
A Methodology for Accelerating the Evaluation of the Mechanical Properties of Polyphase Alloys: *Paul R. Dawson*[1]; Matthew M. Miller[1]; [1]Cornell University, Sibley Sch. of Mechl. & Aeros. Engrg., 196 Rhodes Hall, Ithaca, NY 14853 USA

A system for more rapidly determining critical mechanical properties of polyphase engineering alloys is presented that merges simulation and selective experiments. The system centers around a statistical representation of the material structure based on observable geometric features and their attributes. An example of a feature is a grain; the orientation of the atomic lattice within a grain is an example of one of its attributes. Virtual specimens are instantiated by building polycrystals comprised of grains discretized with finite elements and then assigning attribute values from sampling the corresponding probability distributions. The specimens are tested via finite element simulations to assess their mechanical behavior. Experiments provide key information to validate the simulation tools and to quantify fundamental properties of the constituent phases. The result is a properties representation for the anisotropic strength and stiffness of a multiphase alloy as functions of the microstructural state and the mode of loading.

9:20 AM
Through Process Modelling in Manufacturing of Aluminium Structures for Automotive Applications: *Ole Runar Myhr*[1]; [1]Hydro Aluminium Structures, Product & Process Dvlp., N-2831 Raufoss Norway

Simulation of the material response throughout a multistage manufacturing route, commonly referred to as "through process modelling" (TPM), has gained considerable momentum over the past decade. This is due to an increased need for better control of the end product properties. TPM is particularly useful in fabrication of automotive parts from age-hardening aluminium alloys since the manufacturing is complex and involves several consecutive operations and heat treatments. For such alloys, the material response is intimately linked to a high number density of nano-metre size precipitates evolving in the different processing steps. A model for coupled nucleation, growth and coarsening of precipitates has been fine-tuned for Al-Mg-Si alloys and implemented into a dedicated FE-code. Examples are shown on applications of this FE-code in TPM of manufacturing of aluminium structures for the automotive industry. These examples illustrate how different end product properties predicted by the model can be manipulated and optimised.

9:40 AM
Deformation Behavior and Texture Development During the Thermomechanical Processing of Fe-15 At.% Ga Alloys Containing NbC: *Sivaraman Guruswamy*[1]; Pinai Mungsantisuk[1]; Douglas Barker[2]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA; [2]UEES Inc.(AFRL/MLLMP), Rms. 048/131, Area B, Bldg. 655, 2230 Tenth St., Wright Patteron AFB, OH 45433-7750 USA

Fe-Ga alloys exhibit large magnetostriction in the [001] direction, and [001] oriented single crystals or [100] textured polycrystalline forms of these alloys are therefore highly desirable for use in automotive sensors and actuators. Textured polycrystalline alloys are preferred due to lower cost and better room temperature mechanical properties. This paper examines the feasibility of an inexpensive thermomechnical processing approach involving a sequence of controlled hot rolling, two-stage warm rolling with intermediate anneal, and texture anneal to obtain [001] texture in polycrystalline (Fe-15 at.% Ga) alloys containing NbC. Roll forces during each pass of the hot and warm rolling stages were measured to examine the deformation behavior of the alloys. Textures evolution during different stages of processing was examined using orientation imaging microscopy to identify conditions that favor [001] texture development. The results indicate that an appropriate NbC content and thermomechanical process condi tions can produce FeGa alloys with strong [001] texture. Work supported by NSF-DMR Grant # 0241603.

10:05 AM
Processing and Mechanical Behavior of Lightweight Particle Reinforced Metal Matrix Composites by a Novel Sinter-Forging Technique: *Nik Chawla*[1]; Jason Williams[1]; [1]Arizona State University, Dept. of Chem. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287-6006 USA

In an effort to explore affordable processing for metal matrix composites, this study focuses on the characterization and mechanical behavior of an aluminum matrix composite with SiC particle reinforcement processed by a novel sinter-forging technique. In this technique, reinforcement particles and matrix alloy powders are blended, cold pressed, sintered, and hot forged. This technique has the advantage of eliminating costly extrusion and secondary finishing steps to produce a net-shaped part. The microstructure, as well as the ambient-temperature monotonic and cyclic fatigue behavior of the sinter-forged composites will be reported. The effects of SiC particle size and alloy powder size on processing and properties will be discussed. Comparisons to composites produced by conventional powder metallurgy and extrusion have also been conducted. It will be shown that, although the sinter-forged composites have a somewhat lower ductility than their extruded counterparts, the strength and fatigue resistance are comparable to those of extruded materials.

10:25 AM Break

10:40 AM
Manufacturability of TiAl Alloys for Turbocharger Applications: *Sadao Nishikiori*[1]; Satoshi Takahashi[1]; Nobuhiko Yunoki[1]; Akihiro Ohkita[1]; [1]Ishikawajima-Harima Heavy Industries, Production Engrg. Ctr., 1, Shinnakahara-cho, Isogo-ku, Yokohama 235-8501 Japan

In order for TiAl alloys to be widely employed in turbocharger, it is important to understand effects of process parameters on metallurgical features and to optimize each production process. In previous report, we introduced how TiAl alloy was applied to the product turbocharger, based on the results of material tests, FOB test and several types of reliability tests. Through our manufacturing experience of TiAl turbocharger, further alloy development will be discussed in this study. Then, we focus on various TiAl alloys. Especially, castability,

phase stability, cyclic oxidation resistance and mechanical properties of these alloys have been evaluated. In addition, with an industrial view to application, turbo charger rotor of TiAl-Mo-V-Si alloy (IR-24T) developed by IHI were cast and joined to a shaft by friction welding under the production scale. Hot spin test was also carried out. Potential of this alloy for application will be discussed.

11:00 AM
Processing Ti-Al-Nb Multi-Layered Composites from Elemental Foils Using Accumulative Roll Bonding: *Rengang Zhang*[1]; Viola L. Acoff[1]; [1]University of Alabama, Dept. of Metallurgl. & Matls. Engrg., Tuscaloosa, AL 35487 USA

Intermetallic compounds and alloys in the form of sheet materials are ideal candidates for the manufacturing of supersonic spacecrafts. One particular intermetallic that has been receiving considerable attention for this application is the alloy Ti-46Al-9Nb (at%). In this study, accumulative roll bonding (ARB) is used to process multi-layered composites with a nominal composition of Ti-46Al-9Nb (at%) from elemental foils. The microstructures of the multi-layered composites that were subjected to different levels of rolling reduction were characterized by scanning electron microscopy (SEM). The hard Ti and Nb layers were observed to neck and break down due to the repeated mechanical deformation, and the Ti and Nb particles embedded in the soft Al matrix. X-ray diffraction patterns showed only reflection of the elements, which indicates that no detectable solid-state reactions occurred. Differential thermal analysis (DTA) was also used to characterize the effect of rolling strain on the solid-state reaction and phase formation in the composites during annealing. Tensile testing and fractography of the tensile test specimens were utilized to evaluate the mechanical properties of the processed multi-layered sheet materials.

11:20 AM
Processing of Gamma Titanium Aluminide Sheets Using Cold Rolling and Reactive Synthesis: Gajanan P. Chaudhari[1]; *Viola L. Acoff*[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., 126 7th Ave., Box 870202, Tuscaloosa, AL 35487 USA

Gamma titanium aluminide sheet is a candidate material for aerospace and automotive fields. The importance is due to its low density and superior high temperature mechanical properties. A simple process using a combination of commonly available processing techniques of rolling and heat treatment is presented. Aluminum and titanium foils are cold roll bonded and subjected to a two-stage heat treatment, resulting in gamma-titanium aluminide sheets. Hot rolling of the sheet resulted in a denser product with better mechanical properties. The process parameters and resulting microstructures are presented. Mechanical properties of the sheets are evaluated.

11:40 AM
Directional Recrystallization of High Purity Ni and Ni-V Alloys: Hui Chang[1]; *Ian Baker*[1]; [1]Dartmouth College, Thayer Sch. of Engrg., 8000 Cummings Hall, Hanover, NH 03755 USA

Directional recrystallization process has been performed on both high purity (99.995%) polycrystalline nickel and nickel containing 7 wt. % vanadium. The nickel sheets were cold rolled to thickness reductions of 90%, 95% or 98%, isothermally annealed at their primary recrystallization temperatures for 30 mins and then directionally annealed in an image furnace at 1000°C. A large temperature gradient of 100°C /mm ahead of the hot zone was used during directional annealing and a wide range of hot zone velocities were examined. The as-received, as-rolled, isothermally annealed and directionally recrystallized microstructures were characterized using both optical microscopy and electron back-scattered patterns from a FEI XL30 scanning electron microscope. The results of the different processing and the of the vanadium additions will be presented and contrasted with prior studies on the directional recrystallization of nickel with purity of 99.5% cold rolled to 90% thickness reduction. Research supported by NSF grant DMI 0217565.

Alumina and Bauxite: Bauxite and Bayer Process Red Side

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday AM Room: 2005
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Monique Authier-Martin, Alcan, Arvida R&D Ctr., Jonquière, Québec G7S 4K8 Canada

8:30 AM
Applied Mineralogy Studies: An Important Tool to Understand the Red Mud Sedimentation Process: *Aurea Gomes*[1]; Beatriz Vieira[1]; Nilce Alves Santos[1]; Carlos Alberto Alves[2]; [1]CVRD, Project Dvlp./Tech., BR 262, km 296, Santa Luzia, MG 33030-970 Brazil; [2]CVRD, Project Dvlp./Exploration, Av Governador Jose Malcher, 815/516, Belem, Para 66055-260 Brazil

In the Bayer plant, bauxite mineralogy affects efficiency by driving the chemical reactions that occur in the process. The composition and morphology of the alumina-bearing minerals, as well as those of other impurities with varying solubility in caustic soda, are critical for determining alumina extraction, product purity, caustic soda losses, and energy consumption. In order to understand the factors influencing settling rate, overflow clarity, and mud compaction, the red mud settling performance of several bauxites samples was studied under different digestion conditions. The bauxite samples and their respective red muds were submitted to chemical and mineralogical analysis.

8:55 AM
Effect of Bauxite Microstructure on Beneficiation and Processing: *Károly Solymár*[1]; Ferenc Mádai[2]; Dimitris Papanastassiou[3]; [1]EPU 3000, Engineer's Consulting Ltd., Béla király út 7/A, Budapest H-1125 Hungary; [2]University of Miskolc, Dept. of Mineralogy & Petrology, Miskolc-Egyetemváros H-3515 Hungary; [3]S&B Industrial Minerals S.A., Bauxite Div., 21 A, Amerikis Str., Athens GR-106 72 Greece

The microstructure of bauxite determines to a significant extent the opportunities for its beneficiation and optimum processing downstream. Adequate fine grinding commensurate its microstructure may result in proper mineral liberation and grain size distribution required for effective ore dressing (i.e. H/M or magnetic separation)and digestion respectively. Particle size distribution, mean diameter and amount of ooidal grains as well as degree of dissemination of the impurities in polished sections of raw bauxite, ground bauxite and red mud samples were determined by means of scanning electron-microscope, electron probe micro-analyser and digital image analysis. The results of beneficiation tests (effective removal of liberated limestone but insufficient reduction of finely disseminated reactive silica) and the required digestion parameters of the mainly oolitic Greek diasporic and the Hungarian boehmitic (partly goethitic) bauxite are discussed. Based on the microstructure the effectiveness of beneficiation, the degree of grinding (required particle size) and also the necessary digestion parameters of any bauxite can be predicted.

9:20 AM
Optimation of Bauxite Grinding by Means of Empiric Model: Barnabás Csõke[1]; *Gábor Mucsi*[1]; Károly Solymár[2]; [1]University of Miskolc, Dept. of Process Engrg., Miskolc-Egyetemváros H-3515 Hungary; [2]EPU 3000 Engineer's Consulting Ltd., Béla király út 7/A, Budapest H-1125 Hungary

The grain size distribution of the ground bauxite plays an important role in the extraction yield of alumina and digestion kinetics. The ground bauxite product of ball mills can be characterised by a function of relative size distribution, F (• =X/X50), even at different grinding capacities. The median of the ground product at a given mill depends on the grinding capacity which can be determined by direct measurements (that is X50 = f (Q) function) or can be estimated by equations of Bond-Rowland-Kjos. The expected grain size distribution under modified conditions can also be calculated by means of the above equations, so the grinding process can be optimised. The results of the calculations have been confirmed by plant-scale bauxite grinding tests. A new universal Hardgrove mill was used for fast laboratory determination of grindability of different kinds of bauxite.

9:45 AM
Industrial Test With Mono and Multifilament Cloths in Kelly Filters of CVG-Bauxilum: *Ricardo Alfredo Galarraga*[1]; Rodolfo Díaz[1]; Gisela Quintero[1]; [1]CVG-Bauxilum, Lado Rojo II, Zona Industrial Matanzas, Puerto Ordaz 8015 Venezuela

CVG Bauxilum, who is always open to new technologies, recently evaluated a new filtration fabric with a base specification different any cloth that has previously been tried. The differences are: the fabric construction, which is monofilament polypropylene in the warp direction and multifilament polypropylene in the weft direction and the extraordinarily high number of yarns in the warp direction (250+). For 115 days, the performance of this material was monitored as it was installed on several Kelly filters in the Security Filtration area. The new cloths faced all of the conditions in the plant and the following determinations were made: 1.The cloths withstood the stresses of plant operation for 150 cycles (1500 hours) with no difficulty whatsoever. 2.The number of times caustic cleaning and acid cleaning were required were greatly reduced when compared to previously tried materials. 3.Due to the physical characteristics of the material, cloth manipulation was much easier thereby improving the ease of installation. 4.The quality of the filtered liquor was acceptable. 5.The physical characteristics of the material made it much easier to manually clean than any other previously tried materials.

10:10 AM Break

10:20 AM
Rod Mill Replacement at Aluminium Oxid Stade GmbH: *Hartmut Borchers*[1]; [1]Aluminium Oxid Stade GmbH, Stade 21683 Germany

After 30 years of operation Aluminium Oxid Stade GmbH (AOS) had to replace one out of their two rod mills.The mill showed a lot of cracks at the flange section caused by repair welding and cracks at the foundation. This paper will describe basic tests before replacement, bauxite treatment before installation in order to increase milling capacity of the second old rod mill, modification of the DSM screen, mill installation, main technical differences between old and new rod mill and final grinding test.

10:45 AM
Mechanical Activation of Bauxite-Potential and Prospects in the Bayer Process: *Rakesh Kumar*[1]; T. C. Alex[1]; Z. H. Khan[1]; S. P. Mahapatra[2]; [1]National Metallurgical Laboratory, Jameshedpur, Jharkhand Pin. 831 007 India; [2]National Aluminium Company, P/1, Nayapali, Bhubaneswar, Orissa Pin. 751 013 India

Mechanical activation of bauxite is known to have a beneficial effect on the alkali leaching of gibbsite. Mechanical activation is found to be more effective, in terms of improvement in alumina recovery at lower temperature and soda concentration and minimization of soda loss in leach residue. Coupling of mechanical activation with the leaching process is an important issue in the exploitation of the beneficial effect of the activation. Two separate schemes, namely, "simultaneous milling and leaching" and " separate milling and leaching" have been explored. Both the approaches result in comparable alumina recovery. However, greater soda loss was observed in the case of latter. This is explained in terms of greater duration of leaching and its effect on the dissolution of different Al-bearing phases. The results show that the concept of simultaneous milling and leaching is superior in terms of leaching time, energy utilization and simplicity of operation.

11:10 AM
Prospects of Processing Guyana Bauxite at Sweetening Stage: *Alexander G. Suss*[1]; Anatoly A. Lapin[1]; Andrey V. Panov[1]; Brindley H. Robeson Benn[2]; [1]Russian National Aluminium & Magnesium Institute, 86, Sredny Pr., 199106, St. Petersburg Russia; [2]Guyana Geology & Mines Commission, Upper Brickdam, Georgetown Guyana

Guyana has significant reserves of bauxite (~760 million tonnes) and about 100-years history of its mining and processing – ranging from refractory to metallurgical grade bauxites and alumina. Although Guyana has lost its previous dominance on the world market, due to huge integrated industries created in, for example, Australia, Guinea, Brazil and alumina processing ended in 1983, the country is still in the world's top 10 ranking, in terms of bauxite production and reserves, and has almost no rivals in bauxite quality. This paper investigates the possibility of processing Guyana bauxite at the "sweetening" stage, allowing a refinery to efficiently process medium quality bauxites thereby increasing substantially, digestion capacity at operating alumina plants. Chemical, mineral and process features of these bauxites in comparison with similar "sweetening" bauxites were investigated. It was revealed that Guyana bauxite shows excellent alumina extraction, however, due to specific composition – shell like coarse crystals of kaolinite, secondary gibbsite, low iron-bearing minerals and high kaolinite content – under-recovery of alumina, disilication and thickening problems, and high soda consumption are possible. Additional research is being pursued to reduce these negative impacts.

Aluminum Reduction Technology: Pot Control

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Tor Bjarne Pedersen, Elkem Aluminium ANS, Farsund 4551 Norway; Tom Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday AM Room: 2003
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Thomas Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA

8:30 AM
Challenges in Mass Balance Control of Aluminum Reduction Cells: *Martin Iffert*[1]; Maria Skyllas-Kazacos[2]; Barry Welch[2]; [1]Trimet Aluminium AG, Reduction, Aluminiumallee 1, Essen 45356 Germany; [2]University of New South Wales, Ctr. for Electrochmst. & Minl. Procg., Sydney, NSW 2052 Australia

Today high performance smelters operate with current efficiencies over 94% and energy consumption below 14 kWh per kg of aluminum. The increasing economical as well as ecological pressure makes it necessary to drive the process continuously at the limit. Revamping pots and increasing current intensity are part of the daily process. While this is a challenge, it is a greater challenge for the less energy efficient technology developed before point feeders and modern magnetic compensation. Hence it is important to understand the sources of process variation and disturbances in an early phase and enable the control system to distinguish between energy versus mass balance induced variations. The introduction of superheat measurements has made it possible to identify energy imbalance quicker, but there remain spatial, temporal and material induced fluctuations. This paper, discusses the combined roles of dry scrubbing and different grades and properties of alumina. These influence HF loading of the enriched alumin a, HF emissions and change in the material balance of a pot. Thus contributing to swings in temperature, superheat and bath inventory.

8:55 AM
Diagnosing Iron Contamination in Pot Room Metal: *Stephen J. Lindsay*[1]; [1]Alcoa, Inc., Primary Metals Div., 300 N. Hall Rd., MS S-01, Alcoa, TN 37701-2516 USA

The level of iron contamination in pot room metal is often defined by the average %Fe or by the percentage of the population that is lower in iron than a certain cut-off point. In this paper the author links analysis of the shape of the Fe distribution to practical approaches to improvement and suggests benchmark levels of performance.

9:20 AM
Cell Operation Improvement Using Wireless Human-Machine Interfaces: Leonel Vicente Mota Ivo[1]; *Elias Symphronio Castro Neto*[2]; Otávio Mário Guzzon[2]; [1]Atan Automation Systems, Al. Div., Av. Afonso Pena, 4001 - 9 andar, Funcionarios, Belo Horizonte, MG 30130-008 Brazil; [2]CBA Companhia Brasileira de Alumínio, Controle de Processos, Rua Moraes do Rego, 347, Alumínio, SP 18125-000 Brazil

The improvement of cell operation is one of the most important concerns in primary aluminum production. Substantial gains in productivity, energy consumption, efficiency, working conditions and environment protection can be obtained with better operational procedures. This paper describes the use of a mobile wireless HMI (Human-Machine Interface), mounted in vehicles, cranes and other equipments, along with handhelds used by field personal, to improve the cell operation at CBA, Companhia Brasileira de Alumínio, Brazil. The operational improvements, the features implemented, the architecture of the solution and the technology used are presented. Some problems found and its solutions, along with future implementations, are discussed.

9:45 AM
Experiments on Wireless Instrumentation of Potlines: Mike Schneider[1]; Daniel Steingart[1]; James W. Evans[1]; Paul Wright[1]; *Donald Ziegler*[2]; [1]University of California, Matls. Sci. & Engrg., Berkeley, CA 94610 USA; [2]Alcoa Technical Center, Alcoa Ctr., PA 15069 USA

Hall-Héroult potlines are inefficient, consuming more than twice the electrical energy required thermodynamically. In part this may be a result of inadequate instrumentation. In a typical Hall-Héroult cell the only continuous measurements are of cell voltage and line current. The cells are only minimally outfitted with sensors, mostly due to safety concerns about wires running around potlines where voltage differences can be up to several hundred volts. There is also the difficulty of possible interference with existing hardware, and the lack of reliable, maintenance free, continuous power sources for sensors. This paper presents a tested solution to accurately measure various process parameters via wireless sensing technology, specifically Berkeley Motes running the operating system TinyOS. The investigation is a joint one between Alcoa and UC, Berkeley. Early experiments at Eastalco indicated that the motes, with a few modifications, will be able to operate reliably in industrial conditions, successfully transmitting radio packets, despite the plant's strong magnetic fields, at distances of over 100 feet. The paper describes the successful testing of wireless measurement of a cell parameter and discusses what other measurements are feasible and appropriate. Research supported by the University of California Energy Institute.

10:10 AM Break

10:25 AM
Improving Reduction Cell Metal Level Measurement and Control: *Geoffrey Paul Bearne*[1]; Daniel Whitfield[2]; [1]Comalco Research and Technical Support, PO Box 316, Thomastown, Victoria 3074 Australia; [2]New Zealand Aluminium Smelters Limited, PB 90110, Invercargill New Zealand

A project was recently undertaken at the New Zealand Aluminium Smelter to improve reduction cell metal level measurement and control. The widely used Six Sigma improvement methodology, adopted by Comalco in 2002, was applied to this problem. The capabilities of two alternative measurement techniques - direct "dipping" with a steel rod and indirect measurement from anode position, were compared. Identifying and reducing the causes of variation led to improvements in both systems. The second method, known locally as Rod Height, proved to be more suitable for control purposes. An automated control chart based strategy for determining the mass of metal to be tapped from each cell was developed and implemented in three reduction lines. Key issues and findings from this project are described and the benefits of using the Six Sigma methodology for process improvement are discussed.

10:50 AM
Bath Ratio Control Improvements at Alcoa Poços de Caldas - Brazil: Leonardo Paulino[1]; *Jean Yamamoto*[1]; Jeronimo Coelho Araujo[1]; Roberta Andreia Camilli[1]; [1]Alcoa, Smelter/Potrm., Rod. Poços de Caldas/Andradas, km 10, Poços de Caldas, Minas Gerais 37701-970 Brasil

A systemic approach to improve process control in the potrooms has been in use for several years at Alcoa Aluminio S.A. in Poços de Caldas, Brasil. One of the critical sub-processes in a smelting plant deals with chemical composition control measured as bath ratio. Bath chemistry control measured as percent of pots within a desired range improved from 78% to over 95% from 1998 to 2003. This improvement was achieved due to some key factors: 1) Implementation of a ratio control algorithm to determine fluoride and soda additions using pot age (maintenance) and ratio (corrective); 2) Streamline of the logistic of bath sampling, analyzing and corrective actions; 3) Improvement in analytical techniques from Bard to X-ray diffraction; 4) Increase sampling frequency from each 96 to each 48 hours. As a result, a current efficiency increase from 91.16% in 1999 to 91.65% in 2003 was verified. This paper will present the steps taken by the Ratio Control team to achieve 95% ratio in range.

11:15 AM
A Simple Dynamic Realtime Model for Aluminum Reduction Control System: *Vladimir Yurkov*[1]; Viktor Mann[1]; [1]RUSAL, Engrg. - Technologl. Ctr. Ltd., 37, Pogranichnikov St., Krasnoyarsk 660111 Russia

An aluminum reduction cell is a dynamic essentially nonlinear object and a space-dispersed process. To describe temperature and concentration fields by finite difference or finite element methods requires too much calculation time making its application in control controller in on-line environment conjectural. An extremely simple mathematical model of an aluminum reduction cell developed by RUSAL ETC provide real time calculations which provides sufficient adequacy to the real object. The model is not totally accurate, however the forecasts of the model yield quite reasonable results in predicting the consequences of changes in operating conditions. For example, the model predicts the changes in bath temperature with the corresponding changes in amperage and resultant change in the ledge provide. As a result, the model is sufficient for real time use in the system controlling an industrial cell line.

11:40 AM
Expert System of Electrolysis Diagnostics Using FMEA Technique: Alexander Berezin[1]; *P. V. Polyakov*[2]; O. O. Rodnov[1]; V. L. Yasinski[1]; P. D. Stont[3]; [1]RUSAL Engineering & Techonology Center, Krasnoyarsk 660011 Russia; [2]STC "Light Metals", Krasnoyarsk 660025 Russia; [3]"Mayak PKF" Ltd., Krasnoyarsk 660021 Russia

Reduction of non-productive expenditures at the cost of decreasing of total amount of sick cells is one of the actual targets. Expert diagnostics system is worked out for exposure of sick cells. Diagnostics process consists of the following procedures: -Identification of cell noises and their classification as symptoms of a sickness with the help of specially trained neuronet; -Type definition and calculation of seriousness of sickness according to expert rules with the help of fuzzy logics; -Calculation of priority number of risks PNR - according to FMEA technique (Potential Failure Mode and Effects Analysis) for each symptom, sickness, cell; -Documentation of diagnostics results using FMEA protocols. Cell parameters and SPC data (Statistic process control) are the input information for the expert system of diagnostics. Diagnostics system is able to define PNR of 20 types of potroom sickness, which allows: -to reduce the number of sick cells; -to define the maximum permissible condition of the cell for overhaul.

Applications and Fundamentals of High Aspect Ratio Nanomaterials: Nanostructured Composites

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Nanomaterials Committee
Program Organizers: Jud Ready, Georgia Tech Research Institute - EOEML, Atlanta, GA 30332-0826 USA; Seung H. Kang, Agere Systems, Device and Module R&D, Allentown, PA 18109 USA; Lourdes G. Salamanca-Riba, University of Maryland, Materials Science and Engineering Department, College Park, MD 20742-2115 USA; Nagarajan Valanoor, Forschungzentrum Juelich, IFF and Institute for Electronic Materials, Juelich, Germany D52425

Wednesday AM Room: 3018
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Jud Ready, Georgia Tech, GTRI-EOEML, Atlanta, GA 30332-0826 USA; Seung H. Kang, Agere Systems, Allentown, PA 18109 USA; Nagarajan Valanoor, Forschungzentrum Juelich, Juelich D52425 Germany

8:30 AM Opening Remarks

8:35 AM Invited
Processing of Carbon Nano-Tube and its Composites at High Magnetic Fields: *Hamid Garmestani*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr. NW, Atlanta, GA 30332-0245 USA

Processing of materials under the influence of high magnetic fields has been reported to cause significant enhancements in useful properties of many materials. The mechanisms of influence of magnetic field on texture development, grain growth, and recrystallization need to be understood in order to optimize the processes and to develop commercial applications of in-field heat treatment processes. Canbon nanotubes have been produced using a variety of processing techniques and their use as reinforcements in nano-tube composites have been hindered due to the lack of proper alignment. Using high fields both nanotubes and their composites have been processed using CVD techniques. The results show that although the nano-tubes themselves have very low magnetic susceptibility but with the proper selection of the resin matrix materials a certain level of alignment is achieved. It was also discovered that the high field can adversely affect the structure of the nano-tubes and their morphology.

9:05 AM Cancelled
Fabrication of Nylon-6/Carbon Nanotube Composites

9:35 AM Break

10:00 AM
Carbon Nanotube Nanocomposites and Hybrid Materials for Multifunctional Applications: *Fernand D.S. Marquis*[1]; [1]South Dakota School of Mines and Technology, Dept. of Matls. & Metallurgl. Engrg., 501 E. St. Joseph St., Rapid City, SD 57701 USA

This paper discusses the full integration of carbon nanotubes in polymeric, ceramic, and other materials such as fluids, for the applications as multifunctional components with optimal structural, electrical and thermal properties. The goals are to mimic on a larger scale the properties of carbon nanotubes so that they can be used more aggressively on the micro and macro scales. The idea of mimicking carbon nanotubes involves integration by tip attachment and/or sidewall functionalization, coincident polymerization, and high shear alignment in polymer based composites. These composites are different from the conventional ones, which consist of two distinct phases: matrix and reinforcing phase. Carbon nanotube composites are hybrid materials, which are designed and manufactured in order to expand out the properties of carbon nanotubes by translating their properties to each other. The integration of the carbon nanotubes into these matrices is accomplished through the architecture of special bonds, designed to foster enhanced mechanical, electrical and thermal properties, through dispersion and alignment of the carbon nanotubes. This multifaceted design provides for innovative approaches in order to develop carbon nanotube composites and hybrids materials withn optimized performance.

10:30 AM
Effect of Fabrication Method on the Electrical Properties of ABS/CB Composites: *Sidhartha Gupta*[1]; Runqing Ou[1]; Rosario A. Gerhardt[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr., Atlanta, GA 30332-0245 USA

Acrylonitrile Butadiene Styrene (ABS) is a polymer, which is used in structural applications due to its excellent mechanical properties. Carbon Black is often added as a filler to increase its conductivity. In this study, ABS/CB composites were prepared using two different methods. The first is based on dissolution of ABS in Butan-2-one, and the second on mechanical mixing of the precursor materials. These fabrication methods led to different microstructures, which had vastly different electrical properties. The microstructures were acquired using SEM, AFM and optical microscopy while the electrical conductivity was obtained using impedance spectroscopy. The percolation threshold of the composites fabricated using mechanical mixing was found to be much lower than that of the composites fabricated using the solution method. The carbon black used had 24 nm average particle size and DBPA branching of 63 ml/100gm. This study is critical for the development of composites with more controlled properties.

Arsenic Metallurgy: Fundamentals & Applications: Process Metallurgy

Sponsored by: Extraction & Processing Division, EPD-Copper, Nickel, Cobalt Committee, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, LMD/EPD-Recycling Committee
Program Organizers: Ramana G. Reddy, University of Alabama, Department of Metals and Materials Engineering, Tuscaloosa, AL 35487-0202 USA; V. Ram Ramachandran, Scottsdale, AZ 85262-1352 USA

Wednesday AM Room: 2014
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Corby G. Anderson, CAMP - Montana Tech, Butte, MT 59701 USA; Bill Drinkard, Drinkard Metalox, Charlotte, NC 28205 USA

8:30 AM
The Treatment of Arsenic Bearing Ores, Concentrates and Materials with Alkaline Sulfide Hydrometallurgy: *Corby G. Anderson*[1]; [1]CAMP - Montana Tech, 1300 W. Park St., Rm. 221 ELC Bldg., Butte, MT 59701 USA

Throughout the world, there are many orebodies or materials which have significant value but also contain arsenic. As regulations on the transport, exposure, disposition and emission of arsenic have become more stringent, it has become increasingly more difficult to derive the values from these resources. This paper will outline the fundamentals of alkaline sulfide hydrometallurgy and its successful application to arsenic bearing materials.

8:55 AM
The Simultaneous Oxidation of Sulfide Minerals and the Dissolution of Gold: *Michael J. Nicol*[1]; Suchun Zhang[1]; [1]Murdoch University, Parker Ctr., South St., Murdoch, Western Australia 6150 Australia

The alkaline oxidation of refractory gold concentrates containing arsenopyrite and pyrite at ambient temperatures and pressures has been found to be accompanied by the simultaneous dissolution of gold without the addition of cyanide. A detailed study has been made of the kinetics of the oxidation of the pure minerals and of several concentrates. The reaction products of the oxidation of arsenic and sulphur have been monitored using chromatographic techniques. In the case of arsenopyrite, thiosulfate, monothioarsenate, arsenate and sulfite are the principal products while thiosulfate has been confirmed to be the dominant product of pyrite oxidation. Gold, either as added powder or as a constituent of the concentrates has been found to dissolve simultaneously during the alkaline oxidation of both arsenopyrite and pyrite, and this appears to be associated with the formation of thiosulfate of gold.

9:20 AM
Arsenic - The Technological Motivator for the Chelopech Copper/Gold Mine: *Gavin Beer*[1]; [1]Chelopech Mining EAD, Chelopech Village, Sofia Dist. 2087 Bulgaria

The Chelopech Copper/Gold Mine, located in west-central Bulgaria, has been in operation since 1959 producing a low-grade copper/gold concentrate containing up to six percent arsenic by weight. The penalties and restrictions imposed on smelting this concentrate, have seen the past operators of the mine strive to find a balance between achieving acceptable metal returns from the smelters and installing novel or unproven technologies in the face of changing political and economic climates. This paper documents the colourful history of the concentrate processing alternatives that have been investigated and implemented over the 45 year life of the Chelopech Mine, culminating in the high pressure oxidation option that is now the focus of a Definitive Feasibility Study (DFS) presently being undertaken by GRD Minproc Limited. The fundamental chemistry of the preceding alternatives is outlined followed by a discussion as to why each was ultimately not employed. A detailed description of the technology proposed in the DFS is given including: pressure oxidation, arsenic fixation, SX/EW copper recovery, CIL gold recovery and AVR/SART cyanide/copper recovery processes.

9:45 AM Break

10:00 AM
Gold Recovery from Arsenical Ores and Wastes: *Bill Drinkard*[1]; [1]Drinkard Metalox, Inc., 2226 N. Davidson St., Charlotte, NC 28205 USA

Commercial and demonstrated arsenic separation technologies for stabilization or sale from precious metal and copper ores and some major gold bearing arsenical wastes are presented. Extracted arsenic from ores and wastes has been both stabilized and sold. To date more than 100,000 tons of arsenic (as As2O3) has been profitably converted by our processes into commercial products. Even larger quantities have been safely stabilized. In this presentation, focus will be on new technologies with high gold recoveries, even from multiple refractory ores, and on secure low-cost stabilization.

10:25 AM
Sulfidization of Arsenopyrite: *Vladimir A. Luganov*[1]; Corby G. Anderson[2]; [1]The K. Satpaev Kazak National Technical University, 22 Satpaev Str., Almaty 480013 Kazakhstan; [2]CAMP - Montana Tech, 1300 W. Park St., Rm. 221 ELC Bldg., Butte, MT 59701 USA

The possibility of sulfidization of arsenopyrite with elemental and pyrite sulfur with transfer of arsenic into sublimate forms under the temperature of sulfide roasting is established by thermodynamic analysis. Kinetic investigations allowed to establish that in the process of decomposition the specific surface area and pyrite and arsenopyrite porosity changes with maximum in dependence of process duration. The highest composition velocity of arsenopyrite in the air atmosphere is achieved at 720°C, and pyrite - at 690°C, in the argon atmosphere at 730 and 690°C correspondingly. Addition pyrite to arsenopyrite charge decreases the temperature of decomposition - the highest velocity the process achieves at 580°C, which is connected with formation easily volatile arsenic sulfides. For study arsenopyrite sulfidization process with pyrite in the continuous mode were carried out researches on arsenopyrite roasting in the inert gas media in the stable bed with the consecutive feeding of pyrite into the charge. Initial arsenopyrite contained, %: 34, 8 - iron, 20, 5 - sulfur and 44, 3 - arsenic with the size 80% - 74 μm and presented in itself dense particles of small porosity with the developed surface. Mono-mineral pyrite contained 46, 1% of iron and 50, 3% of sulfur. There was established that the content of arsenic in the cinder under roasting according to the scheme with consecutive pyrite feeding.

Automotive Alloys 2005: Session II

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizer: Subodh K. Das, Secat, Inc., Coldstream Research Campus, Lexington, KY 40511 USA

Wednesday AM Room: 2006
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Subodh K. Das, Secat Inc., Lexington, KY 40511 USA; Tony Zhai, University of Kentucky, Dept. of Chemls. & Matls. Engrg., Lexington, KY 40506 USA

8:30 AM
Electromagnetic Welding of 6061 Aluminum Alloy: Sergey F. Golovashchenko[1]; Vladimir V. Dmitriev[1]; *Al R. Krause*[1]; [1]Ford, Mfg. & Processes, 2101 Village Rd., Dearborn, MI 48124 USA

The process of pulsed electromagnetic welding is similar to explosive welding in terms of the mechanism of metallurgical bonding The blanks are positioned at an angle to one another, and an initial clearance. The coil is positioned near the surface of the blank being accelerated. The coil is connected to a pulsed current generator. Once the capacitors are charged to a designated voltage, the switch connects the battery of capacitors to the coil. During the discharge of the capacitors, a high intensity electromagnetic field is generated in the clearance between the coil and the blank. This electromagnetic field induces an Eddy current in the blank. The interaction between the current in the coil and the induced current generates a high-intensity repulsive force between the coil and the blank. As a result, the latter is accelerated toward the fixed blank. During their impact, a cumulative jet in the contact area is formed, cleaning the surfaces of both blanks and producing a metallurgical bond. The method of p ulsed electromagnetic welding can be employed for the joining of tubes with different thicknesses using radial compression or expansion. Experiments verified the potential of using electromagnetic welding technology to weld 6061-T6 tubes using external mandrels manufactured from similar materials.

8:55 AM
Formability Analysis of Aluminum Welded Blanks: *Susan E. Hartfield-Wunsch*[1]; Nicholas J. Christoff[1]; Sherri F. McCleary[2]; [1]General Motors, Metal Fabricating Div., 2000 Centerpoint Pkwy., MC 483-520-266, Pontiac, MI 48341 USA; [2]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 45069 USA

A study was undertaken to better understand the forming characteristics of aluminum welded blanks. Laser welding, friction stir welding, and variable polarity plasma arc welding were compared to determine the best process for aluminum welded blank fabrication. Blanks were fabricated using AA5754 and AA5182 alloys, with several thickness ratios. Limited Dome Height (LDH) testing was conducted to understand the influence of the weld on formability. Dome heights and forming limit diagrams were used as measures of formability. Weld microstuctures were assessed to determine the relationship between weld geometry and formability. Results from this study indicate that the variable polarity plasma arc welds (VPPAW) offer potential performance enhancements relative to the laser welds or friction stir welds (FSW) when welding 5XXX aluminum alloys.

9:20 AM
Multi-Scale Mechanical Behavior of Open Cell Aluminum Foams: *Jikou Zhou*[1]; Z. Gao[2]; S. Allameh[1]; Alberto M. Cutino[2]; E. Akpan[1]; *W. O. Soboyejo*[1]; [1]Princeton University, Dept. of MAE & PRISM, E-quad, Olden St., Princeton, NJ 08540 USA; [2]Rutgers University, Dept. of Mechl. & Aeros. Engrg., Piscataway, NJ 08854 USA

We will present the results of studies on mechanical behavior of open cell aluminum foams. The multi-scale nature of compressive deformation is examined from individual struts to overall foam deformation. Stress-strain curves of individual struts are investigated using micro-tensile testing. The localization (slip bands) in individual struts is discussed along with evidence of deformation bands at the macroscale. Onset and propagation of deformation localization bands are elucidated via in situ imaging and digital image correlation (DIC) techniques that provide continuous mapping of strain fields across sample sections. A simple unit cell model is then used to estimate the dependence of foam strength and stiffness on relative density and strut properties. Moreover, foam fatigue behavior under cyclic behavior is also studied, and attributed to surface crack nucleation and propagation in individual struts at different fatigue stages.

9:45 AM
Modeling of Precipitation Hardening in Pre-Aged 6000 Series Al Alloys: *Shahrzad Esmaeili*[1]; David J. Lloyd[2]; [1]University of Waterloo, Dept. of Mechl. Engrg., 200 Univ. Ave. W., Waterloo, Ontario N2L 3G1 Canada; [2]Alcan International Limited, Kingston R&D Ctr., PO Box 8400, Kingston, Ontario K7L 5L9 Canada

The 6000 series Al alloys are increasingly used for automotive skin panels for their weight savings and enhanced properties. The paint bake response of these alloys has been significantly improved in recent years by application of pre-aging processes immediately after solution heat treatment. Further optimization of the aging processes and full utilization of the strengthening potential of the commercial sheet requires that the precipitation hardening behavior of the pre-aged alloys to be predictable. Hence, a new physically-based model has been developed to determine the kinetics of precipitation and the evolution of yield strength during artificial aging of pre-aged 6000 series aluminum alloys. The model has been validated with independent experimental results. In this work, the basics of the model development, as well as some modeling and experimental results are presented.

10:10 AM
Aluminum-Ceramic (Flyash) MMCs for Automotive Applications: Graham Withers[2]; *Derek O. Northwood*[1]; [1]University of Windsor, MAME Dept., 401 Sunset Ave., Windsor, Ontario N9B 3P4 Canada; [2]Cyco Tech, 40 Renowden St., Cheltenham, Victoria 3192 Australia

An aluminum-based MMC (metal matrix composite) containing flyash (Ultalite) has been developed for automotive applications which typically involve the replacement of ferrous materials to reduce weight. The flyash particles are hollow microspheres, 20-50 microns in diameter, with a density about 25% of that of aluminum. Ultalite can be processed by all common casting methods. A semi-solid thixotropic casting process (high pressure die casting) has been developed which provides greatly improved casting properties compared to conventional high pressure die casting. Apart from being 1/3 the weight of cast iron and a low cost material, Ultalite does not require special tooling for machining (as is common for MMCs) and has good wear resistance. Potential applications include brake drums and discs, pistons, cylinder heads, cylinder blocks and transmission components.

10:35 AM
A Dislocation-Model of Forming Limit Diagram of Aluminum Sheet with Two Ideal Orientations: *Xiyu Wen*[1]; *Tony Zhai*[1]; Zhong Li[2]; Subodh Das[1]; [1]CAT, College of Engrg., UK, 1505 Bull Lea Rd., Lexington, KY 40511 USA; [2]Commonwealth Aluminum Concast, 1505 Bull Lea Rd., Lexington, KY 40511 USA

In this study, the forming limit diagrams (FLD) of a rate-sensitive FCC sheet with combinations of two different ideal orientations, and orientations are predicted. Unlike the M-K model, no surface groove is assumed on the sheet. On the other hand, due to the effect of segregation in the thermal-mechanical processing of the sheet, narrow bands of grains with similar orientations are assumed to exist. The band will behave like a single orientation and will deform differently from its neighbors. The result of the simulation was compared with two typical FLDs of the O-temper and H-temper aluminum alloy sheets.

11:00 AM Cancelled
Age-Hardening and Plastic Anisotropy in Extruded AA6xxx and AA7xxx Profiles

11:25 AM
Influence of Cu on the Aging Behavior of AlSi7Mg0.5 Alloy: *Yanjun Li*[1]; Stig Brusethaug[2]; [1]University of Oslo, Ctr. of Matls. Sci. & Nanotech., Dept. of Physics, PB 1126, Blindern, Oslo 0318 Norway; [2]Hydro Aluminium, R&D Ctr., 6601 Sunndalsøra Norway

The effect of Cu addition in the range of 0~3 wt.% on the age hardening behavior of AlSi7Mg0.5 alloy during T6 heat treatment has been studied. The evolution of the tensile strength and elongation of the alloys at the peak-aged T6 condition with Cu content has been measured. The tensile strength increases while the elongation decreases with increasing Cu content in the alloy. The alloy with addition of 3.0 wt.% shows the best combination of tensile strength and elongation properties. The investigation on the precipitation behavior of dispersoids during ageing by TEM and HRTEM shows that the precipitation of ϑ-Al2Cu phase caused by the addition of Cu has a strong influence on the aging behavior of the alloy.

11:50 AM
The 4xxx Aluminium Alloys Sheets Use to Deep Drawing: *Marzena Lech-Grega*[1]; Andrzej Klyszewski[1]; Tomasz Stuczynski[1]; Janusz

Zelechowski[1]; Wojciech Szymanski[1]; [1]Institute of Non-Ferrous Metals, Light Metals Div., Pilsudskiego 17, Skawina 32-050 Poland

Recycling of aluminum alloys enforces the manufactures to unify the used alloy types. Hypo eutectic silumins, which have a broad use in automotive industry for cast elements, can be used, in a form of sheets, for deep drew elements. This paper shows mechanical properties (strength, anisotropy) and sheet structure of 4xxx series alloys with addition of transitional metals, appropriate for deep drawing. Results are compared with properties of widely-used AlMg4,5 (EN AW-5082) alloy sheets.

12:10 PM
Effects of Casting Conditions on Quality of Twin-Roll Cast Al-Mg-Si Alloy Strip: *Hiroki Esaki*[1]; Yoshio Watanabe[1]; Hideyuki Uto[1]; Kazuhisa Shibue[1]; [1]Sumitomo Light Metal Ind., Ltd., R&D Ctr., 1-12 Chitose 3, Minato-ku, Nagoya 455-8670 Japan

As for the aluminum alloy 6016, it is the typical Al-Mg-Si alloy which is used as the one for automotive body applications. The AA6016 alloy strips produced experimentally by twin-roll casting (TRC) technology were investigated concerning the surface feature and the microstructure. Both the defects such as the ripple mark and the centre line segregation were clarified to influence the surface quality of the final cold rolled sheet. For example, the ripple mark is detrimental to filform corrosion resistance. Because of that, the optimum casting conditions such as casting speed and set-back distance were clarified to lower the defects. Moreover the Al-Si-Mg alloys containing ferrous impurity from 0.15 to 1% were estimated in order to develop the material recycling technology for automotive body applications by using TRC.

Beta Titanium Alloys of the 00's: Corrosion and Biomedical

Sponsored by: Structural Materials Division, SMD-Titanium Committee
Program Organizers: Rod R. Boyer, Boeing Company, Metall./6-20J1, Seattle, WA 98124-2207 USA; Robert F. Denkenberger, Ladish Co., Inc., Cudahy, WI 53110-8902 USA; John C. Fanning, TIMET, Henderson, NV 89009 USA; Henry J. Rack, Clemson University, School of Materials Science & Engineering, Clemson, SC 29634-0921 USA

Wednesday AM Room: Salon 10/11
February 16, 2005 Location: San Francisco Marriott

Session Chairs: Sreeramamurthy Ankem, University of Maryland, Dept. of Matls. Sci. & Engrg., College Park, MD 20742-2115 USA; Yoji Kosaka, TIMET, Henderson Techl. Lab., Henderson, NV 89009 USA

8:30 AM
Fundamental Corrosion Characterization of Several Newer Generation Beta Titanium Alloys: *James S. Grauman*[1]; [1]TIMET, Henderson Techl. Lab., PO Box 2128, Henderson, NV 89009 USA

Addition of alloying elements to titanium can serve to increase or decrease the inherent corrosion behavior of the underlying titanium base metal matrix. By comparing the corrosion behavior of titanium alloys with commercially pure titanium, interesting observations can be drawn regarding the individual and multi-element effects provided by these alloys. Established beta alloys such as Ti-13-11-3, Ti-38644, Ti-15-3-3-3, and Ti-21S have been fairly well characterized in this regard with respect to basic corrosion behavior, including general and crevice corrosion, and SCC in acid chloride environments. This paper will address a similar corrosion characterization study on several newer generation beta titanium alloys. The alloys involved include TIMETAL LCB (Ti-6.8Mo - 4.5Fe - 1.5Al), TIMETAL 555 (Ti-5.5Al - 5Mo - 5V - 3Cr) , along with other recently developed beta alloys. These alloys are finding interest and application within the automotive and aerospace industries. A direct comparison of their corrosion behavior to other alloys should be of interest to design engineers.

9:00 AM
Corrosion Resistance of Beta Titanium Alloys to Hot Skydrol: *Robert D. Briggs*[1]; Katie J. Schumacher[1]; [1]Boeing Company, Boeing Commercial Airplanes/Matls. & Process Tech., PO Box 3707, MS73-44, Seattle, WA 98027 USA

Skydrol (hydraulic fluid) can cause severe corrosion of titanium alloys at elevated temperature resulting in restrictions on the use of titanium parts in applications subject to elevated temperature and possible skydrol impingement. Several beta titanium alloys were tested for their corrosion resistance to hot skydrol by an immersion testing technique. The corrosion resistance of the beta titanium alloys to hot skydrol will be compared to that of well known alpha-beta alloys.

9:25 AM
Investigation of Ti-Base Alloys with Positron Annihilation Techniques: *Falko Baier*[1]; Wolfgang Sprengel[2]; Jürgen Eckert[1]; [1]TU Darmstadt, Physl. Metall., Petersenstrasse 23, Darmstadt 64287 Germany; [2]Stuttgart University, Inst. of Theoretical & Applied Physics, Pfaffenwaldring 57, Stuttgart 70550 Germany

The research and development of Ti-based alloys for biomedical applications is focused on the development of low rigidity beta-phase Ti alloys composed of non-toxic elements with good mechanical properties and workability. A major drawback of these alloys is their poor workability. In order to overcome these limitations lots of work has been spent in order to find new Ti-alloys by varying the compositions or modifying the existing ones for the improvement of the formability. We present measurements of the positron lifetime and coincident Doppler broadening of the positron-electron annihilation photon line in as-cast and deformed Ti-base alloys in order to show the advantages of this non-destructive method for the field of engineering applications, because the sensitivity of positrons to defects in plastically deformed metals has been well-known since the 1960s. The addition of the element-sensitive Doppler broadening technique gives access to the chemical nature of the dislocation environment.

9:50 AM Break

10:05 AM
Pseudoelasticity in Beta Titanium Alloys with Nitrogen Addition: *Tadashi Furuhara*[1]; Satoshi Annaka[1]; Tadashi Maki[1]; [1]Kyoto University, Dept. Matl. Sci. Engrg., Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501 Japan

A representative metastable beta titanium alloy, Ti-10V-2Fe-3Al (Ti-10-2-3), is known to exhibit good shape memory effect due to stress-induced alpha'' martensite transformation at room temperature. In the present study, nitrogen was added to this alloy to suppress slip deformation by solid solution strengthening of beta matrix and effect on the deformation behavior of beta phase was studied. During quenching after beta solutionizing, thermally-induced martensite is formed in the base alloy (Ti-10-2-3) and the alloy containing 0.1mass%N. When a bending test (of which maximum strain given is 2.5%) is conducted at room temperature, those alloys were deformed by stress-induced martensite transformation and exhibit good shape recovery in heating after deformation. In contrast, the thermally-induced martensite transformation is completely suppressed in the alloy containing 0.2mass%N and the strain provided by the bending test at room temperature is fully recovered in unloading. The forward and reverse stress-induced martensite transformation is observed by in-situ optical microscopy, confirming the occurrence of pseudoelasticity in the 0.2mass%N alloy.

10:30 AM
Phase Stability Dependence of the Plastic Deformation Behavior in Ti-Nb-Ta-Zr-O Alloys: *Junghwan Hwang*[1]; Shigeru Kuramoto[1]; Tadahiko Furuta[1]; Kazuaki Nishino[1]; Takashi Saito[1]; [1]Toyota Central R&D Labs.,Inc., Metallic Matls. Lab., 41-1, Yokomichi, Nagakute, Aichi 480-1192 Japan

We investigated the effects of alloy contents on mechanical properties to make clear a correlation between plastic deformation behavior and β phase stability in Ti-Nb-Ta-Zr-O alloys. It was realized that there was specific compositional area in which the alloy exhibited little work hardening and minimum value of Young's modulus. The specific area was expressed by "bond order" (Bo) based on the DV-X_α method of 2.87 and averaged electron/atom ratio (e/a) of 4.24, which corresponded to those of multi-functional β titanium alloy, "Gum Metal". These electronic conditions also minimized ideal strength required for plastic deformation without any dislocation activity. Actually, the deformation behavior of alloys in the specific compositional area revealed that the unique behavior characterized by "giant fault". We also confirmed that such compositional area corresponded to the phase boundary between α" martensite and β phase at room temperature.

10:55 AM
The Effect of Second Phase on the Deformation Mechanisms of Beta Titanium Alloys: Allan Wayne Jaworski[1]; *Sreeramamurthy Ankem*[1]; [1]University of Maryland, Dept. of Matls. Sci. & Engrg., 090 Stadium Dr., Rm. 1105, College Park, MD 20742-2115 USA

Recent studies have shown that grain size and stability of beta alloys affects ambient temperature tensile and creep deformation

mechanisms. In the case of a single phase beta alloy, Ti-14.8wt%V, the tensile and creep deformation mechanisms were found to be predominantly slip or predominantly twinning, depending on the grain size. However, when the same beta phase is present in an alpha-beta alloy the deformation mechanism in the beta phase is found to be predominantly stress induced martensite. The details of the investigation and the reasons for the second-phase induced deformation mechanisms will be presented. This work is being funded by the National Science Foundation under grant number DMR-0102320.

11:20 AM
Characterization of Ti-15Mo for Orthopaedic Applications: *Brian Marquardt*[1]; [1]Zimmer, Metals Rsch., PO Box 708, Warsaw, IN 46581-0708 USA

Cold hearth melting techniques, with the capability of producing large homogeneous ingots, have generated renewed interest in the Ti-15Mo beta titanium alloy. This alloy was originally developed several decades ago for chemical industry applications but was recently standardized for surgical implant applications in ASTM F 2066. Current processing routes have limited the ASTM standard to one basic microstructural condition which can be produced by beta solution treating and rapidly quenching the material to avoid the formation of alpha and/or omega phases. The equiaxed beta microstructure produced by this process has high ductility and moderate strength. Alternative processing routes and multiphase microstructures have been the subject of recent investigations at Zimmer. A vast range of material conditions and associated mechanical properties can be produced by modifying the rolling, forging, annealing and aging parameters. The purpose of this work was to characterize the influence of some of these processing parameters on microstructure/property relationships and to evaluate Ti-15Mo for applications with high fatigue strength requirements. Tensile and rotating beam fatigue data for an array of processing conditions will be presented along with metallographic results to illustrate the breadth of potential for this beta titanium alloy.

11:45 AM
Evaluation of Ti-Cr-Cu Alloys for Dental Applications: Marie Koike[2]; Masayuki Itoh[3]; Osamu Okuno[4]; Kohei Kimura[3]; Osamu Takeda[5]; Toru H. Okabe[5]; *Toru Okabe*[1]; [1]Baylor College of Dentistry, TX A&M Univ. Sys. Health Sci. Ctr., Biomatls. Sci., 3302 Gaston Ave., Dallas, TX 75246 USA; [2]Nagasaki University Graduate School of Biomedical Sciences, Removable Prosthodontics & Mgmt. of Oral Function, 1-7-1 Sakamoto, Nagasaki 852-8588 Japan; [3]Tohoku University Graduate School of Dentistry, Prosthodontics, 4-1 Seiryo-machi, Aoba-ku, Sendai 980-8575 Japan; [4]Tohoku University Graduate School of Dentistry, Dental Biomatls., 4-1 Seiryo-machi, Aoba-ku, Sendai 980-8575 Japan; [5]University of Tokyo, Inst. of Industl. Sci., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan

To evaluate the suitability of Ti-Cr(7-19mass%)-Cu(3-7%) for dental prostheses, this study examined the characteristics of the cast alloys, including their mechanical properties, grindability (ease of grinding), wear resistance, and corrosion behavior. The grindability of the cast alloys was examined using a SiC wheel at a fixed force and time at a rotational (circumferential) speed of 1250 m/min. Wear was evaluated in a two-body wear testing machine after 50,000 cycles of simulated chewing under water spray at a fixed load. The reduced plastic deformation of the 13% Cr beta titanium alloy resulting from the inclusion of the Ti-Cu eutectoid structure when alloying with Cu significantly improved the grindability and wear resistance. Although the corrosion resistance of the alloys in artificial saliva deteriorated somewhat over the electrode potential range tested, the alloys behaved similar to many other titanium alloys within the normal intraoral oxidation potential. Supported by NIH/NIDCR grant DE11787.

Biological Materials Science and Engineering: Biological Materials Characterization and Biomimetics I

Sponsored by: Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, Society for Biomaterials, Surfaces in Biomaterials Foundation, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), EMPMD/SMD-Biomaterials Committee
Program Organizers: Marc Andre Meyers, University of California, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Roger J. Narayan, Georgia Tech, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Wednesday AM Room: 3009
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Roger Narayan, Georgia Institute of Technology, Dept. of Matls. Sci. & Engrg., Atlanta, GA 30332-0245 USA; Eduard Arzt, University of Stuttgart, Max Planck Inst. Fuer Metallforschung, Stuttgart 70569 Germany

8:30 AM Invited
Tapping the High-Value Secrets Revealed in Biomineralized Nanocomposites: *Daniel E. Morse*[1]; [1]University of California, Inst. for Coop. Biotech., California NanoSystems Inst. & the Matls. Rsch. Lab., Santa Barbara, CA 93106 USA

Biological systems precisely control low-temperature nanofabrication of 3-dimensional mineral-organic composites by mechanisms fundamentally different from those of current technologies. We are working to identify the underlying molecular mechanisms responsible for biological nanofabrication in calcium- and silica-based systems, with the aim of incorporating these principles in new routes to synthesis for advanced technological applications. In sponges, silica nanofabrication is catalyzed and structurally directed by a unique family of enzymes. Higher-order structural control is directed by genetically controlled branching of the catalytic templating proteins operating in conjunction with molding by the surrounding lipid membranes. Biomimetic adaptation of these mechanisms to non-biological materials is now driving industrial research. Biomimetics catalyze and template the structurally controlled synthesis of non-biological semiconductors including titanium dioxide, gallium oxide, ruthenium oxide, cobalt oxide and zinc oxide. These results suggest the feasibility of a low-temperature catalytic route to the synthesis and nanostructural control of metal oxide semiconductors in a biologically inspired process analogous to current molecular organic chemical vapor deposition (MOCVD) technology.

9:00 AM Invited
A New Class of Tough Composite Materials Based on Natural Rigid Biological Systems: *George Mayer*[1]; Bryan J. Gruner[2]; [1]University of Washington, Dept. of Matls. Sci. & Engrg., Seattle, WA USA; [2]Advanced Development Program, Ft. Worth, TX USA

We have studied the structures and properties of a new class of composite materials, containing a predominantly high (95% volume fraction) ceramic or glass phase, combined with minor protein phases, which have unusual combinations of mechanical properties, such as stiffness, strength, and toughness. These composites are based on the architecture of the nacre structure, which is found in the shell of the abalone Haliotis Rufescens. The mechanisms underlying these properties have also been described. Analogs (utilizing high-performance engineering materials), that mimic many of the mechanisms underlying those superior combinations of properties, have been built. The results of the foregoing investigations are presented.

9:30 AM Keynote
Biological and Artificial Attachment Devices: Lessons for Materials Scientists from Flies and Geckos: *Eduard Arzt*[1]; [1]University of Stuttgart, Max Planck Inst. fuer Metallforschung, Heisenbergstr. 3, Stuttgart 70569 Germany

Mechanical performance governs the usefulness of many man-made devices. In biology, mechanics is often essential for survival: this is true on the molecular level, on the cellular level and for whole organisms. This keynote talk will decribe an interdisciplinary study involving materials scientists, biologists, and physicist aimed at elucidating the correlation between structure and performance of attachment devices in insects (flies, beetles), spiders, and geckos. In all of these cases, adhesion is mediated by the interaction of finely-struc-

tured contact elements with the different substrates. We study the structure of these elements on the micro and nano level by different microscopy techniques including SEM, TEM, AFM and X-ray imaging. Local mechanical properties and adhesion forces are measured by nanomechanical test methods and compared with predictions based on theoretical contact mechanics. For example, it has been possible for the first time to measure the adhesion of single gecko spatulae, with dimensions of 200 nm, to selected substrates by atomic force microscopy. Structure, size and shape of the contact elements are found to play important roles; in particular the principle of "contact splitting" has been identified: finer contact elements (down to sub-micron level) produce larger contact forces in heavier animals. The actual dimensions of the contact elements follow exactly the theoretical predictions, a relationship that covers 6 orders of magnitude in animal mass from the fruit fly to the gecko! From our findings, important conclusions can be drawn on the optimal design of artificial contact elements. The talk will present first prototype adhesive surfaces produced with this insight and identify their technical limits by introducing "adhesion mechanism maps". These developments have led to the design of artificial micro-attachment systems ("biomimicry") which are potentially useful in micro-technology.

10:15 AM Break

10:30 AM Invited
Modeling the Role of Nanostructure and Molecular Structure on the Mechanical Response in Nacre: *Kalpana S. Katti*[1]; Dinesh R. Katti[1]; Shashindra Man Pradhan[1]; Pijush Ghosh[1]; Devendra Verma[1]; [1]North Dakota State University, Civil Engrg., CIE 201, Fargo, ND 58105 USA

Nacre, the inner layer of molluscan seashells has mechanical properties that far exceed the properties of its constituents: aragonitic calcium carbonate and organics. The high fracture toughness and strength of nacre is often attributed to the unique nanoarchitecture that consists of laminated structure with about 0.5 micron sized aragonite platelets separated by about 20 nm thick organic layers. Several details of the nanostructure have been recently revealed in literature such as presence of nanoscale mineral bridges through organic layers, nanoscale asperities at organic-inorganic interfaces and rotations between layers. We have constructed three dimensional finite element models that incorporate these details of nanostructure and quantitatively evaluate the role of such details on mechanical response of nacre. Also, we examine the molecular nature of the interfaces and role of molecular structure of the proteins on mechanical response of nacre through molecular dynamics simulations and fourier transform infrared spectroscopy experiments.

11:00 AM
Mechanical Properties and Structure of Haliotis Rufescens, Strombus Gigas, and Tridacna Gigas Sea Shells: A Comparative Study: *Albert Lin*[1]; Kenneth S. Vecchio[1]; Marc A. Meyers[1]; [1]University of California, Dept. of MAE, Matls. Sci. Grp., 9500 Gilman Dr., MC-0411, La Jolla, CA 92093-0411 USA

Shells are composed of aragonite/calcite crystals interleaved with layers of a viscoelastic protein, having dense, tailored structures that impart (relatively speaking) excellent mechanical properties. Shells, such as conch (Strombus Gigas), giant clams (Tridacna Gigas), and Red Abalone (Haliotis Rufescens), have hierarchical architectures that differ from one shell type to another depending on the growth requirements and shell formation used by the particular mollusk. Mechanical test have been carried out on these shells for a comparison of strength with respect to microstructural architecture, sample orientation, hydration level, etc. The mechanical response is found to vary significantly from specimen to specimen and requires the application of Weibull statistics in order to be quantitatively evaluated. The complex micro-laminate structure of these bio-composite materials is characterized and related to both their mechanical properties and growth requirements. The Red Abalone (Haliotis Rufescens) is determined to have the highest mechanical strength in comparison to conch (Strombus Gigas) and giant clam (Tridacna Gigas) shells. This is attributed to an optimization of microstructural architecture in the form of 2-D laminates. The growth mechanisms and structure of abalone is observed through close examination of laboratory-grown flat pearl samples and cross sectional slices of nacreous shell allowing a detailed description of the micro-laminate structure.

11:20 AM
Quantitative Evaluation of Proteins Adsorbed on Polysaccharide Biomimetic Coatings: *Michela Ombelli*[1]; Lauren Costello[2]; Quing Cheng Meng[1]; Russell J. Composto[2]; David M. Eckmann[1]; [1]University of Pennsylvania, Dept. of Anesthesia, 3620 Hamilton Walk, Philadelphia, PA 19104 USA; [2]University of Pennsylvania, Dept. of Matls. Sci. & Engrg., 3231 Walnut St., Philadelphia, PA 19104 USA

Polysaccharide surface coatings hold considerable promise to render implantable medical devices biocompatible. Sugar based biomimetic layers are effective at preventing biofouling, yet a systematic study of the relationship between synthetic surface coating properties and plasma protein adsorption is still lacking. We have developed methods to synthesize and analyze dextran and hyaluronic acid coatings on silicon wafers. We can predict and control thickness, wettability, brushiness and grafting density of thin dextran and hyalurnoic acid layers. We have conducted experiments to quantify competitive protein adsorption (e.g., albumin, fibrinogen) using a novel approach to remove all adsorbed proteins. The method involves use of opportune detergent solutions and subsequent analysis by high performance liquid chromatography to separate and quantify each single protein. Different coating behaviors are correlated to specific coating properties and are used to optimize the synthesis route. Supported by NIH Grants R01 HL60230 and R01 HL67986.

11:40 AM
Preparation and Characterization of Chitosan/Poly(Acrylic Acid) Nanoparticles: Jian-Wen Wang[1]; *Wei-Jen Shih*[2]; Min-Hsiung Hon[2]; [1]Chung Hwa College of Medical Technology, Environml. & Safety Engrg., No. 69, Wen-Hwa Rd., Tainan 701 Taiwan; [2]National Cheng-Kung University, Matls. Sci. & Engrg., No.1, Ta-Hsueh Rd., Tainan 701 Taiwan

Chitosan based nanoparticles, which has a small particle size below 100nm have been developed in this project. Chitosan (CS)/poly(acrylic acid) (PAA) complex nanoparticles with four kinds of solvent have been prepared by a modified dropping method of PAA in chitosan solution. The physicochemical properties of nanoparticles were investigated by using FTIR-ATR, X-ray diffraction, dynamic light scattering, transmission electron microscopy and zeta potential. Chitosan dissolved in acetic acid and lactic acid has the smallest size of CS-PAA nanoparticle about 30nm. It is found that the prepared CS-PAA nanoparticles with a volume ratio of 1 to 1 and incubated in pH 3 PBS buffer solution for 24hr carry a positive charge and show the size in the range from 10 to 30 nm. Different dropping sequence can obtain various surface structures and zeta potentials of CS-PAA nanoparticles and the key factor for controlling the size and structure of the nanoparticles is the incubation pH media.

Bulk Metallic Glasses: Corrosion, Oxidation, and Phase Transformation

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA

Wednesday AM Room: 3006
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Jurgen Eckert, Technische Universitat Darmstadt, Darmstadt D-64287 Germany; Ralf Busch, Oregon State University, Mechl. Engrg., Corvallis, OR 97331 USA

8:30 AM
Intermediate-Range Order of Ni-Based Ternary Amorphous Metals: *Michelle L. Tokarz*[1]; John C. Bilello[1]; [1]University of Michigan, Ctr. for Nanomatls. Sci., Matls. Sci. & Engrg. Dept., 3061 HH Dow Bldg., Ann Arbor, MI 48109-2136 USA

Traditional X-ray experiments determined Radial Distribution Functions (RDFs) of NixNbySn100-x-y bulk amorphous alloys found a divergence from a random hard-sphere model with respect to neighbor shell distances/coordination numbers. However, these functions do not provide information about the specific contributions of any individual element. Solving the Partial Pair Distribution Functions (PPDFs) by varying the composition, or by chemical substitution, assumes similar behavior in different chemical environments, which may not be the case. Anomalous x-ray scattering provides better way to probe the local interactions of specific chemical pairs. Data near and far from the absorption edges of individual elements gives Differential Distribution Functions (DDFs), revealing the atomic arrangements. High-resolution synchrotron anomalous scattering experiments have indicated Ni-based clustering effects. This non-random distribution of atomic species may partially explain the failure of the random model. An

analysis is given in terms of the short and intermediate range order of this series. Research supported by DARPA under contract number: DAAD19-01-1-0525 via a subcontract from California Institute of Technology, and by DOE for use of the synchrotron facilities the Stanford Synchrotron Radiation Laboratories.

8:50 AM

Electrochemical Studies of a $Ti_{43.3}$ $Be_{27.5}$ $Zr_{21.7}$ $Ni_{7.5}$ Bulk Metallic Glass in a Phosphate-Buffered Saline Electrolyte: *Mark L. Morrison*[1]; Raymond A. Buchanan[1]; Atakan Peker[2]; Peter K. Liaw[1]; [1]University of Tennessee, Matls. Sci. & Engrg., 434 Dougherty, Knoxville, TN 37996-2200 USA; [2]Liquidmetal Technologies, 25800 Commercentre Dr., Ste. 100, Lake Forest, CA 92630 USA

Cyclic-anodic-polarization tests were conducted on a Ti-based bulk metallic glass (BMG) with a chemical composition of $Ti_{43.3}$ $Be_{27.5}$ $Zr_{21.7}$ $Ni_{7.5}$ (at.%), commonly known as LM-010. Tests were performed at 37°C in a phosphate-buffered saline (PBS) electrolyte with a physiologically-relevant dissolved oxygen content. The alloy demonstrated passive behavior at the open-circuit potential with a low, mean corrosion penetration rate of 1 μm/year. However, a susceptibility to localized corrosion was observed in all of the tests. The mean difference between the pitting potentials and the open-circuit potentials was high [785 mV]. Furthermore, the mean difference between the protection potentials and the open-circuit corrosion potentials was determined to be high as well [528 mV]. The high, positive values for these parameters signify a high resistance to localized corrosion in the tested environment. Finally, these values are the highest reported in the literature for a BMG alloy in this particular environment. The authors are grateful to the National Science Foundations, Integrative Graduate Education and Research Training (IGERT) program under grant number DGE-9989548, with Dr. L. Clesceri, Dr. W. Jennings, Dr. L. Goldberg, and Ms. M. Poats as the contract monitors, and the Division of Materials Science and Engineering, Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory (ORNL) operated by UT-Battelle, LLC.

9:10 AM

Variation in Cyclic-Anodic-Polarization Behavior as a Function of Bulk-Metallic-Glass Sample Size: *Brandice A. Green*[1]; William H. Peter[1]; Raymond A. Buchanan[1]; Peter K. Liaw[1]; C. T. Liu[2]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., 434 Dougherty Hall, Knoxville, TN 37996-2200 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, MS 6115, Oak Ridge, TN 37831-6115 USA

Cyclic-anodic-polarization experiments were performed on $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (at. %) bulk-metallic-glass specimens, which were obtained from ingots with diameters of 2 and 4 mm. The electrolyte for these experiments was an aerated 0.6 M NaCl solution, simulated seawater, with a pH of 7.00 ± 0.1. Although samples from both the 2 and 4 mm ingots consistently demonstrated passive behavior at the open-circuit potential and susceptibility to localized corrosion at increased potentials, both exhibited considerable variations in the values of the corrosion parameters (the open-circuit potential, pitting potential, and corrosion penetration rate). The samples from the 2 mm ingot proved more resistant to localized corrosion than samples from the 4 mm ingot. Examination of the microstructure and chemical distribution was performed before and after cyclic-anodic polarization experiments to explain (1) variations in corrosion parameters within samples from ingots with the same diameter and (2) differences between samples from ingots of varying diameters. The present work is supported by a National Science Foundation (NSF) Graduate Research Fellowship (B.A. Green); an Integrative Graduate Education and Research Training (IGERT) Program (DGE-9987548) with Drs. L. Clesceri, W. Jennings, and L. Goldberg as the program managers; and the Tennessee Advanced Materials Laboratory (TAML) with Dr. W. Plummer as the director.

9:30 AM

Corrosion of Zr-Based Bulk Metallic Glasses: *Isabella Gallino*[1]; Daniela Zander[2]; Beate Heisterkamp[2]; [1]Oregon State University, Dept. of Mechl. Engrg., Corvallis, OR 97331 USA; [2]University of Dortmund, Dept. of Biocheml. & Cheml. Engrg., Dortmund D-44221 Germany

Zr-based bulk metallic glasses are of increasing interest due to their excellent properties, e.g., the high elastic limit or good corrosion resistance. In general, the amorphous structure is known to improve the corrosion resistance of an alloy. A reason for such a behaviour might be the homogeneity of the metallic glass. Recent results on corrosion of amorphous and crystalline Vit106a and Zr-Cu-Al-Y are presented in comparison to the corrosion behaviour of glassy Zr-Cu-Ni-Al investigated by Gebert et al.[1] The corrosion was studied by potentiodynamic polarization methods at room temperature in 0.001-0.1 M $NaCl_{aq}$ (about pH 8) and in 0.1 Na_2SO_4 adjusted with H_2SO_4 (pH 2-8). The oxide and passivation layers were investigated by X-ray diffraction, SEM and TEM. [1]A. Gebert et al. Material and Corrosion 48 (1997) 293-297.

9:50 AM

Oxidation of $Ni_{60}Nb_{35}Sn_5$ Bulk Metallic Glasses: *Isabella Gallino*[1]; Ralf Busch[1]; Lioba Jastrow[2]; Uwe Köster[2]; [1]Oregon State University, Dept. Mechl. Engrg., 204 Rogers Hall, Corvallis, OR 97331 USA; [2]Dortmund University, Dept. Biocheml. & Cheml. Engrg., Emil-Figge Str. 66, Dortmund D-44221 Germany

Due to the high glass transition temperature (Tg > 881K) and large undercooled region, Ni-Nb-Sn bulk metallic glasses are considered a promising refractory alloy system. In addition, however, adequate oxidation resistance is necessary. The oxidation of $Ni_{60}Nb_{35}Sn_5$ bulk metallic glasses was analyzed in dry air in the temperature range close to the glass transition in order to avoid any crystallization. Thermogravimetric analyses reveal information about the oxidation kinetics. X-ray diffraction and cross-sectional electron microscopy allows phase identification in the scales as well as to reveal the oxidation mechanism. Results will be compared with the oxidation reaction of other metallic glasses as well as crystalline alloys of similar composition.

10:10 AM Break

10:30 AM

Oxidation Reactions of Zr-Based Metallic Glasses: *Uwe Koster*[1]; Lioba Jastrow[1]; [1]University of Dortmund, Dept. Biochem. & Chem. Eng., Dortmund D-44221 Germany

Zr-based metallic glassses are of increasing interest due to their excellent properties, e.g. high elastic limit or catalytic activity, appropriate oxidation behaviour provided. The aim of this paper is a detailed investigation by thermogravimetry and cross sectional microscopy on the oxidation reactions of different Zr-based metallic glasses. Oxidation kinetics seems to be controlled by oxygen diffusion through the scale towards the ZrO_2/glass interface. Two modes of oxidation were observed: depending on the alloy either (1) relative slow growth of continuous scales consisting of nodules of tetragonal ZrO_2 embedding nanocrystals of the late transition metals or (2) formation of fast growing oxide cones exhibiting a lamellar structure of monoclinic and tetragonal ZrO_2 thus allowing very fast diffusion along the interfaces between the lamellae. In order to understand the influence of structure, the oxidation behavior of these metallic glasses was compared with that of nanocrystalline or coarse crystalline alloys of similar composition.

10:50 AM

Air Oxidation and Phase Transformation of Ternary Cu-Zr-Ti Metallic Glasses: *Hsin-Hsin Diane Hsien*[1]; Wu Kai[1]; Yu-Lung Lin[2]; Rong-Tan Huang[3]; [1]National Taiwan Ocean University, Inst. of Matls. Engrg., 2, Pei-Ning Rd., Keelung 20224 Taiwan; [2]Chung-Shan Institute of Science and Technology, Matls. & Electro-Optics Rsch. Div., Taoyan Taiwan; [3]National Tsing Hua University, Dept. of Engrg. & Sys. Sci., 101, Sect. 2, Kuang Fu Rd., Hsinchu 300 Taiwan

Oxidation and phase transformation of the $Cu_{60}Zr_{25}Ti_{15}$ metallic glass was studied over the temperature range 350-450°C in dry air. The oxidation kinetics, as measured by thermogravimetry, generally followed the parabolic rate law, and the oxidation rates increased with increasing temperature. The scales formed on the alloy consisted of mainly Cu_4O_3 and minor amounts of CuO and Cu_2O. The substrate remained an amorphous structure below 400°C, while slightly crystalline characteristic was detected by XRD at 425°C after long time oxidation, indicating that phase transformation has taken place at higher temperatures. The crystalline phases of $Cu_{51}Zr_{14}$ and Cu_4Ti were observed at 450°C.

11:10 AM

Resonant X-Ray Scattering Studies of Structural Order in Pd-Ni-P: *Stephan O. Hruszkewycz*[1]; Todd C. Hufnagel[1]; Sean Brennan[2]; [1]Johns Hopkins University, Matls. Sci. & Engrg. Dept., 3400 N. Charles St., 102 Maryland Hall, Baltimore, MD 21218 USA; [2]Stanford Linear Accelerator Center, 2575 Sand Hill Rd., MS 69, Menlo Park, CA 94025 USA

Recent advances in x-ray scattering instrumentation make possible highly detailed studies of short- and medium-range order in bulk metallic glasses. We have measured the resonant x-ray scattering at the Pd K absorption edge in Pd-Ni-P to determine the local atomic environment around Pd atoms in both as-cast specimens, and specimens relaxed by annealing below the glass transition temperature. In the nearest-neighbor atomic shell, structural relaxation occurs by an increase in the average coordination number (consistent with increased den-

sity), and, interestingly, an increase in the average atomic separation. There is also evidence of enhanced structural order in the second-nearest neighbor shell. We interpret these results in light of recent cluster-based structural models of metallic glasses and a relaxation of free volume regions between clusters.

11:30 AM
Consolidation of Hafnium-Based Amorphous Metal and Composites by ECAE: *Suveen N. Mathaudhu*[1]; K. Ted Hartwig[1]; Ibrahim Karaman[1]; Lazslo J. Kecskes[2]; [1]Texas A&M University, Mechl. Engrg., 3123 TAMU, Coll. Sta., TX 77843-3123 USA; [2]U.S. Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, MD 21005-5069 USA

Warm equal channel angular extrusion (ECAE) in 90° tooling is used to consolidate Hf-based amorphous metal powder (Hf71.3Cu16.2Ni7.6Ti2.2Al2.6 -wt%) and to fabricate an amorphous metal matrix composite (AMMC) when blended and consolidated with pure Cu, Ni and W at temperatures between Tg and Tx for the glassy metal phase. A fully dense and uniformly consolidated product is expected after only one extrusion with good infiltration of the amorphous Hf-based alloy in between the crystalline particles. Hardness, DSC and other experimental results are reported.

11:50 AM
Structural Evolution and Stability of Bulk Zr-Based In-Situ Composites: *Ki Buem Kim*[1]; Jayanta Das[1]; Jürgen Eckert[1]; Sanat K. Roy[2]; Wolfgang Löser[3]; [1]Technische Universität Darmstadt, FB 11 Matl. und Geowissenschaften, FG Physikalische Metallkunde, Petersenstraße 23, Darmstadt D-64287 Germany; [2]Indian Institute of Technology, Dept. of Metallurgl. & Matls. Engrg., Kharagpur 721302 India; [3]Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Postfach 270016, D-01171 Dresden Germany

Bulk scale Zr-based in-situ nanostructured/metallic glass matrix composites have been developed with an addition of Nb as a primary â-Zr stabilizer. According to variation of experimental conditions and alloy compositions, the corresponding microstructures of the Zr-based in-situ composites are changed significantly with different mechanical properties suggesting that the optimum microstructures of these alloys are able to help improve the mechanical properties. In this study in order to optimize the microstructure of the Zr-based in-situ composites the microstructural evolution of the alloys during heat treatment were investigated by X-ray diffraction and transmission electron microscopy. Moreover, the stability of the microstructures also was investigated by differential scanning calorimetry.

Carbon Technology: Anode Baking

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Todd W. Dixon, ConocoPhillips, Borger, TX 79007 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Markus Meier, R&D Carbon, Sierre CH 3960 Switzerland

Wednesday AM Room: 2007
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Theo Mueller, Innovatherm Schweiz AG, CH- 5400 Baden Switzerland

8:30 AM
Enhancement in Baking Furnace Operation: *Masood Talib Alali*[1]; Javed Akhtar Raja[1]; Saleh Ahmed Rabba[1]; [1]Dubai Aluminium Company, Reduction Matl./Anode Plant, PO Box 3627, Dubai 3627 UAE

Dubai Aluminum Company (DUBAL), since its inception in 1979 with production capacity of 135,000 MT per annum has grown to one of the largest single site smelters in the world with production capacity of 683,000 MT by the end of year 2004. The latest expansion which is currently underway will further enhance the capacity to 759,000MT. In order to meet continual growing anode demand, anode baking furnace operations was upgraded and optimized in majority of the operational stages to coincide with the increased aluminum smelting capacity. This article explains the methodology adopted to increase the production by 10% along with improvement in product quality. It also explains the innovative work done to improve the 7% of the product produced during furnace crossover. While enhancing productivity, refractory condition which has a significant impact on unit cost was maintained at a benchmark level reaching 170 fire cycle in one of the furnaces. This article also covers the techniques/approaches adopted to maintain the baked rejection level which is one of the key performance indicators below 0.5% level, along with some other practices to increase the kiln life.

8:55 AM
A New Method to Start Up Fires at Baking Furnaces: *Paulo Miotto*[1]; [1]Consorcio Aluminio do Maranhão, Smelter, Rod. BR 135 Km 18 - Pedrinhas, Electrode Dept., São Luis, MA 65095-604 Brazil

This paper presents a new practice of restarting the fires at pre-baked anodes baking furnaces developed by Consorcio de Aluminio do Maranhão (ALUMAR). This method reduces safety risks and environmental impacts significantly with a lower operational cost in comparison to the conventional approach.The conventional method is based on the use of special burners to provide the needed energy to start the fire. In this case, the control of the process parameters is manual and demand additional care. The cost associated with the conventional method is very high. The new technique consists in using the energy lost in the cooling zone of another fire to restart the process. Basically, the method divides the primary fire in two small parts and then, step by step, creates two new complete fires. The cost associated reduces by around 30% when compared to the conventional method. The results were measured and reported in terms of environmental impact, oil consumption and safety risk analysis.

9:20 AM
Effect of Baking Furnace Fire Pre-Heating Configuration on Environmental Characteristics: *Paulo Miotto*[1]; [1]Consorcio de Alumínio do Maranhão, Smelter, BR 135, km 18, Electrode Dept., São Luís, MA 65095-604 Brazil

This paper shows the experience of Consórcio Alumínio do Maranhão (ALUMAR) in the accomplishment of trials to define the best fire configuration and their impacts on the baked anode properties and environmental results. Pre-heating time effect on the opacity results was studied as a function of stack base temperature and the complete burnt of volatiles. Determination of an adequate configuration of pre-heating zone at baking furnaces was extremely important to guarantee anode quality and minimum environmental impact. Results from this trial show a good correlation between averaged opacity and pre-heating time. Root cause found for this correlation is the incapacity of burning the volatiles completely and the fume profile at the stack plum in specific conditions.

9:45 AM
The Application of Optical Pyrometers in Open Ring-Type Anode Baking Furnaces: *Reinhard Max Heilgendorff*[1]; Cleber Miralha Carneiro[1]; Augusto Giovanni Trindade[1]; [1]ALBRAS Aluminio Brasileiro SA, Carbon Plant Automation, Estrada Pa 483, Km21, Vila Murucupi, Barcarena, Para 68447-000 Brazil

Albras has five open ring-type furnaces with a total of eleven fires, with three burner bridges each. Since startup in 1985, type "S" thermocouples with silicon carbide protection tubes were used for flue temperature measurement and control. With the objective for reducing maintenance time and costs, an extensive test of various combinations of thermocouple and protection tubes types and optical pyrometers was made. The optical pyrometers were found to be a viable alternative. At present two fires are controlled with two color pyrometers withought protection tubes. This paper compares the use of different types of thermocouples, single color pyrometers, with and with ought protection tubes and two color pyrometers. It also shows the advantages of measuring flue wall temperatures as to flue gas temperatures.

10:10 AM Break

10:25 AM
Advanced 3D Modeling for Anode Baking Furnaces: *Dagoberto S. Severo*[1]; Vanderlei Gusberti[1]; Elton C.V. Pinto[1]; [1]PCE Engenharia S/S Ltda, Rua Felix da Cunha, 322, Porto Alegre, RS 90570.000 Brazil

The quality of the anode used in the aluminum industry depends strongly on the baking process. In general, it is desirable to achieve a more uniform temperature inside the anode during the heating process, combined with lower soaking time and energy consumption. The main objective of this study is to present a 3D fully coupled computational model able to take into account a large number of phenomena and parameters that play a role in the baking process, such as coupled fluid flow and transient heat transfer, burning of volatiles, fuel combustion using the Eddy Dissipation model, radiation and control system representation. The simulations were done using the commercial CFD code CFX 5.6. This model can be used as a powerful tool in the development of new furnaces and retrofit of the existent ones.

10:50 AM
Components Analysis of Volatile Released During Carbonization of Coal Tar Binder Pitch: *Kwangeui Yoon*[1]; Dong Jun Lee[1]; Jae Young Jo[1]; Se In Yang[1]; [1]DC Chemical Ltd., R&D Ctr., Carbon Team, 587-102, Hakik-Dong, Nam-Gu, Incheon 402-772 Korea

Coal tar binder pitch is a complex mixture of aromatic compounds. Components having low boiling point in pitch or decomposed compounds at high temperature are released out during the carbonization of binder pitch. It is the source of environmental problem related to binder pitch. We identified the volatile components released at 350C and at 650C carbonization of commercial pitch. Pitch itself and green anode were carbonized and the condensed material from them was analyzed by gas chromatography. We quantitatively analyzed the amount of released components and that of decomposition from various pitches. Volatile controlled pitch was made at laboratory scale, and volatile components and components released during carbonization were compared with those of commercial pitch. From these results, we discussed the possibility of making a pitch with reduced volatile components. Also, we discussed PAH emission from the pitches with different volatile components.

11:15 AM
LP Bricks: A New Generation of Refractories That Meet Higher Demands in Anode Baking Furnaces: *Marcel C. Franken*[1]; [1]Gouda Vuurvast NV, PO Box 56, Gouda 2800 AA Netherlands

There is a tendency in anode baking furnaces to reduce the thickness of the flue walls; the main purpose of this reduction is to increase the size of anodes (spacing). If the thickness of the flue wall is reduced with 10% the life time of the flue wall will be reduced up to 20%. To overcome this problem Gouda Vuurvast NV developed a new generation of bricks with a reduced permeability and a lower alkali content. The lower permeability prevents alkali- and fluoridecontaining gasses to penetrate in the brick. The lower alkali content gives a better starting point of the new flue walls and more "penetrated" alkali can be absorbed by these bricks before the flue walls will collapse. The lower permeability and the lower alkali content will result in a longer life time of the refractories. A number of field tests with this new generation of LP-bricks are running.

11:40 AM
New Developments About Safety and Process in Heating Equipment for the Anode Baking Furnace: *Jean Bigot*[1]; Jean Paul Kreuwen[1]; Jean-Christophe Rotger[2]; Yann El Ghaoui[2]; Hubert Gay[3]; [1]Aluminium Pechiney, Centr' Alp, BP 7, Voreppe Cedex 38341 France; [2]Aluminium Pechiney, LRF, BP114, 73303, Saint Jean de Maurienne Cedex France; [3]Setaram Engineering, 7, rue de l'Oratoire, 69300, Caluire France

Following the issuance of a European safety instruction aiming at improving the safety of firing process and protection of operating personal, all the heating equipment operated in European countries as of 2000 must be designed with regards to the new EN 746-2 safety standard. As this instruction applies also to Anode Baking Furnace, Aluminium Pechiney and Setaram Engineering have worked in cooperation to integrate the recommendation of the new standard in the heating equipment used to bake anode in open type baking furnace. This work of improving safety has led to develop new means, of which the use improves the heating process and reduces fuel consumption and tars emissions. This paper presents the result of this work, which has been implemented in the new heating equipment started last year in Alcan Vlissingen, Aluminium Dunkerque, and Tomago Aluminium.

12:05 PM
Experience with Regenerative Thermal Oxidation as a Fume Treatment Technology for an Open Ring Type Anode Baking Furnace: *Aad Kooijman*[1]; Henry Visser[1]; Karel Verheesen[1]; H. Thalhammer[2]; [1]Aluminum & Chemie Rotterdam B.V, Oude Maasweg 80, 3197KJ Botlek-Rotterdam Netherlands; [2]CTP Chemisch Thermische Prozesstechnik GmbH, Schmiedlstrasse 10, A-8052 Graz Austria

In 2003 Aluchemie has increased capacity with the construction of bake furnace #7 by approximately 25%. The emissions of volatile hydrocarbons from the baking furnaces is a major concern for the environmental authorities. In order to meet the more stringent environmental requirements for the new furnace a technique based on regenerative thermal oxidation for the fume treatment plant was introduced. This paper presents some specific considerations for the configuration of the fume treatment plant together with the experiences gathered in the first year of operation.

Cast Shop Technology: DC Casting: Melt Flow and Cooling

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Gerd Ulrich Gruen, Hydro Aluminium AS, Bonn 53117 Germany; Corleen Chesonis, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday AM Room: 2001
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Rene Kieft, CORUS, Rsch. Dvlp. & Tech., IJmuiden 1970 CA The Netherlands

8:30 AM
An Experimental Heat Flux Measurement of the Wagstaff Water Hole Mold: *Ho Yu*[1]; [1]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 15069-0001 USA

In the high temperature quenching process of aluminum ingot casting, heat transfer from the ingot mold cooling water is one of the key mechanisms that affect casting performance such as ingot cracking and breakout. There are many commercial ingot mold types used within the aluminum industry. Their cooling water heat transfer characteristics, however, are unknown. The scope of this paper includes the construction of the mold secondary cooling water simulator in the Alcoa Technical Center and the experimental heat flux measurement of the Wagstaff water hole mold. The Wagstaff water hole mold was chosen because it is widely used in the aluminum cast shops. In the experiments, heat fluxes were measured as functions of ingot surface temperature at the water impingement point and as well downstream locations. Three water hole mold designs were used in the experiments:15 degree mold, 15 degree mold with inserts and 30 degree mold. Cooling water used in the experiments was de-ionized water in order to eliminate water chemistry effect. The experimental measurements provided the data base for generating empirical correlations of cooling water heat fluxes as functions of ingot surface temperature, ingot location and cooling water flow rate. The correlations are in forms that are suitable to be used as boundary conditions in the in-house Alcoa ingot computer model.

8:55 AM
Calculation of Heat Transfer Coefficients at the Ingot Surface During DC Casting: *Kazunori Kuwana*[1]; Srinath Viswanathan[2]; John A. Clark[3]; Adrian S. Sabau[4]; Mohamed Hassan[1]; Kozo Saito[1]; Subodh K. Das[5]; [1]University of Kentucky, Dept. of Mechl. Engrg., 151 RGAN Bldg., Lexington, KY 40506-0503 USA; [2]Sandia National Laboratories, Matls. & Process Scis. Ctr., MS 0889, Bldg. 701, PO Box 5800, Albuquerque, NM 87185-0889 USA; [3]Albany Research Center, 1450 Queen Ave., SW, Albany, OR 97321 USA; [4]Oak Ridge National Laboratory, Metals & Ceram. Div., Bethel Valley Rd., PO Box 2008, Oak Ridge, TN 37831-6083 USA; [5]Secat, Inc., 1505 Bull Lea Rd., Lexington, KY 40511 USA

Surface heat transfer coefficients representing the various regimes of water cooling during the direct chill (DC) casting of aluminum 3004 alloy ingots have been calculated using the inverse heat transfer technique. ProCAST, a commercial casting simulation package, which includes heat transfer, fluid flow, solidification, and inverse heat transfer, was used for this effort. Thermocouple data from an experimental casting run, and temperature-dependent thermophysical properties of the alloy were used in the calculation. Several variables, such as the use of a structured vs. unstructured mesh, and the presence or absence of fluid flow, were evaluated. The calculated effective heat transfer coefficient, which is a function of temperature and time, covers three water cooling regimes, i.e., convection, nucleate boiling, and film boiling, and the change of water flow rate with time.

9:20 AM
Innovative Technology Uniting New Chemicals with Advanced Monitoring and Control Optimizes the Performance of Cooling Water Systems in Metal Production Processes: *Eugene B. Smyk*[1]; Joseph J. Mazur[1]; [1]Nalco Company, 1601 W. Diehl Rd., Naperville, IL 60563 USA

The consistent performance of a cooling water system is critical to the success of many operations in aluminum, copper and steel production. This paper discusses new technology used to monitor the dynamic stresses of industrial cooling systems that results in fully automating the treatment and operating practice of these critical systems. New molecular chemistry and performance-based sensors that enable

this automation are introduced and discussed. The impact of on-line monitoring and control of the chemical actives on the major stresses experienced in these systems, including corrosion and microbial activity will be presented. Performance results including economic payout to the user, reliability and accuracy of the instrumentation, response to system upsets and the minimal operator involvement are discussed in several case studies.

9:45 AM Cancelled
Molten Aluminum Temperature Measurement with the Use of a Novel Thermocouple Assembly

10:10 AM Break

10:20 AM
Development of a Sensor to Measure Magnitude and Direction of Velocity in Liquid Aluminium: Blas Melissari Cassanello[1]; *Stavros A. Argyropoulos*[1]; [1]University of Toronto, Dept. of Matls. Sci. & Engrg., 184 College St., Toronto, Ontario M5S 3E4 Canada

This paper deals with the development of a sensor to measure magnitude and direction of velocity in Liquid Aluminium. The sphere melting technique was employed to measure magnitude of velocity. In addition using a modification of this technique the direction of velocity was detected. In this development, both aspects, experimental as well as computational work was used in tandem and they will be described in detail. The potential usage of this sensor in other high temperature liquid metals will be also discussed.

10:45 AM
Development and Use of a New Composite Material for Aluminum Contact Applications: *Sylvain P. Tremblay*[1]; Mark Vincent[2]; [1]Pyrotek Inc., 1623 Manic St., Chicoutimi, Quebec G7K 1G8 Canada; [2]Pyrotek Engineering Materials Ltd., Garamonde Dr., Wymbush, Milton Keynes, Buks MK8 8LN UK

A new composite material consisting of fiberglass fabric infiltrated with a CaSiO3 slurry will be described. Its properties as well as its behavior in contact with molten aluminum will be presented. Several plant case studies using this composite material also called "RFM" will be detailed. Utilizing its excellent properties, RFM has improved molten metal quality and brought a new problem-solving dimension to many applications. Applications such as the control pin, auto-pour ladle, continuous rod caster launder and skim dam will be detailed. Actual plant results in terms of improved metal quality and lower cost per ton usage will be shown in these applications.

11:10 AM
New Development of Calcium Silicates Especially for Flow Control and Distribution of Liquid Aluminium and Practical Results: *Volker Krasselt*[1]; Octavian Anton[2]; Mario Peter Görner[1]; [1]Promat GmbH, High Temp. Insulation, Scheifenkamp 16, Ratingen 40878 Germany; [2]Promat International NV, PRTC, Bormstraat 24, Tisselt 2830 Belgium

Within the Promat organization there are 4 different plants for the production of calcium silicate working with 6 different production technologies. This means a wide flexibility for Promat regarding R&D approach and for transfer to the production. Flow control and distribution of liquid aluminium with calcium silicates is an important market which demands precise shaped parts with high resistance to Al and with extended lifetimes. The most important process in calcium silicate technology is the autoclaving where morphology, crystal structures and pore sizes are designed. Promat developed a new method for the production of calcium silicate products: Mineral engineering and engineered matrices. Controlled crystal growth by using advanced technology allows the creation of crystal assemblages with entangled crystals of different dimensions, apparent densities and aggregate shape. Application results of the new development will be illustrated.

11:35 AM
The Effect of Process Parameters on the Metal Distribution for DC Sheet Ingot Casting: *Martin Fortier*[1]; A. Larouche[1]; X.-G. Chen[1]; Y. Caron[1]; [1]Alcan International Limited, Arvida R&D Ctr., 1955, Mellon Blvd., PO Box 1250, Jonquière, Québec G7S 4K8 Canada

The liquid metal flow inside an ingot sump is a key issue in the casting of sound DC sheet ingots. The flow patterns are dependant on the design characteristics of the metal distributor and process parameters used (casting speed, skim dam, dip tube, etc.). To fully understand the effects of process parameter changes on metal distribution, studies were performed using water modelling, measurements during DC casting and mathematical modelling. The parameters studied were: time for transfer and distribution, casting speed, casting temperature, presence of a skim dam, distributor bag deformation and presence of a spout sock. The results show two distinct modes of metal distribution. These modes are respectively caused by the buoyancy driven flow and by the presence of the bag outflow. The interactions between the studied process parameters and the two metal distribution modes are described, giving a better understanding of the resulting variations inside the ingot sump.

12:00 PM
Interaction Between Structure Formation and Melt Flow During Solidification: First Results on Experiments With Electromagnetic Pump: *Andrey Turchin*[1]; Dmitry Eskin[1]; Laurens Katgerman[2]; [1]Netherlands Institute for Metals Research, Al Production, Rotterdamseweg 137, Delft, Zuid Holland 2628 AL Netherlands; [2]Delft University of Technology, Matls. Sci. & Engrg., Rotterdamseweg 137, Delft, Zuid Holland 2628 AL Netherlands

Melt flow is intrinsic in casting processes and influences strongly the resultant microstructure of a cast product. Only few experimental data are available on effects of melt flow on structure formation during solidification. The paper describes a new experimental setup and first results on the interaction between melt flow and structure formation during solidification of an Al-4.5% Cu alloy. An electromagnetic pump is used as a base for the experimental installation that includes also a control system, a metal guiding circuit, and a water-cooled chill for solidification of an alloy under controlled melt flow conditions. Such parameters as melt temperature, flow rate (2 to 25 cm/s) and temperature gradient are controlled. The solidification patterns are formed at the bottom of the water-cooled copper chill placed on top of the channel with the moving melt. The investigated parameters are grain size, growth direction and morphology, dendritic arm spacing, macro- and microsegregation.

12:25 PM
New Insights into Flow Structure in DC Casting of Aluminum Alloys: *Miha Zaloznik*[1]; Bozidar Sarler[2]; [1]Impol d.d., R&D Dept., Partizanska 38, Slovenska Bistrica SI-2310 Slovenia; [2]Nova Gorica Polytechnic, Lab. for Multiphase Processes, Vipavska 13, Nova Gorica SI-5000 Slovenia

DC casting of an aluminum alloy billet is numerically simulated. Of central interest in this paper is the melt flow structure, which is known to affect the predominantly advective species transport and thus macrosegregation. Therefore a more accurate finite-volume method (ULTRA-QUICK) is implemented for the solution of the velocity field, in contrast to popular but inaccurate first-order upwind methods, previously widely used for computations of melt flow. Because the focus is on the flow, a simplified physical model is employed, omitting species transport, but retaining a mushy zone. The results obtained with the more accurate method reveal a much more intricate flow structure than previously known. Several additional circulation cells are present at the bottom of the liquid pool. This result has serious implications for macrosegregation, caused by the flow inside and next to the mushy zone.

