3-Dimensional Materials Science: Modeling and Characterization across Length Scales IV

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Advanced Characterization, Testing, and Simulation Committee
Program Organizers: Michael Uchic, US Air Force; Eric Taleff, University of Texas; Alexis Lewis, Naval Research Laboratory; Jeff Simmons, US Air Force; Marc DeGraef, Carnegie Mellon University

Thursday AM Room: 286
March 13, 2008 Location: Ernest Morial Convention Center

Session Chair: Michael Uchic, US Air Force

8:30 AM
HAADF-STEM Tomography of Intrinsically Low Contrast Materials: *David Morgan*[1]; Miriam Herrera[1]; Shareghe Maheraeen[1]; Volkan Ortalan[1]; Nigel Browning[1]; [1]University of California, Davis

Materials science tomography has traditionally involved materials exhibiting large contrast variation. Examples of such materials are catalytic nanoparticles and quantum dots sitting on or embedded within a matrix of lighter elements. The large contrast difference between such particles and their matrix is highlighted using high angle annular darkfield (HAADF) scanning transmission electron microscopy (STEM) and tomography based on HAADF-STEM images can clearly reveal particle shape and arrangement in three-dimensions. Indeed, data processing for tomography makes use of the high contrast nature of such images. However, materials where the structure is dominated by features such as grain boundaries or dislocations do not exhibit such contrast and have proven difficult to analyze using conventional tomographic methods. We are developing methods to deal with such low contrast materials and will present results based on a variety of image processing filters utilized at various steps during the tomographic data processing procedure.

8:50 AM
Dark-Field Electron Tomography for Three-Dimensional Domain Morphology in Ni-Based Ordered Alloys: *Syo Matsumura*[1]; Kosuke Kimura[1]; Kanae Matsuyama[1]; Satoshi Hata[1]; [1]Kyushu University

Electron tomography is rapidly getting popular these days for three-dimensional material characterization in nanometer scale with development of computer-assisted operation of transmission electron microscopes. So far, this technique has been mostly applied to fine structures and morphologies due to element aggregation with spatial variation of mass density, in which transmittance of incident electrons decays monotonically with mass-thickness. In contrast, dark-filed transmission electron microscopy with diffracted electrons can image morphologies of crystal grains and ordered domains, which are due to spatial change in crystal orientation. In this study, we made a trial to reconstruct three-dimensional morphologies of ordered domains in Ni-based alloys from tilt series of dark-field images by the computed-tomography procedure. In the present talk, we will demonstrate three-dimensional characterization of domain shapes and dispersion of $D1_a$ ordered variants in a Ni_4Mo alloy as well as of precipitates of gamma and gamma-prime phases in Ni-Al-Ti alloys.

9:10 AM
A Femtosecond Laser-Aided Serial Sectioning Process and 3D Dendrite Reconstruction of a Nickel Based Superalloy: *McLean Echlin*[1]; Jonathan Madison[1]; Tresa Pollock[1]; [1]University of Michigan

A laser-aided technique for acquisition of three-dimensional microstructural datasets has been developed. This technique has been utilized to image dendritic structure at the solidification front in a nickel-base single crystal superalloy. The solid-liquid interface is obtained by draining molten metal from an investment mold in a partially solidified casting. The 3D reconstruction was produced using a fully automated serial sectioning process that employs a femtosecond laser to ablate material from the sample surface. Between material removal steps 2D images are captured using an optical lens and a fiber light illumination system. The collection of images are stacked and reconstructed using IDL™ into a 3D dataset. Sectioning slice thicknesses range from the ablation fluence threshold for René N4 (~30-50 μm), and have no apparent slice thickness upper bound. The efficiencies of this serial sectioning process relative to FIB-based and mechanical serial sectioning techniques will be discussed.

9:30 AM
Micromechanics-Based Modeling of Ductile Fracture with Experimental Integration of 3-D Microstructural Data: *Amine Benzerga*[1]; [1]Texas A&M University

In ductile fracture of structural materials, damage initiates at second-phase particles. Therefore, the spacing between these sets the relevant scale of analysis. A unifying framework for analyzing ductile damage by void nucleation, growth and coalescence will be presented. It relies on constitutive descriptions that incorporate shape, relative spacing and orientation of particles in addition to their volume fraction. One peculiar feature of this framework is that crack initiation and growth are natural outcomes to competing plastic mechanisms. The counterpart to the enriched microstructural description is the need to collect more experimental information, both in the undeformed and deformed states. Use of two-dimensional imaging, aided by suitable stereological transformations, has traditionally been the method of choice in providing critical input and model assessment data. In strongly anisotropic materials, however, there is a need for full three-dimensional input and avenues in exploring such input in our modeling strategies will be discussed.

9:50 AM Break

10:10 AM
Three-Dimensional Characterization of Dendritic Structure in Nickel-Base Single Crystals: *Jonathan Madison*[1]; Jonathan Spowart[2]; David Rowenhorst[3]; Tresa Pollock[1]; [1]University of Michigan; [2]US Air Force; [3]Naval Research Laboratory

During solidification, solute-induced convective instabilities at the solid - liquid interface can result in the formation of defects such as freckles and misoriented grains. These defects can be particularly detrimental in the directional solidification of single crystal nickel-base superalloys. Unfortunately, detailed understanding of fluid flow at the scale of the dendritic structure has yet to be fully understood, particularly under conditions in which heat extraction is non-axial. The objective of this research is to develop a technique for quantifying the dendritic substructure at the solid – liquid interface for the purposes of providing direct input into computational fluid flow modeling. Using the RoboMET.3D serial sectioning system, three-dimensional datasets of dendritic structures within decanted René N4 have been obtained and will be shown. Distributions and arrangements of solid and liquid in the vicinity of dendrite tips will also be presented along with discussion of implications for defect formation.

10:30 AM
Advanced Characterization to Determine Chemical Segregation in Nickel Super Alloys: *Jaimie Tiley*[1]; [1]US Air Force

Advanced neutron diffraction, high resolution transmission electron microscopy, and atomic probe tomography techniques were employed to determine the three dimension microstructure characteristics of several commercial nickel superalloys. This includes the volume fraction and morphology of ordered gamma prime phases, the chemical segregation between phases as a function of processing conditions and temperature, and the lattice misfit, site occupancies, and thermal expansion parameters for the studied materials.

10:50 AM
Three Dimensional Characterization of Microstructure in Hot-Deformed AA5083 for Understanding Cavitation Damage: *Jung-Kuei Chang*[1]; Eric Taleff[1]; Paul Krajewski[2]; [1]University of Texas; [2]General Motors Corporation

Fine-grained aluminum alloy AA5083 sheet is hot formed into complex body panels by the Quick Plastic Forming process for the mass production of automobiles. Cavity formation and interlinkage during hot tensile straining can limit the formability of this material in production. Cavitation is strongly influenced by a number of microstructural features, particularly intermetallic particles. The relationship between intermetallic particles and cavities is complex. Standard microstructural observations of two-dimensional material cross sections have not produced data sufficient to understand this relationship. Serial sectioning was used to produce three-dimensional, 3-D, microstructure data sets. These 3-D data sets reveal relationships between intermetallic particles and cavities not previously observable. In particular, cavity percolation and

cavity-particle adjacency are available and quantifiable from the 3-D data. These data provide definitive evidence for the association of cavities with particular intermetallic particle types and particle spatial distributions.

Alumina and Bauxite: Precipitation/Conclusion

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Sringeri Chandrashekar, Rio Tinto Aluminium Limited; Peter McIntosh, Hatch Associates

Thursday AM Room: 296
March 13, 2008 Location: Ernest Morial Convention Center

Session Chair: Luiz Correa, Companhia Vale do Rio Doce

8:30 AM Introductory Comments

8:35 AM
The Effects of Wet Oxidation on Hydrate Yield Inhibitors in Alkaline Aluminate Solutions: *Joanne Loh*[1]; Greta Brodie[1]; Greg Power[1]; Chris Vernon[1]; [1]CSIRO Minerals

Wet oxidation can be an effective means of removing organics from Bayer liquor. Total removal of organics by wet oxidation requires extreme conditions, so partial organics removal is generally considered to be a more economically viable approach. However the mechanisms of degradation by wet oxidation are complex and the products of partial wet oxidation are not well understood. This allows the possibility that there may be conditions under which harmful products, in particular hydrate yield inhibitors, could be produced. This fundamental study was conducted to determine the susceptibility of known yield inhibitors to destruction by wet oxidation. It is shown that of the yield inhibitors investigated, compounds with more than 5 carbons in a chain and aromatic compounds are readily destroyed by wet oxidation at 165°C in the presence of oxygen. Members of the C4 family of inhibitors are more stable and require higher temperatures for full destruction.

9:00 AM
Using Mass Balance for Solids Concentration Control at Precipitation Agglomerator Tanks: *Anderson Amaral*[1]; Cleto Junior[1]; Luiz Gustavo Correa[1]; Jorge Lima[1]; Joaquim Filho[1]; Luiz Santos[1]; [1]Alunorte

The solids concentration control at agglomerator tanks is used as a tool to control the hydrate PSD at precipitation, as well as, to guarantee the alumina attrition index in suitable levels. The range of solids concentration used at Alunorte agglomerator tanks to achieve these objectives is allowed to vary around 180-220 gpl. This paper aims to present the application of one transient mass balance to control the solids concentration at agglomerator tanks. JAVA programming language was used to implement routine for calculations and the PI - Plant Information software, connected with DCS was used for control loop implementation. The relative mean error between the results of calculated solids concentration, by mass balance, and the analyzed samples is around 10%, indicating an excellent applicability of the transient mass balance to control the solids concentration at agglomerator tanks.

9:25 AM
The Most Important Sustainable Development Issues of Chinese Alumina Industry: Wangxing Li[1]; *Jibo Liu*[1]; Zhiming Liu[2]; Yadong Wang[1]; Qiyuan Chen[3]; Zhoulan Yin[3]; [1]Chalco, Ltd., Zhengzhou Research Institute; [2]Chalco, Ltd./Zhengzhou Research Institute, Central South University ; [3]Aluminum Corporation of China Limited

The influence of ultrasonic processing on sodium aluminate solution and alumina trihydrate precipitation process were studied, The cavitation phenomenon caused by ultrasound were detected by hydrophone and sonofluorescence, the structure alterations of sodium aluminate solution were investigated by ESR, 27Al-NMR spectra, and RAMAN spectra, the alumina trihydrate precipitation processes from sodium aluminate solution with ultrasonic processing were also studied, it was found that the ultrasonic processing can cause cavitation and molecular structure change in sodium aluminate solution, the precipitation rate can also be enhanced by ultrasonic processing, and the appearance and granularity of the crystalline produced by the precipitation process were also affected.

9:50 AM Break

10:05 AM
The Impact of Conversion from Batch to Continuous Agglomeration at the Ewarton Alumina Refinery: *Patrick Harris*[1]; [1]West Indies Alumina Company

The agglomeration circuit at the Ewarton Alumina Refinery was converted from batch to continuous mode. The change was achieved by a reconfiguration of existing tanks and pipework. Open launders were installed between the continuous tanks. The final arrangement is a continuous agglomeration circuit followed by a short continuous growth circuit and batch growth precipitators. The impact of the reconfigured precipitation circuit on yield, particle size control and residual soda were assessed and are presented in this paper. There was significant increase in precipitation yield and reduction in residual soda in the final alumina tri-hydrate, while maintaining alumina particle size within customer specification.

10:30 AM
Characterization Profile in Scales from CVG-Bauxilum: *Ricardo Galarraga*[1]; Royman Cañas[1]; Nelson Piñero[1]; [1]CVG Bauxilum

One of the most current and challenging issues affecting Bauxite processing Plants is the constant scale formation in equipment and main process piping. From the Red to the White Side, no one area is exempted from this situation. Based on this, the present work focuses on a detailed investigation of the chemical composition of the scale according to its origin site. Samples were collected, analyzed and dissolution tests made for each of the scales. The purpose of the investigation converges in the study and optimization of the ideal process parameters for the elimination, control or reduction of the formation. The final recommendation is centered around the determination of each type of cleaning system to be used, mechanical, high pressure water, or chemical. For the later case emphasis has been put on temperature conditions, caustic concentration, RMC, contact time and frequency of cleaning that do not impact considerably on plant capacity.

10:55 AM Panel Discussion
Challenges Facing Alumina and Bauxite Industry

11:50 AM Concluding Comments

Aluminum Reduction Technology: Cell Development Part II

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Martin Iffert, Trimet Aluminium AG; Geoffrey Bearne, Rio Tinto Aluminium Tech

Thursday AM Room: 298
March 13, 2008 Location: Ernest Morial Convention Center

Session Chair: Gary Tarcy, Alcoa Inc

8:30 AM
Last Development in AP50 Cell: Jean-Luc Basquin[1]; *Ben Benkahla*[1]; Yves Caratini[1]; Hervé Mezin[1]; Steve Renaudier[1]; [1]Alcan

Alcan has achieved a new step in AP50 technology development: by 2009 44 AP50 cell will be in operation at Jonquiere complex in Quebec, demonstrating on industrial phase the cutting edge of this technology. In the last 3 years an intensive program has been launched to optimize the AP50 design and performances. Using new development of thermo-electrical and MHD models, cell design has been improved. A new anodic assembly, an optimised cathode, has allowed to reduce specific energy comsumption and to improve cell stability. Full measurement campaign and performance test has validated this high level of performance. The AP50 process control has integrated the last development of ALPSYS pot control system insuring a benchmark result for thermal control and Anode Effect frequency. The AP50 technology with a single potline having

an annual output of 500 kt will increase dramatically productivity per employee and reduce investment cost compared to previous technologies.

8:55 AM

Fjardaal Smelter Project, Iceland-Modular Construction: Bernard Cloutier[1]; Joe Wahba[2]; Warren McKenzie[3]; *Sam Philip Maliha*[1]; [1]Fives Solios; [2]Bechtel; [3]Alcoa, Inc

The Construction of the Fjardaal Smelter Project in Iceland represented a challenge in terms of logistics and construction. This challenge is primarily due to the unavailability of a local workforce and the Icelandic climatic conditions. Faced with such constraints, the project Owner ALCOA and the nominated EPC contractor BECHTEL Corp. encouraged the engineering and construction off-site of large pre-assembled modules that would be shipped using specialized maritime transportation vessels . The modules were moved from the plant harbor to the final destination using SPMT's (Self Propelled Mobile Transporters). This paper describes FIVES SOLIOS experience in applying this concept to the potlines Gas Treatment Centers and the Bath Treatment Plant. Large pre-assembled modules weighing from 80T to 340T were delivered in a record time and the construction team managed by Bechtel/Alcoa has received several awards for Health, Safety and Environmental protection. The application of this concept is of high interest for new smelters that are built in remote areas coastal locations and driven by tight schedules.

