ADSORPTION, ION EXCHANGE, AND SOLVENT EXTRACTION: Solvent Extraction II

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee, Copper, Nickel, Cobalt Committee, Lead, Zinc, Tin Committee, Precious Metals Committee
Program Organizer: Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

Wednesday PM Room: Plaza Room C
February 18, 1998 Location: Convention Center

Session Chair: Gus Van Weert, Oretome, Ltd., Caledon East, ON Canada L0N 1E0, Fiona Doyle, University of California, Berkeley, CA 94720-1760

1:45 PM INVITED
SOLVENT EXTRACTION OF FERRIC IRON FROM ZINC SULPHATE SOLUTIONS WITH DEHPA - INVESTIGATION OF NITRIC ACID AS STRIPPING AGENT: *G. Van Weert*[1]; Pieter Hogeweg[2]; [1]Oretome Limited, Caledon East, ON L0N 1E0 Canada; [2]Delft University of Technology, Applied Earth Science, Delft 2628 RX The Netherlands

Solvent extraction of iron from zinc refinery liquors has been investigated before, mainly on the MEHPA/HCl stripping combination. Leakage of chloride into the zinc electrolyte and the costs of handling the ferric chloride eluate have prevented this option from being adopted. This work explores the stripping of the ferric loaded organic phase with nitric acid to take advantage of the possibility of regenerating up to 6N nitric acid, and clean spheriodal hematite by autoclave treatment of ferric nitrate solutions. Since previous work had indicated that MEHPA was attacked by strong nitric acid, work was carried out with DEHPA in kerosene. Degradation testing proved DEHPA to be very stable up to 6N and 70C over a period of five days. It proved possible to remove ferric iron completely from synthetic zinc sulphate solutions irrespective of the DEHPA concentration. Stripping the ferric out proved to be problematic. Although stripping efficiencies were better at 50C than at 20C, it decreased with increasing DEHPA/Fe ratio in the organic phase. Eluates of no more than 5-10 g/l ferric nitrate were produced. Surprisingly, nitric acid was found to be less efficient at stripping than sulphuric acid at equivalent Normality and its efficacy levelled off above 4N. It was concluded that DEHPA is not the SX reagent to take advantage of the low cost autoclave decomposition of ferric nitrate/nitric acid regeneration in zinc hydrometallurgy and that another SX reagent is needed.

2:10 PM INVITED
SOLVENT EXTRACTION REMOVAL OF IRON FROM ZINC PROCESS SOLUTIONS USING ORGANOPHOSPHOROUS EXTRACTANTS: F. Principe[1]; *G. P. Demopoulos*[1]; [1]McGill University, Mining and Metallurgical Engineering, Montreal, Quebec H3A 2B2 Canada

In order for solvent extraction technology to be acceptable as an alternative to existing jarosite precipitation circuits, iron must be cleanly separated and concentrated into a feed stream suitable for downstream iron by-product recovery which meets market specifications and economics. Ten years ago, significant progress was made in a joint McGill University/CANMET project that involved iron extraction with mono(2-ethyl-hexyl) phosphoric acid. Our iron solvent extraction research was reactivated recently by looking into this and other members of the organophosphorous family. Our research discusses the mechanisms and control of anion (SO42-/Cl-) transport (feed/organic/strip), iron build-up in the strip liquor, and the extractant stability/selectivity. An overview of past and current research activity on this project constitutes the subject matter of the communication.

2:35 PM INVITED
SOLVENT EXTRACTION OF COPPER FROM ZINC SULPHATE LEACH SOLUTIONS AND THE EFFECT OF ORGANIC CONTAMINATION ON ZINC ELECTROWINNING: *George Owusu*[1]; [1]Hudson Bay Mining & Smelting Company, Flin Flon, Manitoba R8A 1N9 Canada

A study has been carried out on solvent extraction of copper, instead of the traditional zinc dust cementation process, from zinc sulphate leach solutions. In a series of experiments using plant solution containing 1.9 g/l Cu, 2 g/l Fe, 173 g/l Zn, 7.9 g/l H2SO4, etc. and LIX 622 in SX-1, about 98-99% extraction of copper present in the zinc sulphate solution was achieved with negligible co-extractions of Zn, Fe, Cd, Co, etc. Modification of the pH was not required for this reagent. The copper loaded organic was almost completely stripped using 150 g/l sulphuric acid. Investigation into the effect of any possible organic/extractant contamination on zinc electrowinning showed (if any) little effect on current efficiency when the organic was less than 45 ppm. Current efficiencies of 95-97% were obtained from a continuous electrowinning cell. At organic contaminations higher than 50 ppm, the current efficiency dropped to 94%. Visually, the organic-contaminated cathode sheets had rough surface morphology, becoming more intense with increasing organic concentration compared to non-contaminated cathode sheets.

3:00 PM INVITED
USE OF SOLVENT EXTRACTION TO REMOVE BISMUTH AND ANTIMONY FROM COPPER ELECTROLYTE AT THE SAN MANUEL REFINERY: *Troy A. Leese*[1]; Martin P. Neild[1]; Daniel K. Kim[2]; Benjamin R. Saito[2]; Sharon Young[3]; Charles J. Weidner[4]; [1]Zeneca Specialties, Metal Extraction Products Business, Blackley, Manchester M9 8ZS United Kingdom; [2]BHP Copper, San Manuel, AZ 85631; [3]BHP Copper, Tucson, AZ 85704; [4]Zeneca Specialties, Metal Extraction Products Business, Wilmington, DE 19850-5457

The charge for the copper refinery is a mixture of anodes produced at San Manuel and copper purchased from external sources. Control of unwanted impurities in the tankhouse is very important and beneficial. Currently available removal/recovery technologies were reviewed for the control of bismuth and antimony in the electrolyte. Recent studies have focused on solvent extraction (SX) technology and generated successful results for the removal and subsequent recovery of bismuth and antimony. The SX system employs the reagent ACORGA SBX-50 in conjunction with a patented high chloride stripping system. The latter enables recycle of the eluent, avoiding the high costs associated with conventional systems such as regeneration of resin. Concerns over potential transfer of organics and chloride ion to the electrolyte were readily addressed, solved and demonstrated using conventional established technology. This paper describes the benefits of electrolyte purification, the flexibility afforded by the SX system, the operational practices necessary for maintaining adequate control of bismuth and antimony impurities in the electrorefining environment, and possibilities for future development/exploitation of the Zeneca SX system at the San Manuel refinery.

3:25 PM Break

3:55 PM INVITED
THE OPERATION OF AN INDUSTRIAL COPPER SOLVENT EXTRACTION AND ELECTROWINNING CIRCUIT IN A NITROUS-SULFURIC ACID PRESSURE LEACHING PLANT: *Corby G. Anderson*[1]; [1]Principal Process Engineer, Center for Advanced Mineral and Metallurgical Processing, Butte, MT 59701

Most of the world's industrial copper solvent extraction and electrowinning circuits treat pregnant leach solutions from vat, heap or

dump leaches. However, in one case, copper containing solutions from a nitrogen species catalyzed sulfuric acid oxidative pressure leach of copper sulfide concentrates were treated by a solvent extraction and electrowinning circuit. In this presentation, the complete plant operation will be described including the pressure leaching system. Operating process improvements and challenges in this novel application of established SX/EW technology will be additionally discussed.

4:05 PM INVITED

THE USE OF MIXED EXTRACTANTS IN A UNIQUE MEMBRANE SX SYSTEM FOR THE RECOVERY OF COPPER FROM ACID CUPRIC CHLORIDE SOLUTIONS: *W. Daniel Ernt*[1]; Jeffrey Dimmit[2]; [1]Advanced Recovery Systems, Inc., North Hollywood, CA 91605; [2]AllCo Chemical Corporation, Galena, KS

In secondary metal recovery projects as well as small mining applications, SX system size, cost, and ease of operation are of greater importance than in large mining applications. To broaden the application of SX technology into the recovery of copper from acidic cupric chloride solutions, studies were performed using a mixture of two commercial extractants (adogen 381 and MOC-45). The use of these extractants in combination allows for the transfer of copper from a hydrochloric to a sulfuric medium that permits the isolation of the recovered copper using traditional techniques such as electrowinning or crystallization. In addition to optimizing the extractant chemistry of the system, the testwork focused on the use of a nontraditional separation system, based upon the use of hydrophobic and hydrophilic membranes. The application of this unique hardware system allows for a significant reduction in both the size and cost of the SX system and promises to extend the SX technology into the secondary metal and small mining applications.

4:30 PM INVITED

SIMULTANEOUS AND SELECTIVE EXTRACTION OF ZINC AND COPPER IONS BY TWO PARALLEL MODULES OF SUPPORTED LIQUID MEMBRANES: *Jaechun Lee*[1]; Jinki Jeong[1]; Jin Tae Park[1]; In Ju Youn[1]; Korea Institute of Geology, Mining and Materials, Taejeon 305-350 Korea

One of the main advantages of the supported liquid membrane (SLM) would be that different kinds of ions can be extracted selectively or simultaneously from multi-component solutions by parallel treatments with multi-SLM units. This distinctive feature of SLM extraction originates from its non-dispersive contacting operation between organic and aqueous phases. In this study, simultaneous and selective extractions of zinc and copper ions from their mixed solutions have been demonstrated using two parallel modules of SLMs. PC88A and LIX84 were used as the extractants for zinc and copper, respectively, and the Hoechst Celanese hollow fiber modules (Liqui-Cel Lab Module) as the supporters. The performance and optimum operation of the system were compared with those of the system in which the extraction of each component was achieved by individual runs.

4:50 PM INVITED

POLYMER-STABILIZED SUPPORTED LIQUID MEMBRANES: *Fiona M. Doyle*[1]; Mr. Yuchun Wang[1]; [1]University of California at Berkeley, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720-1760 USA

In principle, supported liquid membranes could be an exceedingly elegant separation process. However they tend to fail by displacement and emulsification of the organic solution in the pores, which allows mixing of the pregnant and strip solutions. We have stabilized supported liquid membranes comprising trioctylamine in nylon and PVDF supports by covering the pores with semi-permeable polyamide films, using an in-situ polymerization technique. Scanning electron microscopy demonstrates that the polyamide films are sensitive to production conditions and the nature of the support. The transport properties of stabilized supported liquid membranes for Cr(VI) are compared with those of unstabilized membranes.

ALUMINUM ALLOYS FOR PACKAGING III: Session III - Applications

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Subodh Das, Arco Aluminum Company, PO Box 32860, Louisvile, KY 40232

Wednesday PM Room: Fiesta B
February 18, 1998 Location: Convention Center

Session Chair: Subodh K. Das, ARCO Aluminum, Louisville, KY 40232

2:00 PM

ADVANCEMENT IN MANUFACTURING DRAWN AND IRONING (D&I) CAN BODIES: *T. C. Sun*[1]; [1]Kaiser Aluminum & Chemical Corporation, Center for Technology, Pleasanton, CA 94566 USA

This paper describes special techniques developed at the Kaiser Center for Technology in acquiring the total forming load and load distribution in a high speed can body-making operation, as well as the surface topographic effects on the forming load. The study led to the development of a much improved D&I process relative to the conventional method, especially in reducing tearoff rate and galling tendency. Factors such as tooling geometry, tooling setup, type of lubricant, delivery system, and basic metallurgical aspects are discussed.

2:30 PM

CAN SHEET PERFORMANCE AS A FUNCTION OF UBC'S RCS (CBS/CES)= (UBC): *W. B. Steverson*[1]; [1]Alcoa, Rigid Packaging Divison, Knoxville, TN 37902

Can customers, as they light weight, add innovation and drive to reduce their manufacturing costs are placing increased performance demands on the sheet being supplied. Customer parallel needs such as strength, formability, low earing, high surface quality and reduced tear offs are increasingly correlated to raw material quality, especially Used Beverage Cans (UBC's). Used Beverage Cans (UBC's) are an increasingly important raw material in the production of Rigid Container Sheet (RCS). This paper will outline the current state of recycling, the quality requirements that should exist on UBC's and how those requirements translate into manufacturing and customer can line performance. Recycling and quality can be aligned provided the customer needs are translated into meaningful raw material requirements and controls. This paper will describe the alignment and detail the associated metallurgical requirements and relationships.

3:00 PM

THE QUANTITATIVE DETERMINATION OF VOLATILES AND ODOR IN ENERGY CURABLE COATINGS FOR FLEXIBLE PACKAGING APPLICATIONS: *Dr. Paul E. Share*[1]; [1]The Valspar Corporation, Packaging Coatings Group, Pittsburgh, PA 15233

Abstract: Recent advancements in Analytical instrumentation have increased our understanding of the factors which determine the quantity and chemical composition of volatile components which may be released from materials coated with Energy Curable Materials. In addition, the correlation of the chemical composition with perceived odor permits us to address complex issues such as degree of cure in a direct and quantitative manner.

3:30 PM Break

4:00 PM

FLANGE FORMABILITY OF THE NECKED CANS BY SDN OR SFN: *Mr. Yoshinari Kikuta*[1]; Mr. Shin Tsuchida[1]; Mr. James E Prichard[2]; [1]Sumitomo Light Metal Ind., LTD, Reseach & Development Center, Nagoya 455 Japan; [2]Reynolds Metals Company, Can Division Machinery Plant, Richmond, VA 23237-1302 USA

Flange formability has been investigated after smooth die necking(SDN) or spin flow necking(SFN) for aluminum D&I cans using three kinds of body sheets. Flange formability after SDN or SFN is superior in the material with softer thickwall after necking of the HR-IA-CR process material. Flange formability is adversely affected during the reduction of the neck diameter by SDN and is not so affected by the thickwall hardness before necking. The reason is that the number of necking stages increases for smaller neck diameters. At that time, the thickwall is subjected to bending-unbending many times, which leads to a fragile thickwall. Flange formability after SFN is better than that after SDN on necked can smaller than 206 diameter, because SFN contains fewer repetitions of bending-unbending.

4:30 PM

NECKING FORMABILITY OF ALUMINUM D&I CANS DURING SDN OR SFN: *Mr. Yoshinari Kikuta*[1]; Mr. Shin Tsuchida[1]; Mr. James E Prichard[2]; [1]Sumitomo Light Metal Ind., Research & Development Center, Nagoya, Aichi 455 Japan; [2]Reynolds Metals Company, Can Division Machinery Plant, Richmond, VA 23237-1302 US

The material's forming behavior has been investigated during the reduction of the neck diameter of aluminum D&I cans using three different kinds of body sheets. In smooth die necking(SDN) with multiple stages the smaller neck diameters lead to thicker and softer thickwalls, and earing increases at the trimmed edge of the can. The earing grows at 45,135,225and 315° to the rolling direction. Thickwall at the 90° and the 270° positions thickens and softens most. It is considered that the softening is due to the Bauschinger effect. In spin flow necking(SFN) the thickwall thins and hardens, and earing increases. The earing increases at various positions to the rolling direction in the material from the HR-IA-CR processes. In spin flow flange reforming, thickwall and earing variations around the circumference are reduced by the effect of a stop ring.

5:00 PM (ORAL ONLY)

STRIP CAST ALUMINUM CAN STOCK PRODUCED BY THE KAISER MICROMILL® PROCESS: *T. C. Sun*[1]; [1]Kaiser Aluminum & Chemical Corporation, Center for Technology, Pleasanton, CA 94566

This paper reviews the metallurgical and forming characteristics of strip cast aluminum can stock made by the patented Kaiser Micromill® process. The high speed Kaiser caster, combined with an in-line thermomechanical process, provides a unique capability to produce all three can stock products - body, end, and tab - utilizing similar alloy compositions around the range of used beverage can scrap. The paper discusses the superior formability, texture control, metal strength and strength retention, as well as the performance of finished products of the in-line processed metal relative to the conventional batch-processed product.

5:30 PM (ORAL ONLY)

PROCESSING OF AA3004 ALLOY SHEET FOR BEVERAGE CAN END APPLICATIONS: Shixi Ding[1]; Yansheng Liu[1]; *James G. Morris*[1]; [1]University of Kentucky, Light Metals Research Labs, College of Engineering, Lexington, KY 40506

In the packaging industry, AA3004 alloy is currently being successfully used to make beverage can bodies. For can end application, the stronger AA5182 alloy is the primary choice to meet the high strength requirements. The present work proposes a modified thermal mechanical processing procedure which allows the production of AA3004 alloy sheet suitable for both can-body and can-end applications. In order to make effective use of precipitation hardening of AA3004 alloys, the modified processing procedure combines the regular work hardening process with a precipitation hardening process. It has been found from this study that a super strengthening effect is achieved in AA3004 alloy sheet subjected to this modified processing. The structures and the properties obtained in AA3004 alloy sheet material through this processing remain relatively stable during a coat baking process. For further comparison, formability of the alloy sheet was evaluated and discussed in terms of tensile elongation, bending ability, Olsen value, and crystallographic texture characteristics (ODF determinations.

ALUMINUM INDUSTRY INITIATIVES

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Jeffrey Keniry, Comalco, Research Center, Thomastown 3074 Australia

Wednesday PM Room: Fiesta D
February 18, 1998 Location: Convention Center

Session Chair: Jeffrey Keniry, Comalco, Research Center, Thomastown 3074 Australia

2:00 PM

ADAPTATION OF THE BAKING PROCESS TO ECONOMICAL DEMANDS AND ENVIRONMENTAL REQUIREMENTS: GENERAL ASPECTS AND TECHNICAL CRITERIA: *Mr. Michael Schneider*[1]; [1]Hoogovens Aluminium, Voerde Germany

The productivity of the VOERDE anode baking furnace was increased during the 26 years of operation by 35%. In the same time the requirements to anode quality, environmental compatibility and economics of the production were increased. Three measures of process-optimisation enable the plant to operate with a high efficiency. These modifications are the installation of "thinwall" flues, the conversion to volatiles-combustion and the replacement of the fume treatment center with tar precipitors and wet scrubbing by a dry-adsorption-system. The benefit of these interacting modifications is not only related to an increasing throughput-rate, a reduced energy-consumption and an improved emission-situation but also to higher and more homogeneous anode baking temperatures, an elimination of tar-wastes and a lowering of production costs. The experiences and results of this optimization can be helpful to other retrofitting projects.

2:25 PM

EXPERIENCES AND PERFORMANCE OF DRY SCRUBBING AT ALBA: *Mr. Geir Wedde*[1]; Mr. Mohammed H.Ghaith[2]; [1]ABB Miljo AS, 0603 Oslo Norway; [2]Aluminium Bahrain BSC, Manama Bahrain

The challenge for dry scrubbing of pot gas from aluminium reduction pots due to high inlet gas concentrations, high ambient and gas temperatures and humidity and meeting low emission levels demand tough plant management and flexible high performance dry scrubbers. Alba's dry scrubbers on pot gas have undergone severe testing and some adjustments to optimize the dry scrubber performance. The results of an extensive testing period are discussed. Experiences of the improved dry scrubbing process (ABBART) applied at Alba's potline 3 expansion are presented.

2:50 PM

ISO 14001: MANAGEMENT TOOL FOR ENHANCING THE ENVIRONMENTAL PERFORMANCE OF AN ALUMINUM REDUCTION FACILITY: *Elbert G. Massad*[1]; [1]Alumax of South Carolina, Goose Creek, S.C. 29445 USA

To remain successful today, aluminum reduction facilities must implement innovative and effective management systems to meet their environmental responsibilities. Alumax of South Carolina has adopted the ISO 14001 standard to help meet its objective of continuously improved environmental performance. ISO 14001 is an international standard designed to promote a commitment for protection of the environment including pollution prevention and continuous improvement. Registration to this standard by a third party is the ultimate way to demonstrate commitment to sound environmental management. Alumax received its certificate of registration in November, 1996. This case study discusses the implementation process employed by Alumax, including lessons learned during the process, anticipated and realized benefits. The paper will share ideas regarding timelines, critical early decisions, methods for meeting the requirements of the standard, and integration of ISO 14001 with an existing ISO 9000 system. Suggested policies, procedures and forms will be made available.

3:15 PM

CURRENT MODULATION ON VALESUL P19 POTS: *Luis Jorge Nunes*[1]; [1]Valesul, 23579-900 Santa Cruzq, Rio de Janeiro Brazil

Current modulation has always been considered as a potential generator of deleterious effects in potline operation, since it put a high variability in a process that intrinsically needs consistency. Historically, current modulation has been adopted whenever any external factor interferes in power supply. In Brazil, depending upon the type of power contract, the energy cost during the called "peak period", normally 3 hours per day, can be five times the normal tax, leading to aluminium production during this period as an unprofitable activity. In order to decrease the power costs, since January 1996, Valesul has decided to implement a current modulation of 20% to the potline during the peak period. The present paper will show the factors considered in the decision, the results obtained and how they were gotten.

3:40 PM

AN ASSESSMENT OF THE AVOIDABLE COSTS OF PRODUCTION FOR WESTERN WORLD ALUMINUM SMELTERS: *K. J. Driscoll*[1]; [1]CRU, London WC1X 0AD England

The full operating costs of production at all Western world aluminium smelters have been reviewed in terms of the fixed and the variables costs of aluminium smelting. The true variable costs of production, or the avoidable costs, represent the short-term costs that an aluminium smelter is no longer obligated to pay immediately upon curtailing any output on a temporary basis. This provided a guideline to those smelters which are most at risk to falling metal prices, and those which are most likely to benefit from closing some or all of their capacity if prices fall below a certain level. This paper describes the procedure for determining avoidable costs, and presents industry-wide results. An avoidable cost schedule is established which represents, in essence, the industry shut-down curve.

4:05 PM

ENERGY AND ENVIRONMENTAL ISSUES OF PRIMARY ALUMINUM PRODUCTION: *Ms. Nancy G. Margolis*[1]; Louis Sousa Sousa[2]; [1]Energetics, Inc., Columbia, MD 21046 USA; [2]U.S. Department of Energy, Office of Industrial Technologies, Washington, D.C. 20585 USA

A report on the energy and environmental issues associated with aluminum production has been prepared by the U.S. Department of Energy, Office of Industrial Technologies. The energy requirements of primary aluminum production have been calculated per ton of metal produced as well as industry-wide for the year 1995. Estimates of both combustion-related emissions and process emissions have also been made, including emissions of CO2 associated with the production of electricity used in reduction. These emissions are undergoing increasing scrutiny in light of government efforts to reduce carbon emissions.

4:30 PM

ALUMINUM INDUSTRY TECHNOLOGY ROADMAP: *Jack Eisenhauer*[1]; Henry Kenchington[2]; [1]Energetics, Inc., Columbia, MD 21046 USA

The U.S. aluminum industry has undertaken a bold technology planning initiative to position itself to compete effectively in global markets. With the help of the U.S. Department of Energy and the Aluminum Association, the aluminum industry has developed a technology roadmap to respond to new market opportunities and challenges. The roadmap will help align the technological resources of industry and government to meet the future demands of established and emerging customers. The roadmap is an initial effort to provide the critical link between the broadly defined strategic goals contained in the industry's "vision" document — "Partnerships for the Future" — and the detailed research portfolio that will be pursued through cooperative R&D partnerships.

ALUMINUM REDUCTION TECHNOLOGY: Cell Performance and Alumina in Potrooms

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Alton Tabereaux, Reynolds Metals Company, 3327 East Second Street, Muscle Shoals, AL 35661-1258

Wednesday PM Room: Fiesta E
February 18, 1998 Location: Convention Center

Session Chair: Mark Read, Kaiser Aluminum, Center for Technology, Pleasanton, CA 94566

2:00 PM

DISSIPATED ENERGY IN THE ALUMINIUM ELECTROLYSIS: *Dr. Signe Kjelstrup*[1]; Ellen Svinsas[2]; Dr. Ellen Marie Hansen[3]; [1]Institute of Physical Chemistry, Faculty of Chemistry and Biology, Trondheim N-7034 Norway; [2]Hydro Aluminium A/S, Technology Center, Ovre Ardal N-5870 Norway; [3]Prediktor AS, Fredrikstad N-1601 Norway

The dissipated energy of a 230 kA aluminium electrolysis cell has been analyzed by irreversible thermodynamics. Energy dissipated as heat in the electrolysis has been explained and located to cell materials. Unavoidable energy losses are specified. Thermal energy losses vary with the amount of aluminium that the cell produces, while the electrical energy losses do not. For a given cell, the energy losses can hence only be minimized to a limited degree. The energy efficiency according to the second law of thermodynamics was calculated and compared to first law analysis data for the cell.

2:25 PM

EFFECTS OF ANODIC GAS RELEASE ON CURRENT EFFICIENCIES IN HALL-HEROULT CELLS.: *Dr. Torstein Haarberg*[1]; Dr. Stein Tore Johansen[1]; Mr. Asbjørn Solheim[1]; [1]Sintef Materials Technology, Process Metallurgy and Ceramics, Trondheim N-7034 Norway

The fluid flow in the electrolyte, caused by anodic bubbles, is computed for different geometries and current densities. The paper will discuss how fluid flow data can be used to compute mass and heat transfer coefficients and how this can be interpreted in terms of current efficiency. The local mass transfer between metal pad and bath is computed and applied in evaluation of the current efficiency. Finally, the interaction of current efficiency and geometry defined by side ledge thickness is discussed in view of the present computations.