Characterization of Minerals, Metals and Materials: Materials Testing and Evaluation

Sponsored by: Extraction & Processing Division, EPD-Materials Characterization Committee
Program Organizers: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; Ann M. Hagni, Construction Technology Laboratories, Inc., Microscopy Group, Skokie, IL 60077 USA; J. Y. Hwang, Michigan Technological University, Institute of Materials Processing, Houghton, MI 49931-1295 USA

Wednesday AM Room: 2010
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Mitch Loan, University of Limerick, Matls. & Surface Sci. Inst., Limerick Ireland; Jeong Guk Kim, Korea Railroad Research Institute, Railroad Safety Rsch. & Testing Ctr., Kyounggi 437-050 S. Korea

8:30 AM
Utilizing the Novel Laser Spallation Technique to Measure Copper-Dielectric Adhesion Strength in Microelectronic Packages: *Arun Raman*[1]; Jun Tian[2]; [1]Intel Corporation, ATD Q&R, Mailstop CH5-263, 5000 W. Chandler Blvd., Chandler, AZ 85226 USA; [2]University of California, Dept. of Mechl. & Aeros. Engrg., 420 Westwood Plaza, Rm. 32-121, Los Angeles, CA 90095 USA

Laser spallation is a novel high strain rate ($10^6 s^{-1}$) metrology to measure thin film adhesion. A typical characteristic of slow strain rate

adhesion tests (10^{-5}-$10^{0}s^{-1}$), such as peel and 4-point bend tests, is in the contribution of plastic and viscoelastic losses to the measured adhesion strength. With laser spallation, due to the very large strain rate, the measured adhesion strength is closer to the true intrinsic value. This study reports copper-dielectric adhesion strengths of about 180MPa measured using laser spallation on test coupons of typical organic substrates used in microelectronic packages. Upon exposure to several hours of high temperature and high relative humidity, there is a change in failure locus, associated with approximately a 25% reduction in adhesion strength. An explanation of the observed phenomena is offered. In addition, laser spallation measured adhesion strengths are also compared with measurements from the more conventionally utilized slow strain rate peel tests.

8:55 AM
Automated Ball Indentation Test Methods: Progress and Accomplishments 1989-2004: *Fahmy M. Haggag*[1]; Robert L. Bridges[2]; [1]Advanced Technology Corp., 1066 Commerce Park Dr., Oak Ridge, TN 37830 USA; [2]BWXT-Y12, LLC, PO Box 2009, Oak Ridge, TN 37831 USA

The Automated Ball Indentation (ABI) test techniques were invented in 1989 to measure key mechanical properties of metallic samples and structures in a nondestructive and localized fashion. A single ABI test replaces the tension test for metallic materials and the fracture toughness test for Ferritic steels. This paper describes the ABI test methods, the progress of their capabilities, and example laboratory and field/in-situ applications in numerous industries. The laboratory version of the patented Stress-Strain Microprobe (SSM) technology has been in commercial use since 1991, and the portable SSM version received a 1996 R&D 100 Award. In 1999, a new miniature SSM system was introduced to provide easier in-situ applicability. The accuracy, reliability, and easy field applicability of the SSM system to test materials with unknown properties have been demonstrated on samples and in-service/operating pipelines as well as on components from other industries.

9:20 AM
A Fully Automated Technique for Twin Identification Through Electron Backscatter Diffraction: *Benjamin L. Henrie*[1]; Thomas A. Mason[1]; [1]Los Alamos National Laboratory, Matl. Sci. & Tech., G755, Los Alamos, NM 87545 USA

A fully automated framework has been developed for extracting twin statistics from deformed microstructure using crystallographic twin identification techniques with spatially correlated electron backscatter diffraction (EBSD) data. The key features of this analysis are the use of the mathematical definition of twin relationships, the inclination of the common K1 plane at a twin boundary, and a voting scheme for determining the parent orientation in a parent/twin pair. Twin area fractions are categorized by operative twin systems, number of active twin variants in each system, and corrected twin widths for α-zirconium and Stainless Steel 316L.

9:45 AM
Recent Advances in Concentration of Fine Particles by Hydroseparation: Vladimir N. Rudashevsky[1]; Nikolay S. Rudashevsky[1]; *Louis J. Cabri*[2]; [1]Center for New Technologies, Roentgena St. 1, St. Petersburg Russia; [2]Cabri Consulting Inc., 99 Fifth Ave., Ste. 122, Ottawa, Ontario K1S 5P5 Canada

Study of rare and accessory minerals in rocks, ores, industrial products, and potentially polluting materials is usually limited by the scarcity and small grain size of the target minerals. Recent advances in laboratory concentration methods have applied the new technology of hydroseparation (HS-01, Rudashevsky et al., 2002; HS-02 Cabri, 2004). This water-based environmentally friendly technology is very efficient in separating trace quantities of dense minerals from fine fractions of powdered, sieved samples, but is also very sensitive to manual adjustments of the water-flow regulator (WFR) and contamination from older plumbing systems. A new model hydroseparator (HS-11) has been specially designed for automatic control of concentration of heavy fine particles,including filtering of pollutants and better control (automated) of the WFR. Tests using the HS-11 will be described, which in addition, also shows promise for scale-up of the methodology for treating coarser particles on a pilot-plant scale.

10:10 AM Break

10:20 AM
Carbothermal Reduction - Nitridation Study of Aluminum-Containing Raw Materials: *F. S. Cinar*[2]; O. Yucel[1]; B. Derin[1]; S. Ercayhan[1]; V. Kizilirmak[1]; [1]Istanbul Technical University, Faculty of Chmst. & Metall., Dept. of Metallurgl. & Matl. Engrg., 34469, Maslak, Istanbul Turkey; [2]Prof. Adnan Tekin High Technological Ceramics and Composites Research Center, 34469, Maslak, Istanbul Turkey

In this study, two different aluminum containing materials (Seydisehir Al(OH)3 and Al2O3) have been used as starting materials to produce AlN powders. For both raw materials, the carbothermal reduction and nitridation process has been carried out in a horizontal tube furnace under flow of nitrogen gas. Starting alumina and aluminum hydroxide powders were wet mixed with carbon black separately in weight ratio of 1:1 (Al2O3:C) and (Al(OH)3:C) in a ball mill for 6 hours. The effects of reaction temperature (1400-1600°C) and time (0-240 min) on the reaction mechanism and morphologies of AlN powder have been investigated using XRD, SEM, BET and sedimentation methods. Full conversion to AlN which is submicron size and spherical particles has been obtained at 1600°C for 1 hour or at 1500°C for 4 hours for experiments used Al2O3 as a starting material. However 100% AlN conversion in the samples used Al(OH)3 powder as a starting material, could not be obtained even by the reaction at 1600°C for 240 min.

10:45 AM
Investigation of Residual Stresses Superposition of D2 Dies Due to Heat Treatment and Multipass Grinding: *Olga Karabelchtchikova*[1]; Iris V. Rivero[2]; [1]Worcester Polytechnic Institute, Matls. Sci. & Engrg., 100 Inst. Rd., Worcester, MA 01609-2280 USA; [2]Texas Tech University, Industl. Engrg., Box 43061, Lubbock, TX 79409-3061 USA

The study investigated residual stresses behaviors and their superposition effect in D2 dies for thread-rolling applications. A nested factorial experiment was applied to test hypotheses that the residual stresses profiles change due to combination of heat treatment and multipass grinding operations, and that certain patterns can be derived due to the memory relationship between pre-existing and final residual stresses distributions. The amount of the retained austenite along with residual stresses in variation with depth was measured using x-ray diffraction technique. Statistical analyses indicate that the proposed hypotheses hold. Residual stresses distributions as well as tensile peak location were found to be significantly influenced by the treatment parameters used. Unique characteristic patterns in the residual stresses profiles were observed due to multipass grinding technique across all experimental conditions. This finding suggested a plausible memory relationship between the cutting passes, and the causes of the foregoing results are further proposed and discussed.

11:10 AM
An Improved Thermal Fatigue Resistance Characterisation Method for Refractories: *Roger Pelletier*[1]; Claude Allaire[1]; [1]École Polytechnique de Montréal, Engrg. Physics, CIREP - Campus CRIQ, 8475, Christophe-Colomb, Montréal, Québec H2M 2N9 Canada

Thermal shock and thermal fatigue resistances (TFR) are traditionally estimated by methods requiring significant human intervention and because of that, suffer from low lab to lab reproducibility. This paper describes a novel TFR characterisation method that reduces to a minimum this problem. In this method, the thermal cycles are produced by moving specimens from a furnace to a copper plate using a fully automated apparatus. The damage level is measured using a non-destructive method. This allows to obtain the damage evolution curve (DEC) with a single pair of specimens. Parameterisation of these curves is used to quantify the evolution of the DEC's as a function of the temperature drop amplitude. The capability of the method is illustrated with experiment results. The shape of the damage evolution curves and the significance of their parameters are also discussed.

11:35 AM
Effect of Microwave Irradiation on the Characteristics of Bentonite Particles: *Bowen Li*[1]; *Janny-Yang Hwang*[1]; Xiaodi Huang[1]; [1]Michigan Technological University, IMP, 1400 Townsend Dr., Houghton, MI 49931 USA

The modification of interlayer structure in montmorillonite is one of the most important fields for the utilization of clay minerals. The effect of microwave energy irradiation to the characteristics of bentonite particles was investigated with laser particle analysis, SEM and XRD. Heating of bentonite powder with microwave energy (2.45 GHz) started at room temperature. The sample was excited to jump around like in boiling state. After 5 minutes of microwave irradiation, there is not significant alternation on the distribution curve of the particle size of bentonite and the surface topography of montmorillonite particle. There is only a slight increase in quantity for particles in 40-90 micron range and a slight decrease in 20-35 micron range. The peak (001) of montmorillonite weakens after 1 minute with microwave irradiation, and disappeared after 5 minutes.

Computational Thermodynamics and Phase Transformations: Theory and Simulation of Alloys

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)
Program Organizers: Corbett C. Battaile, Sandia National Laboratories, Materials and Process Modeling Department, Albuquerque, NM 87185-1411 USA; Christopher Mark Wolverton, Ford Motor Company, Scientific Research Laboratory, Dearborn, MI 48121-2053 USA

Wednesday AM Room: 3005
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Jeffrey J. Hoyt, Sandia National Laboratories, Albuquerque, NM, USA

8:30 AM Invited
Predicting Structures from First-Principles Density Functional Calculations: Smoothing of Total Energy Surfaces: *Vidvuds Ozolins*[1]; Blanka Magyari-Kope[1]; Babak Sadigh[2]; [1]University of California, Matls. Sci. & Engrg., PO Box 951595, Los Angeles, CA 90095-1595 USA; [2]Lawrence Livermore National Laboratory, Livermore, CA 94551-0808 USA

Ab initio density-functional theory (DFT) methods have the potential to fundamentally change the way new material discoveries are made. However, a persistent difficulty in applying these methods to designing new materials is the need to know detailed structural information at the atomic level. Search for thermodynamically stable phases is complicated by the existence of many local minima in the configuration space, the number of which increases exponentially with the number of atoms. Even though the previous 10-20 years have seen remarkable advances in constructing predictive Hamiltonians (e.g., cluster expansion), in practice they are limited to simple lattice-based cases and one- or two-component systems. We suggest an alternative approach which searches for structures directly during a self-consistent DFT calculation. Using smoothing methods to eliminate local minima, we can efficiently search for the most stable structures in systems that consist of many (i.e., more than two) components, are not based on a lattice, and may exhibit broken symmetries. Our approach also permits calculations in the grand-canonical ensemble.

9:00 AM Invited
First-Principles Atomistic Modeling of Ordering Phenomena and Phase Diagrams: *Manfred Fahnle*[1]; Ralf Drautz[1]; Frank Lechermann[1]; Alessandro Diaz-Ortiz[2]; Reinhard Singer[1]; Helmut Dosch[1]; [1]Max-Planck-Institut fuer Metallforschung, Heisenbergstrasse 3, Stuttgart D-70569 Germany; [2]Instituto Potosino, San Luis Potosi 78231 Mexico

In this talk we first review the fundamentals of and the interrelations between the three main techniques used to represent the adiabatic energy hypersurface of a multi-component system, i.e., the expansion into many-body potentials, the cluster functionals and the cluster expansion method (CE). It is shown how perfectly transferable many-body potentials can be defined and determined ab initio, and how the many-body potentials (which focus on the positional degrees of freedom) and the CE (which focusses on the degrees of freedom of chemical ordering) can be merged to a CE not confined to lattices. Concerning the applications of the CE method, we discuss the dense sequence of ground states found for Co-Fe when varying the composition, the rich phase diagram of the ternary system (Fe-Ni)-Al, the unusual ordering phenomena at the (110)-surface of Ni-rich Ni-Al and the search for chainlike adatom configurations on Mo(112).

9:30 AM Invited
Ab-Initio Thermodynamics of Alloys: From the Local Atomic Structure to the Substitutional Ordering of One Million Atoms: *Stefan Müller*[1]; [1]University Erlangen-Nürnberg, Lehrstuhl für Festkörperphysik, Staudtstr.7, Erlangen 91058 Germany

Although density functional theory (DFT) based calculations allow us to study several bulk and surface properties of solids, they are restricted to a small number of atoms.It will be demonstrated how this limitation can be overcome by combining DFT calculations with so-called Cluster Expansion (CE) methods and Monte-Carlo simulations. This concept gives access to both, huge parameter-spaces (e.g. for ground-state searches) and systems containing more than a million of atoms (e.g. for microstructure studies). It permits us to treat alloy properties which possess a delicate temperature-dependence like mixing enthalpies, short-range order or precipitation {\em without} any empirical parameters as input, but with an accuracy that allows the {\em quantitative} prediction of experimental results. The presented examples reach from fcc- and bcc-based disordered alloys up to intermetallic compounds. The approach is extended to alloy surfaces for investigations of ordering phenomena at surfaces and segregation, i.e. the deviation of the alloy's composition in the near-surface region compared to the bulk.

10:00 AM
First Principles Calculations of Alloy Phase Diagrams by Statistical Moment and Cluster Variation Methods: Inclusion of Anharmonicity of Thermal Lattice Vibrations: *Kinichi Masuda-Jindo*[1]; [1]Tokyo Institute of Technology, Matls. Sci. & Engrg., Nagatsuta 4259, Midori-ku, Yokohama, Kanagawa 226-8503 Japan

The thermodynamic quantities of metals and alloys are studied using the moment method in the quantum statistical mechanics, going beyond the quasi-harmonic approximations. Including the power moments of the atomic displacements up to the fourth order, the free energies and related thermodynamic quantities of alloy systems are derived explicitly in closed analytic forms.[1] The configurational entropy term is taken into account by coupling the present moment expansion scheme with the cluster variation method (CVM). The energetics of the binary alloys are treated within the framework of the first-principles TB-LMTO method coupled to CPA and GPM (generalized perturbation method). The applications of the present scheme are given both for the phase separating CuAg and order-disordered binary alloys, NiAl and Ta-W alloys. [1]K. Masuda-Jindo, V. V. Hung and P. D. Tam, Phys. Rev., B67(2003)094301-1.

10:20 AM Break

10:30 AM
Modeling Mg Alloys with a Mixed-Basis Cluster Expansion: *Gus Hart*[1]; Chris M. Wolverton[2]; [1]Northern Arizona University, Physics & Astron., PO Box 6010, Flagstaff, AZ 86011-6010 USA; [2]Ford Research Laboratory, MD3028/SRL, Dearborn, MI 48121-2053 USA

Encouraged by the success of first-principles cluster expansion methods for large-scale modeling of cubic alloys, we are developing a mixed-space cluster expansion approach for hexagonal-close-packed alloys (as well as other symmetries). We have developed an explicit strain model, an essential component of cluster expansion models for modeling precipitate formation. Using the model we demonstrate the contribution of strain to the formation enthalpies of several ordering and phase-separating binary Mg alloys, and demonstrate cluster expansions for each.

10:50 AM
First-Principles Prediction of Metastable Precipitate Phase Boundaries in Al-Cu: *Chinnappan Ravi*[1]; Chris M. Wolverton[2]; Vidvuds Ozolins[3]; [1]Ford Motor Company, (Pennsylvania State University), Physl. & Environmental Scis., MD 3083/SRL Bldg., PO Box 2053, Dearborn, MI 48121 USA; [2]Ford Motor Company, Physl. & Environmental Scis., MD 3083/SRL Bldg., PO Box 2053, Dearborn, MI 48121 USA; [3]University of California, Dept. of Matls. Sci. & Engrg., Los Angeles, CA 90095 USA

In Al-Cu alloys, precipitation strengthening via heat treatment is a common practice to enhance the mechanical properties by the introduction of metastable precipitates. Knowledge of the metastable phase boundaries is important for understanding the strengthening response of various precipitate phases, as these boundaries dictate the maximum possible phase fraction of precipitate for a given composition and temperature. However, these metastable solvus boundaries are often difficult to determine unambiguously from experiment. We present here an entirely first-principles approach to computationally predict the Al-Cu solvus boundaries of the equilibrium θ (Al_2Cu) phase, as well as the metastable θ' (Al_2Cu) and GP zone phases. The calculated boundaries are obtained from first-principles T=0K energetic calculations of precipitate and solid solution phases, as well as first-principles frozen-phonon calculations of the full dynamical matrix for the vibrational free energies. Since the problem involves the dilute limit, configurational degrees of freedom are treated in a mean-field sense.

11:10 AM
The Entropy of Alloys: *Marius Stan*[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech., PO Box 1663, MS-G755, Los Alamos, NM 87545 USA

A major problem in simulating thermodynamic properties of alloys is modeling the entropy. While configurational entropy is incorporated in most stability calculations, the other components, such as the

vibrational and electronic entropy are often neglected or roughly estimated. In this work we propose a method of accounting for both configurational and vibrational entropy and discuss the electronic contribution for several actinide based alloys. The meaning of entropy in non-equilibrium thermodynamic processes is also discussed and illustrated for the case of phase transformations and diffusion.

11:30 AM
Application of the Cluster/Site Approximation to the Calculation of Multicomponent Alloy Phase Diagrams: *W. Wilson Cao*[1]; Y. Austin Chang[1]; J. Zhu[1]; S.-L. Chen[2]; W. A. Oates[3]; [1]University of Wisconsin, Dept. Matl. Sci. & Engrg., Madison, WI 53706 USA; [2]CompuTherm LLC, 437 S. Yellowstone Dr., Madison, WI 53719 USA; [3]University of Salford, Inst. for Matls. Rsch., Salford M5 4WT UK

The Cluster/Site Approximation (CSA) offers computational advantages, without loss of accuracy, over the Cluster Variation Method (CVM) in the calculation of multicomponent phase diagrams. Its ease of use and advantages are illustrated in the calculation of a prototype Cu-Ag-Au fcc order/disorder phase diagram previously calculated using the CVM.

11:50 AM
Defect Structure and Degree of Order in Ni3Ga: Experiment and Modelling: *Olga Semenova*[1]; Hiroshi Numakura[2]; Herbert Ipser[1]; [1]University of Vienna, Inst. of Inorganic Chmst., Waehringerstr. 42, A-1090 Vienna Austria; [2]Kyoto University, Dept. of Matl. Sci. & Engrg., Yoshida Hon-machi, Sakyo-ku, Yoshida Hon-machi, Sakyo-ku, Kyoto, 606-8501, Kyoto 606-8501 Japan

Intermetallic compounds with ordered crystal structure exhibit attractive high-temperature properties because of the long-range ordered (LRO) superlattice which reduces dislocation mobility and diffusion processes at elevated temperatures. In the present investigation, the compound Ni3Ga with L12-structure was employed as a model compound to perform a calculation of LRO on the base of experimental data on measurements of order-disorder kinetics by residual electrical resistometry at respective temperatures. The ordering energies in the pair interaction model and defect concentrations as a function of temperature were estimated from experimental data. It was found that the order-disorder equilibrium in Ni3Ga is reached as a result of two processes with distinctly different rates. The ordering activation energies of both fast and slow processes in Ni3Ga were found equal 1.47 eV (fast process) and 2.66 eV (slow process).The obtained results evaluated in terms of statistical-theoretical model could be compared to the Wagner-Schottky and the Bragg-Williams models, as well as, to Monte Carlo simulations.

Converter and Fire Refining Practices: Advanced Technologies

Sponsored by: Extraction & Processing Division, EPD-Pyrometallurgy Committee
Program Organizer: Alistair G. Ross, INCO, Ltd., Canadian Smelting & Copper Business, Copper Cliff, P0M 1N0 ON Canada

Wednesday AM Room: 2016
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Tim Smith, SNC-Lavalin, Copper, London, England; Phillip J. Mackey, Falconbridge Technology Centre, Falconbridge, Ontario, Canada

8:30 AM
Blister Flash Smelting - Efficient and Flexible Low-Cost Continuous Copper Process: *Jukka Tuominen*[1]; Ilkka V. Kojo[1]; [1]Outokumpu Technology Oy, Riihitontuntie 7E, PO Box 86, FIN-02201 Espoo Finland

The history of making blister copper in an Outokumpu Flash Smelting Furnace dates back to the late 1960's, when Outokumpu first piloted the Outokumpu Direct Blister (ODB) process. The first commercial scale applications have been in use at Glogow, Poland, since 1978 and at Olympic Dam, Australia, since 1988. These applications utilize special concentrates, which are low in iron, and thus the formation of slag is also low. In 1995 the same principle was applied to smelting copper matte into blister copper in industrial scale at Kennecott Utah Copper. This application, the Kennecott-Outokumpu Flash Converting process, will celebrate its 10th anniversary of commercial scale operation this year. This paper outlines the development in efficiency and flexibility of Blister Flash Smelting processes compared to other smelting and converting options. The focus is on the economical aspects i.e. on the total feasibility of both greenfield investment projects and revamping of existing smelters.

9:00 AM
An Update on Flash Converting at Kennecott Utah Copper Company: *Ryan Walton*[1]; Robert Foster[1]; David George-Kennedy[1]; [1]Kennecott Utah Copper Co - Smelter, PO Box 6001, Magna, UT 84044-6001 USA

The Flash Converting Furnace at Kennecott Utah Copper converted over 465kmt of high-grade matte in 2002 but was restricted due to low matte production to 395kmt in 2003. This paper presents updated operational performance data and describes improvements implemented since the mid 2001 rebuild. Matte burner feed distribution, silica and arsenic impacts on settler lime-based slag operability, blister laundering, uptake/boiler accretion control, and dust sulfation will be discussed, as well as current development requirements dictated by operational imperatives and furnace modification plans.

9:30 AM
Risks and Opportunities in Continuous Converting for Nickel at Inco: *Jeff Donald*[1]; Ashok Dalvi[1]; *Tony Warner*[1]; Ken Scholey[2]; *Alistair G. Ross*[2]; Cameron Harris[3]; [1]Inco Technical Services Ltd, 2060 Flavelle Blvd., Mississauga, ON L5K 1Z9 Canada; [2]Inco Ltd, Procg., 18 Rink St., Copper Cliff, ON P0M 1N0 Canada; [3]HG Engineering Ltd, 400 Carlingview Dr., Toronto, ON M9W 5X9 Canada

For processing copper, continuous converting has been successfully employed in a variety of locations, but for nickel, there has yet to be a successful commercial implementation of continuous converting technology. At Inco's Copper Cliff smelter, there are specific requirements for the production of Bessemer matte relating to downstream processing that makes continuous converting for nickel mattes even more challenging. The nickel carbonyl refineries require very low iron levels in the matte, and the sulphur deficiency must be carefully controlled such that the appropriate quantity of PGM-rich metallics are produced from matte separation. The present paper outlines continuous converter technologies that have been implemented in copper, and evaluates their potential for nickel converting. The challenges of producing a Bessemer matte to the required specifications are discussed. The economic and environmental driving forces, and the challenges of justifying a novel technology in place of productive existing equipment, are discussed.

Extractive Metallurgy: Pyrometallurgy II

Sponsored by: Extraction & Processing Division, EPD-Aqueous Processing Committee, EPD-Pyrometallurgy Committee, EPD-Waste Treatment & Minimization Committee
Program Organizers: Thomas P. Battle, DuPont Titanium Technologies, Wilmington, DE 19880-0352 USA; Edgar E. Vidal, Colorado School of Mines, Golden, CO 80401-1887 USA; Courtney A. Young, Montana Tech of the University of Montana, Metallurgical Engineering, Butte, MT 59701 USA

Wednesday AM Room: 2018
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Pat Taylor, Colorado School of Mines, Metallurgl. & Matls. Engrg., Golden, CO 80401 USA; David Robertson, University of Missouri, Dept. of Metallurgl. Engrg., Rolla, MO 65409-1460 USA

8:30 AM Cancelled
Some Fundamentals for Partial Oxygen Lead Softening - The Role of Local Oxygen Partial Pressure

9:00 AM
Some Insights on Low-Temperature Gas-Phase Carbidization of Iron-Bearing Constituents in Red Mud: Regina Caupain[2]; *Gerard P. Martins*[1]; [1]Colorado School of Mines, MME Dept., 920 15th. St, Golden, CO 80401-1887 USA

In an effort to contribute to the research on the minimization of red mud, a study was performed involving low-temperature gas-phase carbidization of iron-bearing constituents of red mud in order to obtain iron carbides, which might serve as a viable feedstock for Electric Arc Furnace steelmaking. A dried precursor red-mud cake was "crushed" and the fraction in the particle size-range, 75µm d_p 150µm, was subjected to gas-phase carbidization, thus: CO-H2 gas mixture, molar ratio: YH2:YCO = 3:1; temperature range: 560°C to 650°C and (batch) reaction times of 15 to 45 minutes. Sooting never occurred during the

carbidization processing. Mössbauer analyses revealed that the iron-bearing phases in the carbidized product constituted 760wt.% cementite (Fe3C), 079wt% Hägg carbide (Fe5C2), 011wt.% Fe2O3, 08wt.% Fe3O4, 012wt.% Fe and 1028wt.% of an unidentified (nano-size) non-magnetic iron oxide phase. With longer reaction-times and higher reaction-temperatures the Hägg carbide content increased – this behavior was ultimately traced to the manner in which the reaction was quenched.

9:30 AM
Carbothermic Reduction of Nickel Oxide and Iron Oxide Containing Kiln Dust in an Inert Atmosphere at Elevated Temperatures: Glenn Hoffman[1]; *Jim McClelland*[1]; [1]Midrex Technologies, Inc., 2725 Water Ridge Pkwy., Charlotte, NC 28217 USA

Carbothermic direct reduction of a saprolite origin kiln dust containing nickel oxide and iron oxide was investigated under FASTMET and ITmk3 process conditions at temperatures ranging from 1,150 to 1,500°C. Carbon containing compacts were produced from the kiln dust and pulverized coal using a hydraulic press. The compacts were heated under inert atmosphere in a tube furnace at various temperatures. Reduction kinetics and rate controlling phenomena regarding thermal processing of the saprolite origin kiln dust will be discussed.

10:00 AM
Solid Oxide Membrane (SOM) Technology for Cost Effective and Environmentally Sound Production of Metals and Alloys Directly from their Oxides and Ore Concentrates: *U. B. Pal*[1]; A. Krishnan[1]; X. Lu[1]; [1]Boston University, Dept. of Mfg. Engrg., 15 St. Marys St., Brookline, MA 02446 USA

Recent progress in the use of Zirconia-based inert anodes for extraction of metals such as Ta and Mg directly from their oxides by the SOM (Solid Oxygen Ion Conducting Membrane) electrolytic process is highlighted. In the case of Mg the oxide is dissolved in the flux, and in the case of Ta the oxide can either be dissolved in the flux or used as part of the cathode. Fundamental aspects of the current-potential behavior are analyzed. Since the Zirconia-based anode is the most expensive part of the system, its long-term stability is critical to the success and eventual commercialization of the SOM process. Different ways to increase membrane stability as well as metal production rate are discussed.

10:30 AM Break

10:45 AM
Crystal Morphologies of ZnO Obtained by Oxidizing Zinc Vapor: *Yi-feng Chen*[1]; Mo-tang Tang[1]; [1]Central-South University, Sch. of Metallurgl. Sci. & Tech., Changsha, Hunan 410083 China

Effects of conditions of oxidizing zinc vapor at high temperature on the crystal morphologies of ZnO and relations of various morphologies are investigated in this paper. Results show that there are five typical morphologies-amorphous, granular, needle, tetrapod and multipod-like ZnO, depending on the physical chemical conditions of oxidizing zinc vapor and having no direct relations with particle size and surface conditions of zinc powders, the raw materials. The behavior of oxidizing zinc vapor varies with oxygen partial pressure, which leads to produce ZnO crystals of different morphologies that can be controlled by the change of preparing conditions.

11:15 AM
Preparation of Fibrillar Nanocrystalline Nickel Powder by Precursor Thermal Decomposition: Wu Jian Hui[1]; *Zhang Chuan Fu*[1]; Zhan Jing[1]; Li Chang Jun[1]; Bai Meng[2]; [1]Central South University, Sch. of Metall. Sci. & Engrg., Changsha, Hunan China; [2]JiangXi Copper GuiXi Smelter HuaXin Metal Liabilities Co., Ltd, Guixi, Jiangxi 335424 China

The precursor thermal decomposition process of fibrillar nanometer scale nickel powder and passivation treatment of obtained powder are investigated, and the composition and morphology of the products are characterized by use of IR, TGA/DTA, XRD and SEM. The results show that the precursor morphology is a decisive factor to the product morphology of the nickel powder. The morphology of the product derived at low decomposing temperature is irregular. The nickel powders produced at temperatures higher than 480 C cohere seriously. The product particles are reunited with the decomposition time prolong. The powder prepared under the optimal condition is fibrillar like woolen yarn and the grain diameter is less than 50nm.

11:45 AM
Reduction Kinetics of Dusts and Pellets from Nickeliferous Laterite Rotary Kiln Treatment: *Emmanuel N. Zevgolis*[1]; Ismene-Polyxeni Kostika[1]; Iliana Halikia[1]; Elias Rigopoulos[2]; [1]National Technical University of Athens, Sch. of Mining & Metallurgl. Engrg., Zografou Campus, 15780, Athens Greece; [2]Silver and Baryte Mines, Metallurgl. Engrg., Milos Island Greece

In this work, the reduction kinetics of dust from nickeliferous Greek laterites is presented. The dust is a by-product from laterite treatment in rotary kilns and it comes from washing towers, electrostatic filters and polycyclones. Pellets made from this dust were also examined. Reducibility was studied in the temperature range of 700°C to 850°C in a laboratory tube furnace. From this study it comes that initially the chemical reaction mechanism prevails in the reduction process, followed by the mixed kinetic model, in the first period of reduction. After that period, reduction becomes diffusion controlled. These results fit well with the experimental data until 800°C. At higher temperatures, diffusion is the rate controlling-step. Activation energy values calculated by Arrhenius law, confirm the proposed mechanisms.

Friction Stir Welding and Processing III: Modeling

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Shaping and Forming Committee
Program Organizers: Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Thomas J. Lienert, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Wednesday AM Room: Nob Hill C/D
February 16, 2005 Location: San Francisco Marriott

Session Chair: Stan A. David, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

8:30 AM Keynote
Using Process Forces as a Statistical Process Control Tool for Friction Stir Welds: *William J. Arbegast*[1]; [1]South Dakota School of Mines and Technology, Advd. Matls. Procg. & Joining Lab., 501 E. St. Joseph St., Rapid City, SD 57701 USA

Many OEM equipment manufacturers now provide for direct measurement of and feedback control on the principle forces (X-, Y-, and Forge) experienced during friction stir welding. Analysis techniques are being developed to convert these force measurements into SPC and feedback control algorithms that can be used to real-time monitor and control weld quality. Descriptions, examples and limitations of the X-Force, Pseudo-Heat Index, Direction Cosine, Resultant Force, and Fourier Transform control algorithms being developed at the Advanced Materials Processing Center are given. Correlations are made between processing parameters, algorithm results, metal flow patterns and the "FSW Metalworking Model", and, their relationship to weld quality.

9:00 AM Invited
Modeling, Analysis, and Validation of Friction Stir Welding and Processing: *Abe Askari*[1]; Stewart Silling[2]; Blair London[3]; Murray Mahoney[4]; [1]Boeing Company, PO Box 3707, MC 7L-25, Seattle, WA 96124-2207 USA; [2]Sandia National Laboratories, Albuquerque, NM USA; [3]California Polytechnic State University, San Luis Obispo, CA USA; [4]Rockwell Scientific, Thousand Oaks, CA USA

We have successfully developed predictive computational tools to model friction stir welding/processing (FSW/P). The model is based on a three-dimensional Eulerian code with complete thermo-mechanical coupling. The code models all the important physical effects with few assumptions. The code includes frictional heating and energy dissipation due to plastic work, thermal convection and conduction, and all relevant geometrical tool details. The Eulerian nature of the code permits modeling very large strains and predicts materials mixing. The model also predicts detailed thermal and deformation histories that impact the final microstructure. Detailed experiments and data analysis in aluminum, bronze, and steel alloys are used to validate the computational models and improve understanding of basic aspect of FSW/P processes. Placement of both tracers and thermocouples in the tool path, metallographic examination, and computed tomography are used to investigate metal flow dynamics and the mixing of material as well as thermal profile and history.

9:20 AM
An Analytical Model for Prescribing the Flow Around the Tool Probe in Friction Stir Welding: *H. Schmidt*[1]; J. Hattel[1]; [1]Technical University of Denmark, Process Modlg. Grp., Dept. of Mfg. Engrg. & Mgmt., Denmark

The objective of this paper is to present a simple model for prescribing a 2D velocity field for the material flow in the shear layer around the probe in Friction Stir Welding (FSW). By introducing an eccentrically shaped shear layer, and assuming a linear velocity profile between the welding flow outside the shear layer and the rotating velocity flow at the probe/shear layer interface, a robust 'model' for evaluating different aspects of the flow is presented. The model takes into account that the material entering the shear layer in front of the probe is transferred around the retreating side of the probe, which in turn calls for a non-symmetrical flow pattern due to the accumulation of material in the shear layer at the leading side and deposition at the trailing side. The rotation zone and transition zone are parts of the model. The model satisfies mass conservation, however, the momentum equations are not solved for. By displaying the velocity vector components, the flow field can be visualized as well as a phenomenological interpretation of a change in welding parameters. As input to the model, at least two parameters out of three variables are necessary. The three variables are: The shear layer thickness at two positions and the contact state variable. The shear layer is characterized by at least one reference thickness, e.g. at the advancing or retreating side. A uniform contact state variable is assumed at the probe/shear layer interface, i.e. the ratio between the tangential speeds of the probe and shear layer interface is constant along the circumference. Based on this, a rough estimate of flow rates in experimental welds can be made. Secondly, by measuring some specific dimensions from welds using marker material, average speeds and shear layer properties can be estimated with the model.

9:40 AM
Three-Dimensional Finite Element Model of the Friction Stir Spot Welding Process: *Karim Heinz Muci-Kuchler*[1]; Sri Satya Teja Kakarla[1]; Casey D. Allen[2]; William J. Arbegast[2]; [1]South Dakota School of Mines and Technology, Mechl. Engrg. Dept., 501 E. St. Joseph St., Rapid City, SD 57702 USA; [2]South Dakota School of Mines and Technology, Advd. Matls. Procg. Ctr., 501 E. St. Joseph St., Rapid City, SD 57701 USA

Friction Stir Spot Welding (FSSW), originally developed by GKSS (Germany), has a strong potential to find applications in both the automotive and aerospace industries. At the present time, research efforts are taking place to gain a better understanding of the process, to explore different tool configurations, and to optimize the set of process parameters. In this regard, having a finite element model capable to simulate FSSW can be very useful to reduce the number of physical experiments required in those studies. In this paper, a simplified isothermal three-dimensional model of the FSSW process is presented. The model, based on a solid mechanics approach, was developed using the commercial software ABAQUS/Explicit. The results of the simulation are compared against available experimental information corresponding to the same tool geometry, sequence of operations, and process parameters.

10:00 AM
Analysis and Numerical Modeling of FSW Spot Welding Al 5754 and AZ91 Base Materials: *Adrian P. Gerlich*[1]; Peter Su[1]; Tom H. North[1]; Gabor Bendzsak[1]; [1]University of Toronto, Matls. Sci. & Engrg., 184 College St., Rm. 140, Toronto, ON M5S3E4 Canada

This paper presents the results produced during friction stir spot welding of Al-alloy (Al5754) and Mg-alloy (AZ91D) base materials for automotive applications. The FSW spot welding process were investigated using a combination of high-speed data acquisition output (axial force, torque, displacement and temperature), metallographic examination of completed joints and numerical modeling. The peak temperatures during FSW spot welding of Al 5754 was 0.96 Ts, where Ts is the solidus temperature of Al 5754 base material (590ºC). The peak temperature attained during FSW spot welding of Mg-alloy base material was 435ºC, which is very close to the melting temperature of the Mg-Al solid solution/Al12Mg17 eutectic (437ºC). Numerical modeling of the spot FSW process is carried out by implementing CFD techniques to simulate flow fields and the temperature distributions during welding. Simulation results are validated using metallographic cross sections and data acquired from thermocouple outputs.

10:20 AM Break

10:40 AM Invited
Modeling the FSW Process Using an Eulerian Finite Element Formulation: *Paul R. Dawson*[1]; Jae-Hyung Cho[1]; [1]Cornell University, Sibley Sch. of Mechl. & Aeros. Engrg., 196 Rhodes Hall, Ithaca, NY 14853 USA

Friction stir welding of stainless steel is modeled using a steady-state Eulerian finite element formulation. The governing equations for the velocity field, temperature distribution, and strength evolution are coupled to determine the thermomechanical history of the workpiece material. The viscoplastic behavior of the steel is modeled using a modified Hart's model in which a staturation flow stress is incorporated into a Voce-type hardening equation. During the welding process, intense shearing near tool causes rapid heating from viscous dissipation and an increased strength from strain hardening. Texture evolution is predicted from the computed velocity gradients along streamlines of the flow field. Upstream and downstream of the tool the deformation is nearly monotonic, causing steady strengthening of the texture. Material rotation around tool pin, however, causes the texture to form, break up, and reform repeatedly and rapidly. Mechanical properties such as elastic modulus, strength and R-value are analyzed from the deformation textures.

11:00 AM
CFD Modelling of the Shear Layer Around the Tool Probe in Friction Stir Welding: *H. Schmidt*[1]; J. Hattel[1]; [1]Technical University of Denmark, Process Modlg. Grp., Dept. of Mfg. Engrg. & Mgmt. Denmark

The present paper focuses on the formation of the shear layer around the probe in Friction Stir Welding (FSW). Aluminium alloys can be characterized as shear thinning or pseudo plastic which is the main reason for the development of very thin shear layer in FSW. A 2D CFD model using the FE software FEMLAB is presented. In order to analyse the flow field, a cylindrical probe rotating co-axially with the tool is modelled. At high shear rates, aluminium is well described by the power law shear rate-shear stress relationship. By changing the power law exponent (m), the degree of non-Newtonian, shear thinning behaviour of the material is investigated, and the effect is reflected in the change in shear layer properties. By following streamlines around the tool probe, a clear definition of the rotation and transition zone is proposed. A uniform contact condition is assumed at the probe/shear layer interface, thus a constant velocity boundary condition is prescribed. The results show that the shape/extent of the shear layer is highly dependent on the power law exponent. Higher shear rates (in the range of 1000 s-1) and narrowing of the shear layer are found for lower exponents. The extent of the simulated shear layer corresponds best to that observed in experiments for m=0.1. Due to the presence of the rotation zone, material entering and exiting the transition zone obtain peak velocities of a fraction (~0.5) of the maximum velocity found at the contact interface.

11:20 AM
Investigation of the Hot Deformation Characteristics During Friction Stir Welding of High-Purity Aluminum: *Bala Radhakrishnan*[1]; Zhili Feng[1]; Gorti Sarma[1]; Oleg Barabash[1]; Stan A. David[1]; [1]Oak Ridge National Laboratory, Computer Sci. & Math., Bldg. 5600, MS 6008, Oak Ridge, TN 37831-6008 USA

The quasi steady-state three-dimensional thermal and flow fields in the vicinity of the tool during friction stir welding of high-purity aluminum are modeled using the commercial flow software, FLUENT. The viscosity of aluminum is calculated from available stress-strain data at various temperatures and strain rates and used in the flow computations. From the steady state temperature and strain-rate fields the operating Zener-Hollomon parameters are calculated at various distances from the tool, and used to predict the size and shape of the swirl zone. The model results are compared with experimentally measured profiles for the swirl zone. The deformation substructure in terms of the grain size, grain size distribution, texture and grain boundary misorientation distribution are measured using orientation imaging microscopy. The model predictions combined with experimental measurements of substructure are used to elucidate whether dynamic recovery or dynamic recrystallization was the operating mechanism during hot deformation in the swirl zone.

11:40 AM
Model for Local Proof Strength of 2xxx Welds: *Marco J. Starink*[1]; Shuncai Wang[1]; Diccon P.P. Booth[1]; Ian Sinclair[1]; [1]University of Southampton, Matls. Rsch. Grp., Sch. of Engrg. Scis., Southampton SO17 1BJ UK

The microstructure development, and resulting hardness and yield strength profiles of 2xxx welds are modelled using a model which combines primary precipitation, coarsening, resolution, partial/full melting and resolidification (Sheil type) and re-precipitation. The strength contribution is dominated by two types of precipitates: the Cu-Mg clusters which form at low temperature and dissolve at temperatures above about 230C, and the S phase which dominates the reaction at the location of peak strength as well as at the locations of minimum strength. The model is compared to microstructural and hardness data on a friction stir weld.

Frontiers in Thin Film Growth and Nanostructured Materials: A Symposium in Honor of Prof. Jagdish Narayan: Advanced Technology and Applications I

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Orin Wayne Holland, University of North Texas, Department of Physics, Denton, TX 76203 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Stephen J. Pennycook, Oak Ridge National Laboratory, Sold State Division, Oak Ridge, TN 37831 USA; Rajiv K. Singh, University of Texas, Austin, TX 78758-4455 USA

Wednesday AM Room: 3020
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Carl C. Koch, North Carolina State University, Matls. Sci. & Engrg., Raleigh, NC 27695-7907 USA; Roumiana S. Petrova, New Jersey Institute of Technology, Physics, Newark, NJ 07102 USA

8:30 AM
Beyond DLC: Development of Atomically Smooth Nanometer-Thick Protective Coatings for Extremely High-Density Recording Applications: *Yip-Wah Chung*[1]; [1]National Science Foundation, Civil & Mechl. Sys., Rm. 545.25, 4201 Wilson Blvd., Arlington, VA 22230 USA

In mid-2004, hard disk drives have storage densities in excess of 50 Gbits/in^2, which will increase to about 1 Tbit/in^2 within the next five years. In order to attain this storage density, the separation between the read-write head and the magnetic layer cannot be more than 5.0 nm. This creates interesting materials and engineering challenges to the manufacturing of such systems. One key challenge is the development of overcoats that are used to protect the disk and head surfaces from wear and corrosion. The thickness of this coating must be 1.0 nm or less. In this talk, we will focus on the development, synthesis, characterization and limitations of these overcoats for future disk drive applications. In addition, we will explore the application of molecular dynamics simulations to aid the synthesis of such coatings.

9:00 AM
Formation of Hydrogen-Free Diamond-Like Carbon: Theory and Experiment: *J. D. Haverkamp*[1]; [1]North Carolina State University, Dept. of Matls. Sci. & Engrg., Raleigh, NC 27695-7916 USA

Hydrogen-free diamond-like carbon films are known to possess interesting mechanical, optical, and electronic properties. These properties are fundamentally related to the fraction of sp^3 coordinated carbon atoms and the ordering of sp^2 coordinated carbon atoms in the diamond-like carbon film. It is therefore of interest to understand the mechanisms by which diamond-like carbon films are formed. To investigate this, diamond like carbon films are grown using pulsed laser deposition over a range of laser energy densities. Film properties are determined via electron energy-loss spectroscopy and visible Raman spectroscopy. Properties of the plasma created in pulsed laser deposition are studied using quadruple Langmuir probes, mass loss measurements, and magnetic field measurements. We propose a new model for the formation of hydrogen-free diamond-like carbon films based upon an activation barrier and electronic excitation of incident atoms. The model quantitatively predicts the sp^3 fraction as a function of pulsed laser energy density. The kinetic energy of incident species is shown to be a leading factor controlling the sp^3 fraction of deposited films, as the kinetic energy controls the interaction of the incident atom with the film. It is shown that the kinetic energy of neutral atoms is an important factor in the growth of diamond-like carbon films with pulsed laser deposition.

9:30 AM
Highly Nonlinear Contact Interaction, Dynamic Energy Dissipation and Nano-Fragmentation of Carbon Nanotubes: *Chiara Daraio*[1]; Vitali F. Nesterenko[1]; Joseph F. Aubuchon[1]; Sungho Jin[1]; [1]University of California, Matls. Sci., 9500 Gilman Dr., MC 0418, EBU2 - Rm. 266, La Jolla, CA 92093 USA

Mechanical response and energy dissipation of an array of carbon nanotubes under high-strain rate deformation was studied using a simple, drop-ball test with measurement of dynamic force between the ball and forest of nanotubes. The contact force exhibits a strongly nonlinear dependence on displacement, which is fundamentally different in comparison with the Hertz law. It is demonstrated that a forest of vertically aligned nanotubes may be successfully used as a strongly nonlinear spring in discrete systems, for monitoring signal propagation speed, and as a novel microstructure for localized energy absorption. We also report a new phenomenon of dynamic nano-fragmentation of carbon nanotubes by high-strain-rate stresses. The drop ball test caused them to break up into short segments in just 15 microseconds with a relatively uniform length range of ~100 - 150 nm. The ends of the fragmented nanotubes often exhibit an irregular oval or hexagonal cross-section. The observed cutting of nanotubes may conveniently be utilized for their resizing and end-opening for a variety of applications.

9:45 AM
Gel Stability in a Liquid Crystal System and Application to a Novel Templating Liquid Crystal: *Christopher R. Lubeck*[1]; Fanny Darmawan[1]; William C. Ewing[1]; Fiona M. Doyle[1]; [1]University of California, Matls. Sci. & Engrg., 210 Hearst Mining Bldg. # 1760, Berkeley, CA 94720-1760 USA

Liquid crystals can template inorganic semiconductors such as cadmium sulfide and zinc sulfide. The efficacy of the liquid crystalline system depends upon two major factors, the stability of the gel and the crystal structure of the inorganic phase. This paper investigates the former. Gel stability can be assessed through differential scanning calorimetry, notably the transition temperature at which the gel goes from an ordered to a disordered state. Various factors that may be manipulated during synthesis, such as the ionic concentration and the relative proportion of solvent to liquid crystal, can affect gel stability. These were examined. In addition, novel liquid crystalline systems were synthesized, and their ability to template inorganic phases was investigated. The resulting particles were characterized via transmission electron microscopy and atomic force microscopy.

10:15 AM Break

10:30 AM
ZnO Nanowire Devices: *Steve Pearton*[1]; [1]University of Florida, Matls. Sci. & Engrg., PO Box 116400, Gainesville, FL 32611 USA

The large surface area of the nanorods makes them attractive for gas and chemical sensing, and the ability to control their nucleation sites makes them candidates for micro-lasers or memory arrays. In addition, they might be doped with transition metal ions to make spin-polarized light sources. To date, most of the work on ZnO nanostructures has focused on the synthesis methods and there have been only a few reports of the electrical characteristics Single ZnO nanowire metal-oxide semiconductor field effect transistors (MOSFETs) were fabricated using nanowires grown by site selective Molecular Beam Epitaxy. When measured in the dark at 25°C,the depletion-mode transistors exhibit good saturation behavior, a threshold voltage of ~-3V and a maximum transconductance of order 0.3 mS/mm .Under ultraviolet (366nm) illumination, the drain-source current increase by approximately a factor of 5 and the maximum transconductance is ~ 5 mS/mm. The channel mobility is estimated to be ~3 cm2 /V.s, which is comparable to that reported for thin film ZnO enhancement mode MOSFETs and the on/off ratio was ~25 in the dark and ~125 under UV illumination. Pt Schottky diodes exhibit excellent ideality factors of 1.1 at 25°C and very low(1.5x10 -10A, equivalent to 2.35A.cm-2, at -10V) reverse currents. The on-off current ratio of the diodes at 0.15/ -5V was ~6. The nanowire diodes show a strong photoresponse, with the current-voltage characteristics becoming Ohmic under ultraviolet(UV) illumination(366nm light) with nanowire conductivity under UV exposure of 0.2 Ohm.cm. The photoresponse showed only a minor component with long decay times (tens of seconds)thought to originate from surface states. The results show the high quality of material prepared by MBE and the promise of using ZnO nanowire structures for solar-blind UV detection. In the temperature range from 25-150 úC, the resistivity of nanorods treated in H2 at 400 úC prior to measurement showed an activation energy of 0.089+/- 0.02 eV and was insensitive to the ambient used (C2H4,N2O,O2 or 10%H2 in N2). By sharp contrast, the conductivity of nanorods not treated in H2 was sensitive to trace concentrations of gases in the measurement ambient even at room temperature, demonstrating their potential as gas sensors. These results show the ability to manipulate the electron transport in nanoscale ZnO devices.

11:00 AM
New Novel Cu-Doped Above Room Temperature: *K. V. Rao*[1]; [1]Royal Institute of Technology, Dept. of Matls. Sci., Stockholm Sweden

Of late, a unusual new type of carrier induced magnetic long range ordering in dilute doped semiconductors has been demonstrated in a number of systems. Among these GaMnAs system has been the most studied material with the highest reported ferromagnetic ordering temperature of around 172K. Dietl et al predicted on a theoretical basis

that ZnO doped with Mn would be an above room temperature ferromagnetic semiconductor. ZnO is a well known electronic material with many desirable features and multivalued properties, with a wide range of applications. However, most of the studies reported on Mn doped ZnO until recently have been misleading, if not unsuccessful, mainly because of the processing conditions. We have for the first time reported in Nature materials (Oct issue 2003) methods to tailor the homogeneous ferromagnetic property into Mn doped ZnO. However, the saturation magnetization Ms and the moment per Mn atom obtained in the actual measurements is much smaller than the expected theoretical value. In order to enhance the carrier concentration and obtain higher Ms values we have co-doped ZnO:Mn with Cu to find that the magnetization can be enhanced by over 150% with as low a concentration as 4 at% Cu. Electronic structures of these materials investigated by using XES, XAS and RIXS confirm that Cu doping increases the hole concentration while maintaining the basic electronic structure of the matrix unchanged. In view of these results we doped ZnO with Cu alone and found it to be ferromagnetic with Tc above 450C. Such a phenomenon observed in ZnO:Cu which contains no magnetic transition elements at all is rather unusual. Some of these studies on new novel oxides, sulphides, and phosphides will be presented. Room temperature ferromagnetism in dilute doped semiconductors containing no magnetic elements is indeed a new challenging phenomenon. * with Amita Gupta, Pamanand Sharma, Jinghua GuO, R. Ahuja and B. Johansson.

11:30 AM

Epitaxial Growth of High Performance Superconducting Wires on Rolling-Assisted Biaxially-Textured Substrates (RABiTS): *Amit Goyal*[1]; [1]Oak Ridge National Laboratory, PO 2008, MS 6116, Oak Ridge, TN 37831-6116 USA

This talk will summarize the development of long lengths of flexible, single-crystal-like wires of YBa2Cu3Ox (YBCO) superconductor via epitaxial growth of the superconductor on Rolling-assisted-biaxially-textured-substrates (RABiTS). The RABiTS technique employs simple and industrially scalable thermomechanical processing routes to obtain long lengths of near single-crystal-like, cube-textured substrates. Epitaxial buffer layers of various cubic oxides (of rock salt, fluorite, perovskite and pyrochlore crystal structures) are then deposited in a reel-to-reel configuration using web-coating employing electron-beam evaporation, sputtering or solution routes. Epitaxial YBCO is then deposited using either ex-situ or in-situ methods to form a single-crystal-like superconducting wire. Such superconducting wires have critical current densities in long lengths of 3 Million Amps/cm2 at 77K in self-field. Incorporation on self-aligned nano-particles of second phases within the YBCO layer further enhances the in-field performance of the superconducting wires. This talk will provide a status of the RABiTS method of fabricating superconducting wire and will outline the path towards eventual realization of large-scale, bulk applications of superconductors.

12:00 PM

Half-Metallic Oxides for Spintronic Applications: *Arunava Gupta*[1]; [1]University of Alabama, MINT Ctr., Dept. of Chmst., Cheml. & Biological Engrg., Tuscaloosa, AL 35487 USA

The emerging field of spintronics aims to exploit the electron spin, in addition to its charge, to create a new class of devices that scale down to much smaller dimensions with possibly added functionalities. Of particular relevance are magnetic tunnel junctions (MTJs), consisting of two ferromagnetic electrodes separated by an insulating barrier, that exhibit large tunneling magnetoresistance (TMR) at relatively low fields. The MTJs are promising for a host of applications including magnetic memory (MRAM), sensors and storage devices. Most of the studies on MTJs have thus far focused on using transition metal ferromagnets (Fe, Ni, Co) and their alloys - typically with spin polarization values less than 50% - where the maximum observed TMR is limited to about 40-50% at room temperature. There is obvious interest in further enhancing the TMR by using materials with a higher degree of spin polarization. Half-metallic systems, which contain a gap in one spin band at the Fermi level and no gap in the other spin band, are expected to have a spin polarization value approaching 100%. Band structure calculations have shown that a number of magnetic oxide materials, such as the mixed-valence manganites (La1-xAxMnO3, A=Ba, Sr, or Ca), magnetite (Fe3O4), and chromium dioxide (CrO2), are half-metallic. With appropriate choice of barrier materials, MTJs have been fabricated using these oxides that exhibit reproducible tunneling characteristics with very high TMR in some cases. However, the enhancement has thus far been limited to low temperatures. I will present an overview of the work in this field over the past few years, including the growth and properties of thin films of this unique class of materials.

General Abstract Session: Mechanical Behavior—Dynamic Loading

Sponsored by: TMS

Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John J. Chen, University of Auckland, Department of Chemical & Materials Engineering, Auckland 00160 New Zealand; James C. Earthman, University of California, Department of Chemical and Materials Science, Irvine, CA 92697-2575 USA

Wednesday AM Room: 2020
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Michael J. Mills, Ohio State University, Matls. Sci. & Engrg., Columbus, OH 43210 USA

8:30 AM

The Ultrasonic Fatigue Behavior of the Ti 6Al-2Sn-4Zr-6Mo: C. J. Szczepanski[1]; A. Shyam[1]; S. K. Jha[2]; J. M. Larsen[3]; C. J. Torbet[1]; S. Johnson[1]; *J. W. Jones*[1]; [1]University of Michigan, Matls. Sci. & Engrg., Ann Arbor, MI 48109 USA; [2]Universal Technology Corporation, Dayton, OH 45432 USA; [3]AFRL/MLLMN Wright Patterson AFB, Matls. & Mfg. Direct., Dayton, OH 45433 USA

A rapid method for characterizing the fatigue crack growth behavior in the short crack regime has been developed and applied to study the fatigue behavior alpha + beta-processed Ti-6246. The measurement of very low fatigue crack growth rates was accomplished by tracking crack initiation and growth from small surface micronotches produced by femtosecond pulsed laser machining. An ultrasonic fatigue apparatus, operating at 20 kHz, was used to grow cracks at room temperature at load ratio of R=0.05. Crack length was acquired in real time using a telescopic digital image acquisition system. The role of microstructural, including micronotch severity, on crack growth was examined and a model for short crack growth in this titanium alloy was developed. This model is used to examine the importance of crack initiation in the very long life fatigue behavior of Ti-6246.

9:00 AM

Characterization of In Vitro Fatigue Crack Growth in Nitinol for Endovascular Stent Applications: *Jessica Stankiewicz*[1]; Scott W. Robertson[1]; Xiao-Yan Gong[2]; Robert O. Ritchie[1]; [1]University of California & Lawrence Berkeley National Laboratory, Matls. Scis. Div., MS 66-202, Berkeley, CA 94709 USA; [2]Nitinol Devices & Components, 47533 Westinghouse Dr., Fremont, CA 94539 USA

The unique mechanical properties, particularly superelasticity, of Nitinol, coupled with its biocompatibility, have made it a preferred choice for many biomedical devices. Prominent among these applications are endovascular stents which have features generally on the order of millimeters or smaller. It is important that the fracture and fatigue properties of Nitinol are characterized on such a size-scale in realistic product forms in order to minimize the chance of in vivo failures. This paper documents research in the area of Nitinol fatigue using a damage-tolerant approach to characterize crack growth. Critical to the validity of testing was conducting these experiments using Nitinol samples with similar texture, heat treatment, and stress history as fully-processed stents. Using thin-walled Nitinol tubes that are the starting material for such stents, this research examines the in vitro behavior of compact-tension specimens that have been cut and flattened from tubes for crack growth studies.

9:30 AM

The Role of Microstructure in Fatigue Life of Colony Ti-6Al-4V: *Alison K. Polasik*[1]; M. J. Mills[1]; J. M. Larsen[2]; H. L. Fraser[1]; [1]Ohio State University, Matls. Sci. & Engrg., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]Air Force Research Laboratory, Matls. & Mfg. Direct., AFRL/MLLMN, Wright-Patterson AFB, OH 45433-7817 USA

A necessary step towards the accelerated insertion of titanium alloys in aircraft engine components is the development of microstructurally-based models of fatigue parameters. Within this goal, the focus of this work is to develop a more detailed understanding of the effect of microstructural features on the fatigue behavior of α/β titanium alloys. Fatigue lifetime tests were conducted for two populations of β-processed Ti-6Al-4V that were subjected to different heat treatments. High resolution SEM imaging was coupled with novel stereological procedures capable of extracting 3-dimensional microstructural information from 2-dimensional micrographs of Ti alloys in

order to quantify key microstructural features in the two sample populations. These numerical values, along with the test conditions, were then used as inputs in a fuzzy logic model to isolate the microstructural features and determine their impact on lifetime, as well as to predict fatigue lifetime based on microstructural parameters were developed. Additionally, this analysis allowed for targeted application of extensive characterization techniques, including OIM, TEM and site-specific TEM foil extraction using the Focused Ion Beam. This research has been supported in part by the US Air Force under the STW-21 Program and by NSF under the Fellowship program.

10:00 AM
High Strain Rate Loading of nc Ni: Experiments and Simulation: *Eduardo M. Bringa*[1]; Y. M. Wang[1]; J. A. Caro[1]; M. Victoria[1]; A. M. Hodge[1]; J. McNaney[1]; B. Torralva[1]; B. A. Remington[1]; R. Smith[1]; C. A. Schuh[2]; B. Wu[2]; H. Van Swygenhoven[3]; [1]Lawrence Livermore National Laboratory, Livermore, CA 94550 USA; [2]Massachusetts Institute of Technology, Cambridge, MA 02139 USA; [3]PSI, Villigen CH-5232 Switzerland

We present experiments and simulations of laser-induced deformation of eletrodeposited nanocrystalline (nc) Ni at strain rates larger than 10^6/s. These strain rates make possible a direct comparison between experiments and molecular dynamics simulations. TEM of material recovered after loading shows that nanograins survive the loading, with some grain growth and grain refinement, and some grains containing large dislocation densities. Nano-indentation of recovered samples gives changes in hardness with complex pressure dependence due to the interplay between: a) large dislocation densities generated during loading, which increase hardness and b) grain growth due to thermal processing, which decreases hardness. Atomistic simulations show high dislocation densities created during loading, even for grains smaller than 10 nm, with partial recovery of the dislocations after unloading and thermal recovery, in agreement with the experimental findings. Work was performed under the auspices of the U.S. DoE by UC, LLNL, contract No.W-7405-Eng-48, LDRD 04-ERD-021.

10:30 AM Break

10:45 AM
On the Failure of NiAl Bicrystals During Laser-Induced Shock Compression: *Eric Loomis*[1]; Pedro Peralta[2]; Damian Swift[3]; Ken McClellan[4]; [1]Arizona State University, MAE, Tempe, AZ 85281 USA; [2]Arizona State University, Dept. of Mechl. & Aeros. Engrg., Tempe, AZ 85287-6106 USA; [3]Los Alamos National Laboratory, Physics, Los Alamos, NM 87545 USA; [4]Los Alamos National Laboratory, MST-8, Los Alamos, NM 87545 USA

Thin NiAl bicrystals 5 mm in diameter and 150 to 350 microns thick were tested under laser-induced shock compression to evaluate the material behavior and the effect of localized strain at the grain boundary on the failure of these specimens. Circular NiAl bicrystal samples with random misorientation were grown and prepared for shock compression at pressures below 10 GPa. Transmission electron microscopy was performed in the bulk of one grain following laser-shock testing and showed that plastic deformation occurred in a periodic fashion through nucleation of dislocation clusters at the shock front. Cracking on the free surface of the samples revealed a clear grain boundary affected zone due to scattering of the shock wave and variations in wave speed across the inclined boundary. The damage locations in these samples correlated well to the regions in which the transmitted waves impinged on the free surface as predicted by elastic scattering models.

11:15 AM
Shock and Recovery of Polytetrafluoroethylene (Ptfe) Above and Below the Phase II to Phase III Transition: *Eric Nathaniel Brown*[1]; Philip J. Rae[2]; Dana M. Dattelbaum[3]; David L. Robbins[3]; G. Rusty Gray[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech., TA-35, Bldg. 455, DCDP 01S, MS E544, Los Alamos, NM 87545 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech., MS G755, Los Alamos, NM 87545 USA; [3]Los Alamos National Laboratory, Dynamic Experimentation, MS P952, Los Alamos, NM 87545 USA

Polytetrafluoroethylene (PTFE) is semi-crystalline in nature with its linear chains forming complicated temperature and pressure dependent phases. Due to its extremely low coefficient of friction, outstanding resistance to corrosion, and range of thermal stability, applications of PTFE include surgical implants, aerospace components, chemical barriers, and structures designed for dynamic large-scale plasticity excursions. Experimental studies on pressure-induced phase transitions using shock-loading techniques and the resulting changes in crystalline structure are presented. Disks of pedigreed PTFE 7C have been shock loaded in momentum trapped assemblies using a 80 mm gas launcher, and recovered in a density graded polymer network. Experiments were performed with impact pressures from 0.4 to 0.85 GPa to investigate the material response above and below the phase II to phase III crystalline transition. Changes in crystalline structure of the recovered materials were quantified using dynamic scanning calorimetry (DSC) and density.

11:45 AM
Microstructure and Mechanical Properties of Investment Cast Ti-6Al-4V: *Kevin L. Klug*[1]; Ibrahim Ucok[1]; Lawrence S. Kramer[1]; Mehmet N. Gungor[1]; Hao Dong[1]; Wm. Troy Tack[1]; [1]Concurrent Technologies Corporation, 100 CTC Dr., Johnstown, PA 15904 USA

The macrostructures, microstructures and mechanical properties of investment cast Ti-6Al-4V shaped components have been studied. The macrostructure investigations were focused on the size distribution of prior-β grains as a function of casting thickness; the microstructure studies were concentrated on α phase and β phase morphology and distribution. Similar studies were conducted on plates cast from lower-cost, alternative Ti-6Al-4V electrodes containing high levels of machining chips and forging scrap. The metallographic analyses of both the components and plates were compared with tensile, fatigue and impact test properties generated for each product form. This work was conducted by the National Center for Excellence in Metalworking Technology, operated by Concurrent Technologies Corporation under Contract No. N00014-00-C-0544 to the Office of Naval Research as part of the U.S. Navy Manufacturing Technology Program.

12:15 PM
Mechanically-Induced Surface Deformation and Associated Stress Whitening in Clay-Containing Nanocomposites: *Rohith Hadal*[1]; Harish Nathani[1]; Shankar Shanmugam[1]; Devesh K. Misra[1]; [1]University of Louisiana, Matls. Sci. & Engrg. Grp., Cheml. Engrg. Dept., PO Box 44130, Lafayette, LA 70504-4130 USA

The lateral resolution of scanning electron microscopy and vertical resolution of atomic force microscopy is combined to examine the surface damage behavior and susceptibility to mechanical surface damage in neat and clay-containing polymer nanocomposites. The surface damage in neat polymers is characterized by "psiloma-type" morphology indicative of compressive plastic deformation and quasi-periodic cracking. While in clay-containing nanocomposites, "ironing," which is a less severe surface damage mechanism was dominant. Also, clay-reinforced nanocomposites experience significantly reduced stress whitening, and is characterized by lower gray level in the plastically deformed surface damage region. This behavior is attributed to the effective reinforcement by clay particles that act in concert increasing the tensile modulus of the composite and restricts plastic deformation of the polymer matrix.

Lead Free Solder Implementation: Reliability, Alloy Development, New Technology: Thermal Fatigue and Reliability of Lead-Free Solder Joints

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Mark A. Palmer, Kettering University, IMEB, Flint, MI 48504-4898 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Ira A. Fulton School of Engineering, Tempe, AZ 85287-6006 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Laura J. Turbini, University of Toronto, Center for Microelectronic Assembly & Packaging, Toronto, ON M5S 3E4 Canada

Wednesday AM Room: 3014
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: K. N. Subramanian, Michigan State University, Dept. of Cheml. Engrg. & Matls. Sci., E. Lansing, MI 48824-1266 USA; Srinivas Chada, Jabil Circuit Inc., FAR Lab/Advd. Mfg. Tech., St. Petersburg, FL 33716 USA

8:30 AM Invited
Supporting Studies to Understand TMF Behavior of Eutectic Sn-3.5Ag Solder Joints: *K. N. Subramanian*[1]; Hongjoo Rhee[1];

[1]Michigan State University, Dept. of Cheml. Engrg. & Matls. Sci., EB2527, E. Lansing, MI 48824-1226 USA

The reliability of the solder joints depends on the material response to imposed service conditions. In order to gain a better understanding of such processes under thermal excursions encountered in service, supporting studies were carried out. Such tests consisted of cyclic shear straining with associated stress relaxation at the shear strain extremes during stress relaxation of pre-strained single shear-lap solder joints at various temperatures. These tests evaluated the roles of pre-strain and pre-strain rate imposed prior to cyclic shear straining, cyclic shear strain amplitude, cyclic shear strain-rate, testing temperature, etc. Acknowledgement: Work supported by the National Science Foundation under grant NSF DMR-0081796.

9:00 AM

Effect of Thermal Cycling on the Electrical Conductivity of Sn-Based Solders: J. G. Lee[1]; N. Meyer[2]; T. Hogan[2]; *K. N. Subramanian*[1]; [1]Michigan State University, Dept. of Cheml. Engrg. & Matls. Sci., E. Lansing, MI 48824-1226 USA; [2]Michigan State University, Dept. of Electl. & Computer Engrg., E. Lansing, MI 48824-1226 USA

Thermal excursions experienced during service result in highly inhomogeneous damage accumulation in electronic solder joints affecting their structural and electrical properties. These properties significantly drop within the first few hundred thermal cycles without any visible surface manifestation of damage. However, surface damage becomes apparent only when the deterioration in these properties stabilized. Electrical conductivity measurements were made with very small probes to quantify the local changes in the electrical conductivity of the thermally cycled Sn-based solder joints. Residual shear strengths and residual electrical conductivities of solder joints that have undergone identical thermal cycles will be compared to gain some insight for reliability predictions. Acknowledgement: Work supported by the National Science Foundation under grant NSF DMR-0081796 and NSF DMI-0339898.

9:20 AM

Evaluation of Solder Joint Reliability in Flip Chip Packages During Accelerated Testing: *Jong-Woong Kim*[1]; Seung-Boo Jung[1]; Dae-Gon Kim[1]; [1]Sungkyunkwan University, Dept. of Advd. Matls. Engrg., 300 Cheoncheon-dong, Jangan-gu, Suwon 440-746 S. Korea

Flip chip soldering technologies are being popular as one of the chip level interconnections to meet a demand for the higher density packages. Solder must act as both the conduits of electrical interconnections and the mechanical support to hold the chip in position on the substrate. When the flip chips are in operation, temperature cycles generate thermo-mechanical fatigue reacting with a substrate and a chip that have different coefficients of thermal expansion. Therefore, a study of thermo-mechanical fatigue behavior and the failure mechanism of the solder joints is very important for guaranteeing the reliability of the flip chip packages. In the present study, the thermal shock test of the flip chip package and a relevant three-dimensional thermo-mechanical finite element analysis using ANSYS were performed. A representative lead-free Sn-3.0Ag-0.5Cu solder was used, and the packages were tested according to JEDEC test method A106B. Finally, the experimental and computational results were related.

9:40 AM

Examination of Failure Mechanisms in Pb Free Solder Joints: *Eric J. Cotts*[1]; Lawrence P. Lehman[1]; Lubov Zavalij[1]; Yan Xing[1]; Ju Wang[1]; Peter Borgesen[2]; [1]Binghamton University SUNY, Physics & Matls. Sci., PO Box 6000, Sci. 2, Binghamton, NY 13902-6000 USA; [2]Universal Instruments Corporation, Rsch., Kirkwood, NY USA

The reliabilities of ball grid array (BGA), chip scale packaging (CSP), and flip chip components with SnAgCu solder joints were examined as a function of long term thermal cycling. All components were assembled on either OSP-coated copper, or electroless-nickel-immersion-gold (ENIG), coated pads on high-Tg FR-4 boards. The samples were subjected to air-to-air thermal cycling between 0C and 100C. The 20 minute cycle had 5 minute ramps and 5 minute holds at the two temperatures. Assemblies were removed for cross sectioning and microstructural characterization at various stages of cycling. Thus damage accumulation was examined using optical and electron microscopy techniques. Polarized light microscopy provided delineation of Sn grains, while electron microscopy with EDS provided compositional analysis. The variation in the thermomechanical loads with solder joint location across an area array allowed detailed study of a range of temperature-damage combinations.

10:00 AM

A Study on Reliability Test of WLCSP Lead-Free Solder Joints: *Huann-Wu Chiang*[1]; Jun-Yuan Chen[1]; Jeffrey C.B. Lee[2]; S. W. Li[2]; [1]I-SHOU University, Dept. of Matls. Sci. & Engrg., #1, Sec.1, Hsueh-Cheng Rd., Ta-Hsu Hsiung, Kaohsiung County, Taiwan 84008 Taiwan; [2]Advanced Semiconductor Engineering, Inc., Engrg. Ctr., 26, Chin 3rd Rd., Nantze Export Procg. Zone, Kaohsiung, Taiwan 811 Taiwan

The interfacial reactions of solder joints between Sn-Ag-Cu solder ball and Sn-Ag-Cu pre-soldered paste will investigated in wafer level CSP package. After appropriate SMT reflow process on PCB with Cu-OSP and Cu-NiAu surface finish, samples will be subjected to either 150°C HTS 1000 hours aging or -40°C -150°C TCT reliability test. Sequentially, the cross-section analysis is scrutinized by SEM/EDX and EPMA to observe metallurgical evolution in the interface and solder buck itself. Pull and shear tests will also be performed on samples. The relationship between the interfacial microstructure and the joint strength will then be analyzed and discussed.

10:20 AM Break

10:30 AM

Nucleation and Propagation of Fatigue Damage in Near-Eutectic Sn-Ag-Cu Alloy: *Tia-Marje K. Korhonen*[1]; Donald W. Henderson[2]; Matt A. Korhonen[1]; [1]Cornell University, Dept. of Matls. Sci. & Engrg., 328 Bard Hall, Ithaca, NY 14850 USA; [2]IBM Corporation, Hopewell Junction 12533 USA

It has been shown that when near-eutectic SAC alloys are used to make BGA solder joints, the grain size is very large, with typically 1 to 12 grains per BGA joint. Often the BGA joints are single crystals. During thermomechanical cycling, the solder joint fatigue process is characterized with recrystallization of the Sn grains, resulting in a smaller grain size in the deformed areas. Grain boundary sliding and increased grain boundary damage then results in intergranular crack initiation and propagation along the recrystallized Sn grain boundaries. In this work, fatigue tests were used to study the initial stages of deformation in Sn-Ag-Cu alloy samples. To separate the solder properties from the constraints introduced by the substrate, the tests were done to free-standing solder specimens, instead of solder joints. The test samples were cast dog-bone specimens that have a cross section of 1mm, which corresponds to the typical solder joint diameter in ball grid arrays. The solder was heated to 245 degrees, held there for ten minutes and then cast and cooled at 1 degree/second cooling rate. Mechanical cycling was performed isothermally at several temperatures, up to 125 C. Typical test conditions were 0.5% strain and 30 minute cycles. Optical microscopy, SEM and electron back-scatter diffraction were used to study the microstructures of the samples before and after fatigue testing.

10:50 AM

Thermal Fatigue Behavior of Sn-Bi Solder Joints: *Mark A. Palmer*[1]; Samir Nashef[1]; [1]Kettering University, IMEB, 1700 W. Third Ave., Flint, MI 48504 USA

A new thermal fatigue test apparatus has been designed to assess the thermal fatigue resistance of solder joints prepared with Sn-30w/oBi, eutectic Sn-Bi, and Sn-70w/oBi alloys. The design of this new apparatus will be discussed. The thermal fatigue behavior will be correlated with the microstructural evolution of the bulk material and the solder joint. Thermal fatigue resistance will be correlated with the temperature dependent strength, temperature dependent fatigue resistance, creep resistance of annealed solder joints and alloys. Funding from the National Science Foundation CMS-0140605 is gratefully acknowledged.

11:10 AM

The Role of Cu Content on Compound Formation Near Chip and Substrate Side for the Flip Chip Sn-3.0Ag-xCu Solder Bump After Aging and Thermal Cycling: *Guh-Yaw Jang*[1]; Li-Yin Hsiao[1]; Jenq-Gong Duh[1]; Hideyuki Takahashi[2]; Szu-Wei Lu[3]; Jen-Chuan Chen[4]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Engrg., 101 Sec. 2 Kuang-Fu Rd., Hsinchu 300 Taiwan; [2]JEOL Ltd., Application & Rsch. Ctr., Tokyo Japan; [3]TSMC Ltd., Flip-Chip Engrg. Dept., 121, Park Ave.3, Hsinchu Sci. Park, Hsinchu 300 Taiwan; [4]ASE, Flip-Chip Operation, 550, Chung-Hwa Rd., Sect. 1, Chung-Li 320 Taiwan

The Sn-Ag-Cu solder is one of the promising candidates to replace the conventional Sn-Pb solder. Interfacial reaction for the flip chip solder bump of Sn-2.3Ag/Sn-3.0Ag-0.5Cu and Sn-3.0Ag-xCu/Sn-3.0Ag-0.5Cu (x = 0.5 and 1.5) combination structure was investigated after aging at 150°C and thermal cycling between -55°C and 125°C. The under bump metallization for the Sn-2.3Ag and Sn-3.0Ag-xCu solders on the chip side was SiO2/Cu/Al/Ni, while the bond pad for Sn-3.0Ag-0.5Cu solder on the plastic substrate side was Cu/electroless Ni/Au. In the Sn-3.0Ag-xCu joints after thermal cycling for 1000 cycles, the Ni layer at the chip side was consumed completely and reacted with Sn and Cu atoms to form $(Cu,Ni)_6Sn_5$ intermetallic compound (IMC). At the plastic substrate side, three reaction compound, $(Cu,Ni)_6Sn_5$, $(Ni,Cu)_3Sn_4$ and Ni_3P, was observed between the solder and the EN

layer. For the Sn-2.3Ag joint, nearly half Ni layer was reacted to form $(Ni,Cu)_3Sn_4$ IMC at the chip side, and $(Ni,Cu)_3Sn_4$ and Ni_3P IMCs were revealed at the solder/EN interface at plastic substrate side. The interfacial reaction in the solder joints could be related to the Cu concentration in the solder joint. In addition, the detailed microstructure evolution of solder joints after aging and thermal cycling was also discussed in this study.

11:30 AM
The Effect of Pb Contamination on Sn-Ag-Cu Solder Joint Reliability: *Masayoshi Date*[1]; Tatsuya Shoji[1]; Masaru Fujiyoshi[1]; Koji Sato[2]; [1]Hitachi Metals, Ltd., Metallurgl. Rsch. Lab., Yasugi-cho 2107-2, Yasugi-shi, Shimane 692-8601 Japan; [2]Hitachi Metals, Ltd., Yasugi Works

The effect of Pb contamination on joint reliability of Sn-3Ag-0.5Cu Pb-free solder was evaluated. In the first reflow, the Sn-Ag-Cu solder balls were bonded to electroless Au/Ni(P) pads of a chip scale package (CSP) by using rosin activated flux. In the following reflow, the package was mounted on a substrate, whose pads were electroless Au/Ni(P) or an organic solder preservative (OSP) coated Cu pads, by using either the Sn-Ag-Cu or eutectic Sn-Pb solder paste. Subsequently, a thermal cycle test was conducted ranging from -55 to 125 °C. The microstructure of the joints and the composition of interfacial compounds were dependent deeply on solder compositions and bond-pads. The joints composed of the SnAgCu balls and the SnPb paste, whose bond-pads of the substrate were Au/Ni(P), were liable to fracture at earlier cycles than others, caused by crack propagation along the bond interface on the substrate side.

11:50 AM
Orientation Imaging Microscopy Studies on Thermomechanically Cycled Lead-Free Sn-3.5Ag Solder Joints: Adwait U. Telang[1]; K. N. Subramanian[1]; Thomas R. Bieler[1]; [1]Michigan State University, Cheml. Engrg. & Matls. Sci., 2527 Eng Bldg., E. Lansing, MI 48824 USA

Single shear lap and double shear lap lead-free solder joints were made using Sn-3.5Ag solder having a 1 mm^2 joint area and solder thickness of about 100μm. Different shear strain states were induced in these joints while undergoing TMF cycling due to the differences in the geometry of the specimens. The microstructural evolution and the damage that developed at the end of 1000 cycles was studied in all joints using Orientation Imaging Microscopy (OIM) and scanning electron microscopy (SEM). Surface topography in the form of grain boundary sliding, ledge development, and further decohesion in the tin matrix that was seen after 1000 TMF cycles was correlated with the crystal orientations and misorientations present in the joint, and the grain boundary character. Slip activity that could cause such surface topography is analyzed and discussed. The effect of different strain histories on evolution of surface damage and microstructure will be discussed and probable cause for such surface damage accumulation will be identified.

WEDNESDAY AM

Magnesium Technology 2005: Magnesium Alloy Processing

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Wednesday AM Room: 2004
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Eric Nyberg, Pacific Northwest National Laboratory, Richland, WA 99352 USA; Menachem S. Pbamberger, Israel Institute of Technology, Technion Dept. of Matls. Engrg., Haifa 32000 Israel

8:30 AM
Comparison of As-Cast and Plasma Deposited Commercial Magnesium Alloys: Dirk Martin Seeger[1]; *Carsten Blawert*[1]; Wolfgang Dietzel[1]; Karl Ulrich Kainer[1]; Yvonne Bohne[2]; Stephan Mändl[2]; Bernd Rauschenbach[2]; [1]GKSS Forschungszentrum Geesthacht GmbH, Ctr. for Mg Tech., Max-Planck-Str. 1, Geesthacht 21502 Germany; [2]Leibniz-Institut für Oberflächenmodifizierung, Permoserstr. 15, Leipzig 04318 Germany

Ion beam sputtering is used to produce magnesium alloy coatings of AM50, AZ91 and AE42 alloys on silicon and magnesium substrates. Due to the specific process conditions, a very fine microstructure will result. We will compare this microstructure with the microstructure of the original commercial AM50, AZ91 and AE42 target materials. The aim is to study the effect of the microstructure on the corrosion properties. Polarisation technique will be used to study the corrosion behaviour of the coatings and the original materials.

8:50 AM
Segregations of Aluminum After Solidification: AZ91D MG-AL-ZN Plate Produced by Die Casting and Gravity Casting: *Chi-Yuan Cho*[1]; Jun-Yen Uan[1]; Huey-Jiuan Lin[2]; Te-Chang Tsai[3]; [1]National Chung Hsing University, Dept. of Matls. Engrg., 250 Kuo Kuang Rd., Taichung 402 Taiwan; [2]National United University, Dept. of Matls. Sci. & Engrg., 1 Lien Da Rd., Kung-Ching Li, Miao Li 360 Taiwan; [3]Hsiuping Institute of Technology, Dept. of Mechl. Engrg., 11Gungye Rd., Dali City, Taichung 412 Taiwan

Segregation of aluminum element in AZ91D magnesium plates produced by die casting and gravity casting was investigated. The aluminum at cast surface have higher concentration than that examined from the interior region, either by die casting or by gravity casting process. The concentration of aluminum in the die cast plate show an increasing tendency along the melt filling direction: from the gating system to the final position the melt can reach. However, for gravity casting plate the alloy elements prefer to accumulate at the position between chill block and the gating system. Before the molten metal solidified, the positions which con-tain high fraction of solid will lead to a relative large amount of alloy element segregating there. As a result, the cast product will have some specific locations where the chemical compositions are lower than the ASTM B-94 AZ91D standard.

9:10 AM
Effects of Grain Refinement and Melt Filtration on the Mechanical Properties of Sand and Permanent Mold Cast Magnesium AZ91D Alloy: *Daryoush Emadi*[1]; Jim Thomson[1]; Kumar Sadayappan[1]; Mahi Sahoo[1]; [1]CANMET, Matls. Tech. Lab., 568 Booth St., Ottawa, Ontario K1A 0G1 Canada

Magnesium finds applications in a multitude of automotive, military and commercial applications because of its lightweight, high strength/weight ratio, high-castability and excellent damping capacity and machinability. Recognition by the auto industry of weight reduction, an increase in energy cost together with government regulations controlling vehicle design has established an environment for increased magnesium use. At present, most of the automotive components in Mg alloys are produced by high-pressure die-casting. However, to increase Mg usage in components, other casting processes such as sand and permanent mold casting should be evaluated. CANMET-Materials Technology Laboratory has taken this approach and initiated a research program to address critical issues relating to high integrity sand and permanent mold casting. The effects of mold design, grain refinement and melt filtration on mechanical properties of sand and permanent mold cast test bars were investigated. The effect of machining on propert ies was also evaluated. The experimental results are presented and discussed in this paper.

9:30 AM
Advances in Technology of Processing Semisolid Magnesium Alloys: *Frank Czerwinski*[1]; [1]Husky Injection Molding Systems Ltd, Dvlp. Engrg., 560 Queen St. S., Bolton, Ontario L7E 5S5 Canada

Since its discovery over thirty years ago, semisolid processing is mainly applied to alloys with relatively low melting temperatures, particularly aluminum. Although historically an interest in magnesium reaches as early as 1974, compared with aluminum, investigations of semisolid magnesium alloys are scarce. This paper presents the key semisolid technologies, available in today's industry, based on thixo- and rheo-routes with particular attention being paid to emerging techniques of injection molding. The major requirements imposed on potential alloys and their transformations during processing are described. For selected alloys the correlation between chemistry and microstructure is analyzed the importance of preheating temperature in semi-solid range is emphasized. Examples of products, manufactured at present worldwide are given.

9:50 AM
Influence of SiC Grain Refiner Additions on the Globular Structure of New Rheocasting Mg Alloys: *Helmut Kaufmann*[1]; Mark Easton[2]; Werner Fragner[1]; [1]ARC Leichtmetallkompetenzzentrum Ranshofen GmbH, PO Box 26, Ranshofen 5282 Austria; [2]CRC for Cast Metals Manufacturing, Australia

The shape of primary phase solid particles, their contiguity and their size are the three major microstructural parameters influencing the castability of semi-solid slurries into high quality magnesium prod-

ucts. New Rheocasting (NRC) is a slurry-on-demand semi-solid casting process where a slightly super heated melt is quenched at the wall of a steel cup and subsequently cooled slowly to achieve globular growth of the primary phase. Fine grain size is extremely important for the overall performance of magnesium alloys in light weight applications. The grain size determines the mechanical properties at room temperature and elevated temperature. In the classical NRC process the grain size is determined by the amount of solidification nuclei formed at the cup wall and their subsequent growth. Typically, particle sizes of the primary phase in the range of 80 to 120 ìm can be reached. In order to achieve even finer particle sizes in the as cast structure, heterogeneous grain refiner particles were added to the melt. Grain refining of aluminium containing magnesium alloys is still an unsolved problem. A newly developed method for preparation and addition of SiC grain refining particles is applied to conventional Mg melts and tested in New Rheocasting. This paper will show the effects of wall mechanisms and heterogeneous nucleation on SiC grain refiner particles on the evolution of the primary phase in NRC semi-solid slurries, as well as their influence on the resulting properties of Mg castings.

10:10 AM Break

10:25 AM
Effects of Processing Parameters on Microstructure of Continuous Cast Magnesium Billets: *Kwang Seon Shin*[1]; Hwa Chul Jung[1]; [1]Seoul National University, Sch. of Matls. Sci. & Engrg., San 56-1 Shinrim-dong Kwanak-gu, Seoul 151-742 Korea

With many advantages derived from the process, semi-solid processing (SSP) is an emerging technology for near net-shape production of engineering components. Although there has been a significant progress in semi-solid processing of Al alloys, very limited information is available on semi-solid processing of Mg alloys. A continuous casting process has been successfully utilized in mass production of the billets of steel, copper, aluminum, etc. In this study, a continuous casting process has been developed for the production of magnesium billets for subsequent semi-solid processing. The processing parameters including melt temperature, stirring force and the withdrawal rate of the solidified billet have been carefully controlled for the successful production of magnesium billets with non-dendritic microstructure. In the present study, the effects of these processing parameters on microstructure of the continuous cast magnesium billets were investigated.

10:45 AM
High Pressure Die Casting Process of Advanced Mg Alloys: *Nir Moscovitch*[1]; Dan Eliezer[2]; Eli Aghion[2]; [1]Dead Sea Magnesium, Rsch. Div., PO Box 1195, Beer Sheva 84111 Israel; [2]Ben-Gurion University, Matls. Engrg., PO Box 653, Beer Sheva 84105 Israel

High pressure die casting (HPDC) is the dominant process technology for the mass production of Magnesium components with complex configuration having typical thin to medium wall thickness. The growing use of die cast Magnesium alloys for the automotive industry, particularly for the production of drive train applications has lead to the development of advanced die casting alloys with improved creep resistance, namely MRI 153M and MRI 230D. MRI 153M alloy can be used in applications with service temperature up to 150°C, while MRI 230D can be used at temperatures up to 190°C. Both alloys have excellent creep resistance at their designated operation temperature. This creep performance is combined with good castability, high strength and superior corrosion behavior. The present paper aims at introducing semi-empiric correlations between HPDC parameters, solidification characteristics and the properties of the die cast component. The paper also includes a systematic evaluation of the heat transfer and energy balance during the die casting process. Adequate implementation of this data can lead to reliable part design and high quality die cast components.

11:05 AM
Numerical Simulations and Experimental Study of Hot Core Distortion Phenomenon in Magnesium Casting: *Sayavur Ispandiyar Bakhtiyarov*[1]; Johnathon Capps[1]; Ruel Overfelt[1]; David Weiss[2]; [1]Auburn University, Mechl. Engrg., 202 Ross Hall, Auburn, AL 36849-5341 USA; [2]ECK Industries, Inc., Manitowoc, WI 54221-0967 USA

This paper presents the results of experimental and numerical studies of hot distortion phenomenon in the phenolic urethane cold box systems during magnesium casting. Dual Pushrod Dilatometer has been used to measure a thermal expansion/contraction of phenolic urethane cold box sand core specimens at temperature range from 200°C to 600°C. The high temperature tensile tests showed that the tensile strength of the phenolic urethane cold box sand cores is significantly affected by the bench life, temperature and binders level. High temperature hot distortion furnace tests on cylindrical cores showed that some coatings increase the temperature limit when distortion starts, but can't prevent it. The hot distortion test during magnesium castings showed that regardless of the application of coating, the type of coating, and anti-veining additives, all cores with density less than the density of the molten metal (magnesium alloy) were significantly distorted. Numerical simulations of the liquid metal flow around the cylindrical sand core and analysis of dynamic forces acting on the core during fill process showed that a buoyancy force is the major contributor to the hot distortion. It is concluded that the one of the solutions in preventing the hot distortion of sand cores is optimizing their weigh, which will balance the buoyancy force and will bring the resultant force to the minimum. The hot distortion test castings using optimized sand cores (both coated and non-coated) with density almost equal to the density of the molten magnesium proved our predictions, and hot distortion has been prevented.

11:25 AM
The Effects of Process Parameters on the Porosity of Die-Cast AM50 Alloys: *Soon Gi Lee*[1]; Gautam R. Patel[1]; Arun M. Gokhale[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr., NW, Atlanta, GA 30332-0245 USA

Pressure die-cast magnesium alloys almost always contain both gas (air) and shrinkage porosity. Quantitative characterization of gas and shrinkage porosity is essential for understanding microstructure and properties relationships. In this contribution, the microstructures of high-pressure die cast AM 50 alloy have been quantitatively characterized to understand the effects of the process parameters such as melt temperature, in-coming liquid metal gate velocity, and intensification. A novel digital image analysis technique has been used to quantify the volume fraction and other geometric attributes of the gas (air) and shrinkage pores. Three-dimensional images of the porosity have been reconstructed using a combination of montage serial sectioning and digital image processing. The differences of the total porosity under different process conditions are mainly due to the number density of large gas pores. Therefore, the large pores, which constitute the upper 10% of the size distribution, have been investigated.

11:45 AM
Macro-Segregation in High-Pressure Die-Cast AM60 Alloy: *Soon Gi Lee*[1]; *Gautam R. Patel*[1]; *Arun M. Gokhale*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr. NW, Atlanta, GA 30332-0245 USA

Macro-segregation is known to occur in the vicinity of cast surfaces in Al and other nonferrous alloy castings under certain conditions and has been well documented, but it has not been investigated in high-pressure die-cast Mg-alloys. Solidification gives rise to transport of interdendritic liquid in order to feed shrinkage, which leads to a solute-rich region close to the cast surface commonly referred to as inverse segregation. Another macro-segregation close to the surface is exudation related to air gaps between the semi-solid shell and the mould caused by solidification contraction. This contribution reports the effects of process parameters such as melt temperature, in-coming liquid metal gate velocity, and intensification on the microstructural aspects of the macro-segregation in a high-pressure die-cast AM60 alloy. These correlations have been quantitatively characterized via quantitative microstructure characterization using stereology and image analysis techniques.

Materials Issues for Advanced Nuclear Systems: Materials for Gen IV and Space Nuclear Systems

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Robert J. Hanrahan, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Sean M. McDeavitt, Argonne National Laboratory, Chemical Technology Division Materials Development Section, Argonne, IL 60439-4837 USA

Wednesday AM Room: 3012
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Robert J. Hanrahan, Los Alamos National Laboratory, ADWP, Los Alamos, NM 87544 USA; Raul B. Rebak, Lawrence Livermore National Laboratory, Livermore, CA 94550 USA

8:30 AM
Materials for Accelerator Driven Systems: *Abderrahim Almazouzi*[1]; [1]SCK.CEN, Reactor Matls. Rsch., LHMA, Boeretang 200, Mol 2400 Belgium

High Chromium ferritic martensitic steels and austenitic steels that are forseen as candidates to build a spallation target as well as fuel cladds, were irradiated in BR2 reactor at 200°C. The post irradiation examination of the irradiated materials, that consist of slow rate tensile testing them in a liquid metal environnment, demonstates that they conserve their performance. The liquid metal embrittlement seems to be hindered by the selfhealing mechanism.

8:55 AM
The Mechanical Properties and Fracture Mechanisms of Wrought LCAC, TZM, and ODS Molybdenum Flat Products: *Brian V. Cockeram*[1]; [1]Bechtel Bettis Laboratory, PO Box 79, ZAP 05R/MT, W. Mifflin, PA 15122-0079 USA

Molybdenum alloys possess excellent strength and creep resistance at high temperatures, with measurable tensile ductility at low temperatures. These properties have attracted interest in the use of molybdenum alloys such as Low Carbon Arc Cast (LCAC) unalloyed molybdenum, Oxide Dispersion Strengthened (ODS) molybdenum, and TZM molybdenum for structural applications at high temperatures, such as vacuum furnace components, forging dies, glass molding, and advanced power systems. Although the tensile properties of molybdenum-base alloys have been well characterized, these alloys are poorly characterized with respect to fracture toughness, and the changes in the Ductile to Brittle Transition Temperature (DBTT) that result from the presence of a notch. Rolling of molybdenum into flat products has the advantage of producing a fine grained microstructure that improves the strength and lowers the DBTT. Detailed examinations of fracture surfaces are used to show that the fracture mechanism is generally the same for these three molybdenum-base alloys. Thin sheet toughening occurs during fracture by the splitting along grain boundaries and/or oxide boundaries to leave ligaments of grains that are stretched to failure with large amounts of plastic deformation. Thin sheet toughening is shown to occur in smooth tensile specimens and pre-cracked fracture toughness specimens. A sampling of tensile properties and fracture toughness data as a function of test temperature are used to identify the DBTT. The fracture mode at the DBTT changes from transgranular cleavage to the thin sheet fracture mode.

9:20 AM
Development of Ni-W Based Alloys for Future Nuclear Reactors: *Rafael Ferreira Cury*[1]; Thierry Auger[1]; Jean-Pierre Chevalier[1]; [1]CECM-CNRS, 15, rue Georges Urbain, Vitry cedex 94407 France

Whether for molten salt or high temperature gas cooled reactor designs, alloys are required to be oxidation and corrosion resistant,to have appropriate high temperature mechanical properties (yield stress and creep resistance) as well as acceptable room temperature toughness. For instance, Hastelloy N (a Ni-Cr-Mo based alloy) was selected for the Oak Ridge experimental molten salt reactor. The related Ni-Cr-W system may offer improvements over Hastelloy N, such as a lower activation and potentially better creep resistance, due to expected lower diffusion of W with respect to Mo, whilst maintaining similar corrosion and oxidation resistance. In an initial approach, the binary Ni-W alloys have been studied, with emphasis on alloy preparation. Using electron diffraction, the structural state (in terms of long and short range order) of the alloys as a function of composition will be presented. The role of short range order on hardening will also be discussed.

9:45 AM
Interpretation of Improved Creep Properties of a 9Cr-1Mo-Nb-V (T91) Steel by Grain Boundary Engineering: *Gaurav Gupta*[1]; Gary S. Was[2]; [1]University of Michigan, Nucl. Engrg. & Radiologl. Scis., 2940 Cooley Bldg., 2355 Bonisteel Blvd., Ann Arbor, MI 48109-2104 USA; [2]University of Michigan, Nucl. Engrg. & Radiologl. Scis., 2408 LEC, 1221 Beal Ave., Ann Arbor, MI 48109-2102 USA

Ferritic-martensitic alloys are expected to play a major role as structural components in Generation IV systems that operate in the temperature range 350-700°C and to doses up to 150 dpa. They exhibit improved irradiation stability and mechanical properties such as reduced swelling, high temperature creep resistance, and thermal shock resistance over austenitic steels but may suffer from grain boundary and/or matrix creep and loss of strength at higher temperatures, and unacceptably low toughness at lower temperatures. The objective of this work is to improve the creep resistance of T91 by grain boundary engineering. Coincident site lattice (CSL) enhancement strengthens the grain boundaries against sliding and deformation, thus improving the creep resistance. High temperature creep experiments in argon are conducted to assess the effectiveness of the CSL-enhanced microstructure on the creep rate. Experimental analysis shows that the CSL-enhanced condition results in a lower creep rate by a factor of 3-4 as-compared to as-received (A/R) condition for T91 at a temperature of 500°C and in the stress range of 200-225MPa by introducing an additional term for internal stress thus reducing the effective stress. Creep experiments are conducted on both A/R and CSL-enhanced T91 to quantify the stress and temperature effect of creep over the range 500-600°C and 150-250 MPa and to determine the mechanism by which Coincident Site Lattice Enhancement affects creep.

10:10 AM Break

10:20 AM
Mechanical Behavior of Neutron Irradiated High Cr Ferritic Martensitic Steels: *Abderrahim Almazouzi*[1]; [1]SCK,CEN, Reactor Matls. Rsch., LHMA, Boeretang 200, Mol 2400 Belgium

High Chromium Ferritic Maetensitic steels are candidates for the traget spallation source and the fuel cladding tubes in the European demonstrator of the accelerator driven system. In this work, we will present new results obtained from the irradiation compaign that has been performed at BR2 within SPIRE project to assess the mechanical behaviour of several standards Fe-9,12%Cr steels. The irradiations have been performed at the lowest temperature limite where the irradiation induced hardening would be the highest (200°C) up to 4.5 dpa. The post irradiation analysis consisted of tensile, charpy and fracture thoughness testing. Discussion on the validity of master curve analysis of this class of materials will be proposed.

10:45 AM
Mechanical Properties and Cracking of High-Temperature Heat-Exchanger Materials: Ajit K. Roy[1]; *Narendra V. Kothapalli*[1]; Raghunanadan A. Karamcheti[1]; Lalitkumar B. Savalia[1]; [1]University of Nevada, Mechl. Engrg., 4505 Maryland Pkwy., Box 454009, Las Vegas, NV 89154 USA

The structural materials selected for high-temperature heat-exchanger applications are expected to withstand very severe operating conditions including elevated temperatures and aggressive chemical species during hydrogen generation using nuclear power source. Currently, three different cycles namely sulfur-iodine, calcium-bromine and high temperature electrolysis are being considered for hydrogen generation. Temperatures ranging from ambient to 1000ºC, and a very low pH (˜ 1) can influence the performance of structure materials such as Alloys C-276, C-22 and Waspaloy. This paper will present the results of stress corrosion cracking, hydrogen embrittlement and localized corrosion studies of all three alloys in related environments. The tensile properties at different testing temperatures will also be included. Further, the results of metallographic and fractographic evaluations of the tested specimens will be presented.

