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March 12-16, 2006
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Technical Program

March 12-16, 2006
Henry B. Gonzalez Convention Center
San Antonio, Texas, USA

THURSDAY

Advanced Materials for Energy Conversion III: A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda: Carbon, Borohydrides and Other Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Reactive Metals Committee
Program Organizers: Dhanesh Chandra, University of Nevada; John J. Petrovic, Petrovic and Associates; Renato G. Bautista, University of Nevada; M. Ashraf Imam, Naval Research Laboratory

Thursday AM
March 16, 2006
Room: 214A
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Daniel Fruchart, CNRS; Joseph Wermer, Los Alamos National Laboratory; Bernard Bonnetot, CNRS-University of Lyon France

8:30 AM Invited
A Fuel Cell Actuated by Sodiumu Borohydride as a Hydrogen Storage Material: *Seiji Suda*[1]; [1]MERIT
Abstract not available.

8:55 AM Invited
Hydrogen Storage Using Borohydrides: *Bernard Bonnetot*[1]; Laetitia Laversenne[1]; [1]University of Lyon-France

Borohydrides, however high hydrogen containing compounds, can hardly be used for hydrogen storage. What ever the solution chosen to recover the stored hydrogen, thermal dehydrogenation or hydrolysis, the regeneration of the borohydride must be operated out of the site of hydrogen utilization. Borohydrides would never be considered as reversible compounds for hydrogen storage. Dehydrogenation yield through thermal decomposition is highly energy consuming because borohydrides, specially alkaline earth derivatives, require high temperatures to be decomposed. More-over the multistep thermolysis of borohydride yield to very stable intermediates as alkaline earth hydrides whose dehydrogenation is rarely performed due to the volatility of the alkaline earth metal. This limitation implies the fact that the announced hydrogen containing must be lowered from 3/4 at least to be realistic. Improvements have been obtained using catalysts which lower the decomposition temperature but they also lower the stored hydrogen amount. The regeneration of the thermolyzed borohydrides would involve a specific chemical treatment which has not be studied up to now because the starting materials of borohydride chemistry are usually oxides. More promising are the developments of hydrogen generation from borohydrides through hydrolyzing process. How ever the hydrogen stored percentage must take into account all the reactants but the technical conditions directed the storage capacity. The hydrogen recovering process involves water as reactant and a key of the "fuel", borohydride plus water, efficiency is the conditions of the reaction of hydrolysis. The amount of recovered hydrogen is fixed by the stœchiometry of the reaction but the ultimate state of the formed borates after hydrolysis fixes the yield of the storage. Water and the borate hydrates formed from borohydrides becomes the most important results of the storage capacity. If all the hydrogen of water can be recovered, the high hydrogen containing of water allows high "fuel" efficiency. If the dehydration conditions of the side products formed after hydrolyze is not possible or required to hard conditions, the storing yield will be lowered. The option of hydrolyzing borohydride-water solution have to face two antagonist conditions: the solution must be as stable as possible to avoid any hydrogen leaking but the hydrolysis reaction must be as fast as possible to feed the fuel-cell with hydrogen. This balance is difficult and choices must be made to favor technical solution. The recycling of the borate resulting of the hydrolysis must be done out of the hydrogen consuming zone and technical points are actually non resolved specially for on board applications.

9:20 AM Invited
Integrated Design of Novel Hydrogen and Ammonia Storage Systems: *Tejs Vegge*[1]; Anders Andreasen[1]; Allan Schrøder Pedersen[1]; [1]Risø National Laboratory

Synthesizing new materials and catalysts for hydrogen storage is complex and expensive task, and a rational materials design process is required. Recent computer advances have made it possible to treat many of the essential materials problems, i.e. structural stability, hydrogen ab-/desorption and diffusion, with high accuracy methods like density functional theory (DFT). DFT calculations can be used to, e.g. provide a physical explanation for the catalytic role of the titanium based additives in complex hydrides or to predict the existence of new hydrogen storage structures with optimized thermodynamic properties. At Risø National Laboratory, we utilize the synergy of integrating theoretical work with in situ x-ray diffraction/SAXS, synchrotron/neutron experiments, and advanced materials testing to expedite the development of improved hydrogen and ammonia storage materials. We rely primarily on i) theoretically and experimentally observed trends, ii) improved nano-scale insight, and iii) structural predictions to guide our materials optimization process.

9:40 AM
Synthesis and Characterization of New Complex Borohydrides for Hydrogen Storage: *Sesha Srinivasan*[1]; Elias K. Stefanakos[1]; [1]University of South Florida

Complex chemical hydrides with high theoretical hydrogen densities have been renewed an interest for hydrogen storage in recent years. The breakthrough discovery of catalyzed sodium alanates for the reversible on-board hydrogen storage may not be the ideal system to realize the 2010 DOE technical targets due to its limited hydrogen storage capacity. On the other hand, sodium borohydride or lithium borohydride is a complex hydride possesses high hydrogen capacity of 10.5 wt.% and 18.2 wt.% respectively. However, the release of hydrogen from sodium borohydride is possible only by hydrolysis (reaction with water) and this process is irreversible. Whereas, the transition metal assisted borohydride derived from NaBH4 (LiBH4) undergoes thermal decomposition of molecular hydrogen at low temperatures. Destabilizing the borohydride complexes by reacting with binary compound yields better reversibility with greater hydrogen storage capacity at moderate temperatures. In search of binary metal hydrides with suitable hydrogen decomposition temperature (Tdec), the surprising correlation was found between Tdec and the standard redox potential (E0) for the Mn+/M0 redox pair in acidic aqueous solutions according to the general equation, Mn+1 (H-1)n = M0 + n/2 H2. Several binary and ternary hydrides which have Tdec values suitable for incorporating with low temperature fuel cells are known. Such hydrides include ZnH2 [Tdec=90°C], Zn(BH4)2 [Tdec= 85°C], KSiH3 [Tdec=70°C], CuH [Tdec=60°C] and LiGaH4 [Tdec=50°C]. Unfortunately, with the exception of Zn(BH4)2 (8.4 wt.% hydrogen capacity), rest of the compounds do not store a sufficient high wt.% of hydrogen to attain the US DOE target of 6.5 wt.%. Keeping these aspects in view, the present work aims to synthesize new complex borohydride, Zn(BH4)2 by mechanochemical milling of NaBH4 and ZnCl2 under inert atmosphere. The as-prepared complex hydride has been characterized extensively using PXD, FTIR, DSC, TGA and PCT techniques to study the structural, B-H bond environment, thermal and volumetric properties. Powder X-ray diffraction analysis of mechanically milled sample exhibits the presence of zinc borate, NaCl, and unreacted NaBH4 as well. The FTIR spectra of BH4- ion in NaBH4 has a characteristic band at 2290 cm-1, and in Zn(BH4)2, it occurs at ~2061 cm-1 (bridging B-H bonds) and ~2451 cm-1 (terminal B-H bonds). It is also interesting to note that Zn(BH4)2 exhibits ~6.0 weight percent of gravimetric hydrogen storage capacity at around 100-150°C as demonstrated by thermogravimetric analysis. The reversibility of the constituent elements to complex hydride phase under H2 atmosphere is presently underway.

10:05 AM

Effect of Catalysts on Hydrogen Sorption Properties of Magnesium: *R. Sundaresan*[1]; R. Vijay[1]; [1]International Advanced Research Centre for Powder Metallurgy and New Materials

Absorption/desorption of hydrogen by magnesium can be enhanced by incorporation of suitable catalysts. Studies have been carried out to evaluate such effects by mechanical alloying (MA) processing of the catalyst addition, when the effects of both grain refinement in Mg and finely distributed catalyst on Mg surface can be combined. Results are presented on the systems (i) Mg-TM (TM = 10-20 wt% Ti), (ii) Mg-IM (IM = 10-50 wt% $MmNi^5$, Mm = mischmetal) and (iii) Mg-Oxide (Oxide = 5-20 wt% Cr_2O_3), milled in Frtisch P5 planetary mill under toluene cover. With the addition of Ti, Mg could absorb 6.1 and 6.0 wt% of hydrogen at 300 and 200ºC, respectively, at 30 bar pressure. The absorption capacity and rate reduced significantly at temperatures below 200ºC. There was no desorption of hydrogen at temperatures below 300ºC at a pressure greater than 1 bar. With the addition of MmNi5, Mg was seen to absorb up to 5.0 wt% at 100ºC and 15 bar pressure. MmNi5 does not itself form a hydride at this pressure and its effect appeared to be only catalytic. The amount absorbed appears to be the saturation limit, rising to only 5.1 wt% at 300ºC. No desorption occurred at temperatures below 300ºC, while at 300ºC and 1 bar pressure, the maximum hydrogen desorbed was 3.1 wt%. Magnesium with the addition of Cr_2O_3 absorbed 5.45, 5.3 and 3.8 wt% at 300, 200 and 100ºC, respectively, at a pressure of 30 bar. The absorption as well as desorption rates increased with increase in Cr_2O_3 content. Mg-15 wt% Cr_2O_3 composite desorbed maximum quantity of 4 wt% at 300ºC and 1 bar pressure. Desorption was marginal at temperatures less than 300ºC. In all cases catalysis is evident since Mg with similar grain size within the three systems behaved differently. In terms of catalytic effect on absorption MmNi5 gave the best results enabling high absorption at temperature as low as 100ºC. In terms of quantity of hydrogen absorbed, Ti addition showed the best results with 6.1 wt% of hydrogen absorbed at 300ºC. Cr_2O_3 addition indicated maximum desorption with 4 wt% at 300ºC and 1 bar pressure. Detailed results are discussed and possible routes in the absorption/desorption processes are considered.

10:30 AM Break

10:45 AM Plenary

Carbon-Based Nanostructured Adsorbents for Hydrogen Storage: J. L. Blackburn[1]; C. Curtis[1]; A. C. Dillon[1]; T. Gennett[2]; K. E. H. Gilbert[1]; *Michael Heben*[1]; K. M. Jones[1]; Y.-H. Kim[1]; P. A. Parilla[1]; L. J. Simpson[1]; S. B. Zhang[1]; Y. Zhao[1]; [1]National Renewable Energy Laboratory; [2]Rochester Institute of Technology

Hydrogen is viewed as a clean energy alternative that could one-day replace fossil fuels in powering vehicles. For this vision to become a reality, significant advances will be required in a wide array of hydrogen related technologies. For hydrogen storage, the U.S. Department of Energy has set a goal of achieving system gravimetric and volumetric storage densities exceeding 6 wt% and 45 kg H2/m3, respectively, to facilitate large scale commercial deployment of hydrogen fuel on several low-demand vehicle platforms by the year 2010. A generic approach to the problem based on nanoscience considerations can offer a new perspective on this problem. In this approach, one considers how suitable binding sites for hydrogen can be designed and arranged in space with sufficient density, using a light host material, to simultaneously achieve high gravimetric and volumetric performance. To minimize energy input requirements during the charge/discharge cycle, and therefore optimize system efficiency, the "suitable" binding sites should stabilize hydrogen with energies in the range of 10 – 50 kJ/mol. We will discuss theoretical and experimental results on carbon nanotubes, fullerenes, and other nanostructured adsorbent materials, and explore the role of composition, doping, and local environment in tuning hydrogen storage properties. We will also describe the research activities of the recently-established DOE Center of Excellence for Carbon-Based Hydrogen Storage Materials which is focused on developing new solutions for hydrogen storage on-board vehicles. The Center is researching systems that reversibly stabilize sufficient hydrogen to meet the DOE targets, and builds on existing experimental and theoretical evidence for (i) dissociative adsorption that is weaker than typical C-H bond formation, and (ii) non-dissociative adsorption that is stronger than pure physisorption. In the first case we consider reversible hydrogen spillover, while in the second the goal is molecular adsorption via structural/chemical modifications to the physisorption potential as well as complexation of dihydrogen. The Center consists of projects at Air Products and Chemicals, Inc., California Institute of Technology, Duke University, Lawrence Livermore National Laboratory, National Institute of Standards and Technology, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Pennsylvania State University, Rice University, University of Michigan, University of North Carolina (Chapel Hill), and the University of Pennsylvania.

11:05 AM Keynote

Metal-Assisted Hydrogen Storage in Nanostructured Carbons: *Nidia Gallego*[1]; Fred Baker[1]; Cristian Contescu[1]; [1]Oak Ridge National Laboratory

First-principle calculations at ORNL on interactions between hydrogen and graphite provided the fundamental basis for experimental work on metal-doped, activated carbon fibers (produced at Clemson). Measurements at ORNL revealed that the Pd doped fibers exhibited a hydrogen storage capacity of about 2 wt% at ambient temperature and a pressure of 2 MPa. This represented an order of magnitude improvement over the capacity of the corresponding Pd free fibers. Further modeling work indicated that, provided the high energy barrier for initial sorption could be overcome, hydrogen could be stored by intercalation between graphene layers. On the basis of these preliminary findings, it is hypothesized that metal assisted hydrogen storage in nanostructured carbon is the result of catalytic activation of molecular H2 and surface diffusion of H atoms, followed by storage on carbon structural defects through either chemical bonding or intercalation. We will present both modeling and experimental results.

11:25 AM Keynote

Low Temperature Hydrogen Adsorption Capacity of Carbon Nanoparticles: *Helmut Hermann*[1]; Melanie Hentsche[1]; Andrei Touzik[1]; Agnieszka Kuc[2]; Roswitha Wenzel[2]; Gotthard Seifert[2]; [1]IFW Dresden; [2]TU Dresden

Accurate quantum mechanical calculations have shown that the effective interaction potential between hydrogen molecules and a graphene sheet has minima at a distance of about 0.3nm from the surface of the graphene layer. Thermodynamic considerations based on this result give an estimate of the hydrogen storage capacity of graphene sheets and its dependence on temperature and pressure (for example, 0.5wt% at 100K and approximately 2wt% at 80K at 0.1MPa). To study this effect experimentally, we built up a Sievert's like apparatus allowing temperature variation between 300K and 40K at a maximum pressure of 200 bar. For C60 fullerenes, the results confirm recent data obtained at 77K. We consider also nanometre-scale carbon powders produced by ball-milling of graphite as a cheap and promising material for hydrogen storage. Variation of the milling conditions including milling at low temperatures is shown to be a way to optimise the storage capacity of carbon powders.

11:45 AM

Electrochemical Hydrogen Storage in Assembly of Nanotubular TiO2 and Carbon Nanotubes: Pradeep Pillai[1]; *Krishnan S. Raja*[1]; Manoranjan Misra[1]; [1]University of Nevada, Reno

Hydrogen storage behavior of carbon nanotubes (CNTs) has been investigated intensely because of its ultra-light weight and large surface area. In this investigation, hydrogen charging and discharging studies were carried out by electrochemical method using an assembly of nanotubular titanium dioxide and carbon nanotubes. Anodization of Ti foil resulted in formation of ordered nanotubular TiO2 layer. This nanoporous TiO2 was used as template for growing carbon nanotubes. Cobalt was the catalyst for chemical vapor deposition of CNTs. Preliminary results indicate a hydrogen discharge capacity of about 1740 mA-h/g(CNT) for the total assembly and 1100 mA-h/g for CNT alone. Hydrogen charging experiments are being carried out by impregnating Mg nanoparticles inside the nanotubular arrays.

Advanced Materials for Energy Conversion III: A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda: Metal, Alloys and Energy Materials

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Reactive Metals Committee
Program Organizers: Dhanesh Chandra, University of Nevada; John J. Petrovic, Petrovic and Associates; Renato G. Bautista, University of Nevada; M. Ashraf Imam, Naval Research Laboratory

Thursday AM Room: 214B
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: M. Ashraf Imam, Naval Research Laboratory; Etsuo Akiba, AIST; Ji-Cheng Zhao, General Electric Company

8:30 AM Invited
Fundamental Analysis of the MM'X Phosphides and Arsenides: A Promising Series Exhibiting Potentially High Magneto-Caloric Performances: *Daniel Fruchart*[1]; F. Allab[2]; M. Balli[1]; P. de Rango[1]; D. Gignoux[1]; E. K. Hlil[1]; A. Lebouc[1]; S. Miraglia[1]; C. Rillo[3]; J. Tobola[4]; M. G. Shelyapina[5]; N. E. Skryabina[6]; P. Wolfers[1]; R. Zach[4]; [1]Centre National de la Recherche Scientifique; [2]LEG, Institut Natinal Polyctechnique de Grenoble; [3]Instituto de Ciencias de Materiales de Aragon; [4]University of Cracow; [5]St. Petersburg State University; [6]Perm State University

The pnictides MM'X, phosphides and arsenides of transition metals can exhibit very peculiar (ferro)magnetic properties. Systematic changes of magnetic ordering occur via first order or meta-magnetic transitions, in such a way that marked contribution of entropy with or without magneto-elastic effects are characteristics of these transitions. E.g. for MnFeP1-xAsx compounds, a large magneto-caloric effect (MCE) was realized by application of moderate magnetic fields only. For a long time, we have analyzed the MM'X series for their fundamental characteristics (magnetization, neutron scattering, specific heat, Mössbauer...) as well from systematic band structure calculations. As for the parent series of monopnictides MnAs-MnP (M' ~ vacancy), we better understand the nature of the magnetic forces (polarization, exchange), that mostly proceeds via electronic unstabilities. Thus a molecular field model looks not the best approximation to develop MCE analyses.

8:50 AM Invited
Synchrotron X-Ray Absorption Spectroscopy (XAS) Studies for Understanding Dopant Effects in NaAlH4: *Tabbetha A. Dobbins*[1]; Roland Tittsworth[2]; John Olivier[1]; Yuri Lvov[1]; [1]Louisiana Tech University; [2]Louisiana State University

Transition metal dopant additions to complex metal hydrides enhance hydrogen adsorption/desorption kinetics. The atomic-scale location of dopants has been reported, however, a mechanism for the kinetic enhancements associated with these dopants has not been fully developed. X-ray absorption spectroscopy (XAS) is an element specific probe for local atomic structure determination. This work explores the local bonding environment around Al in Ti-doped NaAlH4-both before and after dopant additions-using x-ray absorption spectroscopy (XAS). The local bonding environment of Ti is also explored. Layer-by-layer (LbL) nanoassembly is used to catalyze the NaAlH4 powders. LbL allows a more uniform distribution of dopants. Transmission electron microscopy (TEM) is used to study microstructural development.

9:10 AM
Heat Capacity Determination of Organic "Plastic Crystals" by Adiabatic Calorimetry from 3K to 350K: *Anjali S. Talekar*[1]; Raja S. Chellappa[1]; Dhanesh Chandra[1]; Wen-Ming Chien[1]; Alexandra O. Tsokol[2]; J. A. Sampaio[2]; [1]University of Nevada; [2]Iowa State University

Thermal Energy Storage [TES] systems for passive heating systems and other thermal applications invariable use the latent heat effect of solid state phase change materials. Examples of alcohol and amine derivatives of neopentane include: Pentaerythritol [PE:C(CH2OH)4)], Pentaglycerine [PG:(CH3)C(CH2OH)3], Neopentylglycol [NPG:(CH3)2C(CH2OH)2], Neopentylalcohol [NPA:(CH3)3C(CH2OH)], Tris(hydroxymethyl) aminomethane [TRIS:(NH2)C(CH2OH)3], and 2-amino-2-methyl-1,3-propanediol [AMPL:(NH2)(CH3)C(CH2OH)2]. Low temperature heat capacities of such organic compounds with unusually high enthalpies of solid-solid transitions have been determined from 3K to 350K using a semi-adiabatic heat pulse calorimeter. These organic compounds undergo solid-solid phase transitions from low temperature ordered polymorphs (tetragonal, monoclinic, etc.) phase to an orientationally disordered high temperature "Plastic Crystal" modulated cubic phase (FCC or BCC). The effect of the number of hydroxyl groups (that provide the hydrogen bonding for the crystal structure framework) on the heat capacities and the dependence of the Debye temperature (TD) on the number of hydroxyl group is also presented in this study.

9:30 AM
Ionic Conductivity Measurement of Orientationally Disordered Crystals: Tris(hydroxymethyl)aminomethane + 2-Amino-2-Methyl-1,3-Propanediol Binary System: *Md S. Rahman*[1]; Raja S. Chellappa[1]; Suresh Chandra Divi[1]; Dhanesh Chandra[1]; [1]University of Nevada

The amine derivatives of neopentane (Tris(hydroxymethyl)aminomethane: TRIS and 2-Amino-2-Methyl-1,3-Propanediol: AMPL) belong to special class of organic molecular crystals that undergo solid-solid phase transition from a low temperature ordered phase to an orientionally disordered high temperature phase with an unusually high enthalpy of transition. The ionic conductivity of pure TRIS and AMPL show a noticeable increase in the orientionally disordered phase when compared to the low temperature structure. Such an increase in ionic conductivity makes these materials potential candidates for semiconductor applications. In this work, we will present results from our ionic conductivity measurements for pure as well as binary mixtures of TRIS and AMPL. The effect of temperature as well as compositional dependencies on the ionic conductivity of binary solid solutions will be discussed.