9:20 AM

Successful Dry Restart of the Hamburg Smelter: *Till Reek*[1]; Joerg Prepeneit[1]; David Eisma[2]; [1]Trimet Aluminium AG; [2]Timet Aluminum AG

In December 2005, the 133,000 tons smelter in Hamburg, Germany was shut-down. The phase-out process was very controlled and efficient, which was essential for the restart. The assets were acquired by TRIMET ALUMINIUM AG late in 2006. Beginning of March 2007, only 3 months after the transaction took place, the first pot was started successfully. The first two pots were specially prepared with a full-shadow resistor-coke bed for electrical preheating. Temperatures of above 1100°C were reached and pure synthetic cryolite was molten. Seven newly relined pots were started before the first shut down cell was restarted with its original lining. Depending on the condition of the old cathodes either gas or electrical pre-heating was used. This paper highlights the experiences of the dry start-up and the challenges involved in restarting an idle smelter in record time without any pot failures.

9:45 AM

20 Years of Continues Improvements in TALUM Smelter: *Cus Zlatko*[1]; Avgust Sibila[1]; [1]Talum

TALUM is the only primary aluminium producer in Slovenia. In February 1954, the first alumina production plant was introduced, and first aluminium was produced in November of the same year. Various lines and technologies were in operation the last 54 years. Currently the only AP18 technology is used for TALUM primary aluminium production. AP18 pots were started in 1988. During last 20 years the TALUM continues improvements program bring us to be one of the most efficient producer of aluminium in AP18 technology. The average CE of 95,28%, 13.166 kWh/t DC energy consumption and average pot life of more then 3000 days is result of technical improvements using best practice with minimum cost approach which mainly covers optimization of operational parameters, improvement of cathode design, optimization of process control system and application of slotted anodes as well as improvement of anode quality.

10:10 AM Break

10:20 AM

Faster Normalization of Cells after Bath up: *B. Kakkar*[1]; Ali Al Zarouni[1]; Arvind Kumar[1]; [1]Dubai Aluminum Company

It is always the endeavour to normalise cells as early as possible after bath up. A newly started cell has several notable features. current efficiency being one of them. All efforts are directed at improving this aspect right from the time a cell is bathed up. The closely monitored parameters during early operation are bath temperature and excess AlF3. Their control is better in graphitised cathodes due to lower adsorption of sodium. When Dubal switched over to graphitized cathodes, early cell operation strategy was comprehensively revamped in terms of voltage reduction, alumina feed rate, metal level and bath chemistry control. The change in bath up strategy has positively responded and current efficiency of 96.5% could be achieved from second week onwards. Current efficiency improvement in new cells is in line with the strategy of maximising metal output from a cell during it service life.

10:45 AM

Development of New Generation SY300 Technology: Kangjian Sun[1]; *Baoguo Chen*[1]; [1]ShenYang Aluminium and Magnesium Institute

SAMI have developed SY300 technology in 2002. There are more than two thousand SY300 pots in operation. SAMI have made further improvement in SY300 technology and develop the new generation SY 300 technology and and applied the technology in Hennan Wanji smelter. When the first new generation SY300 potline (Wanji) starts up in Jan 2006, the current has increased from 300kA to 335kA. The potline have get the high current efficiency and lower energy consumption than the first generation SY300 pot. SAMI is doing further work to improve the new generation SY300 technology to the world benchmark.

11:10 AM

Thyristor Rectifiers for Aluminium Plants with Advanced Freewheeling Control: Shripad Tambe[1]; Wynand Lauwrens[1]; Markus Rechsteiner[1]; *Eric Lambert*[1]; [1]ABB Inc.

Potline current demand for aluminium plants is constantly increasing. Many potlines with 350 kA are in operation and the trend is to push towards 500 kA in the near future, requiring the installation of many units in parallel. Due to the physical limitations of the size of each unit and the redundancy requirements, it could pose a problem to handle current when all the units are tripped simultaneously. As a result of uneven switching off of the rectifiers, there is a good chance that the last unit will carry full potline current. In a diode plant, this phenomenon can be handled easily as all diodes go into a natural freewheeling mode. Whereas in thyristor plants, special techniques need to be implemented to prevent overloading of the last switched unit. ABB High Power Rectifiers have developed a sophisticated technique which can handle such an occurrence without over sizing any units.

11:35 AM

Alcoa's Pathway to Reliability Excellence: *Vincent Adorno*[1]; Randy Heisler[2]; [1]Alcoa Primary Metals; [2]Life Cycle Engineering

As Alcoa Primary Metals started our journey to limit the cost of unreliability we made early progress, but it was not at a level that was acceptable. Alcoa was in the process of implementing a Lean initiative that required equipment stability – stability that would be provided by Reliability Excellence (Rx). It became apparent that Primary Metals didn't have a global reliability strategy. In 2002 we formed a team to develop a business case and implementation strategy. External consultants were included in this process to insure that best practices and reasonable estimates of potential savings were incorporated. The development of a best practice reliability network was critical to leveraging overall success across Primary Metals. The return on investment has ranged from 5 to 1, to 16 to 1 at individual plants. This success has driven the process forward to all Primary Metals locations with even more tenacity.

Biological Materials Science: Implant Biomaterials II

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Biomaterials Committee, TMS/ASM: Mechanical Behavior of Materials Committee

Program Organizers: Ryan Roeder, University of Notre Dame; Robert Ritchie, University of California; Mehmet Sarikaya, University of Washington; Lim Chwee Teck, National University of Singapore; Eduard Arzt, Max Planck Institute; Marc Meyers, University of California, San Diego

Thursday AM
March 13, 2008

Room: 390
Location: Ernest Morial Convention Center

Session Chairs: Carlos Elias, Instituto Militar de Engenharia; Ryan Roeder, University of Notre Dame

8:30 AM

Fatigue of Zirconia Bioceramics: *Carlos Elias*[1]; Claudinei dos Santos[2]; Renato Souza[2]; Luiz Bicalho[2]; Miguel Barboza[2]; [1]Instituto Militar de Engenharia; [2]Escola de Engenharia de Lorena

When ceramic is used for implant material such as artificial joints or dental implant abutment, it demands for generation of design-relevant fatigue data. In this paper, the fatigue behavior of tetragonal zirconia polycrystals (TZP) with 3mol.% of Y_2O_3 stabilized (3Y-TZP) under four-point bending in load cyclic conditions was investigated. Mechanical properties of hardness, fracture toughness and modulus of rupture were also evaluated. The results showed that dense 3Y-TZP was obtained after sintering, and present HV, K_{IC} and modulus of rupture of 13.5 GPa, 8.15 MPa.$m^{1/2}$ and 880 MPa, respectively. In this ceramic submitted to the 4 point bending cyclic load, the propensity for cyclic fatigue is very strong and presents a considerable range of loading conditions, where cyclic fatigue can be detected. The results obtained indicates that the fatigue strength limit over $5x10^6$ cycles stress is about 550 MPa or around 63% static bending strength.

8:50 AM

Nanocrystalline Hydroxyapatite for Biomedical Applications: *Tien Tran*[1]; Cosan Unuvar[1]; Joanna Groza[1]; James Shackelford[1]; [1]University of California

Hydroxyapatite, a bioactive and resorbable material, has been limited to non-load bearing applications due to its poor mechanical properties. Although nanocrystalline bioceramics exhibit enhanced strength, hardness, and wear resistance as well as protein adsorption and cell adhesion, the fracture toughness of non-cubic ceramics in relation to grain size remains a concern. Conventional processing methods lead to rapid grain coarsening and decomposition making it difficult to achieve fully dense nanocrystalline hydroxyapatite. Consequently, published fracture toughness values at the submicron to nanocrystalline levels often reflect the effects of porosity rather than grain size. Near-theoretical densities can be achieved in minutes by the field-assisted sintering technique (FAST), thereby restraining grain growth to the nanoscale regime and reducing decomposition. Eliminating the effects of porosity allows optimization of the mechanical properties of hydroxyapatite. The application of this approach to producing nanoscale hydroxyapatite is reported, including both biological and mechanical characterization of the resulting material.

9:10 AM

Synthesis and Characterization of Sodium Calcium Phosphate for Biological Applications: *Hande Demirkiran*[1]; Pranesh Aswath[1]; [1]University of Texas at Arlington

New ceramic products were developed by sintering mixtures of Hydroxyapatite (HA) and Bioglass®(BG) at 1200°C. The phase composition and microstructure of the blends were examined by x-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Bioactivity of the ceramics by soaking in simulated body fluid (SBF) solution maintained at 37°C and pH of 7.4 for 10 weeks. Surface compositions and microstructures of the disks were analyzed after immersion in SBF solution by FTIR and SEM, respectively. Sodium, calcium, and phosphorus ion concentrations were examined by inductive coupled plasma. The results demonstrated that the bioactivity of the 25wt% BG-HA blends were found to be the most promising blend among all the blends with crystalline sodium calcium phosphate [$Na_3Ca_6(PO_4)_5$] and amorphous silicon phases. A thick layer of carbonate-apatite covered the surface of sodium calcium phosphate disks after 1 week of immersion.

9:30 AM

In-Vitro Response of Sodium Calcium Phosphate Surfaces to Growth and Proliferation of Bone Marrow Stromal Cells: Hande Demirkiran[1]; Arunesh Mohandas[1]; Motokazi Dohi[1]; Kytai Nguyen[1]; *Pranesh Aswath*[1]; [1]University of Texas at Arlington

Mixtures of $3NaH_2(PO_4) + 2CaH(PO_4) + 4CaO$ were sintered at temperatures ranging from 600–1500°C for 1 hour. The phases formed were characterized using X-ray diffraction and the microstructure of the ceramic product was examined with scanning electron microscopy and optical microscopy. Compositions sintered at temperatures greater than 1200°C or for times longer than 1hour at 1200°C yielded $Ca_{10}Na(PO_4)_7$. In addition blends of Bioglass® and Hydroxyapatite were sintered together to yield new ceramic products with compositions with 25 wt.% Bioglass® yielding $Ca_{10}Na(PO_4)_7$. In this study, compositions that yielded $Ca_{10}Na(PO_4)_7$ were examined further by culturing bone marrow stromal cells on the surfaces over a period of six days. The proliferation and differentiation of BMSC was determined by picogreen DNA assay's and alkaline phosphatase activity.

9:50 AM

Biocompatibility Evaluation of Potassium Mica-Fluorapatite Based Glass Ceramics as a Function of CeO_2 Addition: *Ipek Akin*[1]; Hilal Yazici[1]; Candan Tamerler Behar[1]; Gultekin Goller[1]; [1]Istanbul Technical University

For a material to be machinable and bioactive, it should contain both mica and apatite crystals. Apatite containing glass ceramics are greatly important for surgical implantation due to the high bioactivity, close crystallographic and chemical similarity to human bone tissue. The crystalline phases occurring in these glass ceramics include essentially apatite which provides the biocompatibility and bioactivity of the glass ceramics, and mica phase, crystallized at higher temperature and provides the interesting mechanical properties such as machinability and strength. Osteoblasts are the cells that support the formation, secretion and mineralization of extracellular bone matrix. The purpose of this study is to investigate the behavior of these cells of a glass ceramic having 70wt% potassium mica and 30wt% fluorapatite as a function of 1 and 2wt% CeO_2 addition.

10:10 AM

Influence of ZrO_2 Addition on In-Vitro Bioactivity Properties of Potassium Mica-Fluorapatite Based Glass Ceramics: *Gultekin Goller*[1]; Ugur Ceylan[1]; [1]Istanbul Technical University

Glass ceramics containing microcrystalline phases of mica and fluorapatite can be considered as new materials for bone implants and substitutes in human body. Such a glass-ceramic has a better machinability due to the large amount of layered mica phase which is oriented randomly and distributed uniformly in glass matrix. For a material to be machinable and bioactive, it should contain both mica and apatite crystals. Apatite containing glass ceramics are important due to the high bioactivity, close crystallographic and chemical similarity to human bone tissue. In the production of glass ceramics, nucleating agents (ZrO_2) can be used in order to induce bulk crystallization of the phases. The purpose of this study is to investigate the in-vitro bioactivity character of glass ceramics having 3:7 weight ratio of fluorapatite ($Ca_5(PO_4)_3F$) to potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) as a function of ZrO_2 addition, and compare the morphology of HCA layer formation depending on ZrO_2 addition.

10:30 AM Break

10:40 AM

Nanostructured Silica Enforced Hydroxyapatite: *Tzy-Jiun Luo*[1]; Ching-Chang Ko[2]; [1]North Carolina State University; [2]University of North Carolina

Silica materials synthesized via sol-gel solution have shown excellent biocompatibility towards biomoelcules, cell culture, and tissue engineering. A unique bioceramic based on nanostructured silica, when integrated with gelatin-induced hydroxyapatite (HAP-GEL) nanocrystals (Ko et al., 2006), exhibits enhanced mechanical properties. This new process allowed modification of forming and porosity of the material for potential tissue engineering applications. The nanostructure of silica produced from polycondensation of aminosilane was

found to be affected by HAP-GEL phases allowing chemical additives (e.g. glycerol) for enhanced stability of encapsulated enzyme. Efforts have been made to optimize the synthesis procedure to show short curing time, improved optical properties for bioassay characterization, and tailor-made surfaces for better cell adhesion.

11:00 AM

Microstructure and Bioactivity of Laser Induced Geometrically Textured and Porous Ca-P on Ti-6Al-4V: *Sameer Paital*[1]; Narendra Dahotre[1]; [1]University of Tennessee

In the present work the feasibility of synthesizing porous and geometrically textured calcium phosphate (Ca-P) coating on Ti-6Al-4V by a Continuous wave (CW) Nd:YAG system has been demonstrated. Phases developed due to various laser processing parameters are studied using XRD. TiO_2, Ti and α-TCP phases are obtained as the most predominant phases. Crystallite size for all the above three phases increased with increasing laser fluence. The bioactivity of the coatings was further demonstrated by the formation of an apatite like phase by immersing the sample for varying time periods in a simulated biofluid (SBF). Microstructure and morphological evolutions before and after immersion in a SBF were studied using scanning electron microscopy.

11:20 AM

Control of Microbial and Cell Adhesion to Biomaterials by Ion Beam Implantation: *Robert Zimmerman*[1]; Claudiu Muntele[1]; Daryush Ila[1]; [1]Alabama A&M University

Medical implants usually require seamless adaptation with adjacent living tissue. For example, temporary carbon trans cutaneous electrodes or drainage tubes interface with skin, or permanent replacements of artificial teeth and the femur head interface with bone of the jaw and femur, respectively. We have shown that ion beam induced roughening of specific surfaces of these implanted materials enhance the adhesion with adjacent living tissue, and that implantation of silver ions below the surface of otherwise biocompatible materials completely inhibits cell attachment, while leaving neighboring areas hospitable to cell attachment and adherence. This patterning permits precise control of the formation of tissue on implanted biomaterials. Similarly, we have shown that silver implantation at the surface of Ultra High Molecular Weight Polyethylene (UHWMPE) gives the material anti microbial properties, as well as increasing the wear resistance. Both are improvements to the UHWMPE liner for the acetabular cup replacement for the hip joint.