11:10 AM
Effects of Processing and Prolonged High Temperature Exposure on the Microstructure of Nb-1Zr-C Sheet: *Mehmet Uz*[1]; Robert H. Titran[2]; [1]Lafayette College, Ch. E. Dept., 262 AEC, Easton, PA 18042 USA; [2]NASA-GRC (Retired), Matls. Div., 15976 Walnut Creek Dr., Strongsville, OH 44149 USA

High temperature stability of the microstructure of Nb-1Zr sheets with 0.1 and 0.06 wt.%C was investigated as affected by processing and prolonged 1350-K exposure with and without applied load. Sheets were fabricated by cold rolling bars that were single-, double- or triple-extruded at 1900 K. Creep samples were double-annealed (DA: 1 h \@ 1755 K + 2 h \@ 1475 K) prior to testing at 1350 K for 10,000 - 34,500 h. The microstructures of the as-cast, extruded, rolled, DA and crept samples were characterized using various metallographic and analytical methods. The precipitates were rather coarse Nb2C initially, but transformed to finer (•< 1 mm) carbides of (Zr,Nb)C with each subsequent high temperature process. The grain size, and the relative amount and morphology of (Zr,Nb)C were affected by processing and C-content. However, the microstructures of all the crept samples were similar with (Zr,Nb)C distributed throughout the matrix indicating that prolonged exposure to 1350 K gave rise to complete transformation of Nb2C to (Zr,Nb)C regardless of the processing history. These and other observations are presented with the emphasis on the correlation between processing, microstructure and creep properties. This work was performed for USDOE, Nuclear Energy, Reactor Sys. Development and Tech., Washington, D.C. 20545, under Interagency Agreement DE-Al03-86SF16310.

11:35 AM
Mechanical Behavior, Microstructural Evolution and Grain Morphology Studies in ZrN: *Ilsu Han*[1]; Pedro Peralta[1]; Kenneth J. McClellan[2]; Kirk Wheeler[1]; [1]Arizona State University, Dept. of Mechl. & Aeros. Engrg., PO Box 876106, Tempe, AZ 85287 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., Los Alamos, NM 87545 USA

The mechanical integrity of ZrN as an inert matrix in advanced nuclear fuels can be improved through understanding and control of texture and microstructural evolution. Results of average hardness for 80%, 86% and 90% density samples were 4 GPa, 7 GPa and 8.5 GPa, respectively. This increase in hardness is related to an increase in density and a more homogeneous distribution of porosity in the microstructure. These studies of mechanical behavior are related to texture and microstructural evolution in sintered ZrN. Orientation Imaging Microscopy was performed on a monolithic specimen processed using hot isostatic pressing and a sintered specimen with 80% density. Relationships between grain size and crystallographic orientation were studied to obtain information about microstructural evolution during sintering. A correlation between larger grains and orientations near to <111> is present for both samples. This suggests that <111> is the preferential direction for grain growth during sintering.

Materials Processing Fundamentals: Powders, Composites & Coatings

Sponsored by: Extraction & Processing Division, Materials Processing & Manufacturing Division, EPD-Process Fundamentals Committee, MPMD/EPD-Process Modeling Analysis & Control Committee

Program Organizers: Princewill N. Anyalebechi, Grand Valley State University, Padnos School of Engineering, Grand Rapids, MI 49504-6495 USA; Adam C. Powell, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307 USA

Wednesday AM Room: 3001
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Prince N. Anyalebechi, Grand Valley State University, Padnos Sch. of Engrg., Grand Rapids, MI 49504-6495 USA

8:30 AM
Processing of Vanadiferous Residues to Ferrovanadium: Robert Ressel[1]; *Markus Hochenhofer*[1]; Helmut Antrekowitsch[1]; [1]Christian-Doppler-Laboratory for Secondary Metallurgy of the Non-Ferrous Metals, Franz-Josef-Strasse 18, Leoben 8700 Austria

Recyclable material is rapidly gaining in importance as a source of raw materials in industrialized countries. This is also the case in the production of ferrovanadium, where, increasingly, materials such as discarded capacitors, spent catalysts, slag, dust and sludge are used. As the V-content in the raw material varies greatly, the demands on process technology are very high. The share of unwanted accompanyoning elements depends very much on the source of the raw materials, which, in turn, makes a corresponding optimization of the various refining steps necessary. The raw materials are mostly available as oxides, which means that carbon, silicon or aluminium are used as reducing agents. Thermodynamic calculations were used to show especially the behavior of vanadium and phosphorus at different process conditions.

8:50 AM
Oxidation Behavior of Multi-Phase Mo-Si-B Alloys: *Zhihong Tang*[1]; *Andrew J. Thom*[1]; John Kacuba[1]; Mufit Akinc[1]; Matthew Kramer[1]; [1]Iowa State University, Ames Lab., Dept. of Matls. Sci. & Engrg., Ames, IA 50011 USA

Multi-phase Mo-Si-B alloys, containing intermetallic phases for high temperature properties and a ductile phase for the fracture toughness, are being studied due to their potential for high temperature application. Three alloys have been investigated: alloy 1: Mo5Si3Bx (T1), MoB and MoSi2; alloy 2: T1, Mo5SiB2 (T2) and Mo3Si; alloy 3: Mo, T2 and Mo3Si. In the present study, the effect of water vapor and nitrogen on the oxidation behavior of multiphase Mo-Si-B alloys was examined at 1000°C. The combinational role of nitrogen and water vapor will be examined and compared with both dry and wet air. Oxidation kinetics, scale microstructural analysis and phase chemistry determination will be discussed to give a phenomenological explanation of these effects. Implication of these results for understanding high temperature oxidation behavior of Mo-based alloy as well as their possible application as oxidation-resistant coatings will be discussed.

9:10 AM
The Influence of Mechanical Processing on the Process of Thermal Reduction of SiO_2 by Al and Characterization of the Formed Si-Al_2O_3 Powdered and Compacted Composites: *Aghasi R. Torosyan*[1]; Nshan H. Zulumyan[1]; Zaruhi H. Hovhannisyan[1]; Sona E. Ghazaryan[1]; [1]National Academy of Sciences, Inst. of Gen. & Inorganic Chmst., 2-tup., Argutyan St. 10, Yerevan 375051 Armenia

Chemical reaction between SiO_2 and Al powders induced by heat treatment up to 1000°C has been investigated, depending on SiO_2 modification and time of initial mixture mechanical processing. Differential thermal analysis (DTA) studies have shown that both amorphous and crystalline SiO_2 start interact with Al powder well above the melting point of Al powder if the reactants were not activated mechanically. The situation changed dramatically in the case when the reactants had been undergone to preliminary ball milling and activation. The temperature of Si reduction for all activated (SiO_2-Al) mixtures decreases below 500°C Compat Si-Al_2O_3 ceramic composites have been prepared by compressing and annealing at 550°C the activated Al-SiO_2 powder. The microstructure and mechanical properties of the formed powdered and compacted Si-Al_2O_3 composites have been investigated by XRD, SEM and mechanical testing methods.

9:30 AM
Role of Nitrogen on the Oxidative Stability of Ti5Si3 Based Alloys at Elevated Temperature: *Zhihong Tang*[1]; Andrew J. Thom[1]; Mufit Akinc[1]; [1]Iowa State University, Ames Lab., Dept. of Matls. Sci. & Engrg., Ames, IA 50011 USA

Nitrogen is thought to have a critical role in the oxidation of Ti5Si3. In the present study, the isothermal reaction kinetics of Ti5Si3 at pure nitrogen at 1000°C was intensively investigated. Compared to a slow parabolic oxidation rate in oxygen, a faster linear reaction rate was observed when Ti5Si3 is exposed to nitrogen. Further studies on the oxidation behavior for changing nitrogen/oxygen atmospheres showed that Ti5Si3 is stable for exposure up to 400 hours at 1000°C when nitrogen partial pressure is below 0.5 atm.. Accelerated oxidation occurs after short exposures when the nitrogen partial pressure excess 0.75 atm. And with the increasing nitrogen partial pressure time to breakaway oxidation decreases. Extensive analysis of the oxidation products using SEM and XRD revealed that the formation and fast growth of a nitride-containing subscale interferes with the establishment of the continuous protective silica scale and contributes to the breakaway oxidation.

9:50 AM Break

10:05 AM
Effects of Gravity and Electric Current on Segregation and Permeation in Combustion Synthesis: *Cosan Unuvar*[1]; Daniela M. Fredrick[1]; Jennifer E. Sween[1]; Umberto Anselmi-Tamburini[1]; Anthony Manerbino[2]; Jacques Guigne[2]; Benjamin D. Shaw[3]; Zuhair A. Munir[1]; [1]University of California, Chemical Engrg. & Matls. Sci., 3118 Bianer Hall, 1 Shields Ave., Davis, CA 95616 USA; [2]Guigne Int. Ltd., 685 St. Thomas Line, Paradise, Newfoundland A1L 1C1 Canada; [3]University of California, Mechl. & Aeronautl. Engrg., 2132 Bainer Hall, 1 Shields Ave., Davis, CA 95616 USA

Combustion synthesis involves mixing powder reactants and igniting the mixture. Typically, reactions start when one of the reactants melt and it occurs in the form of a wave through the sample. In Field Activated Combustion Synthesis (FACS), the addition of an electric field has a marked effect on the dynamics of wave propagation and on the nature, composition, and homogeneity of the product as well as capillary flow, and mass-transport in porous media, which are influenced by gravity. Increasing the amount of liquid present in the reaction attenuates the effects of gravity on segregation and permeation. In order to retain sample integrity and maximize the quantity of liquid, chemical ovens with inserts that contain large amounts of molten phase(s) were used. Inserts contained aluminum as the liquid phase and tungsten, tantalum, nickel and titanium as the solid phases. Experiments have been performed in various gravitational conditions.

10:25 AM
Effect of Mechanical Attrition on Dispersion and Cold Compaction of Nickel and Aluminum Powders: *K. Morsi*[1]; Satyajit Shinde[1]; Eugene Olevsky[1]; [1]San Diego State University, Mechl. Engrg., 5500 Campanile Dr., San Diego, CA 92182 USA

Self-Propagating High Temperature synthesis (SHS) has recently been used to produce intermetallics and intermetallics composites, in short processing times and requiring minimal energy inputs. Mixing of elemental powders prior to SHS requires careful consideration for successful processing. This is particularly true for powders with submicron particles sizes. The present paper investigates the low-energy mechanical attrition of mixtures of nickel and aluminum prior to SHS, with the intention of producing a dispersed elemental powder mixture. The process is somewhat different from Mechanically Activated Self-Propagating High-Temperature Synthesis (MASHS) which has recently been successfully employed to produce nanomaterials. The influence of mechanical attrition on dispersion and powder compaction is pre-

sented. The concepts of the theory of plasticity of porous bodies are employed to assess the influence of attrition on the yield stress of thecomposite powder.

10:45 AM
Fully Automated PVD Process for Multilayer Metallic Film Coating: *Eugene Deyneka*[1]; Sergey Yarmolenko[1]; Jag Sankar[1]; [1]North Carolina A&T University, CAMSS, 1601 E. Market St., 242 Ft. IRC Bldg., Greensboro, NC 27411 USA

Automation of the multi-chamber multi-cathode DC magnetron sputtering system for high vacuum metallic film deposition is reported. The PC-controlled system is based on the Opto-22 hardware and software modules, with the computer code written in Microsoft Visual Basic. All three automation scenarios are developed: a) manual (maintenance) mode, including cryopumps regeneration module, b) semi-automated mode with simplified substrate movement between the RIE and sputtering chambers, and c) fully automated recipe-based mode having a total of over twenty etching, general, and sputtering process parameters, where the number of deposited layers is user-defined. The film thickness can range from several nanometers to several microns. The issues of film adhesion to the substrate, sputtering time, layer thickness fine-tuning and control, film uniformity, and incorporating time-depending variables into the code will be discussed. This automation program can be easily modified for a wide range of equipment as a cost-saving alternative to commercial products.

11:05 AM
Synthesis of Al2O3-SiCw Ceramic Matrix Composite by Carbothermal Reduction of Kaolin: *Sutham Niyomwas*[1]; Lek Sikong[2]; [1]Prince of Songkla University, Dept. of Mechl. Engrg., 15 Karnchanawanich Rd., Hat Yai, Songkla 90112 Thailand; [2]Prince of Songkla University, Dept. of Mining & Matls. Engrg., 15 Karnchanawanich Rd., Hat Yai, Songkla 90112 Thailand

The formations of Al2O3-SiCw composite have been obtained in situ by carbothermal reduction of a mixture of Kaolin and activated carbon. The reaction temperature was controlled at between 1400 C to 1600 C. The synthesized products were mixtures of alumina and silicon carbide in the form of whiskers. The effects of milling duration of precursors and reaction temperature are presented. XRD and SEM analyses indicate complete reaction of precursors to yield Al2O3-SiCw as product powders, with the SiC having porous and whisker morphology.

11:25 AM
Morphology Change of AlN with Respect to Starting Materials in SHS Process: Jae R. Lee[1]; Ik K. Lee[1]; Dong J. Kim[1]; Jong G. Ahn[1]; *Hun S. Chung*[1]; [1]Korea Institute of Geoscience & Mineral Resources, Minls. & Matls. Procg., 30 Kajung-dong, Yoosung-Ku, Daejeon 305-350 S. Korea

The particle size and shape effects of starting materials on the preparation of aluminum nitride by self-propagating high temperature synthesis technique under high nitrogen pressure were investigated with various AlN diluents and Al reactants. It was found that the structure of beds of the starting raw particles largely affected the pore channels for nitrogen gas infiltration as well as the passages for combustion propagation before and during the reaction, resulting in the morphology and purity changes of the synthesized products. The AlN product of purity over 98% with size of about 30 microns were obtained.

11:45 AM
Preparation of Sm-Co Alloy Oxide Precursor by Wet-Chemical Coprecipitation: *Guo Xueyi*[1]; [1]Central South University, Sch. of Metallurg. Sci. & Engrg., Yuelu Dist., Changsha, Hunan 410083 China

Sm-Co alloy is a kind of magnetic material with high power and has been applied in modern industry widely. In this study, the wet chemical coprecipitation was developed for synthesis of the Sm-Co alloy oxide precusrsor. The themodynamic analysis of the studied system was done to clarify the solution behavior theoretically based on the themodynamic equilibrium and simulataneous equilibrium. Then,the experiments were done to address the various effects on the wet chemical process, including solution pH, reactant concentration, dispersant,reaction temperature and time, etc. It is found that by precise control of the process, the Sm-Co alloy oxide precursor was synthesized with fine crystallizaion and special size and size distribution.

Mechanical Behavior of Thin Films and Small Structures: Fatigue, Fracture, and Reliability of MEMS and Thin Structures II

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior

Program Organizers: Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA; Brad L. Boyce, Sandia National Laboratories, Materials and Processes Sciences Center, Albuquerque, NM 87185 USA; Evan Ma, Johns Hopkins University, Department of Materials Science & Engineering, Baltimore, MD 21218 USA; Andrew Minor, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA 94720 USA; Christopher L. Muhlstein, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Judy A. Schneider, Mississippi State University, Department of Mechanical Engineering, Mississippi State, MS 39762 USA

Wednesday AM February 16, 2005 — Room: 2024 Location: Moscone West Convention Center

Session Chairs: Christopher L. Muhlstein, Pennsylvania State University, Dept. of Matls. Sci. & Engrg., Univ. Park, PA 16802 USA; David F. Bahr, Washington State University, Mechl. & Matls. Engrg., Pullman, WA 99164-2920 USA

8:30 AM Invited
Understanding and Engineering Reliability in Microelectromechanical Systems: *Srinivas Tadigadapa*[1]; [1]Pennsylvania State University, 111J EE W. Bldg., Univ. Park, PA 16802 USA

The very large surface area to volume ratios of microelectromechanical systems (MEMS) has a very strong influence on their long term stability and performance under dynamic and static loading conditions. The large surface area of such systems offers nucleation sites for the initiation of several surface reactions and modifications to occur under appropriate environmental conditions. Until now these topics have been the subject of study for understanding microstructural reliability and for the development of appropriate packaging strategies for such systems. In this paper the reliability of single crystal silicon microstructures realized using dissolved wafer process will be presented. Micromachined pressure sensor diaphragm characteristics after subjecting to various loading conditions will be discussed. The paper will also discuss the effect of surface treatments of the micromachined structures on the resonant characteristics of these structures and their implications on the performance of MEMS devices. Finally, the paper will present a quick overview of wafer level packaging of MEMS structures and some of our current efforts through wafer level bonding techniques towards achieving such goals.

8:55 AM
Addressing Mechanical Reliability Issues in Sandia MEMS Devices: *Brad L. Boyce*[1]; Thomas E. Buchheit[1]; Steven H. Goods[2]; Danelle M. Tanner[3]; Michelle A. Duesterhaus[4]; [1]Sandia National Laboratories, Dept. 1851, MS 0889, PO Box 5800, Albuquerque, NM 87185 USA; [2]Sandia National Laboratories, Dept. 8754, MS 9409, PO Box 969, Livermore, CA 94551 USA; [3]Sandia National Laboratories, Dept. 1762, MS 1310, PO Box 5800, Albuquerque, NM 87185 USA; [4]Sandia National Laboratories, Dept. 2614, MS: 1310, PO Box 5800, Albuquerque, NM 87185 USA

Sandia National Laboratories is currently developing several MEMS devices. Specific examples include: an electrical contact switch with a spring fabricated from a LIGA Ni-Mn alloy, a low-G accelerometer fabricated from bulk-micromachined single-crystal silicon-on-insulator (SOI), and non-volatile memory fabricated from surface-micromachined polycrystalline silicon. This presentation will provide an overview of mechanical reliability studies motivated by the implementation of these devices. In the case of the electrical contact switch, the LIGA Ni-Mn spring is expected to perform predictably after repeated cycles and thermal exposures. Thus, reliability studies addressed issues of microplastic yielding, subsequent cyclic ratcheting, and thermal stability of the microstructure and resulting properties. The high-cycle fatigue performance will also be discussed with emphasis on the role of oxide-induced crack-initiation sites associated with persistent slip bands. In the case of the low-G accelerometer, the single-crystal silicon is expected to survive quasistatic and shock-loading environments. For this application, device-level tests have been used to evalu-

ate mechanical performance and process-induced failure sites. In the case of the non-volatile memory, the device utilizes thermal actuators and therefore the mechanical reliability at elevated temperatures becomes a primary concern. Micro-tensile tests in ambient and inert environments at temperatures ranging from room temperature to 800C indicated a dramatic decrease in the allowable stresses. In each of these examples, we will show the connection between device-level reliability and underpinning microstructural failure mechanisms. Sandia is a multiprogram laboratory operated by Sandia Corporation, A Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:10 AM
Performance and Durability of Monolayer Coatings Under Monotonic and Fatigue Loading Conditions: R. Kirkpatrick[1]; C. D. McCann[1]; *C. L. Muhlstein*[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Engrg. & the Matls. Rsch. Inst., 310 Steidle Bldg., Univ. Park, PA 16803 USA

Organic monolayer coatings have been used by the authors to enhance the fatigue resistance of silicon microelectromechanical systems (MEMS). The hydrophobic barrier provided by octadecyltrichlorosilane (OTS) and dichlorodimethylsilane (DDMS) layers prevents the intrusion of water and temporarily halts reaction-layer fatigue of silicon films. However, organic monolayer coatings eventually degrade and fail under cyclic loading conditions. In this work the mechanical behavior of organic monolayer coatings on bulk borosilicate glass and polycrystalline silicon are compared. Experimental data suggests that the fatigue susceptibility of these monolayer coatings is limited to the large amplitude, cyclic strains generated in micromechanical systems.

9:25 AM Invited
Characterization of Strength and Fatigue Properties of Thin Polycrystalline Silicon Films: *Joerg Bagdahn*[1]; Jan Schischka[1]; Heiko Knoll[1]; Matthias Ebert[1]; Robert Boroch[2]; Roland Mueller-Fiedler[2]; [1]Fraunhofer Institute for Mechanics of Materials, Heideallee 19, 06120 Halle (Saale) Germany; [2]Robert Bosch GmbH FV/FLD, Postfach 10 60 50, 70049 Stuttgart Germany

Polycrystalline silicon (polysilicon) is a widely used material for MEMS in automotive applications. In order to warranty a reliable function during the whole life of 15-20 years and a high number of mechanical cycles (up to 10^12) a sufficient mechanical strength of the thin films is required. Tensile and bend tests were applied to measure the strength of thin polysilicon films with different sample width and stress concentrations. In addition theoretical studies of the influence of the sample size and stress concentrations on the strength will be shown. The fatigue properties of polysilicon were studied on electrostatic and on external actuated samples under various testing conditions, e.g. the frequency was varied between several and 10^5 Hertz and also the environmental conditions during testing were changed between nearly vacuum and high humidity conditions. Finally, the microstructure of the tested polysilicon film was characterized by TEM, EBSD, FIB and SEM techniques and correlated with the measured strength and fatigue properties.

9:50 AM
Mechanical Behavior of Thin Gold Films for RF MEMS Applications: *I. Chasiotis*[1]; C. Bateson[1]; K. Timpano[1]; D. Koenigkann[1]; N. S. Barker[2]; [1]University of Virginia, Mechl. & Aeros. Engrg., PO Box 400746, Charlottesville, VA 22904-4746 USA; [2]University of Virginia, Electl. & Computer Engrg., PO Box 400743, Charlottesville, VA 22904-4743 USA

The effects of fabrication, film thickness, and strain rate on the mechanical behavior of thin gold films with applications in radio-frequency (RF) MEMS switches have been investigated. Microscale gold specimens with various thicknesses (0.2-2.5 microns) were fabricated using sputtering, evaporation, and electroplating. The gage section width of these free-standing, dog-bone shaped specimens varied between 50-200 microns. The mechanical characterization was conducted via a custom-built uniaxial tensile testing system that employed a low force load cell and a piezoelectric actuator for force and displacement measurements, respectively. The stress-strain curves of the gold films demonstrated elastic-nearly perfectly plastic behavior. The value of Young's modulus was found to agree well with that of bulk gold, averaging 71 GPa. The tensile specimens demonstrated high ductility that increased with decreasing strain rate. For strain rates between 10^{-3} s^{-1} to $10^{-5}s^{-1}$, the ductility was approximately 6% for middle range strain rates and as high as 9% for specimens subjected to monotonic loading at low strain rates. Over the entire range of strain rates the ductility was found to vary by a factor of 4. For the same range of strain rates the peak stress varied between 350-450 MPa and it decreased with decreasing strain rate. The average film strength was comparable to that reported previously for thin films of similar thickness that were also tested in tension. The yield strength was found to be about 300 MPa for low and 350 MPa for high strain rates, respectively, which is also comparable to literature values. Examination of fracture cross-sections indicated a dependence on the material fabrication process and applied strain rate. Furthermore, the effects of specimen thickness and fabrication process on the mechanical properties of thin gold films will be discussed in this presentation.

10:05 AM Break

10:20 AM Invited
Through Thickness Fracture Behavior in Hard Films on Soft Substrates: *D. F. Bahr*[1]; K. R. Morasch[1]; M. S. Kennedy[1]; S. P. Anderson[1]; N. R. Moody[2]; [1]Washington State University, Mechl. & Matls. Engrg., PO Box 642920, Pullman, WA 99164-2920 USA; [2]Sandia National Laboratories, PO Box 969, Livermore, CA 94550-0969 USA

The mechanism of film fracture, particularly in thin (sub micron) films has been difficult to quantify due to the scales of measurement of load and displacements. However, using nanoindentation coupled with atomic force microscopy, it is possible to quantify differences in film fracture in a variety of systems of hard films on soft substrates. This presentation will review 4 different film systems, all of which exhibit similar trends in fracture morphology but span a range of properties. Oxide films on active metals (aluminum and stainless steel), piezoelectric oxides on metallic layers, and tungsten films on polymer substrates have been tested using nanoindentation. Discontinuities in loading behavior have been identified using atomic force microscopy as through thickness fracture events. An applied stress intensity for fracture will be developed based on bending moments on the surface induced by nanoindentation. The wide range of elastic and plastic properties will demonstrate the appropriateness of the model. The stress intensity at fracture is impacted by film growth conditions, for instance in aluminum oxide on aluminum the stress at fracture increases as film thickness increases, but the critical stress intensity for fracture is highest for films thinner than 30 nm, and decreases asymptotically towards a toughness of 1 MPa√m.

10:45 AM
Anomalous Near-Threshold Debond Growth Rate Behavior in Thin-Film Structures: Implications for Device Life: *Bree M. Sharratt*[1]; Lorraine C. Wang[2]; Reinhold H. Dauskardt[2]; [1]Stanford University, Aeronautics & Astronautics, c/o Matls. Sci. & Engrg., Peterson Bldg. 550, 416 Escondido Mall, Stanford, CA 94305-2205 USA; [2]Stanford University, Matls. Sci. & Engrg., Peterson Bldg. 550, 416 Escondido Mall, Stanford, CA 94305-2205 USA

An understanding of the mechanisms associated with interfacial debonding is crucial for designing devices containing thin-film structures where long-term reliability is of concern. We report on an anomalous near-threshold debond growth rate behavior measured at the interface between a thin epoxy layer and an adjacent passivated silicon substrate under both monotonic and cyclic loading. The near-threshold debond growth rates plateaued at ~10^{-9} m/sec and were largely insensitive to the applied loads. The surprising similarity of the plateaus measured under cyclic and monotonic loading indicated that the mechanical fatigue damage accumulation process, a significant accelerant at higher growth rates, was overshadowed in the near-threshold region. The dependence of the plateau growth rates on environmental species and temperature is presented together with a possible chemical reaction based mechanism. These results have significant implications for the operational definition of a crack growth threshold and associated operating life of such thin-film structures.

11:00 AM
Fracture Toughness of Thin Films on Compliant Substrate Using Controlled Buckling Test: *Zhong Chen*[1]; [1]Nanyang Technological University, Sch. of Matls. Engrg., Nanyang Ave. 639798 Singapore

Thin films and multilayered structures are increasingly used in industry. One of the important mechanical properties these thin layers is the fracture toughness, which is not the same as the one obtained from bulk samples. Film fracture toughness is extremely important in design for coatings on plastic or other applications where flexibility is required. This work presents a scheme using controlled buckling experiment to measure the fracture toughness of brittle thin film on compliant substrate. When the film is under tension, steady-state channeling cracks form. Critical fracture strain can be obtained by the displacement in the buckle. Calculation of fracture toughness is presented allowing the substrate to experience plastic deformation. Finally examples are given to illustrate such a test scheme.

11:15 AM Invited
Cohesive and Adhesive Fracture in Complex Device Structures: *Reinhold H. Dauskardt*[1]; [1]Stanford University, Dept. of Matls. Sci. & Engrg., Stanford, CA 94305-2205 USA

Debonding of interfaces and cracking of fragile interlayer dielectrics effects the mechanical integrity of a wide range of thin-film device structures. This results in reduced yield at all levels of device processing including survival through chemical mechanical planarization (CMP) and subsequent device packaging. Two unique challenges for the next technology nodes involve the introduction of new ultra low k dielectric materials and the effect of device architecture including length-scales and aspect ratios, on mechanical and fracture behavior. Materials are nearly always optimized for other desired properties (e.g. dielectric properties or diffusion resistance) and the resulting effects on mechanical performance can be significant. In this presentation, the mechanical and fracture behavior of representative blanket and patterned thin-film structures including glass and organic dielectrics, barriers and metal layers, are examined. The acceleration of crack growth in complex chemical environments typically encountered during processing is discussed. The effects of interface parameters and thin-film composition and porosity will also be considered. Novel strategies to toughen fragile nanoporous materials using molecular remnants of the porogen molecules used to create the porosity are described. Finally, the effect of more complex patterned thin-film structures are examined where length scales are restricted in more than one dimension. Implications for device reliability, integration of new materials, and life prediction are discussed.

11:40 AM
Driving Forces of Bond Coat Surface Rumpling in Thermal Barrier Systems: *K. Jimmy Hsia*[1]; [1]University of Illinois, Theoretl. & Applied Mech., 111B Talbot Lab, MC-262, 104 S. Wright St., Urbana, IL 61801 USA

Failure of thermal barrier coatings is often caused by nucleation and growth of interfacial cracks between the ceramic coating and metallic bondcoat (BC). The underlying process causing such cracking is the progressive rumpling of the BC surface upon thermal cycling. It is believed that the mismatch/growth stresses in the thermally grown oxide (TGO) provide the driving force, and either surface diffusion or plastic ratcheting gives rise to rumpling. Another proposal is the selective diffusion of species and resulting microstructural variations. We carefully studied these mechanisms by critical experiments, focusing in particular on the role of TGO, the role of thermal cycling, the role of microstructural evolution, and the role of the BC. Our findings are: the presence of TGO is not critical for rumpling; thermal cycling is not a necessary condition; there is poor correlation between microstructural variations and peak locations of the rumples. The likely driving force is the mismatch stress in the BC.

11:55 AM
Temperature, Loading, and pH Effects on Debonding of Silica/Adhesive Layered Structures: *Louise Y. Wang*[1]; Reinhold H. Dauskardt[1]; [1]Stanford University, Matls. Sci. & Engrg., 416 Escondido Mall, Bldg. 550, Stanford, CA 94305 USA

Epoxy resins blended with silane coupling agents are widely used adhesives between passivated device substrates and polyimide films in microelectronic packages. However, the resulting silica/adhesive interface and adhesive itself are susceptible to accelerated debonding and cracking in moist, aqueous and corrosive environments. This study focuses on the effects of temperature, pH and more complex mechanical loading on interfacial debonding. Increased debond velocities were apparent with increasing temperature which was related to enhanced reaction kinetics at the debond crack tip. In buffered basic solutions and with increasing temperature, the fracture path was found to meander within the adhesive and adjacent interfaces. In acidic solutions debonding was restricted to the adhesive layer. A plateau growth rate region was apparent at intermediate growth rates in the basic solution. Mechanisms for the accelerated cracking are described and implications for packaging reliability and life prediction considered.

12:10 PM
Tribological Property Investigation for Pulsed Laser Deposited Oxide Thin Films: *Xinyu Wang*[1]; Sudheer Neralla[1]; Sergey Yarmolenko[1]; Dhananjay Kumar[1]; Jagannathan Sankar[1]; [1]North Carolina Agricultural and Technical State University, Dept. of Mechl. & Cheml. Engrg., CAMSS, Greensboro, NC 27411 USA

Tribological properties are an important concern for researchers developing thin films. In this study, alumina (Al_2O_3) and silica (SiO_2) thin films are deposited on silicon (Si) (100) and steel substrates using the pulsed laser deposition (PLD) technique. Different substrate temperatures ranging from room temperature to 800ºC and different laser energies are used. Al_2O_3 and SiO_2 thin films with different thicknesses ranging from 500 nm to 4 µm are developed. Tribological properties such as adhesion, friction, and wear are investigated by performing the nanoscratch test using a nanoindenter and the wear test using a microtribometer. Scratching length of 500 µm and maximum loads of 200 mN are used for the nanoscratch tests. A profilometer, a scanning electron microscope (SEM), a transmission electron microscope (TEM) and an atomic force microscope (AFM) are used to analyze film properties such as surface topography, roughness (RMS) and cross-sectional microstructures. Preliminary results have shown that a strong adhesion between a film and the substrate on which it was deposited existed and different values of adhesion were also found. Direct interfacial fracture observations are made by polishing the film-substrate cross sections. The preliminary observations illustrated the half-penny cracks. Critical loads in the nanoscratch tests and critical number of cycles in the wear tests of different films are compared. The test results provide further understanding into the tribological properties of the oxide thin films.

Metallurgical Technology for Waste Minimization: Session II

Sponsored by: Extraction & Processing Division, EPD-Waste Treatment & Minimization Committee
Program Organizers: Junji Shibata, Kansai University, Department of Chemical Engineering, Osaka 564-8680 Japan; Toru Okabe, University of Tokyo, Institute of Industrial Science, Tokyo Japan; Edgar E. Vidal, Colorado School of Mines, Golden, CO 80401-1887 USA

Wednesday AM Room: 2012
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Yoshiaki Umetsu, Tohoku University, Japan; Pat R. Taylor, Colorado School of Mines, Golden, CO 80401 USA

8:30 AM Invited
Investigation of Ion Exchange Resins for Use in Treatment of Semiconductor Processing Waste Streams: *Jeffrey D. Winterton*[1]; Fiona M. Doyle[1]; [1]University of California, Dept. of Matls. Sci. & Engrg., 210 Hearst Mining Bldg. #1760, Berkeley, CA 94270-1760 USA

The semiconductor industry is rapidly shifting from aluminum to copper as the interconnect material of choice. This shift is accompanied by the creation of several copper-containing aqueous waste streams from different stages of processing. The streams typically have a range of copper concentrations and a variety of additive agents. We are investigating the use of ion exchange resins as a means of recovering the copper from these streams within the processing plant, thereby allowing for the recycling of process waste water and the minimization of hazardous waste generation. Resins of different functionalities have been investigated over a range of processing conditions with the goal of developing a computer based model for the operation. Factors investigated include copper affinity, uptake and elution kinetics, and effect of various plating additives during copper adsorption.

9:00 AM Invited
Adsorption Mechanism of Palladium by Redox Within Condensed-Tannin Gel: *Yoshio Nakano*[1]; [1]Tokyo Institute Technology, Interdisciplinary Grad. Sch. of Sci. & Tech., Dept. of Environml. Chmst. & Engrg., 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502 Japan

Tannin gel particles with polyhydroxyphenyl groups were synthesized as the adsorbent for the new recovery system of palladium(Pd), which was simple and generated little secondary waste in comparison with the conventional recovery processes. The properties of tannin gel particles for the adsorption of Pd were examined in $PdCl_2$ aqueous solution and resulted in that Pd is adsorbed onto the tannin gel particles as a reduced metallic Pd through redox reaction mechanism: chloropalladium(II) species are reduced to Pd(0), while hydroxyl groups of tannin gel are oxidised during the adsorption. Additionally, it was obserbed that Pd species containing fewer Cl, such as $PdCl_2(H_2O)_2$ and $PdCl(H_2O)_3^+$, are more favorable for the adsorption than $PdCl_3(H_2O)^-$ and $PdCl_4^{2-}$. By utilizing such characteristics of tannin gel particles, it is expected that they can be applied to recover Pd efficiently and simply with low cost.

9:30 AM
Heavy Metal Adsorption Properties of Zeolite Synthesized from Coal Bottom Ash: *Jin-Koo Park*[1]; So-Yun Jeon[1]; Ji-Whan Ahn[1]; [1]Korea Institute of Geoscience & Mineral Resources, Minls. & Matls. Procg. Div., Taejon 305-350 Korea

At present, about 70% of the coal fly ash that discharged from domestic thermoelectric power plants is reused as raw materials in the manufacture of cement and concrete. And researches on synthesis of zeolite synthesized from coal fly ash have been performed to obtain the high-value industrial products for the last two decades. However, coal bottom ash occupying about 15% of total coal ash is totally disposed at present. Coal bottom ash can also used as raw materials for the synthesis of zeolites because it contain large amounts of Al and Si. In this study, we synthesized zeolite from coal bottom ash at various NaOH concentrations and reaction times. Then, physio-chemical properties of the synthesized zeolite such as crystal structure, surface area and cation exchange capacity were investigated. Also, characterized adsorption and elution properties of heavy metals for apply the synthesized zeolite to soil improvement agent or water treatment agent.

9:50 AM Break

10:05 AM
Development of Recovery Process of Tetra-Methyl Ammonium Hydroxide from Waste Solution: Junji Shibata[1]; Tomohiro Yanase[1]; *Norihiro Murayama*[1]; Hideki Yamamoto[1]; [1]Kansai University, Cheml. Engrg., 3-3-35, Yamate, Suita, Osaka 564-8680 Japan

Tetra-methyl ammonium hydroxide is used in various electric and electronic parts production processes such as semiconductor, liquid crystal display and printed circuit board. The discharged amount of this chemical reaches about 2,500 ton /year from one factory in Japan. The waste liquor contains a lot of organic matter, which means high BOD and COD. Fundamental study found that tetra-methyl ammonium hydroxide can be separated and recovered from the waste liquor by the ion exchange method, which is one of the hydrometallurgical purification methods. The waste liquor discharged from the liquid crystal display production contains 0.53wt% tetra-methyl ammonium hydroxide, 60mg/dm3 phenol and ppb level of metal ions. We need development of a separation and recovery process for tetra-methyl ammonium hydroxide. In the cation exchange reaction, tetra-methyl ammonium ion is captured on the cation exchange resin. Other non-ionic organic matter like phenol goes through the resin without being captured on it, the separation being attained in this step. In the elution step, tetra-methyl ammonium ion captured on the resin is released as tetra-methyl ammonium chloride into aqueous solution by the action of dilute hydrochloric acid. Tetra-methyl ammonium chloride is converted to tetra-methyl ammonium hydroxide by the reaction between tetra-methyl ammonium chloride and OH-type anion exchange resin. The process is composed of three steps; cation exchange, elution and conversion. The experiments were carried out using ion exchange resin column of 20mmö and 735mm high, and the recovery and purity of tetra-methyl ammonium hydroxide were clarified at each step. They were dependent on various factors such as space velocity in cation exchange, elution and conversion columns, and hydrochloric acid concentration in elution column. One example of experiments exhibited that the recovery of tetra-methyl ammonium hydroxide over three steps was 80% and the purity was 99%, if 10-15 space velocity in each step and 0.3-1.0 mol/dm3 hydrochloric acid in elution step were used. A successive resin column process was developed from the experimental results and then the novel recovery process for tetra-methyl ammonium hydroxide waste liquor was proposed. The assessment of yield and purity at each step was conducted to clarify how the proposed process is effective.

10:25 AM
Biological Fluegasdesulpurization: Sustainable, Effective and Cost-Efficient: *Gerard Schouten*[1]; Jacco Huisman[1]; Henk Dijkman[1]; [1]Paques bv, Business Dvlp., PO Box 52, Balk The Netherlands

Abstract TMS 2005:With the introduction of ever-stricter environmental operating guidelines, capital expenditure restrictions and operational budget cutbacks, the biological method of SO2 removal becomes more and more attractive. Biotechnological treatment of dilute flue gases is a more cost effective technology in comparison to conventional sodium hydroxide scrubbing. Although the investment costs for sodium hydroxide scrubbing are lower, the operational costs are significantly higher. In addition, the end product of the biological installation is sulfur instead of sodium sulfate; and no further wastewater treatment of the bleed from the biological installation is required since heavy metals are removed simultaneously. Another option for the treatment of SO2 containing gas at a sulfuric acid plant is the production of extra sulfuric acid of the discharged SO2 by applying an additional converter. Comparing biological treatment with this option shows much lower investment costs for the biological installation. Sulfur is produced which can be converted to sulfuric acid, so the bio-route will be more cost-effective than an additional converter. In principle, the biotechnological flue gas desulfurisation system (BioDeSOx) is an integration of an absorber with a "biological buffer regeneration facility". In the absorber, the SO2 containing gas is brought into contact with wash liquid (a sodium bicarbonate buffer). The absorber effluent contains a mixture of sulfite and sulfate that is converted into elemental sulfur whereby the wash liquid is regenerated. This conversion takes place in an integrated system; first, the sulfite/sulfate mixture is converted anaerobically into sulfide; secondly, the sulfide is converted aerobically into elemental sulfur. Subsequently the sulfur is separated and the water is returned to the absorber. Due to the buffer capacity of the washing water, removal efficiencies over 98% are possible. In addition to SO2 removal, it is possible to convert for example other bleeds streams such as scrubber acid or weak acid to sulfur in the same SO2 installation. Recent evaluations concluded that biological desulphurization of flue gases is not only economically attractive in comparison to convention sodium hydroxide scrubbing but also in comparison to gypsum producing systems and even seawater scrubbers. This paper describes the technological and economical viability of biological flue gas desulphurization.

Micromechanics of Advanced Materials II (Symposium in Honor of James C.M. Li's 80th Birthday): Mechanics of Nanostructures

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Fuqian Yang, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY 40506 USA; C. C. Chau, Pactiv Corporation, Canandaigua Technology Center, Canandaigua, NY 14424 USA; Sung Nee George Chu, Multiplex Inc, South Plainfield, NJ 07080 USA; M. Ashraf Imam, Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375-5343 USA; Teh-Ming Kung, Eastman Kodak Company, Rochester, NY 14650 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; B. B. Rath, Naval Research Laboratory, Materials Science and Component Technology Directorate, Washington, DC 20375-5341 USA

Wednesday AM Room: 3000
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: C. S. Pande, Naval Research Laboratory, Washington, DC 20375 USA; M. H. Yoo, Korea Advanced Institute of Science & Technology, Dept. of Matls. Sci. & Engrg., Daejeon 305-701 Korea

8:30 AM Invited
Relaxation Effects in Nanocrystalline and Ultra-Fine Grain Metals: Kai Zhang[1]; *Julia R. Weertman*[1]; [1]Northwestern University, Matls. Sci. & Engrg. Dept., 2220 Campus Dr., Evanston, IL 60208 USA

Microhardness measurements on nanocrystalline and ultra-fine grain copper samples show a decrease in hardness over a period of hours. The relaxation rate increases with decreasing temperature, decreasing grain size, and increasing sample purity. Characterization studies examine structural changes in the indent region associated with the mechanical behavior. This research is supported by DOE grant DE-FG02-02ER 46002.

8:55 AM Invited
Effects of Irregular Distribution of Particles on Stress Concentrations in Composites: The Case of Close Approach: *Daniel N. Beshers*[1]; Richard J. Seymour[1]; [1]Columbia University, Matls. Sci. & Engrg., MC 4701, 500 W. 120th St., New York, NY 10027 USA

A common approximation with composite materials neglects the interaction of the particles. For close particles, this neglect is not justified. There are two aspects. One is the appearance of induced stress fields both inside and outside the inclusion. The induced field of one particle adds to the stress on a neighbor and vice versa, leading to a final state with enhanced stress, analogous to interactive effects in electric and magnetic polarization. The second aspect is that there are in general discontinuities of elastic fields at the interface between a

particle and the surrounding matrix. When the inclusions are close, the material between them is subject to finite deformations on each side, but with only a small distance over which to accommodate them. The strain may become very large when the separation is of the order of nanometers. We present analyses of two simple examples.

9:20 AM Invited
Effects of Stress on the Formation of Metallic or Semiconducting Nanostructures on Si and SiGe: *L. J. Chen*[1]; [1]National Tsing Hua University, Matls. Sci. & Engrg., 101, Sec.2, Kuang Fu Rd., Hsinchu 300 Taiwan

Nanostructures, including nanodots and nanowires, are attracting much interest because they are expected to play an important role in nanometer-scale electronics and optoelectronics. Stress has often been found to play an important role in influencing the formation of nanostructures. In this presentation, we provide an overview on the effects of stress on the formation of nanostructures on Si or SiGe. Several examples involving stress-induced effects such as self-assembled NiSi quantum-dot arrays on epitaxial Si0.7Ge0.3 on (001)Si, self-assembled nano-rings in Si-capped Ge quantum dots on (001)Si, growth of TiSi2 and rare-earth silicides nanowires on silicon and self-forming silicide/SiGe-based tube structure on Si will be given.

9:45 AM Invited
Nanomechanical Behaviour of Piezoelectric Nanowire: *Xinyuan (Scott) Mao*[1]; M. Zhao[1]; C. B. Jiang[2]; Suoxing Li[2]; [1]University of Pittsburgh, Mechl. Engrg., 3700 O'Hara St., Pittsburgh, PA 15261 USA; [2]Shengyang Metal Research Institute, Shengyang China

Quasi one-dimensional (1D) solid nanostructures, such as nanobelts of semiconducting oxides, have stimulated considerable interest for scientific research due to their importance in mesoscopic physics studies and their potential applications as nano-devices, nanocantilevers, nanoactuators and nanosensors. A key challenge to today's research is the experimental difficulty in fabricating, manipulating and testing the physical properties of a single nanowire/cantilever whose size is in the nano- to micron-meter range, because the small size (diameter and length) of the object prohibits the applications of the well-established testing techniques. Belt-like oxide nanostructures, so called nanobelts, were successfully synthesized by evaporating ZnO powders at high temperatures without the presence of catalyst. Morphology analysis shows the nanobelts have a rectangle-like cross section with typical widths of several hundred nanometers, width-to-thickness ratios of 5 to 10, and lengths of hundreds of micron meters. Nanoindentations were made on individual ZnO nanobelts by using AFM and Hysitron Triboscope indenters. It was shown that the indentation size effect was still obvious for the indentation depth under 50nm. It is also demonstrated that nanomaching is possible on nanobelt using AFM tip. Piezoelectric behaviour is measured by electric force microscope, which shows strong size effect.

10:10 AM Break

10:15 AM Invited
Dielectric and Mechanical Analysis of Polymer Nanocomposites: *Julie P. Harmon*[1]; Kadine Mohomed[1]; LaNetra Clayton[1]; Timofey Gerasimov[1]; [1]University of South Florida, Chmst., SCA 400, 4202 E. Fowler Ave., Tampa, FL 33620-5250 USA

A variety of polymer nanocomposites were fabricated via in situ ultrasonic polymerization and melt blending. Various techniques were used to characterize the thermal, dielectric and mechanical properties of the nanocomposites. Differential scanning calorimetry (DSC) was used to obtain the glass transition temperature (Tg) of the nanocomposites. Dielectric analysis (DEA) monitored changes in the dielectric response with respect to increasing nanofiller concentration. Dynamic mechanical analysis (DMA) was used to characterize the viscoelastic properties. Nanofiller dispersion quality was tested via scanning electron microscopy (SEM) and optical microscopy. Optimizing dispersion quality enhances the ability to obtain peak performance in key properties. As exptected, DEA results show a dramatic change in the dielectric spectra of the nanocomposites occurring at the point where the percolation threshold is reached.

10:40 AM
Creep-Rupture Behavior of Fine-Diameter Ceramic Fibers with Nano-Sized Grains: *James A. DiCarlo*[1]; [1]NASA Glenn Research Center, Matls. Div., 21000 Brookpark Rd., MS 106-5, Cleveland, OH 44135 USA

The successful application of ceramic matrix composites (CMC) in high-temperature applications depends strongly on developing fine-diameter (~10 μm) ceramic fiber reinforcement with a variety of key thermostructural properties. Foremost amongst these are high as-produced tensile strength and retention of a large fraction of this strength for long times under anticipated CMC service conditions. Using creep-rupture data measured at NASA on single and multi-fiber specimens, this presentation reviews the high-temperature intrinsic strength behavior of commercially available oxide and non-oxide fiber types. It is shown that that there are significant differences in creep-rupture behavior between the various fiber types and that these differences are influenced by such factors as base chemical composition, process-related defect sizes, grain sizes, grain boundary phases, surface chemistry, surface morphology, and test environment. On-going studies at NASA to model the effects of these factors in order to predict and optimize fiber/CMC creep and strength retention are discussed.

11:00 AM Invited
Influence of Grain Size on Deformation Mechanisms in Polycrystalline Materials: *Yuntian Ted Zhu*[1]; Terence G. Langdon[2]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., MS G755, Los Alamos, NM 87545 USA; [2]University of Southern California, Depts. of Aeros. & Mechl. Engrg. & Matls. Sci., Los Angeles, CA 90089-1453 USA

The deformation mechanisms in coarse-grained polycrystalline materials are understood reasonably well. Generally, the primary deformation processes are associated with the movement of dislocations either through crystallographic slip at low temperatures or through a combination of dislocation climb and glide at high temperatures. Additional possible processes include stress-directed vacancy diffusion and grain boundary sliding. It has been shown using molecular dynamic simulations, and confirmed in experiments, that different processes become important when the grain size is reduced to the nanometer level. Partial dislocation emission from grain boundaries becomes a dominant process at grain sizes of 10 to 50 nm and this leads to the formation of deformation twins even in high stacking-fault materials such as aluminum. Grain boundary sliding also becomes dominant at grain sizes below 10 nm at low temperatures. This presentation gives an overview on the influence of grain size on deformation mechanisms in polycrystalline materials.

11:20 AM Invited
A Model for the Inverse Hall-Petch Relation of the Nanocrystalline Materials: *Guojiang Fan*[1]; H. Choo[1]; P. K. Liaw[1]; E. J. Lavernia[2]; [1]University of Tennessee, Matls. Sci. & Engrg., Dougherty Engrg. Bldg., Knoxville, TN 37996 USA; [2]University of California, Cheml. Engrg. & Matls. Sci., Davis, CA 95616 USA

Nanocrystalline (nc) materials have received world-wide research interests due to their superior mechanical properties. Recently, new deformation mechanisms have been identified for the nc materials with the grain sizes on the order of several tens of nanometers, where dislocation pile-ups by the grain boundaries may not be operative. We propose a composite model to explain the phenomena of strength softening with decreasing the grain size, which was reported in some nc materials. We assume that a nc material consists of a grain interior and an amorphous grain-boundary layer. The grain interior deforms elastically under external stresses, while the plastic deformation of the grain-boundary layer was governed by a Maxwell's equation. Based on this model, we will show that the strength of a nc material decreases linearly with decreasing the grain size, when the grain size is below a certain threshold. The model is compared with the experimental data from the published studies on the nc Cu and Ni. The predictions of relevant creep mechanisms for nc materials are also discussed.

11:40 AM
Plastic Flow Localization and Shear Banding in Tungsten: *Q. Wei*[1]; E. Ma[1]; K. T. Ramesh[1]; L. J. Kecskes[2]; L. Magness[2]; R. J. Dowding[2]; R. Z. Valiev[3]; [1]Johns Hopkins University, Ctr. for Advd. Metallic & Ceram. Sys., Baltimore, MD 21218 USA; [2]Army Research Laboratory, Aberdeen Proving Ground, MD 21005 USA; [3]Ufa Technical University, Russia

Over the past twenty years, shear localization in tungsten (W) has been sought after for certain critical applications. We demonstrate that by refining the microstructure of bulk, commercial purity, W into the nanostructured and ultrafine-grained regime, adiabatic shear localization can be induced under dynamic compression in standard Kolsky bar tests. This unusual property is also observed for a number of other fine-structured bcc metals. The propensity for localization is discussed in terms of the strain hardening, strain-rate hardening, and thermal/geometrical softening behavior in bcc metals as a function of microstructure refinement.

12:00 PM
Deformation Behavior and Mechanisms of an Extruded Nanocrystalline Al-Fe-Cr-Ti Alloy: *Hong Luo*[1]; Leon L. Shaw[1]; Lichun Zhang[1]; D. Miracle[2]; [1]University of Connecticut, Inst. of Matls. Sci., 97 N. Eagleville Rd., Storrs, CT 06269 USA; [2]Air Force Research

Laboratory, Matls. & Mfg. Direct., Wright-Patterson AFB, OH 45433 USA

Deformation behavior of an extruded nanocrystalline (nc) Al-Fe-Cr-Ti alloy (80 - 150 nm) has been investigated systematically using compressive tests as a function of temperature and strain rate. A variety of analytical instruments including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS), and electron energy-loss spectrometry are utilized to characterize the material before and after deformation. The TEM analysis reveals the evidence of dislocation activities in the compressive deformation. Furthermore, the dislocation density depends on the test temperature and strain rate. Decreasing strain rate or increasing test temperature decreases the dislocation density. An unusual phenomenon, long stacking fault (SF) which is very difficult to form in aluminum because of the high SF energy, is found in the nc-Al alloy after compressive deformation. The mechanical properties of the nc Al-Fe-Cr-Ti alloy cannot be explained by either coble or power law creep. The strain rate sensitivity of this Al-Fe-Cr-Ti alloy is about 0.02 which is comparable with that of the coarse-grained Al alloys. The deformation mechanism of the nc Al-Fe-Cr-Ti alloy has been discussed based on the microstructure observation and mechanical properties.

Microstructural Processes in Irradiated Materials: He/H Interactions and Ferritic/Martensitic Steels

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Brian D. Wirth, University of California, Department of Nuclear Engineering, Berkeley, CA 94720-1730 USA; Charlotte S. Becquart, Ecole Nationale Superieure de Chimie de Lille, Laboratoire de Metallurgie Physique et Genie des Materiaux, Villeneuve d'Ascq cedex 59655 France; Hideki Matsui, Tohoku University, Institute for Materials Research Japan; Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA

Wednesday AM Room: 3011
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Shigeharu Ukai, Japan Nuclear Cycle Development Institute, Oarai Engrg. Ctr. Sys. Engrg. Tech. Div., Higashi-Ibaraki-Gun, Ibaraki-Prefecture 311-1393 Japan; Yutai Katoh, Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6138 USA

8:30 AM
Ab Initio Study of Helium-Vacancy Defects in Iron: *Chu Chun Fu*[1]; Francois Willaime[1]; [1]CEA/Saclay, SRMP, Gif sur Yvette 91191 France

Ferritic steels are proposed as first wall material in fusion reactors. When submitted to 14 MeV neutron irradiation, not only self-defects but also Helium and Hydrogen atoms are created. Quantitative studies are required to predict the effect of Helium on microstructural and mechanical properties of these materials We report ab initio results on properties of Helium insertion and of small helium and helium-vacancy complexes in bcc Iron, and possible Helium migration mechanisms. Helium atoms prefer to occupy substitutional sites, followed by tetrahedral ones with only 0.17 eV higher in energy. Interstitial Helium migrates very fast (Em = 0.06 eV) and can be easily trapped by vacancy clusters, vacancy-helium complexes and even by helium clusters. We also show here the role of Helium on void and bubble formation. Finally, we use our ab initio data to fit the Iron-Helium interatomic potential.

8:50 AM
Role of Magnetic Interactions on the Properties of He Defects in Iron: *Tatiana Seletskaia*[1]; Yuri Osetsky[2]; Roger E. Stoller[1]; G. Malcolm Stocks[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6138 USA; [2]Oak Ridge National Laboratory, Computer Sci. & Math. Div., Oak Ridge, TN 37831-6138 USA

Density functional theory calculations of He defect properties in iron have shown an unexpected influence of magnetism arising from the defect's electronic structure. In contrast with previous work that neglected such effects, the results indicate that the tetrahedral position is energetically more favorable for the He interstitial than the octahedral site. However, the He substitutional defect is found to be energetically more favorable than the interstitial position. The dissociation energy of He from the vacancy is found to be 2.29 eV which is much smaller than in the previous calculations. This may have significant implications for He diffusion, clustering and its interaction with point defects, which will impact material performance in future fusion reactors. These results provide the basis for development of improved atomistic models.

9:10 AM
Helium - Self-Interstitial Atom Interaction in Fe: *Lisa Ventelon*[1]; Brian D. Wirth[1]; Christophe Domain[2]; [1]University of California, Dept. of Nucl. Engrg., Berkeley, CA 94720-1730 USA; [2]EDF-R&D, Dept. MMC, Les Renardieres, Moret sur Loing 77250 France

We present the result of atomistic calculations to investigate the effect of He impurities on the properties and behavior of self-interstitial atom clusters in Fe. Ferritic alloys are currently being considered for fusion energy first wall applications, and will be exposed to high levels of radiation damage and transmutation production in a 14 MeV fusion neutron spectrum. We present a comparison of the interaction energies between interstitial He atoms and a single self-interstitial atom (SIA) obtained with ab-initio electronic structure and semi-empirical interatomic potentials using molecular dynamics and conjugate gradient molecular statics calculations. These results provide insight into the validity of using semi-empirical interatomic potentials and a basis for extrapolating ab-initio results from small to larger system sizes. We also present the results of a MD investigation into the migration behavior of SIA and SIA clusters in the presence of interstitial and substitutional He. The MD simulations reveal a strong interaction between He and SIA clusters, often resulting in SIA - vacancy reaction that spontaneously eject helium into interstitial sites and provide quantitative information on the interaction radii, trapping - binding energetics and migration behavior of mixed He-SIA clusters.

9:30 AM
Atomistic Modeling of He Binding and Migration at Interfaces in Fe: *Richard J. Kurtz*[1]; Fei Gao[1]; Howard L. Heinisch[1]; Brian D. Wirth[2]; G. Robert Odette[3]; Takuya Yamamoto[3]; [1]Pacific Northwest National Laboratory, Matls. Sci. Div., PO Box 999, Richland, WA 99352 USA; [2]University of California, Dept. of Nucl. Engrg., Berkeley, CA 94720 USA; [3]University of California, Dept. of Mechl. & Environml. Engrg., Santa Barbara, CA 93106 USA

High transmutation He concentrations will be produced in fusion neutron environments. Helium is essentially insoluble and aggregates at grain boundaries, significantly degrading various mechanical properties. So-called nanostructured ferritic alloys are being developed to both improve creep strength and to better manage He by creating a high-density of Ti-Y-O enriched nano-particles to serve as dislocation obstacles and fine-scale He bubble nucleation sites. The binding and migration energies of He atoms and defects at grain boundaries and coherent Cu precipitate interfaces is assessed with molecular dynamics simulations using Fe-Cu-He embedded atom type potentials. Small coherent Cu clusters were used to explore the efficiency of positive misfit nano-particles for trapping He. The energy of substitutional He in grain boundaries and Cu nano-particles is moderately lower than in the matrix, while the corresponding grain boundary energy of interstitial He is much lower than in the matrix. Binding energies roughly correlate with excess volume.

9:50 AM
Atomistic Simulations and Experimental Studies of the Effects of Helium and Hydrogen on Irradiation Damage in BCC Iron: *Maria A. Okuniewski*[1]; Srinivasan G. Srivilliputhur[2]; Chaitanya S. Deo[2]; Stuart A. Maloy[2]; Mike I. Baskes[2]; Mike R. James[2]; James F. Stubbins[1]; Doug P. Wells[3]; Farida A. Selim[3]; [1]University of Illinois, Nucl. Engrg., 103 S. Goodwin Ave., Urbana, IL 61801 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech. Div., Los Alamos, NM 87545 USA; [3]Idaho State University, Idaho Accelerator Ctr., Pocatello, ID 83209 USA

High-energy spallation neutron irradiation in metals results in the production of helium and hydrogen, as well as displacement damage. The displacement damage and the introduction of helium and hydrogen, can lead to altered mechanical and physical properties. Molecular dynamics (MD) and kinetic Monte Carlo (KMC) modeling as well as experimental techniques are used to understand the atomistics and characterize the microstructural evolution during the irradiation processes in Fe, Fe-He, and Fe-H systems. Using MD simulation techniques, pure Fe, Fe-He, and Fe-H systems are subjected to irradiation damage. The effects of incident ion energies, helium and hydrogen concentrations, and temperatures on the evolution of defects, including He and H interstitials, clusters, and bubbles are investigated. The modified embedded atom method potential, which explicitly incorporates angular forces that are essential to model the Fe-He and Fe-H systems, is used. KMC simulations are performed to understand the

evolution of defects and clustering as a function of temperature and varying defect ratios. These stochastic KMC simulations are parameterized by data obtained from experiments and MD calculations. KMC can simulate the system on a timescale much larger than MD (typically picoseconds), which allows for the diffusion of defects. Positron annihilation spectroscopy (PAS) experiments are utilized to characterize irradiation damage in single crystal bcc Fe. PAS is able to measure vacancies, voids, bubbles, and dislocation loops at low concentrations. Bubbles and voids can be detected in the sub-nanometer range, which is below the resolution of transmission electron microscopy. The defect evolution will be studied as a function of implantation dose and temperature. The results obtained from modeling using MD and KMC will be compared with experimental results obtained from PAS.

10:10 AM Break

10:40 AM Invited
Microstructural Development Under Irradiation in European ODS Ferritic/Martensitic Steels: *Robin E. Schaeublin*[1]; Nadine L. Baluc[1]; [1]Swiss Federal Institute of Technology Lausanne, Ctr. of Rsch. in Plasma Physics, Fusion Tech. - Matls., ODGA/105, Villigen 5232 Switzerland

Oxide dispersion strengthened steels based on the ferritic/martensitic steel EUROFER97 are developed within the European fusion program. The reinforcing particles represent 0.3% to 0.5% weight and are composed of yttria, which is incorporated by ball milling. Compaction is made by hot isostatic pressing or hot extrusion. ODS steel samples have been irradiated with 590 MeV protons to 0.3 and 1.0 dpa at room temperature. Microstructure is investigated by transmission electron microscopy and mechanical properties are assessed by tensile and Charpy tests. The ODS material presents a martensitic-like microstructure and a uniform distribution of the yttria particles. While the fracture behavior is drastically degraded by the oxide particles, it can be partially recovered by appropriate thermo-mechanical treatments. At room temperature the yield strength at 0.2% is 1 GPa and plastic strain at failure is 8%. Results of the irradiation on the microstructure and the mechanical properties are presented.

11:20 AM
Microstructural Development in Advanced Ferritic-Martensitic Steel HCM12A: Todd R. Allen[1]; Lizhen Tan[1]; Julie D. Tucker[1]; *Jian Gan*[2]; Gaurav Gupta[3]; Gary S. Was[3]; S. Shutthanandan[4]; S. Thevuthasan[4]; [1]University of Wisconsin, Engrg. Physics, 1500 Engrg. Dr., Madison, WI 53706 USA; [2]Argonne National Laboratory, PO Box 2528, Idaho Falls, ID 83403-2528 USA; [3]University of Michigan, 2522 Bonisteel Blvd., Ann Arbor, MI 48109 USA; [4]Pacific Northwest National Laboratory, Richland, WA USA

HCM12A is an advanced 12 Cr ferritic-martensitic steel designed for higher temperature operation and is under consideration for application in core components in Generation IV nuclear energy systems. This work provides information on the hardening and microstructural changes in HCM12A after irradiation using 2.0 MeV protons at 400°C to 10 dpa, at 500°C to 3 dpa, and 5 MeV Ni-ions at 500°C to 50 dpa. Following irradiation, changes in hardness were measured using Vickers hardness indentation, changes in microstructure and phase stability were studied using transmission electron microscopy, and changes in microchemistry were measured using scanning Auger microscopy. The hardness at 400°C increases by roughly 70% and saturates by roughly 5 dpa. The changes to the microstructure contributing to this hardness increase are mainly the formation of precipitate phases. Chromium is enriched at grain boundaries prior to irradiation, likely due to grain boundary carbides, and increases further during irradiation.

11:40 AM
Microstructural Evolution of Proton Irradiated T91: *Alfred Neal Ham*[1]; Gary S. Was[1]; Gaurav Gupta[1]; [1]University of Michigan, Nucl. Engrg. & Radiologl. Scis., 2940 Cooley Bldg., 2355 Bonisteel Blvd., Ann Arbor, MI 48105 USA

Ferritic-Martensitic alloys are proposed as candidate structural materials for Generation IV reactors, fusion reactors, and accelerator-driven transmutation systems. They are preferred over austenitic stainless steels in these applications due to improved irradiated and mechanical properties such as reduced swelling, high temperature creep resistance, and thermal shock resistance. Understanding radiation effects in these alloys is critical for their success in the advanced reactor and transmutation systems. The objective of this work is to evaluate the microstructural, microchemical, and mechanical property changes in ferritic-martensitic alloy T91 after irradiation. In previous studies, as-received T91 samples have been irradiated using 2.0 MeV protons at 400°C and 450°C to 10 dpa. The hardness at 400°C increases by roughly 78% and saturates by approximately 7 dpa. After 10 dpa at 450°C, the average loop size was 13.4 nm with a dislocation density of 4 x 1021 cm-3. No voids or precipitates are observed following irradiation. Hardness increased approximately 95 kg/mm2 after the same dose. Further irradiations will be performed using 2.0 MeV protons at 500°C to 3 dpa on A/R T91 and coincident site lattice enhanced (CSLE) T91 samples and at 450°C to 10 dpa on He pre-implantation (to 1800 appm) T91. This will provide data as a function of temperature and dose, with and without He pre-implantation and CSL enhancement. Following irradiation, changes in hardness will be measured using Vickers hardness indentation and changes in microstructure, microchemistry and phase stability will be studied using transmission electron microscopy.

Multicomponent Multiphase Diffusion Symposium in Honor of John E. Morral: Computational Tools for Understanding Diffusion Mechanisms

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee, MPMD-Solidification Committee, ASM/MSCTS-Atomic Transport Committee

Program Organizers: Carelyn E. Campbell, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Ursula R. Kattner, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Afina Lupulescu, Rensselaer Polytechnic Institute, Materials Science & Engineering, Troy, NY 12180-3590 USA; Yongho Sohn, University of Central Florida, Advanced Materials Processing & Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816-2455 USA

Wednesday AM Room: 3007
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Ursula R. Kattner, National Institute of Standards and Technology, Metall., Gaithersburg, MD 20899-8555 USA; John A.L. Ågren, Royal Institute of Technology, Dept. of Matls. Sci. & Engrg., Stockholm 100 44 Sweden

8:30 AM Invited
Effective Diffusivity of Heterogeneous Systems: *Y. Mishin*[1]; [1]George Mason University, Sch. of Computatl. Scis., MSN 5C3, 4400 Univ. Dr., Fairfax, VA 22030 USA

We address two related problems dealing with calculations of "effective" diffusion coefficients. One is diffusion in disperse heterogeneous alloys whose phases possess different diffusivities. Assuming that the phase distribution is periodic and diffusion is locally quasi-steady, we show that the average concentration follows an effective diffusion equation. A mathematical procedure for exact and approximate calculations of the effective diffusion tensor is presented and applied to diffusion in a periodic array of cubic particles (prototype of Ni-based superalloys). This analysis can be readily extended to include segregation and driven diffusion. The second problem is diffusion in periodic atomic structures with multiple jump rates, such as grain boundaries, dislocations, or complex crystal structures. A procedure for averaging the spectrum of jump rates to obtain the effective diffusivity is presented and demonstrated by several applications. The continuum and atomistic theories have much in common and are applicable to other properties of heterogeneous systems.

9:00 AM
A Self-Consistent Mean-Field Model for Strongly Concentration Dependent Phenomenological Coefficients: Application to Interdiffusion Kinetics: *Vincent Barbe*[1]; Maylise Nastar[1]; [1]Commissariat à l'Energie Atomique, Service de Recherches en Métall. Physique, Gif-sur-Yvette 91191 France

Starting from an atomic diffusion model which depends on the local composition through the thermodynamic interactions between atoms, we derive the phenomenological coefficients in a multicomponent alloy. The model is based on the master equation and a self-consistent estimation of the non-equilibrium distribution function which is expressed in terms of an effective Hamiltonian (Nastar et al, Phil Mag A 80 (2000) 155). A new decoupling scheme of the kinetic equations is applied, which yields to the prediction of a percolation threshold for the tracer diffusion when the ratio of atom-vacancy exchange frequencies goes to infinity. The resulting transport coefficients show a good agreement with recent Monte Carlo simulations in the particular case of a random lattice gas. We present an application of this self-consistent theory to the prediction of kinetics of interdiffusion of the

ternary alloy Fe-Ni-Cr specifically with a high Ni content to investigate the effect of chromium percolation.

9:25 AM
Reversible and Irreversible Reaction Fronts in Quasichemical Theory of the Multicomponent Diffusion: Misha Sinder[1]; Joshua Pelleg[1]; Sergey Genikhov[1]; [1]Ben Gurion University of the Negev, Matls. Engrg. Dept., PO Box 653, Beer Sheva 84105 Israel

Many systems in physics, chemistry and materials science may be studied by using the concept of the reaction front formed between initially separated reactants. The numerous examples of such applications are known: diffusion flames, internal oxidation of the metals, gas absorption with chemical reactions in liquids, new phase formation in solids, multicomponenets diffusion in semiconductors etc. Recently some new aspects of the reaction front concept have been elucidated.[1-3] The main progress are a simple way to calculate the reaction rate for reversible reactions case and a possibility to analyze the relations between the reversible and irreversible reaction patterns. By this approach the arbitrary reversible reaction - diffusion systems with initially separated reactants may be investigated in detail. The single reversible reaction A + B = C was considered in works.[1-3] In this research the model of the system with initially separated components and two reversible reactions A + B = R and R + B = S is studied. The analysis is done in the framework of the formalism developed in Ref. [3]. Assuming the same diffusion constants of the components, the analytical solution is investigated. On the basis of the obtained results, the relationship between the reversible and the irreversible regime patterns has been determined. Thus, it is shown possibility to predict the long-time behavior of the irreversible or partly irreversible reactions system with two reactions on the basis of the reversible reactions analytical solution. The presented approach could be a useful tool for the study of the multicomponent diffusion accompanied by the quasichemical reactions in solids. [1]M. Sinder and J. Pelleg, Phys. Rev. E 60, R6259 (1999). [2]M. Sinder and J. Pelleg, Phys. Rev. E 61, 4935 (2000). [3]Z. Koza, Phys. Rev. E 66, 011103 (2002).

9:50 AM Break

10:05 AM Invited
Dynamics-Based Microstructural Design in Multicomponent Alloys: *Greg Olson*[1]; [1]Northwestern University/QuesTek, Matl. Sci. & Engrg., 2225 N. Campus Dr., Evanston, IL 60015 USA

Advances in the theory of coarsening kinetics in multicomponent systems have significantly improved the parametric computational design of materials as dynamic systems. These advances have been incorporated in the PrecipiCalc code successfully applied to accelerated thermal process optimization at the component level. Rapid simulations of multicomponent precipitation behavior employing a mean-field approximation can be subsequently refined by rigorous DICTRA simulations of detailed multicomponent diffusion. Development of multicomponent thermodynamic and mobility databases has enabled parametric design of oxidation-resistant Nb-based alloys, and efficient simulation-based process control of the commercial high-temperature carburizing of novel high-alloy steels.

10:35 AM
Analysis of Cu-Ni-Zn Ternary Diffusion Couples Using MultiDiFlux Program: *Kevin M. Day*[1]; Mysore A. Dayananda[1]; [1]Purdue University, Sch. of Matls. Engrg., 501 Northwestern Ave., W. Lafayette, IN 47907-2044 USA

Single phase as well as multiphase diffusion couples assembled with alpha (fcc) and beta (bcc) Cu-Ni-Zn alloys were investigated at 775°C for controlled interdiffusion and development of zero-flux-planes for the individual components. The couples were analyzed by using the MultiDiFlux program developed by Dayananda and Ram-Mohan. Interdiffusion fluxes and average interdiffusion coefficients were calculated over selected concentration ranges from various couples. Such calculations will be presented to demonstrate the capabilities of the MultiDiFlux program. The program will also be employed in the reproduction of concentration profiles on the basis of error functions and the calculated interdiffusion coefficients.

11:00 AM
Effects of Concentration-Dependence of the Effective Diffusivity on Diffusion Paths in Two-Phase Ternary System: *Hongwei Yang*[1]; John E. Morral[2]; [1]University of Connecticut, Dept. of Matls. & Engrg., 97 N. Eagleville Rd., Unit 3136, Storrs, CT 06269 USA; [2]Ohio State University, Dept. of Matls. Sci. & Engrg., 177 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA

In current work, variation of the effective diffusivity with concentration was studied for one hypothetical and two real ternary systems. In order to determine the effects of concentration-dependence of the effective diffusivity on diffusion paths, a DICTRA finite difference simulation of the diffusion paths, which accounts for diffusivity variations was compared to an error function prediction, which assumes a constant effective diffusivity. The effects changed the diffusion path from linear "zig-zag" shape predicted by error function theory to the formation of "horns" in the vicinity of initial interface. The horns may protrude to either the same direction or the opposite direction. Comparison on the results from all three ternary systems shows that how the effective diffusivity varies with concentration is only necessary but not enough condition to led to different pointing directions of the horns.

11:25 AM
Diffusion in fcc and $L1_2$ Phases of Ni-Al-Mo: *T. Wang*[1]; S. H. Zhou[1]; J. Z. Zhu[1]; L. Q Chen[1]; Z. K Liu[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Engrg., Univ. Park, PA 16802 USA

Diffusion in disordered fcc and ordered $L1_2$ phases is a key factor for the high-temperature applications of Ni-base superalloys and is modeled in the present work for the Ni-Al-Mo ternary system. For the fcc phase, atomic mobility in the Ni-Mo and Al-Mo binaries is evaluated from the experimental data in the literature, and the previous modeling in the Ni-Al system is compared with recent experimental results in the literature, and the thermodynamic factors needed for modeling are calculated from the recent Ni-Al-Mo thermodynamic database.[1] For the $L1_2$ phase, the effect of chemical ordering on atomic mobility is described by a phenomenological model.[2] The available experimental data for Ni3Al are used to evaluate model parameters. The diffusion of Al in $L1_2$ is simulated, indicating the anti-site mechanism being dominant. The atomic mobility modeling of Al is then refined based on the anti-site mechanism. As $L1_2$ is not stable in the Ni-Mo and Al-Mo binary systems, no interaction parameter is introduced. By combining the above binary results, atomic mobility in fcc and $L1_2$ are obtained for the Ni-Al-Mo ternary system, and diffusion processing in the ternary system are simulated. [1]S. H. Zhou, Y. Wang, T. Wang, J. Z. Zhu, L. Q. Chen and Z. K. Liu, In Submit, (2004). [2]T. Helander and J. Agren, Acta Mater, 47 (1999) 1141-1152.

Neutron Diffraction Characterization of Mechanical Behavior: Residual Stress I

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Hahn Choo, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996 USA; Camden R. Hubbard, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Xunli Wang, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831 USA

Wednesday AM Room: 3004
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Judy W.L. Pang, Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA; Sven C. Vogel, Los Alamos National Laboratory, Matls. Sci. & Tech. Div., Los Alamos, NM 87545 USA

8:30 AM Invited
Stress Measurements in Welds: Problem Areas: *Thomas M. Holden*[1]; Hiroshi Suzuki[2]; David G. Carr[3]; Maurice I. Ripley[3]; [1]Northern Stress Technologies, 208, Pine Point Rd., Deep River, Ontario K0J 1P0 Canada; [2]Japanese Atomic Energy Research Institute, Tokai Japan; [3]Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW Australia

There have been many stress measurements on welds by neutron diffraction over the past 20 years but there are a number of serious experimental issues that are often not addressed. The primary fact is that the microstructure generally changes across the weld and accompanying this may be a change in the concentration of strengthening elements in solution. This will lead to a shift in lattice spacing which may be incorrectly interpreted as a strain. Secondly, a gradient of plastic deformation near the weld is expected. Since plastic deformation always generates intergranular (type-2) strains this leads to a range of intergranular effects superposed on the conventional weld-related strains. These effects are illustrated by neutron diffraction studies of ferritic, austenitic and Zr-alloy welds where chemistry, inter-

granular effects and often strong crystallographic texture all play a role.

8:50 AM Invited
Residual Stresses in Inertia and Linear Friction Welded Aeroengine Components: *Philip John Withers*[1]; Michael Preuss[1]; Philipp Frankel[1]; [1]Manchester University, Manchester Matls. Sci., Grosvenor St., Manchester SK6 7DT England

Inertia and linear friction welding are candidates for welding 'difficult-to-weld' aeroengine materials used for components such as disc to disc and blade to disc respectively. Furthermore, they allow a movement to new design approaches such as bladed rings and discs. Safe operation of these components requires a good knowledge of the residual stresses that develop during welding and through subsequent post weld heat treatment. In this paper we describe neutron diffraction measurements aimed at measuring the evolution of these stresses. In addition the range of these stresses are compared to the scale of the micrsotructural changes in the near weld zone. Results for both Ni base superalloys and Ti alloys will be presented.

9:10 AM
Processing, Microstructure, Hardness, and Residual Strains of 6061-T6 Aluminum Alloy Friction Stir Welds: *W. Woo*[1]; H. Choo[1]; D. W. Brown[2]; Z. Feng[3]; P. K. Liaw[1]; S. A. David[3]; C. R. Hubbard[3]; [1]University of Tennessee, Matls. Sci. & Engrg., Knoxville, TN 37996 USA; [2]Los Alamos National Laboratory, Matls. Sci. & Tech., Los Alamos, NM 87545 USA; [3]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37830 USA

Friction stir welding (FSW) is a solid-state joining process, which creates a strong bond through severe plastic deformation and frictional heating. The residual stresses (RS) in FSW can approach the yield point of the base material and cause a drastic increase in the crack-growth rate. In this study, we prepared three different weld specimens from 6061-T6 aluminum alloy: (Case 1) a plate processed with both the stirring pin and pressing shoulder, i.e., a regular FSW, (Case 2) a plate processed only with the pressing shoulder, and (Case 3) a plate processed only with the pin. Three residual strain components (longitudinal, transverse, and through-thickness) were measured across the weld line and through the thickness of the specimen using neutron diffraction. The comparison among the three cases shows distinctly different strain profiles revealing de-convoluted effects of the different sources of the residual stress, i.e., plastic deformation, friction heat, or their combination. The relationship among the processing parameters, microstructure, hardness, and sources/distributions of the residual strains in FSW will be discussed.

9:30 AM Cancelled
Neutron Diffraction Strain Measurement in High Strength Steel Welds - A Tool to Aid in Life Prediction

9:50 AM Break

10:10 AM Invited
High-Performance Kirkpatrick-Baez Super Mirrors for Neutron Milli- and Micro-Beams: *Gene Emery Ice*[1]; Camden R. Hubbard[1]; Bennett C. Larson[2]; Judy W.L. Pang[1]; John D. Budai[3]; Stephen Spooner[3]; Sven C. Vogel[4]; Ronald Roggie[5]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Rm. B260, Bldg. 4500S, MS 6118, Oak Ridge, TN 37831-6118 USA; [2]Oak Ridge National Laboratory, Condensed Matter Sci. Div., Rm. B200, Bldg. 3025M, MS 6030, Oak Ridge, TN 37831-6030 USA; [3]Oak Ridge National Laboratory, Oak Ridge, TN USA; [4]Los Alamos National Laboratory, LANCE, PO Box 1663, Los Alamos, NM 87545 USA; [5]Chalk River Laboratories, Bldg. 459, Sta. 18, Chalk River, Ontario K0J1J0 Canada

Kirkpatrick-Baez neutron super mirrors can efficiently focus neutron beams into small areas with a maximum divergence that is limited by the mirror critical angle. The size of the focal spot is primarily determined by geometrical demagnification of the source and by figure errors in the mirror shape. Ray tracing calculations show that high-performance Kirkpatrick-Baez supermirrors can preserve neutron-source brilliance when focusing down to tens of microns and can focus ~ two orders of magnitude greater power into a 100 micron spot than is practical without focusing. The predicted performance is near the theoretical limit set by the source brilliance. We describe the phase space arguments, ray tracing calculations and actual performance of an M3 supermirror system designed to produce a focal spot below 100 microns. Although the current design is optimized for neutron polychromatic microdiffraction, the design principles are widely applicable to a range of neutron science. Some example experiments that exploit the increased flux density of these optics are described.

10:30 AM Invited
Dynamical Diffraction Effects in Neutron Stress Analysis: Ersan Ustundag[2]; Mark R. Daymond[3]; *I. C. Noyan*[1]; [1]Columbia University, Dept. of Applied Physics & Applied Math., 500 W. 120th St., New York, NY 10027 USA; [2]Iowa State University, Dept. of Matl. Sci. & Engrg., 2220 Hoover Hall, Ames, IA 50011-2300 USA; [3]ISIS-Rutherford-Appleton Labs, ENGIN-X, Didcot England

In this presentation we will discuss effects of grain size on the accuracy and precision of stress results obtained with neutron diffraction. In particular, the effects of beam divergence and dynamical diffraction artifacts will be discussed. These effects will be compared to those in x-ray diffraction. Guidelines for avoiding these effects will also be presented.

10:50 AM Invited
Improving the Structural Integrity of Welded Structures Through Reliable Residual Stress Measurements: *Lyndon Edwards*[1]; [1]Open University, Dept. of Matls. Engrg., Walton Hall, Milton Keynes MK7 6AA UK

Many of the factors controlling the structural integrity of welded structures are reasonably well understood and the importance of residual stress is well known. However, previous access to reliable, spatially accurate residual stress field data has been limited so that standards controlling the design of welded structures are typically very conservative. Recent advances in neutron diffraction allow a far more detailed picture of weld residual stress fields to be obtained in increasingly large components and structures. This permits the development and use of predictive models that can be used for the accurate design of new structures or the life extension of legacy plant. This paper uses examples from the aeronautical and nuclear industries to illustrate how fully integrated studies of the 3D residual stress distribution accompanying fusion welds and how they affected by subsequent manufacture and/or service environments can be used to improve the structural integrity of welds structures.

11:10 AM
Residual Stress Measurements in Gas Pipeline Girth Welds: *Michael Law*[1]; [1]Australian Nuclear Science and Technology Organisation, Matls. & Engrg. Sci., PMB1, Menai, NSW 2234 Australia

Gas pipelines have an enviable safety record in transporting energy, however there is still room for improvement. Welding is used extensively in gas pipelines, the welds are made without post weld heat treatment. The welding process generates significant residual stresses along the welding direction with the maximum values occurring in the weld and heat affected zone. The stresses are lower in the axial direction (perpendicular to the weld) but these residual stresses have the most significant effect on fracture and the allowable defect size. Reliable fracture mechanics assessments can only be performed when the residual stresses are known accurately. Neutron residual stress measurements offer many advantages in determining these stresses: the great penetrating power and non-destructive nature of the measurement means that stresses can be measured at a range of depths with good spatial resolution. The residual stresses in the welds are superimposed on those generated by the considerable working during rolling and pipe forming. In the present work, the stress in un-welded pipe, and in girth welded gas pipelines were measured by neutron diffraction. The welds are manual metal arc cellulosic electrode welds made in X70 linepipe with 3 differing wall thicknesses (7.1 mm, 6.4, and 5.2 mm). The full stress tensor was determined for 2 types of sample: - 3 girth welded rings cut from linepipe, and 3 corresponding unwelded rings. The unwelded rings were measured at 5 through-thickness positions with a spatial resolution of 1 mm3. The welded rings were measured at the same 5 through-thickness positions at 19 locations from the center of the weld up to 35 mm away from the weld. The results will be presented and compared.

11:30 AM
The National Science Foundation Major Research Instrumentation [MRI] Program on "Development of an In-Situ Neutron-Scattering Facility for Research and Education in the Mechanical Behavior of Materials": *Peter K. Liaw*[1]; Hahn Choo[1]; Raymond A. Buchanan[1]; Camden R. Hubbard[2]; Xun-Li Wang[3]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., 427-B Dougherty Engrg. Bldg., Knoxville, TN 37996 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37830 USA; [3]Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37830 USA

A National Science Foundation [NSF] Major Research Instrumentation [MRI] Program on "Development of an In-Situ Neutron-Scattering Facility for Research and Education in the Mechanical Behavior of

Materials" is proposed by the University of Tennessee [UT], Oak Ridge National Laboratory [ORNL], and their team members. The collaborating participants come from 16 different universities, 13 industries, and 6 national laboratories with diverse disciplines that include [1] Materials Science and Engineering; [2] Physics; [3] Chemistry; [4] Mechanical, Aerospace, and Biomedical Engineering; [5] Civil Engineering; [6] Nuclear Engineering; and [7] Biochemistry. A four-year development Program has been funded by NSF to establish a suite of instruments for studying mechanical behavior of advanced materials using in-situ neutron scattering at the impending Spallation Neutron Source [SNS, ORNL], which, when completed in 2006, will provide the most intense pulsed-neutron source in the world. The objective of this program is to develop the state-of-the-art in-situ and real-time characterization instrumentation for VULCAN at SNS. The VULCAN diffractometer is designed to conduct fundamental studies in materials science and engineering with a focus on mechanical behavior. The proposed instrumentation will enable VULCAN to fulfill its full potential. The underlying goal of this proposal is to [1] fully exploit the best US neutron-source capabilities, [2] advance neutron science and engineering by providing the most-advanced neutron-scattering instrumentation to the broadest possible materials-research community, and [3] broaden the participation at the frontiers of the scientific/engineering enterprise by educating a diverse cadre of individuals skilled in the applications of advanced, state-of-the-art neutron technologies for fundamental materials studies. We are very grateful to NSF for the support [DMR-0421219]. Drs. Charles E. Bouldin and Guebre Tessema are the Program Directors.

Neutron Scattering in Materials Research: Dynamics and Inelastic Scattering

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee

Program Organizers: Brent T. Fultz, California Institute of Technology, Department of Materials Science, Pasadena, CA 91125 USA; Michael Atzmon, University of Michigan, Department of Materials Science & Engineering, Ann Arbor, MI 48109 USA

Wednesday AM Room: 3022
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Ken W. Herwig, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831-6474 USA; Ron R. Berliner, North Carolina State University, Nucl. Reactor Prog., Raleigh, NC 27695-7909 USA

8:30 AM
Dynamical Sources of Entropy in Phase Transformations in Materials: *Brent T. Fultz*[1]; [1]California Institute of Technology, Mail 138-78, Pasadena, CA 91125 USA

Temperature drives the excitations of phonons, spins, and electrons. In thermal equilibrium these vibrational, magnetic, and electronic contributions to the entropy can be assessed if their energy spectra are known. Each of them can make a significant contribution to the entropy of phase transformations in materials, comparable to the contribution from the configurational entropy that is well known from textbooks. This talk explains how inelastic neutron scattering experiments are used to measure the energy spectra of phonons and other dynamic excitations in materials. Some thermodynamic trends are presented, such as the effect of solute mass and atomic size mismatch on phonon entropies of compound formation. Electronic entropy plays a big role in crystal structure transformations in cerium, uranium and plutonium. Overall, however, an understanding of the entropy of solid state phase transitions requires detailed analyses. Rules of thumb are, unfortunately, inadequate. An excellent opportunity remains for further experimental work.

9:00 AM Invited
Measuring Medium and High Energy Excitations in Condensed Matter Using Spallation Neutrons: *Douglas L. Abernathy*[1]; [1]Oak Ridge National Laboratory, Spallation Neutron Source, PO Box 2008, Oak Ridge, TN 37831-6474 USA

The traditional instrument for measuring inelastic neutron scattering from condensed matter systems has been the reactor-based triple axis spectrometer. More recently, time-of-flight techniques have been developed at spallation neutron sources, which produce thermal and epithermal neutrons in short pulses. The Spallation Neutron Source (SNS) is an accelerator-based neutron source currently under construction at the Oak Ridge National Laboratory in Tennessee. It will provide the most intense pulsed neutron beams in the world for scientific and industrial research and development. Two instruments under development for this facility will specialize in measuring high energy excitations in materials. The operating principles of these instruments will be presented, along with the different optimizations of the two to access a broad wavevector transfer range and offer high resolution for magnetic scattering studies. An example of how single crystal measurements are made on these instruments will be given.

9:30 AM Invited
Thermodynamics of Metals with Strong Electron-Phonon Interactions: *Michael Edward Manley*[1]; [1]Los Alamos National Laboratory, Matls. Sci. & Tech. - 6, MS G770, Los Alamos, NM 87545 USA

Contrary to prevailing wisdom, recent inelastic neutron scattering measurements of phonons indicate that electron-phonon coupling plays a major role in the high-temperature thermodynamics of several actinides and at least one rare-earth. Results are forcing us to rethink the way we approach the thermodynamic problem. For example, the heat capacities of electrons and phonons cannot be separated and the exchange between the phonon entropy and electron energy results in large enhancements of the free energy. For uranium, I will present evidence of the coupling from the perspective of both phonons observed with neutron scattering and electronic distributions observed in photoemission spectra. A simple statistical argument shows how extra entropy generated by phonon softening stabilizes electron distributions to energies higher than that predicted from normal Fermi-statistics. Possible sources of strong electron-phonon coupling will also be discussed.

10:00 AM Break

10:20 AM
Neutron Scattering and Density Functional Theory Study of Lattice Dynamics and Entropy in Dilute Vanadium Alloys: *Olivier Delaire*[1]; Tabitha L. Swan-Wood[1]; Max Kresch[1]; Brent T. Fultz[1]; [1]CALTECH, Matls. Sci., 1200 E. California, MC 138-78, Pasadena, CA 91125 USA

In this study, we investigate the lattice dynamical and entropic effects of alloying dilute impurities into pure bcc vanadium. Using inelastic neutron scattering, we have measured the changes in the phonon density of states (DOS) and entropy of vanadium associated with the alloying of a few percent impurities of the 3d, 4d and 5d series transition metals. A clear trend was observed across the d-series, Ti, Zr and Hf causing a softening of the V phonon DOS, while elements to the right of V in the periodic table induce a stiffening gradually increasing with atomic number. The DOS stiffening observed for 6% of Co or Pt impurities is very large and results in a decrease of vibrational entropy that is larger than the configurational entropy gain of alloying. These changes in the phonons were analyzed both with classical Bornvon Karman lattice dynamics models and with density functional theory computer simulations, using supercells to describe the alloys. We report our findings on the origin of the perturbation of V phonons by transition metal impurities and discuss the consequences on the thermodynamics and transport properties.

10:45 AM
Neutron Scattering Study of the Martensitic Phase Transformation in Fe71Ni29: Olivier Delaire[1]; *Max Kresch*[1]; Tabitha L. Swan-Wood[1]; Brent T. Fultz[1]; [1]California Institute of Technology, Matls. Sci., MC 138-78, Pasadena, CA 91125 USA

Martensitic transformations occur via cooperative and well organized shears of the crystal. Although atoms are displaced, there is no significant change in the disorder of atomic configurations. The entropy of these phase transitions can be entirely vibrational in origin. Inelastic neutron scattering was used to measure elementary exitations in both face centered cubic (fcc) austenite and body centered cubic (bcc) martensite phases of Fe71Ni29. Phonon densities of states (DOS) for the two phases were found by analysis of the incoherent scattering. Comparison of the two room temperature DOS showed a significant change in vibrational entropy: DS(fcc->bcc) = -0.13 kB/atom. Born von Karman (BvK) models of the lattice dynamics were used to relate thermodynamic data to interatomic force constants, which stiffen in the BCC phase. These BvK models took advantage of both coherent and incoherent scattering. We discuss the thermodynamic importance of the results.

11:10 AM
Vibrational Entropy of Mixing and the Phase Stability of Al-Ag: *Tabitha Liana Swan-Wood*[1]; Max Kresch[1]; Jiao Lin[1]; Mike McKerns[1]; Brent T. Fultz[1]; [1]California Institute of Technology, Matls. Sci., MS 138-78, Pasadena, CA 91125 USA

The Al-Ag system has an unusually strong temperature dependence of the solubility of Ag in fcc Al. This phenomena is seen in many binary alloys, particularly those where the impurity has a mass ratio of at least 3 to that of the matrix atom. It is possible this mass ratio causes resonance modes that stabilize the solid solution with a large vibrational entropy of mixing. In our experiments on Al-Ag, phonon density of states (DOS) were obtained from pure Al, and Al-Ag alloys. A distinct resonance mode was found in the 7% Ag DOS. In addition, the hcp phase of Al- 60% Ag showed surprisingly large softening of all phonon modes. An extremely large softening with temperature was seen in the 7% Ag while insignificant softening was seen in the 60% Ag, making a substantial contribution to the temperature dependence of the solvus in this system.

Phase Stability, Phase Transformation and Reactive Phase Formation in Electronic Materials IV: Interfacial Reactions and IMC Formation in Solder Joints

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee

Program Organizers: Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Katsuaki Suganuma, Osaka University, Department of Nanomaterials and Environmental Conscious Technology, Ibaraki, Osaka 567-0047 Japan

Wednesday AM Room: 3016
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: C. Robert Kao, National Central University, Dept. of Cheml. & Matls. Engrg., Jhongli City 320 Taiwan; Kenneth L. Erickson, Sandia National Laboratories, Dept. 9112, Albuquerque, NM 87185 USA

8:30 AM
A Study on Intermetallic Growth Kinetics of Sn-Ag-Cu Lead-Free Alloy on Cu, Ni and Alloy-42 Substrates During Pb-Free Soldering: Nader Dariavach[1]; Paul Callahan[1]; *Jin Liang*[1]; *Raymond A. Fournelle*[2]; [1]EMC, 176 South St., Hopkinton, MA 01748 USA; [2]Marquette University, Milwaukee, WI 53201-1881 USA

Lead-free soldering with Sn-Ag-Cu alloys requires substantially higher temperatures (around 235ºC to 250ºC). The rates for intermetallic growth and substrate dissolution are expected to be significantly greater than those for the current Sn-Pb eutectic solder. This study systematically investigates the intermetallic growth kinetics for Sn3.8Ag0.7Cu lead-free solder with three different substrates: Cu, Ni and Alloy 42, at temperatures ranging from 225ºC to 280ºC for reaction times from 10 sec to 4 hrs. The kinetic reaction rates and temperature-dependency were measured experimentally and simulated with first principle and solid/liquid diffusion theories. A thorough understanding of lead-free solder/substrate interfacial reactions can lead to the optimum lead-free soldering processes and to the optimum lead-free coating thicknesses for component and PCB terminal finishes, as well as to the optimum barrier layers needed for interconnections inside of advanced packages.

9:00 AM
A Study of the Interfacial Microstructures of Sn-Ag-y%Cu Interconnects: *Henry Lu*[1]; Haluk Balkan[1]; Simmon Ng[2]; [1]Flip Chip International, LLC, 3701 E. Univ. Dr., Phoenix, AZ 85034 USA; [2]Wayne State University, Dept. of Cheml. Engrg., Detroit, MI 48202 USA

Sn-Ag-y%Cu interconnects (Cu wt% = 0.0, 0.5, 1.0, and 2.0) were studied after solid-liquid reaction. Combining mechanical testing, surface micro-etching and microanalysis, the 3-D interfacial microstructures were identified, and the relationship between interfacial microstructures and interconnect macro mechanical performances was correlated. The virgin groups had different CuSn IMC morphologies: for Cu 0.5% group, scissors-like; 1.0%, tweezer-like; 2.0%, round clusters. No Ag3Sn platelets were observed. There were no differences in mechanical behaviors. After solid-liquid reactions, there was no CuSn IMC spalling from the interface, except 0.0% group. Ag3Sn platelets were observed for 0.5% group or higher. Cu behaved like a catalyst: the higher Cu content, the more Ag3Sn platelets. CuSn IMC grew as big bricks for the 2.0% group. The interconnect mechanical performance was diverse. Fracture mode was ductile for low Cu content and brittle for 1.0% above. Abnormal growth of Ag3Sn platelets and CuSn bricks were responsible for the interconnects' mechanical degradation.

9:20 AM
Interfacial Reactions in the Pb-Free Composite Solders with Indium Layers: *Sinn-wen Chen*[1]; Shih-kang Lin[1]; Ching-feng Yang[1]; [1]National Tsing-Hua University, Chem. Engrg. Dept., #101, Sec. 2, Kuang-Fu Rd., Hsin-chu 300 Taiwan

A lead-free composite solder is prepared with lead-free solder substrate and a plated-indium layer. The indium containing layers melt during the soldering process, wets the substrates, and forms sound solder joints. Since the melting temperature of indium is 156.6°C, even lower than that of the eutectic Sn-Pb which is at 183°C, so the soldering process can be carried at a temperature lower than the conventional soldering process. During the soldering process, the molten indium alloys with its surrounded Sn based Pb-free solder alloys and then reacts with the nickel and copper substrates. The interfacial reactions between the indium alloys and the substrates are investigated, and binary intermetallic compounds are observed at the interfaces.

9:40 AM
Cross-Interaction Between Au and Cu in Au/Sn/Cu Diffusion Couple: *Chien Wei Chang*[1]; C. Robert Kao[1]; [1]National Central University, Dept. of Cheml. & Matls. Engrg., Jhongli City 320 Taiwan

It was well known that both Au and Cu are fast diffusers in many metals, including Sn. These two metals can diffuse through a long distance in Sn in a relatively short time. In this study, we would like to investigate the cross-interaction between Au and Cu across a thick layer of Sn. In other words, we would like to study the Au/Sn/Cu ternary diffusion couple. Using electroplating method, a 100 microns Sn layer was deposited over Cu plate, and then a 5 microns Au layer was deposited over the Sn layer. The diffusion couples were then aged at 100-200°C for upto 10 days. It was found that Cu and Au can start to cross-interact in a few hours. At the Au/Sn interface, Cu can be detected in the $AuSn_4$ phase. At the Sn/Cu interface, Au can also be detected in the Cu_6Sn_5 phase. The detailed reaction sequence and the mechanism will be presented. Implications related to electronic packaging will also be summarized.

10:00 AM
Study of Interfacial Reactions of AuSn/Au and AuSn/Ag for Flip-Chip RF Assembly: *Yuan-Tai Lai*[1]; *Cheng-Yi Liu*[1]; [1]National Central University, Cheml. & Matls. Engrg., No.300, Jungda Rd., Jhongli, Taoyuan 320 Taiwan

As the signal frequency in RF (Radio Frequency) device approaches several tens of GHz, flip-chip technology has become increasingly important for the chip-assembly of RF device. To meet the requirement of the fluxless process for the flip-chip assembly of RF device, AuSn solder would be the good choice to bond Au bumped RF chips. Hence, the reaction characteristics of eutectic AuSn solder with Au in air ambient are very important. Beside Au substrate, we also studied the wetting reaction between AuSn and Ag, since using Ag substrate could prevent the serious Kirkendall voids forming at the interface between AuSn/Au after thermal aging process. The experiments were carried at four different temperatures, which are 300°, 330°, 360°, and 390° for 30sec, 1min, 2min and 5min. The preliminary results indicated that AuSn has very poor wettability on Au and Ag substrate. The molten AuSn solder ball remained spherical shape on substrates. With increasing of reflowing temperature, the spherical shape of AuSn solder remained, yet, we found that the bottom of the molten AnSu started to spread and wet on substrate. According to the SEM X-section study, Au was found to dissolve into AuSn quickly during the reflowing process. Yet, Ag has much slow dissolution into AnSn comparing to Au. In this talk, we will report the detail kinetics of AuSn/Au and AuSn/Ag reactions and their wetting be.