2:50 PM

CURRENT EFFICIENCY STUDIES IN A LABORATORY ALUMINIUM CELL USING THE OXYGEN BALANCE METHOD: *Mark M. R. Dorreen*[1]; Margaret M. Hyland[1]; Barry J. Welch[1]; [1]The University of Auckland, Dept. of Chemical & Materials Engineering, Auckland New Zealand

The effect of alumina concentration on current efficiency was investigated using the laboratory cell previously described (Light Metals 1997). This method applies an oxygen balance by using on-line mass spectrometric gas analysis. Electrolysis was performed and the efficiency was monitored until an anode effect occurred. Whilst the anode gas CO/CO_2 ratio changes, there was no significant variation in the current efficiency with alumina concentration. This trend applied for electrolyte chemistries in the range of 0-15 wt.% excess aluminium fluoride and for current densities ranging from 0.3-1.1 A/cm^2. Consistent with report trends, the current efficiency increased with decreasing bath ratio. A strong trend for increasing current efficiency with current density was also noted. No influence of inter-electrode distance was detected. However, the mass transfer conditions for dissolving metal would be the same at all inter-electrode distances in the apparatus and therefore no trend is expected by design.

3:15 PM

ESTIMATION OF CELL EFFICIENCY BASED ON THE RATE OF AL TRANSFER TO ANODE: *M. F. El-Demerdash*[1]; E. E. Khalil[1]; S. M. El-Raghy[1]; F. A. Mostafa[1]; [1]Cairo University, Faculty of Engineering, Cairo Egypt

A two dimensional model is developed to estimate current efficiency of the aluminium cell. The transfer rate of aluminium from cathode to anode is estimated as a result of diffusion and mass transfer under velocity field. The mixing differential equation in the homogeneous conditions is solved numerically with suitable boundary conditions at Al/electrolyte and electrolyte/anode interfaces. The diffusion coefficient of Al in the electrolyte is taken as $1*10^{-8}$ m^2/s and the max. solubility of Al in electrolyte as 0.03 wt/wt. The separate diffusion process provides values of 97.5% for a cell of 203 K amp, cell cavity of (9.75 x 3.95 m), and anode to cathode distance of 0.05 m. Under a given velocity field in Y-Z plane, a value of about 90% was obtained.

3:40 PM Break

3:50 PM

THERMAL CONDUCTIVITY IN CRYOLITE MELTS - NEW DATA AND IT'S INFLUENCE ON HEAT TRANSFER IN ALUMINIUM CELLS: *Dr. Asbjorn Solheim*[1]; Vladimir A Khokhlov[2]; Eugene S. Filatov[2]; Jomar Thonstad[1]; [1]SINTEF Materials Technology, Dept. of Electrochemistry, Norway N-7034; [2]Molten Salts Laboratory, Institute for High-Temperature Electrochemistry, Ekatherinburg 620219 Russia

The thermal conductivity (k) was measured for 31 melt compositions in the system NaF-AlF3-CaF3-Al2O3, using the method based on having a stationary temperature gradient in the annulus between two concentric cylinders. It was found that k increases with increasing NaF/AlF3 ratio and increasing concentrations of CaF2, whereas it decreased with increasing content of Al2O3. For normal industrial bath compositions, k is close to 0.8 W/m2K, which is a higher value than suggested earlier in the literature. Thus, reinforcement of old data obtained in a physical model indicates that the heat transfer coefficient between bath and side ledge may be in the range of 800-1200 W/m2K, which is consistent with newer literature.

4:15 PM

RATES OF DISSOLUTION COMMERCIAL ALUMINAS WITH DIFFERENT PHYSICAL PROPERTIES: *L. A. Issaeva*[1]; P. V. Polyakov[1]; V. A. Blinov[1]; I. G. Mikhalev[1]; V. I. Buzunov[1]; [1]Non-Ferrous Metals and Gold Academy, Light Metals Metallurgy Department, Krasnoyarsk 660025 Russia

Rates of dissolution and behavior of commercial aluminas supplied by different refineries in Russian design cells and in laboratory scale experiments have been determined. The smelter uses aluminas with great range of properties, for examples, content (-Al_2O_3changes from 1 to 33%, fines (less, than 44 (m) from 6 to 60%, BET from 32 to 80 m^2g. Dissolution time, determined using ccd measurements and visual observation can differ by 5 times for different aluminas. This difference depends essentially on the amount of alumina and rate of feeding. Secondary aluminas total dissolution times were more or less than that of primary aluminas in unstirring electrolyte. They depend on aluminas properties. Differences in agglomerates formation, their deterioration, floating and sinking are connected with the alumina properties and feeding.

4:40 PM

ON THE OPTIMUM CONDITIONS FOR CONTINUOUS ALUMINA FEED TO ALUMINIUM REDUCTION CELLS: *A. I. Begunov*[1]; B. S. Gromov[2]; R. V. Pak[2]; A. G. Barantsev[2]; A. A. Yakovleva[1]; [1]Irkutsk State Technical University, Irkutsk 664074 Russia; [2]Aluminium Plant, Bratsk 665617 Russia

Earlier, the quasistatistic fields of velocities of electrolyte in the vertical sections of the region between the anode and the sidewall lining were found out on physical models. These data show that the most unfavorable conditions for alumina dissolution occur in the prebake anode cells. But it has turned out that this is not the case. Now the authors put forth the suggestion about the counter pulsating flows of electrolyte being formed both in the vertical sections and in the surface layers of electrolyte in the inter-anode spaces of PA cells. Thanks to this fact, the point-type feeding devices were successfully introduced on PA cells and in the opinion of the authors are not practicable on Soderberg cells, where the alumina dissolution in counter pulsating flows is not possible. The requirements were developed for the designing of simple continuous alumina feed devices, in which the flow of aluminium oxide is fed through the calibrated dosing slot in the thermally insulated cover plate of a cell.

CAST SHOP TECHNOLOGY: Session IIIB - Semi-Solid Processing

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Diran Apelian, Worcester Polytechnic Inst., 100 Institute Rd., Worcester, MA 01609-2280

Wednesday PM Room: River Room B
February 18, 1998 Location: Convention Center

Session Chair: Andreas Alexandrou, Worcester Polytechnic Institute, Semi-solid Materials Processing Laboratory, Worcester, MA 01609 USA; John Jorstad,CMI-Tech Center Inc., Ferndale, MI 48220

2:00 PM

TWO-PHASE MODEL FOR PROCESSING SEMISOLID MATERIALS: *Dr. Andreas Alexandrou*[1]; Gilmer Burgos[1], Vladimir Entov[2]; [1]Worcester Polytechnic Institute, Semi-solid Materials Processing Laboratory, Worcester, MA 01609 USA; [2]Russian Academy of Science, Institute for Problems in Mechanics, 117526 Moscow Russia

The processing of materials in semisolid state offers distinct advantages over similar methods for near-net shaping. This process is ideally suited for die casting. In this process, the raw material is melted and allowed to cool and solidify, while the dendrites formed during solidification are broken up and their morphology is altered using mechanical, electromagnetic or other forces. The resultant slurry has an equiaxed microstructure made up of round, rosette-like crystals and, in some cases, of a fine dendritic microstructure. The process is called rheocasting, as the melt is rheologically manipulated during the liquid-solid transformation. A major benefit to the die-casting industry is that the rheocast ingot has significantly lower viscosity than the solid counterpart. The importance of this is that upon heating of the rheocast ingot to the two-phase region, the semisolid material flows easily under the application of shear. In essence, the semisolid material exhibits both solid-like and liquid-like behaviors. As a "solid", the material maintains its structural integrity; therefore, during processing it is handled like a solid. As a "liquid", the material flows with relative ease and fills die cavities in a progressive fashion. Prediction of the flow of a semi-solid slurry during processing may result in improved quality as well as efficient processes. Since the dynamic response of the material during processing is the result of the combined effect of liquid-solid and solid-solid interactions, we are presenting a mathematical model that takes into account the two-phase nature of the slurry. The model is based on the conservation of mass and momentum for the solid and liquid phases separately and an appropriate constitutive equation describing the interaction between liquid and solid phases. The changes in the rheology caused by the local variation of strain is represented by a continuous relation of the Herschel-Bulkley fluid type. The above model is implemented in a computational code using the classical Galerkin-finite element method with a segregated solution procedure. The code is tested on a three-dimensional flow through a sudden square expansion.

2:20 PM

A COMPARATIVE STUDY OF FRACTION-SOLID EVOLUTION IN ALUMINUM ALLOYS: *Celil A. Aliravei*[1]; Mihriban O.

Pekguleryuz[2]; [1]University of Quebec, Dept of Applied Sciences, Chicoutimi, Quebec Canada

Most solidification models assume that the fraction-solid (f) evolved during solidification is only a function of metal temperature (T) and use of Scheil equation to calculate the f-T curves. Since the fraction-solid is also a function of cooling-rates in castings, it is important to take this into account in the modelling of DC cast aluminum ingots in which cooling-rates can vary locally from <1degree C/s in the center to >10 degrees C/s near the surface. This paper compares (i) int f values determined experimentally for the AA6111, AA5182 amd AA1050 alloys - solidified at cooling rates of 1 degree C/s, 5 degrees C/s and 10 degrees C/s - via the computer aided cooling-curve analysis (CA-CCA) with (ii) the values calculated using the Scheil model in a thermodynamic software, Thermo-Calc. The CA-CCA was found to be a good technique to determine the f as a function of both temperature and cooling-rate. The experimentally determined e-T curves of each alloy exhibited some degree of variation with cooling rates, however, AA6111 showed the least variation. When compared with the experimental f-T curves, calculated curves obtained using the Scheil model failed to correctly predict the fraction solid evolution of all the alloys. However, after normalizing the Scheil f-T curves with the empirical correction factors, very good predictions for AA6111 at all cooling rates, and fairly good predictions for AA5182 at low to medium cooling rates were obtained.

2:40 PM

A MATHEMATICAL MODEL OF INDUCTION HEATING OF THIXOFORMABLE ALUMINUM BILLETS: *Nagy El-Kaddah*[1]; Raphael Craen[1]; Willem Loue[2]; [1]The University of Alabama, Dept. of Metallurgical and Materials Eng., Tuscaloosa, AL 35487-0202 USA; [2]Pechiney CRV, 38340 Voreppe France

Preheating of thixoformable alloys to the semi-solid state is the most critical aspect of the thixoforming process. Successful application of this technology requires uniform heating and accurate solid fraction control during the partial melting stage. This paper describes a comprehensive mathematical model for the analysis, design and optimization of induction heating of thixoformable billets. The model formulation permits full coupling between electromagnetic thermal processes through temperature dependence of physical and electrical properties of the alloy, and also takes into account melting kinetics of thixoformable alloys. A computational approach for solving the coupled electromagnetic and heat transfer equations without meshing and solving the magnetic field in free space is also described. This technique is based on control volume/integral formulation of the electromagnet field problem — the most efficient method for the numerical solution of eddy current problems. The model was validated by comparing numerical predictions against experimental measurements obtained using Pechiney's thixotropic ALTHIX aluminum 357 alloys. Excellent agreement was obtained regarding both evolution of the temperature field during heating and the onset of the billet melting. It is suggested that the model presented here is likely to provide a useful tool for the design, analysis and optimization of induction heating of thixoformable alloys.

3:00 PM

MEASUREMENT AND CALCULATION OF SOLID FRACTION IN QUENCHED SEMI-SOLID MELTS OF RHEOCAST ALUMINUM ALLOY A357: *Merton C. Flemings*[1]; A.M. de Figueredo[1]; Y. Sumartha[1]; [1]Mass. Inst. of Technology, Cambridge, MA 02139-4303

A review is given of recent work at MIT on fluidity and flow behavior of semi-solid alloys. Experiments relating fluidity and flow behavior of a hypoeutectic Al-Si alloy to structure are described, and results presented of high speed video images of the advancing front. It is shown that fluidity of hyper-eutectic Al-Si alloys at a given fraction solid is comparable to that of hypo-eutactic alloys. Thus it seems feasibile to form such alloys at temperatures less than 600°C, including those with Si contents in excess of 60 wt % (and hence with liquidus temperatures in excess of 1100°C).

3:20 PM

A COMPARATIVE EVALUATION OF MHD, SIMA, SPRAY CAST MICROSTRUCTURES: *Evangelos Tzimas*[1]; [1]Drexel University, Department of Materials Engineering, Philadelphia, PA 19104

In this work we identify the differences in the microstructural evolution of spray cast, MHD and SIMA cast and wrought aluminum alloys. Isothermal holding experiments followed by rapid quenching are performed to reveal the true microstructure of these alloys in the semisolid state and to evaluate the connectivity of the solid grains. Spray cast microstructures are initially completely equiaxed. MHD materials exhibit degenerated dendritic features that disappear gradually during heating in the semisolid state. SIMA microstructures contain elongated grains that also spherodize during reheating. The effect of the initial microstructure on grain morphology and growth is discussed. Simple mathematical models for the spherodization of MHD and SIMA microstructures are developed and compared with experimental data. The volume fraction of liquid is evaluated using Differential Scanning Colorimetry (DSC) on both wrought (A2014) and cast (A356) Al alloys produced by MHD, SIMA and Spray Casting and Mg-Al alloys (AZ91D). The effect of microsegregation due to production process of the volume fraction of liquid is studied in detail. Specific guidelines for semisolid processing are generated by exploiting the non-equilibrium state of semisolid materials in order to improve processability.

3:40 - 5:00 PM

PANEL DISCUSSION:

Panelists:
John Boylan, Alumax
Steve Midson, Buhler
Gene Clark, Hot Metal Technologies
Craig Bergsma, Northwest Aluminum
Oliver Gabis, Ormet
Samuel Norville, HPM
Christian Pluchon, Pechiney

CAST SHOP TECHNOLOGY: Session IIIBB - Equipment & Handling

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Diran Apelian, Worcester Polytechnic Inst., 100 Institute Rd., Worcester, MA 01609-2280

Wednesday PM Room: River Room A
February 18, 1998 Location: Convention Center

Session Chair: Jean-Francois Wadier, Aluminum Pechiney, Paris, France 92048

2:00 PM

OPTIMIZED CHARGING AND MELTING MANAGEMENT SYSTEM CMMS IN A SECONDARY ALUMINIUM CASTHOUSE: *Mr. Detlef Michael Maiwald*[1]; [1]LOI/LVE, 45138 Essen Germany

In the secondary aluminium industry various types of aluminium scrap are raw materials in a recycling process for the production of aluminium alloys. Generally the plant comprises melting furnaces, casting furnaces and casting equipment. CMMS is a computer system providing functions for an optimized charging and melting procedure in a secondary (or primary) aluminium casthouse. The charging and melting is integrated in a single automation strategy which ensures best productivity and reliability on high level of quality on the lowest level of production costs. The Charging Control Procedure calculates optimized charges for the best charge combination according to the defined production alloy and lowest input material costs. CMMS can be extended by a charge and equipment tracking system based on a radio frequency network. The Melting Control Procedure achieves the reduction of melt-

ing time, dross and energy costs by increasing the product quality. For this purpose CMMS gets the actual status of temperatures, fuel consumption and charging/melting cycle. From these data CMMS calculates the necessary set points for temperatures and production cycle by fuzzy control.

2:20 PM
TECHNICAL CONCEPT AND EQUIPMENT DESIGN OF THE FIRST SAUDI ARABIAN SECONDARY ALUMINUM SMELTER: *Mr. Christoph Schmitz*[1]; [1]ALPRO-Aluminium Processing GmbH, Bad Muenstereifel 53902 Germany

Large quantities of aluminum scrap, mostly UBC, are collected in the western province of Saudi Arabia. The Moslem pilgrims visiting the holy city of Makkah contribute a substantial share. Up to now this valuable raw material is exported. It appears to be a logical step to process the scrap material within the country in order to arrive at a higher added value. Consequently, SARCO, the first secondary aluminum smelter in Saudi Arabia was established. An analysis of available melting technologies proved that the rotary drum furnace was the best choice for the particular conditions. To improve the somewhat old fashioned technology heat transfer mechanism within the rotary drum furnace have been studied which resulted in the development of a new dual burner system to improve melting efficiency and heat economy. Furthermore, production procedures were established for de-coating and melting with the target to lower the emissions. The entire plant is designed according to German environmental standards.

2:40 PM
FURNACE TENDING BY MECHANIZATION OF THE OPERATIONS: *F. Zannini*[1]; [1]Techmo Car S.p.A., Limena, PD Italy

The traditional melting/holding furnace tending which comprises scraps charging,molten metal accumulation, metal stirring, dross skimming, furnace wall and bottom cleaning involves high volume of manual work, low efficiency, heat losses and drastic degradation of the furnace lining due to frequent temperature drops/heat shocks. Alcoa - Fusina equipped with two different types of melting/holding furnaces worked at traditional technology has decided to upgrade technical level of the operation of his furnaces through introducing a piece of up to date machinery enabled to carry out all the related functions. The paper describes the technical solution worked out by Techmo in close collaboration with Alcoa - Fusina, the main objectives and results to be obtained by the introduction of Techmo's machinery in relation with the furnace run and technology, as well as labour safety and environmental conditions. The solution is flexible and versatile enough to be introduced to the wide range of furnace design.

3:00 PM
THE ECONOMY OF EXTRUSION SCRAP RECYCLING : *Roger A.P. Fielding*[1]; [1]Benchmarks, Kingston, Ontario Canada

Recent advances in melting, metal treatment and casting technologies have a major impact on the economics of recycling aluminum extrusion scrap. Technologies which permit rapid charging, melting and melt preparation, are combined with processes to remove gases and particulates, to refine and to cast uniform ingot structures. The resulting facility is capable of producing a wide range of alloys and ingot sizes with minimum inventory levels while operating at high levels of productivity and energy efficiency.

3:20 PM
CRITERIA FOR CHOOSING REFRACTORIES IN ALUMINUM HOLDING AND MELTING FURNACES: *Claude Allaire*[1]; S. Quesnel[1]; S. Afshar[1], [1]Ecole Polytechnic, Metallurgy and Materials Engineering Department, Montreal, Quebec Canada

Refractories in aluminum holding and melting furnaces are corroded, in service, by the action of molten metal, under the presence of the surrounding atmosphere, as well as the thermal gradient across the metal line, where fluxing agents can be used. Such corrosion leads either to internal and/or external corundum growth, depending on the position of the refractory material in the furnace, with respect to the metal line. Different testing procedures as well as criteria are presented in this paper to permit the selection of refractories offering maximum resistance to corundum growth, at and below the metal line in the above furnaces. The effect of the material's composition and porosity on its corrosion resistance, in such applications, is also discussed.

3:40 PM
THE NEXT GENERATION OF COMBUSTION TECHNOLOGY FOR ALUMINUM MELTING: *Mr. David G. Schalles*[1]; [1]Bloom Engineering Co., Inc., Pittsburgh, PA 15236 USA

This paper will discuss the latest developments in the area of regenerative combustion systems. Field data from the newest generation of "Flameless" Ultra Low NOx and High Efficiency Regenerative systems are used to demonstrate that these systems represent the standard by which alternative combustion system types should be judged. The new generation of regenerative burners will be shown to be technologically superior to other types of combustion systems in the areas of fuel efficiency, emissions (NOx, CO2 and particulates) and productivity. Furthermore, the drawbacks to previous regenerative systems have been reduced or eliminated. The author concludes that the new generation of Flameless Regenerative Burners should be installed on all continuous (sidewell) aluminum melters, and should also be strongly considered for most batch-type melters.

4:00 PM
ELECTROMAGNETIC EDGE DAMS FOR TWIN-ROLL CASTING: *K. R. Whittington*[1]; P. A. Davidson[1]; P. Thomas[2]; L. Wright[2]; J. D. Hunt[3], The Metal Society University of Cambridge, Dept of Engineering, Cambridge, CB2 1PZ U.K.; [2]Kvearner Metals, Sheffield UK

In the roll-casting of ferrous and non-ferrous metals it is necessary to support the liquid metal pool at the edge of the rolls. Conventional refractory edge dams are prone to erosion and need frequent replacement. We have developed a simple, non-contact, electromagnetic edge-dam which works on principle of high-frequency electromagnetic levitation. The device is readily retrofitted to existing casters and recent laboratory tests and casting trials with aluminum have proved successful.

DEFECTS IN CRYSTALS: A SYMPOSIUM HONORING THE CONTRIBUTIONS OF JOHN P. HIRTH: Diffusion and Thermodynamics

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Chemistry & Physics of Materials Committee, Physical Metallurgy Committee, Shaping and Forming Committee

Program Organizers: Craig S. Hartley, National Science Foundation, 4201 Wilson Blvd Room 545, Arlington, VA; Brent L. Adams, Carnegie Mellon University, Dept. of Materials Sci & Eng., Pittsburgh, PA 15213-3890; Richard G. Hoagland, Washington State University, Dept. of Materials Sci & Eng., Pullman, WA 99164-2920; Rob Wagoner, The Ohio State University, Dept. of Materials Sci & Eng., Columbus, OH 43210

Wednesday PM Room: 102
February 18, 1998 Location: Convention Center

Session Chair: Robert Rapp, Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

2:00 PM INVITED
SELF-DIFFUSION WITHIN THE CORES OF A DISSOCIATED GLIDE DISLOCATION IN AN FCC SOLID: *Professor Richard G.*

Hoagland[1]; Dr. Arthur F. Voter[1]; Dr. Stephen M. Foiles[1]; [1]Washington State Univ., Mech. and Matls. Eng, Pullman, WA 99164-2920 USA

An atomistic model is employed to extract details of the energetics of vacancy diffusion within the cores of a dissociated glide dislocation. An elastic band method is applied to the model to explore the migration energies for various paths in the cores of two, closely-spaced, Shockley partials, one of which is pure edge, the other nearly screw. The calculations were performed using an EAM potential for aluminum with a stacking fault energy of about 120 mJ/m**2, and so the partials are separated by about 0.6 nm. Among other things, we find that migration energies parallel to the line of the edge are much higher than in the perfect crystal and instead a zigzag path is favored. Furthermore, a helical path is favored in the mostly screw partial. The migration energy for a vacancy along an infinite stacking fault is found to be somewhat less than in perfect crystal. A kinetic Monte Carlo method incorporates this information to estimate vacancy diffusivity in the cores relative to the perfect crystal. This work was supported by the United States Dept of Energy, Office of Basic Energy Sciences, Division of Materials Science under Grant DE-FG06-87ER45287.

2:30 PM

ROLE OF METAL-OXIDE INTERFACIAL REACTIONS ON THE INTERACTION BETWEEN OXIDATION AND DEFORMATION: *E. Andrieu*[1]; B. Pieraggi[1]; A. F. Gourgues[1]; [1]ENS Chemie Toulouse, Toulouse 31077 France

The influence of oxidation on the creep behavior of Alloy 600 was studied at 300 to 600°C. A strong coupling was observed between oxidation and deformation, related to the growth of fast growing Ni-rich scales such as NiO or $NiCr_2O_4$ spinel. From the influence of oxygen partial pressure, the growth of intergranular Cr_2O_3 particles was found to impede the displacement of the interface between the fast growing oxide and the subjacent alloy, which prevented the annihilation of cation vacancies arriving at the interface. Then vacancies were injected into the alloy with subsequent diffusion and annihilation at internal sinks. For such conditions, the coupling of oxidation and defonnation can be strictly related to the growth of the p-type oxide. An analysis of the embrittlement mechanism involving vacancy injection resulting from interface reactions for the constrained oxide nucleation and growth at the tip of a propagating crack is proposed. According to this mechanism, the passage of vacancies through the oxide-alloy interface induces a change in the local creep properties of the alloy substrate.

2:50 PM

SHOCK-INDUCED DISPLACIVE TRANSFORMATIONS IN TA: *Dr. Luke M. Hsiung*[1]; [1]Lawrence Livermore National Laboratory, Materials Science and Technology, Livermore, California 94551-9900

Deformation substructure developed within shock-loaded pure Ta (45 GPa, room temperature) has been examined using transmission electron microscopy. In addition to a high density of dislocations and {211}<-111> type deformation twins, a β (bcc) -> ω (hexagonal) displacive transformation was found to occur with a plate-like ω phase formed within the β matrix. The orientation relationships between the β and ω phases are $\{211\}_\beta \parallel \{1010\}_\omega$, $\langle 111\rangle_\beta \parallel \langle 0001\rangle_\omega$ and $\langle 0\text{-}11\rangle_\beta \parallel \langle 1210\rangle_\omega$. The lattice parameters of ω phase are $a = 2(d_{011})_\beta = 0.468$ nm, and $c = 3/2(d_{111})_\beta = 0.268$ nm. Mechanism for the β -> ω displacive transformation will be discussed.