9:50 AM
Heat Capacity Measurement of Organic "Plastic Crystal" Thermal Energy Storage Materials Using Modulated Differential Scanning Calorimetry: Tris(hydroxymethyl)aminomethane-2-Amino-2-Methyl-1,3-Propanediol Binary System: Suresh Chandra Divi[1]; *Raja S. Chellappa*[1]; Dhanesh Chandra[1]; [1]University of Nevada

Tris(hydroxymethyl)aminomethane (TRIS) and 2-Amino-2-Methyl-1,3-Propanediol (AMPL) belong to a special class of organic molecular crystals that are potential candidates for thermal energy storage applications. TRIS and AMPL undergo solid-solid phase transitions from a low temperature layered structure (TRIS: orthorhombic, AMPL: Monoclinic) to an orientationally disordered plastic crystal phase (TRIS: BCC, AMPL: BCC). A systematic calorimetric study of organic "plastic crystal" thermal energy storage materials is being conducted using Modulated Differential Scanning Calorimetry (MDSC). The goal of this study is to establish a thermodynamic database of heat capacities of pure as well as binary mixtures of these compounds. Recent calorimetric studies on pure and binary organic "plastic crystals" using MDSC has shown that MDSC is a fast and powerful technique for accurate measurement of absolute heat capacities. In this work, we report the molar heat capacities of ten binary mixtures of TRIS-AMPL from xTRIS=0 to xTRIS=1.

10:10 AM
Comparison of Hydrogen Diffusion Properties of Materials for the Yucca Mountain High Level Waste Repository: *Joshua H. Lamb*[1]; Dhanesh Chandra[1]; [1]University of Nevada

Various materials intended for use at the Yucca Mountain High Level Waste Repository were studied for hydrogen diffusion and trapping effects using the electrochemical method first proposed by Devanathan and Satchurski. The environment present at repository has the propensity to generate hydrogen at the surface of materials leading to the trapping of hydrogen and detrimental effects on material properties. This study looks at these effects resulting from the electrochemical transport through a membrane sample. The electrochemically obtained permeation current is used to calculate the reversible and irreversible hydrogen diffusion properties. This is then related to the total hydrogen stored in and diffused through the material.

Alumina and Bauxite: Precipitation Fundamentals

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Jean Doucet, Alcan Inc; Dag Olsen, Hydro Aluminium Primary Metals; Travis J. Galloway, Century Aluminum Company

Thursday AM
March 16, 2006
Room: 7B
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Songqing Gu, Zhengzhou Research Institute of Chalco

8:30 AM Introductory Comments

8:40 AM
Influence of Alumina Morphology and Structure on Its Strength: *Songqing Gu*[1]; Lijuan Qi[1]; [1]Zhengzhou Research Institute of Chalco

A study of influences of alumina morphology and structure on its strength has been carried out. It is found that agglomerated alumina hydrate particles have many more opportunities to be strengthened than those particles which grow individually. The strength of the agglomerated alumina particles will be kept higher because the water vapor can be released gradually through the gaps among the agglomerated hydrate particles during calcination so as not to damage the whole structure of the particles. In order to obtain alumina with high strength it seems necessary that some small alumina hydrate crystals should be agglomerated in the first step and further strengthened by following growth in the relatively high supersaturation.

9:05 AM
Study on the Oscillation Phenomena of Particle Size Distribution during the Seeded Agglomeration of Sodium Aluminate Liquors: Jianguo Yin[1]; Qiyuan Chen[1]; *Zhoulan Yin*[1]; Jiangfeng Zhang[2]; [1]Central South University; [2]Institute of Technology and Economy in Nonferrous Metals

Chaotic and Fractal theory was used to study the oscillation phenomena of particle size distribution (PSD) in the agglomeration process of sodium aluminate solution. Conclusions were made as follows: PSD of particles is in macroscopic disorder, while it is regular in certain ranges; curves of PSD sometimes appear to oscillate, but particles for a certain range own general rules in the whole process; that is, the curves of PSD oscillating decrease with time for small and median size particles yet oscillating increases for large particles; the minor change of initial conditions can be enlarged in the process, and the particle size information will be affected. As a result, the butterfly effect of the PSD appears; each curve of PSD has the space fractal character for particles of certain range. More precise structure of curves can be identified if smaller divided rule of particle size is adopted.

9:30 AM
Study on the Rate of Crystal Growth and the Phenomena of Template Crystallization during Seed Precipitation from Sodium Aluminate Solutions: *Bai Wanquan*[1]; Yin Zhonglin[1]; Li Wangxing[1]; Qi Lijuan[1]; Yang Qiaofang[1]; [1]Zhengzhou Research Institute Alumimun Corporation of China Ltd.

Seeded, the precipitation from sodium aluminate solutions with high concentration of diasporic bauxite was studied using a laboratory batch crystallizer. The results show that the enhancement of particles is mainly contributed to agglomeration with the speed of 7-8 μm/hour. There are some particles, which are bigger, in the shape of similar sphericity. And the crystallites on the surface are small and identical in size observed by SME. The center of these particles is hollow. It is conjectured that the formation of these particles is based upon some crystal templates, and Al(OH)3 is precipitated layer by layer on the surface of the template. The template is probably dissolved after the shell of Al(OH)3 has formed in the precipitation. That is why the center of the particles is hollow. The alumina particles produced remain the same shape as the original Al(OH)3 particles, and their strength after attrition is still high.

9:55 AM
Effects of Monohydroxy-Alcohol Additives on the Seeded Agglomeration of Sodium Aluminate Liquors: Jianguo Yin[1]; Jie Li[1]; Yanli Zhang[2]; Qiyuan Chen[1]; *Zhoulan Yin*[1]; [1]Central South University; [2]Zhengzhou Research Institute of Chalco

A series of monohydroxy-alcohol additives were adopted in Bayer process. The effects of dosage and carbon chain length on precipitation ratio of sodium aluminate liquors and particle size distribution (PSD) of gibbsite were investigated. Experimental results indicated that: all three monohydroxy-alcohols can increase precipitation ratio of sodium aluminate liquors at the proper dosage. They can accelerate precipitation process obviously at lower dosage at the beginning and yet last longer effects at higher dosage. Particle size of gibbsite products is enlarged when 1-Octadecanol is added at low dosage, yet the product fines under all other conditions. It can be concluded that: long chain additives with low dosage or short chain additives with high dosage is favorable for the seeded agglomeration of sodium aluminate liquors. The relationship between carbon chain length and its dosage may be complementary. Action mechanism among monohydroxy-alcohol additives, sodium aluminate liquors and gibbsite crystals will be further investigated based on the information mentioned above.

10:20 AM Break

10:35 AM
Study on the Effect of K2O on Seed Precipitation in Sodium Aluminate Liquors: *Yanli Xie*[1]; Qun Zhao[2]; Zhenan Jin[3]; [1]Georgia Institute of Technology; [2]Zhengzhou Research Institute of Chalco; [3]Northeastern University

Potassium oxide accumulates during liquor recycling, and its concentration can be up to 55 g/l in pregnant liquor with the total soda 178.4 g/l, which causes negative effects on the seed precipitation procedure. This paper studied the effect of K2O on precipitation yield and hydrate particle size distribution when the concentration of K2O is in the range of 0-60 g/l from 160 g/l caustic soda. The results demonstrated that the potassium contaminated sodium aluminate liquor has higher precipitation ratio, but its effect on particle size distribution is complicated, which varied with time and potassium concentration. The mechanism on why potassium affects precipitation procedure is also studied in this paper.

11:00 AM
Influences of Cation and Anion Ions and Some Kinds of Additives on the Aggregation of Seeds: *Lijuan Qi*[1]; Songqing Gu[2]; [1]Zhengzhou University; [2]Zhengzhou Research Institute Alumium Corporation of China, Ltd

There have been many works on the precipitation mechanism of sodium aluminate solution. However, due to the complexity of the structure of the solution and many factors affecting the process of precipitation, there is no agreement on the mechanism of nucleation, growth, and aggregation of aluminum hydroxide in the process of precipitation so far. In this paper, the influences of cation and anion ions and some kinds of additives on the superficial charges of seeds are investigated, and then the effects of them on the aggregation of seeds are further studied.

11:25 AM
Effects of Power Ultrasound on Precipitation Process of Sodium Aluminate Solutions: *Jilai Xue*[1]; Shaohua Li[1]; Baoping Song[1]; [1]University of Science and Technology Beijing

Sodium aluminate solutions for alumina production have been ultrasound treated to enhance the precipitation seeded in a laboratory Bayer process. The effects of sound power intensity, sonication time, and temperature on the precipitation process were investigated. In this paper the results will be discussed with respect to precipitation efficiency and process kinetics.

Aluminum Reduction Technology: Fundamentals, Emerging Technologies and Inert Anodes - Part II

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee
Program Organizers: Stephen Joseph Lindsay, Alcoa Inc; Tor Bjarne Pedersen, Elkem Aluminium ANS; Travis J. Galloway, Century Aluminum Company

Thursday AM
March 16, 2006
Room: 7A
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Martin Iffert, Trimet Aluminium AG

8:30 AM
On the Entropy Generation in Aluminum Electrolysis Cell: Adam Holda[1]; Janusz Donizak[1]; Juan Mendez Nonell[2]; *Zygmunt Kolenda*[1]; [1]AGH University of Science and Technology; [2]Centro de Investigacion de Quimica Aplicada

Classical thermodynamic analysis of any technological processes is usually based on the First Law of Thermodynamics in the form of energy (enthalpy) balances. However, deeper thermodynamic analysis leads to the conclusion that such approach is not sufficient. The first Law of Thermodynamics guarantees the exact equivalence of the various forms of energy but it does not guarantee interconversibility. One of the possible solutions comes from the Second Law of Thermodynamics using entropy as the state function describing degree of process irreversibility. There are many effects whose presence during electrolysis process renders it irreversible, most important are: heat transfer, spontaneous chemical reactions, electric current flow. Engineers should be able to recognize irreversibilities, evaluate their influence and develop cost-effective means for reducing them. Paper presents the method of calculation of entropy generation occurring during the aluminum electrolysis elementary processes.

8:55 AM Invited
Effect of Additive V2O5 on Sintering and Corrosion Resistance of Inert Anodes of Cermets: *Xi Jinhui*[1]; Yao Guangchun[1]; Liu Yihan[1]; [1]Northeastern University

The inert anodes of nickel ferrite-based cermets doping V2O5 were prepared. The effect of V2O5 on sintering and corrosion resistance was researched. The results indicate that when the additive V2O5 was added, Ni2FeVO6 was produced, which has low melting point 625~652°C. Ag also became liquid at 961°C, so the sintering is liquid sintering. Doping V2O5 makes the grains of ceramic grow completely with the shape of octahedron and grains become coarse. The corrosion rate of samples with V2O5 is much lower than that of sample without V2O5. Ni2FeVO6 concentrated at grain boundary and it has good corrosion resistance. Ni2FeVO6 reinforces the corrosion resistance of the grain boundary and liquid makes the grains of ceramic grow completely, so the corrosion resistance of the sample with V2O5 was strengthened.

9:20 AM Invited
Effect of Additive V2O5 on Conductivity of Inert Adnodes: *Xi Jinhui*[1]; Yao Guangchun[1]; Liu Yihan[1]; [1]Northeastern University

The inert anodes of nickel ferrite-based cermets were prepared by the powder metallurgy method using NiO, Fe2O3, Ag and a little V2O5 as raw materials. The effect of V2O5 on microstructure and conductivity was researched. The results indicate when V2O5 was added, Ni2FeVO6 was produced. During sintering, Ni2FeVO6 became liquid, and it made metal phase distribute in slender strip form; EDX analysis shows there is ceramic phase in the metal phase. The facts show V2O5 can improve the wettability between Ag and ceramics. At the same time, the conductivity is improved remarkably. When the amount of V2O5 is 2.0%, the conductivity is 7 times of that of the sample without V2O5. Moreover, a remarkable change of conductivity took place from 450°C to 650°C. This must be a change in magnetism induced by the V2O5.

9:45 AM
Study on Corrosion of Cermet Inert Anode Based on Nickel Ferrite Spinel: *Tao Luo*[1]; Zhao-Wen Wang[2]; [1]Sunstone Carbon Technology Center; [2]Northeastern University

According to the corrosion comparison of anodes ($NiFe_2O_4$+NiO+Cu+Ni) under different conditions, the paper discusses the corrosion of metal and ceramic phases. The metals Cu and Ni are present as the Cu_xNi_y alloy in the anode. The Ni of Cu_xNi_y alloy was primarily oxidized in an O_2-atmosphere at 900°C. In the polarization experience, the Ni content of the anode decreased remarkably after electrolysis, and the main residual metal was Cu. For the nickel ferrite spinel, the electrolyte did not corrode the anode matrix at 900°C in the absence of oxygen. After adding O_2 to the electrolyte, the corrosion happened. The SEM of an anode after electrolysis showed that the Fe_2O_3 of nickel ferrite spinel dissolved in the electrolyte and hence resulted in corrosion of the anode matrix.

10:10 AM
On the Corrosion Behavior of $NiFe_2O_4$–10NiO Based Cermets as Inert Anodes in Aluminum Electrolysis: *Yanqing Lai*[1]; Xinzheng Li[1]; Jie Li[1]; Zhongliang Tian[1]; Gang Zhang[1]; Yexiang Liu[1]; [1]Central South University

NiFe2O4–10NiO based cermets of different metallic phase compositions (Ni, Cu, and Cu-Ni alloy) were prepared with cold isostatic pressing-sintering process. All samples were pretreated in nitric acid to remove the metal bled out of the sample surface at high sintering temperature. Electrolysis test results showed that, corrosion resistance was difficult to be differentiated effectively just by comparing external changes, mass loss, impurity content in the bath samples taken from the cell during electrolysis or in the aluminum metal. The cermet components, that corrode into the melt follow the Boltzmann distribution with respect to distance from the inert anode. Such distribution may be identified by gathering the impurity ions near the cathode with electric force under polarization condition. This uneven distribution together with different algorithms has great potential to estimate the corrosion rate of inert anodes. An improved test cell configuration and comprehensive evaluation method were used to differentiate the corrosion resistance of cermets.

10:35 AM
Study on Sintering Technique of Nife2O4/Sicw Used as Matrix of Inert Anodes in Aluminum Electrolysis: *Shu-Ting Zhang*[1]; Guang-Chun Yao[1]; Yi-Han Liu[1]; [1]Northeastern University

In order to improve deficiencies of NiFe2O4 spinel used as matrix of inert anode in aluminium electrolysis, NiFe2O4/SiCw were prepared by the solid state reaction for the first time. Microstructural changes were observed by scanning electronic microscope and phase was determined with x-ray detector. Effect of sintering temperature and times on density, porosity and microstructure were researched, and the reasons that caused the difference were discussed deeply. At the same time the thermodynamical compatibility of NiFe2O4 and SiCw was proved under 1200° by DTA. The results showed that the microstructure was more homogeneous when the sintering temperature reached 1180° and the density attained their maximum about 6-hours sintering. The appropriate sintering technique of NiFe2O4/SiCw composite materials selected 1180°×6h.

11:00 AM
Electrolysis Test of 1350A Drained Cathode Reduction Cell with TiB2-Coated Cathode: *Feng Naixiang*[1]; Qi Xiquan[1]; Peng Jianping[1]; [1]Northeastern University

For a new drained cathode cell, detailed operations of cell building, packing, baking, starting-up and normal operations are presented here. Cathode inclination is 10o. TiB2-coated cathode is adopted. The cell is dryly built, carbon-particulate baked and dryly started up. The average current is 1350A. Feeding, tapping, voltage adjustment, etc, are almost the same as those of commercial cells. After 100 hours of continuous electrolysis, it is found that the cell performs rather steadily. Cell noise is about 9mv. The cell performed exactly like industrial cell. Based on metal production and leftover, current efficiency is found not lower than 86% which closes commercial cells. TiB2 coating is firm without any damage and hence effects good protection for carbon cathode. It is analyzed that the dissolution speed of TiB2 is about 1.0g/h-1•m-2. Test results not only

verified the theoretical analysis beforehand, but also proved the feasibility of such cell structure.

11:25 AM
Producing Aluminum-Silicon Alloys from Andalusite Ore by Carbothermal Reduction Method: *Huimin Lu*[1]; Mingfa Chen[2]; Qiang Liu[2]; Shuang Chen[2]; [1]University of Science and Technology Beijing; [2]Beijing Yanhuang Investment Management Company Ltd.

A big andalusite ore bed was found in Kuerle District, Xinjiang, China, and its reserves are the largest and quality best in the world. In this paper, the feasibility of producing aluminum-silicon alloys by carbothermal reduction of andalusite is studied. The mix proportion of furnace charge is as follows, andalusite ore 50~80mass% in which the impurities are quartz, calcium oxide and magnesia etc. and the total impurities amount is not in excess of 20mass%; reducer gas coal and petroleum coke 20~40mass%, the mix proportion of gas coal and petroleum coke 8:2~6:4; adhesive paper industry wastewater 5~8mass%. First, all these raw materials are mixed uniformly in proportion, briquetted and dried, then the carbothermal reduction experiments are conducted in a multifunction sintering kiln with reducing temperature 1950~2150ºC and reducing time 2h, the aluminum-silicon alloys containing 53~58mass% aluminum, 32~37mass% silicon are obtained with aluminum recovery rate 80~85% and silicon 70~75%.

11:50 AM
The Development and Application of Data Warehouse and Data Mining in Aluminum Electrolysis Control Systems: *Xiangtao Chen*[1]; Jie Li[1]; Wengen Zhang[1]; Zhong Zou[1]; Fenqi Ding[1]; Yexiang Liu[1]; Yanqing Lai[1]; [1]Central South University

With the development of network and control systems, the amount of data acquired and stored in aluminum electrolysis control systems has been growing continuously. How to effectively mine useful information hidden in these data is an attractive research topic that will help to enhance the functions of the control systems. In this paper data warehouse and data mining concepts were introduced into aluminum electrolysis control systems and a data-mining tool called "aluminum electrolysis data miner" was developed. There are three core mining components in it: the gray association analysis, the cluster analysis based on connected components and the offset coefficient analysis. For different uses and from different profiles, these component models deeply analyze and mine the data stored in a control system, obtaining the knowledge that can reflect the status of every pot and every potline, in-time adjusting various operating and control parameters and providing decision support for operators.

12:15 PM
Navier-Stokes Equations in Presence of Laplace Forces in the Aluminum Reduction Cell: *Augustin Iosef Moraru*[1]; Aureliu Panaitescu[1]; [1]Politehnica University of Bucharest

Conventional mathematical models of aluminum reduction cells are based on general electromagnetic equations, two-dimensional Navier-Stokes equations and include common turbulence modeling (k-). These models are not able to describe the true mechanisms involved in the motion of two thin liquid layers, because they neglect the vertical transport impulse, which in fact is dominant over the horizontal one. This paper describes the development of a more complete, dynamic, two shallow-layer models which are based on the works of V. Boyarevich. This model takes into account the viscous drag and the surface drag, as well as the variation of the layer thickness.

12:40 PM END

Amiya Mukherjee Symposium on Processing and Mechanical Response of Engineering Materials: Modeling of Material Behavior

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Shaping and Forming Committee
Program Organizers: Judy Schneider, Mississippi State University; Rajiv S. Mishra, University of Missouri; Yuntian T. Zhu, Los Alamos National Laboratory; Khaled B. Morsi, San Diego State University; Viola L. Acoff, University of Alabama; Eric M. Taleff, University of Texas; Thomas R. Bieler, Michigan State University

Thursday AM
March 16, 2006
Room: 217C
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Michael Josef Zehetbauer, University of Vienna; Peter Martin Anderson, Ohio State University

8:30 AM Invited
Uniform Terminology for Strain Induced Boundaries: *Hugh J. McQueen*[1]; Enrico Evangelista[2]; Marcello Cabibbo[2]; [1]Concordia University; [2]University Politecnica delle Marche

The terms for strain induced boundaries should reflect the creating mechanism, the function performed and the regions separated. Dislocation glide is the primary mechanism in creep and hot and cold working, being less influenced by dynamic recovery as temperature T falls and strain rate rises. Dependent on stress, boundaries contain dislocations geometrically necessary for the misorientations and dipoles (denser in cold work); cell walls are rather incidental whereas higher-angle block walls enclose cell clusters developing different slip. After hot forming, polygonized walls consist mainly of low-energy, geometrically-needed dislocations; such subgrain boundaries during steady state straining continually rearrange in a stress-defined substructure. Following Taylor-defined multiple-slip in polycrystals, grains divide into deformation bands slipping on different systems and rotating differently to create texture components. The separating transition boundaries being permanent increase in misorientation with strain, becoming indistinguishable from the grain boundaries that are disturbed by dislocations, extended under strain and serrated.