10:20 AM Break

10:30 AM
Modeling the Effect of Finite Material Boundaries on Multi-Component Base Metal Dissolution and Inter-Metallic Com-

pound Growth: *Kenneth L. Erickson*[1]; Polly L. Hopkins[2]; Paul T. Vianco[3]; [1]Sandia National Laboratories, Dept. 9112, PO Box 5800, MS 0834, Albuquerque, NM 87185 USA; [2]Sandia National Laboratories, Dept. 9114, PO Box 5800, MS 0834, Albuquerque, NM 87185 USA; [3]Sandia National Laboratories, Dept. 1861, PO Box 5800, MS 0889, Albuquerque, NM 87185 USA

Experiments examining multi-component base metal dissolution by molten solders were reported previously. Preferential dissolution of base metal constituents influenced short-term base metal erosion and long-term inter-metallic compound (IMC) growth. A modeling capability is needed to extend observed results to further applications. In one-dimensional, diffusion-controlled systems involving constant properties and time scales for which the solder is semi-infinite with respect to diffusion, interface displacement proceeds monotonically. Relative constituent concentrations in IMC's and solder are established quickly, determined by solubility, and remain constant. Governing equations can be solved analytically. In systems involving variable properties and time-scales for which the solder is finite, interface displacement proceeds non-monotonically. The direction of interface displacement can reverse. Relative concentrations of constituents can change significantly. Governing equations require numerical solution. This paper summarizes numerical simulation of these effects based on data from previously reported experiments involving 63Sn-37Pb solder and 76Au-21Pt-3Pd (wt%) alloy sheet and porous thick film.

10:50 AM
Phase Field Simulations of Liquid Channel Formation and its Influence on the Growth Kinetics of Intermetallic Compound Layer During Soldering Reactions: *Kyoung-Kook Hong*[1]; Joo-Youl Huh[1]; [1]Korea University, Div. of Matls. Sci. & Engrg., 5-1, Anam-Dong, Sungbuk-Ku, Seoul 136-701 Korea

With ever decreasing pitch size in ball grid array (BGA) technology, it has been a crucial issue in electronic packaging to control the intermetallic compound (IMC) layer growth kinetics for the solder joint reliability. In an attempt to understand the drastic difference in the IMC growth kinetics between during the soldering and aging processes, we investigated the influence of the liquid channel formation through the IMC grain boundaries during soldering reactions on the IMC layer growth kinetics using phase field simulations. Computations show that the deeper liquid channel formed into the IMC grain boundaries causes the faster growth of the IMC layer and the increased coarsening rate of IMC grains. This talk will also discuss how the formation of liquid channel into the IMC grain boundaries can be affected by the liquid solder diffusivity and the solder/IMC interface energy.

11:10 AM
Study of Copper Dissolution During Soldering Process: *Mohammad Faizan*[1]; [1]University of Akron, Mechl. Engrg., 302 Buchtel Mall, Akron, OH 44325 USA

During soldering process involving copper and Sn-rich solders, a Sn-Cu interaction takes place at the copper/solder interface. The copper-Sn soldering reaction is very intense at the beginning of the soldering process. Copper is dissolved into the molten solder and subsequently intermetallic compounds (IMCs) are formed at the interface. Due to miniaturization of electronic components and increasing space constraints in the electronic packaging devices, amount of copper available for soldering is very limited. Also, some of the copper must remain intact even after soldering to avoid the dewetting of the solder. Therefore, the rate of copper loss during soldering must be under control. Understanding of the dissolution rate of copper during soldering is critical in achieving reliable soldered joints. This paper presents a numerical analysis of the dissolution process of pure copper, when is comes in contact with the Sn-rich, lead-free molten solder. The results show non-equilibrium dissolution of copper at the early stage of the soldering process.

11:30 AM
Dissolution Behavior of Cu and Ag Substrates in Molten Solders: *Kwang-Lung Lin*[1]; Po-Yi Yeh[1]; Jenn-Ming Song[2]; [1]Cheng Kung University, Dept. of Matl. Sci. & Engrg., No.1, Ta-Hsueh Rd., 701, Tainan Taiwan; [2]Dong Hwa University, Dept. of Matl. Sci. & Engrg., 1, Sec. 2, Da Hsueh Rd., Shou-Feng, Hualien Taiwan

This study investigated the dissolution behavior, at 300~400°C, of Cu and Ag substrates wire in molten Sn-4.0Ag-0.5Cu, Sn-8.6Zn and Sn-8.55Zn-0.5Ag-0.1Al-0.5Ga lead-free solders as well as in Sn-37Pb solder for comparison. Results show that dissolution behavior follows linear kinetics. The dissolution rate was significantly lower for both Cu and Ag in the Sn-8.6Zn and Sn-8.55Zn-0.5Ag-0.1Al-0.5Ga solders than in the Sn-37Pb and Sn-4Ag-0.5Cu solders. This tendency can be attributed to the difference in the interfacial reactions between the substrates and the different solders. The interfacial intermetallic compounds (IMC) formed by the dissolution were investigated after solidification. The Sn-Zn solders produced compact layer IMC while the other solders gave rise to columnar IMCs.

Phase Transformations Within Small-Size Systems: Amorphous to Nanocrystal Transformations

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), EMPMD/SMD-Chemistry & Physics of Materials Committee, EMPMD-Nanomaterials Committee

Program Organizers: Vijay K. Vasudevan, University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012 USA; Robert D. Shull, National Institute of Standards and Testing, Metallurgy Division, Gaithersburg, MD 20899-8552 USA; George Spanos, Naval Research Laboratory, Physical Metallurgy Branch, Washington, DC 20375-5000 USA; Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA

Wednesday AM Room: 3002
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Kazuhiro Hono, National Institute of Materials Science, Tsukuba 305-0047 Japan; Raju V. Ramanujan, Nanyang Technological University, Sch. of Matls. Engrg., Singapore 639798 Singapore

8:30 AM Invited
Nanostructure Synthesis During Devitrification: *J. H. Perepezko*[1]; J. Hamann[1]; W. S. Tong[1]; G. Wilde[2]; R. J. Hebert[2]; H. Roesner[2]; [1]University of Wisconsin, Dept. of Matl. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA; [2]Forschungszentrum Karlsruhe, INT, PO Box 3640, Karlsruhe D-76021 Germany

The recent innovations in metallic glasses involve either bulk volumes slowly cooled to a glass under a nucleation-controlled synthesis or marginal glass formers that are synthesized under growth-controlled kinetics. The new metallic glasses serve as effective precursors to synthesize nanostructured solids. With marginal glass formers, heating often does not yield a clear glass transition, Tg, but instead there is an onset of a partial crystallization into a high number density of nanocrystals (1021-1022 m-3) of the major component (i.e. Al or Fe) within a residual amorphous matrix. The origin of the nucleation sites and the crystallization rate are key kinetics analysis issues. At the same time, alternate strategies involving intense deformation reveals another control over the primary crystallization. These developments represent a major level of microstructure control that have an impact of the structural performance and stability. The support of the ARO (DAAD 19-01-1-0486) is gratefully appreciated.

9:05 AM
Deformation-Induced Devitrification of Al-Based Amorphous Alloys: *Rainer J. Hebert*[1]; Harald Rösner[1]; Gerhard Wilde[1]; John H. Perepezko[2]; [1]Forschungszentrum Karlsruhe, Inst. für Nanotech., PO Box 3640, Karlsruhe 76021 Germany; [2]University of Wisconsin, Dept. of Matls. Sci. & Engrg., 1509 Univ. Ave., Madison 53706 USA

Primary crystallization reactions in amorphous alloys require both, a driving force and a diffusive redistribution of solute atoms in the amorphous matrix. Annealing treatments at temperatures of more than 50 K below the glass transition temperature can induce Al nanocrystals in amorphous Al-Sm alloys. At even higher levels of undercooling, Al nanocrystals develop during intense plastic deformation at ambient temperatures in amorphous Al88Y7Fe5 alloys. Limits to the growth of deformation-induced nanocrystals are examined in this work based on measurements of the nanocrystal size distribution and microstructural investigations of the nanocrystals in the shear bands. A dislocation-based fragmentation process reduces the size of thermally-induced Al dendrites to a minimum size of approximately 18 nm. The formation of dislocations in deformation-induced as well as thermally-induced nanocrystals appears to be crucial for the size distribution evolution during deformation. The possibility of a dynamical steady state of the size distribution is discussed.

9:30 AM
Phase Transformations in Fe-Ni Based Nanomagnetic Systems: *Raju V. Ramanujan*[1]; S. W. Du[1]; [1]Nanyang Technological University, Sch. of Matls. Engrg., Block N4.1, Nanyang Ave., Singapore 639798 Singapore

There is intense current interest in nanomagnetic materials, synthesis of such materials can be carried out by a variety of techniques; phase transformations in mechanically alloyed powders and crystallization of amorphous alloys has been utilized in this investigation. Fe-Ni based alloys with the composition Fe49Ni46Mo5, Fe42Ni40B18 and Fe40Ni38B18Mo4 were processed by mechanical alloying and melt spinning and studied by XRD, SEM and TEM techniques. Nanocrystalline f.c.c. Fe-Ni solid solution as well as amorphous material could be produced by mechanical alloying of the elemental powders. The presence of boron was found to make amorphization easier, phase transformation studies of the as milled powders showed that molybdenum increased the thermal stability. The magnetic properties were studied by VSM. The results obtained from the study of the powders will be compared to the counterpart crystallization studies of initially amorphous Fe40Ni38B18Mo4 ribbons produced by melt spinning.

9:55 AM Break

10:10 AM Invited
3DAP Studies of Amorphous Nanocrystallization - Elemental Distribution Within Small-Size Systems: *K. Hono*[1]; [1]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047 Japan

Nanocrystallization processes of amorphous alloys are widely used for processing nanocrystalline soft and hard magnetic materials, and nanocrystalline ultrahigh strength alloys. Recent studies also reported that many bulk-forming metallic glasses develop nano(quasi)crystalline microstructure after devitrification. In this talk, we will give an overview on our recent studies on the nanocrystallization processes of various amorphous and glassy alloys investigated by the three dimensional atom probe (3DAP) technique complemented by high resolution electron microscopy (HREM). The final nanocrystalline microstructures are very sensitive to alloy compositions, microalloyed elements and heat treatment conditions. Using 3DAP, the distributions of solute atoms in the course of the crystallization processes of Fe, Al, Cu and Zr based amorphous and glassy alloys were analyzed with an atomic resolution, and the overall microstructures were examined by TEM. The factors influencing the nanocrystalline microstructures and the structure-property relationship of nanocrystalline alloys were clarified, by which the optimizations of the microstructures and properties were successfully made in (Fe,Co)-based soft magnetic materials. The possibility and the potential applications of a glass phase separation in bulk-forming metallic glasses will also be discussed.

10:45 AM Invited
Magnetic and Structural Phase Transformations in Nanocrystalline Soft Magnetic Materials: *Matthew A. Willard*[1]; Ramasis Goswami[1]; Vincent G. Harris[2]; [1]Naval Research Laboratory, Code 6324, 4555 Overlook Ave., SW, Washington, DC 20375 USA; [2]Northeastern University, Electl. & Computer Engrg. Dept., Boston, MA 02115 USA

Alloys consisting of nanocrystallites surrounded by a residual amorphous matrix have been produced by rapid solidification processing with subsequent isothermal annealing. The resulting materials, made up of (Fe,Co,Ni)-(Zr,Nb)-B-Cu, possess both high permeability and low core losses making them excellent soft magnetic materials. Characterization of this class of alloys reveals abundant phase transformations, including, primary and secondary crystallization, ferromagnetic-to-paramagnetic phase transformations, polymorphic phase transformations, and order/disorder transformations. This study focuses on magnetic and structural phase transformations and their consequential effects on the properties of these materials. Differential thermal analysis, thermomagnetic analysis, x-ray diffraction, and transmission electron microscopy will explicate the transformations, product phases, and microstructures of these alloys.

11:20 AM
Phase Transformation in Sputter Deposited Al-Zr Thin Film: J. H. Yang[1]; *Y. Yang*[1]; C. X. Ji[1]; Y. A. Chang[1]; [1]University of Wisconsin, Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI USA

The sputter-deposited Al-Zr thin films have been reported in the literature to exhibit either a crystalline or amorphous structure at different compositions. In this study, we first present a thermodynamic argument to calculate the compositions of these binary alloys with tendencies to form amorphous phase. Thin-films of Al-Zr alloys having the compositions predicted by these calculations were prepared by co-sputtering of Al and Zr. These films were found to be amorphous as characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Auger analysis (AES). The thermal stability of these amorphous films has been examined by differential scanning calorimetry (DSC).

Powder Metallurgy Research and Development in the Transportation Industry: Titanium Alloys - P/M Developments

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Powder Materials Committee
Program Organizer: James W. Sears, South Dakota School of Mines & Technology, Additive Manufacturing Laboratory, Rapid City, SD 57701 USA

Wednesday AM Room: 3008
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Eugene A. Olevsky, San Diego State University, Mechl. Engrg. Dept., San Diego, CA 92182-1323 USA

8:30 AM
Influence of Si on the Microstructure of Reactive Sintered TiAl: *David E. Alman*[1]; [1]U.S. Department of Energy - Albany Research Center, 1450 Queen Ave., SW, Albany, OR 97321 USA

TiAl with between 0 and 20 volume percent (v%)Ti5Si3 was produced by reactive sintering of cold pressed compacts of elemental Ti, Al and Si powder mixtures at 700C for 15 minutes in vacuum. The results show that adding Si to Ti and Al reduces the swelling associated with reactive sintering of TiAl, as composites containing more than 5 v%Ti5Si3 densified during reactive sintering. However, composites containing more than 10v% Ti5Si3 did not retain their shape during processing, and the TiAl+20v% Ti5Si3 composite completely melted during the sintering process. The formation of pre-reaction liquid phase and the increase in adiabatic flame temperature with simultaneous compound formation resulted in the melting that occurred and the enhanced densification (minimization of swelling) during reactive sintering of the insitu composites.

8:55 AM
Low-Cost PM Titanium Materials for Automotive Applications: *Orest M. Ivasishin*[1]; Dmytro G. Savvakin[1]; Vladimir S. Moxson[2]; Vlad A. Duz[2]; F. H. Froes[3]; Richard W. Davies[4]; [1]Institute for Metal Physics, 36 Vernadsky St., Kiev 03142 Ukraine; [2]ADMA Products, Inc., 1890 Georgetown Rd., Hudson, OH 44236 USA; [3]University of Idaho, Inst. for Matls. & Advd. Processes, Mines Bldg., Rm. 321, Moscow, ID 83844-3026 USA; [4]Pacific Northwest National Laboratory, 902 Battelle Blvd., PO Box 999, Richland, WA 99352 USA

Titanium alloys are attractive materials for a wide range of applications in automotive industry under condition of noticeable reduction of cost of components made out of them. Blended elemental powder metallurgy (BEPM) is a viable way to achieve this goal. In present study Ti-6Al-4V, Ti-5Al-2.5Fe, and some binary Ti-Mn alloys were synthesized with simplest press-and-sinter BEPM technique. The approach used was based on employment of hydrogenated titanium powder to which alloying elements were added either as elemental or master alloy powders. Minimal content of hydrogen in titanium sufficient to radically influence on the synthesis of titanium based alloys was determined. The advantage of hydrogenated titanium approach in attaining high dense (99%) condition which tensile and fatigue properties are matching the level of corresponding alloys produced with conventional ingot metallurgy will be discussed. Hydrogenated titanium based technology is planned to be tried in manufacturing of various automotive components.

9:20 AM
Fabrication of Titanium Automotive Parts by Laser Powder Deposition: Matt Heath[2]; Bryan Woods[2]; Seth Miller[2]; Aaron Costello[1]; Daniel F. Dolan[2]; *James W. Sears*[1]; [1]South Dakota School of Mines & Technology, Additive Mfg. Lab., 501 E. St. Joseph St., Rapid City, SD 57701 USA; [2]South Dakota School of Mines & Technology, Mechl. Engrg., 501 E. St. Joseph St., Rapid City, SD 57701 USA

Fabrication of titanium components by Laser Powder Deposition (LPD) offers some unique solutions for high performance automotive applications. LPD is a CAD/CAM solid freeform fabrication technology that uses metal powder and laser fusion to produce components. This paper describes the fabrication of titanium engine valves and wheel uprights. LPD's unique capabilities allow direct fabrication of titanium components with design features that are difficult to obtain by other technologies. It has been shown that the titanium valves can be produced lighter and more wear resistant and the wheel uprights 7 times stiffer than existing aluminum designs.

9:45 AM
Processing and Consolidation of Titanium Based Metal-Ceramic Composite, Intermetallic and Alloy Powders for Applications in Transport Industry: *Deliang Zhang*[1]; Zhihong Cai[1]; Gorgees Adam[1]; Stiliana Raynova[1]; Zhiguang Liu[1]; [1]University of Waikato, Dept. of Matls. & Process Engrg., PB 3105, Hamilton, Waikato 2001 New Zealand

Light metallic materials play vital roles in improving the energy efficiency of vehicles used for transport. Titanium based materials are one type of light metallic materials which have not been utilised to their full potential for applications in transport industry because of the limitation of high materials costs and high component manufacturing costs. At Waikato University, we have been working on developing new processes which produce titanium based metal-ceramic composite (such as Ti(Al,O)/Al2O3 and TiAl/Al2O3 composites), intermetallic (such as Ti3Al/TiAl and TiAl), and alloy (such as Ti-6wt%Al-4wt%V) materials directly from low cost raw materials such as titanium oxide and aluminium powders. The new processes involve processing titanium based powders using a combination of several physical and chemical steps, and the powders are consolidated into bulk materials or near net shaped components using novel powder metallurgy processes. This paper will provide an overview of the recent findings and outcomes of the research programme, and discuss the opportunities and issues of using the new materials and the new processes for manufacturing automotive components.

10:10 AM Break

10:20 AM
Synthesis and Characterization of Nanocrystalline Ti Alloys by a Cryomilling Technique: *Fusheng Sun*[1]; P. Rojas[1]; A. Zuniga[1]; E. J. Lavernia[1]; [1]University of California, Dept. of Cheml. Engrg. & Matls. Sci., Davis, CA 95616 USA

The paper reports on the synthesis and characterization of nanocrystalline Ti alloys using a cryomilling technique. The as-received Ti powders with an average powder particle size of 75 mm were cryomilled in a modified Union Process 1-S attritor under a liquid nitrogen medium. The effects of processing parameters such as milling time and ball to powder ratio on the synthesis and structure of the cryomilled Ti powders were investigated. The microstructural evolution of the cryomilled Ti powders were analyzed using XRD, DSC, SEM, and TEM. The results showed that nanocrystalline Ti powders with a grain size of about 5-20nm can be obtained using the cryomilling technique. The grain size and particle size of the cryomilled Ti powders decrease with increasing cryomilling time.

10:45 AM
A Comparison of the Sintering of Various Titanium Powders: *Stephen J. Gerdemann*[1]; David E. Alman[1]; [1]US Department of Energy, Albany Rsch. Ctr., 1450 Queen Ave. SW, Albany, OR 97321 USA

Recently, there has been renewed interest in low-cost titanium. Near-net-shape powder metallurgy offers the potential of manufacturing titanium articles without costly and difficult forming and machining operations; hence, processing methods such as conventional press-and-sinter, powder forging and powder injection molding are of interest. The sintering behavior of a variety of commercial and experimental titanium powders was studied. Commercial powders were acquired that were produced different routes: (i) sponge fines from the primary titanium processing; (ii) via the hydride-dehydride process; and (iii) gas atomization. The influence of vacuum sintering time (0.5 to 32 hrs) and temperature (1200, 1275 or 1350°C) on the microstructure (porosity present) of cold pressed powders was studied. The results are discussed in terms of the difference in powder characteristics; with the aim of identify the characteristics required for full density via press-and-sinter processing. Near-net-shape tensile bars were consolidated via cold pressed and sintered. After sintering, a sub-set of the tensile bars was hot-isostatic pressed (HIPed). The microstructure and properties of the bars were compared in the sintered and HIPed conditions.

11:10 AM
A Novel Method of Injection Molding of Titanium Components: *K. Scott Weil*[1]; Eric Nyberg[1]; Kevin Simmons[1]; [1]Pacific Northwest National Laboratory, Matls. Dept., 902 Battelle Blvd., PO Box 999, Richland, WA 99352 USA

One of the key problems in the powder injection molding (PIM) of titanium components is to minimize the introduction of carbon impurities, because of the deleterious effect they impart on subsequent mechanical properties. We have developed a unique blend of PIM constituents where only a small volume fraction of binder (~5 - 10 vol%) is required for injection molding; the remainder of the mixture consists of the metal powder and binder solvent. Because of the nature of decomposition in the binder system and the relatively small amount used, the binder is eliminated almost completely from the pre-sintered component during the initial stage of a two-step heat treatment process. Results will be presented on the first phase of this research, in which the binder, injection molding, de-binding and sintering schedule were developed. Additional data on the mechanical and physical properties of the material produced will be discussed.

Products, Services, Suppliers Showcase

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizer: David V. Neff, Metaullics Systems Company, Solon, OH 44139 USA

Wednesday AM Room: 2000
February 16, 2005 Location: Moscone West Convention Center

Session Chair: David V. Neff, Metaullics Systems Company, Solon, OH 44139 USA

8:30 AM
Production of High Performance Aluminum Alloy Billet: *Ravi Tilak*[1]; [1]Almex USA, Inc., 1 World Trade Ctr., 8th Fl., Long Beach, CA 90831 USA

Use of Almex LARS TM molten aluminum purification technology along with Almex's Castright II TM casting equipment technology enables cast houses to produce quality products to meet today's increasingly demanding market place for high quality value added products. These innovative technologies address metallurgical issues facing cast houses daily enabling them to produce high quality product on a consistent cost effective basis.

8:50 AM
EcoReg® Continuous Rotating Regenerator - Central Heat Recovery on Large Capacity Aluminum Processing Furnaces: *Michael Shay*[1]; [1]Hauck Manufacturing Company, PO Box 90, Lebanon, PA 17042 USA

The EcoReg® Continuous Rotary Regenerator represents the latest technology in regenerative combustion systems offering higher heat recovery than conventional regenerative systems. Designed to be used for central heat recovery on large capacity furnaces, the EcoReg® replaces the classic recuperator and pulsating dual burner regenerator sets. In the EcoReg®, both principals of a classical regenerator are physically combined in one rotating generator with stationary upper and lower sections. Each section is equipped with two chambers - one for waste gas and one for combustion air. Offering excellent efficiency and productivity increases with low emissions, the regenerator handles 100% of the flue gas, eliminating the need for ancillary flues. As an added benefit, the EcoReg® design does not require burner pairs, allowing for optimum burner number and placement within the furnace design. This paper will present additional information on the EcoReg® technology and a discussion of its application to large capacity aluminum processing furnaces.

9:10 AM
Metaullics Systems Introduces a New High Capacity Pump for Today's Large Reverberatory Furnaces: *Paul Campbell*[1]; [1]Metaullics Systems Co. LP

Forced circulation in a reverberatory furnace by a molten metal pump has long been known to provide benefits in melting rates, reduced energy consumption, higher metal recovery rates, and longer refractory life. The historical recommendation of circulating the volume of the furnace four times per hour is being reconsidered as higher circulation rates are being found to be beneficial. To achieve these higher circulation rates in today's large furnaces new, higher capacity pumps are being developed. Metaullics has recently introduced a pump that has the capacity to circulate a 150 ton furnace ten times per hour.

9:30 AM
Combined Metal Skimming and Melt Treatment System for Metal Transport: *Jan Magnusson*[1]; [1]Altech SMV ehf., Hlidasmara 17, Kopavogur, Reykjavik Area IS 201 Iceland

Abstract not available.

9:50 AM
Brochot Casting System for Aluminum Alloys: *Jean-Jacque Grunspan*[1]; [1]Brochot SA, Tremblay en France 93297 France

The paper defines aluminium alloy families and their characteristics and outlines advantages of Brochot casting system for aluminium alloys. Emphasis is on turbulence-free, non-drossing casting wheel giving controlled and uniforrn ingot filling, constant metal level in

moulds and ingot size. In addition, Brochot's plant-tested programme, which adjusts cooling rate to specific alloys being cast, ensures fine grain, low porosity and minimal shrinkage. Achievenient based on a real industrial scale.

10:10 AM
Main Advantages of the Riedhammer Advanced Baking Furnace System for Production of High Quality Anodes for the Aluminium Industry: *Carmen Porzelt*[1]; [1]Riedhammer GmbH, Industrial Kiln Plants, 90332 Nürnberg Germany

In the last 80 years Riedhammer has been designing and developing Closed Ring Pit Furnaces for t h e baking of high quality anodes for the aluminium industry and more than 105 furnaces have been built or revamped on the basis of this concept in 25 different countries. The most relevant advantages which will be presented are directly related to the achievement of a significant reduction of the capital investment aiming at an increased competitiveness. The introduction of "state of the art" anode baking technology ensures first quality baked anodes in view of the physical and chemical properties directly connected, among others, with the baking process, i.e. heating-up gradients, final baking temperature, temperature homogeneity. Another important improvement is the increase of baking and thermal efficiency positively influencing the fuel consumption as well as the cycle time. A computerised auto firing system permits very high equipment and process reliability together with the optimisation of baking parameters, cycle time ("fast baking") and overall energy balance. Thereby a further strong reduction of the emission levels could be realised emphasising our concern to maintain and improve the environmental friendly characteristics of the equipment.

10:30 AM
Anode Slot Cutting Machine: *Jean-Jacque Grunspan*[1]; [1]Brochot SA, Tremblay en France 93297 France

The paper outlines BROCHOT and ALCO-TEK full pot-rooms installafion project at Alouette sept-Iles in Quebec Canada. It will present four main tasks accurately under progress: Installation and welding of BUS BARS; Installation and alignment of POT Shells; Full lining of the pots; and Superstructure Installation. Moreover, describes BROCHOT/ALCO-TEK contract system for carrying out the plan work schedule along with the specific equipment used for the purpose as well as their relevant appropriate maintenance.

10:50 AM
Latest Developments with TAC: *Martin Taylor*[1]; [1]STAS, Chicoutimi, QC G7K 1H1 Canada

Stas has recently supplied TAC (Treatment of Aluminium in a Crucible) to large aluminium primary smelters, for both <Brownfield> and existing plants. These TAC units are used to remove alkalines, especially sodium, from molten metal using aluminium fluoride. There have also been developments to use a similar technology to remove alkalines .from molten metal in Cast Houses where only recycled metal is processed. Stas will report on the latest developments in this field.

11:10 AM
Bath Crucible Handler, Vehicle Designed to Manipulate Bath Crucibles in the Potroom: *Eloise Harvey*[1]; [1]Mecfor Inc., Chicoutimi, QC G7K 1H1 Canada

Maintaining an adequate level of bath in pots is crucial when a primary smelter wants to achieve high purity aluminium. Indeed, the bath level must be kept just below the cast iron or steel rod in order to minimise its corrosion thus, minimising the deposit of Fe in the aluminium. Mecfor's bath crucible handler allows for precise siphoning and pouring operations to balance bath between pots in primary smelters potrooms. To perform the bath balancing operation, an articulated or rigid bath crucible handling vehicle specially designed for the harsh working environment of aluminium smelter is used. The vehicle is fully autonomous and can pick up a crucible, even from the floor, rotate it and tilt it both ways towards the left or the right of the vehicle to pour bath. The operator can complete his work without ever having to leave his vehicle since the vehicle is equipped with an on-board compressor. Its highly efficient handling system requires only a few seconds to load a crucible. The grip is secured by a manual lock operated from each side of the handler. The rotation allows for a 135° movement, both ways, executed with a hydraulic motor and a slewing bearing. The tilting position is performed by two hydraulic cylinders up to 96°. The bath crucible handler also possesses a high-tech weight scale that indicates the deflection on the horizontal arm of the handler thus providing extremely precise measurements. The system indicates the weight of each load during the siphoning and even during the pouring operation (+/-2Okg or 45 Ibs.). The weight precision is crucial to obtain an adequate mix. The system is composed of strain gauges installed on the horizontal arms and of two weight displays: one on the mast and another one inside the cabin. Another advantage of the bath crucible handler is the bi-directional steering that allows the operator to drive in the forward direction at all time. It provides unobstructed view during the transportation with the bath crucible.

11:30 AM
Cast Aluminium Developments in Automotive Applications: *Nnamdi Anyadike*[1]; [1]APT Aluminum Process and Product Technology, London TW10 6QX UK

Cast aluminium is increasingly gaining in importance, particularly with the growth of highly precise and complex cast products. Each year in Europe alone, more than two million tonnes of aluminium are processed. The shift from grey cast-iron to aluminium casting began in the 1970s and since then weight reductions in the engine block have been in the order of 40-55% compared with the mid-1970s. Further substitutions have been made in areas such as the axle, leading to considerable performance enhancements. Meanwhile, casting methods have been developed in the bid to keep pace with demands from the automotive industry for a lightweight yet robust alternative to iron and steel castings. For aluminium engine blocks the low-pressure casting process has proved to be a high quality technique that satisfies the automotive industry's requiurements. In the case of the 'all aluminium car body' a whole new space frame technology needed to be developed with vacuum pressure die casting at its heart. Automotive aluminium castings are continuing to improve as the technology leaps forward. This paper will look at some of these developments and provide some indication of where the 'next generation' castings are heading.

Recycling - General Sessions: Aluminum and Consumer Goods Recycling

Sponsored by: Extraction & Processing Division, Light Metals Division, LMD/EPD-Recycling Committee
Program Organizer: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA

Wednesday AM Room: 2011
February 16, 2005 Location: Moscone West Convention Center

Session Chair: TBA

8:30 AM
Consolidation of Fine Aluminum Scrap Via the Extrusion Process: *William H. Van Geertruyden*[1]; Wojciech Z. Misiolek[2]; Clifford A. Prescott[2]; [1]EMV Technologies, LLC, 115 Research Dr., Bethlehem, PA 18015 USA; [2]Lehigh University, Inst. for Metal Forming, 5 E. Packer Ave., Bethlehem, PA 18015 USA

In the current aluminum processing industry, there does not exist a cost effective method for remelting fine aluminum scrap. Fine aluminum scrap may include machine chips and swarfs, fine gauge wire, or other particles. Additionally, remelting this type of material is many times not feasible because of considerable oxidation due to the high surface to volume ratio. A new method for consolidation fine aluminum scrap by cold extrusion is proposed in this paper. Cold extrusion experiments have been performed using fine aluminum powder and chopped aluminum wire to understand the effect of particle size and shape on the pressure necessary to produce consolidated aluminum material. These extrusion experiments were performed using a front pad to introduce different levels of counter pressure to control the degree of densification.

9:00 AM
New Experimental Approach in the Search of Intermetallic Compounds for Fe, Mn and Si Removal in Aluminum Recycling: *Alexander Pisch*[1]; Christoph Kraeutlein[2]; Pierre Le Brun[3]; Georg Rombach[4]; Paul de Vries[5]; Marc Ryckeboer[6]; Christian J. Simensen[7]; [1]INPG, LTPCM, Domaine Universitaire, BP 75, St. Martin d'Heres Cedex 38000 France; [2]RWTH Aachen, IME, Intzestrasse 3, Aachen 52056 Germany; [3]Alcan, Voreppe Rsch. Ctr., BP 27, 725 rue Aristide Bergès, Voreppe 38341 France; [4]Hydro Aluminium Deutschland GmbH, Georg-von-Boeselager-Str. 21, Bonn 53117 Germany; [5]Corus Technology B.V., PO Box 10000, CA Ijmuiden 1970 The Netherlands; [6]Remi Claeys Aluminium NV, Kortemarkstraat 52, Lichtervelde 8810 Belgium; [7]SINTEF, Matls. Tech., PO Box 124 Blindern, Oslo 0324 Norway

A new experimental approach has been developed to identify new, unknown higher order intermetallic compounds which can precipitate

and segregate Fe, Mn and Si from a liquid aluminum melt during recycling. For this basic investigation, a complete experimental procedure has been defined and tested in terms of addition elements, melt processing, cooling conditions and crucible material. Large scale analysis has been performed by XRF and ICP by comparing the Fe, Mn and Si content on the top and the bottom of the samples. Several specimens have been analyzed by SEM to investigate the shape and to identify the composition of the observed intermetallics. A list of additional elements have been defined and a maximum amount of nine elements were added at a time. This work was founded by the EEC in the Growth programme (G1RD-CT-2002-00728).

9:30 AM Break

10:00 AM
About the Coalescence Mechanism of Aluminum, the Analysis of the Recent Conceptions: *Anatoly Georgievich Zholnin*[1]; Sergey Borisovich Novichkov[2]; [1]Mosoblprommontazh, Voskresensky region der.Ratmirovo, Ul. Naberezhnaya, 4, Moskovskaya oblast 140207 Russia; [2]Russkiy Aluminiy, Prokatniy Div., Verhniy Taganskiy Typic, 4, Moscow Russia

The overview of articles about confluence of molten aluminum droplets in liquid flux was made. We have reviewed previously published experimental data. The contradiction between conceptions about coalescence mechanism and experimental data was revealed. Mechanisms are proposed which improve conceptions about coalescence. We have shown experimentally that the changes of fusion conditions may principal modify our conceptions about the role of fluoride and chloride additions to the flux. These were revealed to be the determining factors at melting of low-yield aluminum raw material. The basic source of metal loss in reverberatory and rotary furnaces is the mixing of the metal in flux and oxides. Therefore, the determining factors in real fusions are not the flux composition and its behavior, but is instead the viscosity and the wetting ability of flux-oxides substance. On the aluminum drops and flux-oxides substance interaction will be imposed upon mechanical effect, which presents on any fusions.

10:30 AM
The Recovery of Aluminium Metal from Primary and Secondary Drosses by Grinding and Screening: *Warren John Bruckard*[1]; Patrick Walta[1]; James Thorpe Woodcock[1]; [1]CSIRO Minerals, Box 312, Clayton S., Melbourne, Victoria 3169 Australia

Dross is formed during the smelting and remelting of aluminium. It is toxic, and expensive to dump, but contains valuable metallic aluminium. Tests on Australian drosses obtained high recoveries of metallic aluminium in high-grade concentrates by wet milling and screening. Characterisation of the drosses showed mixtures of metallics, oxides, nitrides, carbides, and soluble salts. P80 ranged from 290 µm to 750 µm. After wet grinding in a ball mill the P80 was reduced to 38-74 µm. Assay of the size fractions showed that the malleable aluminium particles had been flattened and reported in the coarser fractions, and that the softer or more brittle non-metallics reported to the fine fractions. For primary dross, screening at 150 µm recovered 95% of the metallic aluminium in a product assaying 90% Al0. Secondary drosses gave about 54% recovery at 70% Al0. It is believed that these products can be directly remelted, thus providing an economic benefit.

11:00 AM
Extraction of Value Added Products from Aluminium Dross Material to Achieve Zero Waste: *Jyoti Mukhopadhyay*[1]; Y. V. Ramana[2]; Upendra Singh[2]; [1]Jawaharlal Nehru Aluminium Research Development and Design Centre, Techl., Amravati Rd., Wadi, Nagpur, Maharashtra 440 023 India; [2]HINDALCO Industries Limited, R&D, PO Renukoot, Renukoot, Uttar Pradesh 231 217 India

Hindalco generates 4,000 tons of dross annually while producing 340,000 tons of aluminium. The dross is disposed as process reject for further processing to downstream industries. The lowest grade of dross normally contains less than 10% metallic aluminium, which is further processed to generate alum as a by-product. Since Hindalco consumed substantial amount of alum for water purification, it was decided to study the scope for internal generation of alum. Accordingly, alum was produced from dross and compared with the alum obtained from the market. It was observed that the cost of indigenous alum is less than half of alum procured from the market. Furthermore, the properties of indigenously produced alum compared very well with commercial alum. The remaining process reject after alum production will be used for making high quality refractory. As a result, a zero waste concept could be achieved, while using waste dross material.

11:30 AM
Characterization of the Hazardous Components in End-of-Life Notebook Displays: A. Mester[1]; N. Fraunholcz[2]; A. van Schaik[1]; *M. A. Reuter*[1]; [1]Delft University of Technology, Mijnbouwstraat 120, Delft 2628 RX Netherlands; [2]Recycling Avenue, Rotterdamseweg 145, Delft 2628 AL Netherlands

The use of notebooks has been strongly and steadily increasing for years in Europe. A corresponding increase in the amount of end-of-life notebooks available for recycling is expected in the coming years. Notebooks are equipped with liquid crystal displays mainly using mercury-containing backlights. The European Directive on waste electrical and electronic equipment (WEEE) requires the save removal of both mercury and liquid crystals. Therefore, the treatment of end-of-life notebooks requires special treatment for which the existing infrastructure for the recycling of traditional desktop computers based on cathode ray tube monitors is not suited. We studied the composition of end-of-life notebook displays in terms of number and mercury content of backlights and main parts such as printed circuit boards. For this, an actual sample of 150 end-of-life notebooks was dismantled manually. Our results indicate that the best option to safely remove mercury is shredding with controlled vapor extraction. Moreover, literature data show that the toxicity of liquid crystals is very low. Therefore, the legislative requirement of their controlled removal appears not justified. The data were also used to predict the material composition of notebook displays for a few years ahead.

Refractory Metals in Electronic Applications: Applications

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Texture & Anisotropy Committee, EMPMD-Thin Films & Interfaces Committee, SMD-Refractory Metals Committee, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Gary A. Rozak, Fabricated Products, Cleveland, OH 44117 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; David P. Field, Washington State University, Pullman, WA 99164-2920 USA; Chris A. Michaluk, Williams Advanced Materials, Gilbertsville, PA 19525 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA

Wednesday AM Room: 3010
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Gary A. Rozak, H.C. Starck, Cleveland, OH 44117-1117 USA; Don Mitchell, Rhenium Alloys Inc., Elyria, OH 44036-0245 USA

8:30 AM
Rhenium, Tungsten and Molybdenum in Electronics: *Don Mitchell*[1]; Todd Leonhardt[1]; James Downs[1]; [1]Rhenium Alloys Inc., 1329 Taylor St., Elyria, OH 44036 USA

Rhenium, tungsten, and molybdenum are used in a wide range of applications for the electronics industry because of the inherent properties of these pure metals and their alloys. These refractory metals have unique properties of high melting points, high temperature strength, high modulus of elasticity, good ductility, and high recrystallization temperatures. A discussion of some of the applications and properties will be presented.

9:00 AM
Applications of Molybdenum in Electronic Materials: *John A. Shields*[1]; Gary A. Rozak[1]; [1]H.C. Starck, Mo/W Ops., Fabricated Products Business Grp., 21801 Tungsten Rd., Cleveland, OH 44117 USA

Molybdenum and molybdenum alloys have thermal, mechanical, electrical and chemical properties that are uniquely applied as electronic materials and in the production of electronic materials. Componant applications include thermal management in electronic packaging, thick film multi-layer ceramic packaging, and thin film metallization and in flat panel displays. Mo and Mo alloys are also employed in manufacturing equipment and tooling for the production of electronic materials. For example, molybdenum is used in masks, ion-implantation equipment and crystal growth furnaces. This presentation will summarize the properties of molybdenum for particular electronic material applications.

9:30 AM
Iridium/Iridium Silicide as an Oxidation Resistant Capping Layer for Soft X-Ray Mirrors: *Shon T. Prisbrey*[1]; Stephen P. Vernon[2];

[1]Lawrence Livermore National Laboratory/University of California, Davis, L-174, 7000 E. Ave., Livermore, CA 94551 USA; [2]Lawrence Livermore National Laboratory, 7000 E. Ave., Livermore, CA 94551 USA

Quarter wavelength multilayer stacks for 13.4 nm light were employed to probe the oxidation resistance of an [Ir/Si] capping layer. Ir thickness values ($7.5 < d_{Ir} < 20$ Å) were investigated. Reflected standing waves were modeled and correlated to Ir thickness, sputtering auger depth profiles, and atomic force microscopy surface measurements. Peak reflectivity determined stability. $7.5 < d_{Ir} < \sim 10$ Å and $15 < d_{Ir} < 20$ Å capping layers were stable after exposure to air for the time measured in this study (~140 days) whereas $\sim 10 < d_{Ir} < 15$ Å capping layers were not. The instability coincides with increased surface roughness (2 -> 5 Å RMS) and the formation of a SiO_2 surface layer. Modeling implied: the formation of iridium silicide, formation of a SiO_2 surface layer for $\sim 10 < d_{Ir} < 15$ Å, and that for $d_{Ir} > 16$ Å, $IrSi_y$ ($y<<1$) is present on the surface.

10:00 AM Break

10:15 AM
Tantalum and Niobium Powder for Electronics Applications: *Leah F. Simkins*[1]; Michael J. Albarelli[1]; [1]H. C. Starck, Inc., 45 Industl. Place, Newton, MA 02161 USA

The tantalum pentoxide as a dielectric film has been the subject of intensive investigation for the last 50 years because of the importance of these insulators in capacitors. Over the past 10 years, capacitors have gotten smaller as technology has developed to make higher surface area powders. In 2002, due to a technology developed at H.C. Starck niobium finally entered the capacitor industry as a viable capacitor substrate. This paper will explore the properties, characteristics, and applications of tantalum and niobium in the electronics industry.

10:45 AM
Tantalum "Spine Anodes" for High Power Electrolytic Capacitors: *Gerhard E. Welsch*[1]; Donald McGervey[1]; [1]CWRU, Matls. Sci. & Engrg., 10900 Euclid Ave., Cleveland, OH 44106 USA

The paper describes how performance criteria of electrolytic capacitors depend on material properties and on capacitor anode design. Various designs will be discussed and a new method for the fabrication of spine-anodes(TM) will be presented using solid tantalum substrates on which layers of high-surface-area tantalum sponge are grown. We will show that capacitors made from thin spine-anodes have higher energy-density and higher power than capacitors made from pressed and sintered powder.

Shape Casting — The John Campbell Symposium: Modeling

Sponsored by: Light Metals Division, LMD-Aluminum Committee, MPMD-Solidification Committee
Program Organizers: Murat Tiryakioglu, Robert Morris University, Moon Township, PA 15108 USA; Paul N. Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Wednesday AM Room: 2008
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Mark R. Jolly, University of Birmingham, IRC in Matls., Edgbaston, Birmingham B15 2TT UK

8:30 AM
Computer Simulation of Shrinkage-Related Defects in Castings - A Review: *Doru Michael Stefanescu*[1]; [1]University of Alabama, PO Box 870202, Tuscaloosa, AL 35487 USA

Simulation of shrinkage-related defects in shape castings has been extensively studied because of its potential contribution to quality improvement of cast products. The location of macro-shrinkage can be estimated rather easily by present solidification models in most casting alloys. The exception is ductile iron, where graphite expansion complicates the physics. For all alloys it is still difficult to quantify macroshrinkage size. In spite of concentrated efforts and numerous claims of success, microporosity prediction is still a problem looking for a solution. After a succinct analysis of the physics of the problem, the paper reviews the various approaches to modeling macro- and micro-porosity evolution, from simple thermal models and criteria functions, to channel and porous medium models based on hydrogen diffusion, and finally to a most recent model based on oxide entrapment. Recent experimental data on microporosity formation in thin-wall ductile iron is also included in the analysis.

9:00 AM
Computational Modelling of Mould Filling and Related Free Surface Flows in Shape Casting: *Mark Cross*[1]; Koulis A. Pericleous[1]; T. Nick Croft[1]; Diane McBride[1]; James Lawrence[1]; Alison J. Williams[1]; [1]University of Greenwich, Ctr. for Numerical Modlg. & Process Analysis, Old Royal Naval Coll., Park Row, London SE10 9LS UK

Accurate representation of the coupled effects between turbulent fluid flow with a free surface, heat transfer, solidification and mould deformation has been shown to be necessary for the realistic prediction of several defects in castings and also for determining the final crystalline structure. A core component of the computational modelling of casting processes involves mould filling which is the most compute intensive aspect of casting simulation at the continuum level. Considering the complex geometries involved in shape casting, the evolution of the free surface, gas entrapment and the entrainment of oxide layers into the casting make this a very challenging task in every respect. Despite well over 30 years of effort in developing algorithms this is by no means a closed subject. In this paper we will review the full range of computational methods used from unstructured finite element and finite volume methods through fully structured and block structured approaches utilising the cut cell family of techniques to capture the geometric complexity inherent in shape casting. This discussion will include the challenges of generating rapid solutions on high performance parallel cluster technology, and how mould filling links in with the full spectrum of physics involved shape casting. Finally, some indications as to novel techniques emerging now that can address genuinely arbitrarily complex geometries are briefly outlined and their advantages and disadvantages discussed.

9:30 AM
Simulation of Casting Complex Shaped Objects Using SPH: *Paul Cleary*[1]; Joseph Ha[1]; Mahesh Prakash[1]; Thang Nguyen[2]; [1]CSIRO, Math. & Info. Scis., PB 10, Clayton S., Victoria Vic 3169 Australia; [2]CSIRO, Mfg. & Infrastruct. Tech., Preston, Victoria Vic 3072 Australia

The geometric complexity and high fluid speeds involved in High Pressure Die Casting (HPDC) combine to give strongly three dimensional fluid flow, with significant free surface fragmentation and splashing. A Lagrangian simulation technique that is particularly well suited to modelling HPDC is Smoothed Particle Hydrodynamics (SPH). Materials are approximated by particles that are free to move around rather than by fixed grids, enabling the accurate prediction of fluid flows involving complex free surface motion. The SPH method will be summarized and its relative strengths and weaknesses for die will be discussed. SPH has other attractive features for the prediction of casting, including ready prediction of shrinkage, feeding, some forms of porosity generation and surface oxide formation. These will be demonstrated using a simple two dimensional Low Pressure Die Casting (LPDC) example. Several examples of SPH simulated HPDC flows for highly complex real three dimensional industrial components/products will be presented. Automotive parts (usually cast with aluminium) range from simple cases such as a servo piston to structural cross members and a full engine rocker cover. Simulation of casting of many household products such as door handles remain large calculations because of the very small gates employed with zinc. A example of zinc die casting will be presented. Together these show unprecedented detail in the fluid free surfaces, particularly in the extent of fragmentation and void formation for the casting of complex shapes. Validation of isothermal SPH flow predictions by comparison with water analogue experiment and MAGMAsoft predictions are summarized for the flow in a single servo piston head. The SPH simulations were better able to capture the key details of the fluid motion and splashing, particularly the relative rates of flow around sharp bends and through thin sections. Some initial validation of flow predictions coupled to temperature and solidification using short shots are also presented. The bulk features of the final solid castings are in good agreement with the predictions. These results together combine to demonstrate that SPH modelling of die casting has now reached a level where both isothermal and thermal simulations can be performed in reasonable computation times for large scale automotive castings and provide a good degree of predictive accuracy.

10:00 AM
Review of Optimisation Methods for Casting Simulation: *Rajesh S. Ransing*[1]; [1]University of Wales Swansea, Civil & Computational Engrg., Sch. of Engrg., Singleton Park, Swansea, W. Glamorgan SA2 8PP UK

The manufacture of defect free components at low cost and high productivity is as important to the casting industry today, as it was thirty years ago. In old days, experience was gained either by using a "trial and error" method or by undertaking expensive experiments. Many "do's" and "don'ts" in the casting process have been evolved over a period of time. However, the important ones that come to mind are so fundamental that they challenge the "academic mind" to think all over again. The rules proposed by Professor John Campbell are classic examples. The message is simple: mathematical complexity in computer models needs to go hand in hand with the rules derived from "first principles." In the optimisation domain, a range of methods have been evolved over a period of years. At the start of the optimisation study, a foundryman has the first option of using simple and well established methods such as the use of orthogonal arrays for optimal design of process conditions or the famous Inscribed or Heuvers circle method for optimal feeding design. With the maturity of computer simulation software, the inverse analysis has also become a popular tool to determine optimal specification of some of the process parameters. The computer simulation software can be based on a variety of computational methods ranging from geometric reasoning techniques (the famous Chvorinov rule and its variants) to solving complex partial differential equations using one of the numerical methods. Optimisation methods based on solving partial differential methods was an active area of research in mid nineties with pioneering work originating from Professor Dantzig's group. This paper will review a variety of optimization methods highlighting their advantages and disadvantages. The paper will raise some of the challenging issues that the optimization community is facing today and also report on our recent work on linking geometric reasoning techniques with the finite element method to achieve optimal and computationally efficient feeding design of castings.

10:30 AM Break

10:40 AM

State of the Art Review of Use of Modelling Software for Shape Casting: *Mark R. Jolly*[1]; [1]University of Birmingham, IRC in Matls. Procg., Edgbaston, Birmingham B15 2TT UK

During the time that John Campbell was developing the Cosworth process for giving quiescent filling in aluminium castings other workers were using the newly developed PCs to help them in the foundry. In the mid-1980s the first 3D PC based casting modelling software, SOLSTAR, was launched into the market. It was developed by a foundryman and used a series of rules to model casting solidification on a cellular automaton based approach. A finite difference type mesh described the geometry and by the early 1990s was using up to 4 million cells. It was solely applicable to prediction primary shrinkage cavities mainly in the ferrous castings. Initially it was sold only to steel foundries, then cast iron and copper and eventually in the early 1990's an aluminium version was developed. However for John Campbell modelling solidification shrinkage was a secondary consideration and it wasn't until software codes were developed that could model flow that he started to take modelling seriously. This was demonstrated in the 1995 conference Modelling of Casting, Welding and Advanced Solidification Processes where, as co-chair, he set up a benchmarking exercise to test the filling algorithms of the software developers. This was made possible by the real-time x-ray equipment that has proved to be invaluable in his recent research work in helping validate and develop his own theories for oxide generation aswell as validate, or not, casting filling simulation software codes. During the following fifteen or so years, many man-hours have been dedicated to developing methods for simulating the whole casting process and to other supplementary processes that exist within the foundry. This review attempts to give the reader an understanding of the special problems that exist within the foundry process and how simulation software has been applied to help give solutions to manufacturing problems.

11:00 AM

Analysis and Optimization of the Transient Stage of Stopper-Rod Pour: *David Goettsch*[1]; Michael Barkhudarov[2]; [1]General Motors, Powertrain, 895 Joslyn Ave., Pontiac, MI 48340-2925 USA; [2]Flow Science, Inc., 683 Harkle Rd., Ste. A, Santa Fe, NM 87505 USA

Stopper-rod controlled pouring system is a simple, efficient method for metal delivery in high production cast lines. However, the raising of the rod from the nozzle creates a complex flow front that results in air entrainment and oxide film creation that are detrimental to casting quality. Three primary factors resulting in defect creation which compromise casting quality are: 1) metallostatic head pressure, 2) shape of the rod, and 3) the speed of its removal from the nozzle. Our present work aims to employ numerical modeling to enhance the understanding of this essentially transient flow. The model will then be applied to optimize the process to minimize the potential for such defects. Real time X-ray visualization will be used to validate the results.

11:20 AM

"Designing-In" Controlled Filling Using Numerical Simulation for Gravity Sand Casting of Aluminium Alloys: *Jean-Christophe Gebelin*[1]; Fu-Yuan Hsu[2]; Mark R. Jolly[1]; John Campbell[1]; [1]University of Birmingham, IRC in Matls. Procg., Edgbaston, Birmingham, W. Midlands B15 2TT UK; [2]Auspicium Co. Ltd., 2F-3, No.4, Sec. 1, Jen-Ai Rd., Taipei Taiwan

In order to achieve good reliable aluminium alloy casting components using gravity sand casting process it is essential to have a good part design, good quality ingots, a good melting process, a good metal transfer system from the furnace to the mould, and use a good running system design. In developing the running system design, and especially in the case of gravity sand casting of aluminium alloys, the first aim of the designer should be the control of the metal stream during the filling. From this statement, it would appear that the only reasonable way forward is to use bottom-gating system, where the liquid metal travels in opposition to the direction of the gravitational force. Only then can the metal stream truly be controlled. This immediately creates a problem in that the metal is going upward in the casting, but in the running system it has first to go downward, in the most controlled possible way. In order to achieve that a number of studies of different parts of the running system has been carried out, such as investigating the pouring basin,[1] down-sprue,[2-3] runner[4] and gating system,[5-6] but putting everything together and looking at the 'junctions' is still a challenging task. In this paper we will present the main results on the 'right' design for the different parts of the running system and some recent work on the "junction" where process modelling and experimental validation have been widely used. [1]Yang X. and Campbell J., Liquid metal flow in a pouring basin, Int. J. Cast Metals Res., 10, pp-239-253, 1998. [2]Campbell J., Castings, Butterworth-Heinemann, 1991. [3]Sirrell B.R., The optimisation of the running and gating of sand casting, M. Ph. Thesis, The University of Birmingham, UK, 1995. [4]Sirrell B. and Campbell J., Mechanism of filtration in reduction of Casting defects due to surface turbulence during mould filling, Trans. AFS, pp 645-654, 1997. [5]Jeancolas M., Cohen de Lara G., Hanf H., Hydrodynamics study of horizontal gating systems, Trans. AFS, v70. 1962. [6]Srinivasan M. N., Applied hydraulics to gating systems, PhD thesis, The University of Birmingham, 1962.

11:40 AM

A Front-Tracking Method of Predicting the Solidification Microstructure in Shape Castings: *Shaun McFadden*[1]; David J. Browne[1]; [1]University College Dublin, Mechl. Engrg., Engrg. Bldg., Belfield, Dublin 4, Co Dublin Ireland

A novel numerical model has been developed that simulates the nucleation and growth of columnar and equiaxed grains from the liquid phase in a casting. This model uses a control volume finite difference method to solve conduction heat transfer over a two-dimensional domain. The evolving columnar front and equiaxed grain boundaries are represented by sharp fronts across the mesh. A front-tracking algorithm is used to predict the evolution of the grains across the grid according to dendrite kinetics. The heat equation is coupled to the front-tracking algorithm by a source term that represents the latent heat that evolves as the dendrite tips advance and the mushy zone solidifies. This model predicts the extent of liquid undercooling ahead of the growing columnar front and this computation is used to determine the likelihood of nucleation and growth of equiaxed grains in the liquid; in particular the columnar-to-equiaxed transition is predicted.

Superalloys and Coatings for High Temperature Applications: Superalloys - I

Sponsored by: Structural Materials Division, SMD-High Temperature Alloys Committee, SMD-Corrosion and Environmental Effects Committee-(Jt. ASM-MSCTS), High Temperature Materials Committee of IoM3

Program Organizers: Roger C. Reed, University of British Columbia, Department of Metals and Materials Engineering, Vancouver, British Columbia V6T 1Z4 Canada; Richard S. Bellows, Solar Turbines, Inc., Materials and Process Engineering, San Diego, CA 92186-5376 USA; Qiang (Charles) Feng, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Tim Gabb, NASA Glenn Research Center, Cleveland, OH 44135 USA; John Nicholls, Cranfield University, Bedfordshire MK43 OAL UK; Bruce A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Wednesday AM Room: Nob Hill A/B
February 16, 2005 Location: San Francisco Marriott

Session Chairs: Malcolm McLean, Imperial College London, London SW72AZ UK; Tim Gabb, NASA Glenn Research Center, Cleveland, OH 44135 USA

8:30 AM Invited
High Temperature Protective Coating Systems, The First 60 Years: *Donald H. Boone*[1]; [1]BWD Turbines, Ltd., 2412 Cascade Dr., Walnut Creek, CA 94598-4300 USA

Protective coating for superalloy components operating in gas turbine engines have been in successful use for over 60 years. Their need and use continues as greater dependencies are placed on coatings for present and advanced designs. A review of this history and the significant understanding attained will be presented as a background to thoughts on present activities and future goals. Some critical achievements, recurring myths, and stumbling blocks will be suggested.

9:00 AM Invited
Improved Single Crystal Superalloy, CMSX-4® (SLS)[La+Y]: *Jacqueline B. Wahl*[1]; Ken Harris[1]; [1]Cannon-Muskegon Corporation, Box 506, Muskegon, MI 49443-0506 USA

Modern turbine engine designs place demanding requirements on single crystal superalloy turbine components. The most stringent applications, such as first stage turbine blades and vanes, require a fully solutioned microstructure to achieve superior high temperature creep and fatigue strength, with excellent oxidation and coating performance, including the use of prime reliant thermal barrier coatings. CMSX-4® [SLS][La+Y] is an improved version of CMSX-4® alloy, with typical sulfur content of 1 ppm and pre-alloyed with lanthanum and yttrium to address these requirements. Significant experience through the manufacture of fifteen heats of alloy and numerous component casting trials will be discussed along with the benefits of lower reactive element additions, pre-alloyed ingot and composite remelt charge blending. This technology has been scaled to 4000 lb. heats to meet initial development and production applications. Current status, including engine service results, will be discussed.

9:30 AM
Surface Modification of Nickel Based Alloys for Improved Oxidation Resistance: *Paul D. Jablonski*[1]; David E. Alman[1]; [1]U.S. Department of Energy, Albany Rsch. Ctr., 1450 Queen Ave., SW, Albany, OR 97321 USA

The present research is aimed at the evaluation of a surface modification treatment to enhance the high temperature stability of nickel-base superalloys. A low Coefficient Thermal Expansion (CTE ~ 12.5x10-6/°C) alloy based on the composition (in weight %) of Ni-22Mo-12.5Cr was produced by Vacuum Induction Melting and Vacuum Arc Melting and reduced to sheet by conventional thermal-mechanical processing. A surface treatment was devised to enhance the oxidation resistance of the alloys at high temperature. Oxidation tests (in dry and wet air; treated and untreated) were conducted 800°C to evaluate the oxidation resistance of the alloys. The results were compared to the behavior of Haynes 230 (Ni-22Cr) in the treated and untreated conditions. The treatment was not very effective for Haynes 230, as this alloy had similar oxidation behavior in both the treated and untreated conditions. However, the treatment had a significant effect on the behavior of the low CTE alloy. At 800°C, the untreated Ni-12.5Cr alloy was 5 times less oxidation resistant than Haynes 230. However, in the treated condition, the Ni-12.5Cr alloy had comparable oxidation resistance to the Haynes 230 alloy.

9:55 AM
Effect of Alloying Elements on the Oxidation Behavior of 4th Generation Ni-Base Single-Crystal Superalloys: *Kyoko Hashi Kawagishi*[1]; Atsushi Sato[2]; Toshiharu Kobayashi[1]; Hiroshi Harada[1]; [1]National Institute for Materials Science, High Temp. Matls. Grp., 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047 Japan; [2]Shibaura Institute of Technology, Dept. of Matls. Sci. & Engrg., 3-9-14, Shibaura, Minato-ku, Tokyo 108-0023 Japan

The 4th generation Ni-base single crystal superalloys, which contain large amounts of refractory metals for strengthening and platinum group metals, e.g., Ru, for TCP-phase prevention, show excellent high-temperature strengths. However, these alloying elements seem to decrease high-temperature oxidation resistance, and the improvement of high-temperature oxidation resistance is one of the important issues for practical use of these superalloys. In this study, Ni-base superalloys with various amounts of Hf, Ta, Re and Ru were examined in isothermal and cyclic exposures at 1100°C to investigate the effect on the oxide growth rate and resistance to scale spallation. Structures of the oxide for the alloys were analyzed by XRD etc, and the oxidation kinetics is discussed.

10:20 AM
High Temperature Corrosion of Ni-Cr Based Superalloys in a LiCl-6% Li2O Molten Salt System: Alberto Polar[1]; Francisco Rumiche[1]; *J. Ernesto Indacochea*[1]; Christine T. Snyder[2]; Leonard Leibowitz[2]; [1]University of Illinois, Civil & Matls. Engrg., 842 W. Taylor St., Chicago, IL 60607 USA; [2]Argonne National Laboratory, Cheml. Engrg. Div., 9700 Cass Ave., Bldg. 205, Argonne, IL 60439 USA

Corrosion tests in molten LiCl-6% Li_2O were conducted on a set of Ni-Cr based superalloys at temperatures ranging from 625°C to 725°C at the Argonne National Laboratory to evaluate their capability to be used for vessels in the electrometallurgical treatment of spent oxide fuels. Ar-10% O_2 gas was bubbled inside the molten salt to simulate the effect of oxygen emission during the reduction phase of the process. Microstructural examination under optical and scanning electron microscopes was performed, and the oxide layers were analyzed using EDS and XRD techniques. Ni-Cr alloys with high Fe content, as well as those where refractory metals were present, produce a highly porous non protective layer. Chlorides formation seems to contribute to the porous character of these layers. Even though different layer morphologies were observed, Ni-Cr alloys with only other minor alloying elements, formed a dense protective layer and they showed the best performance among the analyzed samples.

10:45 AM Break

11:10 AM Invited
An Overview of Modeling Approaches for High Temperature Materials and Coating Design, Processing and Durability for Gas Turbine Applications: *Prakash C. Patnaik*[1]; [1]National Research Council Canada, Inst. for Aeros. Rsch., Bldg. M13, Montreal Rd. Campus, Ottawa, Ontario K1A 0R6 Canada

This paper will present an overview of modeling efforts in design, processing and durability of gas turbine materials and coatings as work continues to advance in this laboratory. Attempts are being made to systematically use first principle calculations of alloying strengthening effects in binary, ternary, quaternary and higher order (up to 5 alloying elements) Ni alloys representing the gamma solid solution and the alloying representing the transition or refractory metals. From superalloy design point of view, one needs to select the alloying additions wisely in order to achieve effective solid strengthening in the gamma matrix. On the processing of materials, understanding the behaviour of chemical microsegregation and the addition of Re, W and Ru on the microsegregation is of paramount importance for modeling purposes. Utilizing a solid-liquid phase equilibria model and a customized chemical thermodynamic database, chemical partitioning predictions are carried out. Future generation of advanced coatings for high temperature applications are addressed through the use of ceramic Thermal Barrier Coatings to increase engine efficiency and enhance component durability.Understanding the physics of the conductive and radiative heat transfer through modeling and the physics of failure have also provided the basis to improve the TBC properties further.

11:35 AM Invited
Effect of Environment on Notch Fatigue Initiation Resistance in CMSX4: *Philippa Ann Reed*[1]; Mark Miller[1]; Mark Joyce[1]; [1]University of Southampton, Sch. of Engrg. Scis., Highfield, Southampton, Hants SO17 1BJ UK

Fatigue initiation in the stress-concentrating fir-tree root fixing of turbine blades is of some concern, and as the turbine blades are often coated, it is assumed that the Ni-base blade will be relatively protected - however fretting may remove this protective coating. Crack initiation at high temperatures has been studied in CMSX4 in both air and vacuum environments, to elucidate the effect of oxidation on the notch fatigue initiation process. In air, crack initiation occurred at sub-surface interdendritic pores in all cases. The sub-surface crack grows initially under vacuum conditions, before breaking out to the top surface. Lifetime is then critically dependent on initiating pore size and distance from the notch root surface. In vacuum conditions, crack initiation has been observed more consistently from surface or close-to-surface pores - indicating that surface oxidation is in-filling/ "healing" surface pores or providing significant local stress transfer to shift initiation to sub-surface pores.

12:00 PM Invited
Mechanical Behaviour of Single Crystal Superalloys Under Cyclic Loading: *Pedro D. Portella*[1]; [1]Federal Institute for Materials Research and Testing, Matls. Engrg., Unter den Eichen 87, Berlin D-12205 Germany

Single crystal superalloy find a wide application as blades or vanes in landbased and airborne gas turbines, especially in the highly loaded first stages. Due to their very regular microstructure it is possible to characterize the changes due to high temperature deformation and correlate them to the mechanical response of these materials. In this work we discuss the microstructural changes in single crystal superalloys observed during cyclic loading at high temperatures. The influence of hold times on cyclic softening, asimmetry in the hysteresis loops and failure mechanisms can be derived from the coarsening in the gamma/gamma' structure. Parallel to this discussion it is possible to modify consistently the constitutive equations designed to predict the mechanical behaviour of these materials in order to simulate these phenomena. We further show the effect of crystal anisotropy and artificially introduced defects on crack initiation in uncoated specimens of single crystal superalloys. We finally propose an approach for lifetime estimation using the constitutive equations derived for these materials.

Surface Engineering in Materials Science - III: Characterization of Surfaces and Films/Coating

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Surface Engineering Committee
Program Organizers: Arvind Agarwal, Florida International University, Department of Mechanical and Materials Engineering, Miami, FL 33174 USA; Craig Blue, Oak Ridge National Laboratory, Materials Processing Group, Metals and Ceramic Division, Oak Ridge, TN 37831 USA; Narendra B. Dahotre, University of Tennessee, Department of Materials Science & Engineering, Knoxville, TN 37932 USA; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Oviedo, FL 32765-7962 USA

Wednesday AM Room: 2022
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Sharmila Mukhopadhyay, Wright State University, Dept. Mech. & Matls. Engrg., Dayton, OH 45435 USA; Craig A. Blue, Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6083 USA

8:30 AM Invited
Improving the Performance of Rolling Contact Bearings With Tribological Coatings: *Gary Doll*[1]; R. D. Evans[1]; C. R. Ribaudo[1]; [1]The Timken Company , Timken Rsch., 1835 Dueber Ave. SW, RES05, Canton, OH 44706 USA

Tribological coatings can improve the performance of rolling contact bearings especially those bearings that are poorly lubricated, subjected to debris, or experience high-frequency oscillatory motion. Whereas coatings such as Ag, MoS2, TiN, and TiC have been used on bearings in niche applications for many years, coatings comprised of amorphous hydrocarbon or diamond-like carbon reinforced with nanocrystalline metal carbides are becoming more broadly used on rolling contact bearings.

8:55 AM
Degradation Mechanisms of Die Coatings Used in Aluminum Pressure Die Casting: *John J. Moore*[1]; *J. L. Lin*[1]; S. L. Meyers[1]; O. Salas[2]; S. Carrera[1]; B. Mishra[1]; [1]Colorado School of Mines, ACSEL, 1500 Illinois St., Golden, CO 80401-1887 USA; [2]Instituto Tecnologico y de Estudios Superiores de Monterrey-CEM, Carretera a Lago de Guadalupe km 3.5, Atizapan Mexico 52926 Mexico

The degradation behavior of five optimized commercial coating systems, developed by different PVD processes, on the H13 hot working steel, has been studied. Data have been generated from both laboratory and in-plant trials with the primary objective of systematically understanding coating degradation mechanisms that occur during aluminum pressure die-casting. The coatings were characterized both before and after subjection to die casting with respect to stress, failure mechanisms and chemical interaction using optical microscopy (OM), scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDS), and glancing incident XRD. The results show that each of the commercial coatings provided improved die performance and die life compared with the ferritic nitrocarburized surface treatment only of the H13 tool steel. The mechanism of degradation, cracking and failure of uncoated and coated H13 dies during aluminum pressure die-casting is proposed. The conjoint action between chemical attack of the liquid aluminum alloy and thermal fatigue cracking in the H13 substrate played an important role in the degradation process.

9:15 AM
Advanced Technologies for Anticorrosive Protection of Canned-Food Steel Sheet: *Oleg B. Girin*[1]; Igor D. Zakharov[2]; Yevgen V. Kolesnyk[1]; Volodymyr I. Ovcharenko[1]; Yuliya O. Proshenko[2]; [1]Ukrainian State University of Chemical Engineering, Dept. of Matls. Sci., Prospekt Gagarina, 8, Dnepropetrovsk 49005 Ukraine; [2]Polimet Research and Technology Center, Lab. of Protective Coatings, Ul. Mandrykovskaya, 169, Dnepropetrovsk 49049 Ukraine

Presented are the developed technologies for anticorrosive protection of canned-food steel sheet that are intended both to upgrade its quality and to reduce the prime cost and the environmental hazards of its production. Discussed are the following technologies for producing on the canned-food steel sheet of: 1) a protective nanostructural composite super-thin chromium coat from a low concentration electrolyte based on hexavalent chromium compounds; 2) a protective amorphous composite super-thin chromium coat from a low toxicity electrolyte based on trivalent chromium compounds, and 3) a protective textural composite super-thin tin coat from a low toxicity electrolyte. In comparison to the conventional these technologies are: 1) more environmentally friendly due to the use of less toxic electrolytes, and 2) more cost and material saving due to the reduction of the coat thickness on the steel sheet. This research project is financed by Science & Technology Center in Ukraine, Project No. 2520.

9:35 AM
Ti Dental Implant Surface Modification by Micro-Arc Oxidation: *Carlos Nelson Elias*[1]; Jose Henrique Lima[2]; Fernando Costa Silva Filho[3]; Carlos Alberto Muller[4]; [1]Military Institute of Engineering, Pr Gen Tibúrcio 80, Rio de Janeiro, RJ Brazil; [2]Odontoclinica Central Exercito, Rua Moncorvo Filho, Rio de Janeiro, RJ Brazil; [3]Intituto de Biofísica, Universidade Federal do Rio de Janeiro, Rio de Janeiro Brazil; [4]Bioterio, Instituto Oswaldo Cruz, Rio de Janeiro, RJ Brazil

Commercial pure titanium (CP Ti) is used as dental implant material because of its excellent chemical stability and biocompatibility. The biocompatibility is closely related to the titanium oxide layer. To increase the biocompatibility of titanium various mechanical and chemical treatments has been proposed. One possibility is increasing the surface roughness and the titanium oxide thickness. In the present work, an electrochemical procedure for modifying the Ti surface was presented. A positive voltage to a CP Ti implant immersed in an electrolyte was applied, anodic oxidation of Ti occurred to form a oxide layer. The morphology of oxide layer was analyzed and the biological properties of the layers were evaluated by in vitro tests, in terms of cell culture. In vivo tests were also done to confirm the biological in vitro tests. The results showed that the dental implant surface modification by oxidation had a beneficial effect on the implant biocompatibility.

9:55 AM Break

10:30 AM Invited
Surface Engineering for Improved Adhesion to Biomedical Implants and Biosensors: *Wole O. Soboyejo*[1]; [1]Princeton University, Dept. of Mechl. & Aeros. Engrg., Princeton Inst. of Sci. & Tech. of Matls., Princeton, NJ 08544 USA

This paper presents an overview of recent efforts to develop biocompatible surface coatings and textures that promote increased

adhesion to biomedical surfaces. These include surfaces that are relevant to orthopedic implants and biosensors at the micro- and nanoscale. In the case of orthopedic implants, alkane phosphonic acid/RGD tethers and laser textures are shown to promote increased adhesion to Ti-6Al-4V surfaces. The adhesion is quantified using shear assay experiments. Similarly, in the case of implantable bio-micro-electro-mechanical structures (bioMEMS), nanoscale biocompatible titanium coatings and alkane phosphonics/RGD tethers are shown to promote increased adhesion to silicon surfaces that are most commonly used in MEMS structures. Finally, the paper highlights the coating of magnetic nanoparticles for specific in-vivo attachment to cancer cells. Examples of such attachment are presented for breast/prostate cancer. The implications of the research are then discussed for the early detection of cancer.

10:55 AM
Plasma Sterilisation and Surface Modification of Thermolabile Materials: *Peter Messerer*[1]; Helmut Halfmann[1]; Marc Czichy[1]; Martin Schulze[1]; Peter Awakowicz[1]; [1]Ruhr-Universitaet Bochum, Inst. for Electl. Engrg. & Plasma Tech. (AEPT), Universitaetsstr. 150, Bochum 44780 Germany

At the institute for Electrical Engineering and Plasma Technology (AEPT) investigations on plasma sterilisation and surface modification of thermolabile materials are performed. Our first field is plasma treatment of medical implants made of titan, UHMWPE and degradable polylactide. In a total treatment time of two minutes the developed process reduces germs and pyrogens by six and more than four decades, respectively. A modified plasma discharge hardens the surface of UHMWPE. Gel content measurements indicate the improvement of abrasion resistance while the bulk material is unaffected. An increasing part of non-carbonated and non-acidic beverages have been bottled in PET. Sensitive products require aseptic filling. Plasma treatment prepares bottles without toxic residua. To improve the shelf-live of oxygen-sensitive soft drinks a diffusion barrier made of a SiOx-layer can be deposited on the inner side of a PET bottle. The combined sterilisation and coating process takes ten seconds.

11:15 AM
Corrosion Resistance Mechanism of Plasma-Based Low-Energy Nitrogen Ion Implanted Austenitic Stainless Steel: *M. K. Lei*[1]; X. M. Zhu[2]; [1]Dalian University of Technology, Surface Engrg. Lab., Dept. of Matls. Engrg., Dalian 116024 China; [2]Dalian Jiaotong University, Dept. of Matls. Sci. & Engrg., Dalian 116028 China

Plasma-based low-energy ion implantation (PBLEII), including plasma source ion nitriding/carburizing and plasma source low-energy ion enhanced deposition of thin films, has emerged as a low-temperature surface engineering technique. A high nitrogen face-centered-cubic phase (gamma-N) layer with peak nitrogen concentration up to 32 at.% was obtained on the nitrided 1Cr18Ni9Ti (18-8 type) austenitic stainless steel. No pitting corrosion for the gamma-N phase was confirmed by electrochemical polarization measurement and immersion corrosion test in a series of NaCl aqueous solutions. In order to explain the pitting corrosion resistance of the gamma-N phase, the passive film formed on the gamma-N phase in 3% NaCl solution was investigated by Auger electron spectroscopy and x-ray photoelectron spectroscopy in conjunction with ion beam sputtering. The protective passive film with a duplex character was by 2-3 times thicker than that of original stainless steel. It was essentially composed of two regions: iron hydroxide/oxides in the outer region and chromium hydroxide/oxides and iron oxides accompanying chromium and iron nitrides in the inner region. The conventional bilayer substructure, e.g. outer hydroxide layer and inner oxide layer, was also detected in the each region. During anodic polarization the chromium nitride with weak Cr-N ionic-type bonds in the gamma-N phase was prone to oxidation and release of nitrogen to form stable oxides and ammonia on the passivating surface. The thick iron hydroxide/oxides region formed on the chromium hydroxide/oxides region due to the increase of alkalinity in the solution, which led to completely barrier the penetration of localized attack of aggressive ions. The role of nitrogen in pitting corrosion resistance of austenitic stainless steel was proved.

The Armen G. Khachaturyan Symposium on Phase Transformation and Microstructural Evolution in Crystalline Solids: Session V

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Phase Transformations Committee-(Jt. ASM-MSCTS)
Program Organizers: Yunzhi Wang, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; John William Morris, University of California, Department of Materials Science and Engineering, Berkeley, CA 94720 USA

Wednesday AM Room: 3003
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Greg Olson, Northwestern University, MSE, Evanston, IL 60015 USA; Long-Qing Chen, Pennsylvania State University, MSE, Univ. Park, PA 16802 USA

8:30 AM Opening Remarks

8:35 AM Invited
Surface-Induced Ordering and Epitaxt-Induced Ordering: The Role of Strain: *Alex Zunger*[1]; [1]National Renewable Energy Laboratory, Golden, CO 80401 USA

It was once thought that the growth method of an alloy does not affect the growth product, as long as one is close enough to equilibrium. It is now realized, however, that while melt-growth and LPE growth of semiconductor alloys produces phase-separation microstructure, vapor-phase (MOCVD, MBE) growth of III-V alloys such as GaP-InP produces ordered atomic arrangements in a spontaneous fashion. The structures obtained are short-period AnBn superlattices along <111> ("CuPt structure") or <001> ("CuAu structure"), and exist even though during growth all atoms are deposited simultaneously. First-principles theoretical calculations have shown that these structures are produced because of surface reconstruction and are, therefore, thermodynamically stable surface-phases that are frozen-in during subsequent growth. I will discuss how strain selects different types of ordering in semiconductor and metal alloys, a field to which A. Khachaturyan contributed significantly. Spontaneous ordering changes the point-group symmetry relative to the random alloy, leading to band gap changes, crystal-field splitting, novel polarizations, as well as changes in effective-masses, pressure coefficients, etc.

9:00 AM Invited
Ab Initio Contribution to Alloy Phase Transformations: Prospects and Challenges: *Patrice E.A. Turchi*[1]; [1]Lawrence Livermore National Laboratory, Chmst. & Matls. Sci. Direct. (L-353), PO Box 808, Livermore, CA 94551 USA

On one hand, first-principles approaches are routinely applied to the study of the statics of phase transformations in alloys. These methodologies seem to impact the field despite, as should often be acknowledged, a lack of experimental validations. On the other hand, phase-field simulations (PFS) have shown in recent years great versatility in predicting various aspects of phase transformations in solids. Moreover the interface between ab initio and the phenomenological CALPHAD approach to thermodynamics and kinetics has recently shown some promise in bringing realism to PFS. Despite this progress, questions remain to be answered on lattice stability, the definition of thermodynamics functions in a broad range of fields, and on the acquisition of realistic kinetic parameters. After a brief survey of the contribution of ab initio to phase transformations in solids, future prospects and challenges are discussed. Work performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

9:25 AM Invited
Aluminum Alloy Thermodynamics and Kinetics from First Principles: *Chris M. Wolverton*[1]; Vidvuds Ozolins[2]; [1]Ford Motor Company, Physl. & Environml. Sci., MD 3083/SRL, PO Box 2053, Dearborn, MI 48121-2053 USA; [2]University of California, Dept. of Matls. Sci., Los Angeles, CA 90095-1595 USA

We present an extensive survey of the thermodynamic and kinetic properties of binary Al alloys, as obtained from first-principles atomistic calculations. We consider a wide range of properties: 1) Energetic properties of ordered compounds, impurities, and mixing energies of solid solutions, 2) first-principles calculations of interatomic force constants, phonon spectra and vibrational entropies, 3) thermodynamic properties and solubility, and 4) kinetic quantities such as solute-vacancy binding, migration energies, and diffusion coefficients. We compare our results critically with experimental and CALPHAD databases to ascertain inaccuracies in the theoretical methods, and cases in which experimental data should be re-evaluated. In addition, the extensive nature of the database facilitates understanding the trends in energetic, thermodynamic, and kinetic properties. In addition, this large first-principles database should enable many future applications, such as improving existing CALPHAD databases, as well as providing key information to phase-field models of microstructural evolution.

9:50 AM
How Well are Higher-Order Correlations in Alloys Determined by Pair Correlations?: Gene Ice[1]; *Rosa Barabash*[1]; Don Nicholson[1]; Lee Robertson[1]; Cullie Sparks[1]; Christopher M. Wolverton[2]; [1]Oak Ridge National Laboratory, Metals & Ceram., One Bethel Valley Rd., MS6118, Oak Ridge, TN 37831-6118 USA; [2]Ford Motor Co., MD 3083/SRL, PO Box 2053, Dearborn, MI 48121-2053 USA

Diffusely scattered x-rays (neutrons) are sensitive to the correlations among atom positions. Only pair correlations can be recovered from diffuse scattering measurements as a measure of the average chemical neighborhood and average spacing between the different atom species. Though it has never been shown that these average pair correlation functions can uniquely determine the actual atomic arrangements, it has been shown that pair correlations do restrict the value of higher order correlations.[1] Here we present numerical analyses of the reconstruction of substitutional crystalline alloys from pair correlations derived from both pair and many-body interactions. With regular, forward Monte Carlo, pair and many-body interactions were used to calculate snapshot images of short-range ordered 64,000-atom periodic cells. We refer to these cells as "input". The averaged Warren-Cowley pair correlations were obtained for each "input" and these pair correlations were then used in a reverse Monte Carlo simulation to reconstruct "output" 64,000-atom configurations. We compare in detail the pair and higher-order (triplets and higher configurations containing up to six atoms) probabilities between the input and output configurations. Pair correlations are shown to strongly constrain the higher-order correlations. For "input" derived from pair-only interactions, the higher-order correlations of the "input" and "output" were in good agreement. For our model system (fcc/AB3), pair correlations are shown to define the morphology of the locally ordered or clustered domains. However, the higher-order correlations in the many body case appear to be restricted but not determined by the pair correlations. Issues of uniqueness are discussed as they relate to pair and many-body interactions. Work supported by DOE Office of Basic Energy Science under subcontract DEAC05-00OR22R725464 with UT-Battelle, LLC. [1]J. Gragg, J. Bardham & J. Cohen, in "Critical phenomena in Alloys, magnets and superconductors", R. Mills, E. Ascher and R. Jaffee, eds., McGraw-Hill NY (1977), pp. 309-337.

10:05 AM Break

10:30 AM Invited
Short-Range Order and Phase Evolution in Au-Ni Alloys: *J.-C. Zhao*[1]; [1]GE Global Research, One Rsch. Cir., K1-MB239, Niskayuna, NY 12309 USA

The Au-Ni system has one of the simplest phase diagrams: complete miscibility at high temperatures and a miscibility gap at low temperatures. Yet it presents one of the very complex systems in terms of short-range order (SRO), and remains one of the most intensively studied binary systems to date. Electron diffraction was performed on two Au-Ni alloys using transmission electron microscopy. Very complex SRO intensities were observed in the diffraction patterns. These intensities match very well with results from first-principles simulation. The good agreement between experimental and simulated patterns indicates that the first-principles calculations have made good progress in modeling the complex behavior in the Au-Ni alloys. In addition to SRO, spinodal decomposition, transient ordering, and continuous and discontinuous precipitation were observed under different annealing conditions.

10:55 AM
Experimental Vertifications of a Ginzburg-Landau Second Order Theory of Autonomous Nanostructural Clustering and Ordering: G. C. Weatherly[1]; K. Janghorbian[1]; G. Radtke[1]; G. A. Botton[1]; *J. S. Jirkaldy*[1]; [1]McMaster University, Brockhouse Inst. for Matls. Rsch., Hamilton, ON L8S-4M1 Canada

An elementary real space theory of clustering (spinodal decomposition) as an autonomous isothermal process starts with the construction of a free energy functional (an integral or lattice sum over a density) which at stationary defines a variational derivative to be entered into a 2nd order non-linear time-dependant Ginzburg-Landau (TDGL) partial differential equation (PDE). Solute conservation is in general entered via a Lagrange Multiplier. Since commonly in cubic crystals the Lagrangian density possesses an even symmetry which is reflected in solute-conserving solutions of the PDE, the additional application of a conserving flux balance represents an over determination which results in a 4th order PDE. Indeed, such a character in a ternary generalization denies a necessary simultaneous diagonalization of the coefficient matrices and so illogically prohibits the mounting of an initial value problem. Unlike the 4th order case, the 2nd order representation in Au-Ni following the Friedel and Eshelby atomistics incorporates coherency strain without a complicating depression of the effective critical point. Our binary TFDL equation(s) incorporating free energy densities associated with Hillert, Khachaturyan, Goryachev and Maugis has been subjected to experimental tests for high temperature clustering, the obligatory coupling of clustering and local long range ordering and extra-spinodal G-P zones in Au-Ni alloys as predicted by Morris and Khachaturyan.

11:10 AM
Ordering in Ternary CuNiZn Alloys: Concentration Wave Consideration and Monte Carlo Simulations: *Andrei V. Ruban*[1]; Sergei Simak[2]; [1]Royal Institute of Technology, Dept. of Matls. Sci. & Engrg, Brinellvagen 23, Stockholm 10044 Sweden; [2]Uppsala University, Condensed Matter Theory Grp., Box-530, Uppsala 75121 Sweden

Concentration wave theory is applied to the case of ternary CuNiZn alloys. Possible ordering scenario are considered. The investigation of the ordering in real system has been performed by Monte Carlo method with effective interactions obtained in the first-principles calculations. We demonstrate that there exist three ordering transitions in contrast to the generally accepted picture, which assumes the existence of only two. We demonstrate that this sequence of phases is a consequence of the symmetry of the ground state and the magnitude of the dominating pair interactions. It agrees with available experimental data.

11:25 AM
Effects of Ordering Phase Transformation on the Evolution of Microstructure During Annealing of Cold Deformed Equiatomic FePd: *Anirudha R. Deshpande*[1]; Jorg M.K. Wiezorek[1]; [1]University of Pittsburgh, Matl. Scis. & Engrg., 864, Benedum Hall, Pittsburgh, PA 15261 USA

Equiatomic L1o ordered FePd intermetallics form a model system for the investigation of the effects of microstructure on hard magnetic properties in the class of L1o ordered ferromagnetic intermetallics. In this system, a microstructural morphology consisting entirely of equiaxed, defect free, L1o ordered grains has been previously reported to exhibit enhanced magnetic properties relative to a characteristic lamellar-polytwin morphology. A combined reaction of FCC to L1o ordering concomitant with annealing of crystal defects introduced during cold working in the FCC stage has been employed to achieve an equiaxed, L1o ordered grain structure. A synergy between the ordering process and the annealing of crystal defects is expected to exist, since previously it has been reported that the preferential nucleation and growth of L1o ordered grains would occur at sites in the microstructure with an appropriate, favorable, localized stress state. Microstructural textures are appropriate signatures of the evolution of the microstructural state. In this study the synergy between the processes of ordering and annealing has been studied using relevant texture evolution. Orientation Distribution Functions coupled with pole figures obtained using X-ray diffraction and orientation imaging microscopy by SEM have been utilized to study the evolution of global and local textures. Local textures have also been probed using TEM. The texture evolution during the combined reaction has been compared with texture evolution during a microstructural change involving solely the annealing of crystal defects in the cold-deformed L1o state. This comparison has yielded new insights into the effects of the ordering phase transformation on the evolution of textures during annealing of these intermetallics after cold deformation.

11:40 AM
Low-Temperature Aging Mechanisms in an U-6Nb Alloy: *Luke L. Hsiung*[1]; [1]Lawrence Livermore National Laboratory, Chmst. & Matls. Sci. Direct., PO Box 808, L-352, Livermore, CA 94551-9900 USA

Aging mechanisms in a water-quenched U-6wt.%Nb alloy isothermally aged at 200°C and naturally aged at an ambient temperature for 15 years have been investigated. The hardness of the isothermally aged samples initially increases from HV 190 (WQ) to HV 255 (200°C, 8h) and subsequently decreases to HV 237 (200°C, 16h). The age hardening phenomenon can be rationalized by the occurrence of spinodal decomposition of the α " matensite phase within the aged alloy. The occurrence of order-disorder transformation is found within the naturally aged alloy based upon the observations of antiphase boundaries (APBs) within the α " phase. An ordered α " phase and a transformation pathway for the aging of U-6Nb at low temperatures are accordingly proposed. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

11:55 AM
Phase Transformations and Microstructure Evolution in Mutlicomponent Nb-Ti-Si-Cr-Al-X Alloys: Raghvendra Tewari[1]; Hyo-jin Song[1]; Amit Chatterjee[2]; *Vijay K. Vasudevan*[1]; [1]University of Cincinnati, Dept. of Cheml. & Matls. Engrg., Cincinnati, OH 45221-0012 USA; [2]Rolls Royce Corporation, 2001 S. Tibbs Ave., Indianapolis, IN 46206 USA

Recently, alloys based on the Nb-Ti-Si system have become of interest for high temperature structural applications. In the present work, the microstructure of multicomponent Nb-30Ti-8Si-10Cr-10Al-X (in at.%) alloys in the as-cast and heat treated conditions was studied utilizing x-ray diffraction, electron probe microanalysis, and scanning and transmission electron microscopy. The effect of temperature and time on phase evolution was examined in detail. The as-cast microstructure was found to be composed of three phases: the matrix b, silicides (of type (Nb,Ti)5Si3)) and a Cr-rich Laves phase. The b phase was found to display in B2-type ordering. The silicides in these alloys were generally quite stable during heat treatment, whereas the Cr-rich Laves phase was observed to dissolve on solutionization at temperatures above 1300°C. Aging of the solutionized materials between 900–1100°C led to the precipitation of fine particles of another Laves phase in b matrix. In addition, the b matrix revealed a tendency toward phase separation into Ti-rich and Nb-rich regions. The volume percentage and chemical composition of each phase has been determined as a function of time and temperature. The changes in the phase constituents have been rationalized in terms of the distribution of elements in various phases. The role of different alloying elements on the formation of these phases has also been critically examined.

The Langdon Symposium: Flow and Forming of Crystalline Materials: Ultrafine-Grained Materials I

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, MPMD-Shaping and Forming Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

Program Organizers: Yuntian Ted Zhu, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA; P. B. Berbon, Rockwell Scientific Company, Thousand Oaks, CA 91360 USA; Atul H. Chokshi, Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India; Z. Horita, Kyushu University, Department of Materials Science and Engineering, Fukuoka 812-8581 Japan; Sai V. Raj, NASA Glenn Research Center, Materials Division, Cleveland, OH 44135 USA; K. Xia, University of Melbourne, Department of Mechanical and Manufacturing Engineering, Victoria 3010 Australia

Wednesday AM Room: 3024
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Alexander H. King, Purdue University, Sch. of Matls. Engrg., W. Lafayette, IN 47907-2044 USA; Yuri Estrin, Clausthal University of Technology, Matls. Sci. & Tech., Clausthal-Zellerfeld 38678 Germany; Evan Ma, Johns Hopkins University, Matls. Sci. & Engrg., Baltimore, MD 21218 USA

8:30 AM
Shear Deformation and the Evolution of Deformation Bands During ECAP of Pure Aluminum: The Formation of High-Angle Boundaries: Keiichiro Oh-ishi[1]; Alex P. Zhilyaev[2]; *Terry R. McNelley*[1]; [1]Naval Postgraduate School, Mechl. & Astronautical Engrg., 700 Dyer Rd., Monterey, CA 93943-5146 USA; [2]Russian Academy of Sciences, Inst. of Mech., Ufa 450000 Russia

Orientation imaging microscopy (OIM) methods have been applied to the evolution of microstructure and microtexture during ECAP of pure aluminum. The influence of strain path has been considered by examination of pure aluminum after four pressing operations by route BC in a die having a 90° die angle, or eight pressing operations by route BC in a die have a 135° die angle. The von Mises equivalent strains were essentially the same for these two procedures. Microtexture results indicate that the distortion during ECAP corresponds to a simple shear in a direction approximately parallel to die-channel exit and on a plane perpendicular to the flow plane and containing the shear direction. Two orientation in the texture correspond to bands of common orientation in the microstructure, and the interfaces between the bands are high-angle in nature. The role of these bands in the formation of high-angle grain boundaries will be discussed.

8:45 AM
Processing Routes Leading to Superplatic Behaviour of ZK60 Magmesium Alloy: *Rimma Ye. Lapovok*[1]; Peter F. Thomson[1]; Ryan E. Cottam[1]; Yuri Estrin[2]; [1]Monash University, Sch. of Physics & Matl. Engrg., Clayton, Melbourne, Vic 3800 Australia; [2]Technical University of Clausthal, Inst. of Matls. Sci. & Tech., 6 Agricolastr., Clausthal, Clausthal-Zellerfeld 38678 Germany

There has recently been discussion on processing of magnesium alloys by ECAE to achieve a high elongation-to-failure during a superplastic tensile test. A two-step processing route was suggested to improve superplastic capabilities of such alloys. In this work superplastic behaviour samples of ZK60 processed by ECAE only and samples which were rolled prior the ECAE processing have been compared. It was shown that the benefit of preliminary deformation is significant for superplastic behaviour at temperatures close to 300°C and low strain rates, while in the area of low temperature superplasticity around 200°C and higher strain rates ECAE processing by itself leads to an elongation of 1700% at a strain rate of 3x10-3.

9:00 AM
Mechanical Properties in Aluminium Alloys Processed by SPD: Comparison of Different Alloy Systems and Possible Product Areas: *Hans J. Roven*[1]; Hakon A. Nesboe[1]; Jens C. Werenskiold[1]; Tanja Seibert[2]; [1]Norwegian University of Science and Technology, Matls. Tech., Trondheim N-7491 Norway; [2]Friedrich-Alexander-Universitat Erlangen-Nurnberg, Inst. fur Werkstoffwissenschaften, Erlangen D-91058 Germany

The present work compares the strength and ductility of a wide range of alloys processed from N= 1 to N= 6 (8) by ECAP: AlMg-, AlMn-, AlMgSi-, AlMnSc-, AlMgSc- and high strength AlZnMg alloys. The plastic deformation has been conducted under controlled conditions with the same deformation tool (ECAP rectangular cross section) in order to make sound comparisons. The initial material conditions are changed, ranging from soft annealed and homogenized to solution heat treated and naturally aged. Post-ECAP heat treatments at different temperatures are also systematically studied. Generally, ECAP route A gives significantly increased strength and combined with non-conventional temperature artificial aging, excellent combinations of strength and ductilty is achieved for age hardening alloys. Generally, the effect of severe plastic deformation is mostly beneficial with high alloy contents, whereas lean alloys tend to be less reacting to SPD. Finally, some believed product areas for selected alloys will be discussed briefly.

9:15 AM
Texture and Microstructural Evolution in Pure Aluminum During High-Pressure Torsion: *Alexander P. Zhilyaev*[1]; Keiichiro Oishi[1]; Terence G. Langdon[2]; Terry R. McNelley[1]; [1]Naval Postgraduate School, Dept. Mechl. & Astronautical Engrg., 700 Dyer Rd., Monterey, CA 93943-5146 USA; [2]University of Southern California, Depts. of Aeros. & Mechl. Engrg. & Matls. Sci., 3650 McClintock Ave., Los Angeles, CA 90089-1453 USA

An orientation imaging microscopy (OIM) investigation was conducted to evaluate the microstructural characteristics in samples of pure aluminum processed by high-pressure torsion (HPT) under both constrained and unconstrained conditions. Electron backscattering diffraction (EBSD) techniques were employed to measure the microtextures and the distributions of the misorientation angles. A thorough analysis of the microtexture has revealed the shear plane normal and direction for aluminum specimens. This paper discusses the common features of the texture components by comparison with aluminum deformed by equal-channel angular pressing. It is shown that the magnitude of the grain refinement depends upon the location in the HPT disc and the pressing conditions.

9:30 AM

Determination of Deformation Mechanisms in Al5083 by Neutron Diffraction: *Sven C. Vogel*[1]; David J. Alexander[1]; Mark A.M. Bourke[1]; Donald W. Brown[1]; Bjorn Clausen[1]; Thomas A. Sisneros[1]; Enrique J. Lavernia[2]; David B. Witkin[3]; [1]Los Alamos National Laboratory, LANSCE, PO Box 1663, MS H805, Los Alamos, NM 87545 USA; [2]University of California, Cheml. Engrg. & Matls. Sci., Davis, CA 95616-5294 USA; [3]University of California, Cheml. Engrg. & Matls. Sci., Irvine, CA 92697-2575 USA

The activity of deformation mechanisms like slip, twinning, diffusion or grain boundary sliding depends on parameters such as grain-size and shape, deformation temperature and strain rate. These activities are typically determined indirectly by fitting parameters of functions describing the strain rate as a function of diffusion constants, stress exponents, flow stress and Young's modulus against experimental results for flow stress vs. strain rate. In the present paper, we describe an attempt to determine the active deformation mechanism directly by neutron diffraction on the SMARTS neutron diffractometer at LANSCE. Available data are peak shifts (lattice strains), peak intensity (texture) and peak width (inter- and intragranuler strains). The various deformation mechanisms have different signatures for these parameters. We will report our initial results on a series of measurements on Al5083. As-received (extruded), 8 pass ECAP and bulk nanograined specimen of <100 nm grain size were tested in tension at room temperature and 275°C. Each specimen was plastically deformed to a logarithmically increasing degree and neutron diffraction data were collected after unloading. Bulk texture was measured on the neutron diffractometer HIPPO before and after the deformation.

9:45 AM

Grain Refinement of Pure Al by ECAP and Simulation of the Process: *Hua Ding*[1]; Wenjuan Zhao[1]; Yuping Ren[1]; Shiming Hao[1]; [1]Northeastern University, Sch. of Matls. & Metall., 3-11,Wenhua Rd., Heping Dist., Shenyang, Liaoning 110004 China

In this paper, microstructures of pure Al after equal channel angular pressing(ECAP) were observed and the effects of purity, initial states of the material and deformation routes on the microstructures were investigated. The results showed that the purity of Al had obvious influnce on the final grain size of the material. The material with 99.999% Al had a tendency to grow after ECAP; while the one with 99% Al remained unchanged. It is also shown that the methods by which the samples were prepared before ECAP and deformation routes affected the microstructures of the material. Meanwhile, the ECAP process was simulated by DEFORM. The results of the simulation can be used to predict the process quite well.

10:00 AM

Elevated Temperature Behavior of SPD Materials: Superplasticity or Enhanced Ductility?: *Alla V. Sergueeva*[1]; Ruslan Z. Valiev[2]; Nathan A. Mara[1]; Amya K. Mukherjee[1]; [1]University of California, Cheml. Engrg. & Matl. Sci., Davis, CA 95616 USA; [2]Ufa State Aviation Technical University, Inst. of Physics of Advd. Matls., Ufa 450059 Russia

The generated results on elevated temperature mechanical behavior of the materials produced by severe plastic deformation (SPD) have established a number of trends: extensive strain hardening; high flow stresses; a correlation between microstructural instability and enhanced plasticity. Moreover, the parametric dependencies such as strain rate exponent and activation energy of the deformation process can range widely. In many materials high elongation (more than 200%) was detected and the resulting structure still had equaxied grains while the values of the strain rate sensitivity and activation energy did not support an implication of superplastic deformation. In most cases, when enhanced ductility was observed, an intensive grain growth occurred in the materials. In current investigation the elevated temperature deformation behavior of metals and intermetallics subjected to SPD was analyzed in order to establish possible deformation mechanisms and microstructural effects. This investigation is supported by NSF, Division of Materials Research (grant NSF-DMR-0240144).

10:15 AM

Grain Boundary Diffusion and Plasticity/Superplasticity of Polycrystalline and Nanostructured Metals and Alloys: *Yury Romanovich Kolobov*[1]; Ilya Vasil'evich Ratochka[1]; [1]Institute of Strength Physics and Materials Science, Physl. Matl. Sci., Academichesky 2/1, Tomsk 634021 Russia

Characteristic features of diffusion and diffusion controlled processes (grain boundary sliding, dislocation accommodation and grain boundary migration) in polycrystalline metals and alloys with bcc and fcc crystal lattice at annealing and creep have been examined. The interconnection and intereffect of diffusion processes, sliding and grain boundary migration as factors, determining the development of plastic deformation at examined conditions are analyzed. The peculiarities of grain boundary diffusion of substitution from impurity environment (coating) in nanostructured metals and alloys relative to the respective ones in coarse grained metals and alloys have been investigated. The physical reasons for considerable (by some orders of magnitude) increase of diffusion penetration of grain boundaries in nanostructured state are discussed. The features of manifestation of low temperature and/or high-strain rata superplasticity in nanostructured metals and alloys have been considered.