3:10 PM

RELAXATION OF COHERENCY STRAINS IN METALLIC DIFFUSION FIELDS VIA POINT, LINE AND SURFACE DEFECTS: *John S. Kirkaldy*[1]; [1]McMaster University, Brockhouse Institute for Materials Research, Hamilton, Ontario L8S 4L7 Canada

The Hirth-Feng representation of coherency strain relaxation in thin films by dislocation multiplication and motion is adapted to three different binary systems previously identified by J.W. Cahn and coworkers as Vegard's law sensitive and therefore potentially subject to diffusional and/or constitutional anomalies due to coherency strains. We conclude that in the case of infinite diffusion couples and solid diffusion profiles in liquid film migration and diffusion induced grain boundary migration the effective film thickness greatly exceeds the critical thickness for onset of multiplication and relaxation, so anomalous diffusion coefficients or interface constitutions are not to be generally expected. In the case of conditions for spinodal decomposition the effective thickness is usually such as to sustain coherency strain and this, on occasion, is known to be strong enough to suppress the spinodal reaction entirely. In this case a unidirectional lamellar discontinuous reaction as in Au-Ni can ensue with s train released by deposit of misfit dislocations along the trailing phase boundaries. This steady state spinodal reaction can be formulated as a solution of the stationary state Ginzburg-Landau equation with the usual wavelength degeneracy making an appearance.

3:30 PM

BIPHASE DIAGRAMS FOR THIN-FILM MULTILAYERS: *Suliman A. Dregia*[1]; R. Banerjee[1]; Hamish L. Fraser[1]; [1]The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

Structural stability in thin-film multilayers is described in terms of classical thermodynamics, involving the competition between bulk and interfacial energies. A new type of phase diagram is introduced, the biphase diagram, in which concurrent phase stabilities are mapped as a function of two degrees of freedom, corresponding to two independent layer thicknesses in a periodic multilayer. The model is illustrated with experimental results from Al/Ti thin-film multilayers. As a function of increasing the periodic size scale of the multilayer, the two metals were found to coexist as hcp/hcp, fcc/fcc, and fcc/hcp biphases. Thus, the behavior of the Ti layers appeared to be unconventional, as they transformed from their bulk structure (hcp) to a metastable structure (fcc)on thickening. The model, including the effects of coherency strains, will be presented to explain the Al/Ti results, as well as to offer a tool for designing and developing metastable multilayered materials.

3:50 PM

DEFECTS IN HfCo2 C15 LAVES PHASE: *Dr. Paul Gabriel Kotula*[1]; Dr. Katherine C. Chen[1]; Dr. Fuming Chu[1]; Dr. Dan J. Thoma[1]; Dr. Terence E. Mitchell[1]; [1]Los Alamos National Lab, Center for Materials Science, Los Alamos, NM 87545 USA

Laves phase intermetallics hold promise for applications such as high temperature structural materials. They are however generally brittle at lower temperatures. One strategy currently being pursued to overcome the poor low temperature mechanical properties is selected alloying of binary Laves phases with ternary additions. $HfCo_2$ is a C15-structured Laves phase with a nearly ideal atomic radius ratio (1.26) and a large solubility range which should allow for a wide range of possible alloying additions. Single-phase $HfCo_2$ alloys have been analyzed by transmission electron microscopy as a baseline for future alloying experiments. It is found that the stacking fault energy of $HfCo_2$ is large relative to other C15 Laves phase alloys (e.g., HfV_2 and $NbCr_2$). Perfect dislocations (i.e., no visible dissociation in weak-beam dark-field images) with (1/2)<110> Burgers vectors are seen to dissociate into partial dislocations with (1/6)<112> Burgers vectors. Dislocation arrays comprising low-angle grain boundaries have also been observed. These observations will be discussed with respect to the observed mechanical properties of $HfCo_2$.

4:10 PM

ATOMISTIC SIMULATION OF POINT DEFECTS AND DIFFUSION IN NiAl: *Dr. Yuri Mishin*[1]; Dr. Diana Farkas[1]; [1]Virginia Tech, Materials Science and Engineering, Blacksburg, VA 24061 USA

Results of atomistic simulations of point defects and diffusion in B2 NiAl are presented. We use an embedded-atom potential fitted to equilibrium properties and planar fault energies of NiAl, as well as the vacancy migration energies in pure Ni and Al. The formation energies of vacancies and antisites are calculated by molecular statics. The equilibrium defect concentrations are determined as functions of temperature and the alloy composition near the stoichiometry using the grand canonic ensemble formalism. The results show good agreement with the experimental data and the triple-defect mechanism of disorder in NiAl. Several mechanisms of self-diffusion are considered, including the mechanism of next-nearest-neighbor vacancy jumps, the 6-jump vacancy cycle mechanism and the 4-ring mechanism. The respective saddle-point energies are calculated by molecular statics. For each mechanism the diffusion coefficients and the effective activation energy of

Ni and Al diffusion are established as functions of the alloy composition and temperature. Diffusion of both Ni and Al in the stoichiometric compound is dominated by next-nearest-neighbor vacancy jumps. The effect of the off-stoichiometry on the diffusion characteristics and the atomicmechanism is also analyzed.

4:30 PM

INTERDIFFUSION RELATED INTERNAL VOLUME CHANGES AND THEIR EFFECTS ON KIRKENDALL SHIFT AND SURFACE CONTOURS OF DIFFUSION COUPLES: *Dr. Volker Ruth*[1]; Reimar Voigt[1]; [1]University Oldenburg, Physics, D-26111 Oldenburg Germany

The imbalance of diffusion fluxes in multi-component diffusion systems gives rise to internal local volume changes in two ways: (i) By incorporation of diffusion induced excess atoms and vacancies in the crystallites and (ii) by composition dependent lattice parameter changes. The incorporation process will proceed via dislocation climb; the vacancies may, however, also coagulate to form pores. The local differences of internal volume changes will cause stress fields that are supposed to play a dominant role during the resulting surface contour changes and that may have a back-effect on the diffusion rates. A phenomenon oriented correction of Darken's second equation is given and a theory for the surface contour changes proposed. For some simple cases the results are compared with experimental findings.

4:50 PM

THE INFLUENCE OF ALLOYING ELEMENTS ON INTERSTITIAL SOLUTES-A THERMODYNAMIC APPROACH: *George R. St. Pierre*[1]; [1]The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 USA

John Hirth has made many critical contributions toward an understanding of the influence of interstitial solutes in alloys and the interactions between alloying elements and interstitial solutes. In this contribution, a thermodynamical model is presented which provides a description of the chemical activity coefficients of interstital solutes. The model extends the salvation shell approach of Wagner and relies on a statistical thermodynamic analysis with one adjustable energy parameter. The chemical potential of the solute is the weighted time average of its value in various couplings. The model is illustrated for over twenty systems containing C, 0, H, N, and S. The one-parameter model based on this analysis provides a significant improvement over current interaction parameter methods.

EDUCATIONAL APPROACHES TO TEACHING INTRODUCTORY COURSES: HOW TO TEACH A BETTER COURSE: Session II

Sponsored by: Education Committee

Program Organizers: Marc DeGraef, Carnegie Mellon University, Dept. Material Sci & Eng., Pittsburgh, PA 15213-3890; Linda Schadler, RPI, Materials Sci & Eng. Dept., Troy, NY 12180-3590

Wednesday PM Room: 103
February 18, 1998 Location: Convention Center

Session Chair: TBA

2:00 PM

THE SCIENCE AND DESIGN OF AN INTRODUCTORY MATERIALS COURSE: *James P. Schaffer*[1]; [1]Lafayette College, Chemical Engineering Dept., Easton, PA 18042-1775 USA

Many factors are important in the design of a successful introductory materials course. The factors discussed in this talk include selection of a text book (emphasis on "The Science and Design of Engineering Materials" since the speaker is one of the authors of this text), selection of topics for general audiences or for selected majors, prioritization of lecture topics on a semester, weekly, and daily basis (how to avoid the rush at the end), incorporating multimedia tools into the traditional interactive lecture setting, design of successful homework assignments which require modest grading effort yet prepare students (both in fact and in their own perception) for exams and future courses, design of successful exams that are fair measures of student knowledge, include open ended questions, and serve to help students learn more than they knew before the exam, and interpreting and responding to student evaluations.

2:20 PM

THE FOUNDATION SERIES: INTEGRATING MATH, SCIENCE AND TECHNOLOGY INTO A INTRODUCTORY MATERIALS LABORATORY COURSE: *Dr. Linda Vanasupa*[1]; Dr. Blair London[1]; Ms. Heather S. Smith[1]; [1]California Polytechnic State University, Materials Engineering Department, San Luis Obispo, California 93407 USA

In looking to the 21st Century, our nation's leading engineering practitioners and faculty have spoken in unison engineering education must move toward more integration, toward experience-oriented learning in team settings. Although several innovative projects and approaches have surfaced since that time, the majority of today's engineering curricula contain subjects in a rather dissociated fashion. We are in the process of developing experiments for the introductory materials course into which are woven math and science. We will present an example of what we call The Foundation Series: "Designing to Withstand the Environment: A Study in Corrosion." Each experiment in our Foundation Series is fashioned around learning outcomes in accordance with ABET Criteria 2000. For the experiment that we will present, students will be able to apply the chemistry of oxidation and reduction, evaluate variation within sample sets and between sample sets, use Ohm's law to measure and calculate corrosion rates, analyze and interpret data, clearly communicate the results in a graphical form and know where he/she could obtain additional information on corrosion protection systems. Our hope is that the Foundation Series will enable engineering students to grasp the "big picture," understanding how materials science and math fit into engineering.

2:40 PM

AN INTRODUCTORY MATERIALS ENGINEERING COURSE, BASED ON MATERIALS PROPERTIES: *Dr. Bruce P. Bardes*[1]; [1]Miami University, Manufacturing Engineering, Oxford, Ohio 45056

The approach used in the popular textbooks intended for introductory courses in materials science and engineering is to begin with atoms, explore atomic structure and atomic bonding, then to progress to aggregations of atoms in crystal structures, to crystal defects, to alloys and phase diagrams, to structures, and to eventually discuss properties. This approach is deriving everything from first principles, and it is very common in science and engineering courses. A problem with this widely used approach is that is does not adequately address the professional needs of students who take only one course in materials engineering. For practicing engineers in disciplines other than materials engineering, materials are most frequently encountered in the context of selecting a material for a particular application. For many practicing materials engineers, a major part of their daily work is assisting other engineers in materials selection. To address this widespread need, an introductory materials engineering course should emphasize materials properties. The course should start by examining service conditions, and translating those conditions into materials properties requirements. Mechanical, physical and chemical properties should be discussed, first in the context of how to measure them, and then in the context of how to manipulate them. After discussing materials properties, it is natural to discuss the structures that account for those properties. Structures can be discussed in whatever detail, and physical size, and may be deemed appropriate. When the context of the course is based on selection and application, it is also natural to discuss engineering materials as items of commerce. This approach also serves particularly well as an introduction to subsequent courses relating to manufacturing processes. The principal advantages of this approach to an introductory materials engineering course are that it serves the future professional needs of students better than the traditional approach, and that it gets students thinking about real materials and real applications,

establishing a high level of interest in the subject matter. This approach also facilitates inclusion of engineering design into the course. It also fits well with concurrent engineering, which is widely used in industry today. The only disadvantage I have found in using this approach has been the need to skip around the textbook, and chapters toward the end of most textbooks presume that the student has already gained command of subject matter presented at the beginning of the book.

3:00 PM Break

3:20 PM Panel Discussion

4:25 PM Poster Session

QUICKNOTES: REFERENCE GUIDES FOR MATERIALS COURSES: *Dr. James B. Adams*[1]; Dr. Stephen Krause[1]; [1]Arizona State University, Tempe, AZ 85287 USA

Quicknotes is a set of reference guides for materials courses. The first quicknotes is for the introductory materials engineering course, and covers all the typical topics from atomic bonding to phase diagrams to mechanical properties. Each quicknotes is a 4-sided laminated handout, with a section for each topic that contains the critical concepts and equations, as well as a glossary and materials database. The guides are intended as an easy reference to help students learn the key concepts of a course, and to review them for exams. These guides have been widely used in physics and chemistry courses, but this is the first time they have been developed for materials courses. The effectiveness of the Quicknotes in an introductory materials course will be discussed, and copies of the Quicknotes will be distributed to the audience.

DEMONSTRATIONS AS TEACHING AIDS IN MATERIALS ENGINEERING: *Joe T. Gregory*[1]; [1]University of Auckland, Dept. of Chemical and Materials Engineering, Auckland New Zealand

Many classical teaching aids have been used over the years to present structural and behavioral concepts in materials: ping-pong balls glued together to represent atomic arrangements in crystals; stretched rubber bands to illustrate Poison's ratio; right angle bend of a paper clip to show elastic spring-back; etc. The one vital element of all such demos is that it has to work - it has to not only mechanistically "work" but it has to be a "good demo," one which does in fact capture only the student's full attention at worse, his entire imagination at best. In recent times, three factors have combined to make teaching aids powerful teaching tools in the modern classroom: (i) the realization of the profound role played by illustrative and even entertaining classroom presentations, (ii) the rapid change and growth in things technological, and (iii) student's conditioning through a constant diet of technicolored, animated, hi-tech media exposure to visual stimuli. With the advent of new materials for model making and the growth of materials technology itself, complex concepts can be grasped more readily by the use of models, demonstrations of mechanisms displaying analogous behavior, enlarged views of critical details, and actual processes/operations brought to the classroom - we think back on hot wax poured into plexiglass models. This paper presents a repertoire of teaching aids in materials science, some detailed, some merely listed - all proven effective over a 30-year span of teaching materials.

TEACHING MATERIALS SCIENCE AND ENGINEERING AT THE UNIVERSITY OF AUCKLAND: *Joe T. Gregory*[1]; W. G. Ferguson[1]; W. Gao[1]; N. D. Broom[1], [1]University of Auckland, Department of Chemical and Materials Engineering, Auckland New Zealand

An introductory course in materials science and engineering has been taught at our university for 30 years. Materials I, and its predecessor Materials Science and Engineering, has been a required course for all engineering students and it is the first of four other materials courses for our Chemical and Materials engineering students. The Chemical and Materials degree is unusual if not unique in that it is chemical engineering with a strong materials content to serve the particular needs of New Zealand while at the same time meeting an international standard at the bachelor level. Chemical as well as metallurgical processing industries are well served by this blend. For any chemical engineer knowledge of materials selection, properties, processing, and behavior is seen to be valuable, not only for day-to-day hands-on engineering but for the broad overview for the process industries.

THREE-YEAR EXPERIENCE IN LECTURING OF INTRODUCTORY JOINT COURSE ON METALLURGICAL TECHNOLOGY AND ENVIRONMENT ENGINEERING: *Dr. Alexey Lozhko*[1]; Dr. Vladimir Gubinsky[1]; Dr. Sidorenkova Ludmila[1], [1]State Metallurgical Academy of Ukraine, Dniepropetrovsk UA-320635 Ukraine

The distinctive feature of university education is disconnection of the learning courses. Usually the lecturers focus attention on information contents of the own courses and intercourses correlation is side issue for them. In our opinion the introduction lecture courses can solve these imperfections. That is why we included in the introduction course the following mandatory points - importance and necessity to study of this course for professional graduation (motivate component), - place of the course among other courses which was gave or will given to the students (orientate component), - fundamental knowledge and practical skills (substantial component). The competence of problems on environment control is necessary for the Ukrainian experts - metallurgists. We have created an introduction course "Introduction in the Specialty", where joined survey information about metallurgical technologies and their damage for an environment. The mission of this course is not student's fundamental knowledge and integrated intuitive conceptions, which we name "Ecological Thinking". Our course bases on business computer games which simulate actual industrial - environmental situations. Will be shown the methodical applications of the course and the software.

INTRODUCTION TO METALLURGICAL & MATERIALS ENGINEERING AT COLORADO SCHOOL OF MINES: *Dr Chester J. Van Tyne*[1]; [1]Colorado School of MInes, Metallurgical & Materials Engineering, Golden, CO 80401 USA

The introductory course in Metallurgical and Materials Engineering for majors in the program at Colorado School of Mines is an intense three week course that occurs during the summer between the sophomore and junior years. This "field session" course allows the opportunity for several unique learning experiences. Among the exercises performed by the students in this course are: 1) field visits to mines, mills and manufacturing plants, 2) a materials design problem, 3) laboratory demonstrations and experiments and 4) library resource exercises. The course also provides the opportunity to welcome the "new" students into the department through interaction with departmental staff. These interactions coupled with the group projects and the picnic at the end of the course provide a cohesiveness for the class which benefits the students during their final two years in the program. Because of the concentrated nature of the course, the faculty are faced with the challenge of conveying the introductory material within the constrained time frame.

EXPERIENCES IN USING MULTIMEDIA MATERIALS TO TEACH FLUID MECHANICS: *Dr. Vaughan R. Voller*[1]; Dr Karl A Smith[1]; [1]CIE, University of Minnesota, Minneapolis, Minnesota 55455-0220 USA

Multimedia materials have a great potential to enhance the teaching of core under-graduate engineering courses. Having access to a range of multimedia materials, however, is only one part of the equation for improving the delivery of the course content. The other critical component is a sound strategy for integrating these materials into the overall teaching objective. Over the past three years we have developed an extensive suite of course ware modules for the teaching of fluid mechanics. These modules include both content and lab based materials. The objective of this paper is to present some of our multimedia materials and more importantly report on our experiences in using these materials to teach a regular undergraduate fluid mechanics course.

GENERAL ABSTRACTS: VI - Microstructure Development

Sponsored by: TMS

Wednesday PM Room: Patio A
February 18, 1998 Location: Convention Center

Session Chair: Jeff Wolfenstine, University of Texas at San Antonio, Division of Engineering, San Antonio, Texas 78249-0665

2:00 PM

COARSENING OF Al_3Sc PRECIPITATES IN Al-Sc ALLOYS: *Alan J. Ardell*[1]; Gabriel M. Novotny[1]; [1]University of California, Dept. of Materials Science and Engineering, Los Angeles, CA 90095-1595 USA

Coarsening of coherent Al_3Sc precipitates in Al-Sc alloys containing 0.06, 0.12 and 0.16 at. % Sc was investigated at 350°C for aging times to 624 h using transmission electron microscopy. The volume fractions, f, of Al_3Sc are very small in this system (<0.007). Thus, though the lattice mismatch is large (~1.4 %), critical tests of current theories of the influence of f on coarsening behavior should be possible since f is so small. The 0.12 and 0.16% Sc alloys contained spherical coherent Al_3Sc precipates at all aging times, but the 0.06% alloy was devoid of homogeneously nucleated precipitates even at the longest aging times. This was unexpected, since the concentration of this alloy exceeds the solubility limit at 350°C. The precipitates nucleate and grow rapidly in the 0.12% alloy to sizes two to three times larger than their counterparts in the 0.16% alloy, but no evidence of coarsening could be detected. Although the particle sizes are smaller in the 0.16% alloy, the precipitates coarsen as expected, i.e. the average particle radius, (r), obeys an equation of the type $(r)3 \propto t$. The particle size distributions in both alloys are similar to those predicted by the LSW theory. It is difficult to reconcile these finds with current theories of nucleation, growth and coarsening. This work is supported by the National Science Foundation.

2:20 PM

COARSENING OF Ni3Si ALLOYS OVER A WIDE RANGE OF VOLUME FRACTIONS: Jim-Hoon Cho[2]; *Alan J. Ardell*[1]; [1]University of California, Dept. of Materials Science and Engineering, Los Angeles, CA 90095-1595

The coarsening kinetics of Ni_3Si precipitates in 6 binary Ni-Si alloys containing 11 to 14.3 at. % Si were investigated at 650°C for aging times at 2760 h. The volume fraction, f, at 650°C varies by about an order of magnitude, from 0.03 to 0.31. The investigation involved measurements of the average radii of the precipitates and particle size distributions (PSD) using transmission electron microscopy, and the kinetics of solute depletion of the matrix using magnetic analysis. To minimize the influence of compositional heterogeneities, alloys containing less than 11.7 % Si(f<0.1) were subjected to an up-quenching heat-treatment involving pre-aging at 530°C. The Ni_3Si precipates become cuboidal in shape with increasing size, and become strongly spatially correlated along <100>, consistent with the results of previous work. However, they never coalesce or bifurcate into a plate shape. The interfacial free energy obtained from the data assuming the matrix is an ideal solution is 5.29+/- 0 .84 m)/m^2. The rate constants for coarsening, as well as the standard deviations of the PSDs, are essentially independent of f, possibly decreasing as f increases at small f (<0.1). Some reasons for this unexpected behavior are discussed. This work is supported by the National Science Foundation.

2:40 PM

AN EXPERIMENTAL TEST OF DIFFUSINE BANDING IN A PERITECTIC SYSTEM: *Dr. Jan-Sik Park*[1]; Dr. Rohit Trivedi[1]; Dr. A. Karma[2]; [1]Ames Lab of U.S. DOE, Material Science and Engineering, Ames, 232 Wilhelm, Ames, IA 50011 USA; [2]Northeastern University, Department of Physics, Boston, MA 02115 USA

Several experimental studies have reported the formation of banded structures in hyperperitectic alloys in Sn-Cd and Pb-Bi systems. Theoretical models based on diffusion and repeated nucleation of the primary and peritectic phases predict that no band formation should occur in hyperperitectic alloys. In order to check the validity of the theoretical models, critical experimental studies have been carried out in the Sn-Cd system. It is found that the reported banded microstructures in hyperperitectic alloys are formed due to the effect of convection, and these structures are in fact oscillatory structures which consist of two continuous phases, i.e. a treelike primary phase that is surrounded by the peritectic phase, and the microstructure appears as bands only due to the cross-section effect. An experimental technique is developed in which several samples sizes, ranging from 0.2 to 3mm in diameter, could be directionally solidified in a single run. As the sample diameter was reduced, the banded structures observed in hyperperitectic compositions were found to disappear. However, discrete band formation was observed only in thin samples of hypoperitectic compositions, as predicted by the theoretical model based on diffusive growth. These discrete diffusive bands were observed only in samples small than 0.6 mm in diameter where convection effect was negligible. The spacing bands was found to decrease as the velocity was increased, and composition measurements show that the banding cycle operates below and above the peritectic temperature. A quantitative comparison of experimental results with the diffusive model will be presented, and a morphology of the two-phase structures due to repeated nucleation and competitive growth of the two phases will be discussed.

3:00 PM

TREATMENT OF AGE-HARDENING KINETICS: HARDNESS VS. RESISTIVITY TECHNIQUES: *W. V. Youdelis*[1]; A. Hatab[1]; [1]University of Windsor, Dept. of Mechanical & Materials Engineering, Windsor, Ontario N9B 3P4 Canada

Measuring hardness or resistivity changes are the two most commonly used methods for studying age-hardening kinetics. Hardness changes are considered more accurate for monitoring the early transformation stages (clusters, GP zone, metastable phase formation), as transitiitions between stages can be identified from slope changes in the rising hardness (H vs. t) curve. On the other hand, the falling resistivity (ρ vs. t) curve is less sensitive to the above transitions, but is more accurate for monitoring the later (overaging or stable phase precipitation) stage. The results of an age-hardening study on the effect of Be addition to an Al-0.7%Mg-0.4%Si are presented, in which it is shown that the two methods give equivalent kinetic parameters (for the Avram i-Johnson-Mehl rate equation) for metastable β' formation, when the transformation start and finish times are more accurately located from dρdt vs. t plots.

3:20 PM

USE OF DIFFUSIONAL CREEP TO INVESTIGATE MASS TRANSPORT IN (La,Sr)MnO3: *Dr. Jeff Wolfenstine*[1]; [1]University of Texas at San Antonio, Division of Engineering, San Antonio 78249-0665 Texas

$(La,Sr)MnO_3$ is considered as one of the most promising materials for use in high-temperature solid oxide fuel cells. Recent measurements of the compressive creep behavior of fine-grained (La,Sr)MnO3 suggest that deformation is controlled by a diffusional creep mechanism over the temperature range of 1150-1300°C. The steady-state creep rate decreases with increasing Sr content and decreasing oxygen activity. This result, when combined with existing point defect models, suggests that the rate-controlling species for mass transport in (La,Sr)MnO3 is the lattice diffusion of La or Mn cations.

3:40 PM Break

3:50 PM

GRAIN DEFECTS IN SUPERALLOY SINGLE-CRYSTAL CASTINGS: *Dr. Ralph E. Napolitano, Jr.*[1]; Dr. Robert J. Schaefer[1]; Dr. Boyd A. Mueller[2]; [1]National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, Maryland; [2]Howmet Corporation, Whitehall, Michigan

The demand for larger and more complex superalloy single-crystal components, in both aerospace and land-based gas turbines, has dramatically increased the degree of process control required for the reliable production of defect-free blades and vanes. Indeed, many types of grain defects, such as stray grains, freckles, slivers, zebra grains, and low angle boundaries, are routinely observed, rendering such components unuseable for their intended application. The conditions which give rise to low angle boundaries and stray grains are not well understood, and these defects have not been well characterized. In this study, single-crystal test-castings of Rene N5 are characterized with respect to low angle boundaries and stray grains. Optical metallography, x-ray topography, and electron backscatter pattern imaging techniques are used to identify and trace crystallographic misorientations. Results are evaluated in conjunction with thermal simulation, providing insight into the mechanisms underlying the degeneration of single-crystal quality in superalloy castings.