8:50 AM
Processing Path Design and the Integration of Texture and Micro-Texture Evolution: *Hamid Garmestani*[1]; [1]Georgia Institute of Technology

A processing path model is proposed to quantitatively describe the texture and micro-texture evolution in an explicit mathematical formula. This model is used to guide the materials design by taking full advantage of the database of experimental data and simulation results from physical models for texture evolution. The streamline grid in material's hull developed from this model is used to investigate if any processing path may exist from an initial texture of raw material to a final texture with desired property. If the solutions exist, the family of processing paths presented by the streamline grid make it possible for further design optimization. This methodology provides a systematic approach to calculate the optimal processing path to the desired texture using statistical continuum mechanics based on one and two-point distribution functions in the calculation of the processing path evolution parameters and the corresponding microstructure.

9:10 AM
Texture Development in BCC Metals during Upsetting: Myoung-Gyu Lee[1]; Levit I. Levit[2]; Charles E. Wickersham[2]; *Peter Martin Anderson*[1]; [1]Ohio State University; [2]Cabot Corporation

A finite element analysis based on rate-dependent crystal plasticity is used to study texture development in BCC metals during upset deformation. Both {110}/<111> and {112}/<111> slip systems are modeled. Each integration point in the finite element mesh follows a polycrystalline constitutive relation for 200 grains that deform according to a Taylor isostrain assumption. Random, <111>, <110>, and <100> transversely-isotropic

initial textures are considered. For zero friction, random initial textures evolve to ~60% <111> and ~30-40% <100>. Transversely-isotropic <111> and <110> textures both produce <111>, but <100> textures remain <100>. Friction induces barreling and shear deformation, so that <111> and <100> textures becomes diffuse. These trends are compared to measured pole figures from upset BCC metal samples.

9:30 AM Invited

Constitutive Modelling of Large Strain Work Hardening of Metals under Different Conditions of Plastic Deformation: *Michael Josef Zehetbauer*[1]; Jan Kohout[2]; Christian Holzleithner[1]; [1]University of Vienna; [2]University of Defence Brno

The paper introduces a composite model which has been originally developed by M. Zehetbauer for a quantitative description of large strain cold working. Later the model has been successfully modified for description of large strain hot working, too. Recently it has been shown that the model also accounts for cases of cold work under elevated hydrostatic pressure (the so-called "Severe Plastic Deformation – SPD") which achieve nanocrystalline structures. All model variants have been tested by strain-dependent measurements of the dislocation density as well as of the cell and/or subgrain size, and – concerning cold work conditions - of the concentration of deformation induced vacancies.

9:50 AM

On the Control of Microstructural Degrees of Freedom in Deformation Processes: *Veera Sundararaghavan*[1]; Nicholas Zabaras[1]; [1]Cornell University

The high cost of manufacturing critical components can be greatly reduced with the development of mathematically and physically sound computational methodologies for multi-scale process design. We present our recent developments in expanding the design space in forming processes by including microstructural degrees of freedom as a design variable in addition to macro-constraints. We have developed a multi-length scale continuum sensitivity method for thermo-elasto-visco-plasticity combined with microstructure evolution in polycrystalline materials. In particular, sensitivities of fields dependent on microstructural degrees of freedom are exactly defined and an averaging principle (linking hypothesis) is developed to compute sensitivity fields at the macroscopic level. These computed sensitivities are used within a gradient-based optimization framework for the computational design of metal forming processes for polycrystalline materials. The effectiveness of the developed design techniques are demonstrated with examples involving control of distribution of elastic and plastic properties in the final product by tailoring the final microstructures.

10:10 AM

Mechanical Modeling of Bimodal Al-5083 Alloys: *K. T. Ramesh*[1]; S. P. Joshi[1]; H. Zhang[1]; E. J. Lavernia[2]; E. S. C. Chin[3]; J. M. Schoenung[2]; [1]Johns Hopkins University; [2]University of California, Davis; [3]Army Research Laboratory

Cryomilled Al-5083, comprising a bimodal mixture of nano-crystalline (NC) and coarse-grained (CG) microstructure (of nominal grain sizes 200 nm and 1 mm respectively) has shown high strength while retaining ductility. The strengthening effect is due to the NC phase whereas the ductility is imparted by the CG phase. The rule-of-mixtures approach is insufficient to model the observed experimental mechanical behavior. In this paper, the Mori-Tanaka mean-field approach is adopted to predict the mechanical response of the alloy. The formulation allows elasto-plastic representation of both phases (Weng et al.) as observed in the material. The analysis indicates that the relative phase distribution appears to promote the strengthening behavior in this material. Acknowledgements: SPJ, KTR and HZ acknowledge the financial support provided by the Army Research Laboratory through Grant No. DAAL01-96-2-0047. JMS and EJL acknowledge the financial support provided by the Office of Naval Research under contract N00014-03-C-0164.

10:30 AM Break

10:40 AM Invited

On the Composition of bcc Cu Alloy Precipitates in bcc Fe: *Morris E. Fine*[1]; Mark D. Asta[1]; J. Zhe Liu[1]; Axel Van De Walle[1]; Gautam Ghosh[1]; [1]Northwestern University

While ab initio calculations of the mixing energy at 0 K predict that bcc Cu precipitates in bcc Fe should be pure Cu, they contain actually a very substantial amount of Fe (almost 50%) according to atom probe studies. Possible sources of this difference include the following. At the aging temperature (approximately 800 K), at metastable equilibrium there may be a substantial amount of Fe in the bcc Cu precipitate. Also at 0 K bcc Cu is mechanically unstable, the elastic constant C' is negative but it increases with Fe content becoming positive near 50% Fe-50% Cu. Additionally, interfacial forces arising from coherency may act to supress the mechanical instability. These possibilities will be discussed in light of the ab initio calculations. The effect of the negative C' on the yield stress will also be discussed.

11:00 AM

An Artificial Neural Network Material Model Implemented within Finite Element Analysis for Prediction of High Temperature Rheological Behavior of Nickel Aluminide: B. Scott Kessler[1]; *Khaled B. Morsi*[2]; A. Sherif El-Gizawy[3]; [1]Kestek; [2]San Diego State University; [3]University of Missouri-Columbia

Accurate virtual modeling and process simulation prior to the start of actual production can many times save considerable time, effort, and money. Conventional constitutive material models have been developed and integrated with finite element analysis in an effort to achieve these ends. These models can only perform accurately if the constitutive model used properly reflects the materials behavior. More recently, artificial neural networks (ANN) have been suggested as a means to more properly describe rheological behavior. In the present work, a robust ANN with the ability to determine flow stresses of a nickel aluminide superalloy based on strain, strain rate, and temperature is developed and linked with finite element code. Comparisons of this novel method with conventional means are carried out to demonstrate the advantages of this approach.

11:20 AM

Influence of Grain Boundary Crystallography on the Flow Stress and Dynamic Failure Strength: *Mukul Kumar*[1]; Roger Minich[1]; Kerri Blobaum[1]; James Stolken[1]; [1]Lawrence Livermore National Laboratory

Recent results show that the Hall-Petch scaling of yield stress needs to take into account a parameter called grain boundary character distribution, which is related to the frequency of crystallographically "special" boundaries in the microstructure. This can be manipulated by a processing methodology called grain boundary engineering. The role of microstructures in the process of void nucleation and growth leading to failure during shock loading of materials is less understood. We shall report on the scaling observed in the case of dynamic failure or spall under shock deformation conditions in high purity copper. The spall strength is observed to increase as the length scales coarsen, which is counter to the Hall-Petch relationship. The role of nucleation site density and grain boundary character distribution in understanding this behavior as a function of impact pressure will be explored in the context of the scaling laws that emerge from this data.

11:40 AM

Molecular-Dynamics Based Cohesive Zone Model for Intergranular Fracture in Aluminum: *Vesselin Yamakov*[1]; Dawn Phillips[2]; Erik Saether[3]; Edward H. Glaessgen[3]; [1]National Institute of Aerospace; [2]Lockheed Martin Space Operations; [3]NASA Langley Research Center

The atomistic mechanisms of grain-boundary debonding during intergranular fracture in aluminum are modeled using molecular-dynamics simulation. Through a developed statistical procedure, a constitutive traction-displacement relationship that characterizes the load transfer across a growing nanoscopic intergranular crack is extracted from the atomistic simulations and is recast in a form that is suitable for inclusion within continuum finite element models. In this way, a finite-element cohesive zone model, which incorporates the atomistic aspects of the elasto-plastic processes at, and near the crack tip is created. Depending on the crystallography of the grain-boundary interface and the dynamics of crack propagation, the model can predict, both, ductile and brittle types of grain-boundary decohesion. The developed procedure represents a multiscale approach to model the influence of the plastic zone around a crack tip using finite-element continuum simulation parameterized by atomistic molecular-dynamics simulation.

12:00 PM

Simulation-Based Investigations of Intragranular Deformations in Single-Phase and Two-Phase Polycrystals: *Paul Dawson*[1]; Jae-Hyung Cho[1]; Tito Marin[1]; [1]Cornell University

Numerical modeling of material systems provides a powerful complement to experiments for investigating the manner in which a system's constituent components individually respond to external loading and collectively act to bear a load. In polycrystalline systems, the elastic and plastic anisotropies of single crystals give rise to heterogeneous mechanical environments at the scale of grains. In responding to load, the crystals deform inhomogeneously with the stress and deformation varying spatially both within and among crystals. In this presentation, we describe three-dimensional, elastoplastic, finite element simulations of polycrystals in which individual crystals are resolved with many elements. Motivated by experimental trends, we examine the spatial distributions of strain and of slip system activity in single-phase and twophase polycrystals comprised of crystals with cubic and hexagonal lattice structures. Attention is given to the influences of such factors as the proximity to grain boundaries, the presence of a free surface, and themorphology of the grains on the distributions of strain and lattice misorientation.

12:20 PM

Modeling the Micro-Indentation of Metal Matrix Composites: *Mario Roberto Rosenberger*[1]; Elena Forlerer[2]; Carlos Schvezov[1]; [1]University of Misiones; [2]National Commission of Atomic Energy

A dynamic finite element model is developed to quantify the effect of the depth and diameter of the reinforcement in the diameter of the indentation in test samples. The model includes a spherical indenter, which is pressed against a metal containing reinforcing particles. The results are validated comparing the predicted values of indentations, the given properties of the model material and the standard indentation given by the Brinell method, showing a very good agreement. The model is employed to predict indentations in simple configurations of composites consisting of a matrix containing one particle of the same diameter as the indenter. The diameters of the impression, and stress and strain fields for reinforced and matrix materials are compared. Impressions of reinforced materials smaller than those for non-reinforced materials were observed, the values depend on the position of the particle. The results are discussed in relation with the scatter of hardness values.

Bulk Metallic Glasses: Characterization and Mechanical Behaviors

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; Raymond A. Buchanan, University of Tennessee

Thursday AM — Room: 217B
March 16, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Ralf Busch, Oregon State University; Yong Liu, Nanyang Technological University

8:30 AM Invited

Thermodynamics, Kinetics and Configurational Entropy in Bulk Metallic Glass Forming Liquids: *Ralf Busch*[1]; [1]Universitaet des Saarlandes

The low critical cooling rate for glass formation in bulk metallic glass (BMG) forming liquids is of thermodynamic and kinetic origin. BMG forming liquids usually exhibit small entropies of fusions, which indicates short range order in the liquid as well as a high entropy of mixing in the crystalline phases. This small entropy difference between liquid and crystalline mixture leads to a small driving force for crystallization. BMG's exhibit small free volumes even at the melting point as well as small compressibilities, which indicates that they are very dense. This is also reflected in their high viscosity and strong liquid behavior, which slows down nucleation and growth kinetics. The strength parameter D increases monotonically with the number of alloy components. Adam-Gibbs equation and Vogel-Fulcher-Tammann equation describe the kinetics very well. Pronounced shear thinning in the equilibrium melt indicates strong short range order and low configurational entropy in the melt.

8:55 AM

Transformations in Supercooled $Pd_{40.5}Ni_{40.5}P_{19}$: *Shantanu V. Madge*[1]; Harald Rösner[1]; Gerhard H. Wilde[1]; [1]Forschungszentrum Karlsruhe GmbH

Previous work on amorphous $Pd_{40.5}Ni_{40.5}P_{19}$ suggests that the alloy phase-separates on annealing in the supercooled liquid region, manifest through the presence of apparent double glass transitions (Tgs) in subsequent differential scanning calorimetry (DSC) runs. In fact, this alloy system presented almost a model system for phase separating, yet thermally rather stable bulk metallic glasses. Here, $Pd_{40.5}Ni_{40.5}P_{19}$ glassy specimens have been investigated by transmission electron microscopy (TEM, including energy-filtered imaging), high-resolution TEM and DSC measurements. Energy-filtered TEM reveals that the specimens showing the supposed double Tgs are free from any compositional inhomogeneities. Results obtained using 3-D atom-probe will also be presented. Additionally, high-resolution TEM image analysis based on Fourier filtering and based on the calculation of the corresponding autocorrelation functions have been applied. The results are critically discussed with respect of possible phase separation reactions in the material. In addition, alternative origins of the apparent double Tgs will also be discussed.

9:15 AM

Effects of Partial Crystallization on the Mechanical Behaviours of Zr and Mg Based Amorphous Alloys in the Supercooled Liquid Region: S. Gravier[1]; S. Puech[2]; A. Eshtewi[1]; *Jean-Jacques Blandin*[1]; J. L. Soubeyroux[3]; P. Donnadieu[4]; [1]INP Grenoble; [2]INP Grenoble/CRETA/CNRS; [3]CRETA/CNRS; [4]INP Grenoble/LTPCM

High temperature deformation of zirconium and magnesium based BMG were studied in compression in the supercooled liquid region. The effects of temperature and strain rate were investigated, showing the usual transitions from Newtonian to non-Newtonian behaviours when temperature is decreased or strain rate is increased. Depending on the conditions of deformation, important hardening can be obtained during testing, attributed to crystallization effects. To study the interaction between crystallization and high temperature deformation, nanocomposites were elaborated thanks to appropriate heat treatments and the crystallisation mechanisms were investigated. Such nanocomposites were tested in the supercooled liquid region and the resulting changes in the viscoplastic rheologies were discussed in terms of predictions of mechanical models used for composite materials but also in relation with the variations in properties of the amorphous matrix.

9:35 AM

A Study on the Change of High Temperature Deformation Behavior for a Zr-Based Bulk Metallic Glass Due to Annealing in an Undercooled Liquid Region: *Min Soo Kim*[1]; Kwang Seok Lee[1]; Hyun-Joon Jun[1]; Young Won Chang[1]; [1]Pohang University of Science and Technology

A study has been made to investigate the influence of isothermal annealing with various times in an undercooled liquid region on structural changes and deformation behavior of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG). Differential scanning calorimetry, X-ray diffraction and transmission electron microscope have been firstly performed to determine the structural state of the pre-annealed specimens with various annealing conditions. High temperature deformation behavior of these pre-annealed samples has been revealed by conducting a series of compression tests with various initial strain rates. Two different types of flow curves, a large plastic deformation after stress overshoot and a steady state plastic flow without stress overshoot, can be observed at various strain rates after different pre-annealing times. From the results, Newtonian and non-Newtonian viscous flows were characterized by the change of steady-state flow stress, and then the transition boundary could be identified as the specific values of critical initial strain rate.

9:55 AM

Dynamic Mechanical Properties of a W-Reinforced Zr-Based Bulk Metallic Glass Composite: *Morgana Martin*[1]; Naresh N. Thadhani[1]; Laszlo Kecskes[2]; Robert Dowding[2]; [1]Georgia Institute of Technology; [2]U.S. Army Research Laboratory

We will report our current work on dynamic high-strain-rate mechanical properties of zirconium-based bulk metallic glass (Vitreloy106) reinforced with tungsten particles. Dynamic mechanical properties measurements were conducted using reverse Taylor anvil-on-rod impact tests to generate strain rates of 10^3 - 10^5 s^{-1}. High-speed digital photography was used to obtain transient images of the deformation history. Velocity interferometry was used to determine the back surface velocity of the impacted rod-shaped sample. These tests provide qualitative and quantitative information about the transient deformation and failure response of the composites, which is used to better correlate the deformation path with the final recovered geometry. The deformation and failure mechanisms of recovered impact specimens are also characterized and correlated with their structure and tungsten phase distribution. In this paper, the dynamic mechanical property results and their correlations with constitutive equations will be presented. Funded by ARO Grant No. E-48148-MS-000-05123-1 (Dr. Mullins program monitor).

10:15 AM Break

10:25 AM

Microstructure and Shear Band Interactions in Amorphous Metal Matrix Composites Consolidated by ECAE: *Suveen N. Mathaudhu*[1]; K. Ted Hartwig[1]; Laszlo J. Kecskes[2]; Ibrahim Karaman[1]; [1]Texas A&M University; [2]Aberdeen Proving Grounds

Severe plastic deformation by warm equal channel angular extrusion (ECAE) in a 90° die is used to consolidate gas atomized amorphous metal powders (Hf-based: $Hf_{71.3}Cu_{16.2}Ni_{7.6}Ti_{2.2}Al_{12.6}$ -wt% and Zr-based: $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$) with pure Cu, Ni and W crystalline powders at temperatures between Tg and Tx. A fully dense and uniformly consolidated product is achieved after one extrusion. Infiltration microstructures are compared for the three different crystalline phases tested. Subsurface shear band interactions between the amorphous matrix and crystalline phase particulate are reported with the bonded interface technique on samples deformed with a Vickers microhardness indentation under loads from 10-1000g. Mechanical properties and hardness for Hf- and Zr-based consolidated composites are compared with the properties of ECAE consolidated monolithic alloy.

10:45 AM

Relationship between Glass Forming Ability and Intermetallics in Fe-Based Multi-Component Alloy Systems: *Satyajeet Sharma*[1]; Umesh Patil[1]; Raj Vaidyanathan[1]; C. Suryanarayana[1]; [1]University of Central Florida

The technique of mechanical alloying has been employed to relate the number of intermetallics in the phase diagrams and glass forming ability in Fe-based multi-component alloy systems. A systematic study has been carried out on binary, ternary and quaternary systems based on the Fe-B system. Special attention was focused on the quaternary Fe42Zr10X28B20 (X = Al, Co, Ge, Mn, Ni, and Sn) alloy systems. The alloying elements were so chosen as to form intermetallics with Zr ranging from 1 (in Zr-Mn) to 10 (in Zr-Al) in number. The powders were milled in a SPEX 8000D milling machine with a ball-to-powder weight ratio of 10:1 and 20:1. The structural evolution was characterized using XRD and TEM techniques. Preliminary results demonstrate that it is possible to relate the number of intermetallics with the ease of amorphization.

11:05 AM

Thermophysical Properties Measurements of $Zr_{62}Cu_{20}Al_{10}Ni_8$ Using Containerless Processing: *Richard C. Bradshaw*[1]; Mary E. Warren[1]; Jan R. Rogers[2]; Tom J. Rathz[3]; Anup K. Gangopadhyay[4]; Ken F. Kelton[4]; Robert W. Hyers[1]; [1]University of Massachusetts; [2]NASA MSFC; [3]University of Alabama, Huntsville; [4]Washington University

Thermophysical property studies performed at high temperature can prove challenging because of reactivity problems brought on by the elevated temperatures. Contaminants from measuring devices and container walls can cause changes in properties. To prevent this, containerless processing techniques can be employed to isolate a sample during study. A common method used for this is levitation. Typical levitation methods used for containerless processing are, aerodynamically, electromagnetically and electrostaticlly based. All levitation methods reduce heterogeneous nucleation sites, which in turn provide access to metastable undercooled phases. In particular, electrostatic levitation is appealing because sample motion and stirring are minimized; and by combining it with, optically based, non-contact measuring techniques, many thermophysical properties can be measured. Applying some of these techniques, surface tension, viscosity and density have been measured for the glass forming alloy $Zr_{62}Cu_{20}Al_{10}Ni_8$ and will be presented with a brief overview of the non-contact measuring techniques used.