11:40 AM

The Effect of Mechanical Processing on the Bio-Corrosion and Fatigue Resistance of Mg Alloy AZ31: *Yuri Estrin*[1]; Hao Wang[2]; H. Fu[2]; Guangling Song[3]; Zuzana Zuberova[4]; [1]Monash University; [2]University of Southern Queensland; [3]University of Queensland; [4]Technical University of Clausthal

The effect of mechanical working by hot rolling and equal channel angular pressing (ECAP) on the fatigue resistance and corrosion kinetics in Hank's solution of Mg alloy AZ31 was studied. This alloy is considered as a possible candidate material for biodegradable implant surgery (possibly for resorbable stents and bone implants), and its suitability depends critically on both the fatigue behaviour and the bio-corrosion resistance. It was shown that grain refinement of the as cast structure by hot rolling leads to a very significant improvement of fatigue properties and a sizeable decrease of the corrosion rate in Hank's solution. However, additional grain refinement by a further processing step (ECAP) did not enhance the fatigue endurance limit and caused a slight increase of the corrosion rate. The study has demonstrated the possibility of improving (and possibly controlling) corrosion and fatigue behaviour of alloy AZ31 using relatively simple mechanical processing routes.

12:00 PM

Corrosion Resistance of Ti_6Al_4V in Fluoride Solutions: *Carlos Elias*[1]; Fabio Souza[2]; Tânia Nogueira[2]; [1]Instituto Militar de Engenharia; [2]Universidade Federal Fluminense

The purpose of this work is to evaluate the electrochemical behavior of Ti_6Al_4V alloy in fluoride solutions after surface treatments with acid and mechanical polishing. The study was carried out by anodic voltammetry in 1% NaCl solutions with 0.1% to 1.6% NaF contents at a pH of 2.0 and 6.50. The samples were observed by SEM before and after the voltammetric assays. The samples submitted to acid etching tested in pH 2.0 solution showed the appearance of pit corrosion at high potentials. The samples submitted to polishing remained passivated. In the case of pH 6.50 solution, a passivation process with the appearance of crystals on the surface of both samples was observed. These results showed that the acid etching treatment, despite leading to better titanium osseointegration, needs careful attention in relation to corrosion. It was observed that the corrosion was more pronounced with increasing fluoride concentration.

Bulk Metallic Glasses V: Processing and Properties

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Peter K. Liaw, University of Tennessee; Wenhui Jiang, University of Tennessee; Guojiang Fan, University of Tennessee; Hahn Choo, University of Tennessee; Yanfei Gao, University of Tennessee

Thursday AM
March 13, 2008
Room: 393
Location: Ernest Morial Convention Center

Session Chairs: Yanfei Gao, University of Tennessee; Marios Demetriou, California Institute of Technology

8:30 AM Invited

Processing of Bulk Metallic Glass: *Jan Schroers*[1]; [1]Yale University

The sluggish crystallization kinetic of bulk metallic glass results in two fundamentally different processing opportunities. BMG can be directly cast. But even for the low critical cooling rates measured for BMGs geometries with high aspect ratio are particularly challenging since during casting cooling and filling of the entire mold cavity are coupled and thereby occur simultaneously. This limits the complexity of the geometries that can be cast even when processing parameters are carefully balanced. Alternatively, BMG can be thermoplastically formed in the supercooled liquid region. In this case the required fast cooling and forming are decoupled. The BMG is formed in a high viscous state where it behaves very similar to plastics when compared by processing temperature and forming pressure. A measure for the formability of BMGs will be introduced. Processing potentials and challenges will be discussed and various examples will be given including blow-molding, microfabrication, and nano-patterning.

8:50 AM Invited

Oxidation Behavior of a $Pd_{43}Cu_{27}Ni_{10}Pb_{20}$ Bulk Metallic Glass in Dry Air: *Wu Kai*[1]; I. Ren[1]; Bryan Barnard[2]; Peter Liaw[2]; Marios Demetriou[3]; William Johnson[3]; [1]National Taiwan Ocean University; [2]University of Tennessee; [3]California Institute of Technology

The oxidation behavior of a $Pd_{43}Cu_{27}Ni_{10}Pb_{20}$ bulk metallic glass (Pd4-BMG) was investigated over the temperature range of 70 to 325°C in dry air. The results showed that virtually no oxidation occurred in Pd4-BMG at T < 250°C, revealing the alloy's favorable oxidation resistance in this temperature range. A very thin film formed on Pd4-BMG at higher temperatures. This film consisted of copper, and its compositions depended strongly on temperature. In addition, the amorphous structure remained unchanged below the glass-transition temperature (T_g), while a duplex structure developed after oxidation at higher temperatures. The duplex structure consisted of Pd-Cu-Ni and Pd-P phases.

9:10 AM

Microstuctural and Mechanical Characterization of a Laser Processed Zr-Based Bulk Metallic Glass: *Hongqing Sun*[1]; Katharine Flores[1]; [1]Ohio State University

Laser processing is a novel manufacturing technology which offers the possibility of creating or repairing metallic coatings and components with highly non-equilibrium microstructures. Due to the localized heat input and high cooling rate inherent to the process, this technology has great potential to be applied in the production of metallic glasses. In the present work, we use the Laser Engineered Net Shaping (LENS™) process to deposit Zr-based glass forming powder on amorphous and crystalline substrates of the same nominal composition. Amorphous melt zones surrounded by distinct crystalline heat-affected zones (HAZs) are observed in single- and multi-layer deposits. The microstructural evolution of the deposits and underlying substrate depend strongly on the total heat input per pass. SEM, TEM, XRD, and DSC analyses are

performed to identify and characterize the observed amorphous and crystalline phases. In light of their unique composite microstructures, the mechanical behavior of laser deposited coatings is also investigated.

9:25 AM Invited
Thermodynamic, Structural and Mechanical Properties of Zr 63-x Alx Cu24 Ni10 Co3 Bulk Metallic Glass Forming Alloys: Rainer Wunderlich[1]; Arnaud Caron[1]; *Hans-Jörg Fecht*[1]; [1]Ulm University

The correlation between thermodynamic, structural and mechanical properties is of strong current interest in bulk metallic glass research in the quest of improving the ductility of metallic glasses. As a model system, the Zr-Al-(CuNiCo) equivalent three component phase diagram has been investigated along the (CuNiCo)=37at% isoconcentration line with the Al-concentration varied from 7 to 20 at%. As a function of Al-concentration, a decrease in the average atomic distance was found which correlates with an increase of the glass transition temperature. An increase in the bulk modulus was observed while the Poisson ratio exhibited a pronounced and unexpected maximum at some intermediate composition. This trend is also reflected in an increase of the cavitation-erosion resistance as a function of Al-concentration. These findings are in contrast to the generally accepted linear rule of mixing, showing that chemical and topological short range order considerably influence the macroscopic mechanical properties of BMGs.

9:45 AM Invited
Thermoplastic Forming Properties and Microreplication Ability of an Mg-Base Bulk Metallic Glass: *Shian-Ching Jang*[1]; C. C. Tseng[1]; Y. C. Yeh[2]; J. L. Jou[2]; Jacob Huang[3]; [1]I-Shou University; [2]Metal Industries Research and Development Centre; [3]National Sun Yat Sen University

The thermoplastic forming properties of Mg58Cu531Nd5Y6 bulk metallic glass (BMG)was evaluated via compressive test at different temperature with various stain rates. Then the process window of thermoplastically forming of the Mg-base BMG is developed according to this data obtained from those compressive tests. The result reveals that the Mg-base BMG possess an excellent superplastic formability with the m-value being nearly 1.0 in the supercooled liquid region under a strain rate around 0.001 ~ 0.01 s-1. In parallel, a relatively low flow stress (less than 10 MPa) within the supercooled liquid region can be obtained with a strain rate of 0.001 s-1. Additionally, the result of replication of a hologram pattern with 10 micro meter depth also shows extremely good microforming ability of this Mg-base BMG in the supercooled liquid region with suitable working condition.

10:05 AM
Tribology Studies of the Zr-Based Bulk Metallic Glasses with Different States: *Feng Jiang*[1]; Jun Qu[2]; Guojiang Fan[1]; Wenhui Jiang[1]; Peter J. Blau[2]; Peter Liaw[1]; Hahn Choo[1]; [1]University of Tennessee; [2]Oak Ridge National Laboratory

The tribological behaviors of a bulk-metallic glass (BMG) Zr52.5Cu17.9Ni14 .6Al10.0Ti5.0 (Vit 105) with different states have been studied. The wear volume order is as followings: the deformed Vit 105, the creep Vit 105, the annealed Vit 105, and the as-cast Vit 105. The results show that despite the hardness, there are other mechanisms, such as the friction heating and embrittlement of the materials which will affect the wear resistance. This work was supported by the National Science Foundation (NSF) International Materials Institutes (IMI) Program (DMR-0231320). Portion of this research was sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Freedom CAR and Vehicle Technologies, as a part of the High Temperature Materials Laboratory User Program, under contract DE-AC05-00OR22725 with UT-Battelle LLC.

10:20 AM Invited
Effects of Processing Conditions on Plastic Deformation of Bulk Metallic Glasses: *Z. P. Lu*[1]; H. Bei[2]; [1]University of Science and Technology Beijing; [2]Oak Ridge National Laboratory

It was recently reported that the misalignment has a great influence on the plastic displacement of bulk metallic glasses under compression. Based on our experimental data, however, the compressive displacement data are quite scattered even for the same bulk metallic glass with reasonable alignment and the same testing conditions including the strain rate and sample diameter. In this talk, we will focus on effects of processing conditions such as purities on the plastic deformation of bulk metallic glasses. Using the recently reported super plastic Zr-based bulk metallic glass and other relatively brittle Zr-based glassy alloys as model systems, we attempt to explore the underlying mechanisms that dictate the localized plastic deformation for the samples with various preparation circumstances and thus understand the fundamental variables that control the mechanical behavior of the bulk metallic glasses investigated.

10:40 AM Break

10:45 AM
Sliding Wear Resistance of the Ni-Based Metallic Glass: *Nozomu Togashi*[1]; Yasunori Saotome[2]; Mamoru Ishida[3]; Hideki Takeda[3]; Yukiharu Shimizu[4]; Nobuyuki Nishiyama[1]; Akihisa Inoue[2]; [1]RIMCOF Tohoku University Laboratory; [2]Tohoku University, Institute for Materials Research; [3]YKK Corporation; [4]Namiki Precision Jewel Corporation

We have reported that wear resistance of the metallic glass (MG) bearing is more excellent than that of the sintered Fe-Cu alloy bearing under lubrication. But then, the worn loss of the MGs is larger than that of the conventional steel in the sliding wear tests under no lubrication.[1] So wear resistance of the MGs changes greatly depending on a lubrication condition. In order to clarify the relation between wear behavior and lubrication, we conducted the pin-on-disk wear tests under lubrication for Ni-based MG. It was found that the wear rate of the MGs under lubrication decreased as the load increases. It was therefore assumed that the friction of MGs made slippy with the oil slick, leading to reduction of the adhesion wear. [1]M. Ishida, H. Takeda, N. Nishiyama, K. Kita, Y. Shimizu, Y. Saotome and A. Inoue, Mater. Sci. and Eng. A, 449 (2007) 149.

11:00 AM
Solid State Joining of a Zr-Based Bulk Metallic Glass: *Nicholas Hutchinson*[1]; Yuan Zhang[1]; Justin Bennet[1]; Glenn Daehn[1]; Katharine Flores[1]; [1]Ohio State University

Bulk metallic glasses have excellent mechanical properties, including exceptionally high strength, high toughness, and low damping, which make them well suited for structural applications. A significant barrier to expanding the use of metallic glasses is a lack of well characterized manufacturing processes, particularly joining techniques to create large scale or complex shaped components. The present work focuses on the characterization and optimization of three solid state welding techniques which rely on mechanical work and plastic deformation at mating interfaces to create joints. Specimens were joined by the friction stir process, a high velocity electromagnetic welding process, and an electro-thermo-mechanical process. The effectiveness of each joining technique and changes in microstructure at the joint are characterized as functions of appropriate operating parameters, applied stress and strain rates and material surface preparation. The results of these experiments will be discussed.

11:15 AM
Solid State Synthesis of Bulk Composites of Amorphous and Nano-Crystalline Structures in Ni-Ti Alloys: *Niven Mosengue*[1]; Kai Zhang[1]; Alex Aning[1]; [1]Virginia Polytechnic Institute and State University

Equimolar powder mixtures of nickel and titanium are cryomilled in a modified attritor mill filled with liquid nitrogen to create lamella structures with 20 to 100 nm spacing in the powder particles. The milled powders are consolidated in a hot isostatic press at temperatures between 300 and 350°C. During the HIPing process, the synthesis of the amorphous structure and the consolidation of the powders take place at the same time. The resulting compacts are composites of amorphous and crystalline nano-structures of the Ni-Ti alloy. Results from TEM, and the dependence of hardness on the microstructure of the composites will be presented and discussed.

11:30 AM
A Continuous Casting Process by Using Electromagnetic Vibrations for Fe-Based Bulk Metallic Glasses: *Takuya Tamura*[1]; Daisuke Kamikihara[1]; Naoki Omura[1]; Mingjun Li[1]; Kenji Miwa[1]; [1]National Institute of Advanced Industrial Science and Technology

It is known that cooling rate from the liquid state is an important factor for producing the bulk metallic glasses. However, almost no other factors such as electric and/or magnetic fields were investigated. The present authors reported that a new method for producing Mg-Cu-Y bulk metallic glasses by

using electromagnetic vibrations is effective in forming the metallic glass phase. Moreover, the present authors have reported that the glass-forming ability of Fe-Co-B-Si-Nb alloys also enhances with increasing the electromagnetic vibration force. Thus, we try to develop a continuous casting process by using the electromagnetic vibrations for Fe-based bulk metallic glasses.

11:45 AM

Effects of Vibration on Micro Forming of an Al Superplastic Alloy and a Zr-Based Bulk Metallic Glass: *Young-Sang Na*[1]; Seon-Cheon Son[2]; Kyu-Yeol Park[2]; Jong-Hoon Lee[1]; [1]Korea Institute of Materials Science, Korea Institute of Machinery and Materials; [2]University of Ulsan

Vibrational micro forming of pyramidal shape patterns was conducted for an Al superplastic alloy, Al5083 and a Zr-based bulk metallic glass, Zr62Cu17Ni13Al8. A PZT actuator combined with a signal generator was adopted for generating vibrational load in a specially-designed vibrational micro forming system. Si micro dies with wet-etched pyramidal patterns were used as master dies for vibrational micro forming. The height of the micro formed pyramids for Al 5083 alloy was increased as the vibrational frequency increased from 1 Hz up to 100 Hz. This was the similar case for Zr62Cu17Ni13Al8 bulk metallic glass. In addition, the micro-formed pattern quality was improved by applying vibrational load and by increasing the vibration frequency in terms of surface defects and in terms of pattern asymmetry, as well.