4:10 PM

A LATTICE MODEL OF DENDRITIC STRUCTURE IN SINGLE-CRYSTAL CASTINGS: *Dr. Ralph E. Napolitano, Jr.*[1]; Dr. Robert J. Schaefer[1]; Dr. Boyd A. Mueller[2]; [1]National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, Maryland USA; [2]Howmet Corporation, Whitehall, Michigan

As a dendritic solid propagates through a mold during single-crystal casting, the mold geometry has a marked affect on the macroscopic shape of the growth front. Because growth may be geometrically constrained in some areas, the structure of the dendritic array may become quite complex. Local primary directions may vary significantly over short distances, and the front may fold onto itself. This breakdown in "order" of the dendritic array indicates the loss of tip-to-tip constraint at the front. Such a change in connectivity of the dendritic network has been associated with several types of grain defects in single-crystal castings. If these patterns can be related to tendency for defect formation, then predictions of such growth patterns would be useful for the intelligent design of single-crystal components. The lattice model presented here is shown to predict the detailed features of a dendritic array as progresses through a 3-D mold. The solid is modeled as an interconnected array of "needles" where the tips are tracked on a square lattice. The needles grow according to the local temperature and a specified relationship for tip kinetics. New tips are generated according to a branch criterion. Each branching event results in four new tips which behave independently. The effect of the temperature gradient vector is examined and compared with experiment. A connectivity parameter is computed and plotted, revealing the effect of the geometry on the "order" of the network. The model also provides the undercooling at the time of solidification and a nucleation parameter which accounts for the complete thermal history of the melt. The model is demonstrated using simple geometries and thermal fields, intended to simulate certain types of features in actual castings, such as expanding cross sections and platforms. Additionally, the model is used with thermal simulation data for an actual casting. The results are compared with microstructural features.

4:30 PM

THE GROWTH-PATH METHOD FOR PREDICTION OF STRAY GRAIN NUCLEATION IN SINGLE-CRYSTAL CASTINGS: *Dr. Ralph E. Napolitano, Jr.*[1]; Dr. Andrew R. Roosen[2]; Dr. Robert J. Schaefer[1]; Dr. Boyd A. Mueller[3]; [1]National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, Maryland USA; [2]National Institute of Standards and Technology, Center for Theoretical and Computational Materials Science, Gaithersburg, Maryland USA; [3]Howmet Corporation, Whitehall, Michigan

The demand for higher combustion temperatures in gas-turbine engines has driven an increase in the complexity of mold designs for single-crystal superalloy components. Such developments require increasingly stringent process control during casting for the production of defect-free castings. The defects most frequently associated with geometric complexity are stray grains, which nucleate in highly undercooled regions, where growth has been geometrically constrained. Prediction of such nucleation is necessary for intelligent design and cost-effective production of these advanced airfoils, and existing modeling techniques have not adequately addressed this phenomenon. In this work, the growth-path method for the prediction of stray grain nucleation is presented. This method incorporates thermal simulation results and anisotropic growth kinetics of a dendritic front to compute the time-minimized path to any given location in a 3-D casting. An empirical or analytical nucleation rate expression can then be integrated along this path to compute a nucleation parameter. The unique feature of the method is that the complete time-temperature history is accounted for. Additionally, the method is efficient since the computation need only be performed for a limited number of paths, eliminating the need for time-consuming 3-D algorithms. The method is demonstrated using a Rene N5 single-crystal casting, and nucleation predictions are compared with experiment.

4:50 PM

COARSENING OF PRIMARY SI IN SPRAY FORMED AL-SI AND AL-SI-CU ALLOYS IN THE SEMI-SOLID STATE: *P.L. Orsetti Rossi*[1]; [1]C.V.B. Industria Venezolana de Aluminio, C.A., Ciudad Guayana, Estado Bolivar Venezuela

Over the past 20 years there have been important efforts for exploiting the attractions of processing in the semi-solid state in comparison with traditional routes involving either liquids or solids. Several prospective metal alloys have been studied including stainless steels, aluminium, copper, magnesium and titanium alloys as well as superalloys and composites, by means of a variety of processes which supply a preform of suitable microstructure. The preforms, in turn, can be further processed to produce near net shape products by using several metal forming processes such as thixocasting, thixoforging, extrusion, rolling and strip casting. The microstructure of the prospective material preform while in the semi-solid state has proved to be essential to the production of quality near net shape products. This paper deals with the coarsening kinetics of primary Si in two spray formed Al-Si in-situ composites, namely Al-36Si and Al-36Si-2.5Cu under isothermal conditions in the semi-solid state, in order to determine the rate constants as well as the operative coarsening mechanism. Small samples were heated to temperatures within the semi-solid state and kept there for various times. The samples were then quenched and prepared metallographically for particles size analysis. Primary Si coarsens relatively rapidly following a bulk diffusion-controlled coarsening kinetics, the experimental rate constants being in reasonable agreement with theory. Coalescence or agglomeration of silicon particles to form big colonies occurs to a great extent in both alloys.

GENERAL RECYCLING OF NON-FERROUS METALS: General Recyling IV - Aluminum Processing

Sponsored by: Extraction & Processing Division, Light Metals Division, Recycling Committee

Program Organizers: Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701; John P. Pickens, Alumitech Inc., 10380 Route 43, Streetsboro, OH 44241

Wednesday PM Room: Plaza Room B
February 18, 1998 Location: Convention Center

Session Chair: Annette Revet, Regina, SK S4P 4L8, Yogeshwar Sahai, Columbus, OH 43210

2:00 PM INVITED

RECYCLING OF ALUMINUM SCRAPS WITH ORGANIC CONTAMINATION - OPERATIONAL EXPERIENCE WITH THE ALCAN FLUIDIZED BED DECOATER: *Michael P. Thomas*[1]; D. Gibson[1]; C. Presley[1]; F. Tremblay[2]; D. Whipple[3]; [1]Alcan Recycling, Technology and Business Development, Shelbyville, TN 37160; [2]Alcan International Limited, Arvida Research and Development Center, Jonquiere, Quebec Canada; [3]N. A. Penta, Charlotte, NC

Alcan has developed a highly efficient thermal decoating system for aluminum scrap based on fluidized bed technology. The new process, which is able to treat aluminum scrap with contaminant levels from a few percent to more than fifty percent organic material content, has been implemented commercially in the form of a full scale operating plant at Alcan's Shelbyville, Tennessee, recycling facility. The decoater has been in operation for three years, during which a comprehensive series of scraps have been characterized and processed. The performance of the decoating facility, on a production scale, will be reported with reference to the types of scraps processed, the decoating efficiency, melt recovery and emission control.

2:25 PM INVITED

DEVELOPMENT OF A SWELL-PEELING METHOD IN UBC RECYCLING SYSTEM: *T. Nakamura*[1]; K. Fujisawa[2]; K. Oosumi[2]; [1]Kyushu Institute of Technology, Materials Science and Engineering, Kitakyushu 804 JAPAN; [2]Kobe Steel, Ltd.

UBC (used beverage cans) are one of the important resources in the aluminum recycling industry. They are able to be recycled into a can body material by remelting. However, there have been some problems pointed out due to paints printed on the can in the remelting process. One is a contamination of unfavorable impurities such as Ti and another is a lower aluminum recovery yield. Although a calcination technique for burning paints and mechanical separation using shot-burst method have been applied for removal of the paints, both methods are not effective. A swell-peeling method has therefore been developed as a pretreatment to remove the films containing the paints. The organic films covering the can surface were easily peeled by a swelling force in a short period after dipping the can in a peeling liquor developed in the present study. The mechanism of peeling the films will be discussed. Subsequent to this pretreatment, aluminum yields were found to be improved upon remelting.

2:50 PM INVITED

A NOVEL METHOD TO AVOID DELETERIOUS EFFECTS OF SULFATES IN INDUSTRIAL SALTS ON ALUMINUM SCRAP RECYCLING PROCESS: *Yogeshwar Sahai*[1]; Donald T. Ireland[1]; Jian Ye[1]; [1]The Ohio State University, Materials Science and Engineering, Columbus, OH 43210

Aluminum Scrap such as Used Beverage Containers (UBC) are melted under a protective molten salt cover. An appropriate salt protects metal from oxidation, promotes coalescence of molten droplets, and separates clean metal from the oxide contamination. Generally, the salt compositions for aluminum scrap recycling are based on equimolar mixtures of NaCl and KCl. A small amount of fluoride is also added to the salt. It has recently been found at The Ohio State University that the presence of sulfates as impurities in industrial salts reduce the metallic yield and efficiency of aluminum recycling processes. In this paper, the role of sulfate in industrial salts in terms of their chemical interactions with aluminum metal are summarized. A novel method which consists of addition of carbon and soda ash to industrial salt has been developed to avoid the harmful effects of the sulfate. Results clearly show that the addition of carbon and soda ash significantly improves the salt characteristics in the recycling process. Industrial implications of this method will be presented in this paper.

3:15 PM INVITED

ROLE OF SALT FLUX IN RECYCLING OF ALUMINUM SCRAP: *Yogeshwar Sahai*[1]; Dr. Raja R. Roy[2]; [1]The Ohio State University, Materials Science & Engineering, Columbus, OH 43210 USA; [2]University of Toronto, Department of Metallurgy and Materials Science, Toronto, Ontario Canada

Recycling of aluminum alloy scrap involves charging it into a bath of molten salt flux, so that the melting of aluminum scrap can take place under the cover of salt flux. One of the main requirements of the salt flux is to promote coalescence of molten metal droplets by stripping the oxide layer from the metal. The salt becomes progressively viscous as the oxide films stripped from metal are suspended in the flux. The coalescence behavior of aluminum and Used Beverage Container (UBC) alloy drops in molten salts based on equimolar NaCl-KCl was investigated. The progress of coalescence in different salts was observed as a function of time. A model to explain the coalescence process is developed. A ternary interfacial energy is constructed for aluminum-a lumina-salt system and its relation to the removal of oxide film from the metal is discussed. The viscosity of molten salts used in aluminum scrap recycling was measured and its importance for the recycling process is discussed.

3:40 PM INVITED

SEPARATION OF INTERMETALLICS USING A CENTRIFUGE TECHNIQUE: *G. H. Nijhof*[1]; [1]Hoogovens Research and Development, Applied Physical Metallurgy, 1970 CA IJmuiden The Netherlands

This report is part of a large research project on the processing of aluminum from household waste. Scrap from waste streams is always contaminated with other metals. The re-use of the remelted material for wrought applications is therefore limited. Previous presentations have discussed the technique to add manganese to the melt to form intermetallic compounds of Fe-Mn. The intermetallics are removed by filtering and the amount of iron can be reduced in a predetermined way. For this technique, patents have been applied. Another technique to remove inclusions is to spin the liquid material in a centrifuge. This technique is used for dross treatment, to separate the oxides from the liquid aluminum. Using the laboratory equipment of FOCON (Austria), a series of experiments were performed. Variables investigated were: 1) Cooling velocity and 2) Centrifugal force (rotational velocity). The material solidified into rings. The distribution of the elements over the cross-section was analyzed to determine the different metallographic phases. The technology and the results are discussed.

4:05 PM Closing Remarks

HARD COATINGS BASED ON BORIDES, CARBIDES & NITRIDES: SYNTHESIS, CHARACTERIZATION & APPLICATIONS: Session IV

Sponsored by: Materials Design and Manufacturing Division, Surface Modification & Coatings Technology Committee

Program Organizers: Yip-Wah Chung, Northwestern University, Dept. of Materials Sci & Eng., Evanston, IL 60208; Ray W.J. Chia, Western Digital Corporation, 2109 Tasman Dr., Santa Clara, CA 95054; Ashok Kumar, University of South Alabama, Dept. of Electrical & Comp Eng., Mobile, AL 36688-0022

Wednesday PM Room: Centro Room C
February 18, 1998 Location: Convention Center

Session Chair: Robert Leuchtner, University of New Hampshire, Department of Physics, Durham, NH 03824, Guanghua Chen, Beijing Polytechnic University, Applied Physics Department, Beijing 100022

2:00 PM INVITED

THE PREPARATION AND CHARACTERIZATION OF CARBON NITRIDE FILMS: *Stephen Muhl*[1]; Adriana Gaona-Couto[1]; Juan Manuel Méndez[1]; Sandra Rodil[1]; Gonzalo Gonzalez[1]; Alexander Merkulov[2]; Rene Asomoza[2]; [1]Universidad Nacional Autonoma de

Mexico, Instituto de Investigaciones en Materiales, Mexico, D.F. 04510 Mexico; [2]Insituto Politécnico Nacional, Centro de Investigaciones y Estudios Avanzados, México D.F 07000 México

A review is made of the methods used and the results obtained by a variety of groups in there attempts to prepare carbon nitride (CN) films. A series of somewhat speculative conclusions are presented which may be of assistance to colleagues working in this field. Following this we describe our results of CN preparation by plasma decomposition of CH_4 and N_2 gas mixtures within a hollow graphite cathode. A significant amount of both physical and chemical sputtering occurs during processing. Langmuir probe measurements of the plasma in the substrate region showed that the electron temperature was of the order of 10 eV with a plasma density ~10^{10} cm^{-1}. Optical emission spectroscopy demonstrated the presence of CN and atomic nitrogen radicals in the plasma plume. The deposit was found to grow preferentially on scratch defects on the silicon substrate surface in the form of cone shaped columns. Characterization of the samples was performed using Profilometry, FTIR, Raman, SEM, EDX, SIMS, x-ray and electron diffraction. Single, double and triple carbon nitrogen bonds were detected in the FTIR spectra; the relative intensities of the associated bands being a function of the deposition time, plasma power and substrate bias. The calibrated EDX elemental analysis of the deposit showed that the nitrogen content was ~57 atomic percent. The matrix affects normally associated with the SIMS technique were avoided by the analysis of MCs+ secondary ions from the samples, where M is either nitrogen or carbon. In this way topographical composition maps of the sample surface were generated. The diffraction techniques demonstrated that small crystals exist in the deposit and that their electron diffraction pattern agrees quite well with that of hexagonal beta C_3N_4. Annealing studies revealed that the material was stable to at least 700°C under vacuum and 500°C in air.

2:30 PM

PREPARATION AND CHARACTERIZATION OF TiB_2 OVERCOAT ON HARD DISK: *Mei-Ling Wu* [1]; Yip-Wah Chung[1]; William D. Sproul[2]; Ray W.J. Chia[3]; Wing Tang[3]; [1]Northwestern University, Robert R. McCormick School of Engineering and Applied Science, Department of Materials Science and Engineering, Evanston, IL 60208; [2]Sputtered Films, Inc., Santa Barbara, CA 93103; [3]Western Digital Corporation, Santa Clara, CA 95054

Thin TiB_2 overcoats were prepared on hard disc substrates by DC magnetron sputtering in a pure, hydrogen-containing, and nitrogen-containing Argon atmosphere. The composition, structure, topography, tribological properties and corrosion resistance are carried out by different techniques, including Auger, Raman spectra, transmission electron microscope (TEM), atomic force microscope (AFM), contact start and stop (CSS), and hot water extraction. It was shown that an optimum combination of the working gas composition and pressure along with substrate bias, and target power are able to produce dense, high resistant and smooth overcoats on hard disc.

2:50 PM

A METHODOLOGY OF MEASURING NITROGEN CONTENT IN THIN NITROGENATED CARBON OVERCOAT ON MAGNETIC THIN FILM MEDIA: *Ray W.J. Chia*[1]; Charles C. Wang[1]; Wing T. Tang[1]; Jerry K. Lee[1]; [1]Western Digital Corporation, Santa Clara, CA 95054

Thin nitrogenated carbon overcoats were deposited on magnetic rigid disks by unbalanced DC-magnetron sputtering using a mixture of argon and nitrogen gases. Nitrogen content of nitrogenated carbon is important in determining its tribological performance. Two techniques, including Raman spectroscopy and reflectometry, were evaluated to measure nitrogen content and/or thickness. It will be shown that conventional deconvolution of Raman spectra into D- and G-band can not be correlated to nitrogen content in thin nitrogenated carbon unambiguously. On the other hand, a trend in the optical constants of nitrogenated carbon will be described that allows rapid quantitative determination of nitrogen content calibrated against ESCA. Measurements of nitrogen content ranging from 0 to 25 at.% will be presented.

3:10 PM

ION-ASSISTED AND SPUTTERED UNDOPED AND CESIUM-DOPED CARBON NITRIDE AND DIAMOND-LIKE-CARBON COATINGS: *I. H. Murzin*[1]; G. S. Tompa [1]; M. A. Hussain[1]; [1]Structured Materials Industries, Inc., Piscataway, NJ 08854

We report on IBAD deposition of CN and DLC films as well as on the design, manufacturing and testing of a new negative carbon ion source that was used to produce some of the carbon nitride and diamond-like carbon (DLC) films. The source consists of a conventional magnetron sputtering gun modified to include the high voltage electrodes and a cesium oven to provide delivery of vaporized cesium to a carbon target installed in the magnetron gun head. The argon and argon-nitrogen gas mixtures were used to ignite the plasma. The sputtered carbon ions were negatively charged because cesium layer on top of a carbon target lowered the surface work function of carbon surface. We compare mechanical and other properties of the several carbon nitride and DLC films de posited without cesium. We also present the results of characterization of the deposition process and the modified sputter gun in terms of such parameters as current absorbed by the substrate, cesium oven temperature, substrate bias, electrodes voltage, deposition rate, r.f. power and other ion source characteristics. We discuss these and other characteristics of the deposition process. This work is supported in part by the BMDO under contract no. DAAH04-95-C-0042.

3:30 PM Break

3:45 PM

APPLICATIONS OF MULTIPHOTON DETECTION IN TRIBOLOGY: *A. K. Drukier*[1]; P. Volkovitskii[1]; [1]Bio Traces Inc., Fairfax, Va 22030

We are currently studying the applications of a new and supersensitive Multiphoton Detection (MPDTM) technique to surface engineering and tribology. The MPD based instruments may advance surface characterization by providing the improved technique for measuring the physical and tribological properties of protective coatings, including thin films of hard material e.g. oxides, nitrides, refractive metals and diamond-like materials. This techniques also permits studies of the nanostructure and wear properties of protective layers. In this talk, we will discuss the methods and instrumentations of MPD technique to measure the tribological and other properties of protective hard coatings.

4:05 PM

CHARACTERIZATION AND TESTING OF LAYERED SiC/HfC PROTECTIVE COATINGS: *Jerry Brockmeyer*[1]; Sangvavann Heng[1]; Brian Williams[1]; [1]ULTRAMET, Pacoima, CA 91331

The harsh environment encountered in aerospace reentry and propulsion applications results in needs for coatings that combine high temperature and corrosion resistance. Hard, refractory carbides, including silicon carbide (SiC) and hafnium carbide (HfC), offer many necessary properties but, typically are limited by the durability and stability of the protective oxide surfaces that form during use. As a result, SiC is limited to a peak sustained use temperature of ~3000°F due to the rapid degradation or loss of the silica (SiO_2) layer at higher temperatures. HfC, with a protective hafnia (HfO_2)layer, offers higher temperature capability but has poor thermal cycling resistance due to spalling of the oxide. A recently develo ped, micro-layered SiC/HfC coating has demonstrated resistance to temperatures (4500°F and excellent thermal cycling resistance. Although not fully characterized, this coating apparently form a complex oxy-carbide surface that is resistant to temperatures significantly greater than those acceptable for SiO_2 and is adherent during cycling. Results of characterization and testing of this coating under severe conditions (e.g., torch, arc jet and rain erosion testing) on various aerospace thermal protection system substrate materials are presented.

4:25 PM

MICROSTRUCTURES OF WC-Co COATINGS PRODUCED BY HIGH ENERGY PLASMA SPRAY (HEPS): J. W. Simmons[1]; *J. A. Hawk*[1]; M. Scholl[2]; [1]Albany Research Center, U. S. Department of Energy, Albany, OR 97321; [2]Oregon Graduate Institute of Science and Technology, Portland, OR 97291

Thermally sprayed tungsten-carbide/cobalt (WC-Co) coatings are used to reduce wear or modify friction in many sliding, abrasive and corrosive wear applications. Decomposition of the WC-Co powders in, primarily through decarburization and thermal decomposition of the WC-Co powders during the thermal spray process, is always a concern. Optimized process parameters may vary considerably for a given process depending upon the initial powder. Currently, the high velocity oxygen-fuel (HVOF) process is considered to produce WC-Co coatings with the best combination of high density, bond strength, and minimum decomposition. However, high energy plasma spray (HEPS) also has the potential to produce high-quality WC-Co coatings and at higher deposition rates. In this study, the microstructures and wear behavior of WC-Co coatings produced using a HEPS system are presented. Microstructures of the coatings were characterized through bulk and micro-chemical analyses, X-ray diffraction, and optical and electron micros copy. The phases and phase morphologies present in the coatings are compared to the original starting powder and coatings produced by HVOF.

4:45 PM

SOME MECHANICAL PROPERTIES OF BORIDED AISI 8620 STEEL: *Sauman Sen* [1]; CumaBindal[1]; [1]Sakarya University, The Department of Metallurgy, Adapazan 54040 Turkiye

In this study, we investigated some mechanical properties of AISI 8620 steel. Boronising was carried out in a salt bath consisting of borax, boric acid and ferrosilicon. The temperature of bath was 950°C and the boronising procedure was conducted at an atmospheric pressure for 2, 4, 6, and 8 hours. The hardness of boride layer formed on surface of AISI 8620 was about 1500 HV. It was found that there is a parabolic relationship between boronising time and boride layer thickness. The presence of FeB and Fe_2B was confirmed by means of x-ray diffraction. It was also observed that fracture toughness of borided layers measured via Vickers indenter was between 9.34 ± 2.2 and 4.65 ± 0.41 $MPa.m^{1/2}$. Increasing boronising time results in low fracture toughness. Metallographic examinations showed those borides have columnar structures.

INTERNATIONAL SYMPOSIUM ON IRON ALUMINIDES: ALLOY DESIGN, PROCESSING, PROPERTIES & APPLICATIONS: Powder Processing

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee, Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Alloy Phases Committee, Materials Design & Manufacturing Division, Powder Materials Committee

Program Organizers: S.C. Deevi, Philip Morris USA, Research & Development Center, Richmond, VA 23234; David G. Morris, University of Neuchatel, Inst of Structural Metallurgy, Neuchatel Switzerland; J.H. Schneibel, Oak Ridge National Laboratory, Metals & Ceramics Division, Oak Ridge, TN 37831; Vinod K. Sikka, Oak Ridge National Laboratory, Metals & Ceramics Division, Oak Ridge, TN 37831

Wednesday PM Room: 108
February 18, 1998 Location: Convention Center

Session Chairs: P. Angelini, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 27831; M. R. Jahabigol, Philip Morris USA, Research & Development Center, Richmond, VA 23234

2:00 PM INVITED

A THERMO-MECHANICAL PROCESS TO MAKE IRON-ALUMINIDE STRIP: *M. R. Hajaligol*[1]; S. C. Deevi[1]; V. K. Sikka[2]; C. R. Scorey[3]; [1]PM USA, Richmond, VA 23261 USA; [2]ORNL, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; [3]AMETEK, Wallingford, CT 06492 USA

Strips of iron aluminide were commercially made using a thermo-mechanical process that includes a series of cold rolling and annealing steps. Green strips of iron aluminide made by roll compacting or tape casting are first de-bindered and sintered to less than full density, then they are rolled to a desirable final thickness and full density through a series of heavy cold rolling and high temperature annealing process. Extreme hardness and lack of ductility of the strips require a special carbide roll with multiple passes of rolling; and because of high work hardening characteristic of iron aluminide, intermediate annealing at about 1000 to 1250 C are essential. Strips made by this process have an excellent set of tensile properties at room temperature, and they keep their properties at a good level up to about 750 C temperature. Strips have a fine and equiaxial grains that range in size from 19 to 25 microns. No major porosity is detected within or on the surface of the strips, and the micro-porosity is in a range that is typical of the other metals made through by other conventional processes.