11:25 AM

Thermodynamic and Experimental Investigation of Plastic Mg-Base Glass Matrix Composite: *X. D. Hui*[1]; W. Dong[1]; Z. G. Li[1]; Z. K. Liu[2]; [1]University of Science and Technology Beijing; [2]Pennsylvania State University

Mg-based bulk metallic glasses (BMGs) are regarded as one of the most attractive structural materials due to their low density and high strength. To date, Mg-based alloys with large glass-forming ability (GFA) have been developed in Mg-Ni-Y, Mg-Cu-Y, Mg-Cu-Al-Y, Mg-Cu-Ag-Y, Mg-Cu-Zn-Y and Mg-Cu-Y-Ag-Pd systems. However, monolithic Mg-based BMGs have been found to be brittle. To overcome the drawback of monolithic Mg-based BMGs alloys, thermodynamic modeling and experimental investigation are conducted on the Mg-base composite alloys with high GFA along with comprehensive mechanical properties. By using CALPHAD technique, we designed a series of Mg-base glass forming alloys, in which Mg-based solid solution phase is expected to precipitate in metallic glass matrix. The significant improvement in plastic strain, fracture strength, and specific strength will be reporeted in this presentation.

11:45 AM

Thermal Stability and Crystallization Behavior of $Cu_{60}Hf_{25}Ti_{15}$ Bulk Metallic Glass: Hsin-Hsin Hsieh[1]; *Wu Kai*[1]; Yu Lung Lin[2]; Ron Tang Huang[3]; [1]National Taiwan Ocean University; [2]Chung Shan Institute of Science and Technology; [3]National Tsing Hua University

Thermal stability and crystallization behavior of $Cu_{60}Hf_{25}Ti_{15}$ bulk metallic glass were studied by means of continuous heating and isothermal method. DSC analyses show that the crystallization process mainly proceeds in three stages. For continuous heating method, the activation energy of these three exothermic reactions are 321, 274, and 309 KJ/mol for the first, second, and third peak, respectively. For isothermal measurement, only one exothermic peak prior to crystallization can be detected. Avrami exponent values of Cu-base glassy alloy is 2.04±0.19, indicating the crystallization behavior of $Cu_{60}Hf_{25}Ti_{15}$ BMG is 3-dimensional diffusion-controlled growth of nuclei at a decreasing nucleation rate.

Characterization of Minerals, Metals and Materials: Advances in Methodologies

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Materials Characterization Committee

Program Organizers: Jiann-Yang James Hwang, Michigan Technological University; Arun M. Gokhale, Georgia Institute of Technology; Tzong T. Chen, Natural Resources Canada

Thursday AM — Room: 205
March 16, 2006 — Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Benjamin L. Henrie, Los Alamos National Laboratory; Jeongguk Kim, Korea Railroad Research Institute

8:30 AM

A New Method for Fracture Plane Determination: *Robert E. Hackenberg*[1]; Robert D. Field[1]; Pallas A. Papin[1]; David F. Teter[1]; [1]Los Alamos National Laboratory

A new method for the determination of the crystallographic indices of planar fracture surfaces is described. The key innovation is the use of an in-situ micromanipulator in a focused ion beam to extract TEM foils from a bulk fracture surface. Selected area diffraction of these foils in the TEM allows the determination of the crystallographic line directions that are contained within the fracture plane. This allows the fracture plane indices

to be characterized. The validation of this method using cleavage fracture in pure Zinc, and its application to other materials will be described.

8:55 AM

Accuracy and Reproducibility of High-Temperature Differential Scanning Calorimetry: *Susan Jacob*[1]; Mark E. Schlesinger[1]; [1]University of Missouri-Rolla

High-temperature differential scanning calorimetry (HTDSC) is a relatively new research tool that offers considerable promise for thermochemical research. However, the reliability and reproducibility of HTDSC measurements is impacted by several experimental variables. The impact of these experimental variables on the results of HTDSC measurement of two well-known thermodynamic properties (the heat capacity of platinum, and the enthalpy of fusion of silver) has been assessed for one well-known model of HTDSC. The results provide a better idea of the conditions needed to obtain optimal experimental results from the instrument, and the degree of accuracy and reproducibility which can be obtained under these conditions.

9:20 AM

Cathodoluminescence Properties of Natural Sphalerite: *Musa Karakus*[1]; Richard D. Hagni[1]; [1]University of Missouri-Rolla

Optical cathodoluminescence (CL) microscopy and spectroscopy was used to study CL behavior of natural sphalerite samples associated with silver, tin, tungsten deposits, and carbonate hosted Zn-Pb-Cu deposits from world famous localities. This study involves determinations of the relationships between CL properties and trace element content of sphalerite. The CL spectrum of natural sphalerite is rather complex due to the presence of more than one luminescence center. Mn2+ activator is the most important activator ion in most sphalerites, and it produces an orange emission band centered at 585 nm. Translucent green sphalerite showed weak orange CL due to Mn2+ but their CL intensity was reduced by the presence of Co2+ and Fe2+. Those sphalerite whose Fe2+ content exceeded 1% did not show CL. Sphalerite from carbonate-hosted deposits exhibited interesting CL colors and spectra. The CL imaging and spectroscopy is found to be extremely useful technique for distinguishing different generation of sphalerite.

9:45 AM

Metallographic Preparation Techniques for Uranium and Its Alloys: *Ann Marie Kelly*[1]; Dan J. Thoma[1]; Robert D. Field[1]; Paul S. Dunn[1]; David F. Teter[1]; [1]Los Alamos National Laboratory

Existing metallographic preparation techniques for uranium and uranium alloys are limited to elucidating specific microstructural characteristics, and some of the techniques are regarded as being environmentally unacceptable. This paper describes a newly developed technique, which is not only more environmentally friendly, but reveals most microstructural features simultaneously. Other attributes include a significant reduction in processing time and with only minor adjustment this technique may be applied to various uranium alloys. Examples of microstructures as revealed during various stages of preparation will be presented to highlight the new technique.

10:10 AM Break

10:20 AM

Using Rietveld Analysis with TOPAS for Modal Analysis of Geological Samples: *Holger Cordes*[1]; [1]Bruker-AXS

X-ray diffraction has long been used for qualitative and quantitative mineral analysis but Rietveld data analysis is still an under utilized method for mineral exploration and processing applications. In this full-profile approach the structural parameters of each mineral phase, together with experimental parameters, are refined by least-squares methods to minimize the difference between observed and calculated diffraction patterns. The result is a standard-less, quantitative analysis of the mineral abundance in the sample that is more accurate and considerably faster compared to traditional methods. The TOPAS software package combines a user-friendly interface with a unique approach to resolve overlapping peaks. Automated analysis options are also available and significantly reduce analysis time for routine samples. Several examples on a wide range of naturally occurring rock types are shown that illustrate the capabilities and limitations of the method. The examples include several options for the quantification of amorphous constituents like volcanic glasses.

10:45 AM

Robotic Automation of the Fire Assay Process for Rapid Quantitative Measurement of Platinum Group Elements in Mineral Concentrator Plants: *Jacques J. Eksteen*[1]; Keith S. McIntosh[2]; Klaus Koch[1]; Derek Auer[2]; [1]University of Stellenbosch; [2]Anglo Platinum Ltd.

The fire assay process for the quantitative recovery of platinum group elements (PGE's) prior to subsequent analysis traditionally is a time-consuming process. Samples derive from various ore types and contain PGE's at the ppm or ppb levels, making concentration of the elements mandatory before assaying. Traditionally sample turn-around times are of the order of 24 hours. The whole sequence of sample preparation, fire assay and subsequent analysis of PGE's have been automated by Anglo Platinum. Some of the major challenges on the road to automation will be discussed and the novel solutions that were implemented. The engineered solution included robotic automation of the whole sequence, from sample preparation, up to the final element by element assay. The final system allowed for rapid (less than one hour) and accurate analysis of PGE's even in streams containing very low levels, such as flotation tailing streams and drill core samples.

11:10 AM

On-Line Radio Frequency Measurement of Bulk Mineralogy: *Daniel Bennett*[1]; David Miljak[1]; Joe Khachan[2]; [1]CSIRO; [2]University of Sidney

There are few methods currently applied towards on-line bulk mineralogical analysis. Yet on line knowledge of process mineralogy could potentially provide large benefits, such as increased extraction efficiency or resource optimization. The work described in this paper involves the development of radio frequency methods for bulk mineralogical analysis. Some "zero field" magnetic resonances that occur in the radio frequency spectrum are mineral specific, and potentially allow quantitative estimation of mineralogy in an ore stream. Results will be presented on the specific detection of chalcopyrite. Initial quantitative measurements investigating matrix effects have indicated the feasibility of on-line mineralogical estimation using radiofrequency techniques.

11:35 AM

Pulsed Power Breaking-Up Technology for Resistant Gold-Containing Ores and Beneficiation Products: Valentin Alekseevich Chanturiya[1]; *Igor Jeanovich Bunin*[1]; [1]Research Institute of Comprehensive Exploitation of Mineral Resources

The aim of this paper is basically to show progress in the study of nanosecond processes involved in the disintegration and breaking-up of mineral complexes with fine noble metals. We studied the influence of nanosecond High-Power Electromagnetic Pulses (HPEMP) on the physicochemical and technological properties of refractory gold-containing ores and beneficiation products. Experimental data are presented to confirm the formation of breakdown channels and selective disintegration of mineral complexes as a result of pulse irradiation, which makes for efficient access of lixiviant solutions to precious metal grains and enhanced precious metal recovery into lixivia during leaching. Preliminary processing of gravity concentrate with a HPEMP resulted in significant increase of gold and silver extraction into lixivia during the cyanidation stage, with gold recovery increased by ~31% (from 51.2% in a blank test to 82.3% after irradiation). Gold recovery from stale gold-containing dressing tailings products increased after pulses-irradiation from 8-12% to 80-90%.

12:00 PM

Applied Mineralogical Studies of Nigerian Bulk Complex Sulphide Ore: *Peter A. Olubambi*[1]; S. Ndlovu[1]; J. H. Potgieter[1]; J. O. Borode[1]; [1]University of the Witwatersrand, Johannesburg

Representative samples of the hydrothermal vein deposits of the bulk complex sulphide ore deposit, 10 km south of Ishiagu, in Ebonyin State, South Eastern part of Nigeria were collected from two small scale mining companies. The samples were mixed and successively crushed in a jaw crusher and cone crusher, and ground in a rod mill. Characterization was carried out with SEM, EDX, XRD, XRF and ICP-OES. Mineralogical analysis revealed the presence of sphalerite, galena, siderite, pyrite, quartz and chalcopyrite. X-ray Diffractometry showed that sphalerite mineral in the ore occurs as sphalerite ferrous with varied percentage of Zn and Fe

within the various sizes while chalcopyrite occurs as a chalcopyrite group mineral with chemical formula Cu2MnSnS4. Results of the elemental analysis showed variations in elemental composition within the different sizes.

Characterization of Minerals, Metals and Materials: Mineralogical Studies

Sponsored by: The Minerals, Metals and Materials Society, TMS Extraction and Processing Division, TMS: Materials Characterization Committee
Program Organizers: Jiann-Yang James Hwang, Michigan Technological University; Arun M. Gokhale, Georgia Institute of Technology; Tzong T. Chen, Natural Resources Canada

Thursday AM Room: 206A
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Jiann-Yang James Hwang, Michigan Technological University

8:30 AM
Temperature Measurements in Microwave Heating: *Xiang Sun*[1]; Jiann-Yang James Hwang[1]; Shangzhao Shi[1]; Bowen Li[1]; Xiaodi Huang[1]; [1]Michigan Technological University

Microwave heating has been used in numerous industrial processes due to its great advantages by comparing with conventional heating method. However, microwave heated products can be affected by non-uniform temperature distribution due to the mechanisms of microwave heating. To overcome this problem, a critical step is to have a temperature-time profile. In order to characterize and diagnose microwave heating effects, an accurate temperature measurement is needed. This paper discusses the possibility of applying several temperature measurement techniques in microwave processing. Both contact and non-contact methods are introduced and compared.

8:55 AM
Mineralogical, Chemical and Ceramic Properties of Kaolinite-Illite Clays from the Tamnava Tertiary Basin – West Serbia: *Ana S. Radosavljevic-Mihajlovic*[1]; Jovica N. Stojanovic[1]; Vladan D. Kasic[1]; [1]Institute for Technology of Nuclear and Other Mineral Raw Materials

Important quantities of ceramic clay, composed of kaolinite-illite with quartz have been determined in the Tamnava tertiary basin. XRPD, DTA/TG and electron microscope investigations were preformed on representative samples. The main mineral association, determined by XRPD analysis, consists of kaolinite-illite, quartz, mica, feldspar, and Fe-oxide. The chemical composition generally shows high silica and alumina contents in all analysed samples, which is typical for strong kaolinized materials. The kaolinite-illite ratio is varying (generally 1:1) and influences in the change of their ceramic properties. These clays are classified as medium-plastic with enlarged range of sintering temperature, what makes them convenient for production of various kinds of ceramic tiles.

9:20 AM
Phase Transitions during Heating of Illite: *Xiaowen Liu*[1]; Hengfeng Li[1]; Jianrong Wang[1]; Yuehua Hu[1]; Danqing Yi[1]; [1]Central South University

The DSC/TGA, IR and XRD analysis were used to characterize the heating phase transformation of illite, which come from Ouhai, Zhejiang, China. It was discovered that the dehydration and dehydroxylation of illite carried out stage by stage during heating. The adsorptive water and layer-inter water were dehydrated from room temperature to 773K; and dehydroxylated in the range of 773K~973K. In these stages of process, illite's layer structure keeped almost unchanged. After 973K, illite began to change into disorder structure. At about 1373K, the layer structure of illite has been destroyed, and a morphous SiO2 and crystallite mullite appeared. At about 1473K, the structure of illite was completely destroyed and mullite crystal phase has become perfect.

9:45 AM
The Direct Test of Swell Stress for Geosynthetic Clay Liners: *Junfeng Shen*[1]; Shengrong Li[1]; Shaohui He[1]; Guangshan Zhang[1]; Jingui Tong[1]; Bokun Yan[1]; [1]China University of Geosciences

Geosynthetic clay liner (GCL) is a kind of waterproofing material used widely in engineering. The waterproof mechanism is understood in terms of bentonite particles becoming a water-obstruct colloid layer after they sorb water and swell. The swell stress, however, has not been determined directly till now. In our experiment, the swell stresses of the GCL, which is made in CETCO company, America, under saturated water-sorbing conditions, are measured directly using a custom-made instrument. The results show that the instrument designed by the authors performed satisfactorily and the test results are reproducible. The drive force for water molecules are able to enter into montmorillonite particles and individual ontmorillonite crystals is understood in term of larger specific surface area, layer structure, layer charge, and broken bound in edge of crystal. Those measurement results will be significant for using GCL appropriately in engineering.

10:10 AM Break

10:20 AM
Mineralogical and Chemical Characterization of the W-Pb-Bi-Ag Ore from the Rudnik Mine, Serbia: *Slobodan A. Radosavljevic*[1]; Jovica N. Stojanovic[1]; Ana S. Radosavljevic-Mihajlovic[1]; [1]Institute for Technology of Nuclear and Other Mineral Raw Materials

The polymetallic W-Pb-Bi-Ag ore from the "Nova jama" ore zone of the Rudnik ore field have been investigated. Contact-pneumatolytic (skarn), pneumatolytic-hydrothermal, and hydrothermal mineralization phases are defined in this ore zone. The most significant mineralization phase that gave compact ore bodies is pneumatolytic-hydrothermal phase. A relatively pure Mo-free scheelite is the only tungsten-bearing mineral. Lead minerals are mostly presented by Pb-Bi sulphosalts and much less with galena. The image analysis coupled with Energy Dispersive Spectrometry (EDS) analysis on a Scanning Electron Microscope (SEM) was applied to the characterization of a W-Pb-Bi-Ag ore as an efficient tool for mineral quantification. Results of EDS (Energy Dispersive Spectrometry) analyses gave the empirical formulae: Pb1.91Ag0.05Cu0.08Bi1.93S5 for cosalite, Pb0.98Ag0.03Cu0.05Bi1.99S4 for galenobismutite and galena Pb0.99Ag0.03S.

10:45 AM
Research on the Dispersion and Aggregation between the Three Clay Minerals and Diaspore: *Xiaowen Liu*[1]; Yuehua Hu[1]; Danqing Yi[1]; [1]Central South University

Slime coating and aggregation between the clay minerals and diaspore should be avoided in the diasporic bauxite flotation. The colloidal stability between the three plate dioctahedral phyllosilicate minerals and diaspore in water was quantitatively calculated by the DLVO theory. It shows that in acidic solution, the particles flocculate by particle (diaspore)-face (clay mineral) form; in neutral solution, they flocculate by particle (diaspore)-edge (clay mineral) form; and disperse in alkaline solution, approximately consistent with the results of measurement in precipitation analysis and the observation of SEM. The results obtained in this study should shed more lights on diasporic bauxite flotation and the dispersion and aggregation of nanoparticles.

11:10 AM
Barite Mineralization in Volcanic Rocks in Southern Flank of East-Magnitogorsk Palaeoisland Arc (South Urals): *Natalya Nikolaevna Ankusheva*[1]; [1]Russian Academy of Science

East-Magnitogorsk palaeoisland arc was formed in devonian-carboniferous on the periphery of Urals palaeocean. Ore-bearing structures are early carboniferous palaeovolcanos. Barite veins are confined to diabase dikes and trachibasalt tuffs. Two barite types are allocated: white and pink. White barite forms crystalline-granular masses, fibrous, tabular, parallel-columnar aggregates, pink – radially-fibrous aggregates, columnar crystals. Roentgenofluorescencal analysis: white barite is enriched Sr (7500 gr/t) and impoverished Pb (120), in pink – more Pb (500–1000) and less Sr (2000). Roentgenostructural analysis: lattice parameters are lower in white barite, than in pink, it is connected to replacement Ba to Sr. There are inclusions of aurichalcite, biotite, rutile, microcline in white barite;

sulfides and hialophane in pink one. The temperatures of hydrothermal solutions were 155–180°C, high salinity (18.6 wt. %), testifying about magmatic origin. Two solutions groups – low- (155–165°C) and high-temperature (170–180°C) are allocated. These barite types concern to two generations – early (white), late (pink).

11:35 AM

Investigation on the Thermal Decomposition of Diaspore: *Xiaowen Liu*[1]; Jianrong Wang[1]; Hengfeng Li[1]; Yuehua Hu[1]; Danqing Yi[1]; [1]Central South University

The kinetic curves are obtained by thermogravimetry(TGA) and differential scanning calorimetry (DSC). The mechanism of thermal decomposition of diaspore is discussed according to Coat-Redfer equation. The phase identification is carried out by X-ray diffraction(XRD) before and after thermal treatments. It is found that after thermal treatment at 500°C, the diaspore is transformed to corundum (a-A12O3) and H2O. The activation energies is 287KJ/mol. The crystal structure also changed greatly during thermal treatment. The value of a parameter, b parameter and the crystal lattice volume (V) of diaspore are increased greatly from 400°C to 500°C. When the heated temperature is below 400°C, the values change inobviously.

Computational Thermodynamics and Phase Transformations: Thermodynamic Models

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Computational Materials Science and Engineering Committee
Program Organizers: Dane Morgan, University of Wisconsin; Corbett Battaile, Sandia National Laboratories

Thursday AM
March 16, 2006
Room: 210A
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Corbett C. Battaile, Sandia National Laboratories

8:30 AM

A Statistical-Thermodynamic Model for Ordering Phenomena in Thin Film Intermetallic Structures: *Olga Semenova*[1]; Regina Krachler[1]; Herbert Ipser[1]; [1]University of Vienna

New advanced nano-crystalline materials are the key to technological progress and a focus of intensive research activity during the last decades. These materials found extensive application in industry in the production of microelectronic and optoelectronic devices and for modern computer technologies. To control the processes occurring in the structure under different treatment conditions during fabrication, a profound basic knowledge of order-disorder phenomena is of paramount importance. This paper presents a new and unified statistical-thermodynamic model for description of ordering phenomena in nano-crystalline intermetallics. The model is developed on the basis of the Ising approach and a Bragg-Williams mean-field approximation which are very powerful tools for studying ordering phenomena as well as order-disorder phase transitions in intermetallic phases. Based on a statistical thermodynamic model previously developed for binary B2 bulk intermetallic phases, the new model allows to estimate point defect concentrations and the degree of long range order in the structure.