12:00 PM

Laser Pulse Induced Shock Processing of Zr-Based Bulk Metallic Glass: *Sameer Paital*[1]; Gong Wang[1]; Peter Liaw[1]; Narendra Dahotre[1]; [1]University of Tennessee

In the present work attempts are made to introduce residual stresses at the surface of Zirconia-based bulk metallic glass (BMG) using a pulsed Nd:YAG laser. Shock processing was carried out in the direct laser impact mode. It is observed that there is an improvement in plasticity due to the residual stresses generated from the shock waves and rise in temperature. This combined effect has resulted in a composite phase microstructure at the near surface region of the bulk metallic glass and resulted in improved plasticity at this region. This improvement in plasticity may be attributed to the retardation in initiation and propogation of the shear bands. The detailed microstructural, stress and strength analyses of laser surface modified Zr-based samples under various laser processing conditions are ongoing and will be discussed during presentation.

12:15 PM

Air-Oxidation of a Cu45Zr45Al5Ag5 Bulk Metallic Glass: *Wu Kai*[1]; I.-F. Ren[1]; C.-P. Chuang[2]; M. Freels[2]; Peter Liaw[2]; [1]National Taiwan Ocean University; [2]University of Tennessee

The oxidation behavior of a Cu45Zr45Al5Ag5 bulk metallic glass (CZA4-BMG) was studied over the temperature range of 375-500°C in dry air. The role of Ag addition on the oxidation kinetics was investigated, and the results were compared to those of the ternary Cu47.5Zr47.5Al5 BMG (CZA3-BMG). In general, the oxidation kinetics of CZA4-BMG followed a multi-stage parabolic rate law, and the oxidation-rate constants at the steady-state stage were slightly lower than those of CZA3-BMG, indicating that the addition of Ag provided a better oxidation resistance for CZA4-BMG. The scales formed on CZA4-BMG consisted mostly of ZrO2, copper oxides, dissolved with Ag, and a minor amount of Al2O3. The exact composition and constitution of the scales strongly depended on the temperature. In addition, the amorphous structure retained unchanged at the temperature below the glass-transition temperature (Tg), while a triple-phase structure was developed after oxidation at higher temperatures, being also temperature-dependent.

Cast Shop Technology: Modelling

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Hussain AlAli, GM Casthouse and Engineering Services, Aluminium Bahrain Company (ALBA); David DeYoung, Alcoa Inc

Thursday AM — Room: 295
March 13, 2008 — Location: Ernest Morial Convention Center

Session Chair: Bjorn Henriksen, Elkem Aluminium ASA Research

8:30 AM Keynote

Mushy Zone Mechanics and the Modeling Solidification Defects in DC Cast Aluminum: *Mohammed M'Hamdi*[1]; [1]SINTEF

Many casting defects occur while the material is in the mushy state. An accurate description of mushy zone phenomena is, therefore, essential for the development of mathematical models and simulation tools for defect prediction, and an important step towards the virtual casthouse. In particular the mechanical behavior of the mushy zone can have a significant impact on several of these defects. The paper focus on the aluminum direct chill casting process, and discusses recent development on the modeling of the mushy zone mechanical behavior and its impact on the modeling of solidification defects such microporosity, hot tearing, surface exudation and bulk macrosegregation.

9:00 AM

Coupled Modeling of Air-Gap Formation and Surface Exudation during Ingot DC-Casting: *Dag Mortensen*[1]; Bjorn Henriksen[2]; Mohammed M'Hamdi[3]; Hallvard Fjær[1]; [1]Institute for Energy Technology; [2]Elkem Aluminium ANS; [3]SINTEF

During casting of aluminium extrusion ingots the surface against the mould experiences a pull-in force that magnifies the air-gap during solidification close to the mould surface. This is a global phenomenon that results in early and large air-gap formations compared to the shape-casting situation. Due to the semi-solid surface created under such conditions, exudation through the surface may appear. In this study a coupled heat and fluid flow, stresses and deformation modelling tool are applied on the process. Results from the mechanical calculation are back-coupled to the thermal boundary conditions. The metallostatic head is the driving force for exudation through the dendritic network and the resulting fluid flow through this network is used to calculate a dynamic thickness of the exuded layer. Measurements from two different alloys, with rather small changes in composition, but with large variations on surface quality, are compared with the modelling results.

9:20 AM

DC Cast Thermal and Fluid Flow Simulation Using a Semi-Permeable Model of TF Combo Bag: Sylvain Tremblay[1]; *Daniel Larouche*[2]; Andre Arseneault[2]; Jean-Philippe Dube[3]; [1]Pyrotek Inc.; [2]Laval University; [3]A.B.I. Aluminerie de Bécancour Incorporated

In the process of aluminum ingot casting, the heat transfer is a key issue in the final quality of the ingot. Hot liquid metal reaches the ingot through the liquid metal distribution system. The distribution action in the pool is mainly acheived by the combo bag as a part of the distribution system. In the present article, we propose a model allowing the coupling between combo bag thermal fluid flow circulations with those into the pool without over-constraints on the physical conservation equations (mass, momentum and energy). The need of such a model is essential to define the complete heat transfer analysis of ingot casting process if pre-imposed solutions are not fed into the mathematical equations. More specifically, it will allow evaluating the impact of combo bag parameter on the thermal flow circulation in metal pool.

9:40 AM
Cyclone Application for Molten Aluminium: Numerical Approach: *Andrey Turchin*[1]; Dmitry Eskin[1]; John Courtenay[2]; Laurens Katgerman[3]; [1]Netherlands Institute for Metals Research; [2]Melt Quality Partnership Ltd.; [3]Technical University Delft

In this paper a numerical simulation technique has been used to evaluate the possibilities of cyclone application in molten aluminium processing by determining the fluid flow for flow velocities of 0.01 m/s, 0.1 m/s and 1 m/s; particle behavior for discrete particle sizes in the range of 20–100 μm; and the collection efficiency of the cyclone. The geometrical aspects have been discussed. The results show that the cyclone concept can be effectively used as an alternative method to remove the impurities from a stream of molten aluminium in a wide range of flow regimes. A pilot installation is being built for validation of the used model in terms of collection efficiency; and for casting trials (see a separate presentation by J. H. Courtenay et al.).

10:00 AM
Heat Transfer during Melt Spinning of Al-7%Si Alloy on a Cu-Be Wheel: *Aravind Sundararajan*[1]; Brian Thomas[1]; [1]University of Illinois

A one-dimensional transient finite-difference heat-transfer model (STRIP1D) has been developed to simulate the Planar Flow Melt-Spinning (strip casting) of Al-7% Si on a Cu-Be wheel. The model includes the effects of two-dimensional fluid flow in the liquid pool on heat transfer and solidification in the strip, coupled with transient conduction in the rotating wheel. The strip-wheel interface is characterized with a time-dependent heat transfer coefficient. The complete model has been validated with experimental data from a pilot caster at Cornell University, and reasonably matches the measured strip thickness, wheel thermocouple temperature, strip surface temperature and secondary dendrite arm spacings. The model provides fundamental insights into the effect of process conditions like wheel speed, gap height, puddle length, and superheat on solidification. Interfacial imperfections observed in the strip are predicted to occur owing to gas bubbles formed at the wheel-strip interface, and have been validated using two-dimensional computations with ABAQUS.

10:20 AM Break

10:30 AM
Inclusion Transport Phenomena in Casting Furnaces: *Stephen Instone*[1]; Andreas Buchholz[1]; Gerd-Ulrich Gruen[1]; [1]Hydro Aluminium Deutschland GmbH

The presence of non-metallic inclusions in Aluminium is one of the most important factors determining its processability and the quality of finished products. The concentration of such inclusions in the liquid metal has been observed to vary greatly. To better understand the contribution of furnace processes to melt quality, a mathematical model of casting furnace processes has been developed at Hydro Aluminium's Research and Development Centre in Bonn, Germany. The model is capable of simulating the most important fluid flow and particle (inclusion) transport phenomena occurring in the furnace during both settling and casting operations. Output from the model is compared with results from industry standard inclusion measurement techniques (LiMCA and PodFA) for different furnace geometries. The results show that the model is a powerful tool and can be used to improve understanding of these processes and help in explaining observations in the cast house.

10:50 AM
Gas Fluxing of Aluminum: Modeling Fluid Dynamics and Magnesium Removal: *Autumn Fjeld*[1]; James Evans[2]; D. Chesonis[3]; [1]University of Leoben; [2]University of California, Berkeley; [3]Alcoa Technical Center

A demagging reaction model was developed which combines the efforts of a multi-part investigation on the gas fluxing of aluminum. Bubble size distribution and residence times taken from a computational fluid dynamics model are incorporated into an external demagging reaction model, which predicts chlorine utilization efficiency. This model includes assumptions regarding the kinetics and reaction path, however the model shows reasonable agreement to prior experimental magnesium removal data and provides insight into the interplay of reaction progress in a fluxing unit and the fluid dynamics in terms of bubble size, trajectory, and resulting bubble residence time. Better understanding of these factors can lead to more sophisticated process control systems and more efficient gas delivery in a gas fluxing unit.

11:10 AM
Analysis of the Interaction of Particles with Non-Planar Solidifying Interfaces: Eliana Agaliotis[1]; Mario Rosenberger[1]; Alicia Ares[1]; *Carlos Schvezov*[1]; [1]CONICET/University De Misiones

The results of model calculations for the interaction of particles with non-planar interfaces during solidification are presented. The model is based on finite element methods for the calculation of the shape of the solidifying interface which is modified by the presence of a solid particle, and for the drag forces resulting on the particle for the geometrical configuration of the system particle-melt-solid. The drag force on the particle is calculated for different conditions of steady pushing by the solid. The results are compared with the corresponding drag force for a planar interface and a particle at the same separation. Thermal conditions resulting in concave and convex interface shapes are considered. The results show that a concave interface generate higher drag forces than a planar interface and the opposite for a concave shape. The magnitude of the force could differ in as much as one order of magnitude.

11:30 AM Panel Discussion

Characterization of Minerals, Metals, and Materials: Characterization of Microstructure and Properties of Materials V

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Materials Characterization Committee
Program Organizers: Jian Li, Natural Resources Canada; Toru Okabe, University of Tokyo; Ann Hagni, Intellection Corporation

Thursday AM — Room: 284
March 13, 2008 — Location: Ernest Morial Convention Center

Session Chairs: Ann Hagni, Intellection Corporation; Mingdong Cai, University of Houston

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8:30 AM
Mechanisms of Texture Evolution in Annealed Wire-Drawn OFHC Copper: *Daudi Waryoba*[1]; Peter Kalu[2]; [1]Florida State University, National High Magnetic Field Laboratory; [2]Florida A&M University

Despite the large volume of research work on texture transformation from strong<111>+weak<100> wire texture into strong<100>+weak<111> on recrystallization or to <111> on secondary recrystallization, there has been limited report on the mechanisms governing this transformation. This study was therefore carried out to present a comprehensive analysis of the mechanisms governing texture transition in wire drawn materials. The investigation was performed on OFHC copper wire drawn to a true strain of 3.56, and annealed at 750°C for durations ranging from 20s to 1 hr. The results show that at the early stage of recrystallization, strain induced grain boundary migration (SIGBM) occurs. This enhances the density of <100> grains which dominate the recrystallization texture due to their higher stored strain energy difference. For prolonged annealing time, continuous recrystallization of the <111> grains coupled with their high grain boundary mobility provide growth advantage of this orientation, leading to a <111> growth texture.

8:50 AM
Rupture Mechanisms in Composites Reinforced with Curaua Fiber: *Sergio Monteiro*[1]; Ailton Ferreira[1]; Felipe Perisse Lopes[1]; [1]State University of the Northern Rio de Janeiro - UENF

A high strength lignocellulosic fiber can be extracted from leaves of the curaua plant to reinforce polymeric composites. Each curaua fiber is composed of naturally bonded aligned filaments that may be separated under applied load and contribute to the composite fracture. This work investigates the rupture mechanism associated with the flexural fracture of polyester composites reinforced with curaua fibers. Plates with up to 50 vol.% of continuous curaua fibers embedded in orthophtalic polyester resin were press-molded at room temperature and cured for 24 hours. Composite specimens cut from the plate were bend tested and had their fracture analyzed by SEM. It was found that the composite rupture is associated with a complex mechanism of individual

interaction of the filaments, which compose each fiber, with the matrix during crack initiation and further propagation. A model of stress concentration due to the specific fiber/matrix interface geometry explains the experimental fracture strength results.

9:10 AM
Local Electrode Atom Probe (LEAP) Analysis of Rhenium Segregation and Secondary Precipitates in Single Crystal, Nickel Base Superalloy PWA 1484: *Brandon Wilson*[1]; Anantha Puthucode[2]; Gerhard Fuchs[1]; Michael Kaufman[2]; [1]University of Florida; [2]University of North Texas

A second generation single crystal nickel base superalloy, PWA 1484, was studied with a Local Electrode Atom Probe (LEAP) to observe Re segregation near gamma/gamma' interfaces as a function of heat treatment. Additionally, the secondary gamma' precipitates that form in the gamma matrix channels were observed as they also strongly influence creep behavior, most notably in the primary creep regime. Two different aging heat treatments were used in order to produce varied amounts of secondary gamma' particles in the alloy. Following aging, samples were also given a brief (30 min) solution heat treatment and rapid quench in an attempt to resolution the gamma' precipitates. This was done to observe any shell or cluster formation along the prior gamma/gamma' interface. Three dimensional composition data as produced by the LEAP allowed for examination of these features as a function of aging heat treatment and subsequent resolution heat treatment.

9:30 AM
Thermal Shock Behaviour and Mechanical Properties of Refractory Materials: *Bouressace Zina*[1]; Meddour Athman[1]; [1]Université de Guelma

Our refractory material was elaborated from grog. It was used as aggregates. Kaolin was also introduced as a binder. An X-ray diffraction (XRD) analysis showed that the prepared basic refractory samples (without addition) are composed obviously, of Mullite and silica in its various forms. In addition, the presence of the Indialite phase was detected for the reinforced talc samples. This phase is characterized by some advantageous properties affecting the thermomechanical properties final material. The porosity of the samples takes diversified values. It differs from one batch to another. Therefore, the mechanical tests and thermal carried out revealed different behaviours of the refractory material according to prepared compositions. The amorphous phase governs considerably the sample thermomechanical properties variation with temperature increasing. This study shows that the thermal shock tests realized proved that our refractory elaborated, by addition of talc particles, takes the good thermal shock resistance.