10:30 AM Break

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Micro SPD: *Yuri Estrin*[1]; Eugen Rabkin[2]; Ralph Hellmig[1]; Michael Kazakevich[2]; Aikaterini Zi[1]; [1]Clausthal University of Technology, Matls. Sci. & Tech., Agricolastr. 6, Clausthal-Zellerfeld 38678 Germany; [2]Technion, Matls. Engrg., Haifa 32000 Israel

It is proposed to use porous steel 'dies' to infiltrate them with a metallic material by a variant of the known forcefill process. Severe plastic deformation (SPD) that occurs in the material due to its flow through a tortuous channel is believed to lead to grain refinement and an improvement of mechanical properties. This process will be referred to as micro SPD. First experimental results on infiltration of steel with aluminum will be presented. The dependence of the penetration depth on the average pore size of the die material in the micrometer range will be discussed along with the results on the effect of the process parameters on the microhardness of Al.

11:00 AM

Processing and Microstructural Modelling of Equal Channel Angular Pressing for Ultrafine Grained Materials: *Hyoung Seop Kim*[1]; Yuri Estrin[2]; [1]Chungnam National University, Dept. of Metallurgl. Engrg., Yuseong, Daejeon 305-764 Korea; [2]Clausthal University of Technology, Inst. of Matls. Sci. & Tech., Agricolastr. 6, Clausthal-Zellerfeld D-38678 Germany

ECAP is a convenient forming procedure among various methods of severe plastic deformation to extrude material by use of specially designed channel dies to make an ultrafine grained material. The properties of the materials are strongly dependent on the plastic deformation behaviour during pressing, which is governed mainly by die geometries, material properties, and process variables. Because the evolution of microstructures and the mechanical properties of the deformed material are directly related to the plastic deformation, the understanding of the phenomenon associated with strain development is very important in the ECAP process. In this study, we describe a range of our continuum modelling and microstuctural modelling results of ECAP in order to illustrate the modelling applicability. For this purpose, the finite element results of ECAP for various geometric factors are described. The inhomogeneous deformation due to the hardening property of the material is explained. Lastly, modelling the microstructural evolution using a dislocation cell model during ECAP is presented.

11:15 AM

Grain Refinement Mechanisms During Severe Deformation of Aluminium Alloys: Effect of Material Variables: *Philip B. Prangnell*[1]; Chris P. Heason[1]; Pete J. Apps[2]; [1]University of Manchester, Matls. Sci. Ctr., Grosvenor St., Manchester M1 7HS UK; [2]Health and Safety Laboratory, Broad Ln., Sheffield S3 7HQ UK

The evolution of the deformed state during the severe deformation of aluminium alloys is discussed, focusing on the mechanisms involved and the effect of important material variables. High spatial and orientation resolution data is presented, obtained using FEG-SEM EBSD orientation mapping and Kuwahara filtering. It has been confirmed that microshear bands are responsible for the majority of new high angle boundary formed at moderate strains. By studying simple model alloys, it has been found that a fine initial grain size increases the rate of grain refinement at low strains, but has little influence at ultra high strains. It has also been show that coarse second phase particles can greatly accelerate the rate of grain refinement, whereas fine coherent particles inhibit the rate of grain refinement. These effects are most noticeable at moderate strains, but still lead to significant differences in the ultra-fine grain structure at very high strains (e.g. strain = 10). The development of strong textures has been found to inhibit, and in some cases, reverse grain refinement.

11:30 AM

Severe Plastic Deformation of Magnesium Alloys: *K. Xia*[1]; J. T. Wang[2]; X. Wu[1]; G. Chen[2]; [1]University of Melbourne, Dept. of Mechl. & Mfg. Engrg., Parkville, Victoria 3010 Australia; [2]Nanjing University

of Science and Technology, Sch. of Matls. Sci. & Engrg., Nanjing, Jiangsu 210094 China

Equal channel angular pressing (ECAP) was applied to magnesium alloys in order to refine grain structures. ECAP was carried out at various speeds for up to 8 passes at temperatures as low as 100°C with or without an applied back pressure at the exit channel. The application of a back pressure and a slower pressing speed were shown to be critical in deforming Mg alloys at lower temperatures without causing cracking. Room temperature mechanical properties were obtained by tensile and micro- and macro-hardness tests. With increasing ECAP strain, the initial coarse grained structure was transformed gradually into a submicron grained microstructure. The kinetics of this strain driven microstructure transformation was analysed. The approaches to refined microstructures and improved mechanical properties in Mg alloys through severe plastic deformation (SPD) were discussed based on a comprehensive review of previous works in the literature.

11:45 AM

Nanoscaled Structure of a Cu-Fe Composite Processed by High Pressure Torsion: *Xavier Sauvage*[1]; [1]Université de Rouen, GPM - UMR CNRS 6634, Inst. des Matériaux de Rouen, Site du Madrillet, Saint-Etienne-du-Rouvray 76801 France

The microstructure evolution of pure metals under severe plastic deformation has been widely investigated during the past decade. Much less is known and reported about the behaviour of multi-phase materials. In this paper, a Cu-Fe(10%vol.) composite material was processed by High Pressure Torsion. The resulting nanostructure was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), micro-hardness measurement and 3D atom probe analysis (3D-AP). Experimental data reveal a strong decrease of the grain size down to 50nm, which is much smaller than in pure iron or pure copper processed by HPT. Moreover, a significant interdiffusion of Cu and Fe was pointed out thanks to 3D-AP investigations. The mutual solubility of these two components is very low at room temperature, thus the alloying mechanism will be discuss as a result of the severe plastic deformation. Finally, this nanostructure will be compared with Fe-Cu nanocrystalline powders prepared by ball milling.

12:00 PM

Microstructure and Properties of an Ultrafine-Grained Low Carbon Steel Processed by Equal-Channel Angular Pressing: *Jing Tao Wang*[1]; Chen Xu[2]; Zhong Ze Du[3]; Terence G. Langdon[2]; [1]Nanjing University of Science and Technology, Sch. of Matls. Sci. & Engrg., No. 200 Xiaolingwei, Nanjing 210094 China; [2]University of Southern California, Depts. of Aeros. & Mechl. Engrg. & Matls. Sci., Los Angeles, CA 90089-1453 USA; [3]Xi'an University of Architecture & Technology, Sch. of Metallurgl. Engrg., Xi'an 710055 China

Ultrafine-grained low carbon steel (Fe-0.15%C-0.52%Mn) was fabricated by equal channel angular pressing (ECAP) at room temperature through routes Bc and C up to 10 passes. With route C, nearly parallel bands of an elongated substructure pertains in the ferrite microstructure after ECAP from 1 to 11 passes, with a slight decrease of the band width from 0.3-0.4 to 0.2-0.3?n micrometers. With route Bc, an equiaxed grain structure with a grain size of about 0.25 micrometers forms after 4 passes of ECAP. A tensile strength over 1000 MPa was achieved after only 2 passes of ECAP via route Bc with limited uniform tensile elongation. Annealing at temperatures below or above the recrystallization temperature after ECAP changes the tensile behavior significantly.

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Strain Rate Sensitivity of Flow Stress of Ultrafine Grained Cu and Ti: *Yujiao Li*[1]; Xiaohui Zeng[1]; Philip Eisenlohr[1]; *Wolfgang Blum*[1]; [1]Universität Erlangen-Nürnberg, Technische Fakultät, Inst. f. Werkstoffwissenschaften LS 1, Martensstr. 5, Erlangen 91058 Germany

The deformation behaviors of ultrafine-grained (UFG) pure Cu with 350nm grain size and of commercially pure (CP) UFG Ti with 300nm average grain size produced by severe plastic deformation through equal channel angular pressing (ECAP) were investigated as function of temperature and strain rate at low homologous temperatures within the range of grain stability. A distinct increase of strain rate ensitivity was observed in UFG Cu with increasing temperature and decreasing train rate which is much stronger than in coarse-grained (CG) Cu. This causes UFG Cu to become softer than CG Cu as temperature and strain increase. This softening effect is explained by diffusion-controlled annihilation of lattice dislocation at grain boundaries. A simple model is used to demonstrate this behavior. For Ti the corresponding difference between UFG and CG variants is much less pronounced. This is discussed in terms of impurities.

6th Global Innovations Symposium: Trends in Materials and Manufacturing Technologies for Transportation Industries: Novel Processes II

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), MPMD-Powder Materials Committee, MPMD-Shaping and Forming Committee, MPMD-Solidification Committee, MPMD-Surface Engineering Committee, MPMD/EPD-Process Modeling Analysis & Control Committee

Program Organizers: Thomas R. Bieler, Michigan State University, Department of Chemical Engineering and Materials Science, East Lansing, MI 48824-1226 USA; John E. Carsley, General Motors Corp, Warren, MI USA; Hamish L. Fraser, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210-1179 USA; John E. Smugeresky, Sandia National Laboratories, Department 8724, Livermore, CA 94551-0969 USA

Wednesday PM, February 16, 2005 — Room: 2009 — Location: Moscone West Convention Center

Session Chairs: John E. Smugeresky, Sandia National Laboratories, Dept. 8772, Livermore, CA 945510969 USA; John E. Carsley, General Motors, Matls. & Processes Lab., Warren, MI 48090 USA

2:00 PM

Nano Metal Powders - Real Life Applications: *Alan Rae*[1]; [1]NanoDynamics Inc., 901 Fuhrmann Blvd., Buffalo, NY 02035 USA

Nanotechnology provides us with a toolkit of techniques that allows us to tailor crystallinity, particle size and surface condition of metals. This allows us to modify reactivity as well as chemical, physical and electrical properties. There are challenges however in preventing agglomeration and unwanted reactions, in scaleup, economics, and applications engineering. This paper reviews specific developments in commercial metal production focusing in particular on Cu, Ag, Fe, Ni and Ti and their applications in electronic, medical and engineering applications.

2:20 PM

Improvement of Ductility and Toughness of Cryomilled Nanostructured Al Alloys for Applications: *Bing Q. Han*[1]; Enrique J. Lavernia[1]; [1]University of California, Dept. of Chem. Engrg. & Matls. Sci., Davis, CA 95616 USA

There are a number of synthesis techniques (for instance, cryomilling) that are capable of producing structural materials with grain sizes of the 10-500 nm range in large quantities. Although a higher strength is generally observed in most of nanostructured materials, their fracture toughness is low and their ductility is limited. These characteristics regarding toughness and ductility have an adverse effect on their potential as structural material. In the present study, two approaches based on microstructural control to improve ductility and toughness of cryomilled Al alloys were reported. The first approach involves architectural designs of nanostructured materials that contain multiple length scales by blending two types of (unmilled coarse grained and cryomilled nanostructured) Al powders, followed by consolidation and extrusion. The second viable approach is to perform a controlled heat treatment on cryomilled nanostructured Al alloys to introduce an intrinsic bimodal microstructure.

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Spray Rolling Aluminum Strip for Transportation Applications: *Kevin M. McHugh*[1]; Yaojun Lin[2]; Yizhang Zhou[2]; Enrique J. Lavernia[2]; Jean-Pierre Delplanque[3]; Sam B. Johnson[3]; [1]Idaho National Engineering and Environmental Laboratory, Industl. & Matl. Tech. Dept., PO Box 1625, MS 2050, Idaho Falls, ID 83415-2050 USA; [2]University of California, Dept. of Cheml. Engrg. & Matls. Sci., Davis, CA 95616 USA; [3]Colorado School of Mines, Engrg. Div., Golden, CO 80401 USA

Spray rolling is a novel technology in which a molten aluminum alloy is atomized and the resulting spray is deposited on the rolls of a twin-roll caster to produce aluminum strip. A combined experimental/modeling approach has been followed in developing this technology with active participation from industry. The feasibility of this technology has been demonstrated at the laboratory scale and it is currently being scaled-up. This paper provides an overview of the process and compares the microstructure and properties of spray-rolled 2124 and 5083 aluminum alloys with commercial ingot-processed material.

3:00 PM
Advanced Atomization Process for Metal Spray Deposition: *Peter Kelly Sokolowski*[1]; Volker Uhlenwinkel[1]; Yunzhong Liu[1]; Iver E. Anderson[2]; [1]Institut fuer Werkstofftechnik, Verfahrenstechnik, Badgasteiner Str. 3, Bremen 28359 Germany; [2]Ames Laboratory, Matls. Sci. & Engrg. Dept., 222 Metals Dvpt. Bldg., Ames, IA 50011 USA

Spray deposition typically utilizes a free-fall atomizer (FFA) with a well established understanding of its capabilities and disadvantages. With an ever increasing demand for superior products and optimal processing conditions in mass production applications, including automotive parts (e.g., cylinder liners), a close-coupled atomizer (CCA) was studied for spray forming. Compared to the FFA, a CCA requires less gas to produce the same particle velocities with the possibility of increasing these velocities and maintaining gas consumption below that of FFA. By increasing particle velocity, it is believed higher densities can be achieved during colder spray conditions. In this study, three materials were sprayed: Sn, bearing steel AISI 52100, and Cu-6wt%Sn on tube substrates with diameters of 80mm and 100mm. Results include density measurements, gas consumption trends, surface temperatures, and particle velocities and diameters obtained with the use of Phase Doppler Anemometry (PDA).

3:20 PM
Control of Mn-Based Precipitate Distribution and Morphology in Aluminum Alloys for Elevated Temperature Applications: *M. C. Carroll*[1]; D. Shull[2]; E. A. Ott[3]; M. J. Mills[1]; G. S. Daehn[1]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., Columbus, OH 43210 USA; [2]Transmet Corporation, Columbus, OH 43228 USA; [3]GE Aircraft Engines, Cincinnati, OH 45215-1988 USA

Manganese is used in small concentrations (generally 1.2 wt% or less) as an alloying element in a number of aluminum alloys, principally as a grain-refining agent. Often overlooked as an important player in emerging aluminum alloy developments, manganese behavior has not been thoroughly evaluated from a processing standpoint in order to improve final material characteristics and achieve more aggressive performance levels. In this study, a more comprehensive understanding of casting and homogenization treatments was sought in order to specifically evaluate Mn-based eutectic constituent and precipitate morphology, and as a result gain a better understanding of high-temperature microstructural evolution. Casting distributions and additional precipitation behavior were evaluated using conductivity measurements that were correlated with direct microstructural observation and characterization via scanning and transmission electron microscopy. Based on the stability of the Mn-based precipitate substructure, novel te chniques for maintaining control over particle distribution along with the resulting increase in potential applications for high-grade Mn-containing aluminum alloys are discussed.

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Laser Direct Fabrication of a Glass-Forming Fe-Based Alloy: *John E. Smugeresky*[1]; Baolong Zheng[2]; Yizhang Zhou[2]; Enrique J. Lavernia[2]; [1]Sandia National Laboratories, Laser Engineered Matls., MS 9402, Livermore, CA 94551 USA; [2]University of California, Dept. of Cheml. Engrg. & Matls. Sci., Davis, CA 95616 USA

Laser Engineered Net-Shaping (LENS®), a promising direct manufacturing technique for fabricating near-net shape fully dense metallic components, tailors microstructures by controlling the cooling rate. A relatively rapid solidification of molten metal occurs as a matter of course. Many new metallic materials for automotive application with isotropic properties and high structural efficiency are dependent upon rapid solidification to achieve appropriate microstructure. In this paper, the potential of LENS® for the fabrication of net-shape parts using a glass-forming Fe-base alloy is explored. Fe-based alloy powder is used for laser deposition of bulk coupons made over a range of process parameters to determine adequacy of the LENS® process solidification rate. The microstructure evolution, thermal stability, transformation sequence and micro-hardness of the laser deposited parts, as a function of processing parameters, are investigated using XRD, SEM, TEM, and DSC. Work by Sandia is supported by the U. S. Department of Energy under contract DE-AC04-94AL85000.

4:15 PM
Segregation Effects During Semi-Solid Forming of Creep Resistant Mg-Al Alloys: *Frank Ajersch*[1]; Faouzi Messaoud[1]; [1]Ecole Polytechnique, Cheml. Engrg., PO Box 6079, Sta. "centre-ville", Montreal, Quebec H3C 3A7 Canada

The forming of Mg-alloy components for structural applications in the transportation industry has gained considerable interest with the development of new creep resistant high strength Mg-Al alloys. The improvement of these properties is based on small additions of structure modifying elements such as Ca and Sr which influence the solidification structure. The properties and microstructure of these alloys formed in the semi-solid state is also highly dependant on the rheological properties. Segregation of the liquid and solid phases are particularly prevalent in slow deformation processes but can be minimized in rapid forming processes such as Thixomolding®. Experiments were carried out using a squeezing flow technique over a range of shear rates in order to quantify the segregation observed for conventional and creep resistant alloys. Correlations between shear stress, shear rates and the microstructure are presented.

4:35 PM
An Investigation of Liquation Formation in the Heat-Affected Zone of Inconel 718 and Inconel 625 Subjected to GTAW: *Shenavia Wilkerson Howell*[1]; Viola L. Acoff[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., PO Box 870202, Tuscaloosa, AL 35487 USA

Nickel-based superalloys Inconel 718 and Inconel 625 are widely used in the aerospace industry, particularly in the gas turbine engine components of aircrafts. During repair welding, these aircraft components are often subjected to numerous cycles consisting of welding followed by postweld heat treatment. Nickel-based superalloys are sensitive to liquation cracking in the HAZ upon postweld heat treating. In the present study, bead-on-plate welds were placed on each specimen using gas tungsten arc welding (GTAW). The effect of welding parameters on liquation in the heat-affected zone (HAZ) of Inconel 718 and Inconel 625 were investigated. The welding current, welding speed and welding environment (i.e. air vs. inert atmosphere) were varied. The resulting welds were characterized using scanning electron microscopy, transmission electron microscopy, and mechanical testing. The purpose of this study is to investigate the conditions that promote liquation in the HAZ during the welding of nickel-based superalloys.

4:55 PM
Welding of Single Crystal Nickel-Base Superalloys: *Sizhao Wang*[1]; Ali Merati[1]; Henry Saari; [1]National Research Council, Inst. of Aeros. Rsch., Bldg. M-13, 1200 Montreal Rd., Ottawa, Ontario K1A 0R6 Canada

Single crystal nickel-base superalloys have been used as gas turbine blade materials for the last few decades due to their excellent high temperature mechanical properties and corrosion resistance. The high costs associated with replacement blades calls for new repair solutions to extend their life cycles, and welding is an efficient process to repair the blades that are worn or damaged during service. Feasibility of both fusion welding and solid state welding is determined by the ability to produce desired microstructures, which yield the required service properties. Therefore, numerous welding trials and mechanical tests must be employed to determine the optimum welding conditions and method. Weldability of single crystal PWA1484 is investigated in this paper in terms of various welding parameters and directions. Pre and post welding heat treatments are applied to the material to optimize the welding conditions. The crack morphology is observed and microstructure development is analyzed using scanning electron microscopy (SEM), optical microscopy (OM) and indexing electron backscattered diffraction (EBSD) patterns. Several potential difficulties of welding single crystal, such as the susceptibility of hot cracking and stray grain formation, which are related to weld pool shape and grain growth orientation, are discussed. Micro-hardness testing is also carried out to characterize the localized microstructural features and mechanical properties of autogenously welded PWA1484.

Alumina and Bauxite: Precipitation

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Dag Olsen, Hydro Aluminium AS, Porsgrunn 3907 Norway; Travis Galloway, Century Aluminum, Hawesville, KY 42348 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday PM Room: 2005
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Chris Vernon, CSIRO Minerals, Bentley, Western Australia 6982 Australia

2:00 PM
Soda Incorporation During Hydrate Precipitation: *Chris Vernon*[1]; [1]CSIRO Minerals, PO Box 90, Bentley, WA 6982 Australia

The economic need to achieve high precipitation yields and tough alumina must be balanced against another important quality consideration - occluded soda. Although there are a number of publications that develop hypotheses for the mechanism of soda incorporation and some that give mathematical relationships to describe the rate of soda incorporation, none attempt to do this with any detailed understanding of the hydrate (gibbsite) growth mechanism. The present work describes sodium incorporation as a function of growth rate and of crystal defect generation, and relates the incorporation of sodium ions into gibbsite crystals to the growth mechanism. A mathematical model for incorporation is developed along statistical mechanical principles and the contribution of organic carbon is explored.

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Dynamic Adsorption Isotherms for Some Hydrate Active Organics and Selected Degradation Products With Implications for Gibbsite Precipitation Yields: Nicolas-Alexandre Bouchard[2]; Raymond Breault[1]; Frédéric Picard[1]; Yannick Chouinard[2]; *Hugues Ménard*[2]; [1]Alcan International Ltd., 1955 Mellon Blvd., Jonquière, Québec G7S 4K8 Canada; [2]Université de Sherbrooke, Dépt. de Chimie, 2500 Blvd. Université, Sherbrooke, Québec J1K 2R1 Canada

The negative impact of organic compounds present in Bayer liquor is well known. To date, the industry mostly relies on bulk removal approaches to control the effect of organics in the Bayer process. However the relationship between total organic carbon and precipitation yield suggests the selective interaction between some organics and precipitating gibbsite is important to plant productivity. These specific organics are referred to as Hydrate Active Organics (HAOs). A better understanding of the characteristics and properties of HAOs could open the way to their selective removal. In this study, the focus was on substituted aromatic compounds that were either detected in Bayer precipitated hydrate or that were generated by the degradation of lignin in caustic solution. Dynamic adsorption isotherms for these compounds obtained using liquid chromatography will be presented to differentiate their adsorptive behaviour towards hydrate. Results for lignin-derived organics and for those obtained from oxygenated and hydrogenated parent molecules, will assist in understanding their relative impacts on gibbsite precipitation yield. These results may show a possible alternative to the complete removal of organics by selective modification of hydrate active organics.

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Boehmite vs Gibbsite Precipitation: *Joanne Loh*[1]; Chris Vernon[1]; Melissa Loan[1]; Greta Brodie[1]; [1]CSIRO Minerals, PO Box 90, Bentley, Western Australia 6982 Australia

Boehmite (monohydrate) precipitation, in place of gibbsite (trihydrate), has been discussed in the literature as a possible energy-saving step in alumina refining. Indeed, the calcination of monohydrate rather than trihydrate would save approximately 12% of the energy consumed in an alumina refinery. These previous investigations have not focussed on the economic and technical feasibility of the process. The current investigation takes a pragmatic approach, measuring precipitation rates, determining product phase and particle size distribution, and assessing the impact of impurities and probe species in an attempt to determine the viability and possible improvements to such a process. The present work indicates that boehmite precipitation rates are approximately 2 orders of magnitude slower than for gibbsite under identical conditions. Agglomeration seems not to occur. The particle size distribution is too fine and the product is unsuitable for calcination. However, the work has further improved the fundamental understanding of gibbsite precipitation and a hypothesis for the mechanism will be presented.

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The Effects of Changes in Solids Concentration on Seed Balance Parameters in Alumina Refinery Seed Classification Systems: *Walter Mason Bounds*[1]; [1]2583 Woodland Ridge Blvd., Baton Rouge, LA 70816 USA

An important consideration in controlling alumina refinery seed classification systems is ensuring that seed produced matches quantity and particle size distribution with seed charged. When this condition is not satisfied, the system may not be stable, resulting in changing seed inventory quantities and particle size distribution. Previous papers have described methods for evaluating operating parameters for individual classifiers as well as seed balance parameters for alumina refinery seed classification systems. In this paper, information from previous papers is utilized to simulate a classification system and determine the effects of changes in solids concentration on seed balance parameters, including mass balance and particle size distribution. Solids concentration effects on out-of-balance cases are also established to aid in illustrating consequences.

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Study of Agglomeration During the Precipitation of Sodium Aluminate Solution: Jiangfeng Zhang[1]; Zhoulan Yin[1]; Qiyuan Chen[1]; [1]Central South University, Physl.-Chmst. Inst., Changsha, Hunan 0086 China

Agglomeration of gibbsite crystals is an important stage in the Bayer process. In the present study, the effect of the crystallization temperature, seed mass, stirring rate, caustic concentration of liquor, molecular rate were investigated. And interpretation of the results was proposed.

4:20 PM

Analysis on the Particle Size Information in Sodium Aluminate Solution During Seeded Agglomeration: Wangxing Li[1]; Jianguo Yin[2]; Qiyuan Chen[2]; Zhoulan Yin[2]; [1]Zhengzhou Research Institute of Chalco, Zhengzhou, Henan 450041 China; [2]Central South University, Physl.-Chmst. Inst., Changsha, Hunan 410083 China

Seeded agglomeration was studied in sodium aluminate solution (Na2Ok=140g?l-1,?¿k=1.37) at 75°.Conclusions were made from the particle size information that agglomeration takes place mainly for particles with the sizes of 0~10?Êm at first and then the larger ones. For particles with certain size, peaks and troughs appear alternately on the curves of the volume percentage to time. The appearance time is basically the same and moves backward when particle size is larger. The kinetic parameters can be further calculated based on the information.

4:45 PM

Study on Negative Effect of K2O on Precipitation Procedure: *Qun Zhao*[1]; *Yanli Xie*[2]; [1]CHALCO, Zhengzhou Rsch. Inst. of Light Metals, No.82, Jiyuan Rd., Shengjie Dist., Zhengzhou, Henan 450041 China; [2]Northeastern University, Sch. of Matls. & Metall., No.11, Ln. 3, Wenhua Rd., Heping Dist., Shenyang, Liaoning 110004 China

The content of impurity K2O in Bauxite is only several thousandths, but it can accumulate in the process and over 10g/l (sometimes ~40g/l), which brings serious negative effect on precipitation, results in fine particles and low strength hydrate. It's demonstrated that the existance of K2O in sodium aluminate liquors can: (1) inhibit the agglomeration between fine particles of hydrates and leads to fine products; (2) change the precipitation mechanism of gibbsite. The products of hydrate grow from sodium aluminate solution is sphere polycrystalline with inlaid structure, which has good ability to resist-attrition. However, the hydrate from potassium aluminate liquor is fragile with needle structure. (3)The existence of K+ in sodium aluminate solution can increase the solubility of SiO2 and then stable the solution, hence decreasing the product yield.

5:10 PM

The Application of Hydrate Seed in Carbonization of Sodium Aluminate Liquors: *Wang Zhi*[1]; Bi Shiwen[2]; Yang Yihong[2]; Yuan Zhangfu[1]; [1]Chinese Academy of Sciences, Inst. of Process Engrg., Zhong Guan Cun, Haidian Dist., Beijing 100080 China; [2]Northeastern University, Sch. of Matls. & Metall, Wenhua Rd., Heping Dist., Shenyang, Liaoning 110004 China

Carbonization was investigated through adding seeds to sodium aluminate liquors in order to improve the particle size and strength of products. All results were explained by analyzing the data obtained and the parameters favoring for improving the product granularity and strength were determined through the orthogonal experiment. By comparison of mean particle size, attrition index and SEM photograph of the products at the conditions with and without seed on operation conditions, it was showed that seeds played important roles in the carbonization process, and the products average particle size was influenced by that of seed, but its effect was related with seed type and seed ratio. In addition, seeds can accelerate the inter-growth of single crystals and gibbsite with inlaid structure had high attrition resistance, as a result the strength of products was increased by 3-25%.

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DFT and Ab Initio Calculation on Thermochemistry of Al6(OH)18(H2O)x(x=0-6), Al(OH)3-3 and Al(OH)4(H2O)2-: Wu Zheng Ping[1]; Chen Qi Yuan[1]; Yin Zhou Lan[1]; [1]Central South University, Coll. of Chmst. & Cheml. Engrg., Changsha City, Hunan Province 410083 China

Enthalpies of formation and Gibbs free energy of formation of Al6(OH)18(H2O)x (x=0-6), Al2O3·2H2O,Al(OH)3-3, Al(OH)4(H2O)2- and Al(OH)4- are calculated at B3LYP/6-31G, 6-31G and B3LYP/6-311++G(3d2p) levels respectively with Dipole & Sphere solvent model by DFT and ab initio methods. Especially, in the process of Al(OH)3 crystals precipitating from supersaturated caustic aluminate solution,

Al6(OH)18(H2O)x(x=0-6) is the favorable growth unit, Al(OH)3-3 is the structure unit of growth units and Al(OH)4(H2O)2- is the minimum growth unit. Using DFT Method with Dipole & Sphere solvent model, ÄfHm(298K)of Al6(OH)18(H2O)x(x=0-6) and Al2O3·2H2O are calculated at B3LYP/6-31G level to be -5419.471013, -5613.439509, -5867.816332, -6018.601893, -6263.675488, -6473.281202, -6698.522508 and -1579.549361 kJ·mol-1, ÄfHm(298K) of Al(OH)6-3, Al(OH)4(H2O)2- and Al(OH)4- are calculated at B3LYP/6-311++G(3d2p) level to be -811.105741, -1993.955225 and -1428.924169 kJ·mol-1. The results are relatively consistent with the available experimental and the theoretical values. ÄrHm(298K)and ÄrGm(298K) of various sorts of hydration reaction of Al6(OH)18(H2O)x (x=0-6) are calculated and the stability of bondage H2O in Al6(OH)18(H2O)x (x=0-6) are discussed. The various combination modes of Al6(OH)18(H2O)6, Al(OH)3-3 and Al(OH)4(H2O)2- are analyzed.

Aluminum Reduction Technology: Cell Stability

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Tor Bjarne Pedersen, Elkem Aluminium ANS, Farsund 4551 Norway; Tom Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday PM Room: 2002
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Donald P. Ziegler, Alcoa Primary Metals, Alcoa Techl. Ctr., Alcoa Ctr., PA 15069-0001 USA

2:00 PM
The Influence of the Basic Flow and Interface Deformation on Stability of Hall-H´eroult Cells: *Haijun Sun*[1]; Oleg Zikanov[2]; Donald Ziegler[3]; Bruce A. Finlayson[1]; [1]University of Washington, Chem. Engrg. Dept., PO Box 351750, Seattle, WA 98195 USA; [2]University of Michigan, Dept. of Mechl. Engrg., 1334 Engrg. Complex, Dearborn, MI 48128-1491 USA; [3]Alcoa Technical Center, 100 Techl. Dr., Alcoa Ctr., PA 15069-0001 USA

We use the method of linear stability analysis to study the effect of background melt flows and interface deformation on stability characteristics of Hall-Héroult reduction cells. The linearized perturbation equations are the two-dimensional shallow water model. Two kinds of background state are generated by using some artificial forcing. The critical friction coefficients for these states and no base flow situation are compared. It is found that some background states, for example, mode (3,1) of melt flows and interface deviation, stabilize the cell. Other states, noticeably, modes (1,1) and (2,1) of interface deviation, have strong destabilizing effect.

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Stability of Hall-Heroult Cells: *Kjell Harald Kalgraf*[1]; [1]Elkem Aluminium, Elkem Al Rsch., Box 8040 Vaagsbygd, NO 4675 Kristiansand Norway

The motion and stability of the metal electrolyte interface is determined by Navier-Stokes equation. The equation may be decomposed into two independent equations by taking the divergence and curl of Navier-Stokes equation. The curl determines the flow of metal and bath and is independent of gravitation and hydrostatic pressure. Using the equilibrium velocity from the flow we find that magneto-gravitational waves depend on the sum of hydrostatic and magnetic pressure.From the divergence we can derive an invariant and a criterium of instability that resembles Sele's criterium of stability. Basically, stability depend on the curvature of hydrostatic and magnetic pressure, and this may in turn be expressed as a dependence on current density, ACD, metal height, and density difference between metal and bath.

2:50 PM
Weakly Coupled Thermo-Electric and MHD Mathematical Models of an Aluminium Electrolysis Cell: *Marc Dupuis*[1]; Valdis Bojarevics[2]; [1]GeniSim Inc., 3111 Alger St., Jonquiere, Quebec G7S 2M9 Canada; [2]University of Greenwich, Sch. of Computing & Math., 30 Park Row, Greenwich, London SE10 9LS UK

In the present study, the full 3D thermo-electric model of a 500 kA demonstration cell has been weakly coupled with the non-linear wave MHD model for the full version of the same cell. In the MHD model, the horizontal ledge distribution calculated in the thermo-electric model has been incorporated as part of the model geometry. In the thermo-electric model, the velocity fields calculated by the MHD model in both the bath and the metal have been used to setup the local heat transfer coefficients at the liquids/ledge interface. Both models have been solved alternatively until a convergence for the horizontal ledge distribution has been obtained.

3:15 PM
Wave Mode Coupling and Cell Instability in Aluminum Reduction Cells: *Nobuo Urata*[1]; [1]Consultant, 770 Cascade Dr., Sunnyvale, CA 94087 USA

The interfacial surface waves cause uneven anode-cathode separation in the electrolytic zone and lower the efficiency of electrolysis in the aluminum reduction cells. In the past, the coupled partial differential equations, describing the electromagnetic perturbation in the cell, were formulated and solved with the various mathematical methods. Fourier expansion method is used for understanding the mechanism of destabilization of the two liquid interface as an interaction of the various non-perturbed waves. A proper mathematical treatment of the boundary condition, a critical factor for solving the equations, is presented. The result is summarized as the mode interactions, governed by the symmetry of the vertical magnetic field and the symmetry of the wave modes. The dominant mechanism of the instability is explained and the various practical methods for magnetic field compensation are discussed.

3:40 PM Break

3:55 PM
Determination and Influence of the Ledge Shape on Electrical Potential and Fluid Motions in a Smelter: *Michel V. Romerio*[1]; Michel Flueck[1]; Jacques Rappaz[1]; Yasser Safa[1]; [1]Swiss Federal Institute of Technology, IACS, Lausanne 1015 Switzerland

The temperature field and the ledge shape in a whole smelter are obtained by solving simultaneously the system of equations formed by: a non-linear convection-diffusion heat equation, which can be considered as a Stephan problem in enthalpy and temperature in the domain of the cell occupied by fluids and ledge, Navier-Stokes equations, with a free interface, in the fluid domains and Maxwell equations in the whole space. The source term of the heat equation results from the Joule effect due to the electrical current crossing the cell. We use artificial time dependence of the heat equation to follow the solidification front with a Chernoff scheme. Results of 3-D numerical calculations showing ledge shape temperature and velocity fields as well as the electrical potential for an operating cell are presented.

4:20 PM
Current Field in an Aluminum Electrolysis Cell: Augustin Moraru[1]; *Nobuo Urata*[1]; Aureliu Panaitescu[2]; [1]"Politehnica" University of Bucharest, Electl. Engrg. Dept., Splaiul Independentei No. 313, Bucharest 77206 Romania

The distribution of the current in an aluminium electrolysis cell is discussed, accounting for the shape and position of the anode blocks and the influences of ledges and cathode bars. The effect of the velocity field in the molten aluminium and electrolyte make the object of a second stage analysis. It is shown that the DC current problem in the electrolysis cell may be split into three almost independent problems related to the cell structure-induced features. The aluminium pad is an almost equipotential body, within the limits of a few tens of millivolt, while the overall voltage drops in the cell are within the order of volts. This allows the separation of electrical problem of the cell into upper, lower and middle parts. In the upper part problem the location of the anodes and ledges, the height of the anode blocks and the distances from the anodes to the aluminium pad are given. In the lower part problem the current distribution is determined by the conductive properties of the carbon lining and the cathode collector bars, as well as the contact resistance between the bars and the cathode blocks. In the middle-part problem the surface current distributions are taken from the previous two problems. The impressed currents produced by the motion within the molten media, due to Laplace forces through the interaction of the current density with the magnetic field intervene in the balance equations. The calculation of the velocity field in the molten media implies the solution to a magnetic field problem and a Navier-Stokes problem, coupled by a Laplace body force term. Because the velocity field may modify the current distribution and the magnetic field, we estimated their influence. The real working conditions lead to a non-symmetrical current distribution, therefore the overall problem must be considered, without simplifying, construction symmetry assumptions. The electrokinetic problem is of very great dimension and only the above mentioned splitting allowed its solution within satisfactory limits.

4:45 PM
Modeling Magnetohydrodynamics of Aluminum Electrolysis Cells with ANSYS and CFX: *Dagoberto S. Severo*[1]; Andre F. Schneider[1]; Elton C.V. Pinto[1]; Vanderlei Gusberti[1]; Vinko Potocnik[2]; [1]PCE Engenharia S/S Ltda, Rua Felix da Cunha, 322, Porto Alegre, RS 90570.000 Brazil; [2]Vinko Potocnik Consultant, Jonquière, Québec G7S 3C7 Canada

Modern aluminum industry is studying ways to increase the efficiency of reduction cells in new and retrofit smelters. Numerical simulation has become a very effective tool for analyzing such complex processes. This paper presents magnetohydrodynamics (MHD) simulations of a new, study case cell technology. A 3-D model was developed by coupling commercial codes ANSYS and CFX, via in-house programs and customization subroutines. A detailed electric-magnetic model was built in ANSYS, which uses Finite Element Method. Steady state and transient MHD flows in the cell were calculated with CFX, which uses Finite Volume Method. Metal and bath were treated as multiphase flow. The homogeneous VOF (Volume of Fluid) model, available in CFX, was used to calculate bath-metal interface in steady state and transient regimes. The transient simulation of the bath-metal interface was used for the study of cell stability.

5:10 PM
Compensation for the Magnetic Field of the End Reduction Cells in Potlines: *Alexander Gusev*[1]; Leonid Krylov[2]; Vitaliy Platonov[1]; Petr Vabishchevich[3]; [1]Engineering-Technological Center Ltd, RUSAL, Pogranichnikov 37, Krasnoyarsk 660111 Russia; [2]RUSAL - Management Company, Nikoloyamskaya 13/1, Moscow Russia; [3]Russian Academy of Science, Inst. for Mathematical Modlg., Miusskaya pl. 4, Moscow Russia

The end reduction cells in potlines at aluminum smelters operate in the conditions, which substantially differ from those of the series reduction cells. This is caused, first of all, by the fact that the magnetic field in the potline substantially changes in going from the series reduction cells to the end ones. To minimize the negative consequences of this effect, nonstandard busbars are frequently used for the extreme reduction cells. In the work, another possibility is discussed, which is characterized by the compensation of the magnetic field by means of the development of special busbar configurations for connecting the end reduction cells, arranged side-by-side, of the adjacent rows in a potline. The efficiency of this technical solution was estimated on the basis of mathematical simulation. The proposed compensation scheme is realized, and its operational capability is proved at the Sayanogorsk aluminum smelter of the Russian Aluminum Company.

WEDNESDAY PM

Aluminum Reduction Technology: Emerging Technologies

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Tor Bjarne Pedersen, Elkem Aluminium ANS, Farsund 4551 Norway; Tom Alcorn, Noranda Aluminum Inc., New Madrid, MO 63869 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday PM Room: 2003
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: John J. Chen, University of Auckland, Dept. of Cheml. & Matls. Engrg., Auckland 00160 New Zealand; Jomar Thonstad, Norwegian University of Science and Technology, Dept. of Matls. Tech., 9471 Trondheim Norway

2:00 PM
Evaluating and Funding New Technologies to Support the U.S. Aluminum Industry: *Thomas Robinson*[1]; [1]U.S. Department of Energy, Industl. Technologies Prog., 1000 Independence Ave. SW (EE-2F), Washington, DC 20585-0001 USA

Proposals for the research and development of new technologies that reduce energy consumption in the U.S. aluminum industry are evaluated and funded by The U.S. Department of Energy, Energy Efficiency and Renewable Energy (EERE) Office's Industrial Technologies Program (ITP). These proposals offer real opportunities to encourage and accelerate the development of new technologies that improve energy efficiency while strengthening the U.S. aluminum industry. ITP's Aluminum Industries of the Future (IOF) is currently partnering with more than 70 firms in over 35 R&D projects. The IOF portfolio of projects ranges from high-risk reduction technologies to high-value melting technologies. This paper reports on how the Aluminum IOF portfolio is performing and how proposals are evaluated, selected and funded. The authors provide researchers with working knowledge of the baselines, benchmarks and bandwidths used to evaluate new technologies and with the proposal merit review selection process.

2:20 PM
Will New Technologies Sustain the U.S. Primary Aluminum Industry?: *William T. Choate*[1]; Majeed Aziz[1]; Rennie Friedman[1]; [1]BCS, Incorporated, 5550 Sterrett Place, Ste. 306, Columbia, MD 21044 USA

The high cost of electricity in the Northwest has resulted in the "moth balling" of nearly forty percent of the U.S. capacity to produce primary aluminum. The very large economies-of-scale needed for Hall-Heroult facilities, coupled with their dependence on a constant low-cost supply of electric power severely limits any potential of locating new primary production facilities in the United States. However, advances in modeling, new materials and novel engineering approaches applied to non traditional primary processes show promise for changing the industry and boosting U.S. primary capacity. This paper speculates on the industrial structure and economic impacts of inert electrodes, multi-polar cells, carbothermic, aluminum chloride and ionic liquid primary production technologies. The projected benefits include: lower electrical use, economies-of-scale at significantly lower volumes, end-user co-location, ability to use off-peak low-cost power, and more... If successfully developed, these technologies could revolutionize the U.S. primary aluminum industry.

2:40 PM
Thermal Stabilities and Viscosities of Low Temperature Aluminum Electrorefining Electrolytes: Di-Alkyl Imidazolium Chloride Ionic Liquids: *Venkat Kamavaram*[1]; R. G. Reddy[1]; [1]University of Alabama, Metallurgl. Engrg., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

Thermal and physical properties of di-alkyl imidazolium chloride ionic liquids were studied for their application in low temperature aluminum electrorefining. The ionic liquids used in this study are 1-butyl-3-methyl imidazolium chloride (C_4mimCl) and 1- hexyl-3-methyl imidazolium chloride (C_6mimCl). Thermal properties of these ionic liquids were studied in the temperature range 150°-200°C under controlled argon atmosphere for 15 hrs. For C_6mimCl, weight loss measured using TG analysis varied from 4 to 85 wt% as the temperature increased from 150° to 200°C. Absolute viscosity of chloroaluminate melts such as C_4mimCl+ $AlCl_3$ and C_6mimCl+$AlCl_3$ were determined as function of temperature and concentration of $AlCl_3$. Non-Arrhenius behavior of absolute viscosities with temperature was observed. Aluminum electrorefining in chloride ionic liquid electrolytes at low temperatures was successfully demonstrated.

3:00 PM
Coprocessing at Cement Plant of Spent Potlining from the Aluminum Industry: *Valerio A. Gomes*[1]; Paulo Z. Drumond[1]; Jose Olimpio P. Neto[2]; Abraão Rodrigues Lira[2]; [1]Consorcio de Aluminio do Maranhao - Alumar, Environml. Safety & Health, Br 135, Km 18 - Distrito Industrial de Pedrinhas, Sao Luis, Maranhão 65095604 Brazil; [2]Cimento Poty S/A, Quality & Environmental, Sítio Santa Helena S/N, Sobral, Ceará 62114-000 Brazil

In line with the concept of Sustainable Development, the Aluminum Consortium of Maranhão [ALUMAR] in partnership with Cimento Poty S/A [Poty Cement Inc.], implemented coprocessing of spent potlining from the aluminum industry, in rotary clinker kilns, on the basis of CONAMA resolution No. 264 of 1999, from the Environmental Council [Conselho Nacional do Meio Ambiente - CONAMA]. Due to its physicochemical characteristics, the addition of Spent Potlining (SPL), as secondary raw material and secondary fuel, entails economic and non-economics benefits for cement production and also safely eliminates a waste considered class I - hazard waste, by Standard ABNT-NBR 10004 of the Brazilian Technical Standards Association. The purpose of the present study is to present the main stages in the process of generation, characterization, and coprocessing of SPL in cement industries, as well as its economic and non-economic benefits and environmental aspects.

3:20 PM
Development of Detoxifying Process for Spent Potliner in CHALCO: *Wangxing Li*[1]; Xiping Chen[1]; [1]Zhengzhou Research Institute of CHALCO, Shangjie, Zhengzhou 450041 China

A novel detoxifying process of spent potliner is described in this paper. Spent potliner is treated in a rotary kiln with special additives, discharge from the kiln reacted with lime solution. Additives are usu-

ally limestone and commercial wastes. The effect of additives, temperature and lime solution on the process is discussed respectively. The result shows that: It is feasible to detoxify SPL by the process, soluble F- and CN- in the spent potliner can be decreased more than 95%, the final solid slag meets the requirement of China national environmental protection standard. There are several advantages of the process: All cuts of SPL can be handled through the process, better utilisation of commercial wastes. The permitting and operating of the process and facilities are verified. A pilot plant is being constructed at a scale of 500-1000 tons per year.

3:40 PM Break

3:55 PM
Greenhouse Gas Emissions from Aluminum Carbothermic Technology Compared to Hall-Hèroult Technology: Hilde Myklebust[1]; *Pål Runde*[2]; [1]Elkem ASA, Energy Div., PO Box 5211 Majorstuen, N-0303 Oslo Norway; [2]Elkem ASA Research, PO Box 8040 Vaagsbygd, 4675 Kristiansand Norway

Introduction of the Aluminum Carbothermic Technology (ACT) in the aluminum industry will lead to significant reductions in emissions of greenhouse gases compared to the traditional Hall-Hèroult process. This is a fact even though twice as much CO2 will be emitted in the carbothermic process based on the process equations. The main reasons for the total reduction are that the ACT-process eliminates PFC-emissions and significantly reduces the power consumption. Calculation of CO2-emissions from power generation is a complex task, but acceptable estimates can be found by means of simplified calculation principles. The results show that replacing the Hall-Hèroult process by ACT will reduce the total greenhouse gas emissions by at least about 30%.

4:15 PM
Performance of Aluminium Bronze as an Inert Anode: *Mark David Glucina*[1]; [1]University of Auckland, Cheml. & Matls. Engrg., 20 Symonds St., Auckland New Zealand

Aluminium bronze alloys have been investigated as a potential inert anode material for aluminium electrolysis. The goal for such a material is to produce an oxide layer at the electrode/anode interface, which will protect the metal from molten cryolite. A lab-scale electrolysis cell has been used for testing potential anodes. The effects of alloy composition, current density, and electrolysis time have been investigated. The scales formed on the anode, both before and during electrolysis, have been characterised through a combination of XRD, SEM, and optical microscopy techniques.

4:35 PM
On the Corrosion Behaviour of Ni-NiO-NiFe2O4 Cermets as Inert Anodes in Aluminum Electrolysis: Yanqing Lai[1]; *Jie Li*[1]; *Huanan Duan*[1]; Xiaogang Sun[1]; Yexiang Liu[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Changsha, Hunan 410083 China

Ni-NiO-NiFe2O4 cermets with different NiO contents were prepared and the corrosion behaviour in Na3AlF6-Al2O3 melts was investigated in laboratory electrolysis tests. The steady-state concentrations of Ni, Fe in these samples were below the corresponding solubility in the similar melts, which implied that the corrosion mechanism in electrolysis might be different from that of unpolarized corrosion. The impurity ions transferred directionally and gathered near cathode, forming a concentration gradient. Such a gradient put the calculation of corrosion rate based on analysis of bath and aluminum into question. Post-electrolysis examination of the anodes showed that Ni metal corroded preferentially at the surface of the anodes, yet the remained ceramic layer prevented the penetration of bath and the loss of the metal phase in the underlying cermets.

4:55 PM
Fabrication of Al-Ni-Cu-O Cermets Inert Anodes and Electrolysis Testing: *Wang Zhao Wen*[1]; Luo Tao[1]; Gao Bing Liang[1]; Qiu Zhu Xian[1]; [1]Northeastern University, Coll. of Matls. & Metall., 3-11 Wenhua Rd., Heping Dist., MB 117, Shenyang, Liaoning 110004 China

An idea about the cermet materials is tested. Al-Ni-Cu-O was applied for the inert anode materials for aluminium electrolysis. The density of samples, fabricated by the hot pressing, is close to the theoretic density. At 900 centigrades the electric conductivity of the samples is >80scm-1. The anode (150×12 mm) was steadily run for 24h at a current of 150A. The deterioration of the anode was analysed. According to the XRD of the electrolysed anode, the NiO content is increasing, and the new phase (NiO) created in the anode, resulted in swelling and delamination. A theory is that a more uniform metal distribution from improving the hot pressing process, gives increased corrosion resistance of the anode.

5:15 PM
Preparation of the Cermet Inert Anode Based on Ferrous Nickel and Electrolysis Study: Luo Tao[1]; *Wang Zhao Wen*[1]; Gao Bing Liang[1]; Qiu Zhu Xian[1]; [1]Northeastern University, Coll. of Matls. & Metall., 3-11 Wenhua Rd., Heping Dist., MB 117, Shenyang, Liaoning 110004 China

Hot pressing-sintering was adopted to fabricate the inert cermets anodes based on the nickel ferrite in aluminum electrolysis. The electrical conductivity of the anodes, with relative density of more than 98%, increases with the increasing of temperature, ranging from $40\Omega^{-1} \cdot cm^{-1}$ to $60\Omega^{-1} \cdot$ cm-1 at 900°C. The electrolysis with the cermet anodes were run at the different anodic current density. The contaminations amount in the aluminium production is increasing with the increasing of anodic current density, and the contaminations (Fe, Ni and Cu) amount is <0.257wt% at 0.8A/cm^2. The main reason of anode corrosion is the ascending activity of Fe^{3+} ions and rich in the outer anode due to the increasing of anodic current density.

5:35 PM
300 A Bench-Scale Aluminum Electrolysis Cell with Fe-Ni-Al2O3 Composite Anode: *Zhong-ning Shi*[1]; Jun-li Xu[1]; Zhu-xian Qiu[1]; Zhao-wen Wang[1]; Bing-liang Gao[1]; [1]Northeastern University, Coll. of Matls. & Metall., PO Box 117, Shenyang 110004 China

A new Fe-Ni-Al2O3 metal matrix composite material was developed for aluminum electrolysis cells. A 300 A experiment for these anodes was operating with wettable cathodes (TiB2) at 960°C for 10 h. The electrolyte consisted of 51NaF-39AlF3-3CaF2-7Al2O3(wt%). The potential from the anode to the aluminum reference electrode was 2.25V. The purity of the produced aluminum was <99% with 75% current efficiency. After electrolysis, the SEM analysis indicated that there was a layer consisting of Al2O3 at the anode surface. To some extent, the layer can prevent the attacks from the melt and oxygen.

Applications and Fundamentals of High Aspect Ratio Nanomaterials: Monitor and Control of Nanostructure Synthesis

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Nanomaterials Committee
Program Organizers: Jud Ready, Georgia Tech Research Institute - EOEML, Atlanta, GA 30332-0826 USA; Seung H. Kang, Agere Systems, Device and Module R&D, Allentown, PA 18109 USA; Lourdes G. Salamanca-Riba, University of Maryland, Materials Science and Engineering Department, College Park, MD 20742-2115 USA; Nagarajan Valanoor, Forschungzentrum Juelich, IFF and Institute for Electronic Materials, Juelich, Germany D52425

Wednesday PM Room: 3018
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Jud Ready, Georgia Tech, GTRI-EOEML, Atlanta, GA 30332-0826 USA; Nagarajan Valanoor, Forschungzentrum Juelich, Juelich D52425 Germany; Lourdes G. Salamanca-Riba, University of Maryland, Coll. Park, MD 20742-2115 USA

2:00 PM Opening Remarks

2:05 PM Invited
Optical and Photoelectron Spectroscopy of Carbon Nanotubes: *Tobias Hertel*[1]; [1]Vanderbilt University, Dept. of Physics & Astron., 1807 Sta. B, Nashville, TN 37235 USA

Carbon nanotubes (CNTs) hold promise for use in a variety of applications owing to a combination of extremely high aspect ratios with unique mechanical and electronic properties of graphene - the building material for CNTs. This presentation will focus on the optical and dynamical properties of CNTs. Specifically, the dynamics of optically excited single- and double-wall carbon nanotubes (SWNTs and DWNTs) will be discussed in some detail. They are investigated in quasi-crystalline form - as so called nanotube ropes - or as individual entities in aqueous solution using CW absorption-, femtosecond time-resolved photoemission- and time-resolved photoluminescence spectroscopy. We discuss the importance of carrier-carrier and carrier-phonon scattering as well as of radiative and nonradiative decay processes for the dynamics of optically excited CNTs.

2:35 PM
Synthesis Optimization and Characterization of Multi-Walled Carbon Nanotubes: *Christian Deck*[1]; Erik McKee[1]; Kenneth S. Vecchio[1]; [1]University of California, Dept. of MAE, Matls. Sci. &

Engrg. Grp., 9500 Gilman Dr., MC-0411, La Jolla, CA 92093-0411 USA

The unique properties of carbon nanotubes have suggested a myriad of applications in a variety of fields. However, consistent and optimal growth of high purity nanotubes has proven to be a challenge. We report on the synthesis optimization of multi-walled carbon nanotubes through the pyrolytic decomposition of benzene and a metal-organic catalyst precursor in a chemical vapor deposition furnace and the subsequent characterization thereof. Variables such as catalyst type, pressure, carrier gas flow rate, gas turbulence, carbon source feed rate, and temperature are optimized so as to produce well aligned multi-walled carbon nanotubes of lengths between a few microns to greater than one millimeter. We also discuss the characterization of our nanotube products through SEM, TEM, XRD, and EDS, focusing on the structure, composition, and purity of the results. Additionally, thermogravimetric analysis was performed to determine characteristic temperatures at which carbon nanotubes and byproducts oxidize in order to find appropriate ranges within which to purify carbon nanotubes. Results show the synthesis of high purity nanotubes of several millimeters in length with a thermal stability to near or above 500°C. As most synthesis byproducts burn off in the proximity of 300°C, a temperature range for nanotube purification is isolated.

3:05 PM
Synthesis and Characterisation of Carbon Nano-Glassy Films: *Marco Giuseppe Beghi*[1]; Antonio Miotello[2]; Paolo Mosaner[2]; Paolo Maria Ossi[1]; [1]Politecnico di Milano, Dip. Ingegneria Nucleare & Ctr. of Excellence Nano Engineered Matls. & Surfaces (NEMAS), Via Ponzio, 34-3, Milano 20133 Italy; [2]University of Trento, INFM-Dip. di Fisica, Povo, TN 38050 Italy

Carbon films were deposited at room temperature onto (100) Si substrates by Pulsed Laser Deposition (PLD) in the UV of highly oriented pyrolitic graphite. By changing deposition conditions (neon and argon atmospheres, at pressures from 0.6 Pa to 2 kPa; laser power density, from 8.5 to 19 MW mm-2) nanosized cluster-assembled films were obtained. SEM determined film morphology, evolves from dense columns to node-like, to an open dendritic structure. The size distribution and relative abundancies of carbon clusters were evaluated by AFM and correlated with film roughness. Visible Raman spectroscopy shows that all films are sp2 coordinated and structurally disordered and belong to the family of nano-glassy carbons. The calculated coherence length is correlated with the size of carbon clusters agglomerated on the surface of the growing film. The number of atoms per cluster, as calculated by a model of aggregation in the plume, depends sensitively on ambient gas pressure.

3:35 PM Break

4:00 PM
In-Situ Monitoring of the Nucleation and Growth Process of High Aspect Ratio Corundum Structures: *Joris Proost*[1]; Elzbieta Koza[1]; [1]University of Louvain, Div. of Matls. & Process Engrg. (IMAP), Place Sainte-Barbe 2, Louvain-la-Neuve B-1348 Belgium

One-dimensional nanostructures of alpha-Al2O3 were successfully synthesized by simple evaporation of the commercial high-purity oxide powders, followed by vapour condensation onto a sapphire substrate under controlled conditions of supersaturation without the presence of a catalyst. Synthesis was carried out in a specially designed reactor equipped with a laser setup that allows to monitor the nucleation and growth process in situ. Detailed in situ interferometric and high-resolution substrate curvature measurements revealed, for the first time, that the growth of these one-dimensional structures is driven by a mechanical stress, which develops in an initially continuous, 2-dimensional layer. This interaction between chemical activity and mechanical stress is shown to provide an important additional parameter to actively control the large-scale synthesis of high aspect ratio oxide nanostructures.

4:30 PM
Effect of Cationic Substituents on Controlling the Aspect Ratio of Goethite and the Magnetic Properties of G-Fe2O3 Nanoparticles Derived from Substituted Goethite: *Sudakar Chandran*[1]; [1]Royal Institute of Technology, Dept. of Matls. Sci., Tmfy-MSE, Brinellvagen 23, Rm. 224, Stockholm SE 100 44 Sweden

The effect of different substitutional impurities such as Al3+, Cr3+, Co2+ or Ni2+ on the particle morphology, shape control and phase stability of goethite and further the understanding of the effect of particle size, shape and compositional variability on magnetic properties of the nanoparticular g-Fe2O3 system are presented. g-Fe2O3 of desired shape and size are obtained by topotactic reaction from the precursor material goethite and magnetic properties are tuned by controlling these parameters. Acicular goethite particles are prepared using morphology controlling cationic additives.[1] The goethite structure is stable in spite of the iso- or aliovalent substitutions. The individual additives have divergent influence on the particle morphology; Al3+ and Cr3+ decreases the particle size to <50 nm and aspect ratio (AR) <2. Co2+ substitution produces slender particles with AR as high as 25. Whereas, Ni2+ does not have any influence on the particle morphology. The attributable factors in morphology control are the increased nucleation rate, restricted growth along needle axes, and the strain induced in the goethite lattice as a result of differences in ionic radii. Maghemite, g-Fe2O3, particles are obtained from goethite wherein the topotactic conversion renders the retention of the particle morphology of the precursor. Maghemite with substituted impurities showed substantial differences in magnetic properties. Saturation magnetization (ss) and coercivity (Hc) go down to very low values due to relaxation of spins on the surface atoms as revealed by Mössbauer spectroscopy. Decrease in coercivity is by way of the presence of diamagnetic ion (Al3+). Whereas, Co-substituted maghemite has enhanced Hc as a result of high magnetocrystalline anisotropy accompanied by the shape anisotropy. [1]C. Sudakar, G.N. Subbanna and T.R.N. Kutty, J.Mater. Chem., 12 (2002) 107-116.

Automotive Alloys 2005: Session III

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizer: Subodh K. Das, Secat, Inc., Coldstream Research Campus, Lexington, KY 40511 USA

Wednesday PM Room: 2006
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Subodh K. Das, Secat Inc., Lexington, KY 40511 USA; Gyan Jha, ARCO Aluminum Inc., Louisville, KY 40223-4032 USA

2:00 PM
Microstructure and Mechanical Properties of Continuous Cast 5754 Alloy Sheet for Automotive Application: *Zhong Li*[1]; Steve Kirkland[2]; Shixi Ding[2]; Paul Platek[2]; [1]Commonwealth Aluminum, 1505 Bull Lea Rd., Lexington, KY 40511 USA; [2]Commonwealth Aluminum, 7319 Newport Rd., SE, Uhrichsville, OH 44683 USA

Commonwealth Aluminum has been developing continuous cast 5754 aluminum alloy sheet for automotive structural part applications over the last several years. The results showed that the Commonwealth Aluminum produced continuous cast (twin belt casting technology) 5754 aluminum alloy sheets can satisfy the formability during the forming process and the strength required by automotive industry. Automotive vehicle internal structural parts have been successfully stamped from CC material manufactured by Commonwealth Aluminum and passed the quality inspection. Commonwealth Aluminum, Newport Rolling Mill, has been approved as a raw material supplier for Ford Motor Company and General Motors Corporation.

2:25 PM
Ultrasonic Fatigue Behavior of E319 Aluminum Alloy at Elevated Temperature: *Xiaoxia Zhu*[1]; J. Wayne Jones[1]; John E. Allison[2]; [1]University of Michigan, Matls. Sci. & Engrg., 3062 HH Dow Bldg., 2300 Hayward Rd., Ann Arbor, MI 48105 USA; [2]Ford Motor Company, Ford Rsch. Lab., Dearborn, MI 48124-2053 USA

The effect of microstructure, temperature and load ratio on the fatigue behavior of an Al-Si-Cu cast alloy was investigated for lifetimes as long as 10^9 cycles using ultrasonic fatigue instrumentation operating at 20 kHz. Fatigue testing was conducted at 20, 150 and 250°C. There was a modest decrease in fatigue resistance from 20 to 150°C, while a significant decrease in fatigue resistance was observed from 150 to 250°C at low stress levels. Fractographic studies indicated that most fatigue cracks initiated from microshrinkage pores at the specimen surface, while a much smaller number initiated from interior pores, twin boundaries and oxides. Microstructure has been quantified and correlated with fatigue behavior. Fatigue lifetime was found to depend primarily on early crack growth behavior, rather than crack initiation. This knowledge has been used to extend a model for fatigue life prediction, based on small crack growth behavior. The effect of frequency and load ratio will also be discussed.

2:50 PM
Deformation Characteristics of AZ31 Magnesium Alloy Under Various Forming Temperatures and Strain Rates: Fadi K. Abu-Farha[1]; *Marwan K. Khraisheh*[1]; [1]University of Kentucky, Ctr. for Mfg., 210 CRMS Bldg., Lexington, KY 40506-0108 USA

The increasing demand for lower fuel consumption vehicles and the associated environmental issues induced the automotive industry to make the commitment to reduce fuel consumption levels, mainly by reducing vehicles' weight. As the lightest constructional metal on earth, Magnesium (and its alloys) has already started to occupy an increasingly big space in the different research fields as an important potential material for various automotive components. Many automotive components have been already produced from different magnesium alloys, but they are mainly cast components. Production of magnesium outer body components is still hindered by the metal's inferior ductility at room temperature; that's why magnesium alloys are usually formed at high temperatures. In this work, the deformation behaviour of Magnesium Alloy AZ31 is investigated under various forming temperatures and strain rates. Tests were conducted in the temperature range between 73 and 932°F and the strain rate range between 1x10-5 to 3x10-2 s-1. Results show the enhanced ductility and strain rate sensitivity of the alloy at higher temperatures. The alloy even exhibits a superplastic-like behaviour within a certain range of strain rates and temperatures. The results of these and other tests will be used to develop a constitutive model that predicts the deformation behaviour of the alloy.

3:15 PM

Quantitative Characterization of AM50 and AS21X Magnesium Alloys to Correlate the Variability in Fracture Properties with Microstructure: *Arun Sreeranganathan*[1]; Soon Gi Lee[1]; Gautam R. Patel[1]; Arun M. Gokhale[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr., NW, Atlanta, GA 30332 USA

Fracture related properties of high-pressure die cast AM50 and AS21X magnesium alloys are studied at six different temperatures ranging from room temperature to 394K. The properties are correlated with the microstructure through quantitative analysis of bulk and fracture surface microstructures. There is a significant variability in the tensile ductility at all temperatures for AM50 specimens and the variability decreases with increase in temperature. The porosity at the fracture surface is found to correlate well with the ductility of AM50 samples suggesting a preferential fracture path through the regions of highly localized clusters of large pores. No such correlation is observed for AS21X where the variability in properties is seen to increase with increase in temperature. Other factors such as the effect of intermetallic compounds like Mg2Si on the fracture properties of AS21X are investigated.

3:40 PM

On the Creep of Die-Cast Magnesium Alloys: *Bimal Kad*[1]; Qingyou Han[2]; Srinath Viswanathan[3]; [1]University of California, 409 Univ. Ctr., La Jolla, CA 92093 USA; [2]Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA; [3]Sandia National Laboratories, Albuquerque, NM 87185 USA

Die cast magnesium alloy design for elevated temperature creep is evaluated from the perspective of strengthening contributions of alloying additions and the microstructure constituents. A new approach[1] to alloy design incorporating Si, Ca, Ce, Zn ternary additions takes into account the inherently non-uniform die-cast microsturture. This leads to a non-uniform distribution of the solidus/homologous temperature in the α(Mg) phase and a non-uniform distribution of deformation stresses and strains in the specimen under creep conditions. The mechanical response of such inherently non-uniform microstructures is evaluated experimentally and via computational means. Both observations suggest that significant creep deformation occurs in the α(Mg) phase in and adjacent to the eutectic regions with the low solidus constituent while deformation in the primary α(Mg) dendrites is less pronounced. Microstructural design efforts that increase the homologous temperature, reduce eutectic volume or reinforce the eutectic α(Mg) phase hold significant promise towards increasing the creep resistance of magnesium alloys. This approach is then applied to predict and validate a ranking of the creep performance of current die-cast alloys under developement. [1]Qingyou Han, Bimal Kad and Srinath Viswanathan (2004) Philosophical Magazine, in press.

4:05 PM

The Role of Microstructural Variability on the Ultra-High Cycle Fatigue Behavior of SiCp-Reinforced Aluminum Composites: *James Huang*[1]; Jonathan E. Spowart[2]; J. Wayne Jones[1]; [1]University of Michigan, Dept. of Matls. Sci. & Engrg., HH Dow Bldg., 2300 Hayward St., Ann Arbor, MI 48109-2136 USA; [2]AF Research Laboratory, Matls. & Mfg. Direct., Bldg. 655, 2230 10th St., Ste. 1, Wright Patterson AFB, Dayton, OH 45433 USA

Compared to their unreinforced counterparts, discontinuously-reinforced metal matrix composites (DRC) generally display improvements in properties such as modulus, wear and creep resistance, and high-cycle fatigue. DRC can also be processed by fairly conventional means, making these attributes increasingly appealing in high-performance structural applications. It has therefore become more important to understand its ultra-high cycle fatigue behavior in order to maximize performance and minimize service costs. The role of microstructural variability on the fatigue behavior of 2124/SiC/15p-T4 MMC was investigated in this study. Ultrasonic fatigue methods were employed in order to specifically explore the ultra-high cycle fatigue regime (10^7 ¡ÜN_f¡Ü10^9 cycles). Although the spatial distribution of SiC particles is known to play a key role in the fatigue behavior of DRC, our data indicate that at these long lifetimes, fatigue life is determined by critical inclusions and not the heterogeneity of the particle distribution. Correlation of fatigue data with inclusion probability studies incorporating serial sectioning and 3-d microstructural characterization is used to examine the role of microstructure on fatigue life and the variability of fatigue life.

4:30 PM

The Effect of Ti Content on Microstructure, Castability and Properties of Foundry Alloy A356.2: *Malcolm J. Couper*[1]; Catherine L. Smith[1]; Mark Easton[2]; Joseph Barresi[1]; [1]Comalco Aluminium Ltd., Comalco Rsch. & Techl. Support, 15 Edgars Rd., Thomastown, VIC 3074 Australia; [2]Monash University, CRC for Cast Metals Mfg., Sch. of Physics & Matls. Engrg., VIC 3800 Australia

The effect of titanium additions on the casting and performance of an Al7Si0.35Mg alloy has been studied. The study investigated various combinations of titanium and grain refiner TiB2 additions and considered grain size, intermetallic phases, age hardening response, tensile properties and fluidity and porosity. Low titanium consisted of 0.01wt% whilst high titanium refers to typically used levels of 0.12-0.14wt%. The results show that high levels of titanium are not required to ensure good performance. In particular, the high titanium levels result in coarse Al-Ti-Si particles, linked to a reduction in tensile elongation in mechanical testing. The fluidity of the alloy with high titanium was reduced. Furthermore, an interaction with hydrogen level in the melt was observed such that this reduction in fluidity was greater in non-degassed melts.

4:55 PM

Development of a Low Carbon Al-Killed/Ti Stabilized Steel for Automotive Applications: *Julio Alberto Juarez-Islas*[1]; Rafael Mendoza[2]; [1]Instituto de Investigaciones en Materiales_UNAM, Materiales Metalicos y Ceramicos, Circuito Exterior S/N, Ciudad Universitaria, Mexico, D.F 04510 Mexico; [2]Ispat Mexicana S.A. de C.V., Aseguramiento de la Calidad, Francisco J Mujica 1B, Lazaro Cardenas, Michoacan 60950 Mexico

An Al-Killed/Ti-Stabilized low carbon steel was produced using the electric arc furnace, vacuum degassing, ladle treatment and continuous casting route. The resulting slabs were then hot rolled at 1100ºC, coiled at 600ºC, cold rolled and annealed at 850ºC. After evaluation of the microstructure, texture and mechanical properties, the fully recrystallized coils fullfilled the target properties stablished by the automotive industry.

5:20 PM

Microstructural Influence on High-Cycle Fatigue Limit of High Carbon Pearlitic Steel Filaments Used for Tires: *Yo Sep Yang*[1]; Seong Yong Park[1]; Chan Gyung Park[1]; Seung Ho Lim[2]; Deok Young Ban[2]; [1]Pohang University of Science and Technology(POSTECH), Matls. Sci. & Engrg., San 31, Hyoja-Dong, Nam-Gu, Pohang, Kyungbuk 790-784 Korea; [2]Trefilarbed Korea, 134, Yusan-dong, Yangsan, Kyungnam 626-230 Korea

Influences of microstructure on high cycle fatigue limit of high carbon steel filaments have been investigated. Fatigue tests were carried out by using Hunter-type tester at a frequency of 60 Hz at bending stress of 900 to 1500 MPa. It was found that fatigue limit and tensile strength were improved with increasing carbon content, which was mainly attributed to decreased lamellar spacing and cementite thickness. However, the fatigue ratio, which is defined as the ratio of the fatigue limit to the tensile strength, was reduced in a higher carbon range of 0.8 to 0.9 wt.%, while the fatigue ratio was nearly constant in a lower carbon range of 0.7 to 0.8 wt.%. Mechanical properties of the filaments have been discussed in terms of the microstructural parameter change of lamellar spacing and cementite thickness. In addition, the variation of cementite morphology on the fatigue crack propagation will be discussed.

5:40 PM

Influence of Additional Mn and Cu Elements on Mechanical Properties of Super High Strength Aluminum Alloy: *Kozo Osamura*[1]; Hiroki Adachi[1]; Tmohiro Sorano[1]; Hidenori Nako[1]; Akihei Tanaka[2]; Ken Kikuchi[2]; Shigeru Okaniwa[3]; [1]Kyoto University, Dept.

of Matls. Sci. & Engrg., Sakyo-ku, Kyoto 6068501 Japan; [2]Toyo Aluminum K.K., Hino 529016 Shiga; [3]Nippon Light Metal K.K., Kanbara 4213203 Shizuoka

One of key technologies for automotive industry is the development of light material with high specific strength. The super high strength Al-Zn-Mg-Cu-Mn-Ag based alloy (Mesoalite20â) includes two type of precipitates of Q and Al6Mn phases. The Q precipitates have a fiber-like shape, but Al6Mn has round and irregular shape. By hot extrusion at 773K, their precipitates flowed along extrusion direction and only Q precipitates aligned well. When increasing Mn content with constant of 1.5mass% Cu, the amount of Al6Mn increased remarkably. The compressive strength decreased with increasing Mn content. When increasing Cu content from 0.5 to 2.5 mass% with constant of 4 mass%Mn, the amount of Q phase increased and their mechanical property improved. Therefore the present study has proposed a new alloy with higher Cu content, which gives higher strength than that of commercial Mesoalite 20, which has tensile strength of 910 MPa.

Beta Titanium Alloys of the 00's: Mechanical Response

Sponsored by: Structural Materials Division, SMD-Titanium Committee

Program Organizers: Rod R. Boyer, Boeing Company, Metall./6-20J1, Seattle, WA 98124-2207 USA; Robert F. Denkenberger, Ladish Co., Inc., Cudahy, WI 53110-8902 USA; John C. Fanning, TIMET, Henderson, NV 89009 USA; Henry J. Rack, Clemson University, School of Materials Science & Engineering, Clemson, SC 29634-0921 USA

Wednesday PM
February 16, 2005

Room: Salon 10/11
Location: San Francisco Marriott

Session Chairs: Robert F. Denkenberger, Ladish Co. Inc., Cudahy, WI 53110-8902 USA; Brian Marquardt, Zimmer, Metals Rsch., Warsaw, IN 46581-0708 USA

WEDNESDAY PM

2:00 PM Invited

Fatigue Performance of Metastable Beta Titanium Alloys: Effects of Microstructure and Surface Finish: *L. Wagner*[1]; A. Boettcher[1]; M. Kocan[1]; H. J. Rack[2]; [1]TU Clausthal, Inst. of Matls. Sci. & Engrg. Germany; [2]Clemson University, Sch. of Matls. Sci. & Engrg., Clemson, SC 29634 USA

Metastable beta titanium alloys may be subjected to a wide variety of thermomechical treatments. For example these materials can be rolled or swaging and statically recrystallization to establish a wide variations in grain size and/or primary alpha size, morphology and volume fraction. Subsequent aging can also result in variations in tensile properties. Finally surface treatment by shot peening or roller burnishing can also be used to alter surface properties. This presentation will review the combined effects of these various treatments on the high cycle fatigue performance of metastable beta alloys either in fully reversed loading(R=-1) or tension-tension loading(R=0.1)of three commercially available metastable beta alloys, TIMET LCB, Beta 21S and Beta C. It is indended to provide a generalized framework of the effects of microstructure, surface roughness, dislocation density and residual stress on the high cycle fatigue crack initiation and propagation in the class of increasingly important titanium alloys.

2:40 PM

High Cycle Fatigue Crack Initiation and Growth in TIMETAL LCB: *B. Yazgan*[1]; Y. Kosaka[2]; H. J. Rack[1]; [1]Clemson University, Sch. of Matls. Sci. & Engrg., Clemson, SC 29634-0971 USA; [2]TIMET, Henderson, NV 89009 USA

This investigation has examined the influence of microstructure variations on the high cycle fatigue behavior of aged TIMETAL LCB, the fatigue performance being evaluated under tension-tension loading conditions at R=0.1 in laboratory air and 25 Hz. Fractographic analysis indicated that fatigue initiation, independent of processing history, involved sub-surface crack formation. Serial sections studies also indicated that crack initiation occurred at the interface between grain boundary alpha and the aged beta matrix. Further BSEI examination of the aged microstructures indicate that the differences in high cycle fatigue behavior can be understood by considering the effect of processing history on the connectivity of grain boundary alpha, decreased connectivity being associated with enhanced fatigue performance.

3:05 PM

Overview of High-Cycle Fatigue of Beta Titanium Alloys: Role of Microstructure on Crack Initiation, Growth and Fatigue Life: *K. S. Ravi Chandran*[1]; Sushant K. Jha[1]; Shankar Srinivasan[1]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City 84112 USA

Results of extensive research on the effect of microstructure on the fatigue behavior of beta-titanium alloys, with an emphasis on the metastable Ti-10V-2Fe-3Al alloy, is presented. The study considered several variations in primary-alpha volume fraction and aspect ratio as well as the varied secondary-alpha distributions resulting from different aging treatments. Previous work from literature on several beta-Ti alloys is also included in the review. It is concluded that the low stress and high cycle fatigue behavior is determined solely by the aging condition or the nature of secondary alpha distribution in beta matrix. The results from the Ti-10V-2Fe-3Al alloy indicate that a fine distribution of secondary-alpha is necessary to achieve maximum resistance to high cycle fatigue. Reanalysis of the literature data on this basis confirmed this finding. Fatigue crack growth in these alloys is largely insensitive to microstructure. Fatigue life is mostly determined by fatigue crack initiation. In most of the microstructures, fatigue cracks initiated in subsurface and surface regions at low and high stress regimes, respectively. The implications of these results on microstructure design for better fatigue resistance and the analysis of mechanisms of fatigue in beta-Ti alloys are discussed.

3:30 PM

Designing a Beta Titanium Alloy for Optimum Fatigue Performance: *Sushant K. Jha*[1]; K. S. Ravi Chandran[2]; [1]Universal Technology Corp., 1270 N. Fairfield Rd., Dayton, OH 45459 USA; [2]University of Utah, Metallurgl. Engrg., 135 S, 1460 E, Rm. 412, Salt Lake City, UT 84112 USA

A systematic study was conducted to establish the microstructure-fatigue correlation in the metastable beta titanium alloy, Ti-10V-2Fe-3Al (Ti-10-2-3). The aging condition significantly affected the damage tolerance of long cracks as well as the fatigue limit. The omega-aged condition showed an increased damage tolerance but lower fatigue lives and the fatigue limit when compared to the alpha-aged microstructure. In the alpha-aged condition, variation at the length scales of prior beta grain and the primary alpha particle had limited effect on the fatigue limit or the long crack growth rates. However, variation at the secondary alpha size scale caused a significant effect on the fatigue life behavior with almost no loss of "long crack" damage tolerance.

3:55 PM Break

4:10 PM

Dynamic Response of Beta-Ti Alloys: *Kenneth S. Vecchio*[1]; Uday Deshmukh[1]; Raghavendra R. Adharapurapu[1]; Fengchun Jiang[1]; Adam Crocker[1]; [1]University of California, Dept. of MAE, Matls. Sci. Grp., 9500 Gilman Dr., MC-0411, La Jolla, CA 92093-0411 USA

Beta-Ti alloys offer attractive alternatives to alpha and alpha+beta Ti alloys due to their increased strength-to-weight ratio, good formability, and excellent fatigue and fracture resistance. With the growing interest in the use of Ti alloys for various defense platforms, the dynamic mechanical response of beta-Ti alloys must be investigated to determine their applicability under impact loading situations. Composition, thermal-mechanical processing, and prestrain level can alter the constitutive response of beta-Ti alloys. Three metastable-beta alloys: Ti-16V-6Cr-4Al, Ti-15V-3Cr-3Sn-3Al, and Ti-10V-2Fe-3Al, in both the annealed+heat-treated and the cold-rolled+heat-treated conditions were investigated to determine the tensile response of these alloys over a broad range of test temperatures and strain rates from 10^{-3}/s to 10^{3}/s. The effect of orientation with respect to the sheet rolling direction was documented. The effect of annealing versus cold rolling on subsequent aging response is discussed, and the relationship between microstructure and mechanical response is established for the various alloy conditions. In general, the flow curves show strong temperature and strain rate dependencies, with relatively little work hardening, consistent with the behavior of many bcc metals. The applicability of existing phenomenological bcc models, such as: Johnson-Cook and Zerilli-Armstrong to these metastable beta-Ti alloys is investigated.

4:35 PM

Quick Reference Guide for Beta Titanium Alloys: *Stacey Nyakana*[1]; John C. Fanning[1]; Rodney R. Boyer[2]; [1]TIMET, PO Box 2128, Henderson, NV 89009 USA; [2]The Boeing Co., PO Box 3707, Seattle, WA 98124 USA

Beta alloys provide useful combinations of physical and mechanical properties as well as a wide range of processing and corrosion properties. Throughout the past several decades, many beta alloys have been researched, yet only a handful of these have currently enjoy

commercial production. While the primary applications continue to be in the aerospace market, beta alloys have demonstrated usefulness in other arenas. This section provides a quick reference guide for a large variety of common and not-so-common beta titanium alloys. Information regarding chemical composition, mechanical properties, physical properties, heat treatment, fabrication, applications, and production status is included.

5:00 PM
Panel Discussion: Beta Titanium Alloys: Future Needs and Opportunities

Biological Materials Science and Engineering: Biological Materials Characterization and Biomimetics II

Sponsored by: Structural Materials Division, Electronic, Magnetic & Photonic Materials Division, Society for Biomaterials, Surfaces in Biomaterials Foundation, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), EMPMD/SMD-Biomaterials Committee
Program Organizers: Marc Andre Meyers, University of California, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Roger J. Narayan, Georgia Tech, School of Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Wednesday PM Room: 3009
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Larry Hench, Imperial College London, Tissue Engrg. & Regenerative Medicine Ctr., Ashford, Kent TN25 4AH UK; Andrea M. Hodge, Lawerence Livermore National Laboratory, Matls. Dept., Livermore, CA 94550-9234 USA

2:00 PM Invited
Rapid In Vitro Testing of Cell-Biomaterial Interactions With Bio-Photonics: *Larry Hench*[1]; [1]Imperial College London, Tissue Engrg. & Regenerative Medicine Ctr., Wye Campus, Ashford, Kent TN25 5AH UK

Obtaining quantitative biological data on the effect of materials on cells and cells on materials is essential in developing new biomaterials and quality assurance testing of commercial biomaterials. Standard biological assays are time consuming and expensive. There is considerable societal pressure to minimize animal testing. However, a limitation of typical in vitro cell culture based tests is monitoring and maintaining a mature cell phenotype during the experiment. A newly developed integrated living cell and bio-photonics system provides rapid in vitro testing of biomaterials using human primary cell cultures with in situ spectroscopic monitoring of the cell phenotype. This bio-photonic based system also can be used for evaluating potentially toxic chemicals, environmental or chemical and biological warfare agents. Advantages of the system include: rapid throughput, non-invasive, real-time monitoring of individual cells, clusters of cells or 3-D assemblages of cells (organoids). Quantitative Raman spectroscopic data are used to follow cell viability, onset of cell death, mechanism of cell death, cell division, cellular differentiation and de-differentiation and cell phenotype when exposed to control environments, biomaterials or chemical, biological, pharmaceutical or environmental elements or compounds. Applications to 10 different types of living cells are presented, including differentiation of embryonic stem cells. Results of using the system on testing the effects of bioterrorism agents, ricin and sulfur mustard, on human lung-derived cells are reviewed.

2:30 PM Invited
Bioactive Ceramic-Tetrahedral Amorphous Carbon Nanocomposites: *Roger Jagdish Narayan*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., 771 Ferst Dr. NW, Rm. 361, Atlanta, GA 30332-0245 USA

We have developed a hydroxyapatite-tetrahedral amorphous carbon nanolayered composite using pulsed laser deposition. The hydroxyapatite surface layer possesses bioactive properties that mimic the properties of natural bone, and the tetrahedral amorphous carbon interlayer possesses biocompatibility, wear resistance, and corrosion resistance properties that hermetically seal the bulk biomaterial. Unfortunately, tetrahedral amorphous carbon thin films exhibit poor adhesion due to internal compressive stress and poor interfacial bonding with the substrate. To solve this problem, we have created multilayered composites using a pulsed laser deposition. These films exhibit significantly higher hardness values than the underlying Ti-Al-V alloy. We envisage numerous applications for these hydroxyapatite/tetrahedral amorphous carbon multilayer coatings, including use in orthopedic and dental implants.

3:00 PM
Net Shape Processing of Functionally Graded Materials by Field Activated Sintering: Vladimir Y. Kodash[1]; *Joanna R. Groza*[1]; Jing Zhang[2]; Antonios Zavaliangos[2]; [1]University of California, Dept. of Cheml. Engrg. & Matls. Sci., One Shields Ave., Davis, CA 95616 USA; [2]Drexel University, Dept. of Matls. Sci. & Engrg., Philadelphia, PA USA

Field Activated Sintering Technique (FAST) is widely used for sintering ceramic and metal products. Processing of the powder is usually conducted in graphite dies and punches and results in simple flat shapes, mainly discs. However, the manufacture of curved surfaces presents some difficulties. A new technique has been developed to produce a non-flat shape made of several layers (functionally graded material, FGM). The FGM was processed by powder cold spraying of several ceramic-metal layers starting with pure materials at each surface and increments of 25% compositions. The final shape was pre-pressed by cold isostatic pressing and then sintered by FAST sintering. The simulation of cold compaction and FAST sintering of non-flat surfaces has been conducted on metal powders. It was found that the temperature homogeneity can be improved by applying thermal insulating coating at the interface between the specimen and the die. The FGM materials may be used for medical applications.

3:20 PM
In Situ Characterization of Ti-Peroxy Gel During Formation on Titanium Surfaces in Hydrogen Peroxide Containing Solutions: *Julie J. Muyco*[1]; Jeremy J. Gray[1]; Timothy V. Ratto[1]; Christine A. Orme[1]; Joanna McKittrick[2]; John Frangos[3]; [1]Lawrence Livermore National Laboratory, Chmst. & Matl. Sci., 7000 East Ave., L-350, Livermore, CA 94550 USA; [2]University of California, Mechl. & Aeros. Engrg., Matl. Sci. & Engrg. Grad. Prog., 9500 Gilman Dr., La Jolla, CA 92093 USA; [3]La Jolla Bioengineering Institute, 505 Coast Blvd. S., Ste. #405, La Jolla, CA 92037 USA

Three possible functions of Ti-peroxy gel are: reduction of the inflammatory response through the reduction of hydrogen peroxide and other reactive oxygen species; creation of a favorable surface for calcium phosphate nucleation; and as a transitional layer between the soft tissue and the stiff titanium. Traditional surface characterization techniques operate in high vacuum environments that alter the actual sample-solution interface. Our studies used techniques that allowed samples to remain in solution and be observed over time. Atomic force microscopy (AFM) force-distance curves, electrochemical impedance spectroscopy (EIS), Raman spectroscopy, and ellipsometry were each used in situ to define kinetic and mechanical properties of Ti-peroxy gel as it formed over time on titanium during exposure to hydrogen peroxide. Our studies enabled us to monitor real-time changes in the native oxide layer on titanium in hydrogen peroxide containing solution, including the formation of a Ti-peroxy gel layer above the native oxide. Peaks attributed to Ti-peroxy gel were seen to emerge over the course of several hours using in situ Raman spectroscopy. Force-distance curves suggest a layer that thickens with time on the titanium sample surface. EIS data showed that changes in the surface layers could be monitored in solution over time. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

3:40 PM
Effect of Post Vacuum Heating on the Microstructural Feature and Bonding Strength of Plasma-Sprayed Hydroxyapatite Coatings: *Chung Wei Yang*[1]; Tzer Min Lee[2]; Truan Sheng Lui[1]; Edward Cheng[1]; [1]National Cheng Kung University, Dept. of Matls. Sci. & Engrg., No. 1, Univ., Rd., Tainan 701 Taiwan; [2]National Cheng Kung University, Inst. of Oral Medicine, Coll. of Medicine, No. 1, Univ., Rd., Tainan 701 Taiwan

Plasma-sprayed HA coatings (HACs) on Ti-6Al-4V substrate with post vacuum heating treatment were employed to improve the properties of HACs. The heating temperatures are 400ºC, 500ºC, 600ºC, 700ºC and 800ºC. According to the experimental results, post vacuum heating treatment could improve the average bonding strength and the minimum life of HACs by using Weibull's reliability analysis. The HACs with 600ºC vacuum heating shows the highest strength value of all. On the other hand, the index of crystallinity (IOC) of heat-treated HACs increases and impurity phase content decreases with increasing heating temperature. The crystallization during vacuum heating also leads the variation in thermal expansion coefficient and the volume

contraction of heat-treated HACs, especially higher than that of 600ºC vacuum heating. Therefore, the volume contraction induces apparent and concentric cracks and reduces the bonding strength of heat-treated HACs.

4:00 PM Break

4:15 PM
Mechanical and Radiographic Properties of a Shape Memory Polymer Composite for Intracranial Aneurysm Coils: *Janet M. Hampikian*[1]; Brian C. Heaton[2]; Frank C. Tong[3]; Zhuqing Zhang[2]; C. P. Wong[2]; [1]Boise State University, Matls. Sci. & Engrg., 1910 Univ. Dr., Boise, ID 83725-2075 USA; [2]Georgia Institute of Technology, Matls. Sci. & Engrg., 771 Ferst Dr., Atlanta, GA 30332-0245 USA; [3]Emory University Hospital, Dept. of Radiology, 1364 Clifton Rd. NE, Ste. A121, Atlanta, GA 30322 USA

An intracranial aneurysm can be a serious condition which may go undetected until the aneurysm ruptures causing hemorrhaging within the subarachnoid space surrounding the brain. An increasingly common treatment method is by embolization using platinum coils. However, in about 15% of the cases treated by platinum coils, the aneurysm eventually re-opens as a result of compaction of the platinum coil ball, incomplete occlusion/thrombosis of the aneurysm, or the inability of tissue to grow on platinum. One solution to this is to develop bio-responsive materials to use as coil implants. In this research, a thermoplastic shape memory polymer (SMP), CalomerTM, produced by The Polymer Technology Group, Inc., was investigated as a potential candidate for aneurysm coils. Small diameter fibers produced from SMPs can be fed through a micro-catheter to adopt a preprogrammed three-dimensional configuration when heated to body temperature. The SMP was tested to determine modulus behavior and shape recovery force. In addition, the polymer was made radio-opaque by adding tantalum filler at 3% volume fraction. Thermo-mechanical testing shows that the material exhibits a shape recovery force near 37° C. Coils produced from the material deployed inside a simulated aneurysm model demonstrate that typical hemodynamic forces do not hinder the shape recovery process. Fluoroscopic imaging of the composite coils in a clinical setting verifies the radio-opacity of the composite material.

4:35 PM Cancelled
Rate- and Cycle Dependence of Deformation of Small-Scaled Materials

4:55 PM
The Recrystallization and Thermal Oxidation Behavior of CP-Titanium: *Fatih Mehmet Güçlü*[1]; *Hüseyin Çimenoðlu*[1]; *Eyüp Sabri Kayalý*[1]; [1]Istanbul Technical University, Cheml. & Metall. Faculty, Metall. & Matls. Engrg. Div.- Maslak, Ýstanbul 34469 Turkey

Titanium and its alloys are used in biomedical industry due to their low weight, excellent corrosion resistance and biocompability. However, wear of these alloys causes adverse tissue reactions in the human body and needs to be replaced short time after implantation. Recently some surface modification techniques are utilized to improve the wear properties of titanium. Thermal oxidation is one these processes which is a low cost and an effective way to form a hard surface coating with an oxygen diffusion zone beneath it. The studies of the thermal oxidation titanium revealed that thermally oxidized samples showed 25 times resistance to wear than non-oxidized samples. Thermal oxidation, which is essentially carried out temperatures about 600°C, may associate with recrystallization of the bulk structure. In this study the recrystallization behavior of cold worked CP titanium are investigated and the relation between thermal oxidation and cold working of the CP titanium is investigated.

5:15 PM
Mechanical Characterization of Coronary Stents Using Nanoindentation and Nanoscratch Testing Techniques: *David J. Vodnick*[1]; Richard J. Nay[1]; Dehua Yang[1]; Thomas J. Wyrobek[1]; [1]Hysitron Inc., Nanomech. Rsch. Lab., 10025 Valley View Rd., Minneapolis, MN 55344 USA

Many generations of coronary stents have been developed, with each succeeding design being more flexible and easier to deliver to the occluded artery. The newest generation contains a drug-eluting coating designed to interfere with restenosis, thrombosis, and scarring. In addition to other biomaterial properties, the mechanical properties of stent material and coatings are of vital importance to product performance and reliability. However, the stent shape, size, and coating thickness have exposed great challenges to existing mechanical testing instruments. Therefore, the nanomechanical properties of several commercially available coronary stents were investigated using nanoindentation and nanoscratch testing techniques for the first time. Hardness and reduced modulus values were utilized to characterize the mechanical properties of various stents and their coatings. Scratching techniques were developed to quantify the interfacial adhesion of thin ceramic and polymeric coated stents. This study demonstrates the capability of nanoindentation and nanoscratch to quantify the mechanical properties and interfacial adhesion strength of coronary stenting systems.

5:35 PM
Effect of Firing Time on the Bonding of Porcelain Fused to Titanium With and Without a Plasma-Sprayed Zirconia Bond Coat: *Tsung Nan Lo*[1]; Truan Sheng Lui[1]; Edward Chang[1]; [1]National Cheng Kung University, Dept. of Matls. Sci. & Engrg., No. 1, Ta Hsueh Rd., Tainan 701 Taiwan

Porcelain and titanium are applied in fixed prosthodontics by porcelain-fused-to-metal (PFM) recently. During firing of porcelain fused to titanium,it was observed that the oxidation of titanium becomes severe under high temperature and longer duration time. The results show that the bonding strength of porcelain fused to titanium decrease from 23.0 MPa to 18.4 MPa with increasing firing time. It is speculated that the titanium might be deteriorated by oxygen dissolution during oxidation process and enable the fracture to occur slightly into the upmost titanium near the porcelain/titanium interface. To alleviate the deterioration of titanium, a plasma-sprayed zirconia layer was introduced to serve as an oxygen diffusion barrier on the titanium prior to fusing of porcelain. Experimental results reveal that the bonding strength of porcelain/zirconia/titanium composite specimen increases (35.8 MPa) and there is no obvious degradation of bonding strength (34.1 MPa) after longer firing time.

Bulk Metallic Glasses: Mechanical Behavior

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Raymond A. Buchanan, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA

Wednesday PM Room: 3006
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Katharine M. Flores, Ohio State University, Matls. Sci. & Engrg., Columbus, OH 43210 USA; John J. Lewandowski, Case Western Reserve University, Matls. Sci. & Engrg., Cleveland, OH 44106 USA

2:00 PM
Ductile vs Brittle Behavior of Metallic Glasses: *J. J. Lewandowski*[1]; W. H. Wang[2]; A. L. Greer[3]; [1]Case Western Reserve University, Dept. of Matls. Sci. & Engrg., Cleveland, OH 44106-7204 USA; [2]Chinese Academy of Sciences, Inst. of Physics, PO Box 603(42-1), Beijing 100080 China; [3]University of Cambridge, Dept. Matls. Sci. & Metall., Cambridge CB2 3Q UK

Notch toughness experiments have been conducted on a variety of bulk metallic glasses in both the fully amorphous condition as well as after annealing. The magnitude of the notch toughness is very dependent on the extent of shear deformation emanating from the notch. The presentation will summarize recent observations of notch toughness in metallic glasses as well as a review of the literature where similar experiments have been conducted. A number of the bulk metallic glasses exhibit exceptionally high values for notch toughness (e.g. > 60 MPa-m1/2) accompanied by extensive shear banding and fracture surface roughness. However, other bulk metallic glasses exhibit much lower notch toughness (e.g. < 10 MPa-m1/2), a lack of extensive shear banding, and fracture surfaces which are very brittle in appearance. The effects of annealing experiments on the change in notch toughness will also be presented, as it is possible to embrittle some, but not all, of the metallic glasses by annealing at temperatures near and above the glass transition temperature. The results will be rationalized by examining the changes to various elastic constants that accompany annealing within one metallic glass system. This approach will also be used to rationalize the difference in notch toughness between the metallic glasses exhibiting high values for notch toughness from those that are brittle. The implications of these correlations will be discussed.

2:20 PM
Structural Changes Associated with Plastic Deformation in Bulk Metallic Glasses: Matthew Lambert[1]; *Katharine M. Flores*[1]; [1]Ohio State University, Matls. Sci. & Engrg., 2041 College Rd., Columbus, OH 43210-1178 USA

It is well known that at low temperatures and high stresses, plastic deformation in metallic glasses is highly localized in shear bands, while at temperatures near the glass transition, deformation becomes homogeneous. Free volume theory indicates that the average free volume increases during flow, and prior studies of free volume distribution suggest that the sizes of free volume sites range from inherent interstitial-like defects to larger defects capable of flow. However, the precise flow mechanism and the evolution of the free volume distribution during flow remain unclear. In this study, the flow behavior of a Zr-based bulk metallic glass was investigated over a range of temperatures and strain rates. The average free volume before and after deformation was quantified using DSC. More detailed information about the evolution of the free volume distribution was obtained using positron annihilation spectroscopy, where an increase in the concentration of flow defects was observed following deformation.

2:40 PM
Cast Bulk Metallic Glass Alloys: Prospects as Wear Materials: *Jeffrey A. Hawk*[1]; Omer N. Dogan[1]; Gary J. Shiflet[2]; [1]U.S. Department of Energy, Albany Rsch. Ctr., 1450 Queen Ave. SW, Albany, OR 97321 USA; [2]University of Virginia, Dept. of Matls. Sci. & Engrg., Sch. of Engrg. & Applied Sci., 116 Engr.'s Way, Charlottesville, VA 22904-4745 USA

Bulk metallic glasses are single phase materials with unusual physical and mechanical properties. One intriguing area of possible use is as a wear material. Usually, pure metals and single phase dilute alloys do not perform well in tribological conditions. When the metal or alloy is lightweight, it is usually soft leading to galling in sliding situations. For the harder metals and alloys, their density is usually high, so there is an energy penalty when using these materials in wear situations. However, bulk metallic glasses at the same density are usually harder than corresponding metals and dilute single phase alloys, and so could offer better wear resistance. This work will discuss preliminary wear results for metallic glasses with densities in the range of 4.5 to 7.9 g/cc. The wear behavior of these materials will be compared to similar metals and alloys.

3:00 PM
Effects of Changes in Notch Radius on Deformation and Fracture of a Bulk Metallic Glass: *T. Jacobs*[1]; J. J. Lewandowski[2]; A. L. Greer[1]; S. Tin[1]; [1]University of Cambridge, Dept. Matls. Sci. & Metall., Cambridge CB2 3Q UK; [2]Case Western Reserve University, Dept. of Matls. Sci. & Engrg., Cleveland, OH 44106-7204 USA

Notched bend bars have been tested with different root radii in order to determine the effects of changes in stress triaxiality on the deformation and fracture of a bulk metallic glass. The evolution of shear bands at the notch surfaces was monitored via sequential loading experiments, while fracture surfaces were analyzed via scanning electron microscopy. FEM analyses were conducted on the bend bars using DEFORM in order to determine the evolution of stress and strain with increased loading, and the results were compared to existing stress analyses of similar specimens. Possible changes in temperature accompanying the deformation at the notches was initially modeled using DEFORM. The effects of changes in notch radius on the extent and magnitude of shear banding and likely locations of fracture initiation will be covered, while estimates of temperature rise predicted by DEFORM will also be presented.

3:20 PM
Effects of Changes in Specimen Geometry and Loading Rate on a Bulk Metallic Glass: *G. Sunny*[1]; A. S. Nouri[2]; J. J. Lewandowski[2]; V. Prakash[1]; [1]Case Western Reserve University, Dept. of Mechl. & Aeros. Engrg., Cleveland, OH 44106-7204 USA; [2]Case Western Reserve University, Dept. of Matls. Sci. & Engrg., Cleveland, OH 44106-7204 USA

The effects of changes in specimen geometry and loading rate have been determined for a Zr-based bulk metallic glass. Right circular cylindrical specimens with length to diameter ratios varying from 0.5 to 2.0 were tested under various strain rates ranging from quasi-static to in excess of 1000/sec. Quasi-static tests were conducted using servo-hydraulic testing machines, while the high strain rate tests utilized both split Hopkinson pressure bar (SHPB) and gas guns. The effects of changes in specimen geometry and loading rate on the deformation and fracture behavior will be presented.