8:50 AM

A Thermostatistical Model for Cell Formation: *Pedro Eduardo Jose Rivera diaz del Castillo*[1]; Mingxin Huang[1]; Sybrand van der Zwaag[1]; [1]Delft University of Technology

A new thermostatistics based approach to describe the conditions leading to the formation of cells is presented. The new theory is based on the minimisation of the free energy for different dislocation arrangements such as homogeneous and pattern distributions. The likelihood of the formation of subgrains is captured by the atom-to-atom computation of the entropy. The differences arising from crystallography and temperature are thus captured by the model. The effects of grain morphology and size on the substructure type are analysed. It is shown that grains in the submicron scale cannot form cells in (meta)equilibrium; whereas deformation of grains in the nanometre scale has to occur with the aid of other mechanisms such as grain boundary sliding.

9:10 AM

Atom Bonds of Al-Zn Solid Solutions and Spinodal Decomposition: *Gao Yingjun*[1]; [1]Guangxi University

The valence electron structures of Al-Zn solid solutions are analyzed according to Empirical Electronic Theory in Solid and Molecule(EET) with the average atom model. The results show that spinodal decomposition produces great change of the valence electron structure in Al-Zn solid solutions. The spinodal decomposition under room temperature enhance hardness and intensity of Al-Zn alloys are rationally explained according to the change of covalent bond in the solid solutions.

9:30 AM

Dilatometric Analysis of Phase Transformation Involving Multi-Phase in Steel: Sang Hwan Lee[1]; Ji Youn Kim[1]; June Yeong Park[1]; *Kyung Jong Lee*[1]; Kyung Sub Lee[1]; Dong Hyuk Shin[1]; Kwang Geun Chin[2]; [1]Hanyang University; [2]POSCO Technical Research Laboratory

Dilatometric analysis is frequently used to figure out the overall phase transformation in steel. However, it is very difficult to separate the transformation for one phase from the others when transformation of two or more phases are superimposed. In this study, the rate of transformation(change of transformed volume fraction per unit time) was applied to step forward to get the individual transformation. Variation of the rate of transformation was first classified by simulating transformation kinetics determined by Avrami equations in the multi-phase system. The systematic analysis was carried out for the experimentally determined dilatation. The start, finish and peak of individual transformation were determined. They were compared with those determined by other methods.

9:50 AM Break

10:10 AM

Bond Analysis of Interface for Strengthening in Al-Mg-Si Alloy: *Gao Yingjun*[1]; [1]Guangxi University

Through the calculation of the electronic bonding density of the main equilibrium phase ß(Mg2Si) and pure Si cell, the result show that the strongest bond in Si cell is more than three times of that in Mg2Si cell, and the (electronic bonding density) in the Si cell is also more than three times of that in the Mg2Si cell. These are the main reason that influences the growth of grain of Mg2Si and the mechanical property of alloy such as hardness and intensity.

10:35 AM

Modeling of Reaustenitization of Hypoeutectoid Fe-C Steels with a Cellular Automaton Method: *B. J. Yang*[1]; [1]Caterpillar Inc.

A model for simulation of reaustenitization of hypoeutectoid Fe-C steel has been developed by using cellular automaton approach(CA). The initial microstructure state for quenching can be predicted with such information as grain size and distribution of carbon concentration. The kinetics of austenitization is modeled by nucleation, grain growth and grain coarsening. The free energy and boundary energy are taken into account for grain coarsening, and carbon diffusion in ferrite and austenite and its interface dynamics are considered for the growth of austenite. The competition between the nucleation and early stage grain growth in the pearlite is investigated, and a simultaneous growth for ferrite to austenite and the grain coarsening is also revealed. A microstructure of hypoeutectic Fe-C steel of 1045 is digitized as an initial microstructure state using various heating rates. The effect of heating rates on the final grain size and homogeneity is studied.

10:55 AM

Thermodynamic Description of Liquid Steels and Metallurgical Slags by the "Generalized Central Atoms" Model: *Jean Lehmann*[1]; Frederic Bonnet[1]; Manuel Bobadilla[1]; [1]Arcelor Research

This paper deals with the latest development in computational thermodynamics currently running at Arcelor Research to improve the representation of the properties of metallurgical slags and liquid steel. This development concerns the unification of two models developed and used by Arcelor Research to represent the properties of the metallurgical slags on

the one hand and of liquid metallic phases on the other hand is presented. These two models are respectively the cell model and the central atoms model as introduced primarly by Lupis and Elliot. The new prospects brought by this unification are explained. In particular, for the metallurgical slags, they arise from a more accurate description of the short-range ordering. Concerning the liquid steel, the model has been assessed on the system Fe-Al-Cr-Mn-Ni-Si-Ti-Ca-Mo-Cu-Nb-C-N-H-O-P-S and applications to nitrogen, sulphur and oxygen in various steel grades show that the central atoms model represents accurately multicomponent systems.

11:15 AM
Thermodynamic and Experimental Simulation of Urinary Stones Minerals Crystallization: *Olga Alexandrovna Golovanova*[1]; Elena Vladimirovna Rosseyeva[1]; Vladislav Jurjevich Yelnikov[1]; Olga Victorovna Frank-Kamenetskaya[1]; [1]St. Petersburg State University

The detail study of inorganic and organic components of Russian inhabitants urinary stones was carried out. Based on these data the thermodynamic model of urinary stones phases crystallization has been constructed. 3D solubility surfaces of a common crystallization of some phases have been calculated. During simulations the composition of the solid phases precipitating from urine-like solutions with different contents of calcium, magnesium, phosphate, oxalate, ammonium, chloride, sulphate, sodium and potassium ions at 37ºC (pH24 h = 6.5 - 7.5) has been determined. Brushite with hydroxyapatite and newburyite at pH24 h = 6.5 have been appeared. Struvite, hydroxyapatite and amorphous calcium phosphates at pH24 h = 7.5 have been precipitated. Good correlation between experimental measured and theoretically predicted data has been revealed.

Deformation and Fracture from Nano to Macro: A Symposium Honoring W. W. Gerberich's 70th Birthday: Environmental and Material Alloying Effects

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Nanomechanical Materials Behavior Committee
Program Organizers: David F. Bahr, Washington State University; James Lucas, Michigan State University; Neville R. Moody, Sandia National Laboratories

Thursday AM
March 16, 2006
Room: 214D
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Neville R. Moody, Sandia National Laboratories; Hussein M. Zbib, Washington State University

8:30 AM Invited
Nanoindentation at Elevated Temperatures: Applied and Fundamental Studies of Materials Mechanics: *Christopher A. Schuh*[1]; [1]Massachusetts Institute of Technology

Recent progress in the development of high-temperature nanoindentation techniques will be discussed. The practices required to obtain artifact-free data at temperatures as high as 410°C are established with reference to experiments on amorphous silica, and subtleties of hardness and modulus measurement at these temperatures will be discussed. The capability of in-situ contact-mode imaging at temperature is also described. Finally, the impact of these techniques for fundamental study of deformation mechanisms is discussed in the framework of the 'incipient plasticity' problem of the elastic-plastic transition.

8:50 AM
Mechanical Grain Growth: *James C. M. Li*[1]; [1]University of Rochester

Grain growth usually takes place at high temperatures without external stress and the driving force is the energy of grain boundaries. However, recent experiments for nanocrystalline materials under an indenter, grain growth is observed at room temperature and even at liquid nitrogen temperatures. So obviously mechanical stress can induce grain growth. Motion of tilt boundaries by mechanical stress was first observed by Parker and Washburn in 1952 in a bent single crystal of Zn. This motion caused one grain to grow into the other. So this is the first observation of grain growth under stress even though it is a bicrystal. In a polycrystal, a boundary can be decomposed by mechanical means after which the two grains merge into one. Some conditions and the critical stress needed to decompose a grain boundary will be shown including the effects of grain size and temperature.

9:05 AM
Stress Induced Grain Growth and Its Effect on the Mechanical Behavior of Nanocrystalline Aluminum Thin Films: Daniel S. Gianola[1]; *Kevin J. Hemker*[1]; [1]Johns Hopkins University

Recent studies of the mechanical behavior of nanocrystalline metals have focused on extensions of the Hall-Petch relation to smaller grain sizes and the identification of the deformation mechanism(s) that become operative when microcrystalline plasticity is abated. Here we report on the observation of high tensile strength and unusually high room temperature tensile ductility in submicron free-standing nanocrystalline aluminum thin films. In situ X-ray diffraction and post mortem transmission electron microscopy point to the importance of room temperature grain growth in transforming the underlying processes that govern the mechanical response of the films; nanoscale deformation mechanisms give way to microscale plasticity. Efforts to model this growth with traditional driving forces for grain boundary migration (e.g. reductions in grain boundary energy, surface energy, and elastic strain energy) have proven to be less than satisfactory, and the importance of grain boundary pinning and role of stress assisted grain boundary migration will be highlighted.

9:20 AM
Forced Chemical Mixing in Nanocrystalline and Amorphous Alloys Subjected to Sustained Plastic Deformation: *Pascal M. Bellon*[1]; Samson Odunuga[1]; Pavel Krasnochtchekov[1]; Youhong Li[1]; Robert S. Averback[1]; [1]University of Illinois

Plastic deformation, at low temperatures, can force the interdiffusion of chemical species and stabilize supersaturated solutions in solid alloys. Despite the information available on that forced mixing, its characteristics are still not well understood, particularly for nanocrystalline and amorphous alloys, for which the mechanisms of plastic deformation remain unresolved. We present here a new method for analyzing forced chemical mixing that offers new insight into the mixing process. The method, which is similar to one used for characterizing turbulent flows, monitors the evolution of the separation distance between pairs of atoms, R, which is quantified by an effective diffusion coefficient. This diffusion coefficient is predicted to increase with R, and to saturate at a value Rc that is characteristic of the length scale of the defects responsible for plastic deformation. Our analytical predictions are tested by 3D molecular dynamic simulations of nanocrystalline and amorphous alloys cyclically deformed in compression.

9:35 AM
Effect of Copper Solution on Deformation Behavior of Nanocrystalline Gold: *Yinmin (Morris) Wang*[1]; Alan F. Jankowski[1]; Alex V. Hamza[1]; [1]Lawrence Livermore National Laboratory

Nanocrystalline gold with copper solution additions in the range of 0-12 wt.% and grain sizes below ~10 nm were prepared using electrodeposition technique. These nanocrystalline foils have a typical thickness of above 10 mm, and thus allow us to carry out mechanical property assessment using traditional mechanical characterization techniques, such as tensile tests and instrumented nanoindentation experiments. The Young's modulus, hardness, tensile strength, and tensile ductility were determined as a function of grain size and solid solute content. Special attention was also paid to interpret the copper solid solute effect on strain rate sensitivity of these materials. New experimental evidence suggests that alloying could not only substantially improve the mechanical properties of nanocrystalline materials, but also fundamentally alternate their deformation behavior. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48. Y.M. Wang acknowledges the support of Graboske Fellowship at Lawrence Livermore National Laboratory.

9:50 AM

The Effects of Solute Impurities on the Onset of Plasticity in FCC Materials: *Gus Vasquez*[1]; David F. Bahr[1]; [1]Washington State University

The ability to quantify the stress required to nucleate dislocations in dislocation free regions in solid solutions of FCC metallic materials has been studied using nanoindentation. The effects of solute impurities in the copper-nickel system on the formation of dislocations in a previously dislocation free region have been demonstrated to be minimal. The shear stress required to nucleate dislocations in copper is approximately 1.6 GPa, while in nickel a 3.9 GPa shear stress is required. Changes in shear stress for nucleation track closely with changes in elastic modulus, showing the nucleation stress is approximately 1/30 to 1/20 of the shear modulus. The expected solid solution strengthening is identified within the same experimental method, demonstrating unambiguously the fact that solid solution impurities in this system will impact the propagation of dislocations during plastic deformation, but not alter the homogeneous nucleation of dislocations in these materials.

10:05 AM

Effect of Passivation on Stress Relaxation in Electroplated Copper Films: *Rui Huang*[1]; Paul S. Ho[1]; Dongwen Gan[1]; [1]University of Texas, Austin

In copper interconnects, mass transport at Cu/passivation interface is the dominant path for electromigration, and the kinetics strongly depends on material and processing of the passivation layer. The present study investigated the effect of passivation on the kinetics of interfacial mass transport by measuring stress relaxation in electroplated Cu films, both unpassivated and passivated, with four different cap layers: SiN, SiC, SiCN, and a Co-based metal cap. Stress curves measured under a thermal cycling condition show different behavior in the unpassivated and passivated Cu films, but indifferent for films with different cap layers. On the other hand, stress relaxation measured under an isothermal annealing condition reveals clearly the effect of the cap layers, indicating that interface diffusion controls the kinetic process of isothermal stress relaxation. A kinetic model based on coupling of interface and grain boundary diffusion was used to deduce the interface diffusivities and the corresponding activation energies.

10:20 AM Break

10:40 AM Invited

Modeling Stress Controlled Crack Tip Hydrogen Embrittlement: *Richard P. Gangloff*[1]; Matthew R. Begley[1]; [1]University of Virginia

Gerberich provided a foundation for micromechanical modeling of H-enhanced subcritical crack growth. This paper reviews improved descriptions of crack tip stress and plasticity central to such predictions. Material models with explicit microstructure (dislocation free zone, strain gradient plasticity, and discrete dislocation) predict near tip stresses higher than those from J_2 plasticity, but only for restricted regimes of alloy hardening and stress intensity. The concentration of trapped H is enriched exponentially by such high local hydrostatic stresses to favor decohesion independent of a requirement for impurity segregation. Material-flow descriptions including length scale can be incorporated into finite element based H damage models to better predict the effects of key variables, and provide a basis for next generation multi-length physics based predictions. Examples elucidate the effects of temperature on internal H assisted cracking of low strength Cr-Mo steel and predissolved as well as environment-produced H concentration on cracking of ultra-high strength steel.

11:00 AM

Investigation of Hydrogen-Deformation Interactions Using Thermal Desorption Spectroscopy (TDS): *Dan Eliezer*[1]; Ervin Tal-Gutelmacher[1]; Thomas Boellinghaus[2]; [1]Ben Gurion University of Negev; [2]Federal Institute for Materials Research and Testing

TDS is a very sensitive and accurate technique for studying hydrogen diffusion and trapping processes in materials. It involves accurate measurement of the desorption rate of gas atoms, soluted or trapped in the material, while heating the sample at a known rate. This study was undertaken to investigate what happens when small amounts of hydrogen are trapped within microstructural defects and the mutual impact of hydrogen and deformation on the behavior of two different systems; hydride- and non-hydride-forming materials, represented respectively by titanium based alloys and stainless steels. The relationships between hydrogen absorption/desorption and deformation, as well as various desorption and trapping parameters, are evaluated in detail. Utilizing TDS provides a comprehensive knowledge of hydrogen-trapping and hydrogen-deformation interactions, necessary to make any decision and/or judgment whether a trap site, or a particular trapped hydrogen content, is either useful or detrimental for safe service conditions of these structural materials.

11:15 AM

Transgranular Hydrogen Embrittlement of Modern Ultra-High Strength Steels: Richard P. Gangloff[1]; *Yongwon Lee*[1]; [1]University of Virginia

Hydrogen severely embrittles modern precipitation hardened martensitic steels in spite of outstanding strength and fracture toughness. AerMet®100 (σ_{YS} = 1750 MPa, K_{IC} =130 MPa$\sqrt{m}$) is susceptible to transgranular cracking from predissolved H (1-8 wppm) or loading in NaCl solution at free corrosion (-470 mV_{SCE}), with a threshold for cracking (K_{TH}) of 15 MPa$\sqrt{m}$. K_{TH} rises toward K_{IC} with cathodic polarization to -625 mV_{SCE}, then falls to 8 MPa$\sqrt{m}$ with polarization to –1100 mV_{SCE}. This behavior is understood based on crack pH and potential governing H uptake. K_{TH} decreases as environmental H concentration increases, paralleling the effect of predissolved H and predicted within a decohesion framework following Gerberich. Slow subcritical H cracking is resolved for potentials where apparent K_{TH} approaches K_{IC}, complicating characterization and consistent with reaction rate limitation dominating H diffusion control of growth rate. Work is in progress to mitigate H cracking by control of carbide and austenite precipitates.

11:30 AM

Cleavage Oriented Iron Single Crystal Toughness Temperature Curves: *Mike Hribernik*[1]; G. Robert Odette[1]; [1]University of California, Santa Barbara

Static, dynamic initiation and crack arrest toughness of cleavage oriented unalloyed Fe single crystals was measured over a wide range of temperatures. The two types of (100)[010] and (100)[011] composite diffusion bonded specimens used in these tests, compression bridge anvil beams and wedge loaded chevron short beams, gave comparable results. Initiation toughness was measured in 4-point bending at rates from < 1 to > $2x10^4$ MPavm/s. Arrest toughness increased slowly from ~ 3-4 MPavm at -196°C up to -50°C increasing more rapidly at higher temperatures. Corresponding initiation toughness curves temperatures where higher, with the shifts depending on the loading rate. Preliminary data suggests an effective activation energy of ~ 0.25±0.05 eV. Implications of the results to a universal master curve toughness temperature curve shape are discussed. Comparisons with limited literature toughness data on Fe-3%Si suggests a significant role of solid solution strengthening in single crystal mediating toughness temperature properties.

11:45 AM

Cleavage Annular Stress Required for Fracture Path Deflection in Cold Drawn Pearlitic Steels: *Jesús Toribio*[1]; Javier Ayaso[1]; [1]University of Salamanca

The fracture performance of axisymmetric notched samples taken from pearlitic steels with different levels of cold drawing is studied. To this end, a real manufacture chain was stopped in the course of the process, and samples of all intermediate stages were extracted. Thus the drawing intensity or straining level (represented by the yield strength) is treated as the fundamental variable to elucidate the consequences of manufacturing on the posterior fracture performance. A materials science approach is proposed, so that the strongly anisotropic fracture behaviour of heavily drawn steels (which exhibit a 90º step in the fracture surface) is rationalized on the basis of the markedly oriented pearlitic microstructure of such steels which influences the operative micromechanism of fracture in this case. A finite element analysis of the stress distribution at the fracture instant allows the computation of the cleavage annular stress required to produce the deflection of the fracture path.

Fatigue and Fracture of Traditional and Advanced Materials: A Symposium in Honor of Art McEvily's 80th Birthday: Fatigue and Fracture XI

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee
Program Organizers: Leon L. Shaw, University of Connecticut; James M. Larsen, U.S. Air Force; Peter K. Liaw, University of Tennessee; Masahiro Endo, Fukuoka University

Thursday AM Room: 216
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Yoshiharu Mutoh, Nagaoka University of Technology; Leon L. Shaw, University of Connecticut

8:30 AM Invited
Striations and Crack-Arrest Markings on Fracture Surfaces: *Stan Lynch*[1]; [1]Defence Science and Technology Organisation

The formation of fatigue striations are reviewed, starting with an historical outline of their first observations, followed by a summary of current understanding, and concluding with a discussion of aspects that are not well understood. Such aspects include: (i) details of the crack-advance process, such as the relative extents of dislocation emission, dislocation egress, and decohesion at crack tips, together with the extent of micro-/nano-void formation ahead of crack tips, (ii) the role of microstructural changes ahead of cracks, (iii) the effects of environment (and cyclic frequency) on striation spacing and appearance, and (iv) the increasing discrepancy between striation spacings and macroscopic crack-growth rates with decreasing stress-intensity-factor range. The formation of crack-arrest markings on sustained-load fracture surfaces are also reviewed, and possible common factors between these markings and fatigue striations, such as microstructural changes and 'damage' ahead of cracks, are discussed.

8:55 AM
Quantitative Analysis of Microstructures and Fracture Surfaces of Common Turbine Engine Materials: *Kezhong Li*[1]; William Porter[1]; James Larsen[2]; [1]University of Dayton Research Institute; [2]Air Force Research Laboratory/MLLMN

To understand the influence of microstructure on fatigue variability, the role of each microstructural feature on crack initiation, micro-crack propagation and macro-crack propagation must be determined. In nickel-base superalloys, features of interest include gamma grain size, primary and secondary gamma prime size and their respective volume fractions. For alpha+beta titanium alloys, features include prior-beta size, primary-alpha size and volume fraction, and secondary-alpha-lath width and volume fraction. Thus, in order to model fatigue performance using microstructure-based models, it is crucial to quantify these and similar features. A detailed investigation was conducted on a nickel-based superalloy, IN100, and an alpha+beta titanium alloy, Ti-6Al-2Sn-4Zr-6Mo, to determine quantitative values for the various microstructural features. Scanning electron microscopy, orientation imaging microscopy and various image-analysis-software tools were employed in the study. The methods used to characterize features of each material are described. Finally, an approach to quantitatively characterize features associated with fatigue-derived fracture surfaces is discussed.