2:30 PM INVITED

THE STRUCTURE-PROPERTY RELATIONSHIPS OF POWDER PROCESSED Fe-Al-Si ALLOYS: Paul D. Prichard[1]; *Iver E. Anderson*[1]; [1]Ames Laboratory-U.S. DOE, Iowa State University, Metallurgy and Ceramics Program, Ames, IA 50011 USA

Fe_3Al alloys have been proposed as alternatives to alloys containing high Ni, Co and Cr for use at temperatures up to 600°C in aggressive environments. This investigation examined the addition of Si to a Fe-15Al at.% alloy to observe the alloy effects on the microstructure during powder metallurgy processing and to measure the resulting mechanical properties. Three alloy powders, Fe-15Al, Fe-15Al-2.8Si and Fe-15Al-5Si were produced with a high pressure gas atomization process to obtain a high fraction of metal injection molding quality powder (D_{84}<32μm). The powders were consolidated by P/M hot extrusion or vacuum sintering to produce samples with density ranging from 87% to

99.9% of theoretical density. Crystallographic faceting and enhanced grain growth was observed with increased silicon content to indicate a change in surface energy. Mechanical property testing was conducted using a small punch test and tensile testing at temperatures from 25° to 550°C to determine the yield strength and fracture energy for each alloy as a function of process conditions. The yield strength, ductile-to-brittle transition temperature and order-disorder transformation temperature were observed to increase with an increasing silicon content. The grain size, porosity and other microstructural features effects on mechanical properties will be discussed. This work was supported by USDOE, Office of Basic Energy Sciences, Div. of Materials Science under contract no. W-7405-ENG-82.

3:00 PM INVITED

PROCESSING AND PROPERTIES OF MECHANICALLY ALLOYED Fe-Al ALLOYS: *F. Moret*[1]; R. Baccino[1]; [1]CEA/CEREM-DEM/SGM, 38054 Grenoble Cedex 9 France

FeAl intermetallic alloys are attractive materials for medium- and high-temperature applications in engines due to their high-mechanical strength coupled with low density and their excellent oxidation resistance. Unfortunately, their use has been restricted until now by their room-temperature brittleness and their poor creep resistance. In this paper, we will review the processing and the properties of mechanically alloyed iron aluminides. We will study how powder metallurgy techniques and mechanical alloying enhance ductility and strength at both low and high temperature. The improvement method combines ductilization by grain boundary strengthening, grain size reduction, and oxide dispersion strengthening. At room temperature, yield strength of such materials can reach 900 MPa and fracture strength at 1150 MPa. Specific stiffness and strength are very high compared to conventional engineering alloys. Potential applications in aeronautical and automotive industries concern the substitution of steels and nickel-based alloys for the fabrication of high-speed rotating or moving engine parts such as shafts and valves.

3:30 PM Break

3:50 PM

TAPE CASTING OF IRON ALUMINIDE STRIP: R. E. Mistler[1]; V. A. Sikka[2]; C. R. Scorey[3]; M. R. Hajaligol[4]; [1]Richard E. Mistler Inc., Morrisville, PA 19067 U.S.A.; [2]Oak Ridge National Laboratory, Metals and Ceramics Divison, Oak Ridge, TN 37831 U.S.A.; [3]AMETEK, Wallingford, CT 06492 U.S.A.; [4]PMUSA

Tape casting as a method of converting iron aluminide powder into a slurry, and then tape casting it into strips was investigated. Typical strip widths, thicknesses, plasticizer and binder formulations, and casting parameters were tested. Application of a thermo-mechanical processing including heat treatment and cold rolling resulted strips with fine grain structure and at essentially 100 percent of theoretical density. The various microstructures developed throughout the process are described, along with physical measurements on the fully dense product. Differences in property with strip made by other processes are described, and it is demonstrated that tape casting is a viable method of making light gauge strip of iron aluminide with different compositions.

4:10 PM

THE CHARACTERIZATION OF IRON ALUMINIDE GREEN SHEET THERMAL PROPERTIES: *Mr. Michael L. Watkins*[1]; Dr. Mark K. Hinders[2]; [1]Philip Morris USA, Research and Development, Richmond, VA 23261-6583 USA; [2]The College of William and Mary, Department of Applied Science, Williamsburg, VA 23187-8795 USA

This paper describes a novel means for inspecting iron aluminide sheet material during processing. The first step in the fabrication of FeAl from metal powder is the formation of a green sheet. Two means are cold rolling and tape casting of a mixture of powder starting material and binding agent. The resulting sheet then undergoes a series of process steps (binder elimination, densification, sintering, annealing to form the final FeAl sheet product. Defects within the green sheet can be a major contributor to material failure in subsequent sheet processing, forming and cutting. The inspection technique takes advantage of the anisotropic heat flow arising from the variations in mass distribution of the green sheet constituents (metal powder, binder and so lvent), voids, cracks and sheet thickness. The ability to detect and control variations during green sheet formation has the potential to significantly improve final sheet quality, reduce waste and costs.

4:30 PM

WETTING BEHAVIOR OF IRON ALUMINIDES: *M. L. Santella*[1]; A. B. Patterson[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6096 USA

A considerable amount of information exists about the welding behavior of iron and nickel aluminides, but little is known about their brazing characteristics. Brazing processes are largely controlled by the wetting phenomenon (i.e., how well a liquid spreads over the surface of a solid metal). These experiments involved melting pure silver, copper, and gold on the surfaces of Fe_3Al and FeAl under closely controlled conditions. Heating of the specimens was done with an induction system in a vacuum chamber. The wetting contact angles were measured as a function of both time and temperature. Wetting (contact angle, $\theta < 90°$) occurred for these combinations: Ag/Fe_3Al, Au/Fe_3Al, Ag/FeAl, and Au/FeAl. Melting of the Ag and Cu always occurred near their normal melting temperatures. However, melting for the combinations involving Au always commenced below its melting temperature of 1063°C. None of the aluminide alloys were wet by Cu. Metallographic examination showed that no interface reaction layers formed between Ag and either Fe_3Al or FeAl. Silver did penetrate the grain boundaries in both Fe aluminides, and significant Al concentrations were detected in the solidified Ag droplets. Similar reactions occurred for Au but more extensive reaction with the aluminide alloys was found in these cases. *Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DEAC0596OR22464 with LockheedMartin Energy Research Corp.

4:50 PM

PROCESSING AND MINOR ALLOYING EFFECTS ON DUCTILITY, IMPACT TOUGHNESS AND FRACTURE BEHAVIOR AT ROOM TEMPERATURE IN FeAl ALLOYS: Dr. Philip J. Maziasz[1]; Mr. Joseph L. Wright[1]; *Dr. David J. Alexander*[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6115 U.S.A.

The ductility, Charpy impact toughness and fracture mode of B2-phase FeAl alloys (36-38 at.% Al) tested in air at room temperature have been recently found to be quite sensitive to combinations of changes in processing-induced microstructure and minor alloying additions. As-cast FeAl alloys with coarse (200-400 μm) grain sizes can have 2-5% ductility in air, and about 15 J impact energy, particularly if heat-treated to form fine ZrC precipitation. In particular, boron microalloying additions change the fracture mode from intergranular to transgranular quasicleavage. Hot-extruded ingot-metallurgy (I/M) FeAl alloys have finer grain sizes (35-50 μm) and 8-10% ductility and 25-65 J impact energy, with B-doped FeAl being best. Hot-extruded powder-metallurgy (P/M) FeAl alloys have an ultrafine grain size (2-5 μm) and 9-15% ductility in air, 85-105 J impact energy and show transgranular ductile-dimple fracture within prior powder particles. The implications of such properties for commercial applications of FeAl will be discussed. Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program under contract DE-AC05-96OR22464 with Lockheed-Martin Energy Research Corp.

5:10 PM

MICROSTRUCTURE AND PROPERTIES OF AN OXIDE DISPERSION STRENGTHENED IRON ALUMINIDE: *Dr. Richard N. Wright*[1]; Mr. Michael T. Anderson[1]; Ms. Jill K. Wright[1]; [1]INEEL, Idaho Falls, ID 83415 USA

Oxide dispersion strengthened (ODS) iron aluminide alloys based on Fe_3Al have been formed by reaction synthesis from elemental powders. The resulting alloys have approximately 2.5% by volume alumina particles dispersed throughout the material. Proper thermomechanical processing results in secondary recrystallization to grain sizes greater than 25mm. ODS material with 5%Cr addition exhibits approximately

an order of magnitude increase in time to rupture at 650C compared to a similar alloy produced by conventional powder metallurgy. The apparent activation energy for creep of the ODS material is on the order of 210kJ/mole and the power law exponent is greater than 9. TEM observations, and the relatively high values for the creep exponent, are indicative of dislocation breakaway from particles as the rate controlling deformation mechanism.

5:30 PM

POLYMER ATOMIZATION OF IRON ALUMINIDE: *J. T. Strauss*[1]; C. R. Scorey[2]; J. McKearn[2]; M. R. Hajaligol[3]; [1]HJE, Glen Falls, NY 12801 USA; [2]AMETEK, Wallingford, CT 06492 USA; [3]PMUSA, Richmond, VA 23261 USA

A method of atomizing a reactive alloy melt with a polymer fluid was investigated. In this investigation, both water based polymer solutions and mineral oil fluids were considered. The prototype powder samples using this method were prepared; and the resultant powder chemistry and morphology were compared to water and gas atomization powders. The advantages of this method over the gas and water atomization along with some properties of an iron aluminum alloy powder prepared in this way are described. The results of some compaction tests made on powder from the different processes are reviewed.

INTERNATIONAL SYMPOSIUM ON SULFIDE SMELTING '98: CURRENT AND FUTURE PRACTICES: Copper Smelting Investments and Plant Modernizations

Sponsored by: Extraction & Processing Division, Copper, Nickel, Cobalt Committee

Program Organizers: Tony Eltringham, BMP Copper, 550 California St., San Francisco, CA 94104-1020; Jussi Asteljoki, Outokumpu Oy, Lansituulentie 7, Espoo Fin-02101 Finland; Pete W.J. Chen, Phelps-Dodge Mining Co., P.O. Box 2860, Silver City, NM 88062; Osamu Ishikawa, Bechtel Corp, Mining & Metals, San Francisco, CA 94119-3965; Robert L. Stephens, Ausmelt Technology Corp., 1331 17th St., Denver, CO 80202; Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

Wednesday PM Room: 207
February 18, 1998 Location: Convention Center

Session Chairs: Osamu Ishikawa, Bechtel Corporation, Mining and Metals, San Francisco, CA 94119-3965 USA; Jussi Asteljoki, Outokumpu Oy, Espoo FIN-02101 Finland

2:00 PM

PRESENT AND FUTURE SITUATION OF THE TENIENTE PROCESS: *Gerardo Achurra*[1]; Roberto Mackay[1]; Ruben Alvarado[1]; [1]Codelco Chile, Division el Teniente, Rancagua Chile

The increasingly demanding markets and environmental regulations have determined that most of the copper smelters have been faced with a dynamic search to find the ways of technological developments and management, to ensure their competitiveness in the short and long range. Since 1993, the basic Smelting-Converting process of the Caletones Smelter of Codelco-Chile, Division El Teniente has been based on the operation of two Teniente Converters, equipment that is being used in most of the Chilean smelters as well as in different smelters throughout the world, such as Peru, Zambia, Mexico and, in the near future, in Thailand. These units, together with the operation of two Fluid Bed Dryers, three Slag Cleaning Furnaces and four Peirce-Smith Converters, give the smelter a concentrate smelting capacity of 1215 kDMT/year with a metallic copper production of 360 kDMT/year. This operational scheme, that mixes traditional and leading edge technologies does not permit us to successfully face the challenges of the modern world in relation to commitment to the environment, competitive costs and the complete satisfaction of the customers. For this reason, a Development Plan has been designed for the period 1996-2000, which considers important technical and management projects that, maintaining its present production capacity, shall permit an increase of the productivity of their equipment, facilities and personnel, and a definitive solution to the environmental regulations compliance. Within the implementation of these projects, the Reverberatory Furnaces will be shutdown. In addition, the installation of two new Slag Treatment Furnaces and the incorporation of two Sulfuric Acid Plants with a production capacity of 4000 TMD, will capture 92% of the sulfur in the process gases.

2:30 PM

IMPROVEMENTS TO STILLWATER MINING COMPANY'S SMELTING FURNACE YIELDING INCREASED CAPACITY AND PRODUCTIVITY: *N. Voermann*[1]; V. Vaculik[1]; T. Ma[1]; C. Nichols[1]; G. Roset[2]; W. Thurman[2]; [1]Hatch Associates, Ltd., Mississauga, Ontario L5K 2 R7 Canada; [2]Stillwater Mining Company, Precious Metals Smelter, Columbus, MT 59019

Stillwater Mining Company operates an electric furnace at its smelter in Columbus, Montana to treat a Ni-Cu platinum group metal concentrate along with secondary PGM bearing materials. Hatch Associates has designed several improvements to this furnace, which was originally built by others. Implementation of these relatively low cost improvements has resulted in substantial increases in furnace availability and capacity, along with reduced unit costs. The improvements included: * Installation of water cooled cooling elements to stabilize refractory wear and increase furnace life. * Improved furnace bindings to enhance the furnace's structural integrity by improving the contact between the refractory and cooling elements and by promoting tight brick joints resistant to matte or slag leaks. * Adjustment of the electrode regulator to allow higher power furnace operation. * Installation of an automated Air-Slide (aeration conveyor) feed system to evenly distribute the furnace feed in an insulating layer on the bath surface. This "black-top" practice reduces unit energy costs and makes available additional smelting capacity. This paper describes the above furnace modifications and the benefits their implementation provides.

3:00 PM

THE DEVELOPMENT, DESIGN, AND OPERATION OF THE REFIMET SMELTER IN CHILE - AN INNOVATIVE AND COST - EFFECTIVE APPROACH TO CUSTOM COPPER SMELTING: *Tim. J. A. Smith*[1]; Rolando Campos[2]; Sergio Miranda M.[2]; Sergio Jara[2]; [1]Kilborn SNC-Lavelin Europe Limited, Melrose House, Croydon, Surrey CR0 2NE United Kingdom; [2]Fundicio Refimet S.A. , Antofagasta Chile

In August 1993, the operation of Refimet Chile's custom copper smelter commenced at La Negra, Near Antofagasta in Northern Chile. Based on conventional reverbatory furnace smelting and Peirce-Smith converting, the initial 90,000 tonne per year copper production plant made use of experience gained in building and operating roasting and leaching facilities both at Rungue, near Santiago, and at La Negra. In particular, with the exception of the reverbatory furnace, the majority of the major equipment was purchased second-hand and rehabilitated or modified for the project. Following success in operating the initial project, plans were approved to implement a phase II expansion to 160,000 tonnes per year copper production. This expansion included conversion of the reverbatory furnace to oxy-fuel firing, addition of a further (second-hand) acid plant and addition of fire refining and anode casting facilities. Parallel development of concentrate injection to converters and enlargement of converter vessels also took place. Phase II was successfully commissioned in 1997. This paper provides an overview of the development of the Refimet smelter including the current phase III expansion plans.

3:30 PM Break

3:40 PM

RECENT IMPROVEMENTS AT THE PHELPS DODGE CHINO SMELTER: *Robert D. Phipps*[1]; Matthew J. King[1]; [1]Phelps Dodge Mining Corporation, Chino Mines Company, Hurley, NM 88043

The Chino Smelter embarked on a program to reduce smelter emissions and improve operating practices. Emissions were reduced by improving converter primary hood design, eliminating the flash furnace settling chamber, and installing a new baghouse to teat converter secondary emissions. Operating practices were improved by quantifying process variables. The use of pilot plants and employee feed back regarding future design changes proved to be extremely valuable in achieving success.

4:10 PM

NAOSHIMA SMELTER OPERATION - PRESENT AND FUTURE: Eiki Oshima[1]; Toshihiko Igarashi[1]; Nozomu Hasegawa[1]; *Kenji Kiyotani*[1]; [1] Mitsubishi Materials Corporation, Naoshima Smelter & Refinery, Kagawa-gun, Kagawa-ken 761-31 Japan

In May 1991, a New Mitsubishi Continuous Copper Smelter Line started operation at Naoshima. Recently, it has been continuing steady operation and one and a half year campaign life has been achieved. In 1996, new records of on-line time, the amount of copper concentrate treated and copper anode production were achieved. The current performance proves the superiority of the process with respect to pollution control, energy efficiency, flexibility and ease of operation and over-all economics including off-gas handling costs. Furthermore, plans are underway to prolong the campaign life for two years and to improve the process efficiency. This paper describes recent operation and improvements, and future capability.

4:40 PM

EXPANSION OF THE COPPER SMELTER IN HUELVA: Patricio Barrios[1]; Miguel Palacios[1]; Henning Donicke[2]; Jean-Paul Nepper[2]; [1]Atlantic Copper S.A., Av. Francisco Montenegro, s/n Huelva 21001 Spain; [2]Lurgi Metallurgie Gmbh, Lurgiallee 5, 60295 Frankfrut am Main, Germany

This paper discusses the revamp and expansion of Atlantic Copper's (formerly Rio Tinto Metal) copper smelter located at Huelva, Spain. The plant was expanded from 150,000 to 270,000 tpy new copper in anodes, and from 133,000 to 215,000 tpy cathodes. Lurgi successfully executed this contact on a lmp-sum, turnkey basis in just 19 months. The Lurgi on-site task force performed this work in close cooperation with Atlantic Copper's personnel, with a minimum of disruption in the plant's ongoing operation. The contractual performance parameters were achieved to the client's satisfaction shortly after the mechanical completion of the respective plant sections.

5:10 PM

THE NORANDA CONVERTER CONSTRUCTION AND START-UP AT THE HORNE SMELTER: *Michel Boisvert*[1]; Guy Janneteau[1]; Jean-Pierre Landry[1]; Charles A. Levac[1]; Donald Perron[1]; Manuel Zamalloa[2]; Frank Poretta[3]; [1]Noranda Metalllurgy, Inc., Horne Smelter, Rouyn-Noranda, Quebec Canada; [1]Noranda Metalllurgy, Inc., Horne Smelter, Rouyn-Noranda, Quebec Canada, [3]Hatch Associates, Mississauga, Ontario L5K 2R7 Canada

Noranda Metallurgy is presently completing the construction of the new Noranda Converter in its Horne Smelter located in Rouyn-Noranda. The capital investment of CDN $53 million is the continuation of the SO2 abatement program that was initiated in the late 80's with the acid plant operation for reactor off-gas treatment. The Noranda Converter is a semi-continuous converter that was studied and pilot-tested at the Horne Smelter in the early 90's. Sulfur emissions fixation will be increased from 70% to above 90% by the end of 2001. The Noranda Converter process will replace the current Peirce-Smith converter operations. The construction site is an extension of the present Noranda Reactor area. Existing off-gas equipment was used to clean and to condition the Noranda converter off-gases to the actual acid plant. This paper describes the history of the Noranda Converter, the general flowsheet of the Noranda Converter, the construction phase, and the human resources coordination in preparation for the start-up.

5:40 PM Closing Remarks

MATERIALS SCIENCE OF CHEMICAL-MECHANICAL PLANARIZATION: Session II

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector/Electronic, Magnetic & Photonic Materials Division, Thin Films & Interfaces Committee

Program Organizers: Krishna Rajan, Rensselaer Polytechnic Inst., Dept. of Materials Sci & Eng., Troy, NY 12180-3590; Rajiv Singh, University of Florida, Dept. of Materials Sci & Eng., Gainesville, FL 32611-6400

Wednesday PM Room: 104
February 18, 1998 Location: Convention Center

Session Chairs: Rajiv K. Singh, University of Florida, Dept. of Materials Sci. & Eng., Gainesville, FL 32611-2066; John Darab, Pacific Northwest Laboratory, Richland, WA 99352

2:00 PM

ADVANCED PROCESSES FOR ORBITAL CMP: *Tom Bibby*[1]; [1]IPEC Planar, Phoenix, AZ 85034

Recent improvements in chemical mechanical polishing (CMP) using orbital polishing methods have resulted in improved performance. In this paper we present the results of recent experiments showing significantly enhanced removal rates and planarization while maintaining high quality non-uniformity. We discuss the methods used to obtain these results as well as consistently tighter process control.

2:30 PM

POST-CMP CLEANING USING ACOUSTIC STREAMING: *Professor and Director Ahmed A. Busnaina*[1]; [1]Clarkson University, Microcontamination Research Laboratory, Center for Advanced Materials Processing, CAMP, Potsdam, NY 13699-5725

Non-contact surface cleaning is a desirable process in post-CMP cleaning . High frequency megasonic cleaning is widely used in the semiconductor industry for the removal of particulate contamination. The megasonic cleaning process proved to be an essential process in cleaning silicon wafers after processes such as CMP, ash, etc. This paper introduces recent results that involve the removal of silica slurry using megasonic cleaning. Results show that removal efficiencies near 100% could be achieved under the right conditions using DI water and SC1. The megasonic input power has a greater effect on the removal efficiency than does temperature. The results also show that when the optimum power is used, the removal efficiency will be high over a wide range of temperatures. The results show that using SC1 chemistry reduces the cleaning time as compared to DI water.

3:00 PM

PARTICLE ADHESION OF CHEMICAL-MECHANICAL PLANARIZED WAFERS: *Rajiv K. Singh*[1]; J. Adler[1]; U. Mahajan[1]; B. M. Moudgil[1]; Y. Rabinovich[1]; K. Rajan[2]; [1]University of Florida, Department of Materials Science & Engineering, Gainesville, FL 32611-2066; [2]Rensselaer Polytechnic Institute, Materials Science & Eng. Dept., Troy, NY 12180-3590

Particle based surface forces play a critical role in particulate adhesion and cleaning during chemical mechanical planarization. Various processing chemistries, film microstructure, deformation, relative humidity, and surface roughness play a critical role in particulate adhesion. In this talk, we investigate the effects of processing chemistries, and particle and surface deformation on particle adhesion using atomic force microscopy (AFM). To simulate particle surface interactions, a particle was attached to the AFM tip and the surface forces were analyzed as a function of different processing chemistries. The role of electrical double layer on particle adhesion characteristics was determined from these measurements. The AFM results were correlated to particle adhesion observed during CMP processing of metal and dielec-

tric surfaces. *This research is sponsored by the Engineering Research Center on particle Science and Technology which has been established by a grant from the National Science Foundation (EEC 94-0929)

3:20 PM
INTERFACIAL REACTIONS BETWEEN A NEW AMINE QUINONE POLYMER AND METAL SURFACES BY ELECTRO-CHEMICAL IMPEDANCE AND FTIR: R. Sharma[1]; *Dr. Gary W. Warren*[1]; [1]University of Alabama, Dept. of Metallurgical & Materials Eng., Tuscaloosa, AL 35487-0202

Electrochemical Impedance Spectroscopy (EIS) experiments were carried out on iron substrates coated with 9µm and 15µm coatings of two different amine-quinon polymers namely AQPU15 and AQPU16. Results showed that these polymers provide better corrosion protection as compared to commercial polyurethane binders used in magnetic recording. The AQPU16 polymer provides an even better protection than AQPU15 as was demonstrated by the changes in the breakpoint frequency over a period of time and the appearance of the second time constant in the case of iron substrates coated with AQPU15. FTIR and XPS experiments on iron and aluminum were done to determine the fundamental mechanisms of interaction interface. Experiments were also carried out using two different monomers. Results showed that the polymers attach to iron and aluminum via the carbonyl and amide groups. In the case of iron, a shift of 15 cm^{-1} in the carbonyl peak and a shift of 30 cm^{-1} in the N-H peak were observed, both toward higher wavenumbers. In the case of aluminum the carbonyl peak shifts towards higher wavenumber by 16 cm^{-1} and the N-H peak shifts to lower wave numbers by 40 cm^{-1}.

3:50 PM
PULSED LASER ASSISTED PARTICULATE CLEANING OF SOLID SURFACES: *D. Kumar*[1]; Rajiv K. Singh[1]; [1]University of Florida, Department of Materials Science & Engineering, Gainesville, FL 32611

In this paper, we have examined the particulate removal efficiency of laser from solid surfaces. The silicon wafers were contaminated with alumina particles with sizes ranging from 0.05 µm to 0.5µm. The silicon wafers with uniform surface-distribution of alumina particles were subjected to pulsed laser beams at varying conditions. The results obtained have shown that line beam lasers can remove submicron particles more efficiently from solid surfaces. The mechanism responsible for higher particulate removal-efficiency of line beam laser has also been discussed.

4:20 PM
DEFORMATION CHARACTERISTICS OF POLISHING PADS: *A. Brennan*[1]; R. Singh[1]; K. Rajan[2]; [1]University of Florida, Department of Materials Science & Eng., Gainesville, FL 32611-2066; [2]Rensselaer Polytechnic Institute, Materials Science & Eng. Dept., Troy, NY 12180-3590

The mechanical behavior of polishing pads is critical to the overall success of the CMP process. Yet little is known about the materials science issues which govern issues such as pad conditioning or pad hardness and stiffness. In this presentation, we present a micromechanics description which takes into account the "microstructure" of the pad and the subsequent inhomogeneities in the pad structure. This model is described in the context of mechanical property measurements of the deformation characteristics of commercial pads. The results of this study are discussed in the context of developing generic guidelines for the design of pads for different applications.