3:40 PM Break

4:00 PM
Effects of Superimposed Pressure on Flow and Fracture of BMGs and Devitrified Amorphous Aluminum Alloys: *P. Wesseling*[1]; L. O. Vatamanu[1]; J. J. Lewandowski[1]; [1]Case Western Reserve University, Dept. of Matls. Sci. & Engrg., 10900 Euclid Ave., Cleveland, OH 44106-7204 USA

Compression tests have been performed with high alignment fixtures on 4 different bulk metallic glass specimens at atmospheric pressure as well as with levels of superimposed hydrostatic pressure up to 700 MPa. The results show essentially no difference in applied flow stress or fracture stress over the range of pressures tested. However, fracture did not occur on the plane of maximum shear, suggesting a normal stress effect on the flow and fracture behavior of the bulk metallic glass specimens. The data is compared to various flow and fracture theories. A Mohr-Coulomb flow theory appears to best describe the data. In contrast, a BMG composite and a devitrified aluminum alloy were tested with different pressures and temperatures. These composite materials fail via ductile fracture under tensile loading at ambient conditions. Initial investigations reveal large increases in ductility due to both increases in pressure and temperature.

4:20 PM
As-Cast Bulk Metallic Glasses Containing Nanocrystalline Particles: *Cang Fan*[1]; Hahn Choo[1]; Peter K. Liaw[1]; [1]University of Tennessee, Matls. Sci. & Engrg. Dept., 434 Dougherty Engrg. Bldg., Knoxville, TN 37996 USA

Bulk metallic glasses (BMG) exhibit heterogeneous deformation under loading at room temperature due to the formation of highly localized shear bands, which leads to a catastrophic failure. Lately, in an attempt to improve ductility, various BMG composites (BMGC) containing crystalline phases have been developed. In this talk, we will present recent advances in the processing technique, and in the understanding of the relationship between the microstructure and mechanical behavior of a Zr-based BMGC. By adding Nb to Zr-Ni-Cu-Al, nanocrystalline-particle-containing BMGCs were synthesized in an as-cast condition without subsequent heat treatments. The HRTEM results show that the addition of 2 at.% Nb introduces nanocrystals with an average size of 3 nm. The x-ray diffraction and DSC results also indicate that the presence of the as-cast nanocrystalline particles strongly influence the crystallization process. The heat flow of the nano BMGCS before reaching supercooled liquid region is different from monolithic BMG. Furthermore, compressive ductility of the Nb-containing BMGC at room temperature is significantly improved (about 3.5%) compared to the monolithic Zr55Ni5Cu30Al10 BMG (about 0.1~0.3%), together with a small increase in the yield strength from 1750 to 1800 MPa.

4:40 PM
High Temperature Hardness Indentation Studies on Metallic Glasses: *P. Wesseling*[1]; J. J. Lewandowski[1]; [1]Case Western Reserve University, Dept. of Matls. Sci. & Engrg., 10900 Euclid Ave., Cleveland, OH 44106-7204 USA

High temperature microhardness indentations were conducted on a variety of metallic glasses, e.g. Al-, Fe-, Cu-, Hf-, Mg-, Ce- and Zr-based metallic glass, using a Nikon QM high temperature hardness indenter. Microhardness indentations were conducted while increasing the temperature up to the glass transition temperature of the material and subsequently during cooling to room temperature. Significant softening is observed as the temperature approaches the glass transition temperature. The softening behavior is further investigated by determining the activation energies for high-temperature flow, which can be derived from the slopes of the hardness versus temperature curves in the high temperature regime. After cooling to room temperature the microhardness of the materials has increased or was unchanged. AFM and SEM studies have been conducted to examine the surface features around the indentations conducted close to or at the glass transition temperature. Comparisons will be made amongst the various systems investigated.

Carbon Technology: Cathode Materials and Corrosion I

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Todd W. Dixon, ConocoPhillips, Borger, TX 79007 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway; Markus Meier, R&D Carbon, Sierre CH 3960 Switzerland

Wednesday PM Room: 2007
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Harald A. Oye, University of Science and Technology, Dept. of Matls. Tech., Trondheim N-7491 Norway

2:00 PM
Revisiting Sodium and Bath Penetration in the Carbon Lining of Aluminium Electrolysis Cell - Part I: *Pierre-Yves Brisson*[1]; Gervais Soucy[1]; Mario Fafard[2]; Guillaume Servant[3]; Hans Darmstadt[3]; Jean Camiré[3]; [1]Université de Sherbrooke, Génie chimique, 2500 boul. de l'Université, Sherbrooke, Québec J1K 2R1 Canada; [2]Université Laval, Génie Civil, Pavillon Adiren-Pouliot, Québec, Québec G1K 7P4 Canada; [3]Alcan Métal Primaire Inc., Arvida R&D Ctr., 1955 Blvd. Mellon, CP 1250, Jonquière, Québec G7S 4K8 Canada

Sodium and bath penetration in the carbon cathode blocks for aluminium electrolysis are known to be amongst the most detrimental phenomena for the cell lifespan. Although much work has been done over the years, some important questions still remain to be answered. In an attempt to adress this problem, we present an ongoing project dedicated to answer specific questions: How the sodium is carried inside the blocks? Which compounds are formed between sodium and carbon? How the bath penetrates the block and how can we model it? What is the connection between sodium, bath penetration and the augmentation of the cathodic voltage drop? This first part will present the background for each question in the form of a literature review. Then we will present the strategies used to try to give some answers to the previously asked questions along with the results obtained so far.

2:25 PM
Development and Validation of a Thermo-Chemo-Mechanical Model of the Baking of Ramming Paste: *Daniel Richard*[2]; Guillaume D'Amours[3]; Mario Fafard[1]; Martin Désilets[4]; [1]Laval University, Civil Engrg. Dept., Pouliot Bldg., Quebec, Quebec G1K 7P4 Canada; [2]Université du Québec, Applied Sci. Dept., 555 boul. de l'Université, Chicoutimi, Québec G7H 2B1 Canada; [3]Aluminium Technology Centre, Natl. Rsch. Council Canada, 501 boul. de l'Université E, Chicoutimi, Québec G7H 8C3 Canada; [4]Alcan International Limited, Arvida R&D Ctr., PO Box 1250, Jonquière, Québec G7S 4K8 Canada

During preheating and the early operation stages of a Hall-Héroult cell, the green ramming paste undergoes several transformations. This cohesive porous granular material will first swell and will lose mass and then, it will develop more porosity and shrink. Moreover, it is also mechanically compressed by the thermal expansion of the cathode blocks. In the on-going project START-Cuve, a new thermo-chemo-mechanical constitutive law has been developed to model the behaviour of the ramming paste. Stresses and strains generated in the rammed seam during baking, can now be accurately predicted. This paper presents some aspects of the mechanical model, which was largely based on extensive experimental observations, both at ambient and at high temperatures. The model was implemented in the finite element code FESh++. To illustrate the complex behaviour of the ramming paste and the capabilities of the model, simulations have been performed using representative temperature evolution scenarios and mechanical loading paths.

2:50 PM
A Laboratory Evaluation of Ramming Paste for Aluminium Electrolysis Cells: *Flemming Bay Andersen*[1]; [1]Corus Research, Development & Technology, Ceram. Rsch. Ctr., PO Box 10000, Bldg. 3J22, IJmuiden 1970 CA The Netherlands

At the primary aluminium smelters of Corus a number of ramming pastes have been used in the pots over the years. Furthermore a lot of new paste qualities are available on the market. The information provided by the suppliers on paste properties is limited and this makes it difficult to compare products. In order to gain knowledge on paste properties and in order to approve ramming paste qualities for use in Corus electrolysis cells we have tested a number of ramming paste qualities. In this paper the results of these tests are presented together with a discussion on expected performance in electrolysis cells. Of special interest are the test results from the so-called "eco-friendly" qualities and how they compare to the standard qualities. Based on the testing results product specifications are proposed to be used for approving ramming pastes from new and existing suppliers.

3:15 PM
Surface Exchange of Sodium, Anisotropy of Diffusion and Diffusional Creep in Carbon Cathode Materials: *Alexander Zolochevsky*[1]; Jørund G. Hop[2]; Trygve Foosnæs[1]; Harald A. Øye[1]; [1]Norwegian University of Science and Technology, Dept. of Matls. Tech., Sem Sælandsvei 12, Trondheim N-7491 Norway; [2]Hydro Aluminium, Tech. & Operational Support, Øvre Årdal N-6884 Norway

Experimental data for the expansion of a semigraphitic cylinder due to sodium diffusion in the axial and radial directions are explained by anisotropic diffusion coefficients and surface exchange coefficients. Compressive creep deformation due to sodium diffusion into the binder phase (short-term creep) produces reduction of the sodium expansion when an external pressure is applied to the material. A constitutive model describes the diffusional short-term creep of an anthracitic material. The long-term creep deformation is considered related to sodium diffusion into grains. Creep measurements have been made for a semigraphitic material under axial loading applied after the maximum value of free sodium expansion. A new constitutive model considering the surface boundary conditions with the exchange rate of sodium describes the carbon swelling and short-term creep. Modeling of the diffusional long-term creep in grains under loading after binder phase sodium saturation is also described. Validation of the proposed model through correlation of theoretical results and experimental data for the sodium concentration, sodium expansion and creep strain is performed. Practical recommendations on how to extend the model to full-scale reduction cells are formulated.

3:40 PM Break

3:55 PM
Influence of Internal Cathode Structure on Behavior During Electrolysis. Part I: Properties of Graphitic and Graphitized Materials: *Frank Hiltmann*[1]; Pretesh M. Patel[2]; Margaret Hyland[2]; [1]SGL Carbon GmbH, Griesheim Plant, Stroofstrasse 27, 65933 Frankfurt Germany; [2]University of Auckland, Dept. of Cheml. & Matls. Engrg., PB 92019, Auckland New Zealand

The internal structure of cathode blocks used in modern aluminium smelting cells will determine their physical, mechanical and operating characteristics. A comprehensive study was undertaken to determine the effect changes in internal structure have on graphitized and graphitic cathodes. Pronounced differences in internal structure were achieved by extreme variation of cathode formulations in lab scale thus allowing characteristics such as porosity and grain orientation to be manipulated. Standard properties such as Young's modulus, electrical resistivity, coefficient of thermal expansion, flexural and compressive strength were measured and the variables most affecting these properties evaluated. Results showed that - for the applied range of formulations - graphitic cathode specimens had superior mechanical properties to graphitized ones, with grain orientation having a significant effect on properties. This is attributed to greater packing efficiency and preferred grain orientation, thus reducing porosity and subsequently improving properties.

4:20 PM
Influence of Internal Cathode Structure on Behavior During Electrolysis. Part II: Porosity and Wear Mechanisms in Graphitized Cathode Materials: *Pretesh M. Patel*[1]; Margaret Hyland[1]; Frank Hiltmann[2]; [1]University of Auckland, Dept. of Cheml. & Matls. Engrg., PB 92019, Auckland New Zealand; [2]SGL Carbon GmbH, Griesheim Plant, Stroofstrasse 27, 65933 Frankfurt Germany

Overall cathode wear in aluminium reduction cells is due to a combination of physical, chemical and electrochemical processes acting simultaneously on cathode blocks during operation. Due to advances in technology graphitized cathode blocks have been more extensively used in the aluminium smelting industry. However, technology progress has also seen the use of high excess AlF3 concentrations and high current densities during electrolysis. These two conditions have been linked to an increase in electrochemical attack on cathode blocks. Research conducted has looked at the chemical and electrochemical wear occurring during lab-scale electrolysis on graphitized cathode samples. Emphasis was placed on the wear mechanisms such as Al4C3 formation within the pores of the cathode sample. During electrolysis pores within the cathode will fill with bath and therefore promote electrolytic sub-surface wear of cathodes. Total porosity and pore-size distributions of cathode blocks will therefore play an important role in cathode wear.

4:45 PM
A Study on the Fundamentals of Pothole Formation: *Eng Fui Siew*[1]; Mark P. Taylor[3]; Toni Ireland-Hay[2]; Gretta Theobald Stephens[2]; John J.J. Chen[1]; [1]University of Auckland, Cheml. & Matls. Engrg. Dept., PB 92019, Auckland New Zealand; [2]Comalco Research and Technical Support, 15 Edgars Rd., Thomastown, VIC 3074 Australia; [3]University of Auckland, Light Metals Rsch. Ctr., PB 92019, Auckland New Zealand

Potholing is a localised and rapid type of erosion through the carbon cathode. It only takes a single pothole to cause a reduction cell failure if the eroded hole is deep enough for the molten aluminium to come in contact with a collector bar. The contact between the molten metal and collector bar allows iron to be dissolved into the molten aluminium, thus contaminating the metal produced. This form of cathode wear is one of the predominant failure modes for aluminium reduction cells. If a better understanding of the contributing factors to the initiation and propagation of potholes can be achieved, then actions may be taken to prevent or reduce their occurrence. This paper discusses the presently held beliefs and hypotheses behind the formation of potholes, compares them to plant data and introduces other possible pothole formation theories.

Cast Shop Technology: DC Casting: Microstructure and Hot Tearing

Sponsored by: Light Metals Division, LMD-Aluminum Committee
Program Organizers: Gerd Ulrich Gruen, Hydro Aluminium AS, Bonn 53117 Germany; Corleen Chesonis, Alcoa Inc., Alcoa Technical Center, Alcoa Center, PA 15069 USA; Halvor Kvande, Norsk Hydro ASA, Oslo N-0240 Norway

Wednesday PM Room: 2001
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Laurens Katgerman, Delft University, Netherlands Inst. for Metals Rsch., Delft 2628 AL The Netherlands; Bjørn-Rune Henriksen, Elkem Aluminium, Rsch., Kristiansand 4675 Norway

2:00 PM
Solidification Studies of 6XXX Alloys With Different Mg and Si Contents: Hu Jin[1]; Majed Jaradeh[1]; *Torbjörn Carlberg*[1]; [1]Mid Sweden University, Engrg., Physics & Math., Holmgatan 10, Sundsvall 85170 Sweden

In choosing alloys for structural applications, a trade off between strength of the material and extrudability is made. A trend is that higher contents of Si than of Mg becomes more common, as this type of alloys tend to give an optimum combination of the mentioned properties. However, in the cast house the experience is that such alloys are more sensitive to surface defects, and thus more difficult to cast than alloys with balanced content of Si and Mg. It is therefore of interest to increase the knowledge of the solidification behaviour of these type of alloys. Directional solidification studies, simulating billet casting, have been made off alloys with balanced and not balanced Mg and Si additions, and with different alloying levels ranging from 6063 to 6082. Effects of growth rate, grain refinement, temperature gradient and composition on structure formation have been investigated.

2:25 PM
Thermo-Inelastic Simulation of Butt Curl Phenomena During Aluminum DC Casting: *Nobuhito Ishikawa*[1]; [1]Furukawa-Sky Aluminum Corp., Melting & Casting Tech. Sec., Techl. Rsch. Div., 21-1 Kurome, Mikuni-cho, Sakai-gun, Fukui-pref. 913-8588 Japan

In an aluminum DC casting, butt curl phenomena are recognized at the short side of its bottom region and they are prone to decrease the productivity through fatal defects such as hot cracking or metal bleeding. In order to evaluate the mechanism of butt curl growth, a thermo-mechanical finite element model has been developed, in which thermally induced strains and stresses associated with solidification are simulated using an elasto-plastic constitutive equation based on an isotropic hardening rule and the Mises yield condition. Comparison of butt curls shows a good agreement between calculations and measurements within tolerance of?\@?}20%. As a driving force of butt curl, a torque moment due to tensile stresses distribution along a mushy region makes the solidified bottom shell bent rapidly when the whole slab surface is covered with secondary coolant.

2:50 PM
The Investigation into Kinked Sheet Ingot Butts at an Alcan Casthouse: Clark Weaver[1]; Yves Caron[2]; Joseph Langlais[2]; Marco Biagioni[3]; *Jean-Claude Pomerleau*[3]; [1]Alcan Primary Metal Group, 1955 Mellon Blvd., Jonquière, QC G7S 4K8 Canada; [2]International Limited, 1955 Mellon Blvd., Jonquière, QC G7S 4K8 Canada; [3]Alcan Primary Metal Group, 1 Smelter Site Rd., Kitimat, BC V8C 2H2 Canada

Sheet ingots that are subsequently to be hot rolled into coils have to meet rather stringent specifications regarding their cross sectional shape and their straightness. The cross sectional shape is fixed by the mould contour and the casting speed for any given alloy and this subject has been the object of many papers in the past. The ingot straightness (i.e. the absence of longitudinal or lateral bow and twist) is dependant on several factors such as casting machine alignment, bottom block condition and starting practices, just to name a few. A rather unique problem of occasional kinked sheet ingot butts was identified in one of Alcan's sheet ingot casting centers about a year ago. This paper describes the methodology that was used to eliminate possible causes as well as the surprising results obtained via a series of short test casts done on the production machine. Upon further investigation, the mechanism causing the kinked ingots was found to exist at many of the other Alcan sheet casting centers. A simple solution was proposed, tested and confirmed as a way to prevent kinking in the bottom butt region of sheet ingots.

3:15 PM Break

3:25 PM
Integrated 3D Model to Simulate Solidification and Predict Hot Cracking: *Zhengdong Long*[1]; Qingyou Han[2]; Srinath Viswanathan[3]; Shridas Ningileri[4]; Subodh Das[4]; Kazunori Kuwana[5]; Mohamed Hassan[5]; Marwan Khraisheh[5]; Adrian S. Sabau[2]; Kozo Saito[5]; [1]University of Kentucky, Ctr. for Al Tech., 1505 Bull Lea Rd., Lexington, KY 40511 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN USA; [3]Sandia National Laboratories, Matls. & Process Scis. Ctr., Albuquerque, NM 87185-0889 USA; [4]Secat, Inc., 1505 Bull Lea Rd., Lexington, KY 40511 USA; [5]University of Kentucky, Dept. of Mechl. Engrg., Lexington, KY 40506-0108 USA

An integrated 3D Direct Chill (DC) casting model was used to simulate the heat transfer, fluid flow, solidification, and thermal stress during casting. Temperature measurements were performed in an industrial casting facility to setup and validate the model. The key features such as heat transfer between cooling water and the ingot surface as a function of surface temperature, cooling water flow rate, air gaps caused by mold and bottom block design were also coupled into the model. An elasto-viscoplastic constitutive model, which was determined based on mechanical testing, was used to calculate the evolution of stress during casting. The stress evolution was compared at various locations and correlated with physical phenomena associated with the casting process. An Ingot Cracking Index, which represents the ingot cracking propensity, was established based on the ratio of stress to strength. The Index calculation results were consistent with cracking observations in industrial casting practice.

3:50 PM
Implementation of a Strain Based Hot Tearing Criterion in Direct Chill Cast Aluminum Ingots: *Andre B. Phillion*[1]; Steve L. Cockcroft[1]; Daan M. Maijer[1]; Mary A. Wells[1]; [1]University of British Columbia, Dept. of Matls. Engrg., Frank Forward Bldg., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

Hot tearing in D.C. ingot castings has been investigated using a strain based hot tearing criterion, implemented into a three dimensional coupled thermal - stress finite element process model. In this presentation, the strain predictions in two different casting simulations will be discussed, as the strain fields from one casting recipe clearly show a high accumulation of tensile strain during solidification on the rolling face, just above the ingot lip. Finally, a comparison of the predicted plastic strain and mushy zone ductility data will be shown. In the critical region just above the ingot lip, the plastic strain accumulated during solidification exceeds the ductility limit at a temperature of about 575°C. Both further up the ingot, and out towards the edge of the rolling face, the accumulated strain was less than the ductility limit.

4:15 PM
Hot Tearing of Aluminium - Copper Alloys: *David Michael Viano*[1]; [1]University of Queensland, Div. of Matls., Sch. of Engrg., St. Lucia, Queensland 4072 Australia

For many aluminium alloys, hot tearing susceptibility follows a lambda curve relationship when hot tearing severity is plotted as a function of solute content. In the past, there has been some difficulty quantifying hot tearing. Traditional methods rely upon measuring electrical resistivity or the number and/or length of cracks in tests such as the ring test. In this experimental program, a hot tear test rig was used. This device measures the load imposed on the mushy zone during

solidification. It was found that the load recorded at completion of solidification (i.e. the solidus) was a good indicator of hot tearing susceptibility. The load measured at the solidus of a range of binary Al-Cu alloys is compared with published results from other researchers. It is found that the results from the hot tear rig are reproducible and correlate well with those obtained by other experimental methods.

Characterization of Minerals, Metals and Materials: Materials Preparation and Characterization

Sponsored by: Extraction & Processing Division, EPD-Materials Characterization Committee
Program Organizers: Tzong T. Chen, Natural Resources Canada, CANMET, Ottawa, Ontario K1A 0G1 Canada; Ann M. Hagni, Construction Technology Laboratories, Inc., Microscopy Group, Skokie, IL 60077 USA; J. Y. Hwang, Michigan Technological University, Institute of Materials Processing, Houghton, MI 49931-1295 USA

Wednesday PM Room: 2010
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: James J.Y. Hwang, Michigan Technological University, Inst. of Matls. Procg., Houghton, MI 49931-1295 USA; Ann M. Hagni, Construction Technology Laboratories Inc., Microscopy Grp., Skokie, IL 60077 USA

2:00 PM
Elastic Properties of FeGa and FeGaAl Alloys with Resonance Ultrasound Spectroscopy: *Pinai Mungsantisuk*[1]; Sivaraman Guruswamy[1]; [1]University of Utah, Metallurgl. Engrg., 135 S., 1460 E., Rm. 412, Salt Lake City, UT 84112 USA

Resonance Ultrasound Spectroscopy is a measurement technique using absorption of sound waves at the natural resonance frequencies of a material body to determine elastic properties. In this work, the elastic properties of Fe-x at.% Ga and Fe-(20-x) at.% Ga-x at.% Al polycrystalline alloys were evaluated. The samples used had parallelepiped shape. The absorption spectra of FeGa and FeGaAl alloys obtained using a Dynamic resonance modulus system over a specific frequency range were analyzed assuming the material to be isotropic. The elastic constant values, C11 and C44, were obtained from which Young's modulus and shear modulus values were determined. The Young's modulus obtained from FeGa and FeGaAl alloys were in the range of 110 to 170 GPa are much greater than those obtained from Terfenol-D alloys. The paper examines the trend in elastic property variation with changes in Ga and Al content. Work supported by NSF-DMR Grant #0241603.

2:25 PM
Lattice Parameter Determinations of Potassium Nitrate (KNO_3)-Ammonium Nitrate (NH_4NO_3) Solid Solutions: *Wen-Ming Chien*[1]; Dhanesh Chandra[1]; Jennifer Franklin[1]; Claudia J. Rawn[2]; Abdel K. Helmy[3]; [1]University of Nevada, Metallurgl. & Matls. Engrg., MS 388, Reno, NV 89557 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6064 USA; [3]Special Devices Inc., 14370 White Sage Rd., Moorpark, CA 93021 USA

The lattice parameters of the low and high temperature phase of KNO_3-rich (in NH_4NO_3) solid solutions have been determined by the X-ray diffraction method. The low temperature single KNO_3 phase (KN II) are from 92%-100% KNO_3 in NH_4NO_3 composition range and from room temperature to 393 K showing in X-ray diffraction patterns. The high temperature KNO_3 phase (KN I) showed very broad composition range between 20% to 100% KNO_3. The lattice parameters of KNO_3-rich (KN II and KN I) solid solutions have been calculated at different temperature range. The volumes of orthorhombic KN II phase decrease from 0.3218(4) to 0.3195(3) nm^3 at the room temperature as the compositions increase from 92% to 100%KNO_3. The lattice constants of the hexagonal KN I phase show that there is no significant change in a-direction when the temperature increases. Detail X-ray results and lattice expansion equations during heating will be presented.

2:50 PM
An EPR Characterization of Vanadium in CaO and Na2O Based Al2O3-SiO2 Glasses: *Humera Farah*[1]; [1]GIK Institute of Engineering Sciences and Technology, Faculty of Metall. & Matls. Engrg., Topi, District Swabi, N.F.W.P. Pakistan

The relationship between glass composition and local structure was examined by Electron Paramagnetic Resonance (EPR) analysis of vanadium (IV) in CaO and Na_2O based Al_2O_3-SiO_2 glasses. The characteristic EPR specrtrum of vanadium (IV) was affected with change in glass composition, equilibrium oxygen partial pressures and melting temperature. From the available previous reports and current study, it seems that a close relationship exists between octahedral and tetrahedral vanadium, which depends upon temperature. The results are important to understanding of vanadium behavior as a candidate in Al-V-Si BMGs and their nano composites.

3:15 PM
Variation in Poisson's Ratio with Other Elastic Constants: An Attempt Towards Rationalization of Elastic Constants for Isotropic Solid Materials: *Anish Kumar*[1]; T. Jayakumar[1]; Baldev Raj[1]; Kalyan K. Ray[2]; [1]Indira Gandhi Centre for Atomic Research, Div. for PIE & NDT Dvlp., Kalpakkam, TamilNadu 603102 India; [2]Indian Institute of Kharagpur, Dept. of Metallurgl. & Matls. Engrg., Kharagpur, W. Bengal 721302 India

The polycrystalline isotropic materials are characterized by only two independent elastic constants. Hence, identification of any new relationship between two independent elastic constants would reduce the number of required independent elastic constants to one. In this direction, an attempt is made to study the variation in Poisson's ratio with other elastic constants using the experimental data generated by the authors and also that collected from the literature for various isotropic solid materials, such as pure elements, ceramics, polymers and intermetallics. The analysis revealed that Poisson's ratio decreases with increase in other elastic constants and a linear correlation is obtained between Poisson's ratio and ultrasonic shear wave velocity. It is also deduced that shear wave velocity is a better parameter for microstructural characterization as compared to longitudinal wave velocity. These observations reveal the possibility for rationalization of elastic constants at least for a group of alloy systems with different microstructural conditions.

3:40 PM Break

3:50 PM
Thermodynamic Analysis on Synthesis of Fibrous Ni-Co Alloy Powder Precursors with Coprecipitation Process: *Zhan Jing*[1]; *Zhang Chuan Fu*[1]; Wu Jian Hui[1]; Masafumi Maeda[2]; Ryoichi Yamamoto[2]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Changsha, Hunan 410083 China; [2]University of Tokyo, Dept. Matls. & Environment, Inst. of Industrial Sci., Tokyo Japan

The mathematics model of Ni(•)-Co(•)-C2O4(2-)-NH3?H2O-H2O of thermodynamic equilibrium system has been developed theoretically according to the law of conservation of mass and the law of simultaneous equilibrium, and the logarithm concentration-pH (log[Me2+]T-pH) diagrams of this system have been made. The effect of ligand and pH value was studied. Two issues in coprecipitation route to synthesize fibrous nickel-cobalt alloy precursor powders, composition and morphology which are a first priority, are addressed based on thermodynamic analysis and experiments. The results show that suitable pH value range of coprecipitation of nickel ions and cobalt ions in theory can be obtained to maintain fibrious, excellent compositional homogeneity and stoichiometry for in coprecipitation products. Experimental demonstration is also carried out.

4:10 PM
Synthesis and Characterization of Fibrous Ni-Co Alloy Precursor Particles by Modified Coprecipitation Method: Zhang Chuan Fu[1]; *Zhan Jing*[1]; Wu Jian Hui[1]; Masafumi Maeda[2]; Ryoichi Yamamoto[2]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Changsha, Hunan 410083 China; [2]University of Tokyo, Dept. Matls. & Environment, Inst. of Industrial Sci., Tokyo, Tokyo Japan

Homogeneous solid-solution oxalates of Ni2+ and Co2+ ions were synthesized by modified co-precipitation method and the composition and morphology of fibrous solid-solution oxalates precursor were characterized by XRD, IR, DTA/TGA and SEM analysis. The effects of feeding methods, pH values, precipitation temperature, reactant concentration, addition surfactant, alcohol washing and drying process on the morphology and dispersion of the precursor were investigated in detail. The experimental results showed that the co-precipitated powders have characteristics that are different from those of the mechanical mixtures with the same stoichiometry. Based on the observations of precursor growth and SEM morphology of the precursor, the oriented attachment was proposed for the well-aligned growth of the fibrous Ni-Co alloy precursor particles.

4:30 PM
Preparation and Characterization of Fibrous Ni-Co Alloy Powders by Thermal Decomposition of Solid Solutions of Complex Ni-Co Oxalates: Zhang Chuan Fu[1]; *Zhan Jing*[1]; Wu Jian Hui[1]; Masafumi

Maeda[2]; Ryoichi Yamamoto[2]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Changsha, Hunan 410083 China; [2]University of Tokyo, Dept. Matls. & Environment, Inst. of Industl. Sci., Tokyo Japan

Synthesis of fibrous Ni-Co alloy powders was achieved by thermal decomposition of solid solutions of complex Ni-Co oxalates precursor obtained via modified coprecipitation method among intimate mixing solution of NiCl2.6H2O, CoCl2.6H2O and H2C2O4.2H2O with surfactant PVP and organic solvent A. Scan electron microscopy(SEM), X-ray diffraction(XRD), X-Ray photoelectron spectroscopy (XPS), energy X-ray analyses(EDX) were used to characterize the structure features and chemical compositions of the as-prepared fibres. The influences of pyrolytic conditions, including temperature, time, the flow rate of N2+H2, and the heating rate, on the morphology, average size and specific surface area of the Ni-Co alloy powders were investigated. It is found that a trend of the mutual alloying of nickel and cobalt: the formation of perfect solid solution for any compositions NixCo100-x was indicated and corresponding NixCo100-x alloys with fcc phase can be obtained under the optimal conditions.

Computational Thermodynamics and Phase Transformations: Thermodynamic Models and Databases

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS)

Program Organizers: Corbett C. Battaile, Sandia National Laboratories, Materials and Process Modeling Department, Albuquerque, NM 87185-1411 USA; Christopher Mark Wolverton, Ford Motor Company, Scientific Research Laboratory, Dearborn, MI 48121-2053 USA

Wednesday PM Room: 3005
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Moneesh Upmanyu, Colorado School of Mines, Matls. Sci. Prog., Div. of Engrg., Golden, CO 80401 USA

2:00 PM
Some Issues on Integration of First-Principles Calculations and CALPHAD Modeling: *Zi-Kui Liu*[1]; [1]Pennsylvania State University, Dept. of Matls. Sci. & Engrg., Univ. Park, PA 16802 USA

CALPHAD modeling has become a mature technique in developing thermodynamic databases of multicomponent systems. It has also been extended to the development of other databases such as atomic mobility and lattice parameters. In the CALPHAD modeling of thermodynamics, the modeling of Gibbs energy of individual phases and the coupling of phase equilibria and thermochemistry are the key in developing internally consistent thermodynamic descriptions of multicomponent materials with sound fundamentals and predictive power because these two sets of data are deduced from the Gibbs energy of individual phases under given constraints. One issue in CALPHAD modeling is the lack of experimental data, particularly for new materials. Experimentally, it is relatively easier to obtain phase equilibrium data in comparison with thermochemical data. On the other hand, first-principles calculations predict thermochemical data better than phase equilibrium data. More and more researchers are using enthalpy of formation from first-principles calculations. In this presentation, the recent research activities at our Phases Research Lab at Penn State will be presented with the following issues addressed. [1]Calculations of enthalpy of mixing in phases with solubility ranges using the special quasirandom structures (SQS). [2]Structure stability related to the SQS calculations. [3]Efficient route in obtaining entropy of formation and entropy of mixing.

2:20 PM
Utilizing Crystal Structure Correlations for Structure Prediction: Kevin Tibbetts[1]; *Chris Fischer*[1]; Dane Morgan[1]; Gerbrand Ceder[2]; [1]Massachusetts Institute of Technology, 77 Mass. Ave., Cambridge, MA 02139 USA; [2]University of Wisconsin, 1509 Univ. Ave., Madison, WI 53706 USA

When faced with the task of determining the stable structure types of a new alloy system, scientists have relied on physical intuition, quantum mechanics, model hamiltonians, and usually a healthy dose of past experience. This talk will present an approach that can combine the guidance of previous data and the accuracy of quantum mechanics. In this approach, the information from past experience, either experimental or computed, is captured in a mathematical framework of correlations, which then in turn can be used to direct accurate first principles computations. As a result, our model is independent of any specific hamiltonian or sophistication of physical understanding. When applied to data taken from a database of experimental information, the extracted structure-structure correlations can be used in a generic manner to predict the stable structure types for new alloy systems. The predictive capability and quality of our model will be shown to expedite the search for stable phases in binary alloy systems. These predictions are applicable to both computational and experimental communities investigating new or partially observed alloy systems. The information content of our model will be compared with the basic behavior of data contained within the experimental database used in this study.

2:40 PM
Modelling Precipitate Evolution in Aluminium Alloys During Complex Processing: *Joseph Douglas Robson*[1]; Nicolas Kamp[1]; [1]UMIST, Manchester Matls. Sci. Ctr., Grosvenor St., Manchester M1 7HS UK

A coupled microstructural modelling approach is described to predict the precipitate evolution in multicomponent industrial aluminium alloys during complex, non-isothermal, processing. The thermodynamic properties of the precipitate phases are calculated using JMatPro, a software package based on Calphad methods. This thermodynamic data is used as inputs to a numerical model for phase transformation kinetics based on classical theory and the Kampmann and Wagner methodology. This framework has been extended to include multiple precipitate phases, as well as both heterogeneous and homogeneous precipitation under non-isothermal conditions. This is demonstrated by predicting the microstructural evolution during welding of a 7xxx series aluminium alloy and comparing with experiment.

3:00 PM
Simulation of the Kinetics of Precipitation Reactions in Ferritic Steels: *Andre Schneider*[1]; Gerhard Inden[1]; [1]Max-Planck-Institut fuer Eisenforschung GmbH, Matls. Tech., Max-Planck-Str. 1, Duesseldorf 41199 Germany

Computer simulations of diffusion controlled phase transformations in model alloys of Fe-Cr-C, Fe-Cr-W-C, Fe-Cr-Si-C, and Fe-Cr-Co-V-C are presented. The compositions considered are typical for ferritic steels. The simulations are performed using the software DICTRA and the thermodynamic calculations of phase equilibria are performed using Thermo-Calc. The thermodynamic driving forces and the kinetics of diffusion controlled precipitation reactions of M23C6, M7C3, cementite and Laves-phase (Fe, Cr)2W are discussed. The simultaneous growth of stable and metastable phases is treated in a multi-cell approach. The results show remarkable effects on the growth kinetics due to the competition during simultaneous growth.

3:20 PM
Phase Equlibria Predictions in Nb-Silicide Based Composites: *Ying Yang*[1]; Bernard P. Bewlay[2]; M. R. Jackson[2]; Y. Austin Chang[1]; [1]University of Wisconsin, Matls. Sci. & Engrg., 1509 Univ. Ave., Madison, WI 53706 USA; [2]General Electric Global Research, Schenectady, NY 12301 USA

Nb-silicide based in-situ composites are promising materials for future high-temperature structural applications. Nb-Si alloys are typically alloyed with Hf, Ti, Cr, and Al to provide a balance of mechanical and environmental properties. In order to develop an improved understanding of phase equilibria in Nb-Hf-Ti-Si quaternary system, a methodology coupling the CALPHAD-type computational thermodynamics with experimental measurement of phase equilibria was used in this study. This paper first describes phase equilibria in the Hf-Ti-Si ternary system determined by experiments. This data was then used to develop a thermodynamic description of the Hf-Ti-Si system. A thermodynamic description of the Nb-Ti-Hf-Si quaternary system was then obtained by extrapolating the thermodynamic descriptions of Hf-Ti-Si, Nb-Hf-Ti, Nb-Ti-Si and Nb-Hf-Si into the quaternary space. The phase equilibria and solidification paths predicted from the currently obtained Nb-Ti-Hf-Si quaternary thermodynamic description are compared with experimental results.

3:40 PM
Incorporating Volume in Thermodynamic Databases: *Suzana G. Fries*[1]; Alan T. Dinsdale[2]; Bo Sundman[3]; [1]ACCESS e. V., Intzestrasse 5, Aachen D-52072 Germany; [2]NPL, Teddington, Middlesex TW11 0LW UK; [3]MSE, KTH, Div. of Computatl. Thermodynamics, Stockholm SE-10044 Sweden

Powerful multicomponent thermodynamic databases based on semi-empirical modelling of the Gibbs energies are able to describe other thermodynamic functions which are related to the Gibbs energy through its derivatives. Such properties include the Enthalpy, Entropy, Heat Capacity etc, as functions of composition and temperature for each phase present. In addition the same properties can be calculated for complex multiphase stable and metastable equilibria. One of the reasons for the success of the use of these databases lies in the standards adopted by Scientific Group Thermodata Europe (SGTE) for the temperature dependence of the Gibbs energy for the pure elements in their stable and metastable states. These values are used internationally and this ensures that the effort of the whole thermodynamic community in the production of data is universally consistent. Calculated results from use of these databases are also being provided as input to other applications involving kinetics eg phase transformation and microstructure simulations require information about other derivatives of the Gibbs energies such as Thermal Expansion and Bulk Modulus as functions of composition. A prerequisite for the incorporation of these and other derivatives of the Gibbs energy in the database is the definition of data for the molar volumes of the pure elements and other end-members and their variation with temperature and pressure. The use of experimental and theoretically calculated information as input for the construction of this set of standard reference data for the molar volumes of phases for a ternary system will be presented.

4:00 PM Break

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Comparison Between Calculations and Measurements of Precipitate Phases and Their Compositions in Cr-Mo Alloys: *J. M. Vitek*[1]; R. L. Klueh[1]; P. J. Maziasz[1]; [1]Oak Ridge National Laboratory, PO Box 2008, Bldg. 4508; MS 6096, Oak Ridge, TN 37831-6096 USA

Calculations of equilibrium phases and their compositions were made for several different Cr-Mo steel alloys that are of interest in high temperature applications. The predicted results were compared with experimental data for extremely long aging times (up to 75,000 h). The experimental data were based on extensive analytical electron microscopy results of extractions made from the aged materials. The comparisons were specifically made with respect to the types of precipitates found, their amounts, and their compositions. The predictions showed reasonably good agreement with experimental results, including the compositions of the precipitates. However, some discrepancies were noted and these will be described in detail. This research was sponsored by the Division of Materials Sciences and Engineering, and the Office of Science, Laboratory Technology Research Program, U. S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

4:35 PM
Phase Diagram Calculations of the NH4NO3-KNO3 Binary System: *Raja Chellappa*[1]; Dhanesh Chandra[1]; [1]University of Nevada, Metallurgl. & Matls. Engrg., MS 388, Reno, NV 89557 USA

The study of ammonium nitrate [AN: NH4NO3]-potassium nitrate [KN: KNO3] binary system is very important for practical applications such as automobile air bag gas generators. In this work, we will present the results of our phase diagram computations of the AN-KN system. The thermodynamic optimization was carried out using our experimental phase diagram as the basis utilizing the PARROT module of the Thermo-CalcTM software. The AN-KN binary system exhibits complex behavior with seven invariant equilibria: three peritectoids, two eutectoids, one congruent, and one eutectic transformation. Interaction parameters were considered only for the high temperature KN-rich phase (subregular solution) and liquid phase (regular solution). All the other phases were assumed to be ideal solutions. The optimized phase diagram under these assumptions is in good agreement with the experimentally determined phase diagram.

4:55 PM
A Thermodynamic Database for Thermal Energy Storage Materials: *Raja Chellappa*[1]; Dhanesh Chandra[1]; [1]University of Nevada, Metallurgl. & Matls. Engrg., MS 388, Reno, NV 89557 USA

Alcohol and amine derivatives of neopentane are potential candidates for thermal energy storage. Examples include Pentaerythritol [PE:C(CH2OH4)], 2-amino-2-methyl-1,3-propanediol [AMPL: (NH2)(CH3)C(CH2OH)2], Pentaglycerine [PG:(CH3)C(CH2OH)3], Neopentylglycol [NPG:(CH3)2C(CH2OH)2], and Tris(hydroxymethyl) aminomethane [TRIS:(NH2)C(CH2OH)3]. In recent times, we have published calculated phase diagrams of NPG-AMPL and PE-AMPL under the CALPHAD framework, based on our experimental phase diagram studies. Work is under progress on other binary systems such as PE-NPG, and TRIS-NPG. We will present the results of our phase diagram computations and discuss the evolution of a thermodynamic database for these organic compounds.

5:15 PM
Experimental Investigation and Thermodynamic Description of the Quaternary Organic Alloy System AMPD -DC -NPG -SCN: *Victor T. Witusiewicz*[1]; Laszlo Sturz[1]; Ulrike Hecht[1]; Stephan Rex[1]; [1]ACCESS e.V., Matls. & Processes, Intzestr. 5, Aachen D-52072 Germany

Transparent organic substances with low entropy of fusion (plastic crystals) for the past seventy years have been used as analogues to metals, because they allow for in situ observation of the microstructure evolving at the solid/liquid interface. Unfortunately, the number of such organic alloy systems is quite limited and experimental information concerning the phase diagrams and related thermodynamic data is scarce. Furthermore, no hints in literature on the existence of ternary or quaternary eutectic alloys formed by plastic crystals have been found. The search for new suitable organic alloys gained new drive within the frame of solidification studies addressing pattern formation in multicomponent, multiphase alloys. We have found experimentally that AMPD-DC-NPG-SCN system is suitable for such purposes. The temperature and enthalpy of phase transformations of organic alloys of the constituent binary and ternary systems of the quaternary AMPD-DC-NPG-SCN system were measured by means of differential scanning calorimetry. The quaternary phase diagram was assessed via the CALPHAD approach using Thermo-Calc by simultaneously optimizing the thermodynamic and phase equilibrium data measured in the present work. A good agreement between the experimental and calculated data for the phase diagram as well as for the thermochemical properties was achieved. Additionally unidirectional solidification of several eutectic alloys was performed in order to verify the nature of the eutectics. We have found the composition region for eutectic alloys that grow with three nonfacetted phases and result in very regular lamellar or rod like patterns. Note: AMPD is 2-amino-2-methyl-1,3-propanediol, CAS No [115-69-5]; DC is (D)camphor or (1R)-1,7,7-trimethylbiciclo[2,2,1]heptan-2-one, CAS No [464-49-3]; NPG is 2,2-dimethyl-1,3-propandiol, CAS No [126-30-7]; SCN is succinonitrile, CAS No [110-61-2].

Friction Stir Welding and Processing III: Microstructure and Texture

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Shaping and Forming Committee
Program Organizers: Kumar V. Jata, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH 45433 USA; Thomas J. Lienert, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Murray W. Mahoney, Rockwell Science Center, Thousand Oaks, CA 91360 USA; Rajiv S. Mishra, University of Missouri, Metallurgical Engineering, Rolla, MO 65409-0340 USA

Wednesday PM Room: Nob Hill C/D
February 16, 2005 Location: San Francisco Marriott

Session Chair: Rajiv S. Mishra, University of Missouri, Rolla, MO 65409-0340 USA

2:00 PM Invited
A Preliminary Investigation on the Microstructure and Properties of Friction Stir Welds in an Al7075/Al2O3/10% Reinforced Alloy: Luisa Marzoli[1]; *Jorge F. dos Santos*[1]; Rudolf Zettler[1]; Mario Volpone[2]; Enrico Rizzuto[3]; [1]GKSS Forschungszentrum, Inst. for Matls. Rsch., Joining Tech., Max-Planck-Str. 1, Geesthacht D-21502 Germany; [2]Fincantieri Cantieri Navali S.p.A, via Cipro, 11, Genova 16129 Italy; [3]University of Genova, DINAV, Ship Structl. Design, Via Montallegro, 1, Genova 16145 Italy

The main objectives of this study were to establish a friction stir welding (FSW) process parameters envelope for an Al7005 alloy reinforced with 10% of Al2O3 and to determine the microstructural features and mechanical properties of the welded joints produced with optimised process technology. Weld thermal cycles recorded during welding have shown that thermal stability conditions could be reached in all investigated welding conditions. Substantial differences have been observed between the microstructures in base material and stir zone. In the latter, a large amount of very small (4 μm and less), rounded particles, totally absent in the base material, has been observed. The tensile testing revealed joint efficiencies of 100% for the yield strength and of around 95% for the UTS. Failure in tensile testing always took place outside the stir zone. The fact that high quality joints could be

obtained in a wide range of parameter combinations indicates that the FSW process has the required robustness for industrial application to the investigated alloys.

2:20 PM
Microstructure Evolution During Friction Stir Welding of Commercial Aluminum Alloys: *Bertrand Huneau*[1]; Xavier Sauvage[2]; Surendar Marya[1]; Arnaud Poitou[1]; [1]Ecole Centrale de Nantes, GeM UMR CNRS 6183, 1, rue de la Noë; BP 92101, Nantes 44321 France; [2]Université de Rouen, Inst. des Matériaux de Rouen GPM UMR CNRS 6634, Ave. de l'univ., BP 12, Saint Etienne du Rouvray 76801 France

The friction stir welds result from frictional heating combined with intense plastic deformation of the material induced by the tool in the processed zone. The joints are free of defects and usually exhibit a fine recrystallised microstructure which make them strong and ductile. However, this microstructure dramatically depends on the rotation and translation speed of the tool, and on the diameter of the pin and of the shoulder. The aim of this work was to investigate thanks to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) the microstructure evolution during friction stir welding of commercial aluminum alloys (cold rolled 1050 and Al-Sc alloys). Grain morphology and size together with precipitates distributions through the welds provide new information about the material flow in the process zone. The influence of the Al2O3 oxide layer prior to the welding process was also investigated.

2:40 PM
Microstructural Details of Friction-Stir Weld Interfaces: *A. C. Somasekharan*[1]; L. E. Murr[1]; [1]University of Texas, Dept. of Metallurgl. & Matls. Engrg., 500 W. Univ. Ave., El Paso, TX 79968-0001 USA

This study dealt with the unique interfaces within the flow regimes observed in the friction-stir welding (FSW) of dissimilar magnesium (Mg) and aluminum (Al) alloys. Mg alloys AZ31B-H24 (hot-rolled), and AZ91D (semi-solid cast, primary solid fractions of ~3% and ~20%) were friction-stir welded to Al wrought alloys 6061-T6, and 5052-H34. Dissimilar Mg alloy welds included the FSW of AZ31B-H24 with AZ91D, and the dissimilar Al alloy welds included the FSW of 6061-T6 and 5052-H34. Optical microscopy, scanning electron microscopy, and transmission electron microscopy were some of the microscopy techniques used in the analysis of the welds and the weld-related interfaces. In the case of dissimilar systems A and B, the transition or interfacial regime from the base metal to the weld zone is characterized by a narrow recrystallized band of A grains, a mixture of A and B, and B grains making up the interfacial regime, especially on the advancing side. The transition from the interface regime to the base material is characterized by a zone of extreme plastic deformation where the grains are distorted, and this distortion decreases into the base material. The complex intercalated mixture of materials within the weld zone of Mg-Al welds is characterized by lamellar and intercalated recrystallized bands of either material, along with swirls and vortexes unique to dissimilar welds. The weld zones of dissimilar Mg alloy and Al alloy welds also show an intercalated mixing of materials, with the interfacial regime from the base material to the weld zone being a sharply transitioning zone of recrystallized grains on the advancing side and a rather diffuse region on the retreating side. An attempt has been made to understand how these interfacial or transition regimes accommodate solid-state flow of the welded materials.

3:00 PM
Microstructure Characteristics of Friction Stir Processed A1 7075 via Macroscopic Approach: *Bin Cai*[1]; Dongfang Huang[1]; Brent L. Adams[1]; Tracy W. Nelson[1]; [1]Brigham Young University, Mechl. Engrg., 435 CTB, Provo, UT 84602 USA

Friction stir welding (FSW) is evolving rapidly as a viable method for joining metals. Developing a deeper understanding of the affects of microstructure on post-stirring mechanical behavior is an important step towards controlling process parameters for optimal performance. However, the traditional vantage point of microscopic observation is on the transverse cross section which is incomplete. Here a new methodology, called the macroscopic or 3-dimensional approach, couples observations of microstructural characteristics with their corresponding geometrical locations. Data is recovered from the plan view in the microstructure, with spatial specificity in the transverse plane. Orientation imaging microscopy (OIM) is extensively employed; and the results via OIM are presented and discussed. Grain sizes at the center line decrease from top to bottom. Very fine grains were found in the weld nugget with prominent alignment. This observation indicates that grains in the nugget are not 3-dimensional equiaxial, but 2-dimensional.

3:20 PM Break

3:40 PM Invited
Analysis of Local Texture and Grain Boundary Structure in Friction Stir Welds of Magnesium Die Castings: *David P. Field*[1]; Naiyi Li[2]; [1]Washington State University, Mechl. & Matls. Engrg., Box 642920, Pullman, WA 99164-2920 USA; [2]Ford Motor Company, 2101 Village Rd., PO Box 2053, MD 3135, Dearborn, MI 48121 USA

Friction stir welding produces severe textural and microstructural gradients in metals. This structural inhomogeneity dominates local properties of the welds that are anisotropic in nature. Because of the limited number of slip systems available in Mg, these include virtually all mechanical and electrical properties of interest for use of a material in structural applications. Friction stir welds of AM60 Mg casting alloys were produced and structural gradients through the weld regions were characterized using electron backscatter diffraction, electron and optical microscopy. The gradients are shown to reflect the metal flow history occurred during welding to some extent. These inhomogeneous structures are discussed in relation to mechanical properties measured on both a local and bulk scale.

4:00 PM
TEM Analysis of Annealed and Thermo-Mechanically Processed Friction Stir Welds in Al-2195: Glen A. Stone[1]; *Anand B. Kaligotla*[1]; Stanley M. Howard[1]; William J. Arbegast[2]; [1]South Dakota School of Mines and Technology, Dept. of Matls. & Metallurgl. Engrg., Rapid City, SD 57701 USA; [2]South Dakota School of Mines and Technology, Advd. Matls. Procg. Ctr., Rapid City, SD 57701 USA

The objective of this work was to investigate the underlying substructural cause of abnormal grain growth (AGG) resulting from the friction stir welding (FSW) of Al-2195. Preliminary investigation has shown that the AGG is eliminated when the FSW Al-2195 is cold-rolled to at least 20%. This investigation continues the earlier work by comparing the substructures of as-FSW, FSW and initiated, and the 20% cold-rolled samples. Factors of interest included dislocation densities, second phase particles, grain substructure, and grain orientation. Samples for analysis were cut parallel to the rolling direction.

4:20 PM
Effect of FSW Parameters on the Evolution of Swirl Zone Grain Structure During Post-Weld Heat Treatment of Commercial Purity Aluminum: *Bala Radhakrishnan*[1]; Gorti Sarma[1]; Oleg Barabash[1]; Zhili Feng[1]; Stan A. David[1]; [1]Oak Ridge National Laboratory, Computer Sci. & Math., Bldg. 5600, MS 6008, Oak Ridge, TN 37831-6008 USA

The deformation substructures in the swirl zone of commercial purity aluminum as a function welding parameters are analyzed using orientation imaging microscopy to determine the microtexture, grain size distribution and grain misorientation distribution. The orientation scan data consisting of the Euler angle set for each site are used as input to a mesoscale substructure evolution model based on a Monte Carlo technique. The relative subgrain energy and subgrain mobility are expressed as a function of the boundary misorientation. The Monte Carlo simulations are used to predict whether normal or abnormal grin growth will occur during post-weld heat treatment of the substructure. The model predictions are compared with experimental measurements of grain structures obtained after annealing.

4:40 PM
Effect of Process Parameters on Mechanical Properties and Microstructure in Friction Stir Welded Thin Sheet 2024-T3: *Alpesh Khushalchand Shukla*[1]; William A. Baeslack[2]; [1]Rensselaer Polytechnic Institute, Matls. Sci. & Engrg., 110 8th St., Troy, NY 12180 USA; [2]Ohio State University, Coll. of Engrg., 142 Hitchcock Hall, 2070 Neil Ave., Columbus, OH 43210-1275 USA

Optimum welding parameters, viz. tool rotation, welding speed, plunge depth and tool design are established for friction stir welding 1mm thick 2024-T3 aluminum alloy by using design of experiments and the effect of these parameters on mechanical properties (hardness and tensile strength) and microstructure is studied. Hardness profiles indicate presence of two minima, one at the TMAZ/HAZ boundary and the other farther away in the HAZ. Average hardness at the TMAZ/HAZ boundary decreases with increase in heat input. Various regions of the welds are characterized by using Transmission Electron Microscopy and the presence, density and coarsening of S type precipitates are related to the changes in hardness across the weld. The hardness minima at the TMAZ/HAZ boundary and farther in the HAZ are found due to presence of overaged S precipitates and dissolution of GPB zones respectively. The hardness peak in the HAZ is found to be due to the presence of GBPII zones.

5:00 PM
Root Flaws of Friction Stir Welds - An Electron Microscopy Study: *Tamara Vugrin*[1]; Martin Schmücker[1]; Günter Staniek[1]; Claudio Dalle Donne[1]; [1]German Aerospace Center, Mech. of Matls. & Joining Tech., Linder Höhe, 51145 Köln Germany

Friction stir welding usually is a stable process that only sporadically produces flaws. In this work flaws in the root region of the weld were examined. These root flaws cause a only partial bonding of the welded material. The origin of the root flaws is not fully understood yet, but it has often been associated with oxides, that are always present on aluminium surfaces. In the present work the root flaws in aluminium friction stir welds were created intentionally by a preoxidation treatment. The surface oxide layer on the aluminium alloys was examined prior to friction stir welding by transmission electron microscopy. The friction stir welds were inspected non destructively by ultrasound. The root flaws were examined by optical-, scanning electron- and transmission electron microscopy. It was possible to trace the oxides that are forming the root flaws.

Frontiers in Thin Film Growth and Nanostructured Materials: A Symposium in Honor of Prof. Jagdish Narayan: Advanced Technology and Applications II

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Thin Films & Interfaces Committee
Program Organizers: N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA; Orin Wayne Holland, University of North Texas, Department of Physics, Denton, TX 76203 USA; Sungho Jin, University of California, Department of Materials Science, La Jolla, CA 92093 USA; Stephen J. Pennycook, Oak Ridge National Laboratory, Sold State Division, Oak Ridge, TN 37831 USA; Rajiv K. Singh, University of Texas, Austin, TX 78758-4455 USA

Wednesday PM Room: 3020
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Nuggehalli (Ravi) M. Ravindra, New Jersey Institute of Technology, Physics, Newark, NJ 07102 USA; John T. Prater, Army Research Office, Research Triangle Park, NC 27709-2211 USA

2:00 PM Invited
Analysis of Defects and Interfaces with Single Atom Sensitivity Through Aberration-Corrected Scanning Transmission Electron Microscopy: *Stephen J. Pennycook*[1]; Matthew F. Chisholm[1]; Andrew R. Lupini[1]; Albina Y. Borisevich[1]; Maria Varela[1]; Yiping Peng[1]; Klaus Van Benthem[1]; Naoya Shibata[2]; [1]Oak Ridge National Laboratory, Condensed Matter Scis. Div., 1 Bethel Valley Rd., Oak Ridge, TN 37831-6030 USA; [2]Universtiy of Tokyo, Sch. of Engrg., 2-11-16, Yayoi, Bunkyo-ku, Tokyo Japan

The ability to correct the major aberrations of the electron microscope is bringing enormous improvements not only in resolution but also in sensitivity. We have recently achieved a resolution of 0.06 nm in a Z-contrast image using a VG Microscopes 300 kV scanning transmission electron microscope (STEM) equipped with a Nion aberration corrector. The small beam size allows oxygen columns to be imaged within perovskite materials, and individual high atomic number dopant or impurity atoms to be imaged on and within specific columns of a crystal. In addition, a simultaneous, aberration corrected, conventional phase contrast image is available which shows oxygen columns with high contrast. Local electronic structure can be studied with electron energy loss spectroscopy, and single atom spectroscopy has been recently been achieved. Applications will be presented on the study of defects and interfaces in perovskite-based oxide materials, structural ceramics, nanomaterials and catalysts, showing how single atom sensitivity and the ability to image dislocation core structures leads to new insights into structure-property relations and has solved some longstanding problems. A previously unanticipated advantage of aberration correction is the reduced depth of focus. It is now possible to perform optical sectioning in the STEM simply be changing the focus of the beam. Single Hf atoms have been imaged in 3D in a Si/SiO2/HfO2 gate dielectric structure; they are not attached to the Si implying good passivation may be possible. In future generations of aberration-corrected STEM, 3D atomic resolution imaging may become routine.

2:30 PM Invited
Bonding Parameters of Cu Wafer Bonding for 3D Integration: *K. N. Chen*[1]; A. Fan[1]; C. S. Tan[1]; R. Reif[1]; [1]Massachusetts Institute of Technology, Microsys. Tech. Labs., 60 Vassar St., Rm. 39-623, Cambridge, MA 02139 USA

A reliable copper wafer bonding process condition, which provides strong bond at low bonding temperature with a short bonding duration, and does not affect the device structure, is desirable for future three-dimensional (3-D) applications. In this work, the effects of different process parameters on the quality of copper wafer bonding are summarized. Various parameters such as bonding pressure and Cu film thickness were studied to investigate the bonding strength. These bonding results were compared with other reported data. Thus, an overall view of Cu wafer bonding for different bonding parameters, including pressure, temperature, duration, copper thickness, clean techniques and anneal option, can be established. In addition, by meeting the process requirement of future IC process, the best bonding condition for three-dimensional (3-D) integration can be decided.

3:00 PM
Nanoengineering Approaches to Self-Assembled InAs Quantum Dot Laser Medium: *Serge Oktyabrsky*[1]; Vadim Tokranov[1]; Mathew Lamberti[1]; Gabriel Agnello[1]; Jobert Van Eisden[1]; Michael Yakimov[1]; [1]University at Albany - SUNY, Coll. of Nanoscale Sci. & Engrg., 251 Fuller Rd., Albany, NY 12203 USA

Interconnect 'bottleneck' in emerging IC's generated a need for alternative signal transmission solutions, such as optical technologies, in chip-level applications. To enhance performance parameters of chip-level active III-V photonic components, several emerging technologies are being developed: shape-engineered InAs quantum dot (QD) laser gain medium, digital alloys for precise control of semiconductor properties, novel "oxidation lift-off technology" for transfer of an optical device layer onto Si substrate. Technological issues and physics of self-assembled QDs with high gain, strong electron-hole coupling and high uniformity will be discussed. Beneficial properties of the developed QD medium are demonstrated by evaluation of laser diodes with unsurpassed thermal stability with a characteristic temperature of 380 K, high modal gain up to 31 cm^{-1} and by implementation of all-epitaxial QD vertical cavity laser. The QD structures are shown to withstand over two orders of magnitude higher defect density than quantum wells typically used in lasers.

3:30 PM Break

3:45 PM
Nanotechnology Related Materials Processing and Future Generation of Computing Systems: *Rajendra Singh*[1]; [1]Clemson University, Ctr. for Silicon Nanoelect. & Holcombe, Dept. of Electl. & Computer Engrg., Clemson, SC 29634 USA

The term nanotechnology has different meanings and expectations to different peoples. In this paper we have defined and examined what really is nanotechnology. Based on the use of fundamental knowledge of science and system level engineering and business knowledge that we know as of today, the role of materials processing of nanotechnology in the development of future generations of computing systems is described. In terms of materials processing techniques, the "top down" approach is already being used in the manufacturing of 90 nm feature size computing systems. The most advanced photomask manufacturing today is already exploiting the ability to manipulate material at atomic level and generate virtually defect free photomasks. However, there is no "bottom up" technique invented as of today that can be used directly in the manufacturing of future generation of computing systems. Future nanotechnology research should be directed in the directions that can lead to materials with very low defect random and systematic defects with lower manufacturing cost that is possible in current methods.

4:15 PM
Pulsed Laser Deposition for Novel Materials: Theory and Experiment: *Rajiv K. Singh*[1]; [1]University of Texas, Microelect. Rsch. Ctr., Austin, TX 78758 USA

Ever since the first successful application of the pulsed laser ablation technique in the deposition of high Tc superconductors in 1987, this method has become the technique of choice for the deposition of other materials such as oxide semiconductors, ferroelectrics, phosphors, colossal magnetoresistance (CMR), high dielectric constant and energy storage compounds. More recently, this method has been found to have excellent potential for the deposition of polymeric thin films for novel applications such a targeted drug delivery systems. The key factors which have led to the widespread use is its ability to maintain chemical stoichiometry, layer by layer thickness control, and relative simplicity of this method. The non-equilibrium nature of species gen-

erated during the laser irradiation process also plays a significant role in low temperature deposition and growth. This talk will focus on the unique fundamental aspects of the PLD process and its applicability to the next generation of oxide thin films and nanoscale materials.

4:45 PM
Recent Trends in Thin Films and Nanostructured Materials: *Ashutosh Tiwari*[1]; [1]North Carolina State University, Matls. Sci. & Engrg., Raleigh, NC 27695-7916 USA

In this talk we will present a brief overview of various research activities and projects currently undergoing in NSF Center of Advanced Materials & Smart Structures (NSF-CAMSS) at North Carolina State University under the director-ship of Prof. Jagdish Naryan. Before starting this talk I would first like to take an opportunity to say few words about Prof. Narayan. In his famous lecture William Arthur Ward said "The mediocre teacher tells. The good teacher explains. The superior teacher demonstrates. The great teacher inspires." Professor narayan belongs to the last category, he indeed inspires. I have had an opportunity to work under his supervision for several years, first as a research associate and then as a senior researcher. I have closely watched his dedication for research, extraordinary scientific vision and a desire to provide exceptional leadership to scientific community. Prof. Narayan has mentored hundreds of students, postdoctoral fellows and scientists, who are spread all over the world and are providing their valuable contribution to science. Prof Jagdish Narayan, known as "Jay" in scientific community, is an exceptional educationalist, outstanding researcher and visionary mentor. In his more than a quarter century long scientific career, he has made numerous outstanding contributions to almost every branch of Materials Science, Physics and Engineering. Prof Narayan has more than 800 papers and patents to his credit and he has written 12 books. His recent inventions in the field of nanostructured materials and Domain matching epitaxy-a new paradigm are attracting tremendous amount of scientific and technological attention. Currently under his direction we are working on several topics. However, the major focus of our research at NSF-CAMSS is on the novel methods of thin film processing, atomic scale structural characterization, physical property measurements and structure property correlation. We study variety of advanced materials and structures including nanostructured magnetic materials, thin film sensors, optically active wide bandgap materials, diluted magnetic semiconductors, perovskite oxides, ultraviolet/infrared detectors, novel diffusion barriers, magnetic superlattices exhibiting interlayer exchange coupling and low-field-magnetoresistance. Recently we have invented a new superlattice structure which exhibits highest magnetoresistance ever observed in any magnetic systems at low magnetic fields. I will discuss all of above mentioned topics in detail and at the end of the talk I will show some of our groundbreaking results related to nanostructured materials for which we have been granted the most recent United States Patent. Ref: J. Narayan and Ashutosh Tiwari "Methods of Forming Three-Dimensional Nanodot Arrays in a Matrix" United States Patent (June 24, 2004).

5:15 PM
Macro Self-Assembly Techniques: *Sudhakar Shet*[1]; Vishal R. Mehta[1]; Anthony T. Fiory[1]; Martin P. Lepselter[2]; Nuggehalli M. Ravindra[1]; [1]New Jersey Institute of Technology, Dept. of Physics, 161 Warren St., Univ. Hgts., Newark, NJ 07102 USA; [2]BTL Fellows Inc., 25 Sweetbriar RD., Summit, NJ 07901 USA

A review of various macro self-assembly techniques for integration of components to create powerful and complex microsystems is presented here. The current status, comparisons and limitations of the approaches to self-assembly methods are described. Applications of macro self-assembly techniques in defense, bio and aerospace industries are summarized.

5:45 PM
Bio-Inspired Designing and Fabrication of Advanced Coating Using Nanomaterials: *Wenping Jiang*[1]; Ajay P. Malshe[1]; [1]University of Arkansas, MMRL, Dept. of Mechl. Engrg., Fayetteville, AR 72701 USA

Nature is the master of organization as evidenced by the complex designs easily seen on the simplest structures and systems with priceless functionality, i.e., the unique nano materials and micro structures giving rise to the color of butterfly wings, super hydrophobic character to lotus leaf and tireless motion to flagella motors in E. Coli cells. The subject addressed in this manuscript is the realization of such structures and systems paralleling to Nature by understanding and controlling the size, shape, and position of nano materials based micro structures, while learning how to tailor nanomaterials with specific performance. We have used electrostatic spray process for self-assembly of nanoparticles to demonstrate surface morphology resembling lotus leaf. This morphology along with combination of hard and soft material phases make such coating an idea candidate for wear and advanced tribological applications.

Lead Free Solder Implementation: Reliability, Alloy Development, New Technology: Mechanical Properties of Lead-Free Solder Alloys and Solder Joints

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Mark A. Palmer, Kettering University, IMEB, Flint, MI 48504-4898 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Nikhilesh Chawla, Arizona State University, Department of Chemical and Materials Engineering, Ira A. Fulton School of Engineering, Tempe, AZ 85287-6006 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; Sung K. Kang, IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA; J. P. Lucas, Michigan State University, Chemical Engineering and Materials Science, East Lansing, MI 48824 USA; Laura J. Turbini, University of Toronto, Center for Microelectronic Assembly & Packaging, Toronto, ON M5S 3E4 Canada

Wednesday PM Room: 3014
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Nik Chawla, Arizona State University, Dept. of Cheml. & Matls. Engrg., Tempe, AZ 85287-6006 USA; Paul T. Vianco, Sandia National Laboratories, Albuquerque, NM 87185-0889 USA

2:00 PM Invited
Creep Behavior of Sn-Rich Solders at Bulk and Small-Length Scales: *Nik Chawla*[1]; Rajen S. Sidhu[1]; Matthew Kerr[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287-6006 USA

The creep behavior and microstructure of bulk solder and solder spheres will be reviewed in this talk. Results on Sn-Cu, Sn-Ag, Sn-Ag-Cu, and pure Sn, will be presented. It will be shown that the creep behavior of Sn-rich solders is very much dependent on: (a) nature and interface between second phase particles and the pure Sn- matrix, (b) Sn matrix microstructure, and (c) temperature. Changes in the creep stress exponent with increasing stress were observed and will be explained in terms of a threshold stress for creep. The activation energy for creep was also found to be temperature dependent. Scanning and transmission electron microcopy were used to characterize the as-reflowed microstructure, as well as to understand creep deformation mechanisms in the solder. Creep mechanisms will be presented and discussed in terms of the creep stress exponents and the solder microstructure.

2:30 PM
Creep Properties of Pb-Bearing and Pb-Free Composite Solder Joints Reinforced with Nano or Micron-Sized Ag Particles: *Fu Guo*[1]; Feng Tai[1]; Yanfu Yan[1]; Jianping Liu[1]; Yaowu Shi[1]; [1]Beijing University of Technology, Key Lab. of Advd. Functional Matls., Ministry of Educ. P.R.C., Coll. of Matls. Sci. & Engrg., 100 Ping Le Yuan, Chaoyang Dist., Beijing 100022 China

Solder alloys are typically subjected to harsh environments and are used at temperatures well above half of their melting points in degrees absolute. Microstructural evolution, recrystallization, superplasticity, creep, and creep-fatigue are operative under normal service conditions, among which creep is the most common and important micromechnical deformation phenomena. Composite approach has been used in an effort to improve the service performance of solder joint including service temperature capability through enhanced creep properties. Systematic creep study was carried out on Pb-bearing (Sn-37Pb) and Pb-free (Sn-3.5Ag and Sn-0.7Cu) solder joints reinforced with nano or micron-sized Ag particles at different temperature and stress levels. Various creep parameters and deformation mechanisms were overviewed and compared with non-composite solder joints. The effects of particle size on the creep properties of different base solder joint materials were also analyzed and extensively discussed.

2:50 PM
Using Different Test Techniques to Investigate the Bond Strength of Cu Wafer Bonding: *K. N. Chen*[1]; S. M. Chang[2]; L. C. Shen[2]; R. Reif[1]; [1]Massachusetts Institute of Technology, Microsys. Tech. Labs., 60 Vassar St., Rm. 39-623, Cambridge, MA 02139 USA; [2]Industrial Technology Research Institute, Elect. Rsch. & Service Organization, Pkgg. Process Tech. Div., APC, Chutung, Hsinchu 310 Taiwan

Direct Cu-to-Cu wafer bonding has been proposed as an attractive method for various applications such as three-dimensional (3-D) IC and package, opto-electronic integration, and micro-electro-mechanical system (MEMS). In order to successfully apply Cu-Cu bonding to these applications, strong bonding strength to support the structure and low bonding temperature to avoid the destruction of the device structure are both crucial. In this paper, to understand more details of the bonding strength of Cu wafer bonding with respect to different bonding temperature and bonding duration, both quantitative and qualitative approaches are proposed, respectively. These investigations include the tensile (or pull) test, the tape test, and the mechanical dicing test.

3:10 PM
High Temperature Hardness of Lead Free Solder: *Joo Won Lee*[1]; Zin H. Lee[1]; Hyuck M. Lee[1]; Sung K. Kang[2]; D. Y. Shih[2]; Paul Lauro[2]; [1]KAIST, Dept. of Matls. Sci. & Engrg., 373-1 Guseong-dong, Youseong-gu, Daejeon 305-338 Korea; [2]IBM T.J. Watson Reaserch Center, Yorktown Hgts., NY 10598 USA

Solder joints are occasionally operated at an elevated temperature in service. They also experience plastic deformation caused by temperature excursion and differences in thermal expansion coefficient. Deformed solders can go through a recovery and recrystallization process at an elevated temperature, which would alter their microstructure and mechanical properties. In this study, to predict the changes in mechanical properties of Pb-free solder joints at high temperatures, the micro-hardness of several Pb-free solders and a composite solder was measured as a function of temperature, deformation, and annealing condition. Solder alloys investigated include pure Sn, Sn-0.7%Cu, Sn-3.5%Ag, Sn-3.8%Ag-0.7%Cu, and Sn-Ag-Cu-Ni (composite). Solder pellets were cast at two cooling rates (0.4 and 7°C/s). The pellets were compressively deformed by 30% and annealed at 150°C for 2 days. The micro-hardness was measured as a function of temperature from 25 to 130°C.

3:30 PM Break

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Isothermal Fatigue of 95.5Sn-3.9Ag-0.6Cu Pb-Free Solder: *Paul T. Vianco*[1]; Mark Grazier[1]; Robert Wright[1]; Eric J. Cotts[2]; [1]Sandia National Laboratories, PO Box 5800, MS0889, Albuquerque, NM 87185-0889 USA; [2]SUNY Binghamton, Physics Dept, PO Box 6016, Binghamton, NY 13902-6016 USA

Isothermal fatigue behavior was investigated of the 95.5Sn-3.9Ag-0.6Cu (wt.%) solder, using shear strain controlled tests on 100 micron solder joints. The samples were tested at 25°C, 100°C, and 160°C. The shear strain ranges were 2.5, 5.0 and 10%. A six minute hold time was introduced at the stain limits and the extent of stress relaxation was documented. The apparent shear moduli were monitored at the loading and unloading terminal points of the cycle. Load drop was and strain energy (area in the hysteresis loop) were computed at benchmarked cycles. Fatigue crack growth occurred along the latter grain boundaries. In some cases, a path was generated in-situ for crack propagation by localized recrystallization of the Sn-rich matrix. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Dept. of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:00 PM
Bending Fatigue Test as a Reliability Evaluation Method for Solder Joints: *Choong-Un Kim*[1]; Jae-Yong Park[1]; Rajendra Kabade[1]; Viswanadam Puligandla[2]; Ted Carper[2]; [1]University of Texas, Matls. Sci. & Engrg., Arlington, TX 76019 USA; [2]Nokia Mobile Phone, Inc., Irving, TX USA

Concerns on the mechanical impact on the chip and package are growing as trends in the electronic industry are heading toward mobile environment. Frequent key pressing, bending due to the bolt fastening, and unexpected drop of the entire device can cause immediate and irrecoverable damage to the device. Consequently, reliability of the electronic device due to the mechanical impact is becoming critical and various test methods such as vibration, bending, and drop test are gaining importance. Among them, bending fatigue test is a promising candidate which provides controlled test environment and also enables us to extract meaningful material properties. This paper introduces the bending fatigue test as a test methodology of solder joint reliability against cyclic mechanical stress. Using a simplified package design for an idealistic test environment, the effectiveness of this methodology and considerations are discussed through the failure analysis.

4:20 PM
Optimization of Pb-Free Ball Grid Array Solder Sphere Reliability: *Daniel Cavasin*[1]; Arthur Huang[2]; [1]Advanced Micro Devices, PCSG, 5204 E. Ben White Blvd., MS: PCS-3, Austin, TX 78741 USA; [2]Advanced Semiconductor Engineering, Inc, 26 Chin 3rd Rd., Kaohsiung 811 Taiwan

A series of statistically-designed experiments were conducted to maximize the long-term reliability of Pb-free Plastic Ball Grid Array (PBGA) components. The primary focus of the experimentation was optimization of the solder sphere/substrate joint integrity. Both Sn-3.5Ag and Sn-4.0Ag-0.5Cu solder alloys were investigated, using substrates with electrolytic Ni/autocatalytic Au plated pads. Components were subject to JEDEC moisture sensitivity level 3 (MSL3)/260C preconditioning, followed by high temperature storage and temperature cycling stresses. Simulated electrical test (test socket insertion/removal) was conducted at each phase of the experimentation, followed by 100% inspection of the solder spheres. Primary response variables included shear strength and presence/absence of solder spheres. Results indicated that the thickness of the plated Au layer on the substrate surface played a key role in determining the components' ability to survive reliability stresses. The formation of complex ternary and quaternary intermetallic compounds in the area of the joint interface was characterized, and the package susceptibility to solder sphere separation due to brittle fracture was defined as a function of process conditions and materials.

4:40 PM
Effects of Strain Rates and Bi-Axial Stress Conditions on Plastic Yielding and Flow Stress of Sn3.8Ag0.7Cu Lead-Free Alloy: *Jin Liang*[1]; Nader Dariavach[1]; Gordon Barr[1]; [1]EMC, 176 South St., Hopkinton, MA 01748 USA

This study systemically investigates the rate-dependent mechanical properties of Sn3.8Ag0.7Cu lead-free alloy and Sn-Pb eutectic alloy under pure shearing and bi-axial stress conditions with thin-walled specimens using a servo-controlled tension-torsion material testing system. The pure shearing tests were conducted at strain rates between 10-6 /sec to 10-1 /sec. In additions, axial tensile and compressive stresses were superimposed onto the shearing samples to examine the effects of bi-axial stress conditions on the yielding and on post-yielding plastic flow of the solder alloys. Strain hardening is observed for the lead-free alloy under all the tested strain rates, while strain softening happens with Sn-Pb eutectic solder under low to moderate strain rates. Special tests were also conducted for sudden strain rates change, load drop and stress relaxation for the purpose to develop a visco-plasticity model to simulate time-depended multi-axial deformation and for damage and fatigue life prediction of real world solder interconnections.

5:00 PM
Evaluation of Solder-to-Chip Attachment, Wafer-Level Bumping Architectures: II. Performance in BHT, Cyclic Mechanical Bending and Temperature Cycling: Ian R. Harvey[1]; *Mark R. Larsen*[1]; David Turner[2]; Ian Doyle[3]; Jim Somers[3]; Jim Ortowski[4]; [1]University of Utah, Coll. of Engrg., 1495 E. 100 S., Kennecott Bldg., Rm. 101, Salt Lake City, UT 84112 USA; [2]Inovar, Inc., 1073 W. 1700 N., Logan, Utah 84321 USA; [3]Bourns Electronics, Microelect. Div., Mahon Industl. Park, Blackrock, Cork Ireland; [4]EDO Ceramics, 2645 S. 300 W., S. Salt Lake City, Utah 84115 USA

We have created a test chip to evaluate the relative tendency for alloy migration under BHT testing, as well as enable comparative thermomechanical performance and induced parasitic effects in standard TC testing and a customized cyclic bending fatigue test with a demonstrated history of reproducing cell phone field failure mechanisms. In this paper, we describe the BHT and failure analysis results indicating robust performance of the NEMI-std lead-free alloy, comparable to the eutectic alloy reference, and demonstrate thermomechanical reliability advantages of two system architectural design features, applicable to both eutectic and lead-free alloys: (1) use of narrow via architecture which acts as a compliant "cushion" under the bump, and (2) use of microvia-in-pad PCB designs.

5:20 PM
The Effect of Aging and Reflow on Shear Behavior of Sn-3.5Ag Lead Free Solder/Cu Joints: *R. S. Sidhu*[1]; X. Deng[1]; P. Johnson[1]; N. Chawla[1]; [1]Arizona State University, Dept. of Cheml. & Matls. Engrg., Fulton Sch. of Engrg., Tempe, AZ 85287-6006 USA

Mechanical behavior of lead free solder/Cu joints is sensitive to the reflow and aging process due to the relatively low melting tempera-

tures of solders and the high growth rate of intermetallics (Cu6Sn5 and Cu3Sn) that form between the solder and Cu substrate. In this study, the effects of reflow time, aging time, and aging temperature on the shear behavior of the Sn-3.5Ag solder/Cu system were investigated. Increasing reflow time changed the intermetallic thickness but not the solder microstructure, since the latter is controlled by cooling rate after reflow. Aging, on the other time, affected both the microstructure of solder and the thickness of the intermetallic layer. These important differences in microstructure significantly affected the strength dependence of the joints. The underlying fracture mechanisms will be discussed and coupled with microstructure-based finite element analysis.

Magnesium Technology 2005: Creep Resistant Magnesium Alloys and Welding-Joining

Sponsored by: Light Metals Division, International Magnesium Association, LMD-Magnesium Committee
Program Organizers: Ramaswami Neelameggham, US Magnesium LLC, Salt Lake City, UT 84116 USA; Howard I. Kaplan, US Magnesium LLC, Salt Lake City, UT 84116 USA

Wednesday PM Room: 2004
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Mihriban O. Pekguleryuz, McGill University, Montreal, Quebec H3A 2B2 Canada; Zi Ki Liu, Pennsylvania State University, State College, PA 16802-5006 USA

2:00 PM
Friction Stir Spot Welding of Mg-Alloys for Automotive Applications: Peter Su[1]; *Adrian Gerlich*[1]; Tom North[1]; Gabor Bendzsak[1]; [1]University of Toronto, Matls. Sci. & Engrg., 184 College St., Wallberg Bldg., Toronto, Ontario M5S3E4 Canada

This paper presents the detailed produced during friction stir spot welding of AZ91D, AM60 and AZ31 Mg alloys. The features of the friction stir spot welding process were delineated using a combination of data acquisition outputs and metallographic examination of completed joints. The peak temperature attained during FSW spot welding of AZ91D, AM60 and AZ91 base materials was very close to the melting temperature of the Mg-Al solid solution/Al12Mg17 eutectic (437ºC), and higher than the reported incipient melting temperature (421°C). Evidence of local liquid film formation is shown in FSW spot welded AZ31 material. Factors determining the tensile shear loads of FSW spot welds in AZ91D and AM60 material were investigated. Higher failure loads during overlap shear testing properties were produced when the projected bonded area immediately adjacent to the keyhole and the amount of mechanical energy delivered during the FSW spot welding operation increased.

2:20 PM
Surface Contamination on Magnesium Ingots: *Anne Kvithyld*[1]; Magdalena Zadrozna[2]; Sean Gaal[1]; Thorvald Abel Engh[1]; [1]Norwegian University of Science and Technology, Dept. of Matls. Tech., Alfred Getz vei 2, Trondheim 7491 Norway; [2]Warsaw University of Technology, Faculty of Matls. Sci. & Engrg., Woloska 141, Warsaw 02-507 Poland

Surface contamination present on magnesium ingots results in increased dross formation. The surface of the ingots primarily reacts with water and carbon dioxide, depending mainly on the humidity, temperature, cooling technique and the alloy of magnesium. Investigations were conducted on shavings from magnesium ingots. Impurities on the surface were studied in a thermo-gravimetric/differential thermal analysis (TG/DTA) furnace, and the evolved gases were measured using quadrupole mass spectrometer (MS). Mass loss curves show two peaks, at low and high temperatures, for pure Mg and AZ91D alloy. For AM20HR alloy only one peak at the higher temperature appears. The lowest total mass loss is obtained for AM20HR, while the highest was measured for pure Mg. The intensity of mass 44 was measured for carbon dioxide. This allowed the mass of the carbon dioxide produced during heating of the magnesium to be calculated, and by difference the quantity of water to be determined.

2:40 PM
Metallurgical Background to the Development of Creep Resistant Gravity Casting Alloys: *Boris Bronfin*[1]; Mark Katsir[1]; Oren Bar-Yosef[1]; Florian Moll[2]; Soehnke Schumann[2]; [1]Dead Sea Magnesium Ltd, Rsch. Div., PO Box 1195, Beer-Sheva 84111 Israel; [2]Volkswagen AG, Rsch., PO Box 1511, Wolfsburg D-38436 Germany

Magnesium alloys being the lightest structural materials, are very attractive in automotive and aerospace industries. New alloys are required that would resist the increasingly onerous operating environment and that would provide more complex components with increased lifetime and reduced maintenance cost. The desire to achive weight reduction of large powertrain components used by the automotive and aerospace industries has resulted in the development of new gravity casting alloys that provide a good combination of service properties and cost. The present paper addresses physical metallurgy principles that enabled to develop new alloys designated MRI201S, MRI202S and MRI203S. New alloys are designed for applications up to 250-300°C and have excelent mechanical properties, corrosion behavior and creep resistance in T6 condition. In addition, the paper will also highlight some practical applications that illustrate the capabilities of newly developed alloys.

3:00 PM
Solid Solution Effects on the Tensile Behaviour of Concentrated Mg-Zn Alloys: *Andrew Blake*[1]; Carlos H. Caceres[1]; [1]University of Queensland, Matls. Engrg., Sch. of Engrg., Brisbane, QLD 4072 Australia

Previous work has suggested that short-range order is responsible for the strengthening in concentrated Mg-Zn alloys. This added strengthening, above the random solid solution hardening observed in dilute alloys, is expected to affect the tensile behaviour of the concentrated alloys through its effects on secondary (prismatic and pyramidal) slip. Solid solution effects on the flow stress, strain hardening rate and ductility of polycrystalline magnesium zinc alloys, with zinc contents between 0 and 3 at.% have been studied. A constant grain size was obtained in all alloys by adding a small amount of Zr. The results are discussed in terms of possible solid solution softening and hardening effects on the different slip systems.

3:20 PM Break

3:35 PM
On the Microstructure and Properties of Friction Stir Welds in AZ31 and AZ61 Alloys: *Jorge F. dos Santos*[1]; Antonio C. Blanco[1]; Rudolf Zettler[1]; Surendar K. Marya[2]; [1]GKSS Forschungszentrum, Inst. for Matls. Rsch., Max-Planck-Str. 1, Joining Tech., Geesthacht D-21502 Germany; [2]Ecole Central Nantes, Welding Joining & Forming Processes, Nantes France

The increased use of Mg in the car manufacturing industry has raised questions on weldability aspects of Mg and its alloys. The Friction Stir Welding (FSW) has the advantage of achieving metallic bonding below the melting point of the base material avoiding metallurgical problems associated with the solidification process. The present study presents the results of a development programme carried out to investigate the response of alloys AZ31 and AZ61 to different FSW tool geometries and process parameters. Temperature development across the weld zone was monitored and the produced welds have been subjected to microstructural analysis and mechanical testing. Defect free welds have been produced with the optimised FSW-tool and parameters. The microstructure of the welded joint resulted in similar ductility and hardness levels as compared to the base material. The results also showed that tool geometry plays a fundamental role on the response of the investigated alloys of the FSW process.

3:55 PM
Effects of Alloying Element on Microstructure and High-Temperature Mechanical Properties of Mg-Al Alloys: *Kwang Seon Shin*[1]; Yeon Jun Chung[1]; [1]Seoul National University, Sch. of Matls. Sci. & Engrg., San 56-1 Shinrim-dong Kwanak-gu, Seoul 151-742 Korea

Magnesium alloys exhibit excellent properties such as high specific strength at room temperature, good damping characteristics and castability. Mg-Al alloys such as AM50, AM60 and AZ91 have been used extensively since these alloys exhibit superior die castability and a good balance of strength and ductility. However, the application temperature of these alloys is generally limited to about 100°C, above which a rapid degradation in mechanical properties was observed due to the presence of Mg17Al12. The poor high-temperature mechanical properties of the commercially available magnesium alloys have prevented their applications at elevated temperatures. In the present study, the effects of alloying elements on microstructure and high-temperature mechanical properties of Mg-Al alloys were examined. The specimens used in this study were die-cast on a 320ton cold chamber high-pressure die casting (HPDC) machine. Tensile and creep tests were performed and the microstructure was examined. It was found that the addition of alloying elements modified the precipitation behavior and improved the high-temperature mechanical properties of Mg-Al alloys.

4:15 PM
DaimlerChrysler Corporation High Temperature (Creep Resistant) Magnesium Alloy Development: *Randy S. Beals*[1]; [1]DaimlerChrysler Corp., 800 Chrysler Dr., Auburn Hills, MI 48326 USA

In the past few years several new magnesium alloys for high temperature applications have been developed. These alloys are typically based on rare earth and alkaline earth element additions to magnesium. Unfortunately, it is very difficult to achieve an adequate combination of properties (die castability, creep resistance, mechanical properties, fatigue resistance, corrosion performance and affordable cost) that allows an alloy to have cost effective performance. In previous studies it has been reported that current alloy systems either achieve a high level of creep resistance or acceptable die castability but never both. This study describes a research and development effort by DaimlerChrysler Corporation's Materials Engineering to arrive at a magnesium alloying system that delivers excellent creep resistance as well as excellent die castability at an affordable cost. This study compares the new alloy with an overview of the various magnesium alloy systems for use in elevated temperature applications (150-175°C).

4:35 PM
Creep Studies of MRI153 Magnesium Alloy Castings: *S. M. Zhu*[1]; B. L. Mordike[2]; J. F. Nie[1]; [1]Monash University, Sch. of Physics & Matls. Engrg., Victoria 3800 Australia; [2]Technical University of Clausthal, Dept. of Matls. Engrg. & Tech., Agricolastrasse 6, D-38678, Clausthal-Zellerfeld Germany

The microstructures and creep properties of three MRI153 alloy castings, die casting, squeeze casting and ingot casting, have been investigated and compared. The stress and temperature dependence of the minimum creep rate suggested that similar deformation mechanisms hold for the three castings. The stress dependence exhibited a transition from power-law creep at low stresses to power-law breakdown at high stresses. In the power-law regime, stress exponents of ~6 and activation energies close to that for lattice self-diffusion in magnesium were obtained. The squeeze-cast alloy showed the highest creep resistance in terms of minimum creep rate or rupture time, while the poorest creep resistance was observed in the die-cast alloy. The creep resistance of the three castings are discussed in terms of grain size, casting porosity and degree of solute supersaturation.

4:55 PM
An Electron Microscope Study of Intermetallic Phases in AZ91 Alloy Variants: *Takanori Sato*[1]; Barry L. Mordike[2]; Jian-Feng Nie[3]; Milo V. Kral[1]; [1]University of Canterbury, Mechl. Engrg., PO Box 4800, Christchurch New Zealand; [2]TU Clausthal, Inst. für Werkstoffkunde & Werkstoftechnik, Agricolastrasse 6, D-38678, Clausthal-Zellerfeld Germany; [3]Monash University, Sch. of Physics & Matls. Engrg., PO Box 69M, Clayton, Victoria 3800 Australia

The magnesium alloy AZ91 has been employed extensively due to its superior castability and mechanical properties at room temperature. New alloys based on AZ91 have been developed to improve creep properties by forming grain boundary and intragranular intermetallic phases via additions of elements such as Ca and Sr. Intermetallic phase stability and distribution are not well understood in these new alloys. In the present work, the various intermetallic phases in two high pressure die cast AZ91-type alloys were characterized using a combination of transmission electron microscopy, selected area and microbeam electron diffraction, scanning electron microscopy, electron backscatter diffraction pattern analysis and energy dispersive x-ray spectroscopy. The crystallographic identification, relative amounts and distributions of phases will be presented.

5:15 PM
Nd:YAG Laser Welding of Magnesium Alloy Castings: *Xinjin Cao*[1]; Min Xiao[1]; Mohammad Jahazi[1]; [1]Institute for Aerospace Research, Aeros. Mfg. Tech. Ctr., 5145 Decelles Ave., Montreal, Quebec H3T 2B2 Canada

Laser welding will become an important joining technique for magnesium alloys with their increasing applications in aerospace, aircraft, automotive, electronics and other industries due to low heat input, small heat affected zone, narrow fusion zone, high welding speed, low residual stress and distortion. The ongoing project on laser welding investigates the laser weldability of cast magnesium alloys and aims to develop a reliable welding and repair process for sand castings. This presentation will report on the progress made in the Aerospace Manufacturing Technology Center of the NRC Institute for Aerospace Research, in studies involving laser welding of Mg-4.2Zn-1.2Ce-0.7Zr (ZE41A-T5) alloy butt joints. The influence of some important processing parameters such as surface condition, defocusing distance, laser power, welding speed, joint gap and filler metal on the welding mode, macrostructure, microstructure, defect and mechanical property of the weld joints will be presented and discussed.

Materials Issues for Advanced Nuclear Systems: Materials for Nuclear Waste Storage

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Robert J. Hanrahan, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Sean M. McDeavitt, Argonne National Laboratory, Chemical Technology Division Materials Development Section, Argonne, IL 60439-4837 USA

Wednesday PM Room: 3012
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Raul B. Rebak, Lawrence Livermore National Laboratory, Matls., Livermore, CA 94550 USA; Robert J. Hanrahan, Los Alamos National Laboratory, ADWP, Los Alamos, NM 87544 USA

2:00 PM
Localized Corrosion Behavior of Alloy 22 Solution Annealed Welded Plates: *Robert A. Etien*[1]; Steven R. Gordon[1]; Gabriel O. Ilevbare[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

Alloy 22 (N06022) may be used in industrial service in the as-welded condition, that is, without prior solution annealing. In some instances, welded Alloy 22 parts may be solution annealed to relieve residual tensile stresses introduced during the welding process. After annealing, it might be necessary to remove the oxide film formed during the heat treatment, depending on the application. Therefore, it is important to determine the corrosion resistance of Alloy 22 in the as-welded condition compared with the annealed condition with and without the annealed oxide film. The crevice corrosion resistance of Alloy 22 (N06022) in these three metallurgical conditions was measured using a number of electrochemical techniques. Studied variables included electrolyte composition (chloride and nitrate ratio), temperature and applied potential.

2:25 PM
Corrosion Behavior of Welded Plates of Alloy 22 With Varying Heat Composition: David V. Fix[1]; Kenneth J. King[1]; John C. Estill[1]; *Raul B. Rebak*[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

The ASTM standard B 575 provides the requirements for the chemical composition of Nickel-Chromium-Molybdenum (Ni-Cr-Mo) alloys such as Alloy 22 (N06022) and Alloy 686 (N06686). The compositions of each element are given in a range; for example, the content of Mo is specified from 12.5 to 14.5 weight percent for Alloy 22 and from 15.0 to 17.0 weight percent for Alloy 686. It was important to determine how the corrosion rate of welded plates of Alloy 22 using Alloy 686 weld filler metal would change if heats of these alloys were prepared using several variations in the composition of the elements even though still in the range specified in B 575. Especially prepared seven heats of plate were welded with seven heats of wire. Immersion corrosion tests were conducted in a boiling solution of sulfuric acid plus ferric sulfate (ASTM G 28 A). The study also covers the effect of solution annealing on the corrosion rate of welded plates.

2:50 PM
Stress Corrosion Cracking of Cladding Materials: Ajit K. Roy[1]; *Unnikrishnan Valliyil*[2]; *Elumalai Govindaraj*[2]; [1]University of Nevada, Dept. of Mechl. Engrg., 4505 Maryland Pkwy., Box 454009, Las Vegas, NV 89154-4009 USA; [2]University of Nevada, Dept of Mechl. Engrg., 4248 Claymont St., Apt #1, Las Vegas, NV 89119 USA

Cladding is the primary structural barrier that prevents the release of radionuclides contained in the spent nuclear fuel (SNF). SNF cladding used in most commercial reactors in the United States is made of zirconium (Zr) alloys such as Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4). This paper is focused on the evaluation of stress corrosion cracking (SCC), hydrogen embrittlement (HE) and localized corrosion susceptibility of Zr-2 and Zr-4 in neutral and acidic solutions at 30, 60 and 90°C. Constant-load and slow-strain-rate (SSR) testing methods were used to evaluate the SCC and HE behavior of both alloys by using smooth and notched tensile specimens. Cyclic potentiodynamic polarization (CPP) technique was used to determine the localized corrosion susceptibility. The morphology of failure was analyzed by optical microscopy and scanning electron microscopy (SEM), respectively.

The SSR testing revealed enhanced ductility and reduced failure stresses with increasing temperature. Fractographic evaluations by SEM revealed dimpled microstructure.

3:15 PM Break

3:25 PM
Effect of Stress Mitigation on the Corrosion Behavior of Alloy 22: *Ahmet Yilmaz*[1]; David V. Fix[1]; John C. Estill[1]; Lana L. Wong[1]; Raul B. Rebak[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

Welding processes may introduce residual stresses in the parts that are joined together. A full solution annealing could eliminate these residual stresses. When annealing is not possible, stress minimization may be applied locally to reduce the level of tensile stresses in the outer layers. Tensile stress minimization techniques include low plasticity burnishing (LPB) and laser shock peening (LSP). It is important to determine if the applied stress mitigation process affects the corrosion resistance of the welded structure. Studies were carried out using welded plates of Alloy 22 (N06022). The corrosion behavior was compared using as welded plates with plates that were treated using LPB and LSP. Immersion tests were carried out in a boiling solution of sulfuric acid and ferric sulfate (ASTM G 28A). Also, cyclic potentiodynamic polarization tests (ASTM G 61) were used to determine the susceptibility to crevice corrosion in brines containing chloride and nitrate ions. Results show negligible effect of the surface treatment on the corrosion resistance of Alloy 22.

3:50 PM
Effect of Stress Mitigation on Precipitation Kinetics in Alloy 22 Welds: *Bassem S. El-Dasher*[1]; Sharon G. Torres[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

Understanding the phase stability of Alloy 22 (N06022) is important since the precipitation of tetrahedrally close-packed (TCP) phases over time has been known to adversely affect corrosion and mechanical properties. Prior observations have shown that these phases precipitate during the welding process. After welding, residual stresses due to the solidification and cooling from temperature remain. When the weld cannot be stress-relieved by solution annealing, the application of commercially available stress-mitigation processes such as low plasticity burnishing (LPB) and laser shock peening (LSP) may be used to produce near-surface compressive stresses. This study involved examination of cross-sectional samples of aged 1.25" thick welds of Alloy 22 plates using electron backscatter diffraction (EBSD) for TCP identification, and micrograph analysis for TCP quantification. Precipitation in the LSP treated weld was observed primarily in inter-dendritic regions, similar to that in the as-welded material. Precipitation in the LPB treated weld however was observed in both inter-dendritic as well as intra-dendritic regions.

4:15 PM
Effect of Heat Treated Oxide Film on the Corrosion Behavior of Ti Gr 7 in Fluoride Containing Solutions: *Tiangan Lian*[1]; Michael T. Whalen[1]; Lana L. Wong[1]; [1]Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94550 USA

Titanium Grade 7 (R52400) is a highly corrosion resistant alloy, mainly due to the spontaneous formation of a stable, protective and strongly adherent passive oxide film in presence of water and oxygen. One of the few environments that may hamper the stability of this oxide film are solutions containing fluoride ions. Welded components of titanium alloys may be used in the as fabricated conditions or either after stress relieving or solution annealing and air-cooling. The stress relief is generally performed at 1000°F (538°C) and the solution annealing at 1300°F (704°C), both for approximately 45 min. It was important to characterize the effect of the high temperature air formed oxide film on the corrosion resistance of R52400 in fluoride containing solutions and to compare the results with the behavior of non-heat treated material. Studied environmental variables included solution composition, temperature and applied potential.

Mechanical Behavior of Thin Films and Small Structures: Advanced Characterization Techniques

Sponsored by: Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS), MPMD-Nanomechanical Materials Behavior

Program Organizers: Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA; Brad L. Boyce, Sandia National Laboratories, Materials and Processes Sciences Center, Albuquerque, NM 87185 USA; Evan Ma, Johns Hopkins University, Department of Materials Science & Engineering, Baltimore, MD 21218 USA; Andrew Minor, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA 94720 USA; Christopher L. Muhlstein, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Judy A. Schneider, Mississippi State University, Department of Mechanical Engineering, Mississippi State, MS 39762 USA

Wednesday PM Room: 2024
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Andrew M. Minor, Lawrence Berkeley National Laboratory, Natl. Ctr. for Electron Microscopy, Berkeley, CA 94720 USA; Kevin J. Hemker, Johns Hopkins University, Dept. of Mechl. Engrg., Baltimore, MD 21218 USA

2:00 PM Invited
Characterisation of the Mechanical Properties of MEMS Devices Using Nanoscale Techniques: *Nicholas X. Randall*[1]; [1]CSM Instruments Inc., 197 First Ave., Needham, MA 02494 USA

This presentation will focus on recent developments in the localised characterisation of the mechanical properties of Microsystems and MEMS devices and structures. Conventional indentation techniques provide a highly powerful method for measuring the load and depth response of bulk and coated materials, but can also be used to measure the mechanical properties of very small micro-machined silicon structures. Beam structures, such as are used for accelerometers, need to be characterised in terms of the number of cycles to failure, the spring constant or the energy required to bend the beam by a required amount. Such localised testing needs to be adapted to work at various distances from the origin of the beam with a positioning accuracy of less than a micron. Initial studies have proved to be highly repeatable. A range of examples is presented which covers a range of application areas, including accelerometer beam structures, microswitches and printer head structures. The basic instrumental concepts are explai ned together with the modifications required for testing small structures in a localised way. In addition, the localised testing of friction and wear in MEMS devices will be covered with some examples of the technology available and how it may be applied to such small contact areas in an accurate and reproducible way.