9:50 AM Break

10:10 AM
Characterization of the Impact Resistance of Coir Fiber Reinforced Polyester Composites: *Sergio Monteiro*[1]; Lucas da Costa[1]; Felipe Lopes[1]; Luiz Augusto Terrones[1]; [1]State University of the Northern Rio de Janeiro - UENF

Polymeric composites reinforced with natural lignocelllulosic fibers are being considered for applications in which low cost and malleability are desirable conditions. In particular, the fibers extracted from the coconut fruit, known as coir fiber, are nowadays used as composite reinforcement in automobile components such as panels and cushions. This investigation focused on the characterization of the impact resistance of coir fiber reinforced composites with polyester matrix. Both Charpy and Izod impact specimens made of polyester composites with up to 40wt.% of coir fibers wee tested in an instrumented hammer pendulum. The results showed that the introduction of coir fibers significantly improves the impact resistance due to the energy transferred to a large number of cracks developed at the fiber/matrix interface.

10:30 AM
Characterisation of Silicon Nitride Thin Films Used as Stressor Liners on CMOS FETS: Measurement of Young's Modulus and Hardness: *Gaetan Raymond*[1]; Pierre Morin[2]; Muriel Braccini[1]; Fabien Volpi[1]; [1]Simap; [2]ST Microelectronics

This paper presents a study of the physical, chemical, and in particular mechanical properties of nitride films used for this application. Its aim is to determine the most important material characteristics and establish the best correlations between these properties. CESL nitride films are deposited by Plasma Enhanced Chemical Vapour Deposition. Thanks to process tuning, film stress ranging from -3 to 1.6 GPa can be achieved. Typical thicknesses used in CMOS technologies are ranging from 30 to 80 nm. For the purpose of the material characterisation, layers up to 300 nm have been deposited on 300 mm silicon substrates. These characterisations and results will help the optimisation of the nitride film used for stressor applications in current and future CMOS technological nodes.

10:50 AM
Challenges in Materials Processing: Role of Heterogeneity in Chemistry and Structure: *Sudha Cheruvathur*[1]; Vijayalakshmi Muraleedharan[1]; [1]Indira Gandhi Centre for Atomic Research

Challenges in the processing of materials arising due to restructuring of microchemistry and microstructure during service life, are illustrated with the following examples: (1)Prediction and experimental confirmation of formation and prevention of hard brittle zone in dissimilar joints of ferritic steels. (2)Optimizing the formation of dilution layer in Colmonoy weld overlay on AISI 304 (L) stainless steel. (3)Prediction and confirmation of alternate structural material for electrodes of elementary neutral particle detectors. (4)"Self wastage" of 9Cr-1Mo steel in Sodium water reaction testing facility In all the above examples, it is demonstrated that detailed computations along with selected confirmatory experiments are essential to recommend appropriate process parameters and also to ensure satisfactory performance of materials.

Computational Thermodynamics and Kinetics: Diffusion and Phase Stability

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Materials Processing and Manufacturing Division, ASM Materials Science Critical Technology Sector, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Computational Materials Science and Engineering Committee, TMS/ASM: Phase Transformations Committee
Program Organizers: Yunzhi Wang, Ohio State University; Long-Qing Chen, Pennsylvania State University; Jeffrey Hoyt, McMaster University; Yu Wang, Virginia Tech

Thursday AM — Room: 288
March 13, 2008 — Location: Ernest Morial Convention Center

Session Chairs: John Morral, Ohio State University; Sujoy Kar, GE Global Research

8:30 AM Invited
The Formation of Single Phase Layers at the Interface of Diffusion Bonded Multiphase Alloys: *John Morral*[1]; Ximiao Pan[1]; Yunzhi Wang[1]; [1]Ohio State University

When multiphase alloys are diffusion bonded there are a number of mechanisms by which a single phase layer can form at the initial interface. Often the formation is predictable by consulting a phase diagram. However in two cases, the phase diagram alone may suggest that the interface will be free of a single phase layer. One is when bonding two phase alloys that only differ in their average composition. Another is when bonding two phase alloys that differ in both their phases and their average composition. In the former case the layer may form if the diffusion path contains a singularity, while in the latter case they will form if the diffusion path passes through a special point on the phase diagram. Both experimental and computer simulation examples of the two cases will be given using diffusion couples made from model systems and Ni-Cr-Al alloys.

8:55 AM
Diffusion Kinetics at Ultra-High Stresses: *Amit Samanta*[1]; Ju Li[1]; Ting Zhu[2]; [1]Ohio State University; [2]Georgia Institute of Technology

We assess point-defect diffusion kinetics in the ultra-strength regime, when materials sustain stresses at significant fractions of their ideal strengths. Since atomic bonds are already weakened, one expects reduced diffusion barrier that could lead to earlier onset of massive processes such as creep. As an example, the formation energy and migration energy barrier of vacancy in Cu are systematically evaluated in bulk, along grain boundaries and inside dislocation

cores, and compared to zero-stress values. Surface diffusion is also modeled at the limit of large surface stresses.

9:10 AM

Multicomponent Diffusion in Single-Phase Multilayered Assemblies: *Kaustubh Kulkarni*[1]; Mysore Dayananda[1]; L. Ram-Mohan[2]; [1]Purdue University; [2]Worcestor Polytechnic Institute

A transfer matrix method is employed to examine concentration profiles developed in multicomponent 'multilayer diffusion assemblies' (MDAs) consisting of a number of finite layers sandwiched between two infinite terminal alloys. Analytical expressions for the temporal and spatial evolution of the concentration profiles are developed for single-phase multilayered assemblies characterized by a set of constant interdiffusion coefficients. The evolution of concentration profiles is explored for test MDAs assembled with ternary, single phase layers characterized by an arbitrary set of interdiffusion coefficients. The results indicate that the diffusion path of an MDA varies with time appreciably and approaches at long times asymptotically that for a solid-solid infinite diffusion couple between the two terminal alloys. Experimental MDAs were also assembled with α(fcc) Cu-Ni-Zn alloys with a thin alloy layer sandwiched between two thick terminal alloys and annealed at 775°C for various times. The results of these studies are also presented and discussed.

9:25 AM

Calculation of Impurity Diffusivities in Ferrite from First-Principles: *Daniel Worthington*[1]; Shenyan Huang[2]; Chris Retford[1]; Gautam Ghosh[3]; Morris Fine[3]; Peter K. Liaw[2]; Mark Asta[1]; [1]University of California, Davis; [2]University of Tennessee; [3]Northwestern University

First-principles calculations of impurity diffusion constants in body-centered-cubic (bcc) Fe have been undertaken in support of an effort aimed at the computationally-assisted design of a creep-resistant precipitate-strengthened ferritic "superalloy." To augment existing kinetic databases, which lack experimental measurements for a number of 4d and 5d solutes, diffusivities have been derived by incorporating first-principles calculated jump-rate probabilities into a generalized five-frequency model of vacancy-mediated diffusion in the dilute limit. We carried out both kinetic Monte Carlo and transition-matrix methods to compute correlation factors incorporating calculated vacancy-solute binding energies, which were found to extend beyond second neighbor. First-principles calculations were also conducted to determine the induced magnetization of the host atoms in the first and second coordination shells of the impurity, to compute the magnetization dependence of the diffusion activation energy, employing a previously published empirical relation between these quantities.

9:40 AM

Multibody Expansions: An Ab Initio Based Transferable Potential for Computational Thermodynamics: *Baskar Ganapathysubramanian*[1]; Nicholas Zabaras[1]; [1]Cornell University

Ab initio based techniques provide by far the most comprehensive and accurate details for computational thermodynamic and structure evolution studies. The computational complexity of these methods precludes the application of such first-principal analysis to configurations beyond a few hundred atoms. But in many cases, long-ranged and many-body interactions are necessary to model the energy accurately. We utilize a multibody based representation of the potential energy landscape to accurately represent these interactions in a computationally efficient manner. The many-body expansion is constructed via accurate sparse grid interpolation over a large database of ab-initio cluster energies. This framework results in the construction of transferable potentials that can be seamlessly integrated into various MD and MC platforms. We will illustrate the accuracy, efficiency and transferability of the proposed potential expansion using several computational thermodynamics based applications including the computation of stable structures of binary alloys.

9:55 AM

Anharmonic Phonons in A15 V3X Compounds: *Oliver Delaire*[1]; Jorge Munoz[1]; Matthew Lucas[1]; Max Kresch[1]; Rebecca Stevens[1]; Brent Fultz[1]; [1]California Institute of Technology

Using inelastic neutron scattering, we investigated the temperature-dependence of the phonon density of states (DOS) in the A15 compounds V3Si, V3Ge and V3Co. Phonons in V3Si exhibit an anomalous stiffening up to temperatures T>500C, while V3Co and V3Ge exhibit the more common softening, expected from thermal expansion. We also measured the heat capacity of the compounds, which could be correlated to the trend observed in the phonons. To help interpret experimental results, we performed Density functional theory (DFT) calculations of these materials. The calculated phonon DOS was in good agreement with the low-T measurements. The electronic part of the heat capacity was also obtained from the DFT computations. V3Si and V3Ge are known to exhibit a fairly strong electron-phonon coupling, as evidenced by their rather high superconducting Tc (Tc=16K for V3Si). Anharmonic couplings arising from phonon-phonon or electron-phonon interactions are used to explain the departure from the quasiharmonic behavior.

10:10 AM Break

10:40 AM

Two-Phase Coexistence in Nanoscale Systems: Peter Bunzel[1]; Gerhard Wilde[2]; *Jörg Weissmüller*[3]; [1]Forschungszentrum Karlsruhe; [2]Westfälische Wilhelms-Universität Münster; [3]Forschungszentrum Karlsruhe and Universität des Saarlandes

We inspect the equilibrium conditions governing the coexistence of two alloy phases within a system of finite size, for instance, a matrix-embedded alloy nanoparticle. The magnitude of the excess energy associated with the internal interface may here be comparable to that of the relevant bulk energy terms, and it depends on the phase fraction in a nonlinear way. Consequently, the common tangent rule does not apply, and the topology of the alloy phase diagram is found to differ from that of macroscopic alloy systems. As an example, we discuss a eutectic alloy system. We find, that the eutectic point splits up into an interval of discontinuous phase change, and that the solidus temperature as well as the compositions of phases coexisting at equilibrium become functions of the overall composition. Calorimetric experiments on Cd-Bi alloy nanoparticles embedded in Al are well compatible with the predictions.

10:55 AM

A Statistical-Thermodynamic Modeling of Behavior and Properties in Thin-Film Intermetallic $L1_2$-Structures: *Olga Semenova*[1]; Regina Krachler[1]; [1]University of Vienna

A statistical-thermodynamic modeling based on an Ising approach and the Bethe-Bragg-Williams random-mixing approximations is proposed for description of thermodynamic behavior and ordering phenomena in many layers nano-crystalline thin-film materials with $L1_2$- structure. New modeling approach takes into account the presence of all possible defects in the structure, both vacancies and anti-structure atoms and includes a description of Long-Range Ordering and Short-Range Ordering in the crystal lattice. The derived equations define the fluctuations of the internal variables, such as interaction energies between atoms and defects and their contributions to macroscopic properties. As a validation of the suitability and high reliability of the chosen methodology, the obtained theoretical results are tested using experimental data on thermodynamic and structural properties of bulk intermetallic phases such as Ni_3Ga, and point defect concentrations, the degree of long-range order in the structure, as well as critical transition temperatures were predicted and compared to the experimental data.

11:10 AM

Ordering and Clustering Instabilities in FCC-Based Alloys: Importance of Second Nearest Neighbors: *Nitin Singh*[1]; David Laughlin[2]; William Soffa[1]; [1]University of Virginia; [2]Carnegie Mellon University

Various investigators have employed the generalized Bragg-Williams model including second-, third-, etc nearest neighbor interactions to describe the energetics and kinetics of the precipitation of ordered phases in FCC-based alloys such as Al-Li, Ni-Ti and Ni-Al. In these systems where the order-disorder transformation is thermodynamically first-order, a synergism between ordering, clustering and spinodal decomposition has been revealed giving rise to a so-called conditional spinodal, for example. In this analysis specific attention is called explicitly to the importance of second nearest neighbour interactions in the occurance of ordering and phase separation in FCC alloys involving the precipitation of an ordered $L1_2$ phase within a supersaturated FCC solid solution. The salient features of the generalized Bragg-Williams model applied to FCC alloys ($A1-L1_2$) will be elucidated and compared to the BCC case (A2-B2).

11:25 AM

Microscopic Phase-Field Simulation of the Ni_3Al Phase Separation Process: *Yanli Lu*[1]; [1]Northwestern Polytechnical University, School of Materials Science and Engineering

The separation process of Ni_3Al phase in Ni-Al alloy containing 12.5at.%Al was simulated at the atomic scale using the microscopic phase-field model and microelasticity theory. The simulation results show that Ni_3Al phases firstly are formed from the disordered solid solution by the mechanism of non-classical nucleation growth, resulting in the appearance of single ordered domain separated by the antiphase domain boundaries (APBs). With the ordered domains isostrcutural decomposing and the Al-lean regions disordering spontaneously, the equilibrium state is formed finally. In the whole stage of precipitation, the shape of Ni_3Al phase becomes more regular and their orientation becomes more obvious, at the later stage, Ni_3Al phases present quadrate shape with round corner and align along the [10] and [01] directions.

11:45 AM

Thermodynamic Modeling of Phase Equilibrium in the Mo-Ti-Zr-C System: *Sujoy Kar*[1]; Don Lipkin[1]; Thomas Tiearney[2]; [1]GE Global Research; [2]GE Healthcare

Alloys in the Mo-rich corner of the Mo-Ti-Zr-C system have found broad application in non-oxidizing environments requiring structural integrity at temperatures well beyond 1000C. Alloys such as TZM (Mo-0.5Ti-0.08Zr-0.03C) and TZC (Mo-1.2Ti-0.3Zr-0.1C) owe much of their high-temperature strength and microstructural stability to MC and M2C carbide phases. The stability of the respective carbides, and the subsequent mechanical behavior of the alloy, is strongly dependent on the alloying additions. A CALPHAD-based thermodynamic modeling approach was employed to elucidate the effect of alloying on the phase equilibrium in the Mo-Ti-Zr-C system. Key aspects of the thermodynamic descriptions of the constituent binary and ternary systems are described, the supporting experimental validation data is reviewed, and implications for developing improved molybdenum-based alloys are discussed.