9:20 AM
In Situ Measurement of Crystal Lattice Strain Evolution during Cyclic Loading: Jun-Sang Park[1]; *Matthew Miller*[1]; Seth Watts[1]; Alexander Kazimirov[1]; [1]Cornell University

Crystals in a polycrystalline material under uniaxial cyclic loading can experience a complicated, multiaxial set of deformation histories. Measuring the crystal aggregate response to a known macroscopic cyclic load can be a first step to understanding the conditions leading to microcrack initiation. This talk will describe a set of experiments using high energy synchrotron x-ray to measure the crystal aggregate lattice strains during cyclic loading. A sophisticated diffractometer/loadframe system, capable of exerting high frequency cyclic load, was employed. The specimen was rotated relative to the x-ray beam to construct lattice strain pole figures. To capture the "real time" lattice strains of different {hkl}s, a rotating shutter was developed and used to synchronize a point in the load history with x-ray beam at every cycle. The results enable us to look at a live picture of the lattice strains and their evolutions in a cyclically loaded specimen.

9:45 AM
Temperature Dependency of Delayed Hydride Crack Velocity in Zr-2.5Nb Tubes: *Young Suk Kim*[1]; [1]Korea Atomic Energy Research Institute

Delayed hydride crack (DHC) tests were conducted on Zr-2.5Nb tubes with different distributions of the b-Zr at temperatures ranging from 125 to 300°C. Compact tension specimens charged to 27 to 100 ppm hydrogen were used to determine the temperature dependences of their DHC velocity (DHCV) and their striation spacing. The CANDU Zr-2.5Nb tube with a higher yield strength and a semi-continuous b-Zr had a higher DHCV and a smaller striation spacing than the RBMK Zr-2.5Nb tube with a fully discontinuous b-Zr and a lower yield strength. It is found that the activation energy for the DHCV is the sum of the activation energies for hydrogen diffusion and the striation spacing representing the hydrogen concentration gradient at the crack tip. Quantitative contribution of hydrogen diffusion and the hydrogen concentration gradient to the DHCV is discussed. This study provides supportive evidence for the feasibility of Kim's DHC model.

10:10 AM Break

10:25 AM Invited
Stress Shielding Phenomena and Fatigue Crack Growth Resistance in F/P Steels with Various Pearlite Morphologies: *Yoshiharu Mutoh*[1]; Akhmad A. Korda[1]; Yukio Miyashita[1]; Teruki Sadasue[2]; [1]Nagaoka University of Technology; [2]JFE Steel

The stage IIb regime of fatigue crack growth is known as the Paris regime, in which microstructure of the material hardly influences fatigue crack growth resistance. It is also well known that stress shielding phenomena at the crack tip, such as crack closure, bridging, phase transformation, microcracking, etc. contribute to reducing the crack tip stress intensity factor and thus enhancing the crack growth resistance. In the present study, fatigue crack growth tests of three kinds of ferrite-pearlite steels with networked, distributed and banded pearlite morphologies were carried out under a constant delta K in the stage IIb regime. During the fatigue tests, detailed in-situ SEM observation of crack growth behavior was conducted. The results obtained suggest some possibilities of microstructural control for improving the fatigue crack growth resistance of steels.

10:50 AM
Superior High Cycle Fatigue Properties of a New High Strength 2026 Al Alloy: *Tongguang Zhai*[1]; Jinxia Li[1]; Matthew Garratt[2]; Gary Bray[2]; [1]University of Kentucky; [2]Alcoa Technical Center

High cycle fatigue was performed on new generation Al alloys, AA 2026, using a self-aligning four-point bend rig, at 20 Hz, R=0.1, room temperature in air. The alloy, developed based on the traditional AA 2024 Al alloys, was hot extruded, and processed to a T3511 condition (solutionized, water quenched, stretched by 1-3% and naturally aged). It was found that the AA 2026 alloy exhibited a fatigue limit of 334 MPa, 90% its yield strength (372 MPa), compared to typically 140 MPa, 43% the tensile yield strength (326 MPa) for an AA2024 Al alloy in a same temper condition. The superior fatigue strength of the 2026 alloy was likely to be attributed to the fewer Fe-containing particles (preferred crack nucleation sites), large crack deflection and plywood-like or fibril grain structure in this alloy. Such grain structure gave rise to crack deflection at grain boundaries, which slowed down growth of fatigue cracks.

11:15 AM
Self-Generated Thermal Fingerprint of Fatigue Damage Process: *Bing Yang*[1]; Peter K. Liaw[2]; J. Y. Huang[3]; R. C. Kuo[3]; J. G. Huang[4]; [1]Oak Ridge National Laboratory; [2]University of Tennessee; [3]Institute of Nuclear Energy Research; [4]Taiwan Power Company

It has always been a great temptation in finding new methods to in-situ "watch" the material fatigue-damage processes so that in-time reparations

will be possible, and failures or losses can be minimized to the maximum extent. Realizing that temperature patterns may serve as fingerprints for stress-strain behaviors of materials, a state-of-art infrared (IR) thermography camera has been used to "watch" the temperature evolutions of reactor-pressure-vessel (RPV) steel "cycle by cycle" during 0.5 Hz low-cycle fatigue experiments in the current research. After using a combination of thermodynamics and heat-conduction theory, key issues in fatigue, such as in-situ stress-strain states, cyclic softening and hardening observations, and fatigue-life predictions, can be resolved by simply monitoring the specimen-temperature variation during fatigue. As a method requiring no special sample preparation or surface contact by sensors, thermography could open up wide applications for in-situ studying mechanical-damage processes of materials and components.

General Abstracts: Light Metals Division: Session III

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS: Aluminum Committee, TMS: Magnesium Committee, TMS: Reactive Metals Committee, TMS: Recycling Committee
Program Organizers: Jim McNeil, Novelis Inc; Neale R. Neelameggham, US Magnesium LLC

Thursday AM
March 16, 2006
Room: 7D
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Dean M. Paxton, Pacific Northwest National Laboratory

8:30 AM
The Influence of Porosity on Compressive Behavior of Closed Cell Aluminum Foams: *Haijun Yu*[1]; Guangchun Yao[1]; Bing Li[1]; Hongjie Luo[1]; Yihan Liu[1]; Yong Wang[1]; [1]Northeastern University

A test is carried out for quasi-static compression of closed cell aluminum foams of different porosities, which is prepared by foaming in melt process. Its compressive stress-stain curves are determined, and its quasi-static compressive mechanic behaviour is studied. The result shows that the compressive process of closed cell aluminum foams is similar to that of brittle material; its stress-stain curves are indented. The compressive strength of closed cell aluminum foams decreases with the increase of the porosity.

8:55 AM
Factors Influence the Preparation of Foam Aluminum by Powder Metallurgy Method: *Guo Zhiqiang*[1]; Yao Guangchun[1]; Liu Yihan[1]; [1]Northeastern University

Foam aluminum is new functional material that has been developed in recent years. In this paper several major factors that influence the process of preparation of foam aluminum by powder metallurgy method were studied: amount of foaming agent, pressure, foaming temperature, protection condition and the amount of additive and so on. Optimal conditions were concluded through the analysis of the foaming process of Al-Si-Ca alloy which has high viscosity thus can improve the stability of foam. The relationships and effects of the factors in the process of the preparation of foam aluminum were studied. It was found out that the pressure is the crucial factor in the foaming process.

9:20 AM
Analysis of Cause of Defect Forming in Aluminum Foam: H. J. Luo[1]; *G. C. Yao*[1]; [1]Northeastern University

Aluminum foam is one of new materials that are of great interest. Aluminum foam is fabricated by foaming in aluminum melt technique in this paper. The above technique is easier than the others in preparing aluminum foam and in which the bigger plate or block of aluminum foam can be made, but inner defect of foam body occurs easily, such as contracted hole, crack and big bubbles, etc. The cause of defect formation is analyzed and the method that avoided these defects is put forward in the paper.

9:45 AM
Study on Preparation of Aluminum Foam Sandwich and Combination Mechanism on Steel Plate/Foam Core Interface: Zhang Min[1]; Yao Guangchun[1]; *Yi-Han Liu*[1]; [1]Northeastern University

Aluminum foam has shown a popular interest in recent years and is potentially used for many applications due to its light weight structure. As engineering structures, aluminum-foam sandwiches have super-light weight and high stiffness and strength. In this paper aluminum-foam sandwiches were manufactured by a Al-Si-Ca alloy powder and two steel plates rolling and foaming process. In this rolling and foaming process, steel-aluminum foam interface was bonded by alloyed process. Asymmetric foaming problem of aluminum foam core was investigated, alloyed combination process between steel plate and aluminum foam core before and after foaming was analyzed. And three combination mechanism was established. By diffusion a good metallic combination in skin-foam core interface was formed.

10:10 AM
Study on the Process of Increasing Viscosity for Producing Foam Aluminum by the Powder Metallurgy Method: *Wei Li*[1]; [1]Shenyang Ligong University

Some of the factors which affect the foaming in a foamed aluminum casting process and microstructural evolution of metal foams have been investigated by applying the powder compact process in many literatures. But few studies on the effect of viscosity of the molten and on the mechanisms stabilizing the pore formation have been undertaken. In this paper, foamed aluminum was preparation by powder metallurgy, the viscosity of the liquid metal was adjusted by Ca-addition into the metal, resulting in improvement of stabilization of bubble and uniformity of pore microstructure. The mechanisms stabilizing of the pore formation have been is investigated, and the effect of Ca addition on porosity and pore microstructure is studied. Moreover, it has been proved that the effect of viscosity on the stabilizing of the molten is more important than oxide layer by means of dynamic observation on foaming course.

10:35 AM
Application of Thread-Forming Fasteners in Net-Shaped Cast Holes in Lightweight Metal Alloys: *Dean M. Paxton*[1]; Greg J. Dudder[1]; John Reynolds[2]; William Charron[3]; Todd Cleaver[4]; [1]Battelle - Pacific Northwest National Laboratory; [2]Research Engineering and Manufacturing, Inc.; [3]Ford Motor Company; [4]Tech Knowledge

The application of thread-forming fasteners (TFFs) in net-shaped cast holes of lightweight materials is being explored by the United States Automotive Materials Partnership (USAMP) through work at the Pacific Northwest National Laboratory (PNNL). Progress has been made applying TFFs in drilled hole applications for general assembly, and have reduced costs, reduced investment, and improved warranty while delivering comparable joint properties in an assembly. Successful application of TFFs in aluminum and magnesium alloy cast products with net-shaped holes will expand the use of lightweight materials due to the proven benefits already achieved in existing applications. This effort includes a parametric study of the relationship between joint strength and fastener reusability versus as-cast hole geometry in lightweight alloy test specimens. The strength of these thread-forming fastener joints with net-shape holes will be compared with two baseline joints, namely standard machine fasteners in tapped holes and thread-forming fasteners in drilled holes.

11:00 AM
Surface and Subsurface Damage in Al-Si Alloys Subjected to Lubricated Sliding Wear: Mustafa Elmadagli[1]; *Ming Chen*[1]; Ahmet Alpas[1]; [1]University of Windsor

Wear and surface damage during lubricated wear of a eutectic Al-Si (12% Si) have been studied and compared with those of the two hypereutectic alloys, an A390 alloy (18.5%Si) and a spray formed alloy (25%Si). The roles of second phase particle fracture and matrix material deformation and transfer on the wear resistance of the alloys have been studied through single pass scratch tests under both dry and oil lubricated conditions. Multi-pass sliding wear tests were also performed using ball-on-disk configuration. Sample surfaces were etched with 10% NAOH solution in order to expose the hard phases. The fracture toughness of secondary phases in these alloys was estimated using micro-hardness tests and

nano-indentation tests. Wear mechanisms will be discussed based on the observations made using focused ion beam, SEM, and a non-contact optical profilometer.

General Abstracts: Structural Materials Division: Microstructure and Properties of Materials II

Sponsored by: The Minerals, Metals and Materials Society, TMS Structural Materials Division, TMS: Alloy Phases Committee, TMS: Biomaterials Committee, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Composite Materials Committee, TMS/ASM: Corrosion and Environmental Effects Committee, TMS: High Temperature Alloys Committee, TMS/ASM: Mechanical Behavior of Materials Committee, TMS/ASM: Nuclear Materials Committee, TMS: Product Metallurgy and Applications Committee, TMS: Refractory Metals Committee, TMS: Advanced Characterization, Testing, and Simulation Committee, TMS: Superconducting and Magnetic Materials Committee, TMS: Titanium Committee
Program Organizers: Rollie E. Dutton, U.S. Air Force; Ellen K. Cerreta, Los Alamos National Laboratory; Dennis M. Dimiduk, U.S. Air Force

Thursday AM Room: 218
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Patrick L. Martin, U.S. Air Force

8:30 AM
Effects of Chromium Concentration on Oxidation and Melting of Ni-Al-Pt-based Alloys: *Donna L. Ballard*[1]; Brian Gleeson[2]; Sarath Menon[3]; Patrick Martin[1]; [1]U.S. Air Force; [2]Iowa State University; [3]Universal Energy Systems, Inc

Chromium has long been seen as a beneficial elemental addition to Ni-based superalloys for oxidation resistance. This will be shown to be particularly true for model Pt-modified γ-Ni+γ'-Ni3Al alloys. However, recent results also indicate that increasing chromium concentration can also be deleterious to bulk alloy melting temperatures. Data will be presented showing the differences in melting temperature ranges for Pt-modified γ+γ' alloys with 0-10 at.% Cr addition. These effects will be described and related to their impact on attaining chemical homogeneity in cast buttons.

8:55 AM
Metal Ion Migration through Surface Oxides on NiTi Alloys: *Emma Jane Minay*[1]; Gerdjan Busker[2]; [1]Imperial College; [2]ClusterVision Ltd

The most widely used shape memory and superelastic alloy, NiTi, is finding increasing use in a diverse range of long and medium term medical implants including orthodontic components, orthopeadic implants and stents. Ni ions are known to have allergic, toxic and carcinogenic effects and hence metal ion release from NiTi is of considerable concern. Experimentally, various single and multiphase oxide films can be formed on NiTi including rutile, anatase, brookite, NiO and nickel titanium oxides. It is generally felt that the production of a TiO_2 -type surface film is desirable as this is known to have excellent biocompatibility, being the surface phase present on Ti and Ti-alloy biomaterials. In this paper solution and migration energies of various defects and ions in these oxide coatings have been determined with the aim of determining the most appropriate surface oxides to minimize Ni ion diffusion and ultimate release into the physiological environment.

9:20 AM
Relationship between Morphological Evolution of the γ/γ' Microstructure and Creep Behavior of Ni-Based Single Crystal Superalloys: *Pierre Caron*[1]; [1]Onera/DMMP

In the high temperature regime (T > 900°C), the creep behavior of the single crystal nickel based superalloys for turbine blade applications is strongly dependent on the morphological evolution of the strengthening γ' particles. In particular, the topological inversion of the γ/γ' rafted microstructure is generally associated with the increase of the creep rate which precedes the final tertiary creep stage. This phenomenon of topological inversion where the initially dispersed γ' phase becomes progressively the matrix was analyzed in a series of single crystal superalloys deformed in creep at temperatures above 1050°C. The aim was to establish relationships between this phenomenon and the chemistry, the volume fraction of γ' phase and the creep behavior of these alloys.

9:45 AM
Metallurgical and Corrosion Behavior of Refractory Materials for Hydrogen Generation: Ajit K. Roy[1]; *Ancila V. Kaiparambil*[1]; Radhakrishnan Santhanakrishnan[1]; [1]University of Nevada, Las Vegas

Hydrogen production using nuclear power is one of the alternate steps being considered by the United States Department of Energy to meet the growing energy crisis. Thermochemical cycle such as the sulfur-iodine process is among the leading technologies presently under consideration. Recently, some refractory materials have been identified as candidate structural materials for heat exchangers to be used in the hydrogen generation. Zr705 have been evaluated for its tensile properties at temperatures ranging between ambient and 400°C. The cracking susceptibility of this material has been determined in an environment relevant to the hydro-iodic acid decomposition process using constant-load and slow-strain-rate techniques. Cyclic potentiodynamic polarization technique has been used to evaluate the susceptibility of this material to localized corrosion in a similar environment. The metallographic and fractographic evaluations of all tested specimens have been performed by optical microscopy and scanning electron microscopy, respectively. This paper presents the comprehensive test results.

10:10 AM Break

10:25 AM
The Effects of Post Heat Treatment in Thermally Sprayed Superfine WC-Co Coatings: *Seongyong Park*[1]; Changyung Park[1]; Munchul Kim[2]; [1]Pohang University of Science and Technology; [2]Research Institute of Industrial Science and Technology

WC-Co coatings with superfine carbide particles near the size of 100nm were fabricated by detonation gun spraying. Fabricated superfine WC-Co coatings showed improved hardness and wear resistance than those of conventional WC-Co coatings. The sprayed superfine coatings, however, revealed degraded properties compared with sintered superfine WC-Co bulk. The degradation of properties are explained as phase decomposition of WC to W2C and amorphous phase due to exposure of carbide particles to high temperature detonation flame during spraying and rapid quenching after spraying. In order to improve the mechanical properties of the coatings by recovering of carbide phases, post heat treatment was conducted in vacuum environment at temperature range of 400~900°C. The improved properties of coatings were elucidated in terms of microstructural changes and the relationship between mechanical properties and phase of carbide was also discussed.

10:50 AM
Performance of Alloy 800H at Elevated Temperature for Heat-Exchanger Application: Ajit K. Roy[1]; *Vinay Virupaksha*[1]; [1]University of Nevada, Las Vegas

The structural materials for high-temperature heat exchangers to generate hydrogen using nuclear power must possess excellent resistance to environment-induced degradations and superior high-temperature metallurgical properties. A primary water splitting cycle known as sulfur-iodine (S-I) process consisting of chemical reactions leading to the production of hydrogen is presently under consideration. Nickel-base austenitic Alloy 800H has been identified as a structural material for heat exchanger to be used in the nuclear hydrogen generation. Since Alloy 800H will be subjected to very hostile environmental conditions, the susceptibility of this material to stress-corrosion-cracking, hydrogen-embrittlement and localized corrosion has been determined by state-of-the-art experimental techniques. The tensile properties of Alloy 800H have also been determined at temperatures ranging from ambient to 600ºC. Scanning electron microscopy has been used to characterize the failure morphology of the tested specimens. Metallographic evaluations has been performed using optical microscopy. The overall data will be presented in this paper.

11:15 AM
The Effect of Heat Damage on the Mechanical Properties of 2014-T6, 2024-T3, 6061-T6,7050-T6, and 7075-T6: Tomas Oppenheim[1]; Kevin

Robinson[1]; Nick Neylan[1]; Rick Clark[1]; *Omar Es-Said*[1]; John Ogren[1]; [1]Loyola Marymount University

In the past couple of months, the Navy in San Diego has been having technical problems with their F-18's. Hot Exhaust began bleeding into the center barrel compartment, weakening the surrounding metal. The Navy had to ground several planes as a result of this. The Navy wants to examine the change in mechanical properties and electrical properties of five Aluminum alloys (7050-T6, 6061-T6, 7075-T6, 2014-T6, 2024-T3) after varying the thermal exposure times (1 min, 10 min, 30 min, 1 hr, 3 hr, 10 hr, 1 day, 10 day, 20 day) and temperatures (350F, 400F, 500F, 600F, 700F, 800F, 900F). Correlations between the yield and ultimate strength and the hardness and conductivity will be made. The Navy would like to use a non-destructive test such as the hardness and conductivity test and correlate the data to the yield and ultimate strength. This will help them prevent future problems.

11:40 AM

Microstructure and Mechanical Properties of Investment Cast Ti-6Al-4V: *Lawrence S. Kramer*[1]; Hao Dong[1]; Kevin L. Klug[1]; Ibrahim Ucok[1]; Laurentiu Nastac[1]; Mehmet N. Gungor[1]; Wm. Troy Tack[1]; [1]Concurrent Technologies Corporation

The microstructures and mechanical properties of investment cast Ti-6Al-4V have been studied as a function of casting thickness, weld-repair and heat treatment. Standard metallography and scanning electron microscopy fracture analysis techniques were utilized to characterize the material specimens. The microstructure study was focused on the size and distribution of prior-b grains, and on a/b phase morphology and distribution. Tensile and fatigue tests were performed on specimens extracted from cast components as well as on separately cast coupons and plates. Metallography and fractography were conducted on selected tensile and fatigue specimens. The results of these investigations are discussed as a function of section thickness, weld repair and heat treatment. This work was conducted by the National Center for Excellence in Metalworking Technology, operated by Concurrent Technologies Corporation under Contract No. N00014-00-C-0544 to the Office of Naval Research as part of the U.S. Navy Manufacturing Technology Program.