2:25 PM
In-Situ SEM Observations of Thermal Fatigue Damage Evolution in Cu Interconnects: Effect of Frequency and Overlayers: *Young-Bae Park*[1]; Reiner Moenig[2]; Cynthia A. Volkert[3]; Guangping Zhang[4]; [1]Andong National University, Sch. of Matl. Sci. & Engrg., Andong S. Korea; [2]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Engrg., Cambridge, MA 02139 USA; [3]Institut fuer Materialforschung II, Forschungszentrum Karlsruhe, Karlsruhe Germany; [4]Chinese Academy of Sciences, Shenyang Natl. Lab. for Matls. Sci., Inst. of Metal Rsch., Shenyang China

It has recently been observed that severe fatigue damage is formed in Cu interconnects due to the cyclic temperatures generated by Joule heating of the metal lines by the passage of alternating currents (AC). However, the effect of the AC frequency on the damage evolution characteristics is not known so far. In this talk, we will summarize our in-situ SEM observations of damage formation during thermal fatigue of polycrystalline sputtered Cu lines (100 to 300 nm thick and 8 um wide) with Ta underlayer on Si. The exact nature of the damage evolution depends on the grain size and orientation, which will be discussed in detail. The higher loading frequency not only accelerated grain growth of damaged grains, but also led to earlier failure. Generally, smaller grained films exhibited longer lifetimes. Finally, it will be shown that the presence of a soft overlayer does not hinder damage formation and fatigue failure. These results imply that thermal fatigue may be a serious reliability threat to Cu interconnects with soft low-k interlevel dielectrics.

2:40 PM
The Nature of Contact Deformation of a Diamond-Like Carbon Coating on Stainless Steel Substrate: *Zonghan Xie*[1]; Mark Hoffman[1]; Singh Rajnish[1]; Avi Bendavid[2]; Phil Martin[2]; [1]University of New South Wales, Sch. of Matls. Sci. & Engrg., Kensington NSW 2052 Australia; [2]CSIRO Division of Telecommunications & Industrial Physics, Lindfield NSW 2070 Australia

Diamond-like carbon films have the unique mechanical properties of high hardness and low friction arising from their amorphous sp3/sp2 structure. For a number of years, these features have drawn considerable interest towards wear applications which seek enhanced surface hardness and abrasion resistance. An understanding of deformation mechanisms of diamond-like carbon coating on ductile substrate systems is therefore critical for design of these coatings to improving their service life. In this work, a diamond-like carbon film was coated onto a stainless steel substrate using a plasma assisted chemical vapour deposition (PACVD) technique. Nanoindentation was undertaken to deform the coating. The indented region was then studied using scanning and focused ion beam (FIB) microscopy of cross-section profiles. Formation and growth of ring cracks in the coating, as well as plastic flow in the ductile substrate, were found to be the predominant deformation processes. Delamination at the interface between the coatin g and substrate occurred upon unloading. No plastic deformation within the coating was observed. Coating deformation was, therefore, controlled by its fracture energy. An indentation-energy based model then allows deconvolution of the coating behavior from that of the substrate, enabling quantification of the fracture toughness of the coating.

2:55 PM Invited
Microsample Tensile Testing and Characterization of Nanocrystalline Aluminum Thin Films: *Kevin J. Hemker*[1]; Daniel Gianola[1]; Derek Warner[1]; En Ma[2]; Jean-Francois Molinari[1]; William N. Sharpe[1]; [1]Johns Hopkins University, Dept. of Mechl. Engrg., Baltimore, MD 21218 USA; [2]Johns Hopkins University, Dept. of Matls. Sci. & Engrg., Baltimore, MD 21218 USA

The mechanical performance of nanocrystalline thin films and MEMS or NEMS materials has been shown to be very different from their bulk microcrystalline counterparts. It is widely recognized that reducing the grain size of a material to nanocrystalline dimensions will result in Hall-Petch strengthening and greatly increased strength and hardness. What is not currently well understood is how nanocrystalline metals accommodate plastic deformation. In the present study fully dense nanocrystalline structures with high angle grain boundaries were fabricated by pulse sputtering of submicron thin films. MEMS-inspired handling procedures and a custom designed load frame were developed to test these nanocrystalline thin films. This presentation will present results of thin film tensile experiments conducted to characterize the strength and in situ transient behavior of nanocrystalline thin films. The results of these experiments will be contrasted with TEM observations, rationalized with regard to possible deformation mechanisms and compared with quantitative atomistic/finite element models that allow for intergranular sliding and capture the composite-like nature of a nanocrystalline solid.

3:20 PM
Real-Time Observation of Plastic Yielding in Aluminum Films During Nanoindentation: *D. Ge*[1]; E. A. Stach[1]; A. M. Minor[1]; M. Jin[2]; J. W. Morris[2]; [1]Lawrence Berkeley National Laboratory, Natl. Ctr. for Electron Microscopy, MS 72, One Cyclotron Rd., Berkeley, CA 94720 USA; [2]University of California, Dept. of Matls. Sci. & Engrg., Berkeley, CA 94701 USA

An experimental study of the initial stages of plasticity in aluminum thin films has been conducted in order to understand the anomalous yielding behavior in instrumented nanoindentation experiments. Typical load-displacement curves from the nanoindentation of aluminum thin films shows a characteristic yielding composed of discrete displacement excursions separated by an elastic response. To clarify the origins of this unique phenomenon, the technique of in-situ nanoindentation in a transmission electron microscopy (TEM) has been applied to aluminum films of different thickness. Taking advantage of the real-time observation of the microstructural evolution in aluminum films under localized loading, the present study focuses on the effect of grain size, penetration depth and indentation position relative to the grain boundary. Possible mechanisms responsible for discrete plasticity have been rationalized based on the observations of dislocation activities. Additionally, ex-situ TEM characterization of nanoindentations are presented for comparison.

3:35 PM Break

3:50 PM Invited
Micro Instrumentation for Studying Mechanical Properties of Free Standing Films: Aman Haque[1]; *Taher Saif*[1]; [1]University of Illinois, Mechl. & Industl. Engrg., Urbana, IL 61801 USA

Investigation of the mechanical behavior of free standing thin films has always been challenged by instrumentation. Most frequently used methods employed to study thin films include nano indentation, wafer curvature, bulge test, and uniaxial tension, to name a few. Except for uniaxial tension, these methods need a material model to extract mechanical properties beyond elastic limit. Furthermore, none of the above methods allow in-situ observation of the microstructure of the specimen while its stress-strain relation is measured. We have developed a MEMS based micro-instrument that allows uniaxial tension of free standing thin films with thickness 30nm and higher. The method also allows in-situ observation of the micro structure so that the mechanism of deformation can be related to the macroscopic stress-strain response. Here, the sample and the measuring instrument are lithographically patterned and co-fabricated. Each instrument is dedicated to one sample. After test, the instrument is discarded. We demonstrate the method by testing 30-300nm thick free standing films of aluminum in SEM (scanning electron microscope) and TEM (transmission electron microscope). We find that as grain size decreases below 50nm, few dislocations exist in aluminum films. They do not generate under high stresses, and even when a crack grows through small grains and grain boundaries prior to failure. Furthermore, as grain size decreases, elastic modulus decreases by a small percentage, and aluminum shows non-linear elastic response with little plastic deformation. We postulate that soft grain boundaries and boundary generated defects are responsible for both reduced elastic modulus and non-linear elastic response.

4:15 PM
Nano- to Micro-Scale Influence of Coating Mechanical Properties Determined Using 3D Omniprobe: *Tathagata Mitra*[1]; Richard J. Nay[1]; Dehua Yang[1]; Thomas J. Wyrobek[1]; [1]Hysitron Inc., Nanomech. Rsch. Lab., 10025 Valley View Rd., Minneapolis, MN 55344 USA

Mechanical characterization of thick coatings presents challenges to nanoindentation due to the ranges of load and displacement it can offer. Additionally, conventional microindentation is unable to probe nanoscale properties of a material, which requires higher measuring and controlling sensitivity. Attempts to bridge nanoscale characterization to macroscale applications have resulted in the emergence of new instrumentation. In this study, a newly developed load and displacement sensing indenter, 3D Ominprobe, capable of both nano- and micro-scale indentation and scratch is introduced. Load- or displacement-controlled indentations were performed on thick DLC, ZrN, and AlTiN coatings. Results on elastic modulus and hardness show depth variation of the properties of the coatings from nano-scale to micro-scale using one instrument. Fracture toughness and indentation size effects are also investigated. Further, interfacial adhesion strength and tribological properties of the coatings are evaluated using the instrument's scratch capability. This study demonstrates the ability of the instrument to integrate nano- and micro-scale mechanical characterization.

4:30 PM
Three-Dimension Imaging of Deformation Modes in TiN-Based Thin Film Coatings: Lok Wang Ma[1]; Julie Marie Cairney[1]; *Paul Richard Munroe*[1]; Mark Hoffman[1]; [1]University of New South Wales, Matls. Sci. & Engrg., Sydney, NSW 2052 Australia

TiN-based thin film coatings are routinely applied to steel substrates to improve their wear-resistance. One method of assessing the deformation behaviour of these coatings is through nano-indentation. However, this method is limited as it provides little microstructural information about the deformation mechanisms that operate under stress. The authors have previously used focused ion beam milling to generate and observe cross-sections through such coatings, where features such as intergranular cracking, transgranular cracking and shear steps at the coating-substrate interface have been observed. However, this method is also limited as it provides data about the crack shape and path in only two dimensions. In this study, we have used a dual-beam focused ion beam miller to create three-dimensional sections of the deformation zones created during nano-indentation. The three-dimensional sections that will be presented provide highly detailed insights into the mechanical behaviour of these coatings.

4:45 PM Invited
X-Ray Diffraction of Small Volumes - Metal Plasticity Under Confinement: *Ralph Spolenak*[1]; [1]Swiss Federal Institute of Technol-

ogy, Dept. of Matls., Wolfgang-Pauli-Strasse 10, Zurich 8093 Switzerland

X-ray diffraction is an important method to study the mechanical properties of thin films and small structures. In this contribution two novel techniques, Laue microdiffraction and in situ diffraction of ultrathin films will be reviewed. Volumes as small as 1 cubic micron can be probed. The results shed new light on thin film metal plasticity on the nanoscale. Examples will be presented on poly- and single crystalline Au and Cu thin films in the thickness range from 1 micron down to 20 nm. The effect of external and internal interfaces on plasticity will be critically discussed.

5:10 PM
Acoustic Methods for the Measurement of the Elastic Properties of Films: Comparative Assessment of Surface Brillouin Scattering and Laser-Induced Ultrasonics: *Marco G. Beghi*[1]; Andrea C. Ferrari[2]; Dieter Schneider[3]; Pavel V. Zinin[4]; [1]Politecnico di Milano, Nucl. Engrg. Dept., Via Ponzio 34/3, Milano I-20133 Italy; [2]Cambridge University, Engrg. Dept., Cambridge UK; [3]Fraunhofer Institut, Werkstoff- und Strahltechnik, Dresden Germany; [4]University of Hawaii, Sch. of Ocean & Earth Sci. & Tech., Honolulu, HI USA

The measurement of the acoustic properties allows the precise determination of the elastic constants in thin films. The main non-destructive techniques using surface acoustic waves (SAWs) in different frequency ranges are Surface Brillouin Scattering (SBS) and laser-induced SAWs (LISAW). We present a critical assessment of their performances, testing them on different diamond-like carbon films of increasing thickness (from 2 nm to microns). Nanometer thick carbon films are used in magnetic hard disk coatings. Two sets of such films were measured by SBS and LISAW. The results of this round robin test show a good correlation, proving the ability of SAW techniques to assess the Young modulus in a thickness range not attainable by techniques such as nano-indentation. Diamond-like carbon films in the micrometer thickness range are widely used for protective coatings and show high promise as low stiction-high Young moduls material for micro electro mechanical systems. For these films the combination of SBS and LISAW achieves a better precision in the elastic properties measurements.

5:25 PM
3D Strain Mapping of Small Structures by Synchrotron X-Ray Microtomography: *JeongJu Ahn*[1]; Hiroyuki Toda[1]; Mitsuo Niinomi[1]; Toshiro Kobayashi[1]; Kentaro Uesugi[2]; Toshikazu Akahori[1]; [1]Toyohashi University of Technology, Dept. of Production Sys., Toyohashi, Aichi 441-8580 Japan; [2]Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198 Japan

With miniaturization of the products, it is difficult or impossible to estimate the mechanical properties of the parts, which form the small products, using a conventional mechanical property assessment technique exactly and quantitatively. For adding the reliability to the mechanical properties of small structures, it needs to evaluate three-dimensional mechanical properties as well as 2D mechanical properties. Therefore, synchrotron X-ray microtomograhpy is applied to real-time measurement and evaluation of the 3D strain distribution of the miniature dog-bone sample of a pure Al with/without artificial circumference notch under the several stroke conditions at the BL47XU of the Spring 8, Japan. It is possible to evaluate 3D local strain mapping of the area or part which is considered to be important as well as whole 3D strain mapping in terms of the stroke using the miniature Al through analyzing 3D images reconstructed from X-ray images.

5:40 PM Closing Remarks: Summary

Metallurgical Technology for Waste Minimization: Session III

Sponsored by: Extraction & Processing Division, EPD-Waste Treatment & Minimization Committee
Program Organizers: Junji Shibata, Kansai University, Department of Chemical Engineering, Osaka 564-8680 Japan; Toru Okabe, University of Tokyo, Institute of Industrial Science, Tokyo Japan; Edgar E. Vidal, Colorado School of Mines, Golden, CO 80401-1887 USA

Wednesday PM Room: 2012
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Yoshio Nakano, Tokyo Institute of Technology Japan; Norihiro Murayama, Kansai University, Cheml. Engrg., Suita, Osaka 564-8680 Japan

2:00 PM Invited
Precipitation of Hematite from Metallurgical Processing Streams by Hydrolysis in the Presence of Anionic Resins: Salima Djaroudib[1]; *Joris Proost*[1]; André Van Lierde[1]; [1]Université Catholique de Louvain, Div. of Matls. & Process Engrg., Place Sainte-Barbe 2, Louvain-la-Neuve B-1348 Belgium

The precipitation of hematite (Fe2O3) from ferric chloride media at ambient pressure and at temperatures below 100°C was studied as part of a program to recover a marketable iron product form metallurgical processing streams and effluents. Hematite was formed in preference to ferric oxyhydroxides (e.g. ß- FeO-OH) by controlling the precipitation conditions, especially by adding Fe2O3 seeds. The extent of the hydrolysis reaction was found to depend primarily on temperature and on the free-acid concentration. As to the latter, the controlled addition of an adsorbant of free acid, in our case the anionic resin polyvinyl-pyridine (PVP), was shown to allow for the nearly complete elimination of iron as readily filterable Fe2O3. The hematite product typically contains > 63% Fe and < 1% Cl, and its composition does not change appreciably upon repeated cycling using regenerated PVP.

2:30 PM Invited
The Transformation of Crystal Structure of Calcium Aluminate Phase and Ettringite as the Solidification of Heavy Metals: *Ji-Whan Ahn*[1]; Kwang-Suk You[1]; Song-Min Chon[1]; [1]Korea Institute of Geoscience & Mineral Resources, Minls. & Matls. Procg. Div., Daejon 305-350 Korea

Tetracalcium sulphoaluminate clinker composed of CaO, Al2O3, SO3 has been synthesized using reagent of CaCO3, Al2O3 and CaSO4?2H2O. The effect of simultaneous addition of heavy metals (Cu, Cr, Pb, Zn) on varying temperature has been investigated. The synthesized solid solutions have been characterized through X-ray diffraction (XRD) and scanning electron microscope (SEM). And the vaporization of them during sintering process was measured by the liquid analysis of clinker. Through the measurements, the solidification and substitution of heavy metal on the crystal structure of tetracalcium sulphoaluminate and Ettringite, which is hydrates, could be evaluated. The morphology of calcium sulphoaluminate phase deformed with increase of heavy metal concentration and the hydraulic reactivity of clinker was changed with the addition of heavy metal. Especially the addition of Cr ion caused to the deformation of Ettringite in the opposition direction of (010).

3:00 PM Break

3:15 PM
Thermodynamic Evaluation of Electronic Waste Treatment: *Scott A. Shuey*[1]; Patrick R. Taylor[1]; [1]Colorado School of Mines, Dept. Metallurgl. & Matls. Engrg., Kroll Inst. for Extractive Metall., 1500 Illinois St., Golden, CO 80401-1887 USA

Electronics disposal has been discussed in some circles for at least the past 25 years. The recycling of electronic waste tends to be a rather complex undertaking when considering the intimate bonding of materials in the average printed circuit board. The development of a recycling process is further complicated when considering the wide variety of products being generated under the heading of "electronics." Ignoring trace elements, and the various halide species generated, will lead process engineers down a development path that is sure to cause material handling issues. Researchers at Colorado School of Mines are modeling the complex chemistry that exists within the body of e-waste. An understanding of the systems thermodynamic behavior will

result in the development of a more robust, long-term process for the recovery of valuable materials from the e-waste stream.

3:35 PM Cancelled
Environmental Control in Russian Alumina and Smelter Plants: Now and the Future

3:55 PM
The Practice on Refining of Impure Indium in Shaoguan Smelter: *Guo Xueyi*[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Yuelu Dist., Changsha, Hunan 410083 China

The coarse indium ingots produced by Shaoguan smelter contained a lot of impurities. In order to produce the high pure indium with the purity more than 99.99%, the appropriate refining processes were designed and the practice of combined use of Glycerin-KI process and electrolysis in Shaoguan smelter was introduced.

4:15 PM
Recovery of Germanium and Indium from Imperial Smelting Process in Shaoguan Smelter: *Guo Xueyi*[1]; [1]Central South University, Sch. of Metallurgl. Sci. & Engrg., Yuelu Dist., Changsha, Hunan 410083 China

The distributions of zinc, indium, and germanium in the smelting process of the closed blast furnace in Shaoguan smelter were analyzed, and the recovery methods of indium & germanium from the slag by the combined processes of separate-blaze-furnace, electrical furnace, the vacuum furnace process, and fusion-electrolysis process were studied systematically. The focus study was put on the small-scale and pilot experiments of zinc removal from the hard zinc by vacuum distillation, indium and germanium enrichment, and a new process, i.e. Ball milling - Neural leaching - Oxidation calcinations - Chloridizing distillation - Hydrolysis, was designed to recover Germanium from the vacuum furnace slag. The suitable process and operational parameters were determined for the practical production.

Micromechanics of Advanced Materials II (Symposium in Honor of James C.M. Li's 80th Birthday): Fatigue, Fracture and Failure

Sponsored by: Structural Materials Division, ASM International: Materials Science Critical Technology Sector, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Fuqian Yang, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY 40506 USA; C. C. Chau, Pactiv Corporation, Canandaigua Technology Center, Canandaigua, NY 14424 USA; Sung Nee George Chu, Multiplex Inc, South Plainfield, NJ 07080 USA; M. Ashraf Imam, Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375-5343 USA; Teh-Ming Kung, Eastman Kodak Company, Rochester, NY 14650 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; B. B. Rath, Naval Research Laboratory, Materials Science and Component Technology Directorate, Washington, DC 20375-5341 USA

Wednesday PM Room: 3000
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: S. J. Burns, University of Rochester, Mechl. Engrg. Dept., Rochester, NY 14627 USA; B. A. MacDonald, National Science Foundation, Arlington, VA 22230 USA

2:00 PM Invited
Alloying Effects on the Fracture Toughness of Nb-Based Silicides and Laves Phases: *Kwai S. Chan*[1]; [1]Southwest Research Institute, Matls. Engrg. Dept., 6220 Culebra Rd., San Antonio, TX 78238 USA

Nb-based in-situ composites are characterized by a large volume fraction of silicides and Laves phase particles in an Nb solid solution matrix. The intermetalllic hard particles can affect adversely the fracture resistance of the composites. Recent work has shown that certain alloy additions can improve the fracture resistance of Nb-based silicides, Laves phases, and the Nb solid solution. In this paper, the effects of alloy addition on the fracture toughness of Nb-based silicides, Laves phases, and solid solutions are summarized. Theoretical calculations have been performed to determine the influence of alloy addition on the bond order, unstable stacking energy, and the Peierls-Nabarro energy for selected slip systems in the intermetallics. The theoretical results will be used in conjunction with experimental data to elucidate the possible roles of alloy addition in the slip process and the fracture resistance in Nb-based silicides and Laves phases.

2:20 PM
Determination of Fracture Toughness of Ferritic Steels by Automated Ball Indentation Tests: Fahmy M. Haggag[1]; *M. Ashraf Imam*[2]; Heshmat A. Aglan[3]; Robert L. Bridges[4]; [1]Advanced Technology Corporation, 1066 Commerce Park Dr., Oak Ridge, TN 37830-8026 USA; [2]Naval Research Laboratory, Matls. Sci. & Tech. Div., Code 6320, Washington, DC 20375-5343 USA; [3]Tuskegee University, Tuskegee, AL USA; [4]Oak Ridge National Laboratory, BWXT Y-12, Oak Ridge, TN USA

The Automated Ball Indentation (ABI) test techniques, invented in 1989, determine key mechanical properties of metallic samples and structures in a nondestructive and localized fashion. The test is based on progressive indentation with or without intermediate partial unloadings until the desired maximum depth (maximum strain) is reached, and then the indenter is fully unloaded. The fracture toughness is calculated from integration of the indentation deformation energy up to the critical depth. The measured key mechanical properties are used with other nondestructive measurements such as crack/defect sizes to determine the safe operating/loading conditions of the Ferritic steel structures or to necessitate certain rehabilitation actions. The new fracture toughness capability is, in practical terms, material thickness independent. Furthermore, its localized nature allows testing welds and heat-affected-zones that cannot be tested destructively because of their irregular shape and small volumes. Applications of ABI test techniques to determine the fracture toughness of steel samples, components, and structures, including welds and heat-affected-zones are discussed.

2:40 PM
In-Situ Investigation on the Mechanical Behaviors of Bulk-Metallic Glasses by Thermography: *Bing Yang*[1]; Peter K. Liaw[1]; Mark Morrison[1]; Gongyao Wang[1]; Chain T. Liu[2]; Raymond A. Buchanan[1]; Y. Yokoyama[3]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., Knoxville, TN 37916 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA; [3]Himeji Institute of Technology, Matls. Sci. & Engrg., Shosha 2167, Himeji City Japan

Since the discovery in the 1990s, bulk-metallic glasses (BMGs) have aroused intense interests because of their ultra-high strengths, super elasticity, and good fracture toughness. Despite these superior properties, the lack of dislocations and plastic deformations in BMGs limits their ductility and fatigue limit in structural applications, especially under tension-loading conditions. In the current research, the mechanical-damage processes of Zr-based BMGs during both fatigue and tensile tests were investigated in-situ by thermography technologies. The thermoelastic effect was used to analyze the stress variations of the BMG specimens during both tensile and fatigue experiments. Except for the final fracture moment, the mechanical behaviors of BMGs have been observed to be dominated by elastic deformations. Multiple shear bands were observed in-situ and analyzed on BMGs before failures during tensile tests by thermography, while no shear bands were observed during fatigue tests, which indicated that the failure mechanism during fatigue could be different from that during the tensile test. As a new nondestructive-evaluation (NDE) method, thermography could open up wide applications in detecting in-situ mechanical damages of materials and structural components.

3:00 PM
Monitoring Tensile Damage Evolution in Nextel/Blackglas Composites: *Jeongguk Kim*[1]; Peter K. Liaw[2]; [1]Korea Railroad Research Institute, Railroad Safety Rsch. & Testg. Ctr., 360-1 Woulam, Uiwang, Kyunggi 437-757 S. Korea; [2]University of Tennessee, Dept. of Matls. Sci. & Engrg., 427B Dougherty, Knoxville, TN 37996-2200 USA

Tensile damage evolution in Nextel/Blackglas composites was monitored with the aid of nondestructive evaluation (NDE) techniques. Several NDE methods, such as ultrasonic testing (UT), infrared (IR) thermography, and acoustic emission (AE) techniques, were employed to analyze damage evolution during tensile testing. Prior to tensile testing, UT was used to characterize the initial defect distribution of the samples. During tensile testing, AE sensors and an IR camera were used for in-situ monitoring of the progressive damages of the samples. AE provided the amounts of damage evolution in terms of the AE intensity and/or energy, and the IR camera was used to obtain the temperature changes during the test. Microstructural characterization using scanning electron microscopy (SEM) was performed to investigate the fracture mechanisms and modes of Nextel/Blackglas samples. Moreover, SEM characterization was used to provide the substantial

evidence of failure behavior, and to show comparable results with NDE signatures.

3:20 PM
Micromechanics of Damage Evolution in Solid Propellants: *Petros Sofronis*[1]; Fengbin Xu[1]; Nikolaos Aravas[2]; [1]University of Illinois, Dept. of Theoretl. & Applied Mech., 216 Talbot Lab, 104 S. Wright St., Urbana, IL 61801 USA; [2]University of Thessaly, Dept. of Mechl. & Industl. Engrg., Pedion Areos, Volos 38334 Greece

Solid propellants are composite materials with complex microstructure. In a generic form, the material consists of polymeric binder, ceramic oxidizer, and fuel particles (e.g. aluminum). Damage induced by severe stress and extreme temperatures is manifested in particle cracking, decohesion along particle/polymer interfaces, void opening or even polymer crazing at low temperatures and inert propellants. In this work, the effect of damage due to void formation on the material macroscopic response is investigated from a solid mechanics perspective. First, issues related with the constitutive behavior of the individual phases in the absence of damage are reviewed. Next, with the use of rigorous composite homogenization theory, a macroscopic constitutive law is proposed that accounts for continuous void nucleation and growth upon straining. Numerical calculations for the uniaxial tension test capture most of the experimentally observed features, namely an initial elastic regime, a viscoplastic regime in which void formation competes with hardening in the matrix, a softening regime, and a macroscopic volume expansion which continuously increases with straining.

3:40 PM Break

3:45 PM
Hold-Time Effects on Low-Cycle-Fatigue Behavior of HAYNES® 230 Superalloy at High Temperatures: *Y. L. Lu*[1]; L. J. Chen[1]; G. Y. Wang[1]; M. L. Benson[1]; P. K. Liaw[1]; S. A. Thompson[2]; J. W. Blust[2]; P. F. Browning[2]; A. K. Bhattacharya[2]; J. M. Aurrecoechea[2]; D. L. Klarstrom[3]; [1]University of Tennessee, Dept. of Matls. Sci. & Engrg., Knoxville, TN 37996-2200 USA; [2]Solar Turbines Inc., 2200 Pacific Hwy., PO Box 85376, MZ R-1, San Diego, CA 92186-5376 USA; [3]Haynes International, Inc., 1020 W. Park Ave., PO Box 9013, Kokomo, IN 46904-9013 USA

Total strain-controlled low-cycle-fatigue tests with and without hold times were performed at temperatures ranging from 816°C to 982°C in a laboratory air on a nickel-based superalloy, HAYNES 230. The influence of hold times on the cyclic-stress response and fatigue life was studied. At the temperatures considered, the alloy exhibited initial cyclic hardening, followed by a saturated cyclic-stress response or cyclic softening under low-cycle fatigue without hold times. For low-cycle-fatigue tests with hold times, however, the alloy showed cyclic hardening, cyclic stability, or cyclic softening, which is closely related to the test temperature and the duration of the hold time. It was also observed that the low-cycle-fatigue life of the alloy considerably decreased due to the introduction of strain hold times. Generally, a longer hold time would result in a greater reduction in the fatigue life. For the tests without hold times, the test temperature seems to have little influence on the fatigue life of the alloy at the test temperatures from 816ºC to 927ºC. However, when the test temperature increased to 982ºC, the fatigue life clearly shortened. In addition, the fracture surfaces of the fatigued specimens were observed, using scanning-electron microscopy, to determine the crack initiation and propagation modes. The fatigue life was predicted by the frequency-modified tensile-hysteresis-energy method. The predicted lives were found to be in good agreement with the experiment results. This work is supported by the Solar Turbines Inc., Haynes International, Inc., the University of Tennessee, the U. S. Department of Energy's Advanced Turbine Systems Program, the National Science Foundation (NSF), under Grant No. DMI-9724476, the NSF Combined Research-Curriculum Development Program, under EEC-9527527, the NSF Integrative Graduate Education and Research Training (IGERT) Program, under DGE-9987548, and the NSF International Materials Institutes (IMI) Program, under DMR-0231320, with Dr. D. Durham, Dr. M. Poats, Ms. W. Jennings, Dr. L. Goldberg, and Dr. C. Huber as contract monitors.

4:05 PM
Experimental Relationships Among Strain, Applied Load and Crack Advance During Stage II Fatigue Crack Growth: *Seon-ho Choi*[1]; Pedro Peralta[1]; James Gee[2]; Zhiyong Xie[2]; [1]Arizona State University, Dept. of Mechl. & Aeros. Engrg., PO Box 876106, Tempe, AZ 85287 USA; [2]University of Pennsylvania Medical Center, Dept. of Radiology, 3400 Spruce St., Philadelphia, PA 19104 USA

The quantification of the strain field ahead of a fatigue crack tip is important to understand fatigue crack growth via plastic blunting and to develop quantitative relationships between crack advance and applied load. The in-plane displacement fields ahead of the tip of a stage II fatigue crack in a CT specimen are measured using the digital image correlation (DIC) method. Pure polycrystalline nickel with an average grain size of 44 ?Ým was used. Cracks were grown under quasi-constant ?´K to prevent excessive stretch of the plastic zone ahead of the crack tip and a half cycle of fatigue load was applied under the scanning electron microscope with different values of the applied load equivalent to a maximum ?´K within the stage II growth regime. The measurements are used to formulate an empirical model to make a connection between the measured strain fields, the applied load and crack advance.

4:25 PM
Prediction of Crack Path Based on Grain Boundary Misorientation and Stress in a Near-Gamma TiAl Alloy: Boon-Chai Ng[1]; *Thomas R. Bieler*[1]; Martin A. Crimp[1]; Darren E. Mason[2]; [1]Michigan State University, Cheml. Engrg. & Matls. Sci., E. Lansing, MI 48824-1226 USA; [2]Albion College, Math. & Computer Sci., Albion, MI 49224 USA

The process of crack propagation in a duplex Ti-48Al-2Cr-2Nb alloy with equiaxed grains has been studied in a notched four point bend Mode I crack growth specimen. OIM (orientation imaging microscopy) is unable to identify the correct orientation of the c-axis, due to the near-cubic crystal structure, so a method to rapidly determine the true c-axis orientation using SACP (selected area channeling patterns) in conjunction with the OIM scans. A phenomenological fracture initiation parameter incorporating the contributions from deformation twinning and ordinary dislocation systems has been developed, that is capable of identifying boundaries that are likely to nucleate microcracks. This parameter was able to account for sharp turns in the crack path in an arrested crack, as well as predict the subsequent crack path after subsequent loading. Based upon this parameter, criteria for crystal orientations and misorientations are proposed for improving the toughness of duplex microstructures. Supported by AFOSR F49620-01-1-0116.

4:45 PM
Failure Mechanism Map and Minimum Weight Design of Sandwich Beam Consisting of Alumina Facesheet and Aluminum Foam Core: Kapil Mohan[1]; *Tick-Hon Yip*[1]; I. Sridhar[2]; [1]Nanyang Technological University, Sch. of Matls. Eng., N4.1 Nanyang Ave., Singapore 639798 Singapore; [2]Nanyang Technological University, Sch. of Mechanical. & Production Engrg., N3 Nanyang Ave., Singapore 639798 Singapore

Aluminum foams are lightweight, recyclable and have high corrosion resistance, high specific strength, isotropic behavior and good formability. Structural performance of these foams can be enhanced by using them as a core of a sandwich structure comprising thin plates of relatively high stiffness and high strength face sheet materials such as alumina and/or aluminum as face sheets. Cost of these structures in terms of bulk material can be reduced by rigorous design procedure along with the definition of constraint specific to the application. Design by minimum-weight involves consideration of failure modes of these sandwich beams, type of loading, geometrical parameters like thickness of core and face sheets, and length of core of sandwich beams. The constraint for the weight design includes stiffness and strength individually. In the present study, three failure modes, indentation, face yield and core shear were identified in the sandwich structure consisting of aluminum foam core and alumina face sheets und er four-point bending. Failure mode is expressed in terms of non-dimensional geometrical variables for a fixed core relative density. Equations for objective function, weight of the beam, were developed separately in terms of different constraints such as strength and stiffness for each of the failure modes. The design analyses was illustrated in terms of weight index plotted against stiffness and strength indices, all being dimensionless quantities.

5:05 PM
Conformation Structure and Chain Rupture Under Deformation of Linear Oriented Polyethylene: *Ulmas Gafurov*[1]; [1]Institute of Nuclear Physics, Tashkent, Ulugbek 702132 Uzbekistan

Macromolecular chain ruptures with different drawing ratio, that is with different molecular ordering, the conformation state of macromolecules in amorphous regions in stretching deformation of oriented linear polyethylene samples were studied. Macromolecular conformation structure and relative number of the chain rupture was determined by IR spectroscopy by concentration of different molecular terminal groupings measuring. Polymer stretching with larger draw ratio (less coiled isomers concentration and larger molecular ordering), in comparison with lower oriented sample, occurred at considerably larger loads and showed decreases in plastic and elastic deformation, increas-

ing in the number of macromolecular ruptures. Deformation at identical values was accompanied by a greater of molecular chain ruptures. It is proposed that main reason of it is decreasing with polymer sample drawing of coiled isomers concentration in amorphous section of interconnecting macromolecules, in folds and loops on crystalline surface and in entanglements leads to difficulty of macromolecular slippage processes that occur through polymer crystallites. The molecular models of chain slippage and chain rupture of a interconnecting macromolecule for an oriented loaded amorphous-crystalline polymer has been suggested. The crystalline polymer is considered as two-phase one with interchanging amorphous and crystalline regions. Using Frenkel-Kontorova's dislocation models tension, slippage of macromolecules are considered. It is taken into account complex interaction between slippage and rupture of polymer chains.

5:25 PM
Nitrogen Diffusion and Fracture of Nitrided and Nitrocarburized Blunt Notch Three-Point Die Steel Specimens: *Donato Firrao*[1]; Daniele Ugues[1]; [1]Politecnico di Torino, Dip. di Scienza dei Materiali e Ingegneria Chimica, Corso Duca degli Abruzzi, 24, Torino 10129 Italy

Nitriding and nitrocarburizing are among the most adopted surface treatments to enhance steel components wear and fatigue resistances. Yet, nitrogen diffusion causes the reduction of impact resistance and low cycle fatigue properties. A complete understanding of the reasons leading to the brittleness of nitrided and nitrocarburized components still lacking, results of studies on impact tested gas and plasma nitrided or nitrocarburized blunt notch die steel samples are presented. A detailed fracture mechanism sequence is proposed encompassing; (i) multiple mode-I radial cracks formation at the root of the notch beyond the N-diffusion zone; (ii) development of a cylindrical stress-free zone practically creating a notch with a radius larger than the previous one; (iii) concurrent mode-II fractures running along logarithmic spirals of the slip line field forming at the new larger notch; (iv) race restricting to two of them, with one hitting the notched sample centerline before the other and further propagating in to the region of minimum thickness with a mode-I fracture. Suggestions for improved treatments are given.

Microstructural Processes in Irradiated Materials: Carbides, Nitrides and Oxides

Sponsored by: Structural Materials Division, SMD-Nuclear Materials Committee-(Jt. ASM-MSCTS)
Program Organizers: Brian D. Wirth, University of California, Department of Nuclear Engineering, Berkeley, CA 94720-1730 USA; Charlotte S. Becquart, Ecole Nationale Superieure de Chimie de Lille, Laboratoire de Metallurgie Physique et Genie des Materiaux, Villeneuve d'Ascq cedex 59655 France; Hideki Matsui, Tohoku University, Institute for Materials Research Japan; Lance L. Snead, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37830-6138 USA

Wednesday PM Room: 3011
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Lance Snead, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6138 USA; Robin Schaeublin, Swiss Federal Institute of Technology Lausanne, Ctr. of Rsch. in Plasma Physics, Villigen 5232 Switzerland

2:00 PM Invited
Microstructural Development in Silicon Carbide During Irradiation at Elevated Temperatures: *Yutai Katoh*[1]; Lance L. Snead[1]; Naoyuki Hashimoto[1]; Sosuke Kondo[2]; Akira Kohyama[2]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., 1 Bethel Valley Rd., Oak Ridge, TN 37831-6138 USA; [2]Kyoto University, Inst. of Advd. Energy, Gokasho, Uji, Kyoto 611-0011 Japan

Effect of atomic displacement damage during irradiation is of particular importance for silicon carbide for advanced nuclear and semiconductor applications. As for nuclear applications, utilization of silicon carbide and composites is proposed for gas reactor fuel coatings, gas fast reactor core structures, and fusion blanket structures including ITER test blanket modules. However, understanding of irradiation effects in silicon carbide and the underlying physical processes is very limited. The present paper discusses irradiation effects in cubic silicon carbide with the emphasis on microstructural evolution at temperatures of interest for nuclear applications. Microstructural examination primarily by transmission electron microscopy was carried out to chemically vapor-deposited high-purity cubic silicon carbide samples which had been either neutron-irradiated in High Flux Isotope Reactor (Oak Ridge, TN) at 300-800C or ion-irradiated at DuET dual-beam static accelerators facility (Kyoto University, Kyoto, Japan) at 600-1400C. Based on the results of microstructural characterization, an attempt was made to develop a map of evolution of various microstructural features in cubic silicon carbide as a function of irradiation temperature and displacement damage level.

2:40 PM
Multi-Time-Scale Approach in Simulations of Damage Accumulation in Silicon Carbide: *Fei Gao*[1]; Matthias Posselt[2]; Ram Devanathan[1]; William J. Weber[1]; [1]Pacific Northwest National Laboratory, Fundamental Sci., MS K8-93, PO Box 999, Richland, WA 99352 USA; [2]Forschungzentrum Rossendorf, Inst. of Ion Beam Physics & Matls. Rsch., PO Box 510119, Dresden D-01314 Germany

Damage accumulation irradiation with electrons, ions, and neutrons is a complex process, which can not completely be modeled by molecular dynamics (MD) method, particularly at low temperatures. MD and long-time dynamics based on the dimer method have been combined to perform multi-time-scale simulations of defect accumulations due to electron irradiation of SiC at room temperature. Molecular dynamics simulations are employed to simulate collisional phase of defect production, while long-time dynamics are used to treat thermally activated processes of defects and defect clusters. The close Frenkel pairs often annihilate within a few hundred nanoseconds, but the recovery events occur within milliseconds for the well separated vacancy-interstitial pairs. Interstitials contribute to long-range migrations at room temperature and thus, aggregate into clusters, forming disordered domains. The significant recovery and annihilation of defects during thermal activated processes explains the high amorphization dose for electron irradiation of SiC at room temperature.

3:00 PM
Modeling Thermal Conductivity Degradation in Irradiated SiC: *Lance L. Snead*[1]; Douglass P. White[2]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831-6138 USA; [2]Merrimack College, N. Andover, MA USA

SiC has many potential applications in Generation IV and Fusion Reactor Components. However, an important consideration is the degradation of thermal conductivity as a result of neutron irradiation. In this work, we present a theoretical mdoel for the thermal conductivity changes expected in neutron irradiated SiC. Phonon scattering by radiation induced vacancies and regions of disorder are considered. The model results are compared to recent experimental observations.

3:20 PM
Irradiation Induced Dislocations and Vacancy Generation in Single Crystal Yttria Stabilized Zirconia: *Jill Noel Johnsen*[1]; Tien Tran[1]; Joanna R. Groza[1]; Fritz Prinz[2]; [1]University of California, Cheml. Engrg. & Matls. Sci., 1 Shields Ave., Davis, CA 95616 USA; [2]Stanford University, Mechl. Engrg & Matls. Sci., Bldg. 530, 440 Escondido Mall, Stanford, CA 94305 USA

A determination of the most effective method of introducing edge dislocations and defect clusters in single crystal Yttria Stabilized Zirconia (YSZ) has been investigated using several techniques. High-energy particle irradiation using 800 keV electrons, 20 MeV protons, or 1 MeV neutrons promotes the introduction of defects. Thermal annealing and temperature cycling were performed both ex-situ and in-situ in a TEM to study the dynamic recovery behavior of the defects introduced by irradiation and to determine the edge character of dislocations. Defect clusters formed in samples exposed to 20.4 MeV protons with a fluence of 1.00×10^{13} p/cm^2 and thermally annealed at temperatures between 800°C and 1000°C. TEM defect analysis offered evidence that edge type dislocations were formed in YSZ irradiated for two hours with 800 keV electrons and thermally annealed at 1000°C for one hour.

3:40 PM
Microstructure Stability of ZrC, ZrN, TiN, TiC and SiC Irradiated with 1 MeV Kr Ions to 10 and 70 dpa at 800°C: *Jian Gan*[1]; Robert C. Birtcher[2]; Mitchell K. Meyer[1]; [1]Argonne National Laboratory, Nucl. Tech. Div., PO Box 2528, Idaho Falls, ID 83403 USA; [2]Argonne National Laboratory, Matls. Sci. Div., 9700 S. Cass Ave., MSD/212, Argonne, IL 60439-4838 USA

Ceramics of ZrC, ZrN, TiC, TiN and SiC have been considered as the candidate materials for dispersion fuel matrix for gas cooled fast reactor (GFR) in Generation-IV nuclear reactor system. TEM disc samples of the hot-pressed ZrC, ZrN, TiN, TiC and SiC were irradiated using 1 MeV Kr ions in an intermediate voltage electron microscope (IVEM) at Argonne National Laboratory. The irradiations were con-

ducted at a dose rate approximately (2.7~4.0)x10-3 dpa/s at 800ºC to a dose up to 70 dpa that is the proposed lifetime dose for GFR fuel. The in-situ microstructural changes were monitored and recorded using a video camera. Post-irradiation microstructural examination will reveal the changes in microstructure such as precipitate development, lattice expansion and phase change. The impact of the microstructure changes on the GFR dispersion fuel development will be discussed.

Multicomponent Multiphase Diffusion Symposium in Honor of John E. Morral: Applications of Multicomponent Multiphase Diffusion

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee, MPMD-Solidification Committee, ASM/MSCTS-Atomic Transport Committee

Program Organizers: Carelyn E. Campbell, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Ursula R. Kattner, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, MD 20899-8555 USA; Afina Lupulescu, Rensselaer Polytechnic Institute, Materials Science & Engineering, Troy, NY 12180-3590 USA; Yongho Sohn, University of Central Florida, Advanced Materials Processing & Analysis Center and Mechanical, Materials and Aerospace Engineering, Orlando, FL 32816-2455 USA

Wednesday PM Room: 3007
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Yuri Mishin, George Mason University, Fairfax, VA 22030 USA; Carelyn E. Campbell, National Institute of Standards and Technology, Metall., Gaithersburg, MD 20899-8555 USA

2:00 PM Invited
Multicomponent Diffusion Effects in Joints of Dissimilar Materials' Engineering Applications: *John A.L. Ågren*[1]; [1]Royal Institute of Technology, Dept. of Matls. Sci. & Engrg., Stockholm 100 44 Sweden

Many engineering applications involve combination of dissimilar materials, as well as processing and usage of such joints at high temperatures where diffusion is rapid. For example, one may mention welded joints of dissimilar steels, composite steel tubes, aluminide coatings on superalloys etc. In addition to the diffusion processes predicted by Fick's law a number of new phenomena occur in multicomponent systems. The Darken effect; up-hill diffusion, is well known in ternary Fe-C-X alloys and of practical importance in steels where carbon is a fast diffusing interstitial. Other effects involve formation of secondary phases even in combinations of one-phase materials of the same phase. Combinations of two-phase materials yield the so-called zigzag diffusion path predicted and analyzed by Morral and coworkers. The Kirkendall effect is caused by differences in individual mobilities and may cause porosity leading to inferior mechanical strength of a joint. Nevertheless, the Kirkendall effect is less well understood in multicomponent systems. A proper understanding of the above phenomena requires a detailed knowledge of the underlying thermodynamic driving forces and phase relations as well as the intrinsic mobilities. In this presentation some recent advances in the modeling of the above phenomena will be discussed.

2:30 PM
Indirect Paths to Final Equilibrium: Kinetics in Multicomponent Systems: *J. M. Vitek*[1]; [1]Oak Ridge National Laboratory, PO Box 2008, Bldg. 4508, MS 6096, Oak Ridge, TN 37831-6096 USA

Currently available software makes it possible to calculate diffusion-controlled phase transformation kinetics in multicomponent systems. However, the paths toward equilibrium are often not direct. Several examples dealing with the austenite/ferrite transformation in steels will be given which reveal the formation and subsequent dissolution of the same phase en route to final equilibrium. While this behavior is certainly indirect, and perhaps not intuitively apparent, the various stages in the transformations can be readily explained by considering the interactions in multicomponent systems. Much of the behavior can be traced to the significantly different diffusion rates in austenite and ferrite, and the same general behavior can be expected in any two-phase system with phases that have grossly different diffusion rates. This research sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

2:55 PM Invited
Simulation of Solution Treatment in Multicomponent Aluminum Alloy Castings: *Harold D. Brody*[1]; [1]University of Connecticut, Matls. Sci. & Engrg., Unit-3136, Storrs, CT 06169-3136 USA

In collaboration with Professor John Morral researchers at the University of Connecticut and the Ohio State University are developing software to simulate the redistribution of alloying elements and the dissolution of intermetallic phases during the solution treatment of Al-Si-Cu-Mg casting alloys. The simulations require increased understanding of solution treatment processes in multicomponent alloys, acquisition and representation in databases of the multicomponent phase equilibria and diffusivity data, and validation of the software by comparison with experiment. The strong dependence of solution treatment kinetics on as-cast microstructure has stimulated revision of solidification models. A major objective of the project sponsored by the Department of Energy and the Center for Heat Treating Excellence is the reduction of heat treatment cycle time. A demonstration project with industry collaborators will test the utility of the simulation to reducing solutionizing time.

3:25 PM
Carburization Process Modeling: *Richard D. Sisson*[1]; [1]Worcester Polytechnic Institute, Ctr. for Heat Treat Excellence, Matls. Sci. & Engrg., Worcester, MA 01609 USA

A brief history of carburization process modeling will be presented followed by an n assessment of the current status of our modeling capability. The database needs will be addressed in terms of the temperature and composition dependence of carbon diffusion coefficients as well as the surface mass transfer of coefficients as a function of temperature, gas composition and steel surface condition. The sensitivity of case depth to process parameters will also be discussed.

3:50 PM Break

4:05 PM Invited
Denisfication of Powdered Steel Preforms by Liquid-Steel Infiltration: *Samuel M. Allen*[1]; Brian D. Kernan[2]; Christoph Sachs[1]; Emanuel M. Sachs[2]; [1]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Engrg., Cambridge, MA 02139-4307 USA; [2]Massachusetts Institute of Technology, Dept. of Mechl. Engrg., Cambridge, MA 02139-4307 USA

The direct manufacture of metal parts by rapid prototyping often employs a metal powder. Densification of the powder can be accomplished either by sintering or infiltration. Infiltration avoids the shrinkage and distortion that typically accompanies sintering. However, conventional steel powder-metal parts are usually infiltrated with copper or bronze infiltrants, and these limit the usefulness of parts because of the resulting non-homogeneous structure and properties. This talk will describe how a gated infiltration process can be used to make parts of a conventional tool steel alloy composition by infiltrating a steel powder preform (made using MIT's Three-Dimensional Printing process) with molten steel alloy having a lower melting point than the base powder. Extensive use of Calphad techniques is necessary to design suitable powder and infiltrant compositions and to select the infiltration temperature. Using this process, we have produced heat treatable D2 tool steel parts having hardness and impact properties comparable to those of wrought D2.

4:35 PM
Interdiffusion and High Temperature Coatings for Gas Turbine Applications: *Jing Liu*[1]; Balaji Jayaraj[1]; Sankar Laxman[1]; Emmanuel Perez[1]; Barbara Franke[1]; Jaewon Byeon[1]; Yongho Sohn[1]; [1]University of Central Florida, AMPAC & MMAE, Box 162455, 4000 Central Florida Blvd., Orlando, FL 32816-2455 USA

Science and technology of high temperature coatings is a subject of great interest for its intellectual merit and practical applications. While a myriad of fundamental concepts in materials engineering can be studied from the processing and degradation of these coatings, the reliability, durability and maintainability of these coatings have a significant impact on the performance and efficiency of critical systems for energy production. This talk will survey the importance of multicomponent-multiphase interdiffusion with specific examples from coating-substrate interdiffusion, high temperature oxidation, and composition-dependent phase transformations in thermal barrier coatings and oxidation-resistant protective coatings for advanced gas turbine applications. Through these examples, the role of multicomponent-multiphase interdiffusion on the reliability and failure mechanisms of the high temperature coatings will be highlighted.

Neutron Diffraction Characterization of Mechanical Behavior: Residual Stress II

Sponsored by: ASM International: Materials Science Critical Technology Sector, Structural Materials Division, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)
Program Organizers: Hahn Choo, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN 37996 USA; Camden R. Hubbard, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; Peter K. Liaw, University of Tennessee, Materials Science and Engineering, Knoxville, TN 37996-2200 USA; Xunli Wang, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831 USA

Wednesday PM Room: 3004
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Ronald B. Rogge, National Research Council, Neutron Prog. for Matls. Rsch., Chalk River, Ontario K0J 1J0 Canada; Thomas Gnaupel-Herold, National Institute of Standards and Technology, Ctr. for Neutron Rsch., Gaithersburg, MD 20899 USA

2:00 PM Invited
Imaging of Single Crystallite Deformation by Neutron Diffraction: *Thomas Gnaupel-Herold*[1]; [1]National Institute of Standards and Technology, Ctr. for Neutron Rsch., 100 Bureau Dr., Stop 8562, Gaithersburg, MD 20899-8562 USA

Diffraction is ideally positioned to study the behavior of grains in select orientations. The domain of neutron diffraction is the analysis of average strains in groups of crystallites having the orientation [hkl] parallel to the scattering vector. This type of investigation often assumes that that sufficiently many grains contribute to the strain measured. This paper will present results of neutron diffraction measurements on deformed coarse grained materials in which the grains are sufficiently large (mm sized) such that the behavior of single grains can be measured. The topics of this investigation are spatially resolved measurements of anisotropic peak broadening and the stress state of selected grains.

2:20 PM Invited
Residual Stress Measurements in Laser Clad Repaired Low Pressure Turbine Blades for the Power Industry: *Philip John Bendeich*[1]; David G. Carr[1]; Ken Short[1]; Richard Blevins[1]; Caroline Curfs[1]; Oliver Kirstein[1]; Gerard Atkinson[1]; Thom M. Holden[2]; Ron Rogge[3]; [1]Australian Nuclear Science and Technology Organisation, Matls. & Engrg. Sci., New Illawarra Rd., Lucas Hgts., New South Wales 2234 Australia; [2]Northern Stress Technologies, Deep River, Ontario Canada; [3]National Research Council, Neutron Program for Matls. Rsch., Chalk River, Ontario Canada

Low pressure turbine blades in power stations suffer from leading edge erosion damage due to water impingement. In an effort to extend the life of these blades, repair of the eroded regions of the blades has been proposed using laser cladding with Stellite material. However, the addition of Stellite results in residual stresses being generated in the parent metal due to contraction during cooling and differences in thermal expansion between the two materials. In this work test coupons and a laser clad blade were examined for residual stresses using both the L3 diffractometer at the NRU reactor, Chalk River, Canada and the TASS neutron diffraction instrument at the HIFAR reactor, Lucas Heights, Australia. In addition XRD results were used to measure residual stresses on the surface of the blade to compliment the neutron measurements. The results of the measurements were used to "calibrate" an FEA model of the weld process.

2:40 PM
Characterization of Residual Stresses in Turbine Discs by Neutron Diffraction and Finite Element Modeling: *Ulrike Cihak*[1]; Peter Staron[2]; Helmut Clemens[1]; Wilfried Marketz[3]; Martin Stockinger[3]; [1]Mining University Leoben, Dept. Physl. Metall. & Matls. Testing, Franz-Josef-Str. 18, Leoben 8700 Austria; [2]GKSS Forschungszentrum, Inst. of Matls. Rsch., Max-Planck-Strasse 1, Geesthacht 21502 Germany; [3]Böhler Schmiedetechnik GmbH & CoKG, Mariazeller Strasse 25, Kapfenberg 8605 Austria

Knowledge of the evolution of residual stresses developing during fabrication of industrial components is steadily gaining importance. Therefore, the prevailing residual stresses in a number of identical, hot-forged, water quenched turbine discs made of nickel-base alloy IN718 have been studied by neutron diffraction. Simultaneously, independent finite element simulations (FEM) have been performed characterizing different quenching rates. The trend of these simulations agrees with that obtained from diffraction measurements. Although the (311) peak was used, which is generally recommended for fcc materials, the results exhibit an offset compared to the FEM results. To clarify this discrepancy further investigations, using an alternative peak, were carried out and a geometrically simple model plate of IN718 applying identical heat treatment conditions was studied. The results, received from the thin model plate and the thick commercial part, are compared with FEM predictions, which are based on detailed measurements of the heat transfer velocity during quenching.

3:00 PM
Residual Strain Distribution in Bent Composite Boiler Tubes and Welded Panels: *Camden Richards Hubbard*[1]; E. Andrew Payzant[1]; Fei Tang[1]; James Keiser[1]; Adam Willoughby[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., MS 6064, Bldg. 4515, Oak Ridge, TN 37831-6064 USA

Kraft recovery boilers, essential chemical and energy recovery units in pulp and paper mills, are typically constructed of carbon steel boiler tubes (SA210 Gd A1) clad with a more corrosion resistant material. These composite tubes are bent and welded together to form air port panels to permit the combustion air to enter at a number of locations around the boiler. Cracking of the bent tubes in the air port is a serious concern. Crack propagation through the clad layer into the carbon steel inner tube likely involves stress corrosion cracking or corrosion-fatigue cracking. The stresses in bent tubes and air ports as manufactured and after service as well as of different designs are being characterized with the goal of contributing to the reduction of failures at air ports.

3:20 PM
Strain Measurements at Railway Wheels: *Mirco Grosse*[1]; Peter Ottlinger[2]; [1]Paul Scherrer Institut, Spallation Neutron Source Div., Villigen 5232 Switzerland; [2]University of Applied Sciences, Dresden 01008 Germany

Strain measurements in railway wheels in the as manufactured state, two usage levels and the end of live state were performed by neutron diffaction using the POLDI facility at SINQ/PSI. In the as manufactured state four railway wheels were investigated. In all four wheels no significant strains were found. After 18400 km usage first strain gradients close to the outer surface of the wheels were detected. In middle ranges including the positions of the nominal highest loads the changes in strain are weak. After an usage of 61000 km the gradients becomes strong at the axial outer position between about +700 ìå close below the tread and - 500 ìå in a depth of 12.5 mm below the tread. At axial middle positions also strain gradients are formed. The end of live state (510000 km) differs only slightly from the state measured after a usage of 61000 km.

3:40 PM Break

4:00 PM Invited
Measurement of Residual and Loading Stress in Composite Materials Using Neutron Diffraction: *Yoshiaki Akiniwa*[1]; [1]Nagoya University, Mechl. Engrg., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

For the composite materials, since the coefficient of thermal expansion of reinforcements is different from that of matrix, the residual stress is induced during cool down from the fabrication temperature. The residual stress has a significant effect on the mechanical properties and strength of the composite. Furthermore, elastic constants of the reinforcement are different from those of the matrix. Then the stress state in each constituent phase during loading depends on the configuration of the composite. In the present study, thermal residual stresses in ceramic composites of alumina mixed with various volume fractions of zirconia and of silicon carbide were measured by the neutron diffraction method. Then phase stresses in an aluminum alloy reinforced with silicon carbide particles were measured under loading. The measured residual stress and the loading stress were compared with the predicted values calculated by the inclusion models.

4:20 PM Invited
Strength Differential Effect in PM 6061Al-15 vol%SiCw Composites: Ricardo Fernandez[2]; *Giovanni Bruno*[1]; Gaspar Gonzalez-Doncel[3]; [1]ILL, Diffraction Grp., 6, rue Jules Horowitz, BP 156, Grenoble F-38042 France; [2]Indo SA, Thin Film Rsch., R&D Dept., Sta Eulalia 181, L'Hospitalet de LLobregat (Barcelona) E-08902 Spain; [3]CENIM, CSIC, Physl. Metall., Avda. de Gregorio del Amo, 8, Madrid E-28040 Spain

The correlation was studied between the strength-differential effect (SDE) in metal-matrix composites and the residual stress (RS)

determined by neutron diffraction (ND). Three 6061Al-15 vol.% SiCw composites were used, with different reinforcement orientations and distributions. Tensile RS in the matrix and compressive in the reinforcement were observed. This agrees with the higher thermal contraction of the matrix than that of the reinforcement. The large hydrostatic microscopic RS agrees with the large fraction of the randomly oriented whiskers. An axial deviatoric stress arises from the remaining whiskers, aligned along the extrusion axis. The RS obtained correlates well with the experimental SDE data. A modified Eshelby model, taking into account the orientation and the spatial distribution of the whiskers was introduced. This agrees with ND results and is able to explain the different SDEs observed in the various composites. The micro-RS can be considered as the origin of the SDE.

4:40 PM
Neutron Diffraction Study of Residual Stress in Thermally Sprayed Metallic Deposits: *Werner Wagner*[1]; Thomas Keller[1]; Nikolaus Margadant[2]; Thilo Pirling[3]; [1]Paul-Scherrer-Institute, Spallation Neutron Source Div., Villigen 5232 Switzerland; [2]EMPA Swiss Federal Laboratories for Materials Testing and Research, Thun Switzerland; [3]Institute Laue Langevin, Grenoble France

The present study investigates metallic NiCrAlY deposits on steel substrates. Neutron diffraction was used to obtain spatially resolved strain and stress profiles in the deposits and the underlying steel substrates. For the neutron diffraction measurements special emphasis was given to a high spatial resolution when entering the surface and crossing the interface to the substrate. Samples of four different spray techniques were analyzed: atmospheric and water-stabilized plasma spraying, flame spraying and wire arc spraying. The results are quantitatively compared with the average in-plane residual stress determined by complementary mechanical profilometry. While the stress profiles are similar for all investigated spray techniques, their absolute values and gradients vary strongly. This is attributed to different quenching stresses from the impinging particles, different thermal histories the deposit/substrate systems undergo during the spraying, and to different coating properties. Crack formation is found to be a dominant mechanism for stress relaxation in the surface plane.

Neutron Scattering in Materials Research: Diffusion and Other Processes

Sponsored by: Electronic, Magnetic & Photonic Materials Division, EMPMD/SMD-Chemistry & Physics of Materials Committee
Program Organizers: Brent T. Fultz, California Institute of Technology, Department of Materials Science, Pasadena, CA 91125 USA; Michael Atzmon, University of Michigan, Department of Materials Science & Engineering, Ann Arbor, MI 48109 USA

Wednesday PM Room: 3022
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Mike Manley, Los Alamos National Laboratory, Matls. Sci. & Tech. - 6, Los Alamos, NM 87545 USA; Doug L. Abernathy, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831-6474 USA

2:00 PM Invited
Opportunities for Quasielastic Neutron Scattering at the Spallation Neutron Source: *Kenneth W. Herwig*[1]; [1]Oak Ridge National Laboratory, Spallation Neutron Source, Bethel Valley Rd., Oak Ridge, TN 37831-6474 USA

The Spallation Neutron Source (SNS) is an accelerator-based neutron source currently under construction at the Oak Ridge National Laboratory in Tennessee. Scheduled for completion in 2006, the facility will provide the most intense pulsed neutron beams in the world for scientific and industrial research and development. Fifteen of the available 24 beam line locations have been assigned through a review process to neutron scattering instruments for condensed matter research and a sixteenth has been assigned for fundamental physics studies. Two of the early instruments will provide exceptional opportunities for quasielastic neutron scattering studies of local diffusive motions on time scales from 100's of psec to 0.1 psec and length scales of 2 to 50 Angstroms. The capabilities of these two instruments will be presented with a particular emphasis on applications in materials science and engineering.

2:30 PM Invited
Scientific Outlook for the SNS Liquids Reflectometer: *John F. Ankner*[1]; [1]Oak Ridge National Laboratory, Spallation Neutron Source, PO Box 2008, MS 6474, Oak Ridge, TN 37831-6474 USA

Neutron reflectivity has evolved in recent years from an exotic method used by a small community of experts to a powerful tool for the investigation of thin films and interfaces on the nanoscale. In contrast to x-ray reflectivity, which provides electron density profiles, neutron reflectivity reveals nuclear and magnetization density variation. This is an essential difference when exploring hydrogenous materials such as polymers, Langmuir-Blodgett films, and membranes. Deuterium (2H) features dramatically different scattering properties from hydrogen (1H), allowing contrast enhancement of hydrogenous materials by selective doping of chemically identical nuclei. The SNS liquids reflectometer, due for commissioning in 2006, is designed to accommodate a wide range of scientific studies of both liquid and solid surfaces, over length scales of 10-10,000 Å. Flexible handling of incident angle, wavelength bandwidth, angular resolution, and position-sensitive detection will allow the user to focus on the length and time scales of interest in a particular material. An increase in beam brilliance of a factor of 20-50 over existing instruments will provide new capabilities for kinetic studies, pump-probe, and small-sample experiments.

3:00 PM Invited
Neutron Diffraction and Neutron Scattering Investigations of Cement: *Ronald R. Berliner*[1]; [1]North Carolina State University, Nucl. Reactor Prog., PO Box 7909, Raleigh, NC 27695-7909 USA

Ordinary portland cement is a mixture of several Ca and Al oxide mineral phases that when mixed with water bind rocks and sand together to make concrete. A basic understanding of this material is desirable because of its widespread use as a construction material. Approximately 80M metric tons of cement is consumed annually in the US. Of particular interest are the structure and chemical activity of the isolated cement minerals, the effect of impurities and polytype structural variations on their chemical activity, the nature of the cement hydration reactions and the structure of hardened cement paste. In addition, much remains to be learned about the chemical and environmental avenues of cement and concrete deterioration. For a variety of reasons, neutron methods are particularly effective in the investigation of this system. Neutron diffraction investigations of cement constituent mineral structure will be described. The results of neutron diffraction and quasielastic neutron scattering experiments on the structure, formation, decomposition and water dynamics of cement hydration products will be presented. Finally, the use of neutron quasielastic and inelastic scattering for the investigation of the cement hydration reactions will be described.

3:30 PM Break

3:50 PM
Neutron Diffraction of Hydrogen Absorption in Potassium-Intercalated Graphite: *Channing Ahn*[1]; John J. Vajo[1]; Rachid Yazami[1]; Brent T. Fultz[1]; [1]California Institute of Technology, Mail 138-78, Pasadena, CA 91125 USA

Stage 2 and higher-stage potassium-intercalated graphites are known to adsorb hydrogen at 77K. In the absence of deuterium, the basal planes of graphite show the expected lattice contraction as a function of temperature reduction. In the presence of 4 bar of deuterium, we observe an increase in the basal plane lattice parameter as the temperature is reduced from ambient to 77K due to the absorption of deuterium into the potassium-containing plane. While deuterium saturation is reached at 77K, further expansion of the basal plane lattice parameter is seen as the temperature is lowered to 16 K. This additional expansion is due presumably to the alignment of deuterium molecules within the intercalated layer. While a basic hard sphere model's can account for the known absorption limits of approx. 1.2 wt% at pressures of below 1 bar, a precise determination of preferred sites gives information on the nature of the interaction between potassium and deuterium. This behavior is also seen in Stage 3 and Stage 4 compounds.

4:20 PM
DANSE (Distributed Data Analysis for Neutron Scattering Experiments): Extending the Scientific Toolkit for the Neutron Community: *Michael M. McKerns*[1]; Michael A.G. Aivazis[2]; Tim M. Kelley[1]; June Kim[2]; Brent T. Fultz[1]; [1]California Institute of Technology, Matls. Sci., 1200 E. Calif. Blvd., MC 138-78, Pasadena, CA 91125 USA; [2]California Institute of Technology, Ctr. for Advd. Computing Rsch., 1200 E. Calif. Blvd., MC 158-79, Pasadena, CA 91125 USA

The DANSE system will merge the various computational tasks of neutron scattering into a unified, component based run-time environ-

ment. Standard components will implement data analysis, visualization, modeling, and instrument simulation for all areas of neutron scattering. A core technology of DANSE is an open source framework that supports the software components and mediates their interactions. DANSE will provide tools to help instrument scientists and expert users migrate their existing routines to components, and allow new and casual users to access a stock set of standard analysis applications or configure their own new computing procedures for novel experiments. The modular structure of DANSE parallels the steps of data analysis performed by scientists, thus making it a natural environment for creating flexible computing procedures. DANSE will lower barriers to sharing software, and extend the experimentalist's toolkit with capabilities of analysis and interpretation such as high-performance simulations (band structure, molecular dynamics, etc.), co-analysis of data from multiple experiments, and real-time feedback for experimental control.

Phase Stability, Phase Transformation and Reactive Phase Formation in Electronic Materials IV: Effects of Alloying Additions on the Microstructural Evolution of Solders and Solder Joints

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, EMPMD/SMD-Alloy Phases Committee

Program Organizers: Douglas J. Swenson, Michigan Technological University, Department of Materials Science & Engineering, Houghton, MI 49931 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; Sinn-Wen Chen, National Tsing-Hua University, Department of Chemical Engineering, Hsinchu 300 Taiwan; C. Robert Kao, National Central University, Department of Chemical and Materials Engineering, Chungli City 32054 Taiwan; Hyuck Mo Lee, Korea Advanced Institute of Science & Technology, Department of Materials Science & Engineering, Taejon 305-701 Korea; Suzanne E. Mohney, Pennsylvania State University, Department of Materials Science & Engineering, University Park, PA 16802 USA; Katsuaki Suganuma, Osaka University, Department of Nanomaterials and Environmental Conscious Technology, Ibaraki, Osaka 567-0047 Japan

Wednesday PM Room: 3016
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Sung K. Kang, IBM, T. J. Watson Rsch. Ctr., Yorktown Hgts., NY 10598 USA; Katsuaki Suganuma, Osaka University, Inst. of Scientific & Industrial Rsch., Ibaraki, Osaka 567-0047 Japan

2:00 PM
Interfacial Reactions of Sn-Ag-Cu Solders Modified by Minor Zn Alloying Addition: *Sung K. Kang*[1]; Da-Yuan Shih[1]; Donovan Leonard[1]; Donald W. Henderson[2]; Sungil Cho[3]; Jin Yu[3]; [1]IBM, Rsch., T. J. Watson Rsch. Ctr., 1101 Kitchawan Rd., PO Box 218, Yorktown Hgts., NY 10598 USA; [2]IBM Microelectronics, Endicott, NY USA; [3]KAIST, Dept. of Matls. Sci. & Engrg., Daejon Korea

The near-ternary-eutectic Sn-Ag-Cu alloys have been identified as a leading Pb-free solder candidate to replace Pb-bearing solders for microelectronic applications. However, recent investigations on the processing behaviors and solder joints reliability assessment have revealed several potential reliability risk factors associated with the alloy system. The formation of large Ag3Sn plates in Sn-Ag-Cu joints, especially solidified in a relatively slow cooling rate, is one issue of concern. In the previous studies, the implications of large Ag3Sn plates on solder joint performance and several methods to control them were discussed. The minor Zn addition was found to be effective in reducing the amount of undercooling required for tin solidification and thereby to suppress the formation of large Ag3Sn plates. The Zn addition also caused the changes in the bulk microstructure as well as the interfacial reaction. In this study, an in-depth characterization of the interfacial reactions of Zn-added Sn-Ag-Cu solders on Cu and Au/Ni surface finishes is presented. The effects of Zn addition on modification of the interfacial IMCs and their growth kinetics are also discussed.

2:30 PM
Effect of Rare Earth Element Addition on the Microstructure of Sn-Ag-Cu Solder Joint: *Bo Li*[1]; Yaowu Shi[1]; Yongping Lei[1]; Fu Guo[1]; Zhidong Xia[1]; [1]Beijing University of Technology, Key Lab. of Advd. Functl. Matls., Ministry of Educ., Coll. of Matls. Sci. & Engrg., 100 Ping Le Yuan, Chaoyang Dist., Beijing 100022 China

Addition of small amount of rare earth (RE) alloying elements has been effective in providing solders with improved strength, creep rupture life, as well as refined microstructure. The current study reports the effects of RE element addition on the microstructure of Sn-3.8Ag-0.7Cu solder joint, especially on the intermetallic compounds (IMCs). The growth of IMCs could be dramatically depressed with appropriate addition of RE elements, resulting in a finer microstructure. The effective range of RE addition was determined. In addition to the typical morphology of Ag3Sn and Cu6Sn5 IMCs, other IMCs that have irregular morphology and uncertain constituents were also observed. The cross sections of Cu6Sn5 whiskers exhibited various morphologies. Different eutectic-like structures, with either lamellar, rod or needle-like morphology, dominated the microstructure with different RE content in the solder alloy. It is suggested that such eutectic-like structures directly affect the creep property of the solder joint.

2:50 PM
Microstructure, Solderability and IMC of Sn-Ag-Cu-RE Lead-Free Solder Alloys: Chi-Man Terence Law[1]; *Chi-Man Lawrence Wu*[1]; Daquan Yu[2]; Lai Wang[2]; [1]City University of Hong Kong, Dept. of Physics & Matls. Sci., 83 Tat Chee Ave., Hong Kong SAR China; [2]Dalian University of Technology, Dept. of Matls. Engrg., Dalian 112063 China

The near-eutectic Sn-3.5wt%Ag-0.7wt%Cu (Sn-3.5Ag-0.7Cu) alloy was doped with rare earth (RE) elements, primarily Ce and La, of 0.05, 0.10 and 0.25 wt% to form Sn-3.5Ag-0.7Cu-xRE solder alloys, to investigate the effect of RE additions on the microstructure and solderability of Sn-3.5Ag-0.7Cu-RE solder alloys on copper coupon, and compared with Sn-37Pb. Their intermetallic layer (IML) thickness between the solder and the Cu substrate was also investigated upon thermal aging at 170°C up to 1000 hr. It was found that, with the addition of RE elements, the microstructure was refined such that the β-Sn grain size was decreased. The Sn-3.5Ag-0.7Cu-0.1RE alloy had the best wetting performance, which had become very close to that of Sn-37Pb. It was also found that the thickness of the IML during thermal aging was decreased after the addition of RE elements to Sn-3.5Ag-0.7Cu.

3:10 PM
Characterizing Metallurgical Reaction of Sn-Ag-Cu Composite Solder by Mechanical Alloying with Electroless Ni-P/Cu Under-Bump Metallization After Various Reflow Cycles: *Li-Yin Hsiao*[1]; Szu-Tsung Kao[1]; Jenq-Gong Duh[1]; [1]National Tsing Hua University, Dept. of Matls. Sci. & Engrg., 101 Sec. 2 Kuang-Fu Rd., Hsinchu 300 Taiwan

Electroless Ni-P/Cu under-bump metallization (UBM) is widely used in electronics packaging. The SnAgCu lead-free composite solder pastes were produced by mechanical alloying (MA) process with doping Cu_6Sn_5 nanoalloys. In this study, the interfacial reaction of SnAgCu composite solders with electroless Ni/Cu UBM was investigated with different reflow cycles. Transmission electron microscopy (TEM) analysis was used to identify the intermetallic compounds by the derived selected area diffraction (SAD) patterns and to observe the interfacial region between the SnAgCu composite solder and electroless Ni-P/Cu UBM by bright field (BF) image. Field-emission scanning electron microscopy (FE-SEM) analysis was employed to analyze the morphology and structure in intermetallic compounds. The intermetallic compound (IMC) formed at the interface between the SnAgCu composite solders and electroless Ni/Cu UBM during reflowing were mainly $(Ni_{1-x}, Cu_x)_3Sn_4$ and $(Cu_{1-y}, Ni_y)_6Sn_5$. The elemental distribution near the interfacial region was evaluated by an electron probe microanalyzer (EPMA). Based on the observation and characterization by FESEM, TEM and EPMA, the reaction mechanism of interfacial phase transformation between Sn-Ag-Cu composite solders and electroless Ni-P/Cu UBM with different reflow cycles was proposed.

3:30 PM Break

3:40 PM
An Investigation of the Formation and Presence of Intermetallic Compounds at the Interface Between Substrate (Copper) and Nanoparticle Reinforced Solder: *D. C. Lin*[1]; G.-X. Wang[1]; T. S. Srivatsan[1]; [1]University of Akron, Dept. of Mechl. Engrg., 302 Buchtel Mall, Akron, OH 44325-3903 USA

Eutectic Sn-3.5%Ag solder is an economically affordable and genetically attractive material for performing research studies primarily because it has a simple eutectic microstructure and is a viable and attractive alternative to replace the lead-containing solders. Using the eutectic solder, a series of experiments were conducted to convincingly demonstrate the role of nano-sized powder additions as a logical

sound and economically feasible method for enhancing the strength of Sn-3.5%Ag solder for even trace additions the nanopowders. The increase in strength is ascribed to be due to the conjoint and mutually interactive influences of interfacial enhancement between the copper substrate and the solder, and a refinement of the solder matrix. This presentation will highlight experimental findings and observations relating to wetting of the copper substrate of the solders: (a) eutectic Sn-3.5%Ag solder, and (b) a composite solder resulting from blending the eutectic solder with nanopowders of nickel. Microstructural observations at the solder-substrate interface revealed the nature and morphology of the intermetallic compounds for the nickel nanopowders reinforced Sn-Ag composite solder to be totally different when compared to the eutectic Sn-3.5%Ag counterpart. The kinetics governing microstructural development and intrinsic microstructural features will be highlighted in light of the conjoint influence of reinforcement influences and its resultant influence of heat transfer.

4:00 PM
Effect of Trace Elements on the Interface Reactions Between Two Lead-Free Solders and Copper or Nickel Substrates: *D. Soares*[1]; C. Vilarinho[1]; J. J. Barbosa[1]; R. Silva[2]; P. Bré[3]; F. Castro[1]; [1]University of Minho, Dept. of Mechl. Engrg., Campus de Azurem, Guimarães 4810-058 Portugal; [2]TecMinho - Associação Universidade Empresa para o Desenvolvimento, Campus de Azurem, Guimarães 4810-058 Portugal; [3]Peixinhos, Lda, Rua Silva Aroso, 1311, Apartado 2136, Perafita 4451-901 Portugal

Traditional Sn-Pb solder alloys are being replaced, because of environmental and health concerns about lead toxicity. Among some alternative alloy systems, the Sn-Zn and Sn-Cu base alloy systems have been studied and reveal promising properties. The reliability of a solder joint is affected by the solder/substrate interaction and the nature of the layers formed at the interface. The solder/substrate reactions, for Sn-Zn and Sn-Cu base solder alloys, were evaluated in what concerns the morphology and chemical composition of the interface layers. It was studied the effect of the addition of P or Al, at low levels, on the chemical composition of the layers present at the interface. The phases formed at the interface between the Cu or Ni substrate and a molten lead-free solder were studied, at 250ºC, with different stage times and alloy compositions. The melting temperatures, of the studied alloys, were determined by Differential Scanning Calorimetry (DSC). Identification of equilibrium phases formed at the interface layer, and the evaluation of their chemical composition were performed by Scanning Electron Microscopy (SEM/EDS). Results of the studied systems were compared with the interface characteristics obtained for a traditional Sn-Pb solder alloy. Different interface characteristics were obtained, namely for the alloys containing Zn. The oxidation susceptibility, of both kinds of solder alloys, was measured by TGA. It was studied the effect of the presence of oxygen on the chemical composition of intermetallic compounds formed at the solder/substrate interface.

4:20 PM
Phase Transformations in Doped Lead-Free Solder Paste: *Mark A. Palmer*[1]; [1]Kettering University, IMEB Dept., 1700 W. Third Ave., Flint, MI 48504 USA

Small amounts of eutectic Sn-Bi powder have been added to eutectic Sn-Ag-Bi solder paste to reduce the processing temperature. Solder joints with mechanical properties comparable to joints prepared with eutectic Sn-Pb solder have been prepared at processing temperatures below 220°C. DSC Analysis has been performed to determine if transient liquid phase sintering has occurs. It will also be determined if the small amount of low melting powder can be used to decrease the reflow time at temperatures just above the melting point, without reducing the melting temperature of the solder paste. Undergraduate students have been extensively involved in this work which has been supported by the Rodes Professorship at Kettering University.

4:40 PM
Effects of Bi and Pb on Oxidation in Humidity of Low Temperature Lead-Free Solder Systems: *Keun-Soo Kim*[1]; Katsuaki Suganuma[1]; [1]Osaka University, Inst. of Scientific & Industl. Rsch., Mihogaoka 8-1, Ibaraki, Osaka 567-0047 Japan

As Sn-Ag-Cu lead-free solder has somewhat higher melting temperature than the conventional Sn-Pb solder, and is much more expensive, it is required to establish a certain kind of low temperature soldering techniques. Sn-Zn and Sn-Ag-In solders with or without Bi have relatively low melting temperature close to Sn-Pb eutectic solder. These solders can provide an excellent solution to those requirements mentioned above. However, there are still unknown features on the effects of Bi, which is added for the improvement of wettability, and of Pb, which can be incorporated from Sn-Pb plated components, on Sn-Zn and Sn-Ag-In soldered joints both on oxidation and on Sn whisker formation in humid atmosphere. The purpose of present work is to investigate the microstructure and joining strength changes of Sn-Zn(-Bi) and Sn-Ag-In-Bi soldered joints during humidity exposure. The formation processes of oxide and Sn whiskers in Sn-Zn-Bi and Sn-Ag-In-Bi soldered joints have been examined.

5:00 PM
Additive Alloying Effects on the Generation of Intermetallic Compounds Between Sn-Ag-Ni-Co Solder and Cu: *F. Gao*[1]; T. Takemoto[1]; H. Nishikawa[1]; A. Komatsu[1]; [1]Osaka University, Joining & Welding Rsch. Inst., Osaka 565-0871 Japan

The characteristics of intermetallic compounds (IMC) generated between Sn-3.5Ag solder alloying with additive element couples (0.2wt%Ni and 0.1wt%Co) and Cu substrate was presented. The additive element couples, say, Ni and Co, were all detected in the IMC produced during soldering. The microstructure of IMC was identified as $(Cu_{(1-x-y)}, Ni_x, Co_y)_6Sn_5$ by EPMA and XRD. However, the morphology of $(Cu_{(1-x-y)}, Ni_x, Co_y)_6Sn_5$ was coral-like, and not as dense as the typical scallop-like Cu_6Sn_5. A duplex structure, say, two distinct regions bearing differing concentration of Ni and Co within the $(Cu_{(1-x-y)}, Ni_x, Co_y)_6Sn_5$ were verified. Much higher Ni and Co concentration were probed in the outer region adjacent to the matrix of solder, while lower concentration of Ni and Co at the inner region of IMC connected with Cu. After aging, the $(Cu_{(1-x-y)}, Ni_x, Co_y)_6Sn_5$ tended to be dense. And the Cu_3Sn phase could not be detected after aging at 110ºC, while appeared at 130ºC and 150ºC for 504h.

Phase Transformations Within Small-Size Systems: Transformations in Thin/Thick Films and Multilayers

Sponsored by: Materials Processing & Manufacturing Division, MPMD-Phase Transformation Committee-(Jt. ASM-MSCTS), EMPMD/SMD-Chemistry & Physics of Materials Committee, EMPMD-Nanomaterials Committee

Program Organizers: Vijay K. Vasudevan, University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012 USA; Robert D. Shull, National Institute of Standards and Testing, Metallurgy Division, Gaithersburg, MD 20899-8552 USA; George Spanos, Naval Research Laboratory, Physical Metallurgy Branch, Washington, DC 20375-5000 USA; Xinghang Zhang, Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843-3123 USA

Wednesday PM Room: 3002
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Xinghang Zhang, Los Alamos National Laboratory, Matls. Sci. & Tech., Los Alamos, NM 87545 USA; Christopher A. Schuh, Massachusetts Institute of Technology, Matls. Sci. & Engrg., Cambridge, MA 02139 USA

2:00 PM Invited
Phase Transformations in Epitaxial Thin Films: Y. L. Li[1]; M. Biegalski[1]; A. Sharan[1]; V. Gopalan[1]; D. Schlom[1]; *L. Q. Chen*[1]; K. J. Choi[2]; C. B. Eom[2]; [1]Pennsylvania State University, Matls. Sci. & Engrg., 102 Steidle Bldg., Univ. Park, PA 16802 USA; [2]University of Wisconsin, Matls. Sci. & Engrg., Madison, WI 53706 USA

Many applications of materials require the growth of thin films on a substrate. It is known that the interface between an epitaxial film and a substrate is coherent when the film thickness is small, i.e. below the critical thickness for interfacial dislocation nucleation. The thermodynamics and kinetics of phase transformations in such an epitaxial film is profoundly affected by both the coherent strain due to the substrate and by the film thickness when it is below a few nanometers. The focus of this presentation will be on the effect of substrate constraint on the phase transformations of an epitaxial thin film. It is shown that for the simple cases of isostructural phase separation of a film or of the transformations of a single crystal film to a single domain state, the shifts in critical temperatures of phase transformations can be analytically calculated using independently measured parameters. As an example, BaTiO3 ferroelectic thin films are studied using thermodynamic theories based on the phenomenological Landau theories. It is shown that ferroelectric transition temperatures can be shifted by about 300°C with about 1% compressive strain and about 450°C with 1.6% strain as compared to the bulk ferroelectric transition temperature of ~ 120°C. The predictions are confirmed by ex-

perimental measurements of lattice parameters and second-harmonic generation on fully coherent (001) BaTiO3 thin films epitaxially grown on (110) GdScO3 and DyScO3 substrates as a function of temperature.

2:35 PM
Grain Boundary Segregation and the Equilibrium Grain Size in Nanocrystalline Ni-W Alloys: Andrew J. Detor[1]; *Christopher A. Schuh*[1]; [1]Massachusetts Institute of Technology, Dept. of Matls. Sci. & Engrg., 77 Mass. Ave., Rm. 8-211, Cambridge, MA 02139 USA

In binary solid solution alloys with a tendency for grain boundary segregation, nanocrystalline grain structures can be thermodynamically stable, and grain size can in fact be controlled quite precisely through tailoring of alloy composition. We have explored this issue in binary Ni-W alloys prepared by electrodeposition, where the alloy composition can be varied through changes in electrolytic current density, the shape of the applied current waveform, and temperature of the deposition bath. Films with grain sizes from d ˜ 50 nm down to the amorphous limit (d ˜ 1 nm) have been produced, and their grain structure correlated with tungsten content. The experimental results are rationalized on the basis of thermodynamic calculations as well as computer simulations employing embedded atom method potentials for Ni and W. Finally, the prospect for fundamental studies of mechanical property variations with changes in grain size will be discussed.

3:00 PM
Phase Transformations in Metals Being Electrodeposited: *Oleg B. Girin*[1]; [1]Ukrainian State University of Chemical Engineering, Dept. of Matls. Sci., Pr. Gagarina, 8, Dnipropetrovsk 49005 Ukraine

It has been found that during electrodeposition of metals a supercooled metal liquid is being formed that is solidified at the deposition temperature in the form of a crystalline and/or amorphous phase. These phase transformations are caused by a very fast (explosive) character of metal precipitation as a result of the chain reaction of electrochemical formation of atoms and of the transfer of atom clusters from the liquid state to a more stable solid state. These phase transitions are proved by the existence in the electrodeposited metals of metastable structures corresponding to the amorphous structure of the solidified metal liquid, the highly defective crystalline structure of the metal quenched from its liquid state, and the intermediate modifications resulting from the super-fast crystallization of the liquid phase in the polymorphous metal. This research project is financed by the Ministry of Education and Science of Ukraine, R&D project No. 0102U001953.

3:25 PM Break

3:40 PM Invited
Size Induced Transformations in Nanostructured Thin Films and Multilayers: *Rajarshi Banerjee*[1]; Arda Genc[1]; Gregory B. Thompson[2]; Sangita Bose[3]; Pushan Ayyub[3]; Hamish L. Fraser[1]; [1]Ohio State University, Matls. Sci. & Engrg., 477 Watts Hall, 2041 College Rd., Columbus, OH 43210 USA; [2]University of Alabama, Metallurgl. & Matls. Engrg., Tuscaloosa, AL USA; [3]Tata Institute of Fundamental Research, Condensed Matter Physics & Matls. Sci., Mumbai India

Size effects in nanostructured materials have attracted a lot of attention in recent years. The dimensional constraints imposed on either one, two, or all three dimensions in such materials often results in interesting structural changes and consequently influences their properties. In this presentation illustrative examples from our work on a number of different systems will be discussed. Firstly, the case of stabilization of pseudomorphic phases in nanoscale metallic multilayers will be discussed wherein reduction in the layer thickness to the nanometer regime results in one of the layers undergoing a structural transformation and adopting the same crystal structure as that of the adjacent layer. Secondly, size-induced structural transformations in nanostructured thin films will be discussed, including a fcc to hexagonal 4H phase transformation in nanocrystalline Ag and a hexagonal 2H to cubic 3C phase transformation in nanocrystalline CdS. Finally, an interesting example of size-induced metal-insulator transition in nanocrystalline Nb will be presented.

4:15 PM
Atom Probe Tomography of Pseudomorphic Phases in Thin Multilayered Films: *G. B. Thompson*[1]; M. K. Miller[2]; R. Banerjee[3]; H. L. Fraser[3]; [1]University of Alabama, Metallurgl. & Matls. Engrg., A101, Box 870202, Tuscaloosa, AL 35487-0202 USA; [2]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN USA; [3]Ohio State University, Dept. of Matls. Sci. & Engrg., 2041 College Rd., Columbus, OH 43210 USA

Ti/Nb and Zr/Nb thin film multilayers have been sputtered deposited. As the individual layer thickness of either Ti or Zr is decreased, an allotropic phase transformations from hcp to bcc occurred within the Ti or Zr layer. Using a thermodynamic model, the stabilization of the pseudomorphic bcc phase has been rationalized as a competition between interfacial and volumetric free energies. These energies are sensitive to the compositional variations within the layers and at the interfaces. Atom probe tomography (APT) has been used to characterize the interdiffusion and intermixing between the layers. It was found that the amount of interdiffusion and interfacial intermixing was significantly influenced by the stacking sequence of the films as well as the phase of the individual layer. For example, Nb achieved a pseudo-equilibrium concentration of ~ 20at%Nb in the bcc Ti layer where as it had negligible interdiffusion into the hcp Ti layer.

4:40 PM
Oscillatory Reaction in Nanostructured Multilayer Foils: *Jiaping Wang*[1]; Jonathan C. Trenkle[1]; Etienne Besnoin[2]; Omar M. Knio[3]; Todd C. Hufnagel[1]; Timothy P. Weihs[1]; [1]Johns Hopkins University, Matls. Sci. & Engrg., 102 Maryland Hall, 3400 N. Charles St., Baltimore, MD 21218 USA; [2]Reactive Nanotechnologies, 111 Lake Front Dr., Hunt Valley, MD 21030 USA; [3]Johns Hopkins University, Mechl. Engrg., Baltimore, MD 21218 USA

We have observed oscillatory self-propagating exothermic reactions in both Al/Ni and Zr/CuNi/Al multilayer foils. Self-propagating reactions can be initiated in these foils with a small thermal pulse and are driven by a reduction in atomic bond energy. As atoms mix normal to the layers, heat is released and conducted parallel to the layers. Experimental studies and numerical models have demonstrated that the formation reactions propagate in the foils in an unsteady way, characterized by superadiabatic temperature excursions and large variations in instantaneous reaction velocity. Evidence for the oscillations can be seen in the microstructure of the reaction products, the length scale of which correlates with an observed texture on the surfaces of reacted foils. This texture arises from differential thermal expansion in the foil as the reaction propagates unsteadily. We examine and describe the effects of bilayer (or trilayer) thickness, heat of reaction, premixing, ambient temperature, and cooling rate on the magnitude and period of the oscillatory reactions.

5:05 PM Closing Remarks: Vijay Vasudevan, George Spanos, Robert Shull and Xinghang Zhang

Powder Metallurgy Research and Development in the Transportation Industry: Sintering and Densification - P/M Processing

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Powder Materials Committee
Program Organizer: James W. Sears, South Dakota School of Mines & Technology, Additive Manufacturing Laboratory, Rapid City, SD 57701 USA

Wednesday PM Room: 3008
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Fernand D.S. Marquis, South Dakota School of Mines & Technology, Dept. of Matls. & Metallurgl. Engrg., Rapid City, SD 57701 USA

2:00 PM
Microwave Sintering of Functionally Graded Composites (Preliminary Study): *Eugene Al Olevsky*[1]; Xuan Wang[1]; Mark Russakoff[1]; Marc Andre Meyers[2]; [1]San Diego State University, Mechl. Engrg. Dept., 5500 Campanile Dr., San Diego, CA 92182-1323 USA; [2]University of California, MAE Dept., La Jolla, CA 92093-0416 USA

Functionally graded materials (FGM) are a promising class of materials for a broad range of industrial applications. In automotive industry, graded composites for claddings, exhaust valves, coatings for tribological applications, electronic circuitry components are examples of the potential usage of FGM where gradual spatial distribution of material composition is essential for solving the problem of thermomechanical properties' mismatch. Due to the inherent nonuniformity of properties, the fabrication of functionally graded materials offers substantial challenges. In particular, during sintering a differential shrinkage can lead to distortions and damage of produced components. In the present study a mathematical model for microwave sintering of functionally graded composites is developed. Based on the model, the evolution of sintered macroscopic shape is predicted

and optimized. The modeling effort is supported by experiments on microwave sintering of green parts shaped by electrophoretic deposition. For several metal/ oxide ceramics material systems it is shown that microwave sintering of graded composites provides both high process efficiency and high final relative density.

2:25 PM
Characteristics of W-Ni-Fe-(Cr) Powder in Metal Injection Molding: *Fei Yi Hung*[1]; Truan Sheng Lui[1]; [1]National Cheng Kung University, Dept. of Matls. Sci. & Engrg., No.1, Univ., Rd., Tainan 701 Taiwan

W-Ni-Fe-(3~6Cr) alloy powders used for metal injection molding (MIM) to understand the sintering structures. The effect of Cr content and tungsten-powder particle size in mechanical properties of W-Ni-Fe-(Cr) alloy were also discussed. According to the experimental results, the shrink rate of volume in W-Ni-Fe alloy decreased with decreased the particle size of tungsten-powder. Even if slightly decreased the particle size of tungsten-powder that could still play an important role on raising fracture resistance and matrix hardness. If added the Cr element, the fracture strength decreased but the salt spray property could be improved. Besides, the Cr element affected the microstructure and it's concentration was also different in composed of phases.

2:50 PM
Repair of Gas Turbine Engine Components with Laser Powder Deposition: Seth Miller[1]; Eric Henderson[1]; Bryan Woods[1]; Matt Heath[1]; *James W. Sears*[1]; [1]South Dakota School of Mines & Technology, Additive Mfg. Lab., 501 E. St. Joseph St., Rapid City, SD 57701 USA

Laser Powder Deposition (LPD) for component repair offers some unique solutions for Gas Turbine Engine applications. LPD is a CAD/CAM solid freeform fabrication technology that uses metal powder and laser fusion to repair components. Inherent to LPD is the ability to add material for repair of critical GTE components with minimal heat affect to the under lying material. Also, due to the nature of LPD, hard coatings can be achieved without heat treatment allowing for repair of heat-treated steels. In some cases LPD repair can be used to replace hard chrome or carburized surfaces. Details of several GTE components that have been repaired will be disclosed.

3:15 PM Break

3:25 PM
Use of Combustion Synthesis in Preparing Ceramic-Matrix and Metal-Matrix Composite Powders: *K. Scott Weil*[1]; John Hardy[1]; [1]Pacific Northwest National Laboratory, Matls. Dept., 902 Battelle Blvd., PO Box 999, Richland, WA 99352 USA

A standard combustion-based approach typically used to synthesize nanosize oxide powders has been modified to prepare composite oxide-metal powders for subsequent densification via dynamic compaction into ceramic- or metal-matrix composites. Metal nitrate salts of interest were dissolved in the appropriate ratio in water and combined with glycine, then heated to cause autoignition. The resulting product consists of an intimate and well-dispersed mixture of nanometer size oxide and metal cystallites. The effects that various processing parameters, such as metal salt ratio, salt-to-glycine ratio, and combustion atmosphere, have on powder composition, reinforcement phase dispersion, and reinforcement and matrix particle size distribution have been examined and will be discussed.

3:50 PM
Structure Property Characteristics of Shock Compacted Bulk Exchange-Coupled Pr2Fe14B/a-Fe Nanocomposite Magnets: Zhiqiang Jin[1]; *Naresh N. Thadhani*[1]; [1]Georgia Institute of Technology, Matls. Sci. & Engrg., 771 Ferst Dr., Erskine Love Mfg. Bldg., Atlanta, GA 30332-0245 USA

Shock compaction offers the potential of fabricating bulk nanocrystalline materials via consolidation of amorphous and/or nanocrystalline alloy powders, while retaining the metastable structure and nano-scale grain size. In this work, shock waves generated using explosives and gas-gun impact, were utilized to consolidate exchange-coupled Pr2Fe14B/a-Fe hard/soft phase nanocomposite powders into bulk compacts. Design of the consolidation fixtures, densification conditions, and starting powder properties allowed control of the final density and retention of the nanoscale structure of the hard/soft magnetic phases in the recovered shock-compacted samples compacts of ~99% of full density. TEM observations revealed retention of ~15-25 nm grain size, ensuring exchange coupling between the hard and soft phases. The resulting properties including remnance, coercivity, and energy product, indicate potential for the use of shock compaction for making bulk nanocomposite magnets for applications in motors for military vehicles. The unique attributes of shock-densification in forming and retaining the nanocrystalline structure, and therefore leading to improved magnetic properties will be described. Funded by DARPA through ARO under grant DAAD19-03-1-0038.

4:15 PM
Bi-Material Transportation Components Using Powder Injection Molding: Densification, Shape Complexity, and Performance Attributes: *Randall M. German*[1]; John L. Johnson[1]; [1]Pennsylvania State University, Ctr. for Innovative Sintered Products, 147 Rsch. W., Univ. Park, PA 16802 USA

Tailored materials, possible via selective placement of different compositions within a component, are useful in several transportation systems ranging from rocket nozzles to automotive engine fuel injectors. Research at Penn State has focused on use of powder injection molding to combine shape complexity with functional design. Controlled sintering of two different compositions within the component is the major difficulty with these structures. Differential shrinkage strains during heating often result in delamination, warpage, or cracking. Via experimentation and modeling, options have been isolated to allow co-sintering; these are through adjustments in solids loading, particle size, minor alloying, and heating cycle to minimize damage during heating. Consequently, co-injection molding of bi-material structures has been realized in several material and property combinations, such as glass sealing alloys linked to heat dissipation alloys, and other combinations based on magnetic response, corrosion resistance, hardness, and low cost. This presentation will introduce the problems, opportunities, sintering protocol, and show a products fabricated using this new technology.

4:40 PM
Preparation and Evaluation of Magnetic Fe-Zn Alloys by Explosive Compaction: *Robert Pennington Corson*[1]; Sivaraman Guruswamy[1]; Michael K. McCarter[2]; [1]University of Utah, Metallurgl. Engrg., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA; [2]University of Utah, Mining Engrg., 135 S. 1460 E., Rm. 313, Salt Lake City, UT 84112-0113 USA

Gallium has been shown to significantly change the magnetic properties of Fe relevant to automotive sensor applications. Like its neighbor gallium in the periodic table, zinc has a large solubility in Fe and a completely filled "d" shell. In this work, the effect of alloying Zn with Fe on the magnetic properties is examined. The low boiling point of Zn makes it difficult to alloy with Fe which has a higher melting point. A novel method of creating Fe-Zn alloys is examined. Powders of each metal are mixed together, and are dropped through a magnetic field to enhance sample texturing. Then the sample is liquid phase sintered to create a compact which is then explosively compacted. The resulting alloy is annealed to ensure chemical homogeneity. An examination of the influence of different processing parameters and the Zn content on the alloy properties is presented. Work supported by NSF-DMR Grant #0241603.

Rare Earths: Science, Technology and Applications V: Reactive Metal Processing

Sponsored by: Light Metals Division, LMD-Reactive Metals Committee
Program Organizers: Renato G. Bautista, University of Nevada, Department of Chemical and Metallurgical Engineering, Reno, NV 89557-0136 USA; Dhanesh Chandra, University of Nevada, Chemical and Metallurgical Engineering, Reno, NV 89557 USA; John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA

Wednesday PM Room: 3001
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: John N. Hryn, Argonne National Laboratory, Argonne, IL 60439-4815 USA; Renato G. Bautista, University of Nevada, Cheml. & Metallurgl. Engrg., Reno, NV 89557-0136 USA

2:00 PM
Thermodynamic and Phase Diagram Studies of Some Rare Earth Compounds and Nitrogenation of Fe17Nd Alloy: R. E. Aune[1]; *S. Seetharaman*[1]; [1]Royal Institute of Technology, Div. of Matls. Process Sci., SE-100 44 Stockholm Sweden

With a view to enable a deeper understanding of the electrolytic process route for the manufacture of rare earth alloys, the thermodynamic properties of the rare earth oxides have been compiled and compared with earlier compilations. The data has been corrected for differences in molecular weights and temperature scales. The vapor-

ization of DyF3 was studied by high temperature mass spectrometry. Using the value of enthalpy of formation of solid DyF3 available in literature, the enthalpy of formation of gaseous molecule of DyF3 and its atomization energy were estimated. The Gibbs energy of the gaseous reaction Dy2F6 2DyF3 was evaluated. Mass spectroscopic studies were also carried out in the present laboratory in the case of the system DyF3-Dy2O3 at 1357 K. Phase diagram studies in the case of NdF3-Nd2O3 were also carried out in the present laboratory. Nitogenation studies of Fe17Nd alloys were carried out in the temperature range 1173-1473 K at different N2 partial pressures in a thermogravimetric equipment. The mass changes indicate that there is a long incubation period before the alloy starts picking up nitrogen. This is followed by a sharp mass increase and later a slower increase. At extremely low oxygen partial pressures in nitrogen, the nitrogenated alloy exhibited a Curie temperature of about 600 K. Magnetization studied that the alloys were soft magnets contrary to the behaviour reported in literature.