12:00 PM

Phase Equilibria and Thermodynamic Assessment of the Ti-Al-Nb System: Hans Seifert[1]; *Damian Cupid*[2]; Olga Fabrichnaya[1]; Orlando Rios[2]; Fereshteh Ebrahimi[2]; [1]Technische University Bergakademie; [2]University of Florida

Alloys in the Ti-Al-Nb system are promising for many high-temperature applications such as turbines for aero-engines. To refine the currently available thermodynamic description of the Ti-Al-Nb system, the extension of the bcc primary solidification field of the liquidus surface was investigated by observing the as-cast microstructures of selected alloys using optical microscopy, X-ray diffraction, scanning electron microscopy, and electron probe microanalysis. Also, differential thermal analysis was performed to determine the temperature of the invariant reaction between the liquid, sigma-Nb_2Al, bcc, and gamma-TiAl phases. The results of the experiments were used to re-optimize the Gibbs energy descriptions of the phases in the Ti-Al-Nb system for better agreement between calculated and experimentally observed liquidus surfaces. For further refinement during optimization, the calculated temperatures of predicted solid state reactions in the Ti-Al-Nb system were checked using differential thermal analysis and also additionally included as experimental data in the optimization.

12:15 PM

Phase Stability between the $(Al_{1-x}Mg_x)B_2$ Phase and the Al-Mg Intermediate Phases: *Sungtae Kim*[1]; Donald Stone[1]; Jae-Ik Cho[2]; Chang Yeol Jeong[2]; Chang-Seog Kang[2]; Jung-Chan Bae[2]; [1]University of Wisconsin - Madison; [2]Korea Institute of Industrial Technology

In-situ composites based on Al-Mg matrices and $(Al_{1-x}Mg_x)B_2$ reinforcement phases are being investigated as candidate alloys for transportation applications where such alloys offer the potential to reduce weight and improve fuel efficiency. A key to the synthesis of these alloys is the ability to tailor their microstructures, an issue that is intimately related to phase stability in the Al-Mg-B system. Therefore, we investigate that stability; but in order to avoid attempting alloy system design with an arbitrary selection of composition and temperature, we utilize additive entropy formulation and ab initio calculations to estimate thermodynamic properties of phases in the Al-Mg-B system. Based on experimentally updated and theoretically evaluated thermodynamic properties of intermediate phases, the CALPHAD method has constructed the Al-Mg-B phase diagram over a wide range of temperature and composition to guide in alloy design. The financial support of the Korea Institute of Industrial Technology is gratefully acknowledged.

Electrode Technology Symposium (formerly Carbon Technology): Inert Anode

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Carlos Zangiacomi, Phelps Dodge International Corporation; John Johnson, RUSAL Engineering and Technological Center LLC

Thursday AM Room: 299
March 13, 2008 Location: Ernest Morial Convention Center

Session Chairs: Odd-Arne Lorentsen, Hydro Aluminium; Jomar Thonstad, Norwegian University of Science and Technology

8:30 AM

Inert Anodes: An Update: *Rudolf Pawlek*[1]; [1]Technical Information Services and Consulting

This overview covers the development of inert anodes for the primary aluminium industry in the period 2003-2007. It reviews further on cermets, including their mechanical and physical properties and their behaviour and their manufacture; especially Cu (NiO-$NiFe_2O_4$) cermets in cryolite melts. However, the overview focuses particularly on the manufacture and behaviour metal anodes, including steels and Ni-Fe alloys. These alloys must be passivated before use in electrolysis, otherwise they will dissolve in the cryolite electrolyte. Low temperature electrolytes are used to avoid aggravated corrosion; KF-based electrolytes for low temperature electrolysis have proved suitable. Multi-polar electrolysis in a mushy electrolyte using metal electrodes could be a solution in the future. Inert anodes were tested on laboratory and batch scales, but no information about industrial scale tests is yet available.

8:55 AM

Effects of the NaF to AlF_3 Ratio on Fe-Ni-Al_2O_3 Anode Properties for Aluminum Electrolysis: *Junli Xu*[1]; Zhongning Shi[1]; Zhaowen Wang[1]; [1]Northeastern University

Fe-Ni-Al_2O_3 anodes for aluminum electrolysis were prepared by powder metallurgy method and were tested in different ratio of NaF to AlF_3. It was discovered that the anode corrosion rate increased with the decrease of the ratio of NaF to AlF_3. The appropriate ratio was between 1.6~1.8, and the produced aluminum purity reached 98% while the corrosion rate of anode was about 22mm/a. The effects of the ratio of NaF to AlF_3 to the corrosion rate of Fe-Ni-Al_2O_3 anode were explained using electrochemical impedance analysis and cyclic voltammetry.

9:20 AM

Anti-Oxidation Properties of Iron-Nickel Alloy at 800–900°C: *Xingliang Zhao*[1]; Xiaozhou Cao[1]; Zhongning Shi[1]; Zhaowen Wang[1]; Ying Nie[1]; [1]Northeastern University

Fe-Ni base alloy as a kind of candidate materials for metal inert anode in aluminum electrolysis, three Fe-Ni (with different wt %) alloys with mass ratio of 50:50, 60:40 and 70:30 respectively were prepared by powder metallurgy process. Oxidation behavior of the three alloys were studied at 900°C. The results indicated that the oxidation kinetic curves follow the parabolic law and anti-oxidation properties enhanced with increasing ratio of Fe to Ni in the alloy. X-Ray Diffraction showed that the oxide film formed on the anodic surface consisted of Fe_2O_3 and Fe_3O_4. 5wt% Al and 30wt% Co were added in different Fe-Ni alloy respectively. The results showed that anti-oxidation properties of Fe-Ni-Co is better than Fe-Ni-Al at 900°C

9:45 AM Break

9:55 AM

Effects of Rare Earth Element on Oxidation Behavior of Fe-Ni Metal Anode for Aluminium Electrolysis: *Xiaozhou Cao*[1]; Zhongning Shi[1]; Zhaowen Wang[1]; Ting'an Zhang[1]; Xianwei Hu[1]; Xingliang Zhao[1]; [1]Northeastern University

The addition of rare earth elements have significant effect on the oxidation behavior of Fe-Ni metal anode for aluminium electrolysis in air at 900°C by thermogravimetry method. The microstructure and composition of oxide film have been analyzed by XRD and SEM. The results show that rare earth element can change the content of oxide film on the surface of metal anode. Rare earth element is inclined to distribute on grain interfaces and refined casting grains. The oxide film is compact and can prevent the matrix from oxidizing further. The oxidation mechanism was suggested by the component of oxide film of metal anode.

10:20 AM

Effect of Additive CaO on Corrosion Resistance of 10NiO-$NiFe_2O_4$ Ceramic Inert Anodes for Aluminium Electrolysis: Zhongliang Tian[1]; Lifeng Huang[1]; Yanqing Lai[1]; *Jie Li*[1]; Yexiang Liu[1]; [1]Central South University, School of Metallurgical Science and Engineering

10NiO-$NiFe_2O_4$ composite ceramic inert anodes with additive CaO content of 0, 1, 2 and 4%(mass fraction) were prepared and their corrosion resistance to Na_3AlF_6-K_3AlF_6-Al_2O_3 melts was studied in laboratory electrolysis tests. The results show that the content of additive CaO in anodes had little effects on the steady-state concentrations of impurities in electrolyte. Considering the corrosion resistance and thermal shock resistance, among 10NiO-$NiFe_2O_4$ ceramic anodes with different content of additive, 2% CaO/(10NiO-$NiFe_2O_4$) ceramic inert anode behaves best and should be further studied.

Hael Mughrabi Honorary Symposium: Plasticity, Failure and Fatigue in Structural Materials - from Macro to Nano: Cyclic Deformation and Fatigue of Metals II

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS Materials Processing and Manufacturing Division, TMS: High Temperature Alloys Committee, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Nanomechanical Materials Behavior Committee
Program Organizers: K. Jimmy Hsia, University of Illinois; Mathias Göken, Universitaet Erlangen-Nuernberg; Tresa Pollock, University of Michigan - Ann Arbor; Pedro Dolabella Portella, Federal Institute for Materials Research and Testing; Neville Moody, Sandia National Laboratories

Thursday AM — Room: 386
March 13, 2008 — Location: Ernest Morial Convention Center

Session Chairs: J. Wayne Jones, University of Michigan; Tatsuo Sakai, Ritsumeikan University

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8:30 AM Keynote

Mechanisms of Fatigue Failure of Polycrystalline Copper in the VHCF-Regime: Stefanie Stanzl-Tschegg[1]; B. Schönbauer[1]; *Campbell Laird*[2]; [1]Boku University Vienna; [2]University of Pennsylvania

In order to understand the mechanisms of fatigue damage of metallic materials, ductile single-phase metals have been studied by distinct authors like Mughrabi extensively in the past. More recently, since the non-existence of a fatigue limit in inhomogeneous high-strength steels became evident in tests in the VHCF regime, the question on the microstructural mechanisms of cyclic deformation in ductile metals was actualized by Mughrabi, and investigations with new testing techniques were started. Some results are reported in this paper, like on the formation of persistent slip bands (PSBs) in the VHCF regime and their role for the initiation of fatigue cracks in polycrystalline copper. The experiments were performed with the ultrasound fatigue technique up to 10^{11} cycles, and AFM as well as SEM and TEM studies were performed. The existence and correlation of PSB threshold and a questionable fatigue limit are treated.

9:00 AM Invited

Microstructure Variability and Fatigue Behavior at Very Long Life Fatigue: *J. Wayne Jones*[1]; John Allison[2]; Tresa Pollock[1]; Christopher Szczepanski[1]; Xiaoxia Zhu[1]; Jiashi Miao[1]; Liu Liu[1]; [1]University of Michigan; [2]Ford Motor Company

The is a growing body of research on the interesting and sometime unique interactions between microstructure, cyclic deformation mechanisms and damage accumulation that affect very high cycle fatigue behavior (VHCF) at lifetimes at or beyond 10^9 cycles. Models have emerged, such as proposed by Mughrabi, that extend our current understanding of cyclic deformation processes and microstructure variability to explain VHCF behavior. At such long lifetimes, critical microstructure features (e.g. large grains, inclusion, pores, surface condition) exert a strong influence on fatigue damage accumulation and, hence on the variability of fatigue life. This presentation describes recent research that uses ultrasonic fatigue to investigate VHCF behavior in a wide range of structural alloys, including cast aluminum alloys, wrought titanium alloys, particulate reinforced aluminum alloys and nickel-base single crystal and polycrystalline superalloys at ambient and elevated temperature. Current understanding from these studies of the role of microstructure in VHCF behavior will be summarized.

9:20 AM Invited

Long Life Fatigue-Critical Crack Length Concept: *Alan Plumtree*[1]; [1]University of Waterloo

Long life fatigue is expressed by examining the critical lengths and threshold stress ranges for small surface and internal cracks. Competition between the two occurs after a very large number of cycles. The crack (surface or internal) that attains the critical length first becomes dominant, causing eventual failure. The critical length of surface cracks is related to crack closure and surface strain distribution. Failure occurs at the corresponding maximum threshold stress range ie. endurance limit. For much longer lives, the maximum threshold stress range for the initiation and growth of internal cracks exceeds that of surface cracks. The more highly stressed internal regions such as flaws are preferred sites for the critical cracks. This critical length concept is applied to describe the long life fatigue of aluminum alloys and steels.

9:40 AM Invited

Development of Multi-Type High Efficiency Fatigue Testing Machines in Rotating Bending and Axial Loading: *Tatsuo Sakai*[1]; Tatsuya Furusawa[2]; Ryohei Takizawa[3]; Noriyasu Oguma[4]; Hiroshi Hohjo[5]; Hajime Ikuno[5]; [1]Ritsumeikan University; [2]Tokyokoki Seizosho Ltd.; [3]Toyota Motor Corporation; [4]University of Toyama; [5]Toyota Central Research and Development Laboratories, Inc.

In usual fatigue tests, cyclic load are applied to the specimens toward ten million cycles to obtain S-N characteristics of the structural materials. But, the fatigue property in gigacycle regime is also focused as an important subject in recent years. In such a long life region, a tremendous long period is required to perform fatigue tests. In order to overcome this difficulty, the authors have developed special types of fatigue testing machines under rotating bending and axial loading in which some multiple specimens can be tested simultaneously. In rotating bending, two different type of testing machines for 4 or 10 specimens were developed. On the other hand, two different types of testing machines in axial loading were also developed by using special hydraulic technology. Their fundamental performance was confirmed through actual fatigue tests in gigacycle regime.

10:00 AM

Focused Ion Beam Tomography for the 3D-Investigation of Fatigue Cracks and Their Interaction with Micro-Structural Barriers: *Horst Vehoff*[1]; Michael Marx[1]; Wolfgang Schaef[1]; [1]Saarland University

The influence of the microstructure on fatigue is often discussed on the basis of mean values. For developing materials with a better fatigue resistance, local information about the interaction of cracks with microstructural obstacles is needed. The problem is how to image three dimensional cracks with the available techniques? Imaging by SEM or AFM is two dimensional, the resolution of high resolving x-ray tomography is not sufficient to image crack opening displacements in the order of less than one micron and in TEM only thin films can be investigated. Therefore three dimensional FIB tomography is used to visualize the crack path inside the specimens. It will be shown, by which mechanisms cracks interact with grain boundaries and how precipitates are bypassed by activating additional slip systems. Microstructural data like

the inclination angel of the active slip systems can be coupled with the crack propagation rate which decreases significantly during interaction.

10:15 AM
High Cycle Fatigue Behavior of Copper Deformed by High Pressure Torsion: *Golta Khatibi*[1]; Jelena Horky[1]; Brigitte Weiss[1]; Michael Zehetbauer[1]; [1]University of Vienna

So far, investigations of fatigue behaviour of bulk nanomaterials achieved by Severe Plastic Deformation (SPD) have been restricted to those from Equal Channel Angular Pressing (ECAP). This contribution presents first results of fatigue tests of Cu processed by High Pressure Torsion (HPT). A special resonance ultrasonic fatigue testing system has been used which allows for symmetrical loading (R = -1) of freestanding small samples with thicknesses down to 10µm. From disk-shaped HPT samples, miniaturized dumbbell-shaped specimens were cut and subjected to 10^6 to 10^9 loading cycles. The influence of purity and of grain/subgrain size on high cycle fatigue of HPT copper was investigated. Comparing the fatigue life curves of HPT Cu with those of coarse grained Cu, a significant increase of fatigue life was found. During cycling, high purity copper specimens showed softening and related grain coarsening while specimens of commercially pure copper did not reveal this effect.

10:30 AM
Microstructural Effects on Length Scales for Plastic Blunting of Stage II Fatigue Cracks in Metallic Materials: *Pedro Peralta*[1]; Rikki Teale[1]; Andrea Keck[1]; Seon-Ho Choi[1]; [1]Arizona State University

A length scale has been recently proposed for plastic blunting of stage II fatigue cracks in metals that is proportional to the product of the cyclic plastic zone radius and the average shear strain ahead of the crack tip. This quantity is measured via in-situ loading experiments in compact tension specimens of Al 2024-T351 and Ti-6Al-4V, where the strain fields ahead of the crack tip are quantified using Digital Image Correlation (DIC) for several values of applied load. Microstructure at the tip is characterized using Electron Backscattering Diffraction (EBSD) and correlations between local microstructure, cyclic strain fields and the plastic blunting length scales are sought. Results are compared to similar measurements in pure polycrystalline nickel and the effects of microstructure are discussed in terms of differences and similarities between the results for the engineering alloys and pure nickel. Funding by Department of Defense AFOSR Grant FA95550-06-1-0309, Victor Giurgiutiu program manager.