4:50 PM
ABSTRACT TITLE NOT AVAILABLE: *A. Maury*[1]; [1]Lucent Technologies

Abstract Not Available

MICROSTRUCTURE AND ITS EFFECTS ON AMORPHOUS NANOPHASE & NANOCRYSTALLINE MATERIALS: Session VI - Semiconducting, Magnetic and Opto-electronic Properties

Sponsored by: ASM International: Materials Science Critical Technology Society, Flow & Fracture Committee, Jt. Electronic, Magnetic & Photonic Materials Division, Alloy Phases Committee, Chemistry & Physical Metallurgical Committee, Structural Materials Division, Physical Metallurgy Committee
Program Organizers: Ram B. Bhagat, Pennsylvania State University, 227 Hammond, University Park, PA 16802; Robert D. Shull, NIST, Bldg. 223 Rm. B152, Gaithersburg, MD 20899; Stephen Spooner, Oak Ridge National Lab, Solid State Division, Oak Ridge, TN 37831

Wednesday PM Room: 205
February 18, 1998 Location: Convention Center

Session Chairs: Stan Veprek, Tech. University Munich, Institute for Chemistry of Inorganic Materials, Garching, Munich D-85747 Germany; Akihisa Inoue, Tohoku University, Institute for Materials Research, Sendai 980-77 Japan

2:00 PM Opening Remarks

2:10 PM INVITED
SURFACE PROPERTIES CONTROL OF SEMICONDUCTING METAL OXIDE NANOPARTICLES: *Marie-Isabelle Baraton*[1]; Lhadi Merhar[2]; [1]LMCTS-ESA 6015 CNRS, Faculty of Sciences, Limoges F-87060 France; [2]Ceramec, European Research Centre for Environmental and Medical Applications of Ceramics, Limoges F-87000 France

When properly synthesized, handled and processed, nanocrystalline materials show superior properties in a wide range of applications including sintering, catalysis, microelectronics, optoelectronics, magnetism, medicine ... It has been realized lately that for these materials which exhibit a high surface-to-bulk ratio, the chemical composition of the first atomic layer is of utmost importance in the macroscopic properties of the final product. Control and tailoring of the surface of nanocrystalline materials are the key to solve problems currently hindering the development of nanoparticle-based materials. Although for semiconducting materials electronic and geometric structures of their surfaces are closely related to each other, these structures are usually studied with different experimental probes. The reason is that most techniques that are sensitive to the geometric structure cannot address the electronic structure, and vice versa. In this paper we show how surface Fourier transform infrared spectrometry can successfully probe both the surface chemistry related to geometry and electrical properties of metal oxide nanoparticles. This is achieved by performing selective gas adsorption and making use of the Drude-Zener theory. Nanosized titania has been used as a prototypical transition-metal-oxide and subjected to various surface treatments to show how surface chemistry tailoring can modify the electronic properties.

2:50 PM
SMALL-ANGLE NEUTRON SCATTERING AND MAGNETIZATION MEASUREMENTS ON NANOCRYSTALLINE Ni3Fe: *H. N. Frase*[1]; B. Fultz[1]; S. Spooner[1]; R. Shull[1]; [1]National Institute of Standards and Technology, Gaithersburg, Maryland 20899; [2]California Institute of Technology, Materials Science, Pasadena, CA 91125 USA

We made small angle neutron scattering (SANS) and magnetization measurements on nanocrystalline Ni3Fe samples prepared by mechani-

cal attrition. The materials were studied: 1) as-milled, when the material had a characteristic nanocrystallite size of 9 nm, 2) after annealing at 260^{0}C, which relieved residual stress but caused little grain growth, and 3) after annealing at 600°C, when the material had a characteristic crystallite size of >30 nm. The SANS measurements were performed under various applied magnetic fields up to 8 kG in order to separate the nuclear and magnetic scattering. From this data, the Guinier radii were found to be characteristic of grain boundaries and crystallite sizes. The SANS data were also parameterized in terms of the slope of the ln(I) vs. ln(Q)plot at large Q. Differences were found in the slopes for the nuclear and magnetic scattering, consistent with a change in magnetic structure when the crystals grew to sizes characteristic of the magnetic exchange length. The macroscopi c coercivity appears to be related to the internal strain in the samples. This work was supported by the U.S. Department of Energy under contractDE=D0FG03=D096ER45572.

3:10 PM INVITED

Fe-BASED BULK ANORPHOUS ALLOYS WITH ULTRAHIGH MECHANICAL STRENGTH: *Akihisa Inoue*[1]; Tao Zhang [1]; Masayuki Kobayashi[1]; [1]Tohoku University, Institute for Materials Research, Sendai 980-77 Japan

Since bulk amorphous alloys were prepared in multiconponent systems such as Mg-Ln-TM, Ln-Al-TM and 2r-A1-TM (Ln=lanthanide metal, TM=transition metal), the new alloys have attracted rapidly increasing interest because of the importance from materials science and engineering aspects. In addition to the above-described systems, some bulk amorphous alloys of Zr,-Ti-Al-TM Zr-Ti-TM-Be and Pd-Cu-Ni-P systems have subsequently been synthesized. These nonferrous bulk amorphous alloys have good mechanical properties of high tensile strength of about 1700 MPa. High Vickers hardness (H) of about 500 and high impact fracture energy, of about 70 kJ/m. More recently, we have also succeeded in finding Fe-based bulk amorphous alloys with good soft magnetic properties in Fe-(Al,Ga)-(P,C,R,Si) and Fe-(Co.Ni)-(Zr,Nb,Ta)-B systems. Besides, the bulk amorphous alloys in Fc Co Nb (Mo, W)-B system were also found to exhibit high mechanical strength, i.e., compressive fracture strength of 3800 MPa, bending fracture strength of about 3700 MPa and H of 1200. The Fe-based amorphous alloys with good mechanical properties also exhibit a wide supercooled liquid region reaching 90 K and T2 is as high as about 880 K. The high stability of the supercooled liquid against crystallization causes the large glass-forming ability (GFA). Furthermore, the high T2 implies strong bonding nature among the constituent elements in the Fe-based alloys. The finding of the new Fe-based amorphous alloys with large GFA, good soft magnetic properties and high mechanical strength is important for future development of bulk amorphous alloys.

3:50 PM

QUANTUM CONFINEMENT PHENOMENA AND MECHANISM OF PHOTOLUMINESCENCE IN NANOCRYSTALLINE SILICON PASSIVATED WITH SiO2 GRAIN BOUNDARIES: *S. Veprek*[1]; Th. Wirschem[1]; Ch Ossadnik[1]; [1]Technical University Munich, Institute for Chemistry of Inorganic Materials, Garching b. Munich D-85747 Germany

Compact films of nc-Si with a crystallite size D controllably varied between 1.5 and 10 nm were prepared by plasma CVD. Posttreatment consisting in a two stage oxidation and annealing in forming gas allowed us to passivate the dangling bonds and to control the average distance between the crystallites which is important because the "quality" of the grain boundaries significantly influences the optoelectronic properties of the films. A systematic studies on a large series of such films clearly support the early theoretical calculations of the band gap widening (up to $\geq$ 3 eV for D $\leq$ 1.5 nm), of the increase of optical transition probability and resulting efficiency of the PL due to the quantum confinement. However, the excitors are trapped at the Si/SiO2 interface and, therefore, the properties of such trapped excitors determine the characteristics of the PL. Doping of the nc-Si/a-SiO2 films with appropriate "luminophors", such as W. Mo, Cr results in a 50 ps fast and efficient PL, because these dopants act as efficient and fast radiative centers. This opens up new possibilities for the development of optoelectronic devices based on Si-technology.

4:10 PM

NANOPHASE MATERIALS FOR PHOTON-DRIVEN DISPLAYS: *R. Brotzman*[1]; H. Sarkas[1]; J. Aikens[1]; D. Gamota[2], [1]Nanophase Technologies Corporation, Burr Ridge, IL 60521; [2]Motorola,Corporate Manufacturing Research Center, Schaumburg, IL 60196[2]

Competition is intensifying in critical high-technology electronic markets. Efforts to incorporated nanophase materials into display manufacturing systems to improve the quality, lower the production cycle time, and reduce to cost of will be discussed. Materials of interest include nanophase phosphors, semiconductors, and dielectrics forintegrated electronics.

4:30 PM INVITED

PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE OF NANOCRYSTALLINE SI POWDER PREPARED BY LASER CVD: 19th Berger[1]; S. Tamir[2]; [1]Technion, Department of Materials Engineering, Haifa, Israel; [2]Technion, Metal Institute, Haifa, Israel

Nanocrystalline silicon powder was prepared by decomposition of SiH_4 gas using an excimer laser beam operated at 193nm, repetition rate of 10-70 Hz, and pulse duration of 24ns. The Si crystallites have a spherical shape and narrow size distribution. The average crystallite size decreases with increasing the laser repetition rate from 45nm at 20Hz to 15nm at 70Hz. The Si powder shows photoluminescence(PL) at room temperature in the following wavelengths: 610-670nm and 510-550 when excited at 488nm, and at 430-510nm when excited at 330nm. The powder also shows electroluminescence(EL) in aqueous $K_2S_2O_8$ and H_2SO_4 solution at wavelengths between 500nm and 800nm under applied voltage of about -1.0 V. The nanocrystalline Si powder has several advantages on porous Si. It can be deposited on any substrate, the fabrication process is dry and can be integrated in various microelectronic processes, the cystallites in the clusters are not oxidized w hen the powder is exposed to air, and the powder has high mechanical and thermal stability. In this paper the microstructure, composition, PL, and EL of the Si powder will be presented and the mechanism of PL and EL will be discussed.

5:10 PM

NANOCRYSTALLINE HARD MAGNETIC COP ALLOY FILMS: *Dr. Vladimir Grigor'evich Shadrow*[1]; Dr. Lyudmila Vasil'evna Nemtsevich[1]; Dr. Tadeush Antonovich Tochitskii[1]; [1]Inst. Solid State Physics, Acad. Sci. of Belarus, Minsk, Belarus 220072 Belarus

Structure and magnetic properties of nanocrystalline electrodeposited CoP films have been investigated by means of EM, XRD and AFGM. It is shown that sodium hypophosphite addition up to 5 g/l to the cobalt electrolyte results in the aggregates (~700nm) formation, consisting of a small crystallites (~10 nm) with the hcp [00.1] orientation. A further hypophosphite content increasing (up to 30 g/l) leads to the nanocrystalline (~10 nm) film formation and the [00.1] texture perfection increasing first and then some decreasing. The structure change observed are accounted for by proposed hypophosphite- ions adsorption mechanism and explain the magnetic parameters changing. In particular, crystallite separation by P rich regions results in a sharp coercivity increasing and in a dipolar magnetic intergranular interaction, which extent according to the remanence and delta M curves measurements depends on P content and the [00.1]texture perfection promoting P incorporation in the grains boundary regions. Two peaks in irreversible susceptibility curves confirm the existence of the [00.1] and [10.0] oriented crystallites and correlate with the XRD data.

MODELING THE MECHANICAL RESPONSE OF STRUCTURAL MATERIALS: Session IV: Microstructural Evolution

Sponsored by: Structural Materials Division, Structural Materials Committee

Program Organizers: Eric M. Taleff, The University of Texas, ASE/EM CO600, Austin, TX 78712; Rao Mahidhara, Cypress Semiconductor Corp, San Jose, CA 95134

Wednesday PM Room: 202
February 18, 1998 Location: Convention Center

Session Chairs: T. R. McNelley, Naval Post Graduate School, Department of Mechanical Engineering, Monterey, CA 93943-5146; R. S. Mishra, University of California, Department of Chemical Engineering and Materials Science, Davis, CA 95616

2:00 PM INVITED

MICROSTRUCTURAL EVOLUTION DURING EQUAL-CHANNEL ANGULAR PRESSING: M. Furukawa[1]; Z. Horita[2]; *N. Nemoto*[2]; T. G. Langdon[3]; [1]Fukuoka University of Education, Munakata 811-41, Japan; [2]Kyushu University, Fukuoka 812-81, Japan; [3]University of Southern California, Los Angeles, CA

The equal-channel angular pressing (ECAP) procedure is known to be extremely effective to produce fine grained materials which may show superplasticity, high strength and/or high ductility. This process involves pressing a material repeatedly through a channel of equal cross-sections intersecting at a certain angle. The experimental results show that deformation is homogeneous throughout the sample and dense dislocation walls intersected by dislocation cells are formed always parallel to the shear plane. With increasing strain, the misorientations between the walls and cells increase and finally result in being high enough to form equiaxed fine grains with high angle boundaries. In the present work, experiments were conducted to investigate the effects of the combination of shearing directions, number of pressings and angle of channel intersection on the microstructural evolution in pure Al and Al-Mg alloys in terms of optical and transmission electron microscopy.

2:30 PM

PROCESSING OF SUPERPLASTIC ALLOYS USING THE EQUAL-CHANNEL ANGULAR PRESSING TECHNIQUE: *P. B. Berbon*[1]; N. K. Tsenev[2]; R. Z. Valiev[3]; M. Furukawa[4]; Z. Horta[4]; M. Nemoto[4]; T. G. Langdon[1]; [1]University of Southern California, Los Angeles, CA 90089-0241 USA; [2]Ufa State Petroleum Technical University, UFA, Russia 450062; [3]Ufa State Aviation Technical University, UFA, Russia 450000; [4]Kyushu University, Fukuoka 812 Japan

A fine-grained structure with equiaxed grains is a well-known requirement for a material to exhibit superplasticity. A series of experiments was undertaken to demonstrate the ability of the equal-channel angular (ECA) pressing technique to introduce the required microstructure in commercial alloys. Mechanical testing of the processed materials was performed in the temperature range 0.5-0.8 Tm, where Tm is the absolute melting temperature, and in the strain rate range 10-3 to 1 s-1. Superplastic behavior, characterized by low flow stresses and very large elongations to failure, was achieved after ECA pressing. These results demonstrate the potential for low temperature and/or high strain-rate superplasticity.

2:50 PM

BEHAVIOR OF TITANIUM ALLOY UNDER UNIAXIAL AND BIAXIAL SUPERPLASTIC CONDITIONS: Z. Chen[1]; Z. Li[1]; P. Dang[1]; *N. Chandra*[1]; [1]Florida A&M University, Florida State University, Department of Mechanical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310 USA

The validity of extending constitutive relationships established under uniaxial condition to biaxial forming is important from both basic and applied interests. Titanium alloy under superplastic condition is studied under both uniaxial and biaxial states to understand the relationships. Ti-6Al-4V alloy is tested at uniaxial condition to establish the mechanical constitutive equation and also study the evolution of certain metallurgical parameters (e.g., grain size, grain shape, phase distribution, and grain size distribution). The same material is then subjected to biaxial condition in a multi-cone testing setup. In this testing, the sheet is subjected to a balanced biaxial state with varying levels of strain-rate. Comparison between the mechanical and metallurgical states of the specimen under the two types of loading is made.

3:10 PM

SUPERLASTICITY IN NEAR-ALPHA TITANIUM ALLOY 685: *V. Gopala Krishna*[1]; V. V. R. K. Prasad[2]; N. C. Birla[3]; G. Sambasiva Rao[4]; B. Gupta[4]; [1]Governament of India Defense Research & Development Organization, Ministry of Defense, Hyderabad, India 500058; [2]Indian Institute of Science, Bangalore, India; [3]Defense Metallurgical Research Laboratory, Hyderabad, India 500058; [4]Warangal Regional Engineering College, Warangal, India

Dynamic Materials Mode (DMM) is one among science based methodologies, developed in recent years to understand deformation processing and to optimize the process parameters for net shape or near-net shape processing of structure-sensitive titanium alloys, since trial and error techniques may not lead to successful solutions. Accordingly, isothermal hot compression tests in the temperature range 775°C to 1025°C and strain rate-range 10-3 s-1 were conducted on the cylindrical specimens of near-

3:30 PM Break

3:40 PM

GRAIN BOUNDARY AND MICROTEXTURE DEVELOPMENT BY CONTINUOUS REACTIONS IN SUPERPLASTIC ALUMINUM ALLOYS: *Prof. T. R. McNelley*[1]; M. E. McMahon[1]; M. T. Perez-Prado[2]; [1]Naval Postgraduate School, Department of Mechanical Engineering, Monterey, CA 93943-5146; [2]Centro Naciona1 de Investigaciones Metalurgicas (CENIM), CSIC, Avda., Department of Physical Metallurgy, Madrid, Spain 28040

The development of microtextures and grain boundary misorientation distributions during processing of superplastic aluminum alloys have been studied by means of computer aided electron backscatter diffraction (EBSD) analysis methods. Two alternative microstructural transformation processes that enable superplastic response in aluminum have been characterized using such methods. Here, results for materials that transform by continuous reactions will be presented. Such reactions are characterized by the de velopment during processing of deformation textures that are retained during subsequent heating and superplastic straining of the material. Bimodal misorientation distributions are frequently observed in association with the continuous reaction. Such misorientation distributions may be interpreted by models combining misorientations determined by components of the texture with misorientation relationships that reflect the influence of recovery on the deformation microstructure.

4:00 PM

ANISOTROPIC BIAXIAL CREEP OF TEXTURED CP-TITANIUM TUBING - EFFECT OF COLD-WORK: *Prof. K. Linga Murty*[1]; B. V. Tanikella[2]; Ratnaja R. Kola[3]; [1]North Carolina State University, Nuclear Engineering, Raleigh, NC 27695-7909; [2]St. Gobain/Norton Company, Northboro, MA 01532; [3]AT&T Laboratories, Murray Hill, NJ USA

Biaxial creep behavior of thin-walled tubing of recrystallized (Rx) cp-titanium alloy was investigated using internal pressurization superimposed with axial load at 723 K from which the creep locus was

constructed at a constant energy dissipation. Similar study was made at 573 K on cold-worked stress-relieved (CWSR) tubing. The experimental loci were fit to the modified Hill's equation with anisotropy parameters, R and P, which are also the contractile strain (-rate) ratios. The normalized loci for both the CWSR and Rx clearly deviated from that for isotropy. The crystallographic texture of the tubing was characterized through inverse and direct pole figures from which the crystallite orientation distribution functions (CODF) were derived. The CODF was combined with plasticity model based on power-law stress dependence of the strain-rate and dominance of basal prism and pyramidal slip systems were considered. Experimental results deviated from the prism-model predictions albeit the deformed microstructures revealed only prism dislocations. These differences are attributed to the relatively high O-equivalent content while grain-shape anisotropy due to cold-work seems to have a negligible influence. This work is supported by the National Science Foundation.

4:20 PM
RELATIONSHIP BETWEEN TEXTURE AND FRACTURE TOUGHNESS IN AA 7050 PLATE: *Dr. Armand J. Beaudoin*[1]; W. A. Cassada[2]; [1]University of Illinois , Urbana-Champaign, Illinois; [2]Reynolds Metals Company, Mill Products Division, Richmond, VA 23261 USA

Aluminum alloy 7050 was rolled using an experimental regime designed to vary texture development at the t/4 (quarter-plane). Samples of 5" gauge plate were finished processed to a T7451 temper. Samples were prepared for evaluation of plane strain fracture toughness (KIc) using compact specimens. Tests were carried out with normal to the crack in the transverse direction (T-L) as well as in the longitudinal direction (L-T). Experimental pole figures were measured and quantitative texture analysis was performed to develop the orientation distribution function. Yield surfaces were derived for each sample using polycrystal plasticity theory. Metrics developed through the quantitative texture analysis exhibited correlation with the difference in fracture toughness measured in the T-L and L-T samples. The texture development at the quarter-plane was further compared to texture development predicted through finite element modeling of the rolling process using material response derived from polycrystal plasticity.

MOLYBDENUM & MOLYBDENUM ALLOYS: Metallurgy and Properties

Sponsored by: Structural Materials Division, Refractory Metals Committee

Program Organizers: Andrew Crowson, U.S. Army Research Office, PO Box 12211, Research Triangle Park, NC 27709; Edward S. Chen, U.S. Army Research Office, PO Box 12211, Research Triangle Park, NC 27709; John A. Shield, Climax Specialty Metals, 21801 Tungsten Rd., Cleveland, OH 44117; P.R. Subramanian, UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432-1894

Wednesday PM Room: 203
February 18, 1998 Location: Convention Center

Session Chair: K. J.A. Mawella, Defence Research and Evaluation Agency, Structural Materials Centre, Farnborough, Hampshire GU14 OLX

2:00 PM
IMPROVED UNDERSTANDING OF MOLYBDENUM AND MOLYBDENUM ALLOYS: *Dr. T. G. Nieh*[1]; Dr. J. Wadsworth[1]; [1]Lawrence Livermore National Laboratory, Livermore, CA USA

Refractory metals, and particularly molybdenum, are prime candidates for many high temperature aerospace components because of their high melting points, dimensional stability, and inherent creep resistance. The use of refractory metals is often limited, however, by poor room temperature properties, inadequate oxidation resistance at elevated temperatures, or difficulties associated with joining or welding. In this paper, the understanding of the role of oxygen on these room temperature brittle behavior problems, especially in molybdenum alloys, is described. The effect of rhenium addition on the room temperature ductility of Mo is discussed. The effects of thermomechanical processing on the texture development and, thus, the subsequent mechanical properties in Mo are presented. In addition, alloying effect, e.g. potassium doping, on the thermal stability of Mo has been examined. The effectiveness of carbides in molybdenum alloys designed for high temperature creep resistance has been analyzed. The origins of brittle behavior in welded alloys are described. Examples are also given of novel solid state joining developments in molybdenum alloys below and above their recrystallization temperatures.

2:30 PM
THE INFLUENCE OF IRRADIATION CONDITIONS AND HEAT TREATMENTS ON THE MECHANICAL PROPERTIES OF NEUTRON-IRRADIATED MOLYBDENUM AND ITS ALLOYS: *Dr. K. Abe*[1]; Dr. K. Ueda[1]; Dr. A. Hasagawa[1]; Dr. M. Satou[1]; [1]Tohoku University, Dept. of Quantum Science and Energy Engineering, Aobaku, Sandai 980-77 Japan

Molybdenum and its alloys are candidate materials for high heat flux components of fusion reactors and facilities, because of their good properties in high-temperature strength and thermal conductivity etc. The important materials issues in the application for radiation field are degradation of mechanical properties caused by neutron irradiation. This paper describes the general tendency of the change in mechanical properties of molybdenum and its alloys caused by high-fluence neutron irradiation at high temperatures, and discusses the important factors to control the irradiation embrittlement of the materials. The microstructural evolution depended strongly on the irradiation temperature. The influence of heat treatment and of alloying with rhenium on the irradiation hardening and embrittlement were studied in detail. The irradiation embrittlement was improved appreciably by refining the grain size before irradiation. The evaluation of irradiation effect using a miniature type bend test and the stress-strain analysis by finite element method are also discussed.

2:50 PM
EFFECTS OF IMPURITIES ON GRAIN SIZE DEPENDENCY OF YIELD STRENGTH IN PURE MOLYBDENUM: *Dr. Kyu Cho*[1]; Dr. Robert J. Dowding[1]; [1]U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069 USA

Molybdenum and its alloys are being utilized in electronic, electrical, nuclear reactor, aerospace, and defense applications. It has been well known that residual impurities in molybdenum greatly influence its ductility, yield strength, and ultimate tensile strength. The primary impurities governing the mechanical properties are oxygen, nitrogen, and carbon. The level of these impurities is strongly dependent on its processing history and often exceeds the solid solubility limits at room temperature. On the other hand, molybdenum has been shown to obey the Hall-Petch relationship, which states that the yield stress is a strong function of average grain size. This dependency is, however, strongly affected by microstructure, chemistry, processing history, and anisotropy. Therefore, the objective of this work is to investigate the possible influence of the residual impurity level on its grain size dependency of yield properties in commercially available molybdenum processed by vacuum arc casting and powder metallurgy techniques.

3:10 PM
CURRENT STATUS OF IMPROVED RESISTANCE TO RECRYSTALLIZATION AND IRRADIATION EMBRITTLEMENT IN MOLYBDENUM: *Dr. Hiroaki Kurishita*[1]; [1]Tohoku University, Institute for Materials Research, Oarai, Ibaraki 311-13 Japan

Since molybdenum and its alloys suffer from significant embrittlement by recrystallization and neutron irradiation, it is needed to develop molybdenum alloys with improved resistance to such embrittlement. In this paper, our efforts made to improve the resistance are presented. First an explanation of embrittlement is given. Then a successful idea of alloys design and microstructure control to improve the resistance is described. The essential point of the idea is to

introduce a large number of grain boundaries that are strengthened by finely dispersed transition-metal-carbide particles by using mechanical alloying and hot isostatic pressing treatments. For molybdenum alloys developed by applying the idea, the recrystallization behavior and impact bending properties before and after high-temperature vacuum heating to 2000°C and neutron irradiation to 0.1 displacement per atom are shown and compared with those for TZM alloy. Finally, the occurrence of radiation-induced ductilization found in the developed alloys is stated.