2:20 PM

Direct Electro-Deoxidation of Metal Oxides to Form Ti-Al and Ti-V Alloys: Stuart L. Finch[1]; *Derek J. Fray*[1]; [1]University of Camabridge, Dept. of Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

Porous pellets containing TiO2, Al2O3 and V2O5 were sintered and then reduced by making the pellet the cathode in a bath of molten calcium chloride. It was found that all the oxides were readily reduced to form Ti-Al and Ti-V alloys. In the case of Ti-Al, there was some loss of aluminium from the pellet. It was found that the final oxygen concentration depended upon the time and temperature of reduction. After 25 hours of reduction the oxygen content of the reduced pellets varied from 600 pmm to 2500 ppm and this was a function of the starting oxides and was in the order TiO2-V2O5<TiO2<TiO2-Al2TiO5<TiO2-Al2O3. The mechanism of the reduction process will be discussed.

2:40 PM

A New High Speed Titanium Production by Subhalide Reduction Process: *Osamu Takeda*[1]; Toru H. Okabe[2]; [1]University of Tokyo, Grad. Sch. of Engrg., 7-3-1 Hongo Bunkyo-ku, Tokyo 113-8656 Japan; [2]University of Tokyo, Inst. of Industl. Sci., 4-6-1 Komaba Meguro-ku, Tokyo 153-8505 Japan

A new titanium production process by magnesiothermic reduction of titanium subhalides using a titanium reaction vessel was investigated. This study discusses the possibility of establishing a high speed, semi-continuous process for the production of high-purity titanium. The titanium subhalide feed material, either titanium dichloride (TiCl2) or titanium trichloride (TiCl3), and magnesium reductant were charged into a titanium reaction vessel, and the vessel was heated at rate 3.3 K min-1 in an argon atmosphere. In the experiment, the sample temperature rapidly increased from around 973~1003 K, and magnesiothermic reduction of titanium subhalide proceeded at high speed. After the reaction, excess magnesium and reaction product magnesium chloride (MgCl2) were removed by draining and vacuum distillation. At this stage, titanium sponge with 99.2% purity was successfully obtained. The titanium reaction vessel showed no signs of damage and thus showed itself to be suitable for magnesiothermic reduction of titanium subhalides.

3:00 PM

Ti Via the Reaction of Molten TiCl2-MgCl2 Salt With Molten Mg: *Akio Fuwa*[1]; S. Takaya[1]; E. Fukasawa[3]; N. Nakahara[3]; [1]Waseda University, Dept. of Matls. Sci. & Engrg., Okubo 3-4-1, Shinjuku-ku, Tokyo 169-8555 Japan; [3]Toho Titanium Co, Chigasaki, Kanagawa 253-8510 Japan

TiCl2 and the molten TiCl2-MgCl2 salt can be well considered as reaction intermediate species in the present Kroll process, where TiCl2 can be considered being produced in the reaction between incoming TiCl4 gas with sponge Ti produced. In this present investigation, this molten salt of TiCl2-MgCl2 has been focused and taken as a reactant in titanium metal production process. First, the molten TiCl2-MgCl2 salt of a specific composition was made through the reaction of solid Ti sponge placed in molten MgCl2 salt with TiCl4 bubbling gas of specific quantity at around 900C, and then, this molten mixed salt was reacted with molten Mg added at the similar temperatures. In our study, titanium metal has been successfully obtained and observed with SEM for their physical characterization. Further, the reaction mechanism of Mg reduction of the TiCl2 constituent in the mixed salt has been discussed in terms of "Electronically Mediated Reaction" mechanism.

3:20 PM

Study on Improving the Current Efficency of the Direct Reduction TiO2 to Ti in Molten CaCl2: *Huimin Lu*[1]; *Chunsen Xu*[1]; *Chunfa Liao*[1]; *Huanqing Huan*[1]; [1]University of Science and Technology, Metallurg. Engrg. Sch., No. 30 Xueyuan Rd., Beijing 100083 China

The direct reduction experiments of TiO2 to Ti in molten CaCl2 (FFC process) are conducted. Reaction mechanism of reduction TiO2 into Ti in molten CaCl2, and the relationships of reduction potential with temperature are studied by Cycle Voltammetry and Chronoamperometry in the range of 800ºC~860ºC. The results of V-A curves, SEM and micro-area elemental analysis show that TiO2 can be reduced to Ti by molten salt electrolysis, and the reduction is conducted in two steps, firstly TiO2 is reduced to TiO, then TiO is reduced to Ti, The reduction potentials in both steps are decreased with the increase of the temperature. In the experiments, the current efficiencies are also estimated; the main reasons of lower current efficiency of FFC process are parasitic reactions such as carbon precipitation and the back-reaction. Some important measures like the modification of cell design are adopted for improving the current efficiency.

3:40 PM Break

3:50 PM Invited

Hydrogen Desorption of TiCl3-Doped NaAlH4 and Na3AlH6: *J. H. Schneibel*[1]; S. A. Speakman[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., Oak Ridge, TN 37831 USA

Commercial NaAlH4 was doped in a Spex mill with varying amounts of TiCl3 and then desorbed resulting in Na3AlH6. The Na3AlH6 obtained in this manner was doped again with varying amounts of TiCl3. In agreement with work by Kiyobayashi et al. (J. Phys. Chem. A, 2003, vol. 107, pp. 7671-7674), programmed thermal desorption of Na3AlH6 occurred at lower temperatures, when the dopant was primarily added to the Na3AlH6 instead of the NaAlH4. In-situ x-ray diffraction work is in progress to determine the structural reasons for this effect. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

4:10 PM Invited

Fabrication and Testing of a Larger Scale Reactive Materials Processing Facility for the Development of Sodium Based Complex Hydride Materials: *Thad M. Adams*[1]; H. B. Peacock[1]; C. S. Stripling[1]; G. B. Rawls[1]; R. Zidan[1]; M. G. Scott[1]; [1]Savannah River National Laboratory, Matls. Applications & Process Tech. Grp., Bldg. 773-41A/151, Aiken, SC 29808 USA

Many of the materials used in hydrogen service including advanced metal hydride systems are based on highly reactive metal systems. These materials tend to be moisture sensitive, pyrophoric, and/or toxic. Additionally, many of these materials can only be synthesized from their elemental or precursor components under high pressures and at temperature. These aspects make synthesis of both lab scale (gms) and prototype scale (kgs) quantities extremely difficult. The design and implementation of a processing system at SRNL capable of producing and handlingconsolidating/loading—prototype scale quantities of these new storage materials is paramount for SRNL and for the success of a national hydrogen economy. The focus of this paper will be a presentation of the development program related to the design, fabrication, install, and start-up an inert high pressure processing and handling station for the production and loading of environmentally sensitive particulate materialsNaAlH4, Mg-Ni, Li alloys and initial results from processing runs on sodium aluminum hydride materials.

4:30 PM

Annealing and Mechanical Property Study of Processed Zirconium: *Joel W. House*[1]; Philip Flater[1]; Robert J. De Angelis[2]; [1]Air Force Research Laboratory, Eglin AFB, FL 32542 USA; [2]University of Florida/GERC, Shalimar, FL 32579 USA

A study of pure zirconium was conducted to develop an engineering specification of structure for use in high strain rate applications. All specimens were water jet cut from a disk. The disk was 228 mm (9 in) in diameter and 6.4 mm (0.25 in) thick. The annealing specimens were cut in a circular pattern centered about the plate axis. These specimens were annealed one hour in vacuum at temperatures between 150 and 700°C. Compression specimens were cut for quasi-static and high rate mechanical properties. These cylindrical specimens had their axis oriented either in the plane of the plate or through the plate thickness. The hardness values of the specimens annealed at the various temperatures were determined. Optical microscopy was used to characterize the microstructural changes with annealing temperature. These data showed slow grain growth in the zirconium material at low temperatures, less than 400°C, but at higher temperatures grain growth was rapid. X-ray texture determinations were made on the mid-plane of the annealed specimens. Grain growth was accompanied by the formation of a strong basal plane texture. Based on the annealing study,

compression specimens with two different grain sizes were fabricated. The effects of grain size, specimen orientation, and texture on mechanical properties will be reported.

4:50 PM
Recovery of Neodymium from NdFeB Magnet Scrap by Leaching with Sulfuric Acid: *Ho-Sung Yoon*[1]; Sung-Don Kim[1]; Jae-chun Lee[1]; [1]Korea Institute of Geoscience and Mineral Resources, Minerals & Matls. Procg. Div., 30 Gajeong-dong, Yuseong-gu, Daejeon 305-350 Korea

The recovery of neodymium from NdFeB magnet scrap has been investigated by roasting in air and leaching selectively with sulfuric acid. The selective extraction of neodymium was examined in terms of roasting temperature, sulfuric acid concentration, and leaching temperature and time. The solubility difference between ferrous sulfate and neodymium sulfate was utilized to precipitate neodymium as neodymium sulfate which was separated as residue during the solid/liquid separation process after leaching of NdFeB magnet scrap. Also, neodymium could be separated from iron by double salt precipitation using sodium sulfate and neodymium hydroxide was prepared easily by adding double salt to sodium hydroxide solution.

5:10 PM
CFD Modeling of the Vacuum Refining of a 2% Na - 1% K - Li Melt: *Ioannis John Roumeliotis*[1]; Ka Wing Ng[1]; Mainul Hasan[1]; Ralph Harris[1]; [1]McGill University, Metals & Matls. Engrg., 3610 Univ. St., M.H. Wong Bldg., Rm. 2160, Montreal, Quebec H3A 2B2 Canada

CFD modeling was performed using FLUENT to predict the performance of a prototype vessel for the vacuum refining of molten lithium containing 2 wt% sodium and 1 wt% potassium. Refined, high purity lithium metal would find application in the production of thin foil lithium electrodes for rechargeable lithium metal polymer batteries. These batteries are prone to failure when there is an excess of 200 ppm alkali metal impurities such as sodium and potassium in the lithium foil. The modeling has identified design issues that need to be addressed.

5:30 PM
Calciothermic Reduction of Neodymium Fluoride: *R. G. Reddy*[1]; P. T. Velu[1]; [1]University of Alabama, Metallurgl. & Matls. Engrg., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

Metallothermic reduction is an important industrial process route for the production of high purity rare earth metals. Production of neodymium metal by the reduction of NdF3 with calcium in the presence of CaCl2 flux, effect of various parameters such as temperature, pressure and salt composition on the yield and impurities content of the Nd metal was analyzed. Thermodynamic calculations using Gibbs energy minimization method was used to characterize the process. Both commercial grade and pure NdF3 showed yield greater than 97%. The yield of Nd decreased with increase in temperature and the flux, and increased with increasing pressure. An excellent agreement was obtained between the calculated and process results. Application of the results to industrial Nd processing systems was discussed.

Recycling - General Sessions: Non-Ferrous Recycling

Sponsored by: Extraction & Processing Division, Light Metals Division, LMD/EPD-Recycling Committee
Program Organizer: Mark E. Schlesinger, University of Missouri, Department of Metallurgical Engineering, Rolla, MO 65409-0001 USA

Wednesday PM Room: 2011
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Mark E. Schlesinger, University of Missouri, Dept. of Matls. Sci. & Engrg., Rolla, MO 65409-0340 USA; Ragnhild Aune, Kungliga Tekniska Högskolan, Dept. of Matls. Sci. & Engrg., SE-100 44 Stockholm, Sweden

2:00 PM Cancelled
Recovery of Chromium and Nickel from Stainless Steel Dusts

2:25 PM
Bench-Scale Study of the Chromium and Nickel Recovery from Dusts and Sludges Generated in the Stainless Steel Production: *Pedro José Nolasco-Sobrinho*[1]; *Jorge Alberto Soares Tenório*[1]; [1]University of São Paulo, Metallurgl. & Matls. Dept., 2463, Prof. Mello Moraes Ave., São Paulo 05508-900 Brazil

Currently Brazilian stainless steel production is around 350,000 t per year. The stainless steel industry generates dusts and sludges with high amounts of chromium, nickel, and iron. The recycling of these wastes is the best means of treatment. The waste characterization is an essential step in a recycling process definition. The techniques used to characterize the wastes were chemical analysis, particle size distribution, determination of the apparent density, X-ray diffraction analyses, and SEM/EDS. Briquettes were prepared using the wastes, Fe-Si and CaO. The briquettes were introduced in molten liquid steel at 1570°, 1600° and 1635°C. A bench-scale piece of equipment was used to melt the steel. A high recovery of chromium (99%) and nickel (100%) from dusts was found. The time required to recover both chromium and nickel was about 15 minutes at 1600°C.

2:50 PM Cancelled
Kinetics Study of the Chromium Oxide Reduction from Brazilian Stainless Steel Dusts

3:15 PM
Electroslag Crucible Remelting for In-House Recycling Heavily Contaminated Scrap of Ni-Base Superalloys: *Vladyslav M. Sokolov*[1]; Vitaly D. Babyuk[1]; Ewgeny A. Zhidkov[1]; [1]PTIMA, Recycling, 34/1 Vernadsky Ave., Kiev-142 03680 Ukraine

Generation of the significant amount of the scrap contaminated by detrimental admixtures is common in the manufacture of nickel-base superalloy components. The analysis of the current technologies for scrap recycling has demonstrated their complexity and expense. All valuable alloying elements with strong affinity for oxygen are irreversibly lost. Besides, the technologies realization requires additional facilities of outside contractors. A novel cost-effective approach has been proposed for increasing the part of the scrap that can be recycled in-house. It is based on the rarely-used electroslag crucible remelting furnace where a charge is melted and refined in an ambient flux. The furnace replaces a traditional induction furnace in basic application. Moreover, the usage of the specific environmentally friendly flux protects the melt from oxidation. The trials have demonstrated that the recycled metal tolerates the stringent requirements of the superalloy industry for wrought and cast products.

3:40 PM Break

3:55 PM
The Dynamics of an ISF Recycling Zn Containing Materials: *Markus Andreas Reuter*[1]; Antoinette van Schaik[1]; [1]TU Delft, Applied Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

Due to the large variation in recycled materials fed to an industrial Imperial Smelting Furnace in Germany, the operation can vary much. With the aid of sophisticated data analysis including neural nets, PCA and decision tree analysis it will be shown how an industrial furnace moves between different operational states. These states are for example a stable thermodynamic state, a mass transfer driven state and various in-between transitional (dynamic/chaotic) states. It will be shown what drives these states and what initiates them. Furthermore, it will be shown that if these states are not identified it is rather difficult to model this type of reactor, especially since the feed varies so often. This analysis has also been applied on a pig-iron blast furnace showing similar trends.

4:20 PM
Kinetic Study on the Volatilization Reaction of Lead in Electric Arc Furnace Dust: *Jae-Min Yoo*[1]; Byung-Su Kim[1]; *Jae-Chun Lee*[1]; Min-Suck Kim[1]; Jin-Ki Jeong[1]; [1]Korea Institute of Geoscience & Mineral Resources, Minls. & Matls. Procg. Div., 30 Gajeong-dong, Yuseong-gu, Daejeon 305-350 Korea

The volatilization reactions of lead by chlorine components as NaCl and KCl in EAF dust were investigated in the temperature range of 973 to 1223 K under an air atmosphere by using a weight-loss technique. The main volatilization reaction of lead was: 2NaCl + PbO + 2SiO2 + Al2O3 = PbCl2(g) + 2NaAlSiO4. At 1223 K with a reaction time of 180 minutes, the volatilization ratio was 99.0% for lead and 98.3% for chlorine, while only 1.3% for zinc. The Jander equation was found to fit the volatilization reaction rate well over the entire temperature range. The volatilization reaction rate of lead was controlled by solid-solid diffusion. An activation energy of 175 kJ/mol (41.8 kcal/mol) was obtained.

4:45 PM
A Thermochemical Study of Different Options for Halogen Removal from Nonferrous Metal-Containing Wastes: *Jürgen Antrekowitsch*[1]; *Markus Hochenhofer*[2]; Dieter Offenthaler[1]; [1]University of Leoben, Nonferrous Metall., Franz-Josef-Straße 18, Leoben, Styria 8700 Austria; [2]Christian Doppler Laboratory for Recycling of Nonferrous Metals, Franz-Josef-Straße 18, Leoben, Styria 8700 Austria

The recyclability of various nonferrous metal wastes often suffers from a relatively high fluorine and chlorine content. Both are inserted in most cases by the use of plastic contaminated scrap and a wide variety of different coatings. These halogens lead to poor product qualities and off gas contamination. Especially the history of zinc recovery from steel mill dusts shows, that the today common hydrometallurgical options are on their limit and therefore are not sufficient in most cases. This thermochemical study should give more information about different pyrometallurgical options, that offer both a chlorine and fluorine reduction and efficient zinc recovery, preferably in one process step. Selective evaporation in different atmospheres and conversion with the use of hydrogen are the main parts in this study. The results combined with the relatively small information available from literature should provide a basis for further investigations in this field.

5:10 PM
Plutonium Pyrochemistry Spent Salts Treatment by Oxidation and Distillation: *Christophe Robert Thiebaut*[1]; Gilles Bourges[1]; David Lambertin[1]; Laurent Pescayre[1]; [1]CEA Centre de Valduc, Bâtiment 119, Is Sur Tille 21120 France

The pyrochemical processing of actinide metals generates pure metal and contaminated by-products such as salts, crucibles, agitators, anodes and cathodes. Chemical treatment can be used to remove these actinides from metal or refractory material. It is more difficult to treat ceramic materials and the salt baths themselves. We propose a way to treat these salts baths: first, an oxidation of the salt bath; then, the chlorides are removed from this concentrate and separated from the actinide oxides by vacuum distillation. This requires a specially designed apparatus, due to the temperature. We will present the results obtained so far: inactive qualification of the process for NaCl/KCl base salt, carried out with lanthanide surrogates; design and inactive tests of pilot equipment for production scale distillation of oxidized plutonium salts; and modifications in order to nuclearize the pilot plant in order to have the first active tests done in 2005.

Refractory Metals in Electronic Applications: Processing and Properties

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Structural Materials Division, ASM International: Materials Science Critical Technology Sector, ASM/MSCTS-Texture & Anisotropy Committee, EMPMD-Thin Films & Interfaces Committee, SMD-Refractory Metals Committee, EMPMD-Electronic Packaging and Interconnection Materials Committee
Program Organizers: Gary A. Rozak, Fabricated Products, Cleveland, OH 44117 USA; Srinivas Chada, Jabil Circuit, Inc., FAR Lab/Advanced Manufacturing Technology, St. Petersburg, FL 33716 USA; David P. Field, Washington State University, Pullman, WA 99164-2920 USA; Chris A. Michaluk, Williams Advanced Materials, Gilbertsville, PA 19525 USA; N. (Ravi) M. Ravindra, New Jersey Institute of Technology, Department of Physics, Newark, NJ 07102 USA

Wednesday PM Room: 3010
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Gary A. Rozak, H.C. Starck, Cleveland, OH 44117-1117 USA

2:00 PM
A Model for the Consolidation of Ultrafine Refractory Metal Powders: *Randall M. German*[1]; [1]Pennsylvania State University, Ctr. for Innovative Sintered Products, 147 Rsch. W., Univ. Park, PA 16802 USA

The refractory metals are fabricated from powders and often this is via the press and sinter route. The resulting components are used in electronic applications ranging from heat sinks to capacitors. However, the unique properties required in the final product often create challenges in processing. A model has been formed for the press-sinter processing of ultrafine and nanoscale refractory metal powders. It predicts apparent density, green density, sintered density, sintered grain size, sintered hardness and strength, and performance attributes using simple inputs of particle size, temperature, pressure, impurity level, and sintering time based on our current understanding of the microstructure evolution during processing. It has been applied to several refractory metal systems. The success is contingent on a new work of sintering concept captured in a single parameter master sintering curve. Demonstrations of property predictions show how novel press-sinter cycles can be isolated for a variety of applicatio ns. This predictive capability allows for process and product optimization based on selected performance features.

2:30 PM
The Effect of Geometry on Residual Strains in Graphite-Mo-Cu Brazed Heatsinks: *F. Michael Hosking*[1]; John J. Stephens[1]; Michael K. Neilsen[2]; [1]Sandia National Laboratories, PO Box 5800, MS 0889, Albuquerque, NM 87185-0889 USA; [2]Sandia National Laboratories, PO Box 5800, MS 0893, Albuquerque, NM 87185-0893 USA

Copper backing-plates are routinely used to dissipate heat from temperature-sensitive components. Heat sinks intended for higher temperature service conditions can be attached by brazing. We will describe an application where graphite is brazed to copper with a molybdenum interlayer to mitigate residual stresses caused by thermal expansion and contraction differences during heating and cooling. The effects of brazing area, interlayer thickness, and heat sink thickness on flatness were investigated. The experimental results are compared against finite element analysis, which incorporates unified creep-plasticity constitutive relationships for the Ag-Cu-Ti filler metal. The molybdenum interlayer is generally effective in maintaining flatness with thinner copper substrates. Residual strains increase as the brazing area increases, although smaller vertical displacement occurs if the rigid interlayer is thicker. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:00 PM
Direct Brazing Process to Alumina Ceramic Using Conventional Braze Alloys and a Niobium Interlayer: *John J. Stephens*[1]; Gordon E. Boettcher[1]; Charles A. Walker[1]; Paul F. Hlava[1]; Thomas J. Headley[1]; [1]Sandia National Laboratories, Dept. 1861, PO Box 5800, MS0889, Albuquerque, NM 87185 USA

We will present the results of an exploratory study conducted to determine if hermetic seals could be made between bare (non-metallized) sapphire and niobium piece parts using the following three braze alloys: AWS BVAu-3 (62Cu-35Au-3Ni), BVAu-8 (92Au-8Pd), and BVAu-10 (50Au-50Cu). We chose to evaluate these alloys with ASTM F19 tensile buttons pairs made from AL-500 alumina ceramic, brazed in a configuration containing a 0.010 inch thick interlayer of unalloyed Nb. With respect to the tensile button results, the highest loads to fracture and 100% hermeticity were observed with the BVAu-10 alloy. This talk will present the results of microstructural analysis of the braze/ceramic interface region, in order to characterize the bonding mechanism. We will also compare the tensile button test results with the results for brazing sapphire parts to unalloyed Nb with the same three braze alloys. This work was conducted at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:30 PM Break

3:45 PM
New Approach to Direct Element Analysis of Refractory Metals and Their Carbides and Oxides: *Karol Putyera*[1]; Damodaran Sathymurthy[1]; [1]6707 Brooklawn Pkwy., Syracuse, NY 13211 USA

A number of analytical techniques can be used for elemental survey analysis of refractory metals or their carbides and oxides. The techniques currently in use include wet chemistry, X-ray fluorescence and spark source mass spectrometry in the middle of others. However, these hard-to-dissolve materials tend to require complex fusion/dissolution procedures and the use of combinations of nitric, hydrochloric, hydrofluoric and perchloric acids prior to introduction to solution-based methods. Wet chemical methods can be laborious and time consuming, they also dilute the sample by several fold, introduce contaminants, and may result in partial loss of some of the volatile analytes during the fusion/dissolution processes. The disadvantages and limitations of the wet methods prompted us to develop new analytical procedures for glow discharge mass spectrometry (GDMS), which compliment and/or supersede the wet techniques. The most dramatic change is the development of a new flat cell arrangement, in which samples can be analyzed as bulk solids, coatings, films or powders using the same plasma sputtering conditions. In addition, a new approach has been developed for analyzing non-conductive coatings.

4:15 PM
Thermophysical Properties of Molten Refractory Metals Measured by an Electrostatic Levitator: *Takehiko Ishikawa*[1]; Paul-Francois Paradis[1]; Shinichi Yoda[1]; [1]Japan Aerospace Exploration

Agency, Inst. of Space & Astronautical Sci., 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505 Japan

Thermophysical Properties such as the density, the surface tension, and the visocsity of molten refractory metals including Ti, Zr, Nb, Ta, Mo, and W were measured by non-contact techniques combined with an electrostatic levitator. Due to their high melting temperatures and risk of contamination from crucibles, measurements of their properties in liquid phase are very difficult with conventional techniques. Principle of electrostatic levitation, measurement techniques, and experimantal results will be presented.

Shape Casting — The John Campbell Symposium: Applications

Sponsored by: Light Metals Division, LMD-Aluminum Committee, MPMD-Solidification Committee

Program Organizers: Murat Tiryakioglu, Robert Morris University, Moon Township, PA 15108 USA; Paul N. Crepeau, General Motors Corporation, MC/486-710-251, Pontiac, MI 48340-2920 USA

Wednesday PM Room: 2008
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Murat Tiryakioglu, Robert Morris University, Moon Township, PA 15108 USA; Paul N. Crepeau, General Motors Corporation, Pontiac, MI 48340 USA

2:00 PM

Development of Cast Steel Backup Roll: *Xiuhong Kang*[1]; *Dianzhong Li*[1]; Lijun Xia[1]; John Campbell[2]; Li Yiyi[1]; [1]Chinese Academy of Sciences, Inst. of Metal Rsch., Special Environment Matl., 72 Wenhua Rd., Shenyang, Liaoning 110016 China; [2]University of Birmingham, Metall. & Matls., Elms Rd., N. Campus, Edgbaston, Birmingham, W. Midlands B15 2TT UK

This paper concerns the development of a novel casting process for a heavy cast steel backup roll. Total weight of the roll was about 50 tones and the mold was about 7m tall. A "naturally pressurized" gating system was employed to avoid air and inclusion entrainment and to ensure smooth filling. In this way high quality liquid steel was introduced into the mold. It included an offset stepped pouring basin with stopper, hyperbolic-tapered down-sprue with 113 mm entrance diameter and 63 mm exit diameter, radiussed transition between down-sprue and runner, and tangential ingate. The thickness of the sand lining of the steel die at the barrel and journals was optimized by computer simulation to guarantee that the casting solidified progressively towards the feeder. In addition, all shrinkage was arranged to be completely located in the feeder by use of insulation tiles and exothermic powder. Sound castings were produced with zero defects.

2:20 PM

Applications of Campbell's Casting Rules on High Quality Aluminum Castings: *Chen-Chieh Wong*[1]; [1]Metal Industries Research & Development Centre, Casting Tech. Sect., 1001 Kaonan Hwy., Kaohsiung, Taiwan China

Professor Campbell's 10 casting rules have great help in developing high quality aluminum castings. In our research, we apply these concepts to produce CVD heater and gate valve body castings for semiconductor equipment used under vacuum environment. Housings for aerospace purposes are also developed. At first, Campbell's rules are adopted to design runner and gating system. The proper designs of runner and gating system include bottom filling, low filling rate, and good design of pouring basin, riser size and venting. Then CAE software is used to confirm the designs. By such process, we are able to reduce to the leadtime of development and to achieve low scrap ratio and cost as well. To meet the first requirement of the rules, good quality liquid metal, special degassing method is used to reduce the hydrogen content below 0.02cm3/100g measured by first bubble detection. The CVD heater is cast by sand casting and the gate valve body is cast by permanent mold die casting process. Aerospace housing is cast by the Quickcast process. Instead of wax patterns, SLA pattern — resin model — is used to make ceramic mold for investment casting in Quickcast process. All these three castings pass X-ray examinations and even fluorescent penetrant inspections.

2:40 PM

A Rational Approach to Casting—Building Quality into the Process: Marcos I. Cardoso[1]; Andres F. Rodriguez[1]; Geoffrey K. Sigworth[1]; Jose Talamantes[1]; [1]Nemak, S.A. de C.V., R&D Dept., A.P. 100, Bosques del Valle, Garza Garcia, Nuevo Leon 66221 Mexico

During the last twenty years producers and consumers of aluminum castings have increasingly come to realize the importance of eliminating defects (inclusions and gas porosity) to obtain highest quality. And the procedures used in the cast shop determine metal cleanliness, which is why the plant processes are often qualified when a new part goes into production. In this paper, a review is first presented of the theoretical and experimental data which quantify the loss of tensile and fatique strength when defects are found in a casting. Then liquid metal treatment procedures are considered, and their effect on metal cleanliness presented. The review shows that modern fluxing, degassing and filtration procedures must first be used to clean the metal. Then, clean metal must be introduced directly into the mold, without any splashing or metal turbulence. It is only in this way that castings of consistently high quality may be produced.

3:00 PM

Campbellology for Ferrari: *Vian Francis Coombe*[1]; [1]Ferrari Spa/ Gestione Sportiva, Direction Tecnica - Metall., Via Ascari 55/57, Maranello, Mo 41053 Italy

With the ever-increasing demands to save weight, increase performance and reduce costs, the auto industry is increasing the use of light alloy materials. Ferrari Auto is no exception. Ferrari,in 1996 adopted to use an all aluminium space frame chassis for their new 360 Modena car. The design partnership of Ferrari and Alcoa called for a mix of extrusions welded to 12 strategic castings. The quality and mechanical characteristic requirements of the castings meant considerable changes to the Ferrari in-house foundry. Using an example of the methods and process route of the Apost door pillar casting, this paper describes how the foundry was transformed utilising the philosophy of John Campbell as a base for achieving the specification aims for the casting components.

3:20 PM

Controlled Diffusion Solidification - Manufacturing Quality Net Shaped Al Based Wrought Alloy Parts: *Deepak Saha*[1]; Sumanth Shankar[2]; Diran Apelian[1]; Makhlouf M. Makhlouf[1]; [1]Worcester Polytechnic Institute, Metal Procg. Inst., 100 Inst. Rd., Worcester, MA 01609 USA; [2]McMaster University, Dept. of Mech. Engrg., 1280 Main St. W., Hamilton, ON L8S 4L7 Canada

Aluminum combined with differing percentages of other metals such as silicon, copper, magnesium, and manganese form alloys that are used in many domestic, automotive and aerospace applications. Net shape manufacturing of wrought alloys (via casting) has been prohibitive due the proclivity of these alloys to "hot tears". Hot tearing tendency coupled with coherency temperature, that is close to the liquidus temperatures, lead to the development of cracks in the final "as cast" structure. The microstructure of wrought alloys is predominantly dendritic, and by altering the dendritic morphology to a globular one (providing a continuous interdendritic liquid network) one can considerably reduce the hot tearing issues. A novel method has been developed at WPI, termed Controlled Diffusion Solidification or CDS. In this process, two precursor liquid alloys of precisely controlled chemistry and temperature are mixed to produce a predetermined alloy composition. CDS provides an effective process for the net shape manufacturing of these alloys. The CDS process is discussed and reviewed; results from industrial trials utilizing a variety of different casting processes are presented, along with the resultant microstructural data and mechanical properties.

3:40 PM Break

3:50 PM

Effect of Die Temperature and Melt Quality on a Low Pressure Die Cast Engine Cylinder Head: *Geoffrey Robert de Looze*[1]; [1]CSIRO, Mfg. & Infrastruct. Tech., Locked Bag 9, Cnr. Albert & Raglan Sts., Preston, Victoria 3072 Australia

Automotive casting plants are traditionally interested in reducing in-house scrap and increasing productivity. The global research effort supporting this activity is arguably separated into pragmatic factory-based developments, and simplified laboratory investigations. To help bridge this gap, this paper describes a laboratory-based investigation into the production of a low pressure die cast (LPDC) engine cylinder head made using a modified water-cooled casting die mounted on a commercial LPDC machine. Comprehensive process temperature measurements were combined with quantitative metallography. These measurements showed how the machine operating parameters and the melt quality level affected the casting cooling rate and/or microstructure. Micro-porosity form and distribution in the castings was used as an indicator of casting quality and solidification conditions, and experimental evidence for the operation of burst feeding in LPDC was detected. Significant improvements to casting directional solidification and microstructural refinement were shown with use of forced die

cooling, however the limitations of this technique also became apparent. These results are illustrated in terms of the geometry of the casting cross-section.

4:10 PM
Breaking the Grip of Quartz: Silica-Free Foundry Sands at Silica Sand Prices: *Kenneth Peter Harris*[1]; [1]Noram Technology Ltd., Britannia House, 960 High Rd., London N12 9FB England

Noram Technology has developed technology that is being used to convert surplus fine fractions from construction aggregate manufacture to good quality, silica-free foundry sand. Since very many foundries are located within 200 miles of a quarry producing suitable aggregates, foundry sand made this way can be offered for sale at prices close to silica sand. Unlike quartz, these silica-free sands have low, linear thermal expansions; they are compatible with all commonly used binders and free from the health and safety issues affecting silica. A Noram plant also recycles foundry sand at exceptionally high yields, enabling sand consumption per ton good of casting to fall by 50% or more independent of binder system. If local demand for foundry sand is insufficient to warrant manufacture at the quarry, a foundry operating a Noram recycle plant can make its own from the abovementioned fine fractions. This technology will allow many foundries to replace silica sand and increase the use of low-cost environmentally benign inorganic binders.

4:30 PM
The Cosworth Casting Process: Evolution and Benchmark: *Nicholas R. Green*[1]; Andrew M. Tomkinson[1]; Thomas C. Wright[1]; Jon P. Evans[1]; [1]Cosworth Technology Ltd., Wainwright Rd., Shire Business Park, Worcester WR4 9FA UK

The Cosworth Casting Process was developed to allow manufacture of small volumes of high performance castings and the pedigree of the process established through a record number of wins in Formula 1 racing. The process has evolved successfully into high volume production through the application of rollover of the mould under pressure from the pump immediately after filling. To benchmark the reliability of components manufactured with the high volume casting process, elevated temperature fatigue tests were performed and fatigue life distributions characterised with Weibull statistics. Material samples from the bearing panels of precision sand-cast AlSiCuMg production cylinder blocks from Cosworth Technology and two other European suppliers to Audi were tested at 85 MPa and 150°C under fully reversed rotating-bending. All materials exhibited similar upper fatigue life limits. However, the Cosworth Technology cast material exhibited a Weibull modulus of fatigue of 3.0, whilst the other precision sand processes each showed significantly greater scatter in fatigue life with Weibull moduli of only 1.5. No correlation was found between initiating defect size and fatigue life. It is concluded that the presence of oxide films entrained in the gravity casting of the other components accounted for their increased unreliability.

4:50 PM
John Campbell's Closing Remarks: *John Campbell*[1]; [1]University of Birmingham, Metall. & Matls., Elms Rd., N. Campus, Edgbaston, Birmingham, W. Midlands B15 2TT UK

Prof. Campbell will offer his unique perspective on the papers presented during this conference.

5:30 PM Conference Close

WEDNESDAY PM

Superalloys and Coatings for High Temperature Applications: Superalloys - II

Sponsored by: Structural Materials Division, SMD-High Temperature Alloys Committee, SMD-Corrosion and Environmental Effects Committee-(Jt. ASM-MSCTS), High Temperature Materials Committee of IoM3
Program Organizers: Roger C. Reed, University of British Columbia, Department of Metals and Materials Engineering, Vancouver, British Columbia V6T 1Z4 Canada; Richard S. Bellows, Solar Turbines, Inc., Materials and Process Engineering, San Diego, CA 92186-5376 USA; Qiang (Charles) Feng, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; Tim Gabb, NASA Glenn Research Center, Cleveland, OH 44135 USA; John Nicholls, Cranfield University, Bedfordshire MK43 OAL UK; Bruce A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Wednesday PM Room: Nob Hill A/B
February 16, 2005 Location: San Francisco Marriott

Session Chairs: Qiang (Charles) Feng, University of Michigan, Dept. of Matl. Sci. & Engrg., Ann Arbor, MI 48109 USA; Richard S. Bellows, Solar Turbines Inc., Matls. & Process Engrg., San Diego, CA 92186-5376 USA

2:00 PM Invited
Advances in Material and Coating Technologies for Industrial Gas Turbine Applications: *Zaher Z. Mutasim*[1]; [1]Solar Turbines, Matls. Engrg., 2200 Pacific Hwy., San Diego, CA 92101 USA

The demand for increased gas turbine efficiency and improved durability, while reducing life cycle cost, has evoked a lot of attention from gas turbine original equipment manufacturer (OEMs) and end users. While OEMs are continuing their drive to improve engine performance by introducing novel concepts to the engine designs, it becomes apparent the many limitations the engine designer experiences. These include the levels of mechanical and thermal stresses that the turbine will experience at the expense of improved performance. This presentation describes the applications and the environment that industrial gas turbines experience, and the consequent degradation mechanisms that the turbine materials are subjected to. Market and customer drivers are also defined, and used to develop new material and coating solutions to satisfy customer demands. Advances in materials and coating systems are presented for gas turbine combustor liner and gas turbine blades and nozzles.

2:30 PM Invited
Crystallographic Implications of Creep Deformation of Single Crystal Superalloys Subject to Multiaxial Loading: Hector C. Basoalto[1]; Mamoud G. Ardakani[1]; R. N. Ghosh[2]; Barbara A. Shollock[1]; *Malcolm McLean*[1]; [1]Imperial College London, Exhibition Rd., London SW72AZ UK; [2]National Metallurgical Laboratory, Jamshedpur India

Most models of anisotropic creep appeal to two or more active slip systems to account for the observed creep behaviour as a function of orientation, stress and temperature. Validation of the models by comparing predicted crystal rotations for uniaxially loaded off-axis specimens with EBSD measurements is complicated by the progressive development of triaxial stresses in nominally uniaxial tests due to geometrical constraints. The present paper presents a comparison of (i) predictions of creep deformation in multiaxial stresses, including crystal rotations, from an implementation of a multiple slip model in ABAQUS via a User Creep Sub-Routine and (ii) EBSD measurements of the spatial variation in crystal rotation in circumferentially-notched creep specimens.

3:00 PM
Creep of Ru-Containing Nickel-Base Single Crystal Superalloys: *Laura J. Rowland*[1]; Q. Feng[1]; T. M. Pollock[1]; [1]University of Michigan, Dept. of Matls. Sci. & Engrg., 2300 Hayward, Ann Arbor, MI 48109 USA

There is a continuing demand for development of nickel-base superalloys that can maintain structural integrity at temperatures of 1100°C and beyond. Ru additions have been found to increase the liquidus temperature of nickel-base superalloys, reduce the propensity for formation of TCP phases, and improve creep rupture strength at 1100°C. The experimental Ru-containing nickel-base single crystal superalloys investigated had cuboidal, intermediately-shaped, or spherical γ' precipitates. The rafting behavior of the experimental alloys

also varied dramatically indicating there is a range of γ-γ' lattice misfit from negative to near zero to positive. The objective of this study was to investigate the role of Ru in influencing creep properties in a matrix of alloys with a wide range of composition, with moderate amounts of Re and W, and Ru content up to 9.7 wt%. It was determined the impact of Ru on creep strength is strongly dependent on microstructure, rafting direction and dislocation substructure.

3:25 PM
Miniature Specimen Creep Testing of a Low Density Single Crystal Super Alloy: *Gotthard Mälzer*[1]; Aleksander Kostka[1]; Gunther Eggeler[1]; Thomas Mack[2]; [1]Ruhr-Universität Bochum, Lehrstuhl Werkstoffwissenschaft, Bochum D-44780 Germany; [2]MTU Aero Engines, München 80995 Germany

We present mechanical and microstructural results on miniature specimen creep testing of a low density Ni-base superalloy in the 1000°C temperature regime. We give some back ground information on the development of our miniature specimen creep testing procedure. We show that the main features of creep can be captured. We present creep curves and show how the secondary creep rate depends on stress and temperature for three crystallographic directions (tensile loading in <100>, <110> and <111> directions). Moreover we use scanning and transmission electron microscopy to characterize the microstructural evolution during creep. Emphasis is placed on the coarsening of the ã/ã?-microstructure (rafting), the nucleation of cracks at cast micro pores, the appearance of rupture surfaces and on the cutting of the ã?-phase by dislocations. Our results show that our miniature test technique provides reasonable creep data and is ideally suited to study the microstructural processes occurring.

3:50 PM Break

4:15 PM
Microstructural Study of Nickel-Base Superalloys for Ultra Supercritical (USC) Coal Power Plants: *Quanyan Wu*[1]; Vijay K. Vasudevan[1]; John Shingledecker[2]; Robert Swindeman[2]; [1]University of Cincinnati, Cheml. & Matls. Engrg., 2624 Clifton Ave., Cincinnati, OH 45221 USA; [2]Oak Ridge National Laboratory, Ceram. & Metals, Bldg. 4500S, MS6155, PO Box 2008, Oak Ridge, TN 37831 USA

The demand for higher efficiency and reduced environmental effects in coal-fired power boilers has to result in the use of higher steam temperatures and pressures. A significant materials effort is to reach a target steam condition of 760°C and 35MPa to meet USC requirements. This will require the use of Nickel-base superalloys, in which long-term creep strength is a critical factor. In this study, the microstructural stability and evolution of Haynes 230, CCA617 and HR6W after ageing and creep-test under various temperatures are examined and discussed. Creep test results at ORNL showed that CCA617 exhibits a significant improvement over the standard alloy 617 in creep rupture strength while in HR6W, failure to meet the expected performance was encountered. Microstructural analysis focusses on the formation, distribution, size and volume fraction of gamma prime, carbides, and their interaction with dislocations. TEM is the main characterization tool in addition to SEM, EDS and microhardness tests.

4:40 PM
Nondestructive Characterization of Microstructural Degradation in Creep Damaged Ni-Based Superalloys by Ultrasonic Techniques: *Jaewon Byeon*[1]; Jinhun Song[2]; Sookin Kwun[2]; Yongho Sohn[1]; [1]University of Central Florida, AMPAC & MMAE, Box 162455, 4000 Central Florida Blvd., Orlando, FL 32816-2455 USA; [2]Korea University, Matls. Sci. & Engrg., Anam-dong, Sungbuk-gu, Seoul 136-701 Korea

The creep damage of two Ni-based superalloys, IN738LC and PM1000 were non-destructively examined by ultrasonic velocity and attenuation. Microstructural features related to creep damage were quantitatively correlated to the ultrasonic velocity and attenuation. The creep damage in PM1000, at 1000°C under the tensile stress range of 110-123MPa, occurred by the formation of cavity, and decreased the ultrasonic velocity, because the increase in the volume fraction of creep cavity decreased the Young's Modulus. The creep damage in IN738LC, at a temperature range of 850-950°C and tensile stress range of 116-255MPa, occurred by the directional coarsening (rafting) of gamma-prime precipitates. A linear correlation was observed between the ultrasonic attenuation coefficient and the mean length of precipitates in IN738LC. The potential of ultrasonic technique to assess creep damage in high temperature alloys is discussed with an emphasis on the relationship between the microstructural damage mechanisms and the governing principles of ultrasonic response.

5:05 PM
Ultrasonic Fatigue of a Single Crystal Superalloy at Elevated Temperature: *JianZhang Yi*[1]; Chris J Torbet[1]; Tresa M Pollock[1]; J Wayne Jones[1]; [1]University of Michigan, Matls. Sci. & Engrg., H. H. Dow Bldg., Ann Arbor, MI 48109-2136 USA

Turbine airfoils are usually subjected to high temperatures, aggressive environment and vibratory stresses arising from a wide range of stimuli, such as the turbulent flow around the airfoil itself. Traditionally, high cycle fatigue testing is confined to 10^7 cycles due to the time consumed with the conventional testing equipment. In the present study, an ultrasonic fatigue testing system, operating at a frequency of approximately 20kHz, was used to explore the high cycle fatigue behavior of a single crystal PWA 1484 superalloy at high temperature (1700°F) and in the lifetime regime of 10^6-10^9 cycles. The resultant fatigue properties were thus analyzed and discussed by identifying the crack initiation and characterizing the development of fatigue damage evolution in the superalloy.

5:30 PM
The Effect of Stress on the Long-Term Phase Stability of Ni-Base Superalloy U720LI: *Satoshi Takahashi*[1]; Yoshinori Ito[1]; Sadao Nishikiori[1]; [1]Ishikawajima-Harima Heavy Industries Co., Ltd., 1 Shin-Nakaharacho, Isogo-ku, Yokohama, Kanagawa 235-8501 Japan

Ni-base superalloy U720LI has been widely used for the rotating components in aircraft-engines. In this study, we focused on the effect of stress on sigma phase precipitation. Alloy forged and heat-treated consists of duplex grain size, which is caused by distribution of primary ã'. Exposure heat treatments were performed at 700°C and 750°C for times up to 3000 hours in air. For evaluation of mechanical properties, creep rupture test, LCF test and dwell LCF test were carried out at temperatures described above. Microstructural observation was conducted for these specimens, and then the influence of the stress on precipitation kinetics was discussed. From this work, it is found that stress accelerates the precipitation of sigma phase, and regardless of stress present, sigma phase is prone to precipitate in fine grain area.

Surface Engineering in Materials Science - III: Plasma Processing for Surface Modification

Sponsored by: Materials Processing and Manufacturing Division, MPMD-Surface Engineering Committee
Program Organizers: Arvind Agarwal, Florida International University, Department of Mechanical and Materials Engineering, Miami, FL 33174 USA; Craig Blue, Oak Ridge National Laboratory, Materials Processing Group, Metals and Ceramic Division, Oak Ridge, TN 37831 USA; Narendra B. Dahotre, University of Tennessee, Department of Materials Science & Engineering, Knoxville, TN 37932 USA; John J. Moore, Colorado School of Mines, Department of Metallurgy and Materials Engineering, Golden, CO 80401 USA; Sudipta Seal, University of Central Florida, Advanced Materials Processing and Analysis Center and Mechanical, Materials and Aerospace Engineering, Oviedo, FL 32765-7962 USA

Wednesday PM Room: 2022
February 16, 2005 Location: Moscone West Convention Center

Session Chair: Arvind Agarwal, Florida International University, Dept. Mech. & Matls. Engrg., Miami, FL 33174 USA

2:00 PM Invited
Extended Thermal Cycle Lifetime in Thermal Barrier Coatings with Bond Coats Made from Cryomilled Powders: *Julie M. Schoenung*[1]; Feng Tang[1]; Leonardo Ajdelsztajn[1]; George Kim[2]; Virgil Provenzano[3]; [1]University of California, Chem. Engrg. & Matls. Sci., 2017 Kemper Hall, Davis, CA 95616 USA; [2]Perpetual Technologies, Montreal H3E1T8 Canada; [3]National Institute of Standards & Technology, Gaithersburg, MD 20899 USA

The objective of this study is to increase the thermal cycle lifetime of thermal barrier coatings (TBCs) by modifying their bond coats. The main idea is the cryomilling of the NiCrAlY powder that is used to make the thermal sprayed bond coat. The cryomilled powder has nanocrystalline grains and contains in-situ dispersed nano-scale oxides and nitrides. These features are expected to remain in the bond coat after thermal spray and, therefore, to modify the oxidation behavior of the TBC. LPPS and HVOF thermal spray processes have been used to produce the bond coats. The top coats have been applied with the APS process. The thermal cycle test is conducted in air at 1121°C with a one-hour cycle. Our results show that the lifetime of the TBCs with

cryomilled bond coats can be greater than 1300 cycles, which is comparable to the longest lifetimes reported for high-cost EB-PVD TBCs.

2:25 PM
Synthesis and Characterization of Vacuum Plasma Sprayed Tantalum Carbide Coating: *Kantesh Balani*[1]; Gabriela Gonzalez[1]; Arvind Agarwal[1]; Robert Hickman[2]; [1]Florida International University, Mechl. & Matls. Engrg., EAS 3400, 10555 W. Flagler St., Miami, FL 33174 USA; [2]Plasma Processes Inc., 4914 Moores Mill Rd., Huntsville, AL 35811 USA

Tantalum carbide (TaC) is a candidate coating material for high temperature applications as in rocket nozzle throats and liners. But, the high melting temperature and brittleness of TaC poses hurdles in synthesizing such coatings with conventional processing routes. Vacuum plasma spraying (VPS) has been employed for coating TaC and surpassing processing difficulties. High cooling rates experienced during the VPS process inherently leads to formation of non-equilibrium phases in the final microstructure. X-Ray Diffraction analysis has detailed the generation of Ta2C phase during VPS. SEM and TEM studies clearly show the disparity of non-homogeneous and non-stoichiometric phases in the sprayed coating. Microhardness analysis was extended to gather fracture toughness data through Vicker indentation cracks in the vacuum plasma sprayed TaC. The dissociation of decarburization of TaC to form Ta2C during plasma spraying is a processing problem and requires further optimization work for ongoing research.

2:40 PM
Molybdenum Silicides as High-Temperature Corrosion-Resistant Coatings: *Peter F. Tortorelli*[1]; Michael P. Brady[1]; Ian G. Wright[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, Oak Ridge, TN 37831-6156 USA

The high-temperature corrosion behavior of Mo-Si-B alloys under various environmental conditions is being studied for possible use in advanced fossil-fuel systems as corrosion-resistant coatings. Alloys of Mo-Mo5SiB2-Mo3Si with different compositions and phase morphologies were oxidized in dry air or exposed to an H-2-H2S-H2O-Ar environment. Effects of the multiphase nature (composition, morphology) of the Mo-Si-B system on environmental resistance under these conditions were evaluated. Microstructural characterization indicated that the oxidation reactions resulted in cooperative behavior among the different phases while preliminary analyses suggested that sulfide formation mimicked the starting alloy microstructure. Quite low corrosion rates under sulfidizing conditions were observed. Implications of these findings for design of smart coatings for oxidation and/or sulfidation resistance will be discussed. Research sponsored by the Advanced Research Materials Program, Office of Fossil Energy, U. S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

2:55 PM
Plasma Spray Formed Near-Net-Shape MoSi2-Si3N4 Nanocomposites: *Viswanathan Venkatachalapathy*[1]; [1]University of Central Florida, Mechl., Matls. & Aeros. Engrg., 381 Engrg. Bldg., 4000 Central Florida Blvd., Orlando, FL 32816 USA

The commercial applications such as high temperature aerospace (gas turbine engines) and automotive applications of MoSi2 based nanocomposites rely on the successful consolidation of these materials into bulk-sized components while preserving their nanostructures. This article summarizes the challenge for the successful consolidation of MoSi2-Si3N4(nano/micro) nano-composite by plasma spray forming. Plasma sprayed cylindrical reinforced MoSi2 composite have been fabricated by the plasma spray forming without any defect on the surface. A detail characterization of the spray formed bulk nano-composite has been performed along the radius of the composite using optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Vickers hardness tester. Vickers hardness and fracture toughness of the nanocomposite showed a little deviation from the expected, that might be due to the difference in particle size and distribution in the MoSi2 matrix as a funct ion of component thickness. The higher hardness and fracture toughness were observed at the middle of the composite and the average fracture toughness of the plasma sprayed bulk nanocomponent was 6.3 MPa m1/2. The higher fracture toughness value could be attributed to the retention and the presence of nanoparticles in the matrix, though with some porosities. High temperature oxidation behavior was studied and showed excellent high temperature resistance. Furthermore, the electronic structure of the composite was studied using the ab-initio QM principles and the DFT theory. The changes of the density of states and the band structure, together with the decreased Fermi energy and the total energy of the reinforced MoSi2 system were calculated and related to its superior mechanical and physical properties.

3:10 PM
Erosion-Oxidation Behavior of Steels and Thermal Sprayed Cermet Coatings: *Lalgudi V. Ramanathan*[1]; [1]Cidade Universitaria, IPEN, Matls. Sci. & Tech. Ctr., Av. Prof. Lineu Prestes 2242, São Paulo 05508-000 Brazil

An apparatus consisting of a fluidized bed of erodent particles through which a specimen assembly enters and leaves at periodic intervals has been used to determine the erosion-oxidation (E-O) behavior of various steels and HVOF sprayed alloy and cermet coatings of Ni20Cr, WC-20Cr7Ni and Cr3C2-Ni20Cr on a steel substrate. Alumina powder (~200 μm) was used as the erodent. The E-O tests were carried out in the range 100-850ºC, with particle impact velocities of 3-19 ms-1 and impact angle of 90º. The erosion-oxidation behavior was determined as wastage, as a function of temperature. The effect of chromium content on E-O behavior of the steels was determined. Above 500ºC, wastage increased with temperature, reaching a maximum at 700ºC and then decreased with further increase in temperature. The surface roughness of the coatings was determined to corroborate the E-O regimes.

3:25 PM Break

3:40 PM Invited
Recent Advances in Thermal Spray Processing of Materials: *Sanjay Sampath*[1]; [1]State University of New York, Ctr. for Thermal Spray Rsch., Stony Brook, NY 11794-2275 USA

Thermal sprayed coatings is a highly versatile tool for surface engineering. These coatings have found wide spread applicability in both aero and power generation turbine engines. In the past, coatings have been principally added as an after thought with the goal of life extension of engineering components, however, as the need for prime reliant coatings grow, so do the requirement of reliability and reproducibility. Depositing reproducible coatings is an implicit requirement for the application of prime reliant coatings, so as to reduce/eliminate infant mortality of coatings. Advances process diagnostics and property extraction for these lamellar materials has significantly enhanced our understanding of the process dynamics during thermal spray. This has enabled improving performance as well as assessing process sensitivity, establishing optimizing protocols and reducing variability. In this presentation, we will discuss a fundamental approach to understanding the process through complete plume diagnostics, singe and multiple point measurement of particle state and measuring deposit properties insitu. The outcome of this effort is displayed in what is referred to as 1st order (process-particle interactions) and 2nd order (particle-coating interactions) process maps. For example, these maps allow reducing variability for deposition of ceramic thermal barrier coatings. Implications of these maps towards industrial applications will be addressed. Acknowledgements: Supported by the NSF MRSEC program DMR 0080021.

4:05 PM
Plasma Sprayed Multicomponent Coatings for Textile Machinery with Emphasis on Self Lubrication: *Suman Saurabh*[1]; Krishna M. Gupt[1]; [1]Indian Institute of Technology Bombay, Dept. of Metallurgl. Engrg. & Matls. Sci., Rm. No-B402, Hostel-13, Powai, Mumbai, Maharastra 400076 India

All textiles manufacturing machines encounter continuous friction between machine components and moving thread. It leads, among other things to wear of components, thus causing mis-alignment, vibration and damage to fibers and yarn. Although lubrication is universally used to avoid friction related wear, but in case of fiber processing lubrication can deteriorate fiber/fabric quality. The development of self lubricating multicomponent coatings with solid lubricants is an answer to industry's increasing demand for alternatives to oil lubricating systems. The present work aims to study and analyze the tribological properties of plasma sprayed (Cr2O3.CaF2, Cr2O3.BaF2, Cr2O3.Ag2O) coatings for textile machinery components. Effect of addition of solid lubricants (CaF2, BaF2, Ag2O) and its self lubricating nature were studied. The influence of different process parameters on coating properties were studied by SEM and TEM analysis. Coatings were analyzed and were found to have much superior wear resistance and lower friction coefficient.

4:20 PM
Measurements of Residual Stresses in Plasma-Sprayed Hydroxyapatite Coatings on Titanium Alloy: *Yungchin Yang*[1]; [1]National Taipei University of Technology, Matls. & Minl. Resources Engrg., 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106 Taiwan

In an attempt to investigate the stress state and stress distribution in hydroxyapatite coatings (HAC), the residual stresses in thick HACs

on titanium alloy were studied by the materials removal method, as a function of cooling media during spraying. In addition, and the x-ray diffraction sin2?é method was adopted as a comparison. The Young's moduli of hydroxyapatite coatings were measured on separated free coating by a three-point bending test. The results show that the measured Young's modulus of the HACs with an average of 22.8 GPa was found to be much lower than the theoretical value of bulk HA. During measurements by the materials removal method, on the three types of HACs using different cooling media, the interface between the HAC and Ti-substrate displays higher residual stress than the top surface of HAC. The residual stresses in all the HACs measured by both methods were in a compressive mode, and the residual stresses on the top surface obtained from the two methods are consistent. It was also found that the compressive residual stresses on the top surface of HAC and at the interface between the coating and the substrate both increased with increasing temperature of the HAC. Therefore, the coating temperature, and the effect of varying the cooling media during plasma spraying, had a significant effect on the residual stress states of the HACs.

4:35 PM
Surface Mechanical Alloying Between an Aluminum Plate and Oxide Powders: *Laszlo Takacs*[1]; Aghasi R. Torosyan[2]; [1]University of Maryland, Dept. of Physics, 1000 Hilltop Cir., Baltimore, MD 21045 USA; [2]National Academy of Science, Inst. of Gen. & Inorganic Chmst., Yerevan 375051 Armenia

Mechanical alloying is usually carried out via ball milling a mixture of components in powder form. It is also possible to place a plate into the milling chamber and mill only the other component(s), pressing their particles onto or into the surface of the plate and inducing surface modification and alloying. As the processes at a macroscopic surface are less stochastic than between the powder particles during ordinary mechanical alloying, it is easier to understand the microscopic details of mechanical alloying in the powder-plate geometry. It is also possible to prepare a variety of coatings this way. In the present report, the interaction between an aluminum surface and PbO and WO3 powders is discussed from both points of view. It is shown that both mechanical and chemical processes contribute to the formation of the surface layer.

4:50 PM
Design and Tuning of a Micro Vacuum Plasma Spray System: *W. Scott Crawford*[1]; Mark A. Cappelli[1]; Friedrich B. Prinz[2]; [1]Stanford University, Mechl. Engrg., Bldg. 520, Rm. 520-I, Stanford, CA 94305-3032 USA; [2]Stanford University, Mechl. Engrg., Matl. Sci. and Engrg., Bldg. 530, Room 220, Stanford, CA 94305-3030 USA

A system has been developed and refined for small-scale vacuum plasma spraying of metals. This table-top system operates at arc power 1.5-3 kW and deposition rates below 0.1 g min^{-1}. System design is described with attention to issues heightened at these low levels of power and flow rate. These issues include design and operation of powder feeder and powder flow path, injector design, and momentum interactions between plasma jet and obliquely injected stream of powder and carrier gas. Tuning of operating conditions is also described, by a combination of system decomposition, scaling analysis and experiment. Key experiments included planar laser scattering for imaging of particle trajectories. Coating materials studied include 316L stainless steel and titanium alloy.

The Armen G. Khachaturyan Symposium on Phase Transformation and Microstructural Evolution in Crystalline Solids: Session VI

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Materials Processing & Manufacturing Division, EMPMD/SMD-Chemistry & Physics of Materials Committee, MPMD-Computational Materials Science & Engineering-(Jt. ASM-MSCTS), MPMD-Phase Transformations Committee-(Jt. ASM-MSCTS)
Program Organizers: Yunzhi Wang, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA; Long-Qing Chen, Pennsylvania State University, Materials Science and Engineering Department, University Park, PA 16802-5005 USA; John William Morris, University of California, Department of Materials Science and Engineering, Berkeley, CA 94720 USA

Wednesday PM Room: 3003
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Chris Wolverton, Ford Motor Company, Physics & Environml. Sci., Dearborn, MI 48121 USA; J.-C. Zhao, GE Global Research, Niskayuna, NY 12309 USA

2:00 PM Opening Remarks

2:05 PM Invited
Precipitates in Ni-Rich Alloys: *Gernot Kostorz*[1]; [1]ETH Zurich, Angewandte Physik, Zurich 8093 Switzerland

A survey will be given on the numerous studies of phase separation in Ni-rich solid solutions initiated at the author's laboratory. Especially for Ni-Al and Ni-Ti, small-angle scattering of neutrons, diffuse scattering of neutrons and X-rays, and transmission electron microscopy have been combined to follow the transformation from the early stages. While in Ni-Al, initially coherent $L1_2$-ordered precipitates represent the stable decomposition product, they appear as a metastable phase in Ni-Ti. In both cases, elastic interactions lead to preferred alignments of the precipitates along the elastically soft directions, but there are also important differences in shape, chemical composition, degree of order, and temporal evolution of precipitates. While the alloys decompose, short-range order is also established in the matrix phases. From the wealth of experimental data, a comprehensive description of the differences and similarities of the two systems emerges.

2:30 PM Invited
Coarsening of Ni-Al Solid Solution Precipitates in a γ (Ni_3Al) Matrix; Contrasting Behavior Between Inverse and Conventional Alloys: Y. Ma[1]; *A. J. Ardell*[1]; [1]University of California, Dept. of Matls. Sci. & Engrg., Los Angeles, CA 90095-1595 USA

Coarsening of γ (Ni-Al solid solution) precipitates in a γ' (Ni_3Al) matrix (the inverse alloy) was investigated in 5 alloys aged at 650°C. The rate constant for the kinetics of particle growth increases very rapidly as the equilibrium volume fraction, f_e, increases. This normal behavior contrasts dramatically with the coarsening of γ' precipitates in conventional Ni-Al alloys, wherein the rate constant is either independent of, or decreases anomalously, as f_e increases. The dependence of the rate constant on f_e in the inverse alloy agrees quantitatively with the predictions of the old MLSW theory of Ardell. Coalescence of γ precipitates is very easy, in stark contrast to the strong resistance to coalescence of γ' precipitates in conventional alloys. We regard this finding as indirect proof of the important role of anti-phase relationships during coarsening of γ' precipitates in conventional alloys, postulated by Wang and Khachaturyan.

2:55 PM
Experimental Study of Microstructural Evolution in Coherent System: *Y. S. Yoo*[1]; D. Y. Yoon[2]; [1]Korea Institute of Machinery and Materials, Dept. of Matls. Procg., 66 Sangnam-dong, Changwon, Kyungnam 641-010 S. Korea; [2]Korea Advanced Institute of Science and Technology, Dept. of Matls. Sci. & Engrg., Daejon 305-701 S. Korea

The g/g' system in Ni base alloys shows various microstructural phenomena including alignment, splitting, morphological instability, and solid state dendrite. Experimental conditions for these microstructural evolutions are presented. Possible origin and mechanism of these phenomena are also discussed and compared with theoretical works. Initial precipitate density seems to be a crucial variable in determining the shape and distribution of gamma prime affecting both the strain field and the diffusion field of each particle. By deeply

etching the matrix and observing under a scanning electron microscope, the three dimensional precipitate morphologies are determined accurately.

3:10 PM Invited
Role of Composition During the Chessboard Pattern Formation in Co-Pt Alloys: *Y. Le Bouar*[1]; A. Loiseau[1]; A. G. Khachaturyan[2]; [1]LEM, CNRS/ONERA, 29 Ave. de la Division, Leclerc, BP 72, 92322, Châtillon France; [2]Rutgers University, Dept. of Ceram. & Matls. Engrg., Piscataway, NJ 08855-0909 USA

Co-Pt Binary alloys form at high temperature a FCC solid solution, and order on this lattice to form either the cubic L1_2 or the tetragonal L1_0 structure. For a small concentration range, the two ordered structure coexist at equilibrium, and we observe the formation of a chessboard-like microstructure. In this work, we present both a experimental investigation based on TEM observations and a phase field modelling of the chessboard pattern formation. We focus on the the role of the composition on the microstructural evolution. We show that the microstructural pattern is very sensitive to the concentration and that very surprising transient patterns can appear during an isothermal annealing.

3:35 PM
A Combined Study of Solid State Phase Changes in Steel Through Confocal Microscopy and Orientation Imaging: *Eric D. Schmidt*[1]; [1]Carnegie Mellon University, Dept. of Matls. Sci. & Engrg., 5000 Forbes Ave., Pittsburgh, PA 15213 USA

A Confocal Scanning Laser Microscope (CSLM) has been used to directly observe austenite formation during heating and ferrite formation during cooling. The final microstructure can then be analyzed via electron backscattering diffraction (EBSD) to determine the crystallographic orientation relationship of the various ferrite morphologies—primarily allotriomorphic and Widmanstatten. These ferrite orientations can then be used to determine the prior austenite grain locations and orientations. A detailed and accurate analysis of the phase change kinetics is then possible by comparing direct observations and orientation relationships from the exact same location. The effect of heating rate, cooling rate, annealing temperature, annealing time, and atmosphere have all been explored in this study.

3:50 PM Break

4:15 PM Invited
Temporal Evolution of the Nanostructure of Ni-Al-Cr Base Alloys: *David N. Seidman*[1]; Chantal K. Sudbrack[1]; Kevin E. Yoon[1]; Ronald D. Noebe[2]; [1]Northwestern University, Matls. Sci. & Engrg., Cook Hall, 2220 Campus Dr., Evanston, IL 60208-3108 USA; [2]NASA, MS 49-3, Glenn Research Ctr., 21000 Brookpark Rd., Cleveland, OH 44135 USA

The temporal evolution of the nanostructure of Ni-Al-Cr base alloys is studied employing three-dimensional atom-probe (3DAP) and transmission electron microscopies. The decomposition kinetics of the gamma (FCC)phase into the gamma and gamma prime (L12 structure), which is a first-order phase transformation, is followed through the nucleation, growth and coarsening stages from its genesis, initially employing radial distribution functions (RDFs) to detect local ordering in the absence of detectable gamma prime precipitates. The smallest detectable gamma prime precipitates contain about 20 atoms. The temporal evolution is followed by measuring the mean precipitate radius, the number density, and the supersaturations of all the solute elements in both the gamma phase and gamma prime precipitates. In addition, the width of the gamma/gamma prime interface and its interfacial free energy is determined from the 3DAP microsope observations. The coarsening process involves coalescence of gamma prime precipitates, in addition to classical Ostwald ripening.

4:40 PM Invited
Numerical Calculation and Atom Probe Analyses of Kinetics in Ni-Al-V System: *Hélèna Zapolsky*[1]; Sebastien Ferry[1]; Didier Blavette[1]; Long-Qing Chen[2]; [1]University of Rouen, GPM, UMR 6634, Ave. de l'univ., BP 12, Saint-Etienne-du-Rouvray 76801 France; [2]Pennsylvania State University, Dept. of Matls. Sci. & Engrg., 102 Steidle Bldg., Univ. Park, PA 16802 USA

The ternary Ni-Al-V compound is a rare system where in some temperature domain the three different phases coexist at equilibrium. As follow from the experimental and theoretical phase diagram at 800°C, the ordered Ni3Al phase (with L12 structure) coexists with the ordered Ni3V phase (with the DO22 structure) and with the disordered matrix which have fcc lattice. An important feature of the current study is to analyze coarsening data in ternary Ni-based alloys. The morphological evolution and coarsening kinetics of ordered intermetallic precipitates with coherency stress were studied using the Önsager-type microscope diffusion equations and three dimensional atom probe (3DAP) analyses. The emphasis is on the effects of precipitate volume fraction. Specifically, we predict the variation of the rate constants - of coarsening with precipitate volume fraction. Comparison of numerical simulation results with experiments shows good quantitative agreement.

5:05 PM
Computer Simulation of Phase Decomposition in Fe-Cu-Mn-Ni Quaternary System Based on the Phase-Field Method: *Toshiyuki Koyama*[1]; Hidehiro Onodera[1]; [1]National Institute for Materials Science, Computatl. Matls. Sci. Ctr., 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan

The phase decomposition in Fe-Cu-Mn-Ni quaternary system during isothermal aging is simulated based on the phase field method. Since the chemical free energy used in this simulation is obtained from the CALPHAD database, i.e. the thermodynamic database of phase diagrams, the calculated microstructure changes are directly related to the phase diagram of the Fe-Cu-Mn-Ni system. At the early stage of aging, the Cu-rich zone with bcc structure begins to nucleate, and the component X (=Mn, Ni) is partitioned to the Cu-rich phase. When the Cu composition in the precipitate reaches equilibrium, the component X inside the precipitates moves toward to the interface region between the precipitate and matrix. Finally, the shell structure that the Cu precipitates surrounded by the thin layer with high concentration of component X appears. This microstructure change is reasonably explained by considering the local equilibrium at the diffused interface region of nano-particles.

5:20 PM
Compositional Pathways in a Model Ni-Al-Cr Alloy: *Chantal K. Sudbrack*[1]; Ronald D. Noebe[2]; David N. Seidman[1]; [1]Northwestern University, Dept. of Matls. Sci. & Engrg., 2220 Campus Dr., Evanston, IL 60208 USA; [2]NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH 44135 USA

Due to complex interactions in multi-component metallic alloys, as well as experimental limitations, insight on the decomposition pathways of isothermal precipitation from a supersaturated solid solution is limited. We present a detailed three-dimensional atom-probe microscope study of the earliest stages of decomposition, γ (fcc) —> γ (fcc) + γ' ($L1_2$ structure), in a model Ni-Al-Cr superalloy. Short-range order and clustering tendencies are evaluated from the direct space images. It is found that Cr atoms are trapped in the forming precipitates, and that an increased solubility of Al can be attributed to capillarity effects. The composition trajectory of the matrix follows the tie-lie, while the precipitates' trajectory does not.

The Langdon Symposium: Flow and Forming of Crystalline Materials: Ultrafine-Grained Materials II

Sponsored by: Materials Processing & Manufacturing Division, Structural Materials Division, MPMD-Shaping and Forming Committee, SMD-Mechanical Behavior of Materials-(Jt. ASM-MSCTS)

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Wednesday PM Room: 3024
February 16, 2005 Location: Moscone West Convention Center

Session Chairs: Terry R. McNelley, Naval Postgraduate School, Mechl. & Astronautical Engrg., Monterey, CA 93943-5146 USA; Kenong Xia, University of Melbourne, Dept. of Mechl. & Mfg. Engrg., Parkville, Victoria 3010 Australia; Yuntian T. Zhu, Los Alamos National Laboratory, Los Alamos, NM 87545 USA; Ruslan Z. Valiev, Ufa State Aviation Technical University, Inst. of Physics, of Advd. Matls., Ufa 450000 Russia

2:00 PM
Lattice Defect Investigation of SPD Cu by Means of X-Ray Line Profile Analysis, Calorimetry and Electrical Residual

Resistivity: Erhard Schafler[1]; *Gerd Steiner*[1]; Elena Korznikova[1]; Michael Kerber[1]; Michael J. Zehetbauer[1]; Leonhard F. Zeipper[2]; [1]University of Vienna, Matls. Physics Inst., Boltzmanngasse 5, Wien A-1090 Austria; [2]ARC Seibersdorf Research GmbH, Matls. Rsch., Seibersdorf, Austria A-2444 Austria

Samples of pure Cu have been subjected to different modes of SPD (ECAP, HPT), and deformation induced defects such as vacancies, dislocations and local internal strains have been studied by means of Calorimetry, Residual Electrical Resistivity (RER) and X-Ray Line Profile Analysis (XPA). The densities and arrangements of defects have been measured as a function of deformation degree and - in case of HPT - extent of hydrostatic pressure. It has been found that both the vacancy concentration and the dislocation density are higher than with usual deformation like torsion and rolling, and that they still increase with increasing deformation degree as well as increasing hydrostatic pressure. For both quantities, however, a saturation has been observed with respect to deformation and hydrostatic pressure applied. With the help of measurements of internal strains, the saturation effect is discussed in terms of static and dynamic recovery.

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Defect Based Micromechanical Modelling and Simulation of NanoSPD CP-Ti in Post-Deformation: Leonhard F. Zeipper[1]; *Michael J. Zehetbauer*[2]; [1]ARC Seibersdorf Research GmbH, Matls. Rsch., 2444-Seibersdorf Austria; [2]University of Vienna, Matls. Physics Inst., Boltzmanngasse 5, 1090 Vienna Austria

The paper concerns the modelling and simulation of dislocation based hardening at room temperature compression after Equal Channel Angular processing of CP-Ti (grade2). For the first time the post-deformation behaviour is successfully simulated for a nanoSPD material by the use of the Zehetbauer model, which was already applied on cubic materials during conventional and Severe Plastic Deformation. Unsuccessful calculations by the Estrin-Toth model support the numerical interpretations given in this paper. Based on the experimental data of uniaxial compression and the measured total dislocation density, the hardening behaviour is characterized and physical quantities are calculated. The results, like the calculated cell size, the dislocation evolution in the cell interior and the cell walls as well as the deformation induced vacancy concentration versus strain are discussed. Experimental data from TEM and residual electrical resistivity measurements confirm the simulation results.

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Tensile Properties of Consolidated Nanocrystalline Cu: *Evan Ma*[1]; Sheng Cheng[1]; [1]Johns Hopkins University, Matls. Sci. & Engrg., 3400 N. Charles, Baltimore, MD 21218 USA

Over the past fifteen years, nanocrystalline (nc) Cu has been a primary model material for understanding the deformation behavior of nanocrystalline metals. To obtain truly nc grain sizes (well below100 nm), the nc Cu was usually obtained in powder form, via the gas phase condensation route for example. A consolidation step is then needed to obtain bulk compacts for mechanical testing. Due to the residual porosities, the intrinsic tensile behavior of nc Cu remains unclear so far. In fact, all the consolidated nc Cu (and other nc metals as well) showed virtually no ductility in tension. The strength values vary over a wide range and are often lower than expected. Many models have appeared over the years trying to fit to these experimental data, causing major confusions in understanding the intrinsic nc behavior. We have prepared nc Cu powder through ball milling at 77 K. The severe plastic deformation processing yields powders with internal grain sizes well below 100 nm. We used an in situ consolidation technique to produce fully dense bulk nc Cu millimeters in thickness. In this talk, we report the high tensile strength and the ductility achieved, as well as the strain rate and temperature dependence. The impurity effects on the properties above are examined. We also analyze the deformation localization observed, and discuss the results in comparison with those of other nc metals and in light of the proposed/established deformation mechanisms/modes in nc metals.

2:45 PM

Severe Plastic Deformation Through Adiabatic Shearing Banding in Fe-C Steels: *Donald R. Lesuer*[1]; Chol K. Syn[1]; Oleg D. Sherby[2]; [1]Lawrence Livermore National Laboratory, L-175, Livermore, CA 94551 USA; [2]Stanford University, Dept. of Matls. Sci. & Engrg., Stanford, CA 94305 USA

Severe plastic deformation takes place within adiabatic shear bands in iron-carbon steels. Strains in the order 5 or greater are commonly observed. These shear bands form under conditions of high strain rate in excess of 1000 s-1. Studies on shear band formation in an ultrahigh carbon steel (1.3%C) are described in the pearlitic and martensitic conditions. Extremely high hardness is obtained in the shear band in excess of Vickers Hardness of 10 GPa (equivalent to 4000 MPa tensile strength). A mechanism is described to explain the high strength based on phase transformation to austenite from adiabatic heating resulting from severe deformation. Rapid re-transformation leads to an ultrafine ferrite grain size containing carbon principally in the form of nanosize carbides. It is proposed that the same mechanism explains the ultrahigh strength of iron-carbon steels observed in ball-milling, ball drop tests and in severely deformed wires. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

3:00 PM

Nanostructure Formation in Pure Copper Deformed by Rolling: Mariana Gheorghe[1]; *Naresh N. Thadhani*[1]; [1]Georgia Institute of Technology, Matls. Sci. & Engrg., 771 Ferst Dr., Erskine Love Mfg. Bldg., Atlanta, GA 30332-0245 USA

Severe plastic deformation of copper at liquid nitrogen temperature suppresses dynamic recovery and allows formation of stable nanocrystalline structure. The effect of rolling conditions on the strength and microstructure of copper was investigated in this work. Pure copper (99.99%) was rolled to similar total reductions by single or multiple passes, at ambient and liquid nitrogen temperatures. The specimens rolled at liquid nitrogen temperature (-150°C) had strength and hardness higher than those rolled at room temperature. The crystallite size was found to decrease to 20-40nm, as the degree of deformation at liquid nitrogen reached 100%. Such a reduction in grain size was not obtained in the room temperature rolled samples due to effects of recovery and recrystallization. In this paper, the correlation of grain size, retained strain, and dislocation density and character (determined using x-ray diffraction and transmission electron microscopy), with microstructure evolution and properties, will be presented. The authors acknowledge the funding available through AFOSR Grant No. 1606U81 (Craig S. Hartley, program monitor).

3:15 PM

Mechanical Behavior of a Mg AZ61 Alloy Processed by Accumulative Roll Bonding: *Jorge Antonio del Valle*[1]; María Teresa Pérez-Prado[1]; Oscar Antonio Ruano[1]; [1]CENIM,CSIC, Physl. Metall., Gregorio del Amo,8, Madrid 28040 Spain

Research on the processing, structure and mechanical behavior of nanocrystalline ($d < 100$ nm) and ultra-fine grained ($100 \text{ nm} < d < 1$ mm) materials has thrived. These materials have promising structural properties, such as elevated strength, good wear resistance and high toughness, as well as the potential for superplasticity at low temperatures and high strain rates. In this work an ultra-fine grained AZ61 Mg alloy has been fabricated via accumulative roll bonding (ARB), using large thickness reductions per pass. The resulting microstructure is analyzed by optical microscopy as well as macro- and microtexture analysis in order to study the mechanisms responsible for grain refinement. The mechanical behavior of the processed material is investigated, both at room temperature and at high temperatures, with the aim of establishing a relationship between the initial microstructure and the operative deformation mechanisms.

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High Temperature Behavior of a Cryomilled Ultrafine-Grained Al-7.5%Mg Alloy: *Bing Q. Han*[1]; Enrique J. Lavernia[1]; [1]University of California, Dept. of Cheml. Engrg. & Matls. Sci., Davis, CA 95616 USA

In the present study, the tensile behavior at temperatures of 298 K to 673 K of an ultrafine-grained Al-7.5%Mg alloy processed by consolidating cryomilled powders was investigated. Microstructure of the Al-Mg alloy shows a high thermal stability with the insignificant grain growth after high-temperature testing. The Al-Mg alloy exhibits an intrinsic behavior similar to that of other mechanically alloyed aluminum alloys, but different from that of classic superplastic aluminum alloys although the grain size of the cryomilled Al-Mg alloy is much smaller than that of superplastic aluminum alloys. The possible effect on the ductility and deformation mechanisms at elevated temperatures of the cryomilled Al alloys is discussed.

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4:00 PM

Characterization of Severely Deformed Cu/Ag and Cu/Zr Nanolamellar Structure: S. Ohsaki[2]; S. Katoh[3]; N. Tsuji[3]; *K. Hono*[1]; [1]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047 Japan; [2]University Tsukuba, Grad. Sch. of Pure & Appl. Scis., Tsukuba 305-8571 Japan; [3]Osaka University, Dept. Adaptive Machine Sys., Suita, Osaka 565-0871 Japan

To investigate the nanostructure evolution process by the accumulative role bonding (ARB) process of two phase lamellar structures, we have selected a Ag-Cu eutectic alloy and Cu/Zr stacked plates as model systems. A round bar of a Ag-39.5at.%Cu eutectic alloy with a diameter of 10 mm was first cold-rolled and then ARB processed to cumulate a large plastic strain of 6.8. 5 pieces of Cu sheets 0.2 mm thick and 4 pieces of Zr sheets 0.2 mm thick were mutually stacked and then roll-bonded, so that the total composition of the stacked material was Cu-45at%Zr. The ARB process was repeated for the multilayered material up to a total strain of 13.6. An intermixing of Ag and Cu layers was observed in the Ag-Cu eutectic lamellae. 3DAP analysis showed that the compositions of Cu and Ag lamellae are 60at.%Cu and 5 at.%Cu, respectively. Although such a mixing was observed in Cu/Ag lamellae, no amorphization was confirmed. On the other hand, the Cu/Zr stacked lamellae deformed to a total strain of 13.6 exhibited various interesting local nanostructures such as the amorphous/nanocrystal composite and the amorphization of some of the Zr lamellae. In both systems, substantial mixing was observed in the shear bands, where large shear deformation localized without any remains of the lamellar structure.

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Large Strain Deformation and Ultra-Fine Grained Materials by Machining: *Alexander H. King*[1]; Srinivasan Chandrasekar[2]; W. Dale Compton[2]; Kevin P. Trumble[1]; Travis L. Brown[2]; Seongeyl Lee[2]; Balkrishna C. Rao[2]; M. Ravi Shankar[2]; Srinivasan Swaminathan[2]; [1]Purdue University, Sch. of Matls. Engrg., 501 Northwestern Ave., W. Lafayette, IN 47907-2044 USA; [2]Purdue University, Sch. of Industl. Engrg., 315 N. Grant St., W. Lafayette, IN 47907-2023 USA

The characteristics of deformation field in plane strain machining, including the distributions of strain, strain rate and strain gradient, are reviewed with reference to recent experimental and analytical results. The nature of this deformation field is compared and contrasted with that prevailing in Equal Channel Deformation processing. The creation of ultra-fine grained materials by high strains produced in machining is demonstrated in pure metals, age hardening aluminum alloys, carbon steels, high temperature materials and amorphous alloys. These results indicate that machining provides a simple experimental configuration for studying various effects of large strain deformation in materials.

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Electron Microscopy of Mechanically Alloyed Oxide-Dispersion-Strengthened 14YWT Ferritic Steel: *James Bentley*[1]; David T. Hoelzer[1]; Dorothy W. Coffey[1]; Kathy A. Yarborough[1]; [1]Oak Ridge National Laboratory, Metals & Ceram. Div., PO Box 2008, Oak Ridge, TN 37831 USA

Advanced characterization techniques have revealed that the exceptional high-temperature mechanical properties of a new class of mechanically alloyed (MA) oxide-dispersion-strengthened (ODS) ferritic steels are due to a high concentration (~1 x 10^{24} m^{-3}) of small (a few nanometers diameter) Ti-enriched oxide clusters that are resistant to coarsening even at 1200°C. Pre-alloyed powders of the base alloy are ball-milled with yttria powder (to incorporate supersaturations of oxygen, yttrium and vacancies) and then extruded at typically 850°C to produce Fe-14.2%Cr-1.95%W-0.22%Ti-0.25%Y_2O_3, designated MA 14YWT. In order to complement atom probe tomography and small-angle neutron scattering, energy-filtered transmission electron microscopy (EFTEM) has been used to image the clusters and reveal intergranular segregation. Additional analytical electron microscopy has been used to supplement the EFTEM. Examination of as-milled powders was enabled by focused ion beam (FIB) milling for TEM specimen preparation. The electron microscopy results have provided useful guidance for helping to optimize processing conditions.

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Computational Description of Nanocrystalline Deformation Based on Crystal Plasticity: Hsueh-Hung Fu[1]; David Benson[1]; *Marc A. Meyers*[1]; [1]University of California, Dept. of Mechl. & Aeros. Engrg., 9500 Gilman Dr., La Jolla, CA 92093-0411 USA

The effect of grain size on the mechanical response of polycrystalline metals was intestigated computationally and applied to the nanocrystalline domain. A phenomenological constitutive description is adopted to build the computational crystal model. Two approaches are implemented. In the first, the material is envisaged as a composite: the grain interior is modeled as a monocrystalline core surrounded by a mantle (grain boundary) with a lower yield stress and higher work hardening rate response. Both quasi-isotropic and crystal plasticity approaches are used to simulate the grain interiors. The grain boundary is modeled either by an isotropic Voce equation (Model I) or by crystal plasticity (Mode II). Elastic and plastic anisotropy are incorporated into this simulation. An Implicit Eulerian Finite Elemene Formulation with von Mises plasticity or rate dependent crystal plasticity is used to study the non-uniform deformation and localized plastic flow. The computational predictions are compared with experimentally determined mechanical response of copper with grain sizes of 1 micro meter and 26 nm. Shear localization is observed during work hardening in view of the inhomogeneous mechanical response. In the second approach, the use of a continuous change in mechanical response, expressed by the magnitude of the maximum shear stress orientation gradient, is introduced. It is shown that the magnitude of the gradient is directly dependent on grain size. This gradient term is inserted into a constitutive equation that predicts the local stress-strain evolution.

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Severe Plastic Deformation Within a Friction-Stir Weld: *John F. Bingert*[1]; Richard W. Fonda[2]; [1]Los Alamos National Laboratory, MST-8, MS G755, Los Alamos, NM 87545 USA; [2]Naval Research Laboratory, Code 6324, 4555 Overlook Ave. SW, Washington, DC 20375 USA

The deformation gradient within the stir zone of a friction-stir weld results in locally severe plasticity. The dominant stress state is simple shear resulting from the interaction between a rotating cylindrical tool and the workpiece. This shear, combined with rigid rotations due to bulk material movement from the baseplate, introduces significant microstructural evolution. Friction-stir butt welds in 2195 and 2519 aluminum alloys were interrogated by optical and electron microscopy to elucidate some of the details of the structural changes. In particular, the post-mortem microhardness, precipitation reactions, and crystallographic texture were characterized to provide insight into the thermomechanical history experienced during the weld. Consequences of rigid-body spin and elevated-temperature shear deformation will be explored in relation to their influence on the observed texture. Experimental results were compared to polycrystalline plasticity simulations performed to predict texture evolution in the stir zone. LA-UR-04-4936.

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Bimodal Structured Bulk Nanocrystalline Al-Mg Alloys: *Zonghoon Lee*[1]; Enrique J. Lavernia[2]; Steven R. Nutt[1]; [1]University of Southern California, Matls. Sci., 3651 Watt Way, VHE-602, Los Angeles, CA 90089-0241 USA; [2]University of California, Dept. of Chem. Engrg. & Matls. Sci., Bainer Hall, Davis, CA 95616-5294 USA

The microstructure, mechanical properties and deformation mechanism of bimodal structured nanocrystalline Al-Mg alloys were investigated. Grain refinement was achieved by cryomilling of atomized Al-Mg powders, and then cryomilled nanocrystalline powders blended with 15%, 30% and 50% unmilled coarse-grained powders were consolidated by hot isostatic pressing followed by extrusion to produce bulk nanocrystalline alloys. Bimodal bulk nanocrystalline Al-Mg alloys, which were comprised of nanocrystalline grains separated by coarse-grain regions, show balanced mechanical properties of enhanced ultimate strength and reasonable ductility/toughness compared to conventional Al-Mg alloys and other nanocrystalline metals. The investigation of tensile test, TEM analysis and finite element analysis suggests unusual deformation mechanisms and interactions between ductile coarse-grain and nanocrystalline regions. The bimodal microstructure and its ductility toughening effect inspire us to design microstructures and to select processing parameters leading to optimal performance characteristics on various nanocrystalline metals.

5:30 PM

The Use of Severe Plastic Deformation for Consolidating Nanostructured Metallic Powders: *Deliang Zhang*[1]; Nathan J. Scott[1]; Carl C. Koch[2]; [1]University of Waikato, Dept. of Matls. & Process Engrg., PB 3105, Hamilton, Waikato 2001 New Zealand; [2]North Carolina State University, Dept. of Matls. Sci. & Engrg., Raileigh, NC 27695-7907 USA

Certain severe plastic deformation processes such as equal channel angular pressing have been widely used to process bulk metallic materials to generate ultra fine grained structures with grain sizes greater than 100nm. In the meantime, high energy mechanical milling, as another severe plastic deformation process, has been widely used to produce nanostructured metallic powder materials with grain sizes as small as a few nanometres, but turning the nanostructured powders into bulk nanostructured materials is a great challenge. Severe plastic deformation, on the other hand, is also capable of producing a large area of new surfaces of powder particles due to the large amount of shear deformation. Under certain conditions, the large area of new surfaces can be well utilised to cause cold welding, or cold sintering in powder metallurgy term. This paper will critically examine the relationships between processing conditions, microstructure and quality of

a few nanostructured copper based metallic materials produced by consolidating nanostructured powders using severe plastic deformation processes such as high energy mechanical milling, rolling and forging, and discuss the associated scientific and technological issues.

TMS Featured Presentations

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February 16, 2005 Location: Moscone West Convention Center

Session Chair: Richard Wright, Idaho National Engineering Laboratory, Idaho Falls, ID 83415-2218 USA

2:00 PM
Bauxite Mining Sustainability: *Patrick Riley Atkins*[1]; [1]Alcoa, Inc., 390 Park Ave., New York, NY 10022 USA

Beginning in 1990, The international Aluminum Institute began a program to report on the bauxite mineing and rehabilitation activities of the worldwide industry. A survey process was initiated and reports were published in 1992, 1998 and 2004. The recently published 2004 report includes extensive data on mines that represent over 70% of the world's output of bauxite. This paper describe the latest report and will focus on the mine rehabilitation technologies,progress and performance, on company/community interactions and the sustainability goals of the industry.

2:25 PM
On the Preparation and Stability of Scorodite: *George P. Demopoulos*[1]; [1]McGill University, Metals & Matls. Engrg., 3610 Univ. St., Montreal, Quebec H3A 2B2 Canada

Scorodite is advocated as a viable option for the fixation of arsenic from aqueous process effluents, especially for arsenic-rich and iron-deficient solutions. It has a high arsenic content, it requires stoichiometric amounts of iron, and it has excellent dewatering and disposal characteristics. Because of its high degree of crystallinity and small specific surface area, scorodite is also, very importantly, thought to have high inherent stability at least from a kinetic point of view. As a mineral, scorodite can be found in a wide variety of geological settings. This suggests that it is stable under specific weathering conditions. Hence our interest in designing a cost-effective process for returning arsenic to the environment in this mineral form. In this paper, (1) the preparation of scorodite in lime neutralisation ?type circuits is discussed and (2) the long term stability of scorodite is evaluated in the light of newly generated accelerated ageing kinetic data.

2:50 PM
Use of CO2-Snow for Protecting Molten Magnesium from Oxidation: Friedrich-Wilhelm Bach[1]; *Alexander Karger*[1]; Christoph Pelz[2]; Mirko Schaper[1]; [1]University Hanover, Inst. for Matls. Sci., Schoenebecker Allee 2, 30823 Garbsen Germany; [2]Linde Gas AG, Unterschleissheim Germany

When processing magnesium alloys, prevention of oxidation of the liquid metal is of prime importance, because of the high oxygen affinity of molten magnesium. A special danger of environmental pollution occurs from the usage of protective gases for molten magnesium. The protective gas SF6, which is widely used nowadays, increases the greenhouse effect due to it's GWP of approximately 23900 relative to CO2. At the Kyoto summit in 1997, this gas was detected as one of six gases to be restricted in use. The environmentally friendly alternatives are being examined by authors of this paper. The research goals of this group are to develop and to evaluate new methods for protecting the surface of magnesium melts. One possible alternative is covering the magnesium melt with CO2-snow. The current results will be presented in the following paper.

3:15 PM
Identifying Economic and Scrap Reuse Benefits of Light Metals Sorting Technologies: Preston P. Li[1]; Sigrid Guldberg[2]; Hans Ole Riddervold[2]; *Randolph E. Kirchain*[1]; [1]Massachusetts Institute of Technology, Matls. Sys. Lab., Rm. E40-421, 77 Mass. Ave., Cambridge, MA 02139 USA; [2]Hydro Aluminum, Drammensveien 264, N-0240, Oslo Norway

The changing pattern of aluminum scrap usage has created material reuse challenges for the industry. For instance, mixed scraps consisting of wrought and cast alloys often cannot be directly re-melted and reused due to compositional incompatibility. Various new sorting technologies promise to address these challenges. It is critical to understand how, when, and to what extent sorting should be applied in different circumstances. This paper examines the use of linear programming methods to identify economically efficient sorting strategies and their impact on scrap usage. Economic efficiency was tested for various states of scrap material supply, finished good demand, sorting technology type, and sorting performance. The model can be used to identify optimized specific sorting schemes. The overall goal is to support industry decision-making regarding the application of sorting technologies to increase scrap use and lower production costs.

3:40 PM Break

3:50 PM
Developing an Atomic-Level Understanding of the Mechanisms that Govern CO2 Mineral Carbonation Reaction Processes: *Michael J. McKelvy*[1]; Andrew V.G. Chizmeshya[1]; Jason Diefenbacher[2]; Hamdallah Béarat[2]; R. W. Carpenter[1]; George Wolf[3]; [1]Arizona State University, Ctr. for Solid State Sci., Sci. & Engrg. of Matls. Grad. Prog., Tempe, AZ 85287 USA; [2]Arizona State University, Ctr. for Solid State Sci., Tempe, AZ 85287 USA; [3]Arizona State University, Dept. of Chmst. & Biochmst., Tempe, AZ 85287 USA

Mineral carbonation is an intriguing CO2 sequestration candidate technology, which produces environmentally benign and geologically stable materials. The primary challenge is economically viable process development. Serpentine and olivine minerals are exciting candidate feedstock materials, due to their wide availability, low-cost, and rapid mineral carbonation potential. Cost-effectively enhancing their carbonation rate is critical to reducing mineral sequestration process cost. We will discuss our recent research into the mechanisms that govern serpentine/olivine mineral carbonation reaction processes, including in situ observations of the mineral carbonation process and a novel mechanistic approach to enhance carbonation reactivity that avoids the cost of mineral activation. Our goal is to develop the necessary atomic-level understanding to engineer improved carbonation materials and processes to reduce process cost.

4:15 PM
Diffusion Paths and Interdiffusion Microstructures: Applications and Remaining Challenges: *John E. Morral*[1]; [1]Ohio State University, Dept. of Matls. Sci. & Engrg., Columbus, OH 43210 USA

Interdiffusion can influence the properties and cost of products that experience high temperature during processing or service (e.g. coated turbine blades, solid oxide fuel cells, carburized sun gears, etc.). Accordingly the ability to predict interdiffusion microstructures can be a useful alloy design tool. Software such as DICTRA can predict interdiffusion microstructures via diffusion paths and phase diagrams. Although useful for certain applications, both DICTRA and the theory of diffusion paths have serious limitations. Software for the Phase Field Method (PFM) requires more computer time, but has fewer limitations and can predict microstructures directly. Also the PFM takes into account both precipitate morphology and diffusion in precipitates, which yields a more accurate result. However without adequate databases and a better understanding of interdiffusion fundamentals, the value of these programs to alloy design will be limited.

4:40 PM
Deformation at the Nanometer and Micrometer Length Scales: Effects of Strain Gradients and Dislocation Starvation: *William D. Nix*[1]; Gang Feng[1]; Julia R. Greer[1]; [1]Stanford University, Dept. Matls. Sci. & Engrg., 416 Escondido Mall, Stanford, CA 94305-2205 USA

Size effects in plasticity are now well known. Plastic deformation in small volumes requires higher stresses than are needed for plastic flow of bulk materials. Here we review the various effects that appear to be responsible for this. The size dependence of the hardness of metals at the micron scale can be described in terms of the geometrically necessary dislocations or, correspondingly, the strain gradients, created in small indentations. But such accounts break down when the size of the deformation volume begins to approach the spacing of individual dislocations or when the crystal becomes dislocation starved. Nanoindentation of epitaxial films at the nanometer depth scale reveals irregular load-displacement curves. In this domain the nucleation of dislocations and plasticity under dislocation-starved conditions appears to be more important than strain gradients. Recent uniaxial compression experiments on tiny samples of gold made by focused ion beam machining and integrated circuit fabrication methods show strong size effects on plasticity, with sub-micron sized crystals showing remarkable strengths after plastic deformation. These experiments involve small deformation volumes and minimal strain gradients. These size effects may be explained by considering a process of strain hardening by dislocation starvation, wherein existing dislocations leave the crystal more frequently than they reproduce themselves by multiplication.

5:05 PM
Semiconducting and Piezoelectric Nanobelts, Nanosprings, and Nanorings: *Zhong Lin Wang*[1]; [1]Georgia Institute of Technology, Sch. of Matls. Sci. & Engrg., Atlanta, GA 30332-0245 USA

Nanowire and nanotube based materials have been demonstrated as building blocks for nanocircuits, nanosystems and nano-optoelectronics. Quasi-one-dimensional nanostructures (so called nanobelts or nanoribbons) have been successfully synthesized for semiconducting oxides of zinc, tin, indium, cadmium and gallium, by simply evaporating the desired commercial metal oxide powders at high temperatures. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. Using the technique demonstrated for measuring the mechanical properties of carbon nanotubes based on in-situ transmission electron microscopy, the bending modulus of the oxide nanobelts has been measured, and the nanobelt is shown to be a dual mode nanoresonator for NEMS technology. Field effect transistors and ultra-sensitive nano-size gas sensors, nanoresonators and nanocantilevers have also been fabricated based on individual nanobelts. Thermal transport along the nanobelt has also been measured. Very recently, nanobelts, nanorings and nanosprings that exhibit piezoelectric properties have been synthesized, which are potential candidates for nano-scale traducers, actuators and sensors. The discovery of single-crystal perfect nanorings and its "slinky" growth model will be presented.

5:30 PM
Aluminum Alloy Thermodynamics and Kinetics from First Principles: *Chris Wolverton*[1]; Vidvuds Ozolins[2]; [1]Ford Motor Company, Physl. & Environml. Sci., MD 3083/SRL, PO Box 2053, Dearborn, MI 48121-2053 USA; [2]University of California, Dept. of Matls. Sci., Los Angeles, CA 90095-1595 USA

We present an extensive survey of the thermodynamic and kinetic properties of binary Al alloys, as obtained from first-principles atomistic calculations. We consider a wide range of properties: 1) Energetic properties of ordered compounds, impurities, and mixing energies of solid solutions, 2) first-principles calculations of interatomic force constants, phonon spectra and vibrational entropies, 3) thermodynamic properties and solubility, and 4) kinetic quantities such as solute-vacancy binding, migration energies, and diffusion coefficients. We compare our results critically with experimental and CALPHAD databases to ascertain inaccuracies in the theoretical methods, and cases in which experimental data should be re-evaluated. In addition, the extensive nature of the database facilitates understanding the trends in energetic, thermodynamic, and kinetic properties. In addition, this large first-principles database should enable many future applications, such as improving existing CALPHAD databases, as well as providing key information to phase-field models of microstructural evolution.

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