10:45 AM
Development of Damage in Cast Iron During Superimposed Low Frequency Thermal-Mechanical and Higher Frequency Mechanical Loading: Thilo Hammers[1]; Andreas Uihlein[1]; *Karl-Heinz Lang*[1]; Detlef Loehe[1]; [1]Universitaet Karlsruhe (TH)

More and more thermally and mechanically highly stressed components fail due to the superposition of low and higher frequency loadings. A typical example are cylinder heads of combustion engines. Permanently rising temperatures and pressures of the combustion increase both the thermal-mechanical loading as well as the superimposed higher frequency mechanical induced loadings. The superposition of a higher frequency loading may reduce the number of low frequency basic cycles to failure drastically. It has to be assumed that the superimposed loading changes both the conditions for the initiation as well as the growth behaviour of fatigue cracks. To clarify the mechanisms of the damage development thermal-mechanical fatigue tests without and with a superimposed higher frequency loading were carried out on a cast iron material. Broken specimens as well as specimens from disrupted experiments were examined using light and scanning electron microscopy to identify the fatigue damages on hand.

11:00 AM
Investigation of Microstructure for AA7050 to Assist in Identifying the Fatigue Crack Initiation Sites: *Jonathan LeDonne*[1]; Steve Sintay[1]; Anthony Rollett[1]; [1]Carnegie Mellon University

The fatigue life of aerospace aluminum alloys is governed primarily by crack initiation, which is accelerated by the presence of particles in the microstructure. Although much is known qualitatively about the relationships between fatigue life and the size of microstructural features, quantitative models suffer because of the lack of detailed microstructural data. Characteristics of coarse constituent particles are investigated for AA7050. Size distributions of second phase particles are characterized. The sizes and positions of particles are analyzed for 2-dimensional orthogonal sections, which are then used for reconstruction of a 3-dimensional microstructure of particles. The conversion assumes that the particles can be approximated as ellipsoids. Fracture surfaces are also investigated to establish a defined fatigue crack-initiating feature. The results are compared to previous results on AA7075.

11:15 AM Concluding Comments

Materials in Clean Power Systems III: Fuel Cells, Hydrogen-, and Clean Coal-Based Technologies: Hydrogen Technologies

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Corrosion and Environmental Effects Committee
Program Organizers: Zhenguo "Gary" Yang, Pacific Northwest National Laboratory; Michael Brady, Oak Ridge National Laboratory; K. Scott Weil, Pacific Northwest National Laboratory; Xingbo Liu, West Virginia University; Ayyakkannu Manivannan, National Energy Technology Laboratory

Thursday AM — Room: 392
March 13, 2008 — Location: Ernest Morial Convention Center

Session Chairs: Leon Shaw, University of Connecticut; Guozhong Cao, University of Washington

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8:30 AM Invited
Coherent Carbon-Cryogel-Ammonia-Borane Nanocomposites for H_2 Storage: *Guozhong Cao*[1]; [1]University of Washington

Coherent carbon cryogel - ammonia borane (C-AB) nanocomposites are synthesized and the improved H_2 storage properties are reported. Porous carbon cryogels were impregnated with AB in tetrahydrofuran solution at 25°C under Argon. 30% of the carbon cryogel pore volume was filled to produce a 24 wt% C-AB nanocomposite. Nitrogen sorption isotherms, X-ray diffraction, differential scanning calorimetry, differential thermal / thermal gravimetric analyses, mass spectrometry, Fourier Transform Infrared Spectroscopy and 11B NMR were used to characterize the coherent C-AB nanocomposites. Findings include a merged two-step hydrogen release reaction with an appreciable reduction in the dehydrogenation temperature to <90°C, as well as the suppression of borazine release. Our results indicates that incorporation of AB in CC will lead to its destabilization, which is responsible for the improvement of hydrogen release kinetics as well as formation of different nonvolatile products for thermally reacted CC-AB compared to solid state AB.

9:00 AM
Hydrogen Uptake and Release Behavior of Lithium Amide and Hydride Systems for Hydrogen Storage Applications: W. Osborn[1]; T. Markmaitree[1]; X. Wan[1]; *Leon Shaw*[1]; Z. Gary Yang[2]; [1]University of Connecticut; [2]Pacific Northwest National Laboratory

The DOE FreedomCAR requires that the on-board hydrogen storage system for PEM fuel cells can provide stable hydrogen fuel in about 1,500 uptake and release cycles. This study investigates the reaction pathway and rate-limiting step of dehydrogenation of the nanostructured LiNH2 + LiH mixture in order to identify the strategy for enhancing its hydrogen uptake and release rates. The study reveals that dehydrogenation of the LiNH2 + LiH mixture is diffusion controlled and the rate-limiting step is NH3 diffusion through the Li2NH product layer outside the LiNH2 shrinking core. Furthermore, long-term hydrogen uptake/release stability is observed. These phenomena are explained based on a model describing the major steps of the dehydriding reaction of the mixture, and related to the evidence obtained from X-ray diffraction and specific surface area measurements of the mixture before and after isothermal hydrogen uptake/release cycles at high homologous temperatures.

9:25 AM
Structural Behavior Studies of Li-Based Hydrogen Storage Materials during Pressure Hydriding/De-Hydriding Cycling: *Wen-Ming Chien*[1]; Joshua Lamb[1]; Dhanesh Chandra[1]; [1]University of Nevada

Li-based complex hydrides (imide/amide and $LiNH_2/Li_3AlH_6$) have been performed X-ray diffraction studies during pressure hydriding/de-hydriding cycling.

The degradation of hydrogen storage capacities after pressure cycling was also determined. Equilibrium isotherms were obtained by Sievert's apparatus after 1, 56, 163, 501 and 1100 pressure cycles on imide/amide system, and observe hydrogen capacity changes as a function of cycles at 255°C. Structural studies of the products after pressure cycling showed mainly Li_2NH and LiH phases, and the impurity Li_2O phase. X-ray diffraction results showed the Li_2NH reduced from 77% to 13%, and LiH phase increases from 18% to 57% after 1100 cycles. Pressure cycling results showed 2.55 (~10.25 bar) and 2.95 wt% (~0.86 bar) hydrogen storage loss after 1100 cycles. X-ray diffraction study results of $LiNH_2/Li_3AlH_6$ system show that there is a phase transformation between 165°C to 200°C. Detail results of structural behaviors and pressure isothermals of different cycles will present.

9:50 AM

Development of Catalysts for Hydrogen Generation from Hydride Compounds: *Valentina Simagina*[1]; Pavel Storozhenko[2]; Olga Netskina[1]; Oksana Komova[1]; [1]Boreskov Institute of Catalysis; [2]State Research Institute of Chemistry and Technology of Organoelement Compounds

Investigation of hydrogen generation from NaBH4 and NH3BH3 over catalysts has been carried out. It was shown, that the nature of a support and an active component of the catalyst affects the rate of H2 generation. Development of active and stable catalysts, optimization of the catalytic bed and application of new engineering solutions have permitted to develop of hydrogen generator providing uniform hydrogen generation both in uninterrupted and in periodic modes of operation.

10:15 AM Break

10:30 AM

Elastic Constants and Internal Friction of Beta-Phase and Alpha+Beta-Phase Pd-Hydride between 1.4 and 300 K: *Douglas Safarik*[1]; Ricardo Schwarz[1]; [1]Los Alamos National Laboratory

Recently we measured[1] the room-temperature elastic constants of single-crystal PdHx, where $0.01<x<0.62$. In this composition range, the crystals are two-phase mixtures of coherent beta-hydride precipitates in an alpha-hydride matrix, or coherent alpha-hydride precipitates in a beta-hydride matrix, depending on the value of x. We found that C44 and B decrease linearly with increasing x, whereas C'=(C11+C12)/2 shows a parabolic dependence on x. The unusual composition dependence of C' was attributed[1] to anelastic relaxations involving changes in the shape of the coherent lenticular-shaped precipitates when subjected to an acoustic stress. To further investigate this anomalous behavior, we have measured the elastic constants and internal friction of single crystal PdHx in the temperature range $1.4<T<300$ K and the composition range $0.58<x<0.72$. We discuss our results in terms of thermally activated relaxations of the coherent precipitates and ordering of the H-atoms in the beta phase. [1]R.B. Schwarz,H.T. Bach,U. Harms,D. Tuggle,Acta Mat.53,569(2005).

10:55 AM

Effects of Partial Substitution of Al for Mg on the Electrode Properties of Mg2Ni Thin Film: *Junli Xu*[1]; Ying Li[2]; Fuhui Wang[2]; [1]Northeastern University; [2]Institute of Metal Research of Chinese Academy of Sciences

Mg2Ni films with Mg partially substituted by Al were prepared by magnetron sputtering. Their charge-discharge property was tested, and the effect of the partial substitution of Al for Mg on thermal parameter of the films was studied. The charge-discharge experiments showed that the discharge property of Mg2Ni film was improved by the substitution of Al for Mg. The gradation of discharge capacity of Mg2-xAlxNi film was: Mg1.8Al0.2Ni > Mg1.7Al0.3Ni > Mg1.6Al0.4Ni > Mg2Ni. P-C-T curves revealed that the equilibrium hydrogen pressure increased and the formation enthalpy of hydrides in Mg2-xAlxNi film decreased with the increment of Al content, which indicated that the stability of the hydrides in Mg2-xAlxNi film decreased with the increment of Al content.

11:20 AM

Cytotoxicity and Reactive Oxygen Species Generation for Aggregated Carbon and Carbonaceous Nanoparticulate Materials: *K. Garza*[1]; K. Soto[2]; Lawrence Murr[1]; [1]University of Texas; [2]Lockheed Martin Aeronautics Company

We have investigated the cytotoxicity and reactive oxygen species (ROS) generation for indoor and outdoor soots: candle, wood, diesel, tire, and natural gas burner soots – along with surrogate black carbon, various multiwall carbon nanotube aggregate materials, TiO2 (anatase) and chrysotile asbestos as reference materials. All soots were observed by TEM and FESEM to be composed of aggregated, primary spherules (20-80 nm diameter) forming complex, branched fractal structures. These spherules were composed of intercalated, turbostratic arrangements of curved graphene fragments with varying concentrations of polycyclic aromatic hydrocarbon (PAH) isomers. In vitro cultures with an immortalized human lung epithelial cell line (A549) treated with these materials showed decreased cell viability and variations in ROS production, with no correlations to PAH content. The data demonstrates that soots are cytotoxic and that cytotoxicity is not related to PAH content but is a function of ROS generation, suggesting that soot induces cellular oxidative stress.

Refractory Metals 2008: Properties of Refractory Metals

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Refractory Metals Committee
Program Organizers: Todd Leonhardt, Rhenium Alloys Inc; Jim Ciulik, University of Texas at Austin

Thursday AM
March 13, 2008
Room: 388
Location: Ernest Morial Convention Center

Session Chairs: Todd Leonhardt, Rhenium Alloys Inc; Brian Cockeram, Bechtel Bettis Inc.

8:30 AM

Influence of Microstructure on the Fracture Toughness of Tungsten Alloys: *Bernd Gludovatz*[1]; Mario Faleschini[2]; Andreas Hoffmann[3]; Reinhard Pippan[2]; [1]Christian Doppler Laboratory for Local Analysis of Deformation and Fracture; [2]Austrian Academy of Sciences, Erich Schmid Institute of Materials Science; [3]Plansee Metall GmbH

Tungsten and tungsten alloys show the typical change in fracture behaviour from brittle (low temperatures) to ductile (high temperatures). In order to improve the understanding of the effect of microstructure the fracture toughness of pure tungsten, potassium doped tungsten and tungsten with 1wt% La_2O_3 has been investigated by means of 3-point bending -, double cantilever beam - and compact tension specimens. Though all these materials show the expected increase in fracture toughness with increasing temperature, influences like texture, chemical composition, grain boundary segregation and dislocation density have an extreme influence on the obtained results. These influences can especially be seen in the fracture behaviour and morphology, where two kinds of fracture can occur: on one hand the transcrystalline and on the other hand the intercrystalline fracture. Therefore techniques like electron backscatter diffraction, auger electron spectroscopy and x-ray line profile analysis were used to determine the parameter influencing fracture toughness.

8:55 AM

Physical Properties of Tungsten Wire for Halogen Lamp Manufacture: *James Downs*[1]; [1]Rhenium Alloys Inc.

Tungsten is the choice for halogen lamp filaments because of its good conductivity, high melting point, and low vapor pressure. Controlling the mechanical properties of the tungsten wire is critical to meet the demand for high intensity infrared lamps, for industrial and semiconductor industry that last longer and perform better. This presentation examines physical properties of tungsten, metallurgic structure and halogen cycle and how these affect fabrication and manufacture of the lamps and lamp performance.

9:20 AM

Microstructural Characterization of Dynamic Abnormal Grain Growth in Molybdenum: *James Ciulik*[1]; Eric Taleff[1]; [1]University of Texas at Austin

Large single crystals of commercial-purity molybdenum were grown by dynamic abnormal grain growth (DAGG). The microstructures were characterized using several methods: serial sectioning to show the three dimensional microstructure at the polycrystalline/single crystal interface; electron backscatter diffraction (EBSD) to characterize the crystallographic orientations of the grown single crystals and the crystallographic texture of the parent polycrystalline molybdenum; and Laue backscatter X-ray diffraction to

identify the orientation of the single crystals grown. Results are presented to show that DAGG is a viable method of growing large single crystals of refractory metals at temperatures well below the melting temperature.

9:45 AM

High Temperature Properties of Molybdenum-Rhenium Alloys: *Jason Wood*[1]; Samuel Causey[1]; Randall Jenkins[1]; Jennifer Gaies[2]; Mark Opeka[2]; Keisha Sylvester[2]; Xian Zhang[2]; [1]Southern Research Institute; [2]Naval Surface Warfare Center – Carderock Division

Mechanical and thermal properties were obtained from different alloy compositions of molybdenum-rhenium (Mo-Re). The Mo-Re compositions characterized were Mo-41%Re, Mo-44.5%Re and Mo-47.5%Re and the manufacturing processes for these compositions were sinter and hot isostatic press (HIP) or swaged. Mechanical and thermal properties for these materials were obtained from room temperature to 3500°F. Manufacturing process differences and material property comparisons will be presented.