12:05 PM

Effects of Thermal Aging on 6061-T6 Aluminum Alloy: *Wail Salim Dahir*[1]; Dalal S. Hassouna[2]; Bryan M. Gayer[1]; Omar S. Es-Said[3]; Richard Clark[4]; John Ogrin[3]; [1]Los Angeles Unified School District; [2]New Horizon School; [3]Loyola Marymount University; [4]College of the Canyons

The influence of varying the thermal aging parameters on the physical and mechanical properties of 6061-T6 aluminum alloy was studied. The variables altered were heat exposure to temperatures ranging from 120-230°C in 10 degree intervals over variable ranges of time from 5-30 minutes in 5 minute intervals. This envelope was chosen to encompass the range of conditions used in the curing of a proprietary powder coating on an aluminum alloy. The purpose of this work is to determine whether or not the curing process for the coating in any way degrades the properties of the aluminum alloy. The influence of varying these parameters on the tensile strength, electrical conductivity, and hardness of the alloy is discussed and correlated. The completion of low temperature testing revealed no significant changes, while higher temperature exposures revealed degradation in the properties of the samples. A correlation between hardness and yield and hardness and ultimate yield is presented.

Magnesium Technology 2006: Alloy Development II

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Thursday AM
March 16, 2006
Room: 6B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Wayne Jones, University of Michigan; Per Bakke, Hydro Aluminium

8:30 AM

Behavior of Alkaline Earth Metal Oxides in Magnesium Alloys: *Shae K. Kim*[1]; Jin-Kyu Lee[1]; [1]Korea Institute of Industrial Technology

Magnesium alloys are gaining increased importance for many applications. Their range of applications could be further extended if their safety and elevated temperature properties were improved without damaging their original properties and increasing cost. The aim of this research is to manufacture CaO or SrO added magnesium alloys in terms of 1. increasing burning temperatures of alloys for ensuring safety during manufacturing and application, 2. reducing protection gas amount during melting and casting, 3. eliminating protection gas during forming processes of extrusion and rolling, etc., 4. maintaining or improving elevated temperature properties with lower amount of Ca or Sr than conventionally developed high-temperature magnesium alloys, 5. easy alloying of inexpensive CaO or SrO instead of expensive Ca or Sr with high oxidation tendency even during alloying. In this paper, effects of CaO or SrO on burning phenomena, oxidation resistance and optimum cover gas usage of magnesium alloys were evaluated.

8:55 AM

Computation of Local Constitutive Equations for Eutectic and Mg-Rich Dendritic Regions in High-Pressure Die-Cast AE44 Alloy: *Arun Sreeranganathan*[1]; Arun M. Gokhale[1]; [1]Georgia Institute of Technology

For modeling and simulations of the micro-mechanical and mechanical response of high-pressure die-cast Mg-alloy components, it is essential to have reliable quantitative data on the local constitutive behavior of various constituents (for example, eutectic region, Mg-rich dendrites, etc.) present in the microstructure. It is not possible to get such data from macro-scale mechanical tests. In this contribution, we present application of micro-indentation technique for computation of local stress-strain behavior of the eutectic constituent and Mg-rich dendrites in a high pressure die-cast AE44 alloy. The local constitutive equations of these constituents are computed through solution to an inverse problem using finite element (FE)-based numerical analyses. The computed constitutive equations are then utilized to simulate the overall global mechanical response of virtual alloys having different amounts of eutectic and dendritic constituents.

9:20 AM

Effect of Sr Additions on the Microstructure and Mechanical Properties of Mg-Al-Ca Alloys: *Akane Suzuki*[1]; Nicholas D. Saddock[1]; J. Wayne Jones[1]; Tresa M. Pollock[1]; [1]University of Michigan

The effect of Sr additions on the microstructure and mechanical properties was investigated in Mg-5Al-3(Ca, Sr) and Mg-4Al-4(Ca, Sr) quaternary alloys (wt%). The Mg-5Al-3(Ca, Sr) quaternary alloys consist of the dendritic α-Mg phase and intermetallic phases, C36-$(Mg, Al)_2Ca$ and $Mg_{17}Sr_2$, along the grain boundaries. The $Mg_{17}Sr_2$ phase forms with the addition of more than 0.25wt% Sr. The mechanical properties of these alloys were tested in compression at room temperature and 448 K. At both temperatures, the flow stress exhibited a minimum at 0.5wt% Sr. The effect of Sr additions on the flow stress will be discussed from the viewpoints of intermetallic compounds at grain boundaries and the solid-solution strengthening of the α-Mg phase.

9:45 AM

Effects of Alloying Elements on Microstructures and Mechanical Properties of Mg-Mm-RE Alloy System: *Hyun Kyu Lim*[1]; Ju Yeon Lee[1]; Tae Eung Kim[1]; Won Tae Kim[2]; Do Hyang Kim[1]; [1]Yonsei University; [2]Cheongju University

Although aluminum and zinc elements have been used as the most favorite alloying elements in magnesium alloys, their usage has been limited when the improvement of high temperature is required due to their lower eutectic temperatures. It has been reported that the addition of rare earth (RE) elements improves elongation as well as strength, thus improving high temperature formability. In the present study, the effects of rare earth elements, especially neodymium and yttrium, on Mg-Mm (Ce-based misch-metal) system have been investigated by observing the microstructures and mechanical properties. Moreover, we evaluated the properties of Mg-Mm-RE-X (X: Zn, Sn and In) alloy system. For example, the Mg-Re-Nd-Zn alloy sheet exhibited high yield strength and elongation at room temperature. Specimens have been fabricated by a hot-rolling method and tensile properties at ambient and elevated temperatures have been investigated. Phase identifications have been performed by X-ray diffraction and transmission electron microscope.

10:10 AM

Microstructure and Mechanical Properties of Mg-Zn-Si Wrought Alloys: *Kwang Seon Shin*[1]; Ji Hoon Hwang[1]; Young Gee Na[1]; Dan Eliezer[2]; [1]Seoul National University; [2]Ben-Gurion University of Negav

Mg-Zn alloys have a large age hardening response, stemming from the precipitation of a transition phase (ß'). The objective of this study is to develop new wrought Mg alloys with improved strength based on the Mg-Zn alloy. The effects of Si addition on the microstructure and mechanical properties of the Mg-Zn alloys were investigated. The addition of Si introduces the intermetallic compound, Mg2Si, which has high hardness and melting point, and thus improves the mechanical properties of the Mg-Zn alloys. However, it was found that the addition of more than 2 wt.% Si deteriorated the tensile properties of the Mg-Zn alloys, due to the occurrence of premature fracture along the interface between the polygonal Mg2Si particles and the Mg matrix. It was also found that the double aging treatment after extrusion and solution heat treatment significantly increased both yield and tensile strengths of the ZS alloys, but at the expense of tensile ductility.

10:35 AM Break

10:55 AM

Effect of Ca, Sr, and Zn on Phase Stability in Mg-Al Based Alloys: *Yu Zhong*[1]; Alan A. Luo[2]; Zi-Kui Liu[1]; [1]Pennsylvania State University; [2]General Motors Research and Development Center

Mg-Al based alloys are one group of the most popular magnesium-based alloys that are under development. The AM series with 2-6% Al and the AZ91 alloy offer good performance at room temperature. They have poor creep resistance at temperatures over 100°C, largely due to the g-Al12Mg17 phase. The additions of Ca and Sr into AM and AZ series alloys have been found to be beneficial not only to keep costs low but also to improve the mechanical properties, especially the creep resistance at elevated temperatures. In the present work, the effect of Ca, Sr, and Zn on phase stability of Mg-4.5wt.%Al alloy were investigated through thermodynamic modeling of the multicomponent system and by means of Scheil simulation and equilibrium calculations. Good agreement with available experimental observations was achieved. Proper Ca and Sr additions reduce the stability of g-Al12Mg17 in Mg-4.5wt.%Al alloys, while Zn addition does not.

11:20 AM

Microstructure and Thermal Response of Mg-Sn Alloys: Okechukwu Anopuo[1]; Yuanding Huang[1]; *Norbert Hort*[1]; Carsten Blawert[1]; Karl Ulrich Kainer[1]; [1]GKSS Research Centre

The future demand for light weight constructions requires alloy development to achieve an appropriate combination of mechanical properties and corrosion behavior of modern magnesium alloys. Therefore a new class of magnesium alloys based on the Mg-Sn system has been developed. Besides the combination of alloying elements in the new Mg-Sn alloys the property profile is ruled by the development of microstructure during solidification and subsequent heat treatments. To obtain deeper knowledge of the occurring phases Mg-Sn-Ca and Mg-Sn-Si alloys have been investigated in the F, T4 and T6 condition by means of electron microscopy, XRD and Vickers hardness to determine phases in accordance to the as cast and heat treated conditions. These experiments have been accompanied by the investigation of the corrosion behavior using salt spray tests and potentiodynamic measurements.

11:45 AM

Effects of Minor Addition and Cooling Rate on the Microstructure of Cast Magnesium - Silicon Alloys: *Patrick D. Quimby*[1]; Shu-Zu Lu; [1]Michigan Technological University

Minor additions of antimony, calcium, sodium, and phosphorus were added to Mg-Al-Si alloys with the intention of refining/modifying the microstructure, thereby increasing its mechanical properties. The high cooling rate of the die-casting process was simulated using a graphite wedge mould. The effects of cooling rate and minor addition on the microstructure of both Mg-Si hypoeutectic (AS21) and hypereutectic Mg-3%Si-2%Al cast alloys were examined. It was found that antimony does not show any obvious refinement or modification effect, sodium shows some limited modification, while phosphorus and calcium show a significant refinement and modification effect on both primary and eutectic Mg2Si phase. This may lead to the development of low cost, high temperature creep-resistant and wear resistant magnesium alloys for the automotive industry.

Magnesium Technology 2006: Welding and Joining

Sponsored by: International Magnesium Association, TMS Light Metals Division, TMS: Magnesium Committee
Program Organizers: Alan A. Luo, General Motors Corporation; Neale R. Neelameggham, US Magnesium LLC; Randy S. Beals, DaimlerChrysler Corporation

Thursday AM Room: 6A
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Naiyi Li, Ford Motor Company; Dan Eliezer, Ben Gurion University of Negev

8:30 AM

Effect of Grain Refinement on the Strength and Corrosion of Magnesium Alloy AZ31 Weld Metal: *Dan Eliezer*[1]; Carl E. Cross[2]; Thomas Boeelinghaus[2]; [1]Ben Gurion University of Negev; [2]Joining Div V5-BAM

Gas tungsten arc welds made on wrought magnesium AZ31 plate have been characterized for corrosion in saline solution (3.5% NaCl). Microstructural changes induced by the welding process resulted in different environmental behaviour of each zone (BM-base metal, HAZ-heat affected zone and FZ-fusion zone). The faster kinetics of corrosion in FZ and especially HAZ are attributed to (a) the coarse microstructure, consisting of large grains, and (b) very small amounts of ß-phase in the grain boundaries. Also, hardness traverses have shown that these zones are weaker than the base metal. Based on the significant effect of grain size on strength in magnesium alloys, the weld metal grains have been systematically refined using controlled oscillation during welding, and by adding a grain refiner to the weld pool. Detailed microstructure analyses have been carried out and the relationships between corrosion behaviour, mechanical properties and microstructure (grain refinement and second-phases formation) are highlighted.

9:00 AM

Friction-Stir and Surface-Friction Welding of Twin-Roll Strip Cast Mg Alloy Sheets: Sung S. Park[1]; C. D. Yim[2]; *C. G. Lee*[2]; Nack J. Kim[1]; [1]Pohang University of Science and Technology; [2]Korea Institute of Machinery and Materials

Mg alloys have the great potential for automotive applications mainly due to their low density and high specific strength. Recent development of twin-roll strip casting technology has shown that it can efficiently produce low cost, high performance wrought Mg alloy sheets. For the successful application of twin-roll strip cast Mg alloys, however, cost-effec-

tive and reliable ways of joining are needed. The present research is aimed at investigating the response of twin-roll strip cast Mg alloys to friction stir welding (FSW). In addition to FSW, surface friction welding (SFW), novel welding technique suited for thin sheets, has also been investigated. Two twin-roll strip cast alloys, AZ31 alloy and dispersion strengthened ZMA611 alloy, were subjected to FSW and SFW. Microstructure and mechanical properties of welded alloys will be discussed with respect to the effects of alloying elements and welding conditions. Comparison will also be made with commercial ingot cast AZ31 alloy.

9:30 AM

Micro-Alloying of Magnesium Wrought Alloys for Improved Electro-Magnetic Joining of Extruded Hollow Profiles: *Martin Bosse*[1]; Friedrich-Wilhelm Bach[1]; [1]University Hanover

Due to their low density, sufficient stability and high recycling potential, magnesium alloys offer an important potential as structural component in automotive and rail vehicle structures. In order to push the application of magnesium profiles in lightweight constructions, intensive research regarding an appropriate joining technology and the processing of alloys, which have to be adapted to this joining technology, is required. Therefore the essential aim of IW in the presented joint research project of the German Research Foundation (DFG) is to develop and characterize new alloys for joining extruded hollow profiles by electro-magnetic deformation. The electrical conductivity and formability of the base materials are of special importance for the electro-magnetic forming process. Therefore low-content wrought alloys are suited for the optimization by micro-alloying. Starting from known magnesium wrought alloys of the categories AZ, ZEK and ZME modified alloys are developed by addition of alloying elements such as calcium and zircon.

10:00 AM

The Laser Welding Characteristics of AZ31 Mg Alloy by Continuous Rolled for Automobile: *Mok-Young Lee*[1]; Woong-Seong Chang[1]; Byung-Hyun Yoon[1]; Yeong-Gak Kweon[1]; [1]Research Institute of Industrial Science and Technology

Magnesium alloys are becoming important material for light weight car body, due to their low specific density but high specific strength. However they have a poor weldability, caused high oxidization tendency and low vapor temperature. In this study, the welding performance of magnesium alloys was investigated for automobile application. The material was continuously rolled magnesium alloy sheet contains 3% Al and 1% Zn. Mg alloy sheets were welded using high power continuous wave Nd:YAG laser according to process parameters such as laser output power, travel speed, shielding conditions. The mechanical properties were evaluated for laser welded specimen and the microstructure was investigated also. For the results, the tensile properties of welded specimen were decreased obviously. The surface of welding bead was covered with oxidized magnesium dust but it was removed by simple cleaning work as wipe-out with paper tissue. Also under cut, that caused vaporization of base metal was occurred.

10:30 AM Break

11:00 AM

Intergranular Strains in the Dynamic Recrystallized Zone of a Friction-Stir Processed AZ-31B Magnesium Alloy: *Wanchuck Woo*[1]; H. Choo[1]; D. W. Brown[2]; Z. Feng[3]; P. K. Liaw[1]; S. A. David[3]; C. R. Hubbard[3]; Mark M. A. Bourke[2]; [1]University of Tennessee; [2]Los Alamos National Laboratory; [3]Oak Ridge National Laboratory

Friction-stir processing (FSP) is a solid-state joining technique, which creates a strong bond through the frictional heating and severe plastic deformation. The heat and plastic deformation, however, can induce a significant amount of the residual stresses, which may approach the yield point of the base material and cause a drastic increase in the crack-growth rate. In the present study, the residual strains were measured using the spallation neutron source in a FSP AZ-31B magnesium alloy plate. The residual intergranular stresses were observed in the dynamic recrystallized zone, which has experienced the severe plastic deformation, using 2 x 2 x 2 mm 3 dimension of macroscopic-stress-released coupons taken out of the FSP plate. The results of the macroscopic stresses, intergranular strains, and other properties (e.g., chemical compositions, textures, tensile properties, and hardness) of FSP AZ-31B will be discussed.

11:30 AM

Interface Chemistry and Mechanical Behavior of Fe Base Metals/Magnesium Alloys Assemblies: *Myriam Sacerdote-Peronnet*[1]; Jean-Claude Viala[1]; [1]University of Lyon

Bimetallic joints resulting from the association of Mg alloys and ferrous substrates are interesting in the scope of manufacturing low-weight components for the automotive and aeronautic industries. To obtain assemblies with optimized properties, it is necessary to acquire a thorough understanding of their interface chemistry and mechanical properties. The interface reactivity of different Fe/Mg-M systems (M=Al, Si, Mn, Zn, Zr is an alloying element of magnesium) was studied by two complementary approaches: determination of the phase equilibria in the ternary systems at 730°C, characterization of the reaction zones formed at the interfaces. Synthetic Mg-M alloys and commercial magnesium alloys: GA6Z1, GM2, M2 and RZ5 were used. We determined the growth kinetics and mechanism at these interfaces. Mechanical characterizations were carried out ("push-out"). We will point out the relations existing between the mechanical behaviour of the assemblies and the composition of the corresponding reaction zones.

Phase Stability, Phase Transformation and Reactive Phase Formation in Electronic Materials V: Damage Structures: Ni Plating, Tin Whiskers and Thermal Cycling

Sponsored by: The Minerals, Metals and Materials Society, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Structural Materials Division, TMS: Alloy Phases Committee
Program Organizers: Katsuaki Suganuma, Osaka University; Douglas J. Swenson, Michigan Technological; Srinivas Chada, Jabil Circuit, Inc.; Sinn Wen Chen, National Tsing-Hua University; Robert Kao, National Central University; Hyuck Mo Lee, Korea Advanced Institute of Science and Technology; Suzanne E. Mohney, Pennsylvania State University

Thursday AM
March 16, 2006
Room: 213B
Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Srinivas Chada, Jabil Circuit, Inc.; K. N. Subramanian, Michigan State of University

8:30 AM

High Energy Synchrotron X-Rays Study of Service-Related Damages in Lead-Free Solders: *K. N. Subramanian*[1]; Deep Choudhri[1]; Andre Lee[1]; [1]Michigan State University

Due to its geometry, solder joint is modeled as a highly constrained, heterogeneous, layered composite. When exposed to external fields, highly inhomogeneous stresses arise in a very heterogeneous manner. The observed surface damage appears after a few hundred TMF cycles and intensified on further TMF cycling. However, effect of TMF on residual performances of joint is quite the opposite to the observed surface damage. Rapidly decreases in properties occur after few cycles, a stage with no visible surface damage, and then stabilize after several hundred cycles, a stage in which surface damage intensifies to form the catastrophic crack. Obviously, the surface damages cannot be used to predict the service reliability of solders. Using the high penetration depth of high-energy synchrotron X-rays, we examined the internal changes in tin-based electronic solder joints. X-ray results gave a more complete picture of internal changes in solder joints relating to applied fields.

8:55 AM

Impact of Thermal Cycling on Intermetallic Growth and Void/Crack Formation for SAC/ENIG PBGA Solder Joints: *Luhua Xu*[1]; John H. L. Pang[1]; Faxing Che[1]; [1]Nanyang Technological University

Intermetallic growth and interfacial voids/crack formation between SAC/ENIG solder joint in 316I/O PBGA soldered assembly subject to thermal cycling are reported. The IMC thickness was measured on all solder joints and plotted vs location. Higher thickness was observed at the outermost solder after 1000 to 3000 thermal cycles. IMC growth under thermal cycling is faster than isothermal aging and subject to the loca-

tions. This indicates that thermal stress might accelerate element diffusion. The interfacial failure was commonly found at the component side of outmost solder joint. Voids/crack forms not only at the joint corners but also at the center of the interface. Coalescence of multiple voids causes the final breakdown. Young's Modulus of IMCs was characterized by Nanoindentation after different cycles. The modulus reduced from 180-200GPa to 130-150GPa after 3000 cycles. The impact of IMC thicknesses and Young's modulus was analyzed by Finite Element Modeling and shows different fatigue lifetime.

9:20 AM

The Kinetics of AuSn4 Migration in Solders: *Chien Wei Chang*[1]; C. E. Ho[1]; C. Robert Kao[1]; [1]National Central University

The fast migration of Au atoms in eutectic PbSn matrix was known as one of the main factors contributing to the Au embrittlement phenomenon in solder joint. In this study, we investigate whether such behavior also occurred in high-tin lead-free solders. Experimentally, Sn3.5Ag (wt.%) spheres with 500 microns diameter was soldered on BGA Au/Ni pads. It was found that those AuSn4 also migrated back to the solder/pad interface during thermal aging, and formed discontinuous or continuous layer at solder/pad interface. The AuSn4 layer became continuous when the Au in Au/Ni was thick. Finally, a simple sandwich structure of Au(1 micron)/Sn(100µmicrons)/Ni was applied to study the kinetics of Au migration in tin-matrix.