3:30 PM Break

3:50 PM

MICROSTRUCTURAL DEVELOPMENT IN Mo-RICH Mo-Si-B ALLOYS: *Mr. Ridwan Sakidja*[1]; Dr. Heino Sieber[1]; Prof. John H. Perepezko[1]; [1]University of Wisconsin-Madison, Materials Science and Engineering, Madison, WI 53706 USA

Based upon extended isothermal annealing treatments on arc-cast and rapidly solidified splat samples, the high temperature phase equilibrium has been established for Mo-rich alloys in the Mo-Si-B system. At both 1600°C and 1200°C a prominent feature of the phase stability is the development of a two phase field involving a Mo solid solution (Mo-ss) and a Mo_5SiB_2 (T2) intermetallic (D8l) phase. For alloys with compositions covering the (Mo-ss + T2) two-phase field, the annealing of arc-cast samples results in the formation of Mo-ss precipitates with a faceted morphology within the supersaturated T2 intermetallic phase. This reaction provides for the in-situ formation of a ductile phase dispersion within T2. Preliminary indentation tests demonstrate that the Mo-ss precipitates do act to enhance the crack growth resistance and contribute to toughening of the two phase microstructure. For an alloy with composition Mo-20B-10Si some of the overall features of the microstructural evolution have been characterized by X-ray diffraction and SEM/EDX studies. The crystallographic orientation of the Mo-ss precipitates within the T2 matrix have been determined by TEM/SAED studies to show mainly the relation: Mo-ss {111} || T2 {001}; Mo-ss <011> || T2 <110> and are considered in terms of a HRTEM analysis of interfacial structure. The support of AFOSR (F49620-96-1-0286) is gratefully acknowledged.

4:10 PM

PROCESSING, MICROSTRUCTURE, AND PROPERTIES OF MOLYBDENUM-SILICON-BORON INTERMETALLICS: *Dr. Joachim H. Schneibel*[1]; Dr. Chain T. Liu[1]; Dr. Matthew J. Kramer[2]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6115 U.S.A.; [2]Iowa State University, Ames Laboratory, Ames, IA 50011-3021 USA

Molybdenum-silicon-boron intermetallics based on Mo-10.5Si-1.1B, wt% (Mo-26.7 Si-7.3 B, at. %) were fabricated by powder and ingot metallurgy. Powder-processed materials were usually free of macrocracks and contained no or only few microcracks. In materials processed by ingot metallurgy, fast cooling rates resulted in macrocracks and only little microcracking. Slow cooling rates minimized the incidence of macrocracks, but led to many pores and/or microcracks. Depending on the processing, flexure strengths approaching 300 MPa at room temperature, and 600 MPa at 1200°C were obtained. The microstructures and mechanical properties will be discussed in terms of the type of processing as well as the carbon and oxygen contents of the materials. This research was sponsored by the Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program, U.S. Department of Energy, under contract number DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation, and in part by USDOE through Iowa State University under contract No. W-7405-Eng-82

4:30 PM

NANOINDENTATION STUDIES OF STRESS RELAXATION IN MOLYBDENUM THIN FILMS: *Dr. Donald S. Stone*[1]; Karl Yoder[1]; Richard A. Hoffman[2]; Jen C. Lin[2]; [1]University of Wisconsin-Madison, Materials Science and Engineering, Madison, WI 53706 USA; [2]Alcoa Technical Center, Alcoa Center, PA

The mechanical properties of thin film molybdenum are of interest because of the exceedingly small grain-size and high defect densities that can be achieved. In this work we have applied nanoindentation techniques to characterize the hardness and rate sensitivity of the hardness in 1-2 -thick molybdenum films deposited on silicon. Grain sizes range between 20 and 100 nm and hardness levels range from 6 to 16 GPa. Based on the rate sensitivity of the hardness, it is possible to calculate an activation area. We find that for arc evaporated films the activation areas agree with data obtained from bulk molybdenum suggesting the operation of bulk-like dislocation mechanisms. In e-beam evaporated thin films the activation areas are lower. Differences in microstructure can account for the differences in mechanical behavior. The data obey a Hall-Petch relationship extending out two orders in magnitude in grain size the data from bulk materials.

4:50 PM

OXIDATION BEHAVIOR AND MECHANICAL PROPERTIES OF Mo-Mo_5Si B_2-Mo_3Si THREE-PHASE ALLOYS: *Dr. M. G. Mendiratta*[1]; Dr. P. R. Subramanian[1]; [1]UES, Inc., Dayton, OH 45432 USA

Alloys in the three-phase field Mo-Mo_5Si B_2-Mo_3Si are being investigated as high temperature structural materials. The compositions encompass a wide range of B and Si contents to vary the volume fractions of the intermetallic phases Mo_5Si B_2(T2) and Mo_3Si in equilibrium with the Mo phase. The materials are mainly fabricated by arc-melting of elemental mixtures and casting in the form of 300 gm buttons followed by prolonged heat treatments. The alloys are subjected to static and cyclic oxidation exposure in the temperature range 800 - 1400°C. High temperature creep rates (1200 - 1400°C) and toughness (25 - 1000°C) are also being determined. The results will be discussed in comparison to the behavior of other potential high temperature material systems. This research was performed at the Wright Laboratory Materials Directorate with support from AF Contract F33615-96-C-5258.

NON-AEROSPACE APPLICATIONS OF TITANIUM & ITS ALLOYS: Session VI - Miscellaneous Applications; Sporting Applications

Sponsored by: Structural Materials Division, Titanium Committee
Program Organizers: F.H. (Sam) Froes, University of Idaho, IMAP-Mines Bldg. #321, Moscow, ID 83844-3026; P.G. Allen, Timet, P.O. Box 2128, Henderson, NV 89009; M. Niiomi, Toyohashi Univ of Technology, Dept. of Production Systems Eng., Toyohashi 441 Japan

Wednesday PM Room: 101
February 18, 1998 Location: Convention Center

Session Chair: Chenggong Li, AVIC/BIAM, Bejiing China

2:10 PM

TITANIUM ALLOY COIL SPRING APPLICATIONS IN NON-AEROSPACE INDUSTRIES: *Mr. Alan Caddey*[1]; [1]Renton Coil Spring Company, Renton, WA 98057-0880

Beta titanium alloys offer a unique combination of properties for springs. Their relatively high strength, low elastic modulus, low density and excellent corrosion resistance make them ideal for aerospace applications. These same attributes are increasingly being recognized by other industries as well, and titanium is quickly finding its way into various non-aerospace applications. The front running aerospace titanium alloy Ti-3Al-8V-6Cr-4Mo-4Zr, commonly known as ABeta-C, is leading the way into the non-aerospace arena. To a lesser degree, other titanium alloys, including Ti-6.8Mo-4.5Fe-1.5Al-0.15O, (more commonly known as ATIMETAL7 and Ti-6Al-4V, are also being used in the aerospace and non-aerospace industries. This paper will discuss

several non-aerospace titanium alloy coil spring applications, including Pro-Stock Car valve springs, off-road (desert) racing vehicle suspension springs, various motorcycle and bicycle springs, and Formula 1 and Indy Car (CART) suspension springs.

2:30 PM
TITANIUM USE IN AUTOMOBILES—DOES DETROIT REALLY WANT IT?: *F. H. (Sam) Froes*[1]; O. N. Senkov[1]; V. Moxson[2]; [1]University of Idaho, Institute for Materials and Advanced Processes (IMAP), Moscow, ID 83844-3026; [2]Advanced Materials, Inc. (ADMA, Inc.), Twinsburg, OH 44087

Programs such as the Partnership for Next Generation Vehicle (PNGV) are promoting the use of lightweight, albeit expensive, materials such as aluminum, magnesium and titanium for automobile use. However, does Detroit really want these materials or are they happy to sell steel cars? What difference would it make if gasoline prices in the USA rose by a factor of 3 to European levels? These and other issues will be discussed using titanium as an example of an expensive lightweight material.

2:50 PM
THE DEVELOPMENT OF TITANIUM ALLOYS FOR NON-AEROSPACE APPLICATIONS: *Mr. James S. Grauman*[1]; [1]TIMET Henderson Technical Laboratory, Henderson, NV 89009

As with most industrial laboratory settings these days, basic R&D has given way to applied R&D. The focus is on fulfilling a customer's requirements, as it should be. In the area of non-aerospace applications, recent market developments have led to new or, in some cases, modifications of mature titanium alloy systems. The recent trend has been to utilize existing alloys and tailor fit them for a specific application or market by adjusting their mechanical or corrosion resistant properties. The advantage being rapid deployment into the marketplace and an immediate high level of acceptance by the end users. This paper will review several recent titanium alloy introductions, commenting on the application demands placed on the alloys and the means by which the demands were met. In addition, laboratory test results will be presented which show the necessity of careful scrutiny prior to introduction of alloy modifications.

3:10 PM
PROPERTIES AND POTENTIAL APPLICATIONS OF HYBRID TIMETAL® 15-3/PMC LAMINATES: *Mr. J. C. Fanning*[1]; Mr. W. R. Kingston[2]; [1]TIMET Henderson Technical Laboratory, Henderson, NV 89009; [2]TICOMP, Chino, CA 91710

Hybrid TIMETAL® 15-3 / Polymeric-Matrix-Composite (PMC) laminates consist of layers of titanium foil bonded together with polymer prepreg and reinforced with fibers. Very high strength (1590-2340 Mpa [230-340 ksi]), high elastic modulus (138-200 Mpa [20-29 Msi]), and moderate density (2.77 g cm-3 [0.10 lbs in-3]) make the laminates very attractive for numerous aerospace and non-aerospace applications. General configuration, mechanical properties and potential non-aerospace applications of the laminates will be discussed in this paper.

3:30 PM
IS IT ETHICAL TO USE TITANIUM TO ENHANCE SPORTS PERFORMANCE?: *F. H. (Sam) Froes*[1]; O. N. Senkov[1]; [1]University Of Idaho, Institute for Materials and Advanced Processes (IMAP), Moscow, ID 83844-3026

Use of advanced materials such as titanium, can result in dramatically improved performance in sports. The ethics of this use will be discussed and some possible scenarios for restricting use, so that all competitors can compete solely based on athletic ability, will be presented.

3:50 PM
THE USE OF TITANIUM TUBING IN THE SPORTS INDUSTRY: *Steven E. Meredith*[1]; [1]Sandvik Special Metals Corp., Kennewick, WA

High strength, light weight, and excellent corrosion resistance; the properties that made titanium a common aerospace material have also given titanium a growing position in the sporting goods industry. Tubing made from commercially pure titanium as well as alloys such as Ti-3Al-2.5V, Ti-6Al-4V, and Ti-15V-3Cr-3Sn-3Al have been used in a myriad of sports equipment including golf shafts, bicycle and motorcycle frames, wheelchair frames, hockey sticks, baseball bats, lacrosse sticks, snowshoes, and pool cues. In the pursuit of better performance, sports equipment has become high tech with titanium competing against not only conventional steel and aluminum alloys, but also advanced composite, thermal plastic, and intermetallic materials. The designer of such sports equipment must be aware of titanium's unique properties to take full advantage of the material while avoiding some of the pitfalls.

4:10 PM
TITANIUM IN GOLF CLUBS: *Chet Shira*[1]; Oleg N. Senkov[2]; F. H. (Sam) Froes[2]; [1]Carbite Golf, San Diego, CA 92121; [2]IMAP, University of Idaho, Carbite Golf, Moscow, ID 83844-3026

Because of its attractive combination of properties, including high-strength and corrosion resistance, titanium and its alloys are currently the number one choice for golf club head applications, particularly metal woods. In this paper the characteristics of golf clubs made from titanium will be discussed and related to performance. This will include both casting techniques to produce hollow titanium woods with a large "sweet spot". It will also include use of titanium in irons with tungsten inserts to lower the center of gravity. Recent advances including a powder metallurgy approach to production of inserts will also be discussed.

4:30 PM
TITANIUM GOLF CLUB HEADS: *Chenggong Li*[1]; J. Ma[1]; [1]BIAM, Beijing China

Because of its high strength-to-density ratio and excellent corrosion characteristics titanium and its alloys are an excellent choice for "metal" wood golf club heads. This paper will review developments in this area at BIAM, including recent "value added" activities which take the golf club head closer to the final product.

PROCESSING-STRUCTURE-PROPERTY RELATIONSHIPS OF COMPOSITE INTERFACES: SESSION V: PHYSICAL CHEMISTRY OF INTERFACES

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector/Structural Materials Division, Composite Materials Committee, Materials Design & Manufacturing Division, Powder Materials Committee

Program Organizers: Sunil G. Warrier, UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432-1894; Mary Lee Gambone, WL/MLLM, Wright Lab Materials Directorate, WPAFB, OH 45433; Ray Y. Lin, University of Cincinnati, Dept. of Materials Sci. & Eng., Cincinnati, OH 45221-0012; Benji Maruyama, WL/MLLM, Wright Lab Materials Directorate, WPAFB, OH 45433

Wednesday PM Room: Centro A
February 18, 1998 Location: Convention Center

Session Chair: Sunil G. Warrier,UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432-1894; Kishore U. Pichuraja, Stevens Institute of Technology, Hoboken, NJ

2:00 PM INVITED
EXPERIMENTAL SIMULATION OF THE INTERFACIAL REACTIONS IN METAL MATRIX COMPOSITES: *Constantin Vahlas*[1]; I. W. Hall[2]; I. Haurie[1]; [1]Laboratoire de Cristallachimie et Réactivité de Matériaux, INPT-CNRS ENSCT, F-31077 Toulouse Cedex 4 France;

[2]University of Delaware, Mechanical Engineering and Materials Science Program, Newark, DE 19716-3106

The chemical vapor deposition and the powder techniques have been used for the ex-situ experimental simulation of the of interfacial reactions in a titanium and in an orthorhombic aluminide matrix, silicon carbide based reinforcement composites. The results obtained by both methods are similar to the ones in the real composites. This new approach allows for a rapid, economic and easy to use evaluation and contributes to the optimization of the interfacial characteristics in MMC's.

2:45 PM

MECHANICAL PROPERTY MICROSTRUCTURE RELATIONSHIP AND THERMAL STABILITY OF METAL CERAMIC INTERFACES: *Manfred Ruhle*[1]; [1]Max-Planck-Institut fur Metallforschung, Stuttgart German

The mechanical properties of metal/ceramic interfaces play a critical role for an understanding of the properties of metal ceramic composites. In this paper, results on model systems will be described (M/Al_2O_3, M-Nb, Cu, Ni). The structure, composition and bonding across the interface and the fracture resistance of the interface will be determined experimentally as a function of the processing conditions. Furthermore, the influence of reactions at the interface during high temperature annealing on the mechanical properties will be studied. After annealing, the appearance of reaction phases are investigated and their influence on the mechanical properties determined.

3:10 PM

TUNGSTEN FIBER-REINFORCED COPPER MATRIX COMPOSITES: *H. G. Wheat*[1]; J. E. Orth[2]; [1]University of Texas at Austin, Mechanical Engineering Department, Austin, TX 78712; [2]United Defense, Munford, TX 36268

The corrosion behavior of several copper metal matrix composites has recently been investigated in sodium chloride solutions. The research focussed primarily on graphite/copper composites and secondarily on tungsten/copper composites. The graphite/copper composites offer a wider range of potential applications than the tungsten composites due to their decreased density and superior mechanical and thermal properties. Tungsten/copper composites, however, are ideal for high strength, high thermal conductivity applications where component weight is not a limiting criterion and therefore they offer potential as components in high temperature aircraft and rocket engine turbines. In addition, they suffer less severe galvanic corrosion than their graphite counterparts as a result of interfacial interactions. The results of the electrochemical testing and surface analysis of these composites will be described.

3:35 PM

REACTIVE SPUTTER DEPOSITION OF CHROMIUM NITRIDE COATINGS: *M. Pakala*[1]; Ray Y. Lin[1]; [1]University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221

Deposition of chromium coatings using electrodeposition is accompanied by emission of hexavalent chromium mists which is a carcinogenic. Hence alternative chromium deposition technologies are being investigated. Sputter deposition is a strong candidate to economically deposit hard chromium coatings in an environmentally friendly way. Chromium coatings of 2-3 mm thickness were deposited on mirror finished plain carbon steel coupons using RF magnetron sputter deposition. Depositions were carried out with 0 to 22 volume percent nitrogen in the plasma. Structure and composition of the coatings were studied using x-ray diffraction, energy dispersive x-ray analysis (EDAX) and x-ray photoelectron spectrometry (XPS). With increasing nitrogen content formation of the two nitride phases is observed. Quantitative values of the nitrogen content in coatings are obtained using EDAX. Chromium phase is observed for nitrogen contents about 7%. Qualitatively the solid solution of nitrogen in the Cr phase coating can be observed by shifting of x-ray diffraction peak to higher d-spacings and also by XPS analysis. Measurement Scratch test wear track widths indicate that the Cr_2N coatings have better wear resistance than Cr coatings and CrN coatings. The wear resistance also increases with nitrogen content in single phase Cr coatings.

4:00 PM Break

4:15 PM

KINETIC CONTROL OF SILICON CARBIDE/METAL REACTIONS: *J. S. Park*[1]; K. Landry[1]; J. H. Perepezko[1]; [1]University of Wisconsin-Madison, Department of Materials Science and Engineering, Madison, WI 53706 USA

The kinetic features governing SiC/metal reactions have been investigated to identify the operating mechanisms and diffusion characteristics. With respect to the contact metal components, the reaction characteristics were identified by two separated modes - formation of carbides and silicide (Mode I), and formation of silicides and free carbon (Mode II). The analysis was confirmed experimentally by diffusion annealing of SiC/Ni and SiC/Cr at 1173K. The diffusion pathways of both reactions were examined in terms of a chemical potential framework. The application of the analysis has been extended to in-situ interface reactions of SiC/Cu/Ni and SiC/Cr/Ni. New reaction modes representing SiC/Metal reactions and a strategy to control reaction pathway are discussed. The support of ONR (N00014-92-J-1554) is gratefully acknowledged.

4:40 PM

COMPOSITION AND ENERGETICS OF METAL/SiC INTERFACES: *Mr. Zhangmin Wang*[1]; Dr. Paul Wynblatt[1]; [1]Carnegie Mellon University, Dept. of Materials Science and Engineering, Pittsburgh, PA 15213 USA

This paper will report the result of studies of Au/SiC and of Au-alloy/SiC interfaces by a solid state wetting technique. The technique, which involves the equilibration of small metal crystallites on ceramics, under ultrahigh vacuum conditions, has been applied to the study of pure Au and of Au-Sn, Au-Ge and Au-Si alloys, on monocrystalline alpha-SiC substrates. Contact angles made by the crystallites on the SiC substrate have been determined, and the surface compositions of the crystallites and of the substrate have been measured. From these measurements, it is possible to extract both the compositions as well as the energies of the metal/SiC interfaces, and thus assess the effects of alloying on interfacial energetics. Support of this work by DOE under grant DE-FG02-88ER45358 is gratefully acknowledged.

5:05 PM

INTERFACE PHASES DESIGN AND PROCESSING OF POWDER METALLURGY ALUMINIUM/GLASS COMPOSITES: *Wang Dajian*[1]; He Aiping[1]; [1]Kunming University of Science And Technology, Department of Metallurgy, Kunming 650093 P.R. China

There has been increasing interest in the development of metal matrix-particulate ceramic composites through powder metallurgy. The materials with reduced thermal expansion and wear resistance can achieve the combination of properties of Al and glass in response to requests from the machine or automotive industry. Work on the dispersion of amorphous materials like glass in aluminium and its alloy are likely to be greatly different in view of their different physical and chemical properties. The structure of glass, physic-chemistry of interfaces must be carefully considered to improve the joining strength of the composite. In the experiment, glass particles containing 72.04%SiO_2, 2.55%Al_2O_3, 0.16%Fe_2O_3, 6.48%CaO, 4.02%MgO, 14.32%K_2O+Na_2O and waste Al powders with a composition of 2.59%Si, 1.55%Ti, 0.82Mn%, Fe_1.24%, Mg0.80%, Cu0.95% and 90.34% (all percentages are weight percent), which was fabricated from waste beverage aluminium cans, were primarily used as matrix materials for preparing aluminium/glass composites. The materials adopted results in a more complicated multicomponent and multiphase system on the interfaces to be investigated in detail. The phase diagrams and phase equilibrium of Al-Si, Al-Cu, Al-Mg, Al-Zn and oxide systems during solid or liquid sintering are considered by TGA-DSC thermal analysis, XRS or SEM analyses. The structure and properties are analyzed to optimized the preparing process. The research results may be furtherly applied to practical waste glass/Al composite fabrication process.

SOLIDIFICATION AND DEPOSITION OF MOLTEN METAL DROPLETS: Session III

Sponsored by: Materials Design and Manufacturing Division, Solidification Committee

Program Organizers: Men G. Chu, Alcoa Technical Center, Molten Metal Processing Center, Alcoa Center, PA 15069; Jung-Hoon Chun, M.I.T., Dept. of Mechanical Engineering, Cambridge, MA 02139; Enrique J. Lavernia, Univ of California-Irvine, Dept. of Chem. Engrg & Matls. Sci, Irvine, CA 92717-2575

Wednesday PM Room: Plaza Room D
February 18, 1998 Location: Convention Center

Session Chair: Jung-Hoon Chun, M.I.T., Dept. of Mechanical Engineering, Cambridge, MA 02139

2:00 PM

EVALUATING POROSITY IN SPRAY DEPOSITED MATERIALS: *Dr. J.-P. Delplanque*[1]; W. D. Cai[1]; Dr. E. J. Lavernia[1]; [1]University of California at Irvine, Chemical and Biochemical Engineering & Materials Science Department, Irvine, CA 92697-2575 USA

A heuristic model is proposed to evaluate porosity in spray deposited materials. It is assumed that the actual deposition process can be conceptualized as an equivalent discrete process resulting in a stratified build-up of the deposit. This model also incorporates the effect of the relative magnitude of the fluid flow characteristic time and the solidification characteristic time plays on the porosity formation process. Based on these assumptions, expressions for the porosity are derived as functions of the particle size distribution, the average solid fraction of the incident spray, and the solidification contraction. The average solidification of the incident spray is estimated from the droplet size distribution and the solid fraction of a single droplet of a given size. The latter is determined by calculating the droplet dynamics and thermal history, including the effect of undercooling. This model is used to investigate the effect of undercooling and process parameters (melt superheat, atomization pressure, deposition distance, and melt mass flow rate) for a variety of materials. The model's predictions are compared to available experimental data.

2:20 PM

AN APPROACH TO MINIMIZE POROSITY IN SPRAY FORMED DEPOSIT THROUGH A MODEL-BASED DESIGNED EXPERIMENT: *Dr. Robert L. Kozarek*[1]; Dr. Men G. Chu[2]; Dr. S. John Pien[1]; [1]Alcoa Technical Center, Fluid State Processing Center, Alcoa Center, PA 15069 USA; [2]Alcoa Technical Center, Molten Metal Processing Center, Alcoa Center, PA 15069 USA

Spray forming technology is based on the atomization of liquid metals and subsequent deposition on a substrate. In the process, gas atomized metal droplets are simultaneously cooled as they are conveyed to the substrate by the atomizing gas. The extent of cooling is dependent on the characteristics of the spray such as particle and gas velocity, the particle size, and the time of flight. Depending on the thermal history, the impacting droplets will arrive at the substrate in either a fully solid, fully liquid or mushy state. Under the proper conditions, the mixture of droplets will consolidate to form a thin mushy or semi-solid deposit on the top surface of the spray formed deposit. This layer solidifies incrementally as heat is transferred into the substrate. The thickness and average solid fraction of the mushy layer are important parameters which have been strongly correlated to the porosity and product microstructure of the deposit. Unfortunately, neither quantity can be experimentally measured directly. This paper describes a designed experiment to develop a process map of spray conditions in relation to porosity in the bulk deposit. The experiments were performed on a small bench scale unit. The process conditions were selected on the prediction of fraction solid using mathematical models of the process. Process parameters considered include gas pressure, gas/metal ratio, spray distance, average droplet velocity, average droplet diameter and melt superheat. An operating window for minimizing porosity in the bulk was identified. A methodology for applying the results to a larger scale unit by using a transient model to describe the thermal history and fraction solid at each location in the small scale deposit will be described.

2:40 PM

DEFORMATION AND SOLIDIFICATION BEHAVIOR OF A MOLTEN METAL DROPLET COLLIDING WITH A SUBSTRATE: MODELING AND EXPERIMENT: *Dr. Jun Fukai*[1]; Haruhisa Asami[1]; Osamu Miyatake[1]; [1]Kyushu University, Department of Chemical Systems And Engineering, Fukuoka 812-81 Japan

A mathematical model for predicting deformation and solidification of a molten metal droplet impinging on a substrate was developed. The model was numerically solved utilizing deforming finite elements to simulate accurately the large deformations. Experiments in which a molten tin droplet of an order of millimeter in diameter impinges on metal and nonmetal substrates were used to test the numerical results. The experiments demonstrated that the splat diameter made dimensionless with the droplet diameter, was correlated with the Weber number in the range of interest in this study. Little difference in the splat diameter for different metal substrates (copper, stainless-steel and brass plates) was observed. Good agreement was found between the model and the experiment. The numerical results were moreover compared to several published experimental data in terms of time variation of temperature at the droplet/substrate interface.