10:10 AM Break

10:20 AM

Oxidation Behavior of Alloys from the Nb-W-Cr System Containing C Modifiers: *Maria Gonzalez De Moricca*[1]; Shailendra Varma[1]; [1]University of Texas at El Paso, Department of Metallurgical and Materials Engineering

A comparison of the oxidation behavior between alloys of the Nb-W-Cr System containing C as a modifier has been performed. Selection of alloy compositions was based on the ternary isothermal sections of Nb-W-Cr at 1000 and 1500°C. Oxidation experiments were conducted in air at different time intervals in a range of temperatures from 700 to 1400°C. Mass gain per unit area as function of the temperature was used to determine the alloy's oxidation resistance. The oxidation products were characterized by XRD, EDS, SEM, and XPS. An intermediate temperature range indicates the formation of complete powder after 24 hours. The oxidation resistance at 1200°C and above has been found to be superior to their monolithic form as well as the alloys with boron (B) addition. The characterization results will be presented to delineate the effect of the carbon as a modifier to the ternary alloys on the oxidation kinetics.

10:45 AM

Effect of Al on High Temperature Oxidation of Cr-W Alloys: *Omer Dogan*[1]; [1]Albany Research Center, National Energy Technology Laboratory

There is an increasing demand for new materials with good high temperature properties for new energy technologies developed to increase generating efficiency and reduce environmental pollution. Along with other refractory metals, chromium-tungsten alloys possess good strength well above the application temperatures of Ni-based superalloys. However, they have limitations with room temperature ductility and elevated temperature oxidation. The Cr-W alloys develop Cr_2O_3 scale under oxidizing conditions at elevated temperatures. Under cyclical temperature conditions, the oxide scale spalls resulting in a mass loss. In this study, effect of Al on the high temperature oxidation behavior of Cr-10wt%W alloy was investigated using a pseudo-cyclical oxidation test. Forming an Al-Cr layer on the Cr-W alloy reduced oxidation rate significantly and eliminated spalling completely.

11:10 AM

Mechanical Properties of High Purity Niobium Processed via Severe Plastic Deformation: *Shreyas Balachandran*[1]; Richard Griffin[1]; Robert Barber[2]; Karl Hartwig[1]; [1]Texas A&M University; [2]Shear Form Inc

High purity Niobium (Nb) is used for superconducting radio frequency accelerator cavities. This application requires the Nb sheet to have good formability and uniform mechanical and physical properties. The motivation of the study is to develop a fabrication process for Nb sheet with a more uniform microstructure and improved ductility. In order to obtain such sheet, the authors have worked bulk Nb by multipass equal channel angular extrusion (ECAE) and then rolled the bars to sheet. Preliminary results of tensile test and hardness measurements along with microstructural analysis shows improved ductility and mechanical property uniformity when compared to commercially available Nb sheet.

Structural Aluminides for Elevated Temperature Applications: Environmental Effects and Protection

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: High Temperature Alloys Committee, TMS/ASM: Mechanical Behavior of Materials Committee

Program Organizers: Young-Won Kim, UES Inc; David Morris, Centro Nacional de Investigaciones Metalurgicas, CSIC; Rui Yang, Chinese Academy of Sciences; Christoph Leyens, Technical University of Brandenburg at Cottbus

Thursday AM
March 13, 2008

Room: 394
Location: Ernest Morial Convention Center

Session Chairs: Christoph Leyens, Technical University of Brandenburg at Cottbus; Guo Liang Chen, University of Science and Technology Beijing

8:30 AM Invited

Recent Progress on Oxidation Resistance of High Nb Containing TiAl Alloys: *Guo Liang Chen*[1]; N. Zhang[1]; L. L. Zhao[1]; W. J. Wang[1]; J. P. Lin[1]; [1]University of Science and Technology Beijing

The presentation deal with the oxidation behavior of high Nb containing TiAl alloys. It has been confirmed that the outside thin layer of scale is Al2O3 at initial stage of the oxidation of high Nb containing TiAl alloys. The depletion in Al from surface is consistent with the selective oxidation of the alloy to form the alumina oxide layer. But the growth of the alumina layer is limited by the diffusion of Al in the underneath oxide layer. The depletion of Al leads to the onset of (Ti,Nb)O2 layer. The (Ti,Nb)O2 layer consists of two sublayers, (Ti,Nb)O2 and (Ti,Nb)O2+ Al2O3. The morphology of (Ti,Nb)O2 layer is finer and denser than TiO2 layer of the TiAl alloys without Nb content. The alloying Nb significantly reduces the diffusion of oxygen in the scale, resulting in great improvement of oxidation resistant. The long time oxidation resistant can be significantly improved by Y additions. Suitable Y content can completely depress the abnormal increase of the oxidation of TiAl + 7/8 Nb alloys after about 500 hr long time exposure at 900. The optimum content is related to the Nb content in the alloy. Adding Y to high Nb containing TiAl alloys is a suitable way to keep excellent oxidation resistance after long time exposure at high temperature. The detailed effects of Y addition on the oxide scale are also discussed.

9:00 AM

Oxidation Behavior of TiAlYN and CrAlYN Nanocomposite Coatings Deposited on γ-TiAl Based Alloy Ti-45Al-8Nb: *Reinhold Braun*[1]; David Müßener[1]; Martin Moser[2]; Florian Rovere[2]; Paul Mayrhofer[2]; Christoph Leyens[3]; [1]DLR - German Aerospace Center; [2]Montanuniversität Leoben; [3]Technical University of Brandenburg at Cottbus

The oxidation behaviour of nanocomposite TiAlYN and CrAlYN coatings was investigated in the temperature range between 750 and 950°C conducting cyclic oxidation tests in air. The about 4 µm thick layers were deposited on γ-TiAl samples using unbalanced magnetron sputtering. The yttrium content varied from 0 to 4 at%. Post-oxidation micro-structural examination was carried out using scanning electron microscopy and energy-dispersive X-ray spectroscopy. The TiAlYN coatings provided reasonable oxidation protection to γ-TiAl alloy at 750°C, but they decomposed after short time periods at 850°C. Samples with nanocomposite CrAlYN coatings exhibited significant lower mass gains in comparison to the bare substrate material when thermally cycled at 900°C. Although the coatings were entirely oxidised, oxidation of the substrate was considerably reduced compared to uncoated samples. When exposed at 950°C, the CrAlYN coatings with 1 and 4 at% Y provided initial protection which vanished after longer exposure times.

9:20 AM

High Temperature Oxidation of Beta-Gamma Ti Alloys: *Michiko Yoshihara*[1]; Young-Won Kim[2]; [1]Yokohama National University; [2]UES Inc

A new class of TiAl based multi-component alloys, called beta gamma alloys, have been explored at UES/AFRL in an effort to ease the processing and improve the machinability of gamma-TiAl alloys. Additional requirements were that the new alloys should have refined structures and also adequate resistance to creep and oxidation at high temperatures. It was found out that such alloys may exist within the broad composition range of Ti-(40-45)Al-(1-7)Nb-(1-8)(Cr,Mn,V,Mo)-(0-0.5)(B,C). In the present study, the cyclic oxidation behavior of several beta-

gamma alloys has been investigated in air in the temperature range between 600°C and 870°C. The results show that the oxidation resistance varies widely depending upon the phase distribution and alloying elements. Some of beta-gamma alloys show the oxidation resistance as good as that of best conventional gamma alloys. The results will also be compared with those of representative titanium alloys and explained in terms of beta distribution and alloying elements.

9:40 AM

Influence of Oxidation Protective Coatings on the Ductility of γ-TiAl Based Alloys: *Martin Moser*[1]; Florian Rovere[1]; Reinhold Braun[2]; Helmut Clemens[1]; Paul Mayrhofer[1]; [1]Montanuniversität Leoben; [2]DLR-German Aerospace Centre

Using γ-TiAl alloys in high temperature applications requires coatings that effectively protect the material from oxidation. Here, three commercial coating systems, Al/Cr deposited by pack-cementation, NiAl prepared by Ni-electroplating, and a CoNiCrAlY coating deposited by atmospheric plasma spraying, as well as two novel physical vapour deposition (PVD) films, AlAu and CrAlYN are investigated. Ti-47Al-2Cr-0.2Si sheet material was selected as substrate as this alloy exhibits high ductility at room temperature but low oxidation resistance. Thermal exposure in air reveals that all selected coatings improve significantly the oxidation resistance of the base material. The interaction between the coatings and γ-TiAl was investigated by 4-point-bending tests at room temperature. After coating all samples show a decrease in bending strength. The PVD coatings as well as the CoNiCrAlY films show the smallest influence on ductility, whereas the pack cementated Al/Cr- and electroplated Ni-films resulted in strong degradation of mechanical properties.

10:00 AM

Oxidation Characteristics of γ-TiAl-8Nb Coated with a CrAlYN/CrN Nanoscale Multilayer Coating: *William Rainforth*[1]; Ian Ross[1]; Christina Reinhard[2]; Papken Eh.Hovsepian[2]; Arutium Ehiasarian[2]; Reinhold Braun[3]; Christoph Leyens[4]; [1]Sheffield University; [2]Sheffield Hallam University; [3]German Aerospace Centre (DLR); [4]Technical University of Brandenburg at Cottbus

There is a major desire to introduce gamma-TiAl into a range of high performance applications in order to reduce weight. However, this will require the development of coatings that protect against oxidation at high temperature, but do not adversely affect the mechanical properties. This work reports the high temperature degradation mechanisms of a nanoscale CrAlYN/CrN multilayer coating deposited on gamma-TiAl(8Nb) by a combined high power impulse magnetron sputtering/unbalanced magnetron sputtering. Detailed TEM/STEM analysis of FIB prepared specimens from isothermal static oxidation tests at 850°C for up to 1030 hours is presented. The evolution of the complex oxide and significant structural modification of the gamma-TiAl(8Nb) substrate is reported. The implication of these observations for future coating development is discussed.

10:20 AM Keynote

Recent Progress in the Science and Technology of Gamma Titanium Aluminides: *Christoph Leyens*[1]; Janny Lindemann[1]; Maria Glavatskikh[1]; Susanne Gebhard[2]; Maik Fröhlich[2]; Dan Roth-Fagaraseanu[3]; [1]Technical University of Brandenburg at Cottbus; [2]German Aerospace Center; [3]Rolls-Royce Deutschland

Titanium aluminides have attracted significant attention since materials properties have been strongly improved over the last years, and engineers have become more familiar to design with a material that shows limited ductility and damage tolerance. Part of the reason of slow introduction into service is the complexity of materials processing which is attributed to a strong dependency of component properties on alloy chemistry and microstructure. Among others, the paper will provide an overview of recent progress in the understanding of processing-related fluctuations in chemical composition and their effects on the mechanical properties of Ti-Al-Nb- and Ti-Al-Nb-Mo-based gamma TiAl alloys which are designed for moderately elevated temperature applications. Moreover, recent results on the retained strength of these classes of modern alloys and materials behavior after impact will be highlighted. Also, latest findings regarding mechanical and chemical surface treatments including coatings will be discussed.

11:00 AM

Hot Corrosion Behavior of Nanostructured Coatings on Gamma-TiAl for High Temperature Applications: *Francisco Perez-Trujillo*[1]; Juan Nieto Hierro[1]; Maria Hierro de Bengoa[1]; Sonia Mato Díaz[1]; [1]Universidad Complutense

Gamma-TiAl aluminides have a temperature limit for high temperature applications. In order to increase the operation temperature, different micro and nano structured coatings have been applied in order to increase this temperature. Among the different corrosive environments at high temperature, molten salts are the most aggresive environment to test. To know the hot corrosion resitante of this novel coatings, experiments in sulfate-chloride molten mixtures have been perform at 750°C for more than 300 h. Since this test have not been perform before, equivalent circuits have been established, as well as the corresponding modelling. The advantages to establish coatings performance of the elctrochemical impedance spectrosocpy (EIS)appled will be established. Mechanistic approach and coatings peformance will be given.

11:20 AM

Oxidation Behavior of Nb Additional TiAl Alloys: Wei Lu[1]; *Lianlong He*[1]; [1]Institute of Metal Research

The oxidation behavior of different stages of three kinds of Nb additional TiAl based alloy, Ti-46.5Al-5Nb, Ti-45Al-8Nb-0.2W-0.2B-0.02Y and Ti-45Al-15Nb (at%) have been investigated at 900°C in static air. The adherence between nitride layer and base alloy is good. However, an obvious interface between the mixed layer and the under layer existed at the initial oxidation stage. Meanwhile, oxygen absorption and refining of the base alloy lead to the increase of the volume fraction of grain boundary at the initial stage. The first reason why Nb addition improves the oxidation resistance of TiAl alloys is that the doping of Nb^{5+} in the TiO_2 enriched layer can not only reduces the diffusion path of Ti cation and O anion but also promote the formation of Al_2O_3 enriched layer. The second reason is that Nb based compound was formed at the subsurface layer, which can prevent a continuous formation of X phase.

11:40 AM

The Fluorine Effect for High Temperature Oxidation Protection of TiAl-Alloys for Automotive and Aero-Engine Applications: *Alexander Donchev*[1]; Michael Schütze[1]; Rossen Yankov[2]; Andreas Kolitsch[2]; [1]Society for Chemical Engineering and Biotechnology; [2]Forschungszentrum Dresden Rossendorf

The insufficient oxidation resistance of TiAl above roughly 800°C is a major disadvantage for its use but it can be improved significantly by small amounts of halogens in the surface zone of the TiAl-material. Especially fluorine has proven to be a beneficial doping element. The fluorine effect is stable at least for one year at temperatures up to 900°C under thermocyclic conditions. In this paper results of fluorine treated and untreated TiAl-coupons, turbocharger rotors for automotive use and turbine blades for aero-engines are shown. The specimens were exposed isothermally and thermocyclically in the temperature range from 700–1050°C in laboratory air or synthetic air. The specimens can be treated with fluorine in several ways e.g. spraying. Without any treatment some components were totally destroyed during high temperature oxidation but after fluorine treatment the components were still intact. Post oxidation investigations showed the formation of a thin and protective Al2O3-scale.

12:00 PM

Ti-Al-Cr-X Coatings for High Temperature Oxidation Protection of Gamma Titanium Aluminides: *Maik Froehlich*[1]; Reinhold Braun[1]; Christoph Leyens[2]; [1]DLR-German Aerospace Center; [2]Technical University of Brandenburg at Cottbus

To extend the oxidation resistance of gamma titanium aluminides for applications above 750°C the formation of non-protective titania has to be prevented. The primary objective to improve the resistance of titanium aluminides against oxidation is the use of alumina forming coatings. The paper is focussed on the development of oxidation resistant metallic coatings on the basis of Ti-Al-Cr. Ti-Al-Cr and Ti-Al-Cr-X coatings with X=Ag,Hf,Y,Si were produced by magnetron-sputtering-techniques. The coated specimens were examined under cyclic conditions at 900°C and 950°C up to 1000 cycles, respectively. All coatings formed a thin alumina layer on top providing a diffusion barrier for oxygen at the beginning. But internal diffusion between substrate and coating led to a depletion of Laves phase which promotes the formation of alumina. The effect of cross diffusion between coating and substrate for the various coating chemistries will be discussed on the basis of post-oxidation SEM/EDX and oxidation kinetics analysis.