9:45 AM

Kirkendall Voids at Cu/Solder Interface and Their Effects on Solder Joint Reliability: *Zequn Mei*[1]; Sue Teng[1]; [1]Cisco Systems Inc

Recent studies, especially by Chiu et al and Date et al in the 2004 ECTC conference, demonstrate extensive Kirkendall voids at the interface of solder joint to Cu substrate, and their significant effects on the impact and shock strength of the solder joints. In this study, we focus on two issues, the condition for the void formation, and effect of voids on solder joint reliability. Samples of electronic assemblies of different packages aged or thermal cycled were cross-sectioned by either FIB or sputtering etching. The results show that voids at Cu/solder interface formed extensively in some cases, but not so much in others. So far, we are not clear exactly what factors control the void formation; it seems that the Cu plating process and the small concentration of Ni in either solder or substrate influences the void density and distribution. Shock strength at 400G of BGA packages aged for 20 days at 125°C did not degrade; the failure occurred by either delamination at the fiber/resin interface underneath the non-solder mask defined Cu pads, or inside the solder where close to the solder mask defined Cu pads. We also curve-fitted the Chiu's result of voids growth vs time at different temperatures with the equation of A = C t 0.5 exp (-Q/RT), to use it for prediction of the voided area at the product service condition.

10:10 AM Break

10:20 AM

Optimal Phosphorous Content Selection for Ni-P UBM with Sn-Ag-Cu Solder: *Yung-Chi Lin*[1]; Jenq-Gong Duh[1]; [1]National Tsing Hua University

The nickel plating has been used as the under bump metallurgy (UBM) in the microelectronic industry. In this study, the electroplated Ni-P UBM with different phosphorous content (7, 10, and 13wt%) was used to evaluate interfacial reaction during multiple reflow between Ni-P UBM and Sn-3Ag-0.5Cu solder paste. $(Cu,Ni)_6Sn_5$ IMC formed in the SnAgCu solder/Ni-P UBM interface during the first cycles of reflow. With increasing cycles of reflow up to 3 times, $(Ni,Cu)_3Sn_4$ IMC formed, while $(Cu,Ni)_6Sn_5$ IMC spalled into the solder matrix. With further increasing cycles of reflow, the Ni-Sn-P layer formed between $(Ni,Cu)_3Sn_4$ IMC and Ni-P UBM for Ni-10wt%P and Ni-13wt%P UBM. However, almost no Ni-Sn-P layer was revealed for the Ni-7wt%P UBM even after 10th cycles of reflow. In consideration of surface morphology, wettability of Ni-P UBM, and interfacial reaction of SnAgCu/Ni-P, the optimal phosphorous content selection of Ni-P UBM was decided and also discussed.

10:45 AM

Root Cause of Black Pad Defect of the Electroless Nickel/Immersion Gold Plating on BGA Pads: *Kejun Zeng*[1]; [1]Texas Instruments

Presence of high phosphorous (P) content in the failed pad surface was often cited as the evidence for black pad defect of the ENIG plating. It was proposed to decrease the P content in the nickel plating. On the contrary, some companies are proposing to use high P content to avoid the black pad defect. In the present work, solder reaction with ENIG plating and the resulted interfacial structure are studied. FIB polishing was used to reveal details of the microstructure of the ENIG plated pad with and without soldering. High speed pull test of solder joints was performed to expose the pad surface. Results of SEM/EDX analysis of the cross sections and fractured pad surfaces suggest that the black pad is the result of the galvanic corrosion of the electroless nickel plating by the gold plating bath. High P content is not the signature of black pad.

11:10 AM

Microstructural Feature of "Black Pad" Ni-P/Sn-Pb Interface: *Katsuaki Suganuma*[1]; Keun-Soo Kim[1]; Naoya Murata[2]; [1]Osaka University; [2]JEOL

The microstructure of back pad Au/Ni-P and its soldered interface was analyzed primarily by TEM. Seriously oxidized crack-like structure, which is localized, was observed under Au thin layer. This region has amorphous porous structure containing Cu as well as Ni and O. The oxidized region does not form intermetallic compounds at the interface while the sound Ni-P surface react to form Ni-Sn intermetallic growing into the solder layer with a P-rich layer into the original Ni-P plating. The degradation mechanism will be discussed based on the observation.

11:35 AM

Tin Whisker Prevention by Treatment of Substrate Surface Structure: *Makoto Takeuchi*[1]; Kouichi Kamiyama[1]; Katsuaki Suganuma[2]; [1]Victor Company Japan, Ltd.; [2]Osaka University

Tin coating on Cu substrate will cause tin whisker formation resulting in short circuit damage. Fine pitch connectors have serious problem of forming tin whisker under a pressure caused by mechanical connection. The authors have developed a new process for the prevention of whisker formation. The auhtors focused on the surface chemical treatment of substrates. The surafce chemical state has a great influence on whisker formation. The various chamical conditions of subsrates, especially Cu, are analysed and the most influential treatment will be proposed.

12:00 PM

JEITA Whisker Testing Methods for Connectors: *Hiroyuki Moriuchi*[1]; [1]Fujikura Ltd

JEITA has proposed a new testing method for tin whisker formationespecially for fine pitch connectors. This paper describes the details of this method and various factors on whisker formation will be discussed. Mechanical compression stress influences on whisker growth rate. Whisker is growth in room temperature rapidly. Tin thickness also influences whisker growth. Testing parameters will be also discussed in this paper.

Phase Transformations in Magnetic Materials: Processing and Characterization

Sponsored by: The Minerals, Metals and Materials Society, TMS Materials Processing and Manufacturing Division, TMS/ASM: Phase Transformations Committee
Program Organizers: Raju V. Ramanujan, Nanyang Technological University; William T. Reynolds, Virginia Tech; Matthew A. Willard, Naval Research Laboratory; David E. Laughlin, Carnegie Mellon University

Thursday AM Room: 213A
March 16, 2006 Location: Henry B. Gonzalez Convention Ctr.

Session Chairs: Ganapathiraman Ramanath, Rennsselaer Polytechnic Institute; Matthew A. Willard, Naval Research Laboratory

8:30 AM Invited
Effects of Large Magnetic Fields on FeCo-Based Alloys: Phase Transformations and Induced Anisotropy: Paul R. Ohodnicki[1]; Yuranan Hanlumyuang[1]; David E. Laughlin[1]; *Michael E. McHenry*[1]; [1]Carnegie Mellon University

FeCo-based nanocrystalline/amorphous nanocomposites are interesting due to large saturation inductions and high Curie temperatures. Structure sensitive properties can be tailored by inducing magnetic anisotropy through field annealing resulting in reduced high frequency core losses. In addition to directional ordering in the crystalline and amorphous phases, it may be possible to induce anisotropy by establishing some crystallographic texture in the nanocrystals through large field crystallization. It is therefore desirable to understand the effects of strong magnetic fields on relevant phase equilibria to design thermomagnetic processing schedules. Models of field induced anisotropy through directional pair ordering in crystalline FeCo alloys using Monte Carlo simulations will be discussed taking into account the tendency for chemical ordering. Effects of applied fields on the equilibrium bulk FeCo phase diagram will also be discussed including a predicted shift in the critical temperatures with increasing field for first (bcc to fcc) and higher order (order-disorder) phase transitions. The authors gratefully acknowledge financial support from the National Science Foundation through award number DMR-0406220.

9:05 AM Invited
Search for Very Large Magnetocaloric Effects in Materials with Field-Induced Crystallographic Phase Changes: *Robert D. Shull*[1]; Virgil Provenzano[1]; Alexander J. Shapiro[1]; [1]National Institute of Standards and Technology

It has been found in the recent past, initially in $Gd_5Ge_2Si_2$, that large magnetocaloric effects can be obtained in materials which possess a crystallographic phase change induced by the application of a magnetic field. As a consequence of this discovery, many investigators have looked for the next breakthrough in magnetic refrigerants exclusively in such systems. Unfortunately, this investigation model may not be correct as these same systems usually also possess large magnetic hysteresis losses which must be subtracted from the magnetocaloric effects to determine the material's usefulness. Recently, it was shown[1] that when such a subtraction is performed, the resulting refrigeration "capacity" is not as good as expected. Here a new model is presented for circumventing this "show stopper" by changing the phase equilibria of the system upon the addition of small amounts of an additional constituent. [1]V. Provenzano, A.J. Shapiro, and R.D. Shull, Nature 429, 853 (2004).

9:40 AM
Rapid Solidification of Sm-Co Permanent Magnets: Vinod K. Ravindran[1]; Shampa Aich[1]; *Jeffrey E. Shield*[1]; [1]University of Nebraska

Rapid solidification has been used effectively to produce Nd-Fe-B-based permanent magnets. It has, however, been less widely investigated for the production of Sm-Co-based materials. Here, we report the microstructural evolution of rapidly solidified Sm-Co alloys from 6 to 16 atomic percent Sm. We have observed a wide variety of phase formation and microstructures, ranging from primary Co dendrite formation to eutectic structures to the hard magnetic $SmCo_7$ compound. Particularly, we observed non-equilibrium formation of Co along with $SmCo_7$, whose presence caused a decrease in coercivity from ~10 kOe to 500 Oe. Alloying elements reduced the scale of the microstructure, effectively offsetting the detrimental effects of the Co phase formation and leading to a recovery of the coercivity. The eutectic structure with Co rods surrounded by $SmCo_7$ provides a natural path to nanoscale hard/soft magnetic nanocomposites, where control of scale and phase content is critical.

10:05 AM Break

10:25 AM
Ordering in Combined Reaction Processed FePd Bulk Intermetallics: Andreas Kulovits[1]; Anirudha R. Deshpande[1]; *Jorg Michael Wiezorek*[1]; [1]University of Pittsburgh

It has been shown in numerous works that ordering heavily deformed Fe-50at%Pd via a combined reaction transformation mode leads to a fine grained equiaxed structure with enhanced magnetic properties as compared to the polytwinned micro - constituent that forms upon conventional ordering of undeformed gamma Fe-50at%Pd. In this study FePd alloys of different composition Fe-Xat%Pd, X=34, 50, 61, were severely plastically deformed in the gamma FePd state by an equal channel angular pressing or ECAP operation. The structural evolution of the phase - transformation of the combined reaction in Fe-50at%Pd was investigated by means of XRD, SEM and TEM and compared to the combined ordering and decomposition reactions for the off-stoichiometric compositions. The change in magnetic properties during the different phase – transformation modes was monitored via VSM. The magnetic domain structures in the different alloys were compared and correlated to the individual microstructures by means of AFM and MFM.

10:50 AM Invited
Advanced Transmission Electron Microscopy on Magnetic Phase Transformations: *Yasukazu Murakami*[1]; Daisuke Shindo[1]; [1]Tohoku University

This paper reports recent technical advances in electron holography and its applications to some issues on magnetic phase transformations in smart materials. Taking advantages of the direct observation of magnetic flux and the peripheral techniques aiming at in situ observations, the holography studies have revealed correlations between magnetic domains and crystallographic microstructures (twins, antiphase domains, precursor lattice modulation of the matrix, etc.) in ferromagnetic shape memory alloys. The observations demonstrate that this magnetic imaging can be a powerful tool for explorations of transformation mechanisms, e.g., pattern formation and its temperature dependence above the transformation point. Updated results will be also presented with respect to the simultaneous measurement of magnetism and conductivity, which will provide beneficial information about magnetic inhomogeneity as observed near phase transformation temperatures in several compounds.

11:25 AM Invited
Magnetoelastic Precursor Effects in Ferromagnetic Shape Memory Alloys: *Sai Prasanth Venkateswaran*[1]; Marc J. DeGraef[1]; [1]Carnegie Mellon University

Ferromagnetic shape memory alloys in the Ni-Mn-Ga and Co-Ni-Ga alloy systems exhibit pre-transformation modulations of two types: one modulation is structural, and gives rise to the conventional tweed contrast in electron microscopy two-beam observations. The other modulation has a magnetic origin, and is visible only in the out-of-focus Lorentz observation mode. In this contribution, we will review the contrast mechanisms that are responsible for this type of modulation contrast. A strong magnetoelastic coupling in these materials is responsible for the modulations, which occur upon approaching the martensitic transformation temperature. We will present detailed results of phase-reconstructed Lorentz observations, which enable us to study the modulations with high spatial resolution. The pre-transformation behavior in these materials will be contrasted with that in other non-magnetic systems.

12:00 PM

Micromagnetism in a Nanophase Alloy Studied by Small-Angle Neutron Scattering: *Werner Wagner*[1]; Joachim Kohlbrecher[1]; [1]Paul Scherrer Institute

Magnetic structures on the nanometer scale were studied by Small-Angle Neutron Scattering (SANS) in a two-phase alloy of the CuNiFe system. This system, upon annealing, undergoes a phase transition forming ferromagnetic Fe/Ni rich precipitates embedded in a paramagnetic Cu-rich matrix. Small Angle Neutron Scattering, with the dual interaction of neutrons with atoms, i.e. nuclear and magnetic, offers the unique opportunity to study both, compositional and magnetic correlations, accessing the size range of 5 to 200 nm. Further, in the case of non-isotropic magnetic alignment, the magnetic SANS turns anisotropic following the orientation distribution of the magnetic moments in the samples. In the present work a detailed analysis of the field dependent magnetic SANS signal from the alloy for different stages of aging has been carried out, aiming to show how the magnetic moments of the ferromagnetic precipitates, combined a preferred crystallographic orientation, react in the presence of the external field.

12:25 PM Concluding Comments by Raju V. Ramanujan

Simulation of Aluminum Shape Casting Processing: From Alloy Design to Mechanical Properties: Prediction of Mechanical Properties

Sponsored by: The Minerals, Metals and Materials Society, TMS Light Metals Division, TMS Materials Processing and Manufacturing Division, TMS Structural Materials Division, TMS: Aluminum Committee, TMS/ASM: Mechanical Behavior of Materials Committee, TMS: Process Modeling Analysis and Control Committee, TMS: Solidification Committee, TMS/ASM: Computational Materials Science and Engineering Committee
Program Organizers: Qigui Wang, General Motors Corporation; Matthew Krane, Purdue University; Peter Lee, Imperial College London

Thursday AM
March 16, 2006

Room: 6D
Location: Henry B. Gonzalez Convention Ctr.

Session Chair: Paul N. Crepeau, General Motors Corporation

8:30 AM Invited

Multistage Fatigue Modeling of Cast A356 and A380 Aluminum Alloys: *Mark F. Horstemeyer*[1]; Yibin Xue[1]; David L. McDowell[2]; Christina Burton[1]; [1]Center for Advanced Vehicular Systems; [2]Georgia Institute of Technology

We present a multistage fatigue model with microstructure-property relations and descending order capturing deleterious effects inclusions: (1) Pores/Oxides > 200 microns, (2) > 100 microns free near-surface pores/oxides, (3) 60-90 pores/oxides microns w/large volume porosity fractions, (4) Pores/Oxides < 60 microns w/large volume porosity fractions, (5) Pores/Oxides w/low volume porosity fractions, signifying different casting features dominating fatigue life. Capturing cyclic responses, fatigue life compartmentalizes into four stages, fatigue crack growth incubation stage is modeled. Assuming a near-micron initial crack size, Microstructurally Small Cracks (MSC) initiate and grow to Physically Small Crack (PSC) to several dendrite cell sizes. Usually, 60-80% of life is spent in these three domains. Researchers combined these stages into crack initiation. We separate these mathematically different stages. Using the multistage fatigue model, two different cast aluminum alloys (A356 and A380) were studied in context of actual cast shapes.

8:55 AM Invited

Overview: Prediction of Fatigue Performance in Cast Aluminium Alloy Components: *Trevor Charles Lindley*[1]; Peter D. Lee[1]; Peifeng Li[1]; Daan M. Maijer[2]; [1]Imperial College; [2]University of British Columbia

The influence of cast processing conditions on the microstructure (SDAS) and defect population (pores, oxide films, intermetallic particles) has been studied in cast aluminium alloys. The size, distribution and complex three dimensional shape of the pores was characterized using 3-Dimensional X-ray tomography, giving more realistic dimensioning of pores compared to conventional 2–D metallography. For each cast condition, tensile and S-N fatigue properties were measured in the heat treated T6 condition. Using scanning electron microscopy, fractographic examination was performed in order to reveal the defect responsible for fatigue crack initiation. Models for situations where either crack initiation or small crack growth constituted the dominant phase of fatigue life were reviewed before formulating a methodology for the prediction of fatigue life of components. Residual stress effects resulting from machining or from the quench step in the T6 heat treatment were also included in life assessment.

9:20 AM Invited

Simulation of Tensile Test Bars: Does the Filling Method Matter?: *Mark R. Jolly*[1]; [1]University of Birmingham

Tensile testing is used throughout the Aluminium shape casting industry as a method for proving quality of both materials and process. Simulation work at the University of Birmingham, combined with experimental work by NTec, has demonstrated that the very method of filling can significantly influence the distribution and location of porosity within cast tensile test pieces. Simulations are carried out for two Al-Si alloys covering eutectic and long freezing ranges. Test parameters such as pouring temperature and filling rate are also evaluated. Comparisons with previously published mould designs are made using simulation as the experimental tool. Validation of the simulations are made using the new mould designs and the new Crimson up-casting facility located at the University of Birmingham.

9:45 AM

Fatigue Life Prediction in Defect-Containing Aluminum Castings: *Qigui Wang*[1]; Peggy Jones[1]; [1]General Motors Corporation

Increasing use of aluminum shape castings in structural applications has drawn great concern in fatigue properties of cast aluminum alloys. Fatigue life of cast aluminum components is controlled by maximum defect size in the material. The larger the defect size the lower the fatigue life. In defect-containing aluminum castings, the fatigue life can be predicted using fracture mechanics models together with the estimated extreme defect size in the castings by Extreme-Value Statistics (EVS). The maximum defect size predicted by EVS agrees quite well with measurements of the initiation pore sizes from the fracture surface.

10:10 AM Break

10:25 AM

Characterization of Small Fatigue Cracks in an Aluminum Casting Alloy A356: *Jingen Zhou*[1]; Guang Ran[1]; Yongfang Wang[1]; Qigui Wang[2]; [1]Xian Jiaotong University; [2]General Motors Corporation

In this paper, a cast aluminum alloy A356 was used to study small fatigue crack behavior. The da/dN-delta k curves, fatigue thresholds and closure stresses of fatigue cracks with different sizes were measured. The effects of crack size and shape on crack growth behavior and their closure are discussed. It is showed that the anomalous growth behavior of physically small fatigue crack and mechanically small fatigue crack is due to lower and various closure level and the effect of notch field and excessive plastic zone, respectively. The models for characterizing thresholds of physically small fatigue cracks and predicting lifetime of mechanically small fatigue cracks in notch field are proposed by taking account of these factors based on experiments.

10:50 AM

Modeling of Creep and Bolt-Load Retention Behavior of a Die Casting A380 Aluminum Alloy: *Qigui Wang*[1]; Cherng-Chi Chang[1]; [1]General Motors Corporation

Aluminum casting alloys exhibit creep behavior when the materials are exposed to high temperature and load. The creep properties of aluminum castings strongly depend upon porosity level and microstructural constituents. In this paper, the stress- and temperature-dependent creep behavior of a die casting A380 aluminum alloy is simulated using a classical constitutive model. The bolt-load retention behavior of the material is analyzed in a head bolt joint in an aluminum engine under thermal cycle condition using finite element method. The analytical model for the bolt-load retention simulation comprehends not only the plasticity in all

metal components but also the creep properties of aluminum threads in the engine block. The predicted head bolt load loss during engine thermal cycle is in good agreement with the experimental measurement. The simulation results also indicate that aluminum thread creep in the engine block is responsible for the load loss in the head bolt joint.

11:15 AM

Mechanical Properties Prediction Using MAGMAsoft for 319 Alloy Products with Copper Contents Variations: *Carlos Esparza*[1]; Alejandro Escudero[1]; Salvador Valtierra[1]; [1]NEMAK

Determination of the relationship between the local solidification time and copper contents to predict UTS, Yield Stress and Hardness for Cylinder Heads casted on a gravity semi permanent mold process with variations of a typical 319 alloy.

11:40 AM

Brief Review of Multiaxial High Cycle Fatigue: Ding Xiangqun[1]; *He Guoqiu*[1]; Chen Chengshu[1]; Zhu Zhengyu[1]; Liu Xiaoshan[1]; [1]Tongji University

In this paper the mechanism of multiaxial high cycle fatigue, especially under nonproportional loading is reviewed. The criteria used for life estimate in the multiaxial fatigue are discussed. Among the criteria reviewed, energy approach appears to be the most promising criterion for multiaxial fatigue life prediction. Accordingly, some suggestions are made for further work.

NOTES