3:00 PM

MODELING OF RAPID SOLIDIFICATION DURING SPLAT QUENCHING: *Dr. Guoxiang Wang*[1]; Dr. Sanjay Sampath[1]; Dr. V. Prasad[2]; Dr. Herbert Herman[3]; [1]State University of New York at Stony Brook, Center for Thermal Spray Research, Stony Brook, New York 11794 USA; [2]State University of New York at Stony Brook, Depatment of Mechanical Enginering, Stony Brook, New York 11794 USA; [3]State University of New York at Stony Brook, Department of Materials Science &Engineering, Stony Brook, New York 11794 USA

In thermal spray deposition, splats are formed by the impact of molten droplets on a solid substrate or a pre-deposited layer. As a first approximation, melt spreading and subsequent solidification can be decoupled and, therefore, the analysis of the heat transfer and rapid solidification of the splat can be greatly simplified. This paper presents some recent developments in modeling of rapid solidification during such a splat quenching process. Specifically, an integrated heat and rapid solidification model has been developed to study the microstructure formation in the splat. The model is based on a unified dendrite tip growth theory, developed recently by the present authors, which employs the marginal stability criterion derived by Trivedi and Kurz for rapid solidification and is applicable for both free dendrite growth in an undercooled melt and constrained dendrite growth under a positive temperature gradient. The unified dendrite tip growth model also determines the solidification morphology, i.e. , planar or dendritic growth. For planar solidification, a heat and mass diffusion will be solved with the solid/liquid interface following the kinetic liquidus curve. For dendritic solidification, dendrite tips are tracked numerically and the latent heat release in dendritic region is simulated by a microsegregation model considering the tip undercooling. The model is used to predict the microstructure development of impacted droplets of various materials. This work was supported by the MRSEC Program of the National Science Foundation under Award Number DMR-9632570

3:20 PM

ON MODELING AND OPTIMIZATION OF SPRAY FORMING PROCESS FOR PRODUCING LINEAR ALUMINUM SHEET: *Dr. S. J. Pien*[1]; Dr. M. G. Chu[2]; Dr. M. K. Chyu[3]; [1]Alcoa Technical Center, Fluid State Processing Center, Alcoa Center, PA 15069 USA; [2]Alcoa Technical Center, Molten Metal Processing Center, Alcoa Center, PA 15069 USA; [3]Carnegie Mellon University, Mechanical Engineering Department, Pittsburgh, PA 15213 USA

This paper describes a three-dimensional computational simulation of transport phenomena in spray forming process as well as the appli-

cation of optimization technology to study the effect of process parameters in the making of aluminum sheet by using a linear spray nozzle. The modeling and simulation have been focused on investigation of the effects of three-dimensional gas flow characteristics on the aluminum droplets deposition in an actual spray chamber. The numerical procedure employed here for the gas/droplet phase is a fully interacting combination of Eulerian flow and Lagrangian droplet calculation. The related gas turbulence parameters are modeled through two equation, k-e model. Modeling of aluminum droplet solidification uses a five-stage process evolution involving undercooling and recalescence. The rebound velocity of an impinging droplet is modeled based on the size, velocity and solid fraction of the droplet. The preform shape resulted from the chamber conditions is statistically calculate d and it agrees well with what measured experimentally. Thermal condition of the preform is also modeled and the results suggest a correlation to the porosity formation in the preform. This paper also describes the work of using optimization technique to determine the conditions to which a desired process can be reached. The optimization approach utilizes the aforementioned simulation models to search for the objective function and the associated process conditions under which optimal solution can be obtained. Due to the complex nature of the problem and the multiplicity of process parameters, application of optimization technique is found to be an effective way to study the spray forming problem. Examples of sensitivity information on the effect of process parameters are also presented.

3:40 PM Break

3:50 PM

SIMULATION OF LAYER GROWTH IN LINEAR NEAR-NET-SHAPES IN INDUSTRIAL SPRAY FORMING APPLICATIONS: *Dr. Jorge E. Gonzalez*[1]; [1]University of Puerto Rico, Department of Mechanical Engineering, Mayaguez, Puerto Rico 00680

This paper deals with the numerical simulation of the phase change and heat transfer processes that occurs during the growth of a solidifying layer under high melt rates that result from linear atomization. The coupled problem that results from conservation of mass, including a surface source effect, with conservation of energy in both the mushy region and the cold substrate was formulated. The problem assumes that the entrained liquid mass from the linear atomization is continuous with spatial distribution, and non-slip of the resulting liquid layer at the cold substrate. Furthermore, the problem considers the presence of a moving domain that commonly occurs in conveyering arrangements. Undercooling was considered as a linear function of the velocity of the solidification front. Energy entrainment of the continuous liquid film was considered at the outside boundary along with contact thermal resistance between the solid layer and the cold substrate. The liquid entrainment was approximated as a continuous Gau ssian distribution which is typical of linear atomizers. The full two-dimensional set of the resulting equations was discretized using finite differences with a control volume approach. Results are presented for the particular case of the fabrication of aluminum sheets solidifying on a stainless-steel cold substrate. Solutions for the solidification front and for the full thickness of the layer are obtained as function of the horizontal direction for several conveyor speeds and mass entrainment rates. The accuracy of the numerical scheme was assessed by comparing results with simplified limiting cases. Grid size independence is also demonstrated.

4:10 PM

ANALYSIS OF TRANSIENT HEAT CONDUCTION WITH PHASE CHANGE IN A SPRAY DEPOSITED BODY: *Dr. Shinill Kang*[1]; Dong-Hoon Chung[1]; Eon-Sik Lee[2]; Sangho Ahn[2]; [1]Yonsei University, Department of Mechanical Design and Production Engineering, Seoul 120-749 Korea; [2]Research Institute of Science and Technology, Advanced Materials Division, Pohang, Kyungbuk 790-600 Korea

A numerical method is presented to predict and analyze the shape and the temperature history of a growing billet produced from the "spray forming" which is a fairly new near net-shape manufacturing process. It is important to understand the mechanism of billet growing and the cooling history of the spray deposited body, because one can obtain a billet with the desired final shape without secondary operations by accurate control of billet shape and, moreover, growing velocity together with the cooling rate define the microstructure of the final formed product. The shape of a growing billet is determined by the flow rate of the alloy melt, the mode of nozzle scanning which is due to cam profile, the initial position of the spray nozzle, scanning angle, and the withdrawl speed of the substrate. The temperature history of a growing billet is governed by heat flux input from the spray, gas convection on the surface of the deposited body, heat conduction to the substrate. In the present study, a theoretical model is first established to predict the shape of the growing billet and next the transiet axisymmetric heat conduction problem with growing domain is solved using the so-called "deforming finite element technique". The range of mushy zone near the surface of the deposited body is predicted, and the effect of cooling history on the microstructure and possible pore developments is discussed.

4:30 PM

SIMULATION OF THERMAL MECHANICAL BEHAVIOR DURING METAL DROPLET SOLIDIFICATION: *Dr. Brian G. Thomas*[1]; Mr. Jon T. Parkman[1]; [1]University of Illinois, Mechanical & Industrial Eng., Urbana, IL 61801 USA

A finite-element model has been developed to predict the evolution of temperature, stress, and shape of a molten metal droplet solidifying against a chilled substrate. Thermal contraction causes the quenched surface of the impinged droplet to bend away from the substrate, which creates interfacial resistance that is critical to subsequent heat transfer. The model is applied to predict the behavior of 10-mm diameter droplets of molten steel solidifying against a chilled copper substrate. Temperatures calculated by the heat flow model are input to an elastic-viscoplastic finite-element stress model. The stress model features an efficient algorithm to integrate the highly non-linear constitutive behavior of steel at high temperature. It includes the effects of phase transformation on both the thermal linear expansion / contraction behavior and the creep behavior, which varies with carbon content. The droplet shape is predicted to evolve almost entirely during the first 0.1 seconds, when a thin solid skin first forms and is strong enough to contract. The final shape of the droplet interface predicted by the model agrees both qualitatively and quantitatively with previous measurements reported by Dong and coworkers. The shape is predicted to vary with carbon content, due to the different strengths and contractions of the phases according to the peritectic transformation, which agrees with measurements. This work aims to shed light on the development of surface roughness and accompanying non-uniform solidification, which is responsible for many casting defects.

4:50 PM

EFFECT OF THERMOMECHANICAL TREATMENT ON THE DAMPING CAPACITY OF AL-ZN-X ALLOYS PRODUCED BY SPRAY FORMING PROCESS: B. C. Moon[1]; *Dr. Z. H. Lee*[1]; [1]RASOM, KAIST, Department of materials Science and Engineering, Yusong, Taejon 305-701 Korea

The effect of thermomechanical treatment on the structure and the damping behavior of Al-Zn-X alloys produced by spray forming was studied. Various compositions of Al-Zn binary alloys and Al-Zn-X ternary alloys were made by spray forming and ingot casting. The third elements were Cu, Mg, Mn, and Si. Specimens were machined and heat-treated at various conditions. The difference between the microstructure of spray formed and cast specimens after heat treatment was compared. The microstructure of these alloys show either lamella or equiaxed fine grains. These alloys were then rolled at various conditions. The damping capacity and the tensile properties of each alloys were measured and the changes of their microstructure with initial microstructure and rolling conditions was observed. Damping capacity was measured by logarithmic decrement of freely decayed vibration of strip specimen. Resonance frequency was 10 Hz.

5:10 PM

DEPOSITION OF HIGH-MELTING POINT MATERIALS ON A SUBSTRATE: SUBSTRATE MELTING AND RESOLIDIFICATION: *S. P. Wang*[1]; G. X. Wang[1]; E. F. Matthys[1]; [1]University of California, Department of Mechanical Engineering, Santa Barbara, CA 93106-5070 USA

The melting and resolidification of the substrate or of previously deposited layers may play an important role in many processes such as thermal spray coating, microcasting, spray deposition, and high-temperature casting. A good understanding of this phenomenon would help us to achieve better bonding between deposited layers in some cases or to avoid damage to the substrate in others. In the present work, these processes are looked at as the melting and resolidification of a substrate in contact with a layer of molten metal which may also solidify. Both the solidification of the deposited layer and the melting and then resolidification of the substrate or previous layer are calculated using non-equilibrium phase change kinetics conditions at the solid/liquid interfaces and an implicit finite difference method with interface tracking. A non-dimensional analysis of the controlling parameters under various conditions was conducted, and allowed us to generate non-dimensional operational maps that can tell us whether there will be substrate melting or not. If there is, other non-dimensional maps were generated to quantify the maximum achievable melting depth for various process conditions. Some results on the interface velocity during substrate melting and resolidification for various process conditions and for variations in interfacial heat transfer coefficient with time will be also presented. Of particular interest were high-melting-point metal and ceramic materials (such as molybdenum, tungsten, zirconium, and alumina) which are in wide usage in the automotive and aerospace industries because of their refractory, fracture toughness, and corrosion resistance qualities. A better understanding of the bonding mechanism between the coating layer and the substrate is then a very important issue in the thermal spray processing of these high-melting-point materials because it is directly related to the quality and durability of the coating layer.

STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS VI: Gamma Titanium Aluminides 3

Sponsored by: Structural Materials Division, Mechanical Metallurgy Committee

Program Organizers: Young-Won Kim, UES, Inc., Materials & Proc. Division, Dayton, OH 45432-1805; Michael J. Kaufman, University of Florida, Dept. of Materials Sci & Eng., Gainesville, FL 32611-2066; Chain T. Liu, Oak Ridge National Lab, PO Box 2008 Bldg 4500S, Oak Ridge, TN 37831-6115

Wednesday PM Room: 107
February 18, 1998 Location: Convention Center

Session Chairs: Maria Morris, University of Neuchatel, Institute of Structural Metallurgy, Neuchatel Switzerland; Michael J. Mills, The Ohio State University, Dept. of Mat. Sci. & Eng./CISM, Columbus, OH 43210

2:00 PM

STRENGTHENING OF TiAl ALLOYS BY DIRECTIONAL SOLIDIFICATION: Dr. David J. Johnson[1]; Dr. Haruyuki Inui[1]; *Prof. Masaharu Yamaguchi*[1]; [1]Kyoto University, Department of Materials Science and Engineering, Kyoto 606-01 Japan

Studies of TiAl polysynthetically twinned (PST) crystals where the entire ingot consists of only a single TiAl/Ti3Al lamellar grain have shown that the mechanical properties of the lamellar structure are extremely sensitive to the orientation of the lamellar boundaries with respect to the loading axis. For these PST crystals, optimum properties are measured when the lamellar boundaries are parallel to the loading axis. We recently showed that the lamellar structure can be aligned along the growth direction for some TiAl alloys containing Si and Nb by directional solidification. Recent work on high temperature strength of such directionally solidified TiAl alloys is promising due to strong retention of the inherent high strength of the lamellar structure with temperature. For example, the strength of a directionally solidified Ti-46.5Al-3.0Nb-0.5Si (at %) alloy is higher than 350 MPa at 1100°C. In this paper, our recent results on the strength, microstructure and deformation behavior of directionally solidified TiAl alloys are presented.

2:30 PM

EFFECT OF ß-PHASE FORMATION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF LAMELLAR TiAl ALLOYS: *Dr. C. T. Liu*[1]; Dr. P. J. Maziasz[1]; Dr. J. H. Schneibel[1]; [1]Oak Ridge National Laboratory, Metals and Ceramic Division, Oak Ridge, TN 37831-6115 USA

Ti-47Al-2Cr-2Nb (at. %) with and without additions of Mo and Cr were prepared by hot extrusion of alloy powder at temperatures above and below T_α. The additions of Mo and Cr were added for stabilizing the ß phase, which was enriched in these two elements. The refined lamellar structures (< 80 μm) produced by hot extrusion above T_a were stress relieved at temperatures to 1050°C in order to achieve an improved tensile ductility at room temperature. The formation of ß phase is effective in refining colony size and increasing the tensile ductility at room temperature. The ß phase also improves the tensile ductility above 600°C, but this increase is at the expense of the alloy strength. Three-point bend tests show that the fracture toughness is sharply reduced with the ß -phase formation. The results will be discussed in terms of the intrinsic properties of the ß phase and its associated change in microstructural features. Research sponsored by the U.S. Department of Energy, Division of Materials Sciences and Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

2:50 PM

TEXTURE AND STRENGTH IN ALIGNED LAMELLAR TiAl ALLOY PROCESSED BY ALPHA-FORGING: *Dr. Zhe Jin*[1]; Dr. Y-W. Kim[2]; Mr. Bill Konkel[3]; [1]Los Alamos National Laboratory, MST-5, Los Alamos, NM 87545 USA; [2]UES, Inc., Dayton, OH 45432 USA; [3]Wyman-Gorden Forging, Research and Development, Houston, TX 77095-5038 USA

Production of aligned lamellar-grains in TiAl alloys has been found to be feasible in laboratory-scale samples through employing the "alpha-forging" process which was developed at Wright Laboratory, Wright-Patterson. When properly processed, the aligned microstructures result in significant improvements in both strength and ductility. Recently, scaled-up alpha-forging experiments were conducted on alloy KDCBS (Ti-46.5Al-2Cr-2.8Nb-0.25W-0.22C-0.1B-0.15Si) in collaboration between Wright-Laboratory/Materials Directorate and Wyman-Gordon Forging. The present report is concerned with texture analysis and its effect on the strength in the alloy forgings (33cm diameter x 2.5cm thick) produced under two different alpha-forging rates. Three (111), (200) and (220) pole figures were measured from various locations in the radial direction as well as thickness direction. The crystal orientation distribution function (CODF) calculated at each location showed a general trend toward the formation of a {011}<uvw> fiber texture, although some scattered individual texture components are also observed. The orientation density distribution along the {011}<uvw> fiber texture depended on strain rate and location. These results are analyzed to elucidate the yield-strength increases obtained in both radial as well as transverse directions.

3:10 PM

FLOW RESPONSES OF PST AND FULLY LAMELLAR POLYCRYSTALS OF Ti-48Al IN THE MICROSTRAIN REGIME: *Dr. T. A. Parthasarathy*[1]; Dr. Madan G. Mendiratta[1]; Dr. M. Dimiduk[2]; [1]UES, Dayton, OH 45432 USA; [2]Wright Laboratory, Materials Directorate, Ohio 45433 USA

The flow behavior of polysynthetically-twinned (PST) crystals of a Ti-48Al alloy was studied as a function of orientation in the microstrain regime (10^{-5} to $2x10^{-2}$) at room temperature, to understand the evolution of the anisotropy of flow stress with strain. The variation with orientation of the resolved shear stress was observed to be only 10-15

MPa at near zero (10^{-5}) strain, but it increases rapidly to ~70 MPa at $2x10^{-3}$. The results were analyzed and rationalized using a mechanistic model that takes into account the distribution of the lamellar sizes. The flow behavior is predicted to be sensitive to both the mean and the standard deviation of the lamellar size distribution with sources from only a fraction of the lamellar contributing to the deformation process even at 0.2% strain. Combining the data of the hard orientations of the PST material and those of a polycrystal of the same composition, an apparent Taylor factor for fully-lamellar polycrystal line Ti-48Al was determined to be in the range of 3.2 to 3.8. * UES, Inc., Dayton, Ohio

3:40 PM

THE IMPORTANCE OF STRAIN AGEING EFFECTS IN INTERMETALLICS (SUCH AS TiAl AND Al_3Ti): *Prof. David G. Morris*[1]; Prof. Maria A. Morris[1]; T. Lipe[1]; M. M. Dadras[1]; [1]University of Neuchâtel, Institute of Structural Metallurgy, Neuchâtel 2000 Switzerland

Strain ageing effects have been reported in many intermetallics, but there appears to be no general consensus as to the controlling mechanisms and the importance of such effects in affecting the general deformation behavior of such materials. Deformation instabilities observed during continuous deformation (dynamic strain ageing) and during stress or strain rate jump tests on TiAl alloys are considered, and interpreted on the basis of static strain ageing data. Such experiments have been carried out on a variety of TiAl alloys, examining the sensitivity of strain ageing to the chemical composition and the microstructure. The results are analysed in terms of diffusion models, considering the role of substitutional and interstitial solutes as well as volume and local, pipe diffusion mechanisms. As a final point, the importance of such temporary, local dislocation locking on more macroscopic mechanical properties, such as the flow stress and anomalous hardening, and the overall ductility, is considered

4:00 PM

HIGH CYCLE FATIGUE INITIATION IN FULLY LAMELLAR Ti-46Al-2Nb-2Cr-1Mo-0.2B: *Mr. W. John Porter, III*[1]; Dr. A. H. Rosenberger[2]; Dr. J. M. Larsen[2]; [1]University of Dayton Research Institute, Dayton, OH USA; [2]Air Force Research Laboratory, Materials Directorate, OH 45433-7818 USA

Gamma titanium aluminide alloys are reaching a level of maturation in terms of processing and property understanding where application in rotating aerospace components is probable. To enhance the likelihood of near-term application, the relationships between microstructure and high cycle fatigue crack initiation need to be better understood. To address this issue, high cycle fatigue testing of fully lamellar Ti-46Al-2Nb-2Cr-1Mo-0.2B was performed at room temperature with a stress ratio of 0.1. Five samples per stress level were tested at each of the six stress levels chosen. Detailed fractography was performed on selected samples. Variability in test results and the relationship between high cycle fatigue initiation and fatigue performance are discussed. Comparisons of high cycle fatigue behavior are made to various gamma alloys tested under similar conditions. Design implications concerning the high cycle fatigue behavior of this alloy are addressed.

4:20 PM

EFFECT OF MICROSTRUCTURE ON STRENGTH IN HIGH-NB CONTAINING TiAl ALLOYS: *Prof. Guo Liang Chen*[1]; Dr. W. J. Zhang[1]; Mr. Z. C. Liu[1]; Young-Won Kim[2]; [1]University of Science and Technology Beijing, State Key Laboratory for Advanced Metals & Materials, Beijing 100083 China; [2]UES, Inc., Dayton, OH 45432 USA

From the considerations of oxidation resistance and high-temperature strength retention, conventional gamma TiAl alloys do not appear to be suitable for long-term use at temperatures higher than 815°C. It has been demonstrated that high Nb-additions (8-15 at%) in TiAl improve the properties at higher temperatures, resulting in for example, the yield strength at 900°C even greater than 650 MPa in certain microstructural forms. This paper is aimed to understand these strengthening aspects in Ti-45Al-10Nb and Ti-45Al-10Nb-2Cr alloys. The alloy ingots were thermomechanically processed to produce two types of microstructures: fine equiaxed $\alpha 2+\gamma+(ß)B2$ microstructures (~40&microm) with varying amounts of (ß) B2 phase; and a fully-lamellar microstructure (~100&microm) with small B2 grains decorating the colony boundaries. Both compressive and tensile tests were performed for selected microstructures at room-temperature and 900°C. Deformation structures were investigated to characterize dislocation interactions, climb, and twinning, and the role of (ß) B2 phase on the yielding behavior was studied. The results are analyzed to explain the strengthening behavior and its dependency on microstructure.

4:50 PM

STRENGTHENING OF TiAl ALLOYS BY SB ADDITION: *Prof. Baiyun Huang*[1]; [1]Central South Univ. of Technology, Powder Metallurgy Research Lab., Hunan 410083 China

The objective of this study is to strengthen two-phase TiAl alloys based on Ti-48Al (at.%). It is found that with the addition of up to 0.15 Sb, the room temperature ductility and fracture strength can be enhanced significantly. For example, the fracture strength reaches as high as 1345 MPa in the alloy of Ti-48Al-0.15 Sb. These improved properties are attributed mainly to the refinements of the colony grain size and the interlamellar spacing with the addition of Sb. Besides, the high-temperature oxidation resistance can also be substantially increased in the presence of 0.15 Sb, being higher than those for Ti-48Al and Ti-48Al-2Cr-2Nb. The cause for this increase is suggested to be the formation of a protective layer of Al2O3 stabilized by Sb.

5:10 PM

THE EFFECT OF PROLONGED HIGH TEMPERATURE EXPOSURE ON MONOTONIC AND CYCLIC PROPERTIES OF A GAMMA TITANIUM ALUMINIDE: *Stetson K. Planck*[1]; [1]University of Dayton Research Institute, Dayton, OH USA

It is known that titanium aluminides suffer from poor ductility and toughness at temperatures below the ductile to brittle transition temperature and may suffer a further reduction in tensile ductility following high temperature exposure in air. Currently, however, there is not a clear understanding of the effect of high temperature exposure on the fatigue performance of this class of alloys. Experiments are underway to determine the degree of degradation of the monotonic and cyclic properties due to prolonged high temperature exposure of a gamma titanium aluminide (Ti-46Al-2Nb-2Cr-1Mo-0.2B, at%). Tensile and fatigue tests at room temperature, 540°C and 760°C were conducted following 50 and 500 hour exposures at 760°C. The embrittled layer that formed during exposure was characterized using hardness and scanning electron microscopy. It is proposed that fracture of this layer leads to lower ductility and shortens the time to crack initiation and that its removal restores the virgin properties. Examination of the failed specimens using scanning electron microscopy will be used to identify the relationship between the embrittled surface and mechanical performance of the bulk.

SUPERPLASTICITY AND SUPERPLASTIC FORMING: Session VI - Modeling and Control of Forming Operation

Sponsored by: Materials Design and Manufacturing Division, Shaping and Forming Committee

Program Organizers: Amit K. Ghosh, Univ of Michigan, Dept. of Matls Sci & Eng., Ann Arbor, MI 48109-2136; Thomas R. Bieler, University of Michigan, Dept of Matls Sci & Mechanics, E. Lansing, MI 48824-1226

Wednesday PM Room: 106
February 18, 1998 Location: Convention Center

Session Chair: N. Chandra, Florida State University, Dept. of Mechanical Engineering, Tallahassee, FL 32310

2:00 PM INVITED

NUMERICAL MODELING OF TRANSFORMATION SUPERPLASTICITY FOR AN ELASTIC, IDEALLY-PLASTIC MATERIAL: P. Zwigl[1]; *D. C. Dunand*[2]; [1]Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139; [2]Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208

Finite-element modeling is used to simulate transformation superplasticity for an elastic, ideally-plastic material. The internal stresses created during a phase transformation by the density mismatch between the two allotropic phases are superimposed to a biasing, externally-applied uniaxial stress. The resulting stress-, strain-, and energy fields are determined as a function of time in a coupled temperature-displacement formulation which takes into account discontinuous changes in the material mechanical and thermal properties at the phase transformation. A parametric study is conducted where the density mismatch, the external stress, and the yield stress of the weakest phase are systematically varied. The numerical results show that the uniaxial strain increment accumulated after a full temperature cycle is proportional to the first two variables, and inversely proportional to the last one. Furthermore, the simulation predicts a non-linear increase in strain increments when the applied stress approaches the plastic limit. All these trends are in qualitative agreement with experimental data on pure iron and with analytical closed-form solutions.

2:25 PM

BEHAVIOR OF TITANIUM ALLOY UNDER UNIAXIAL AND BIAXIAL SUPERPLASTIC CONDITIONS: *Z. Chen*[1]; Z. Li[1]; P. Dang[1]; N. Chandra[1]; [1]Florida State University, Department of Mechanical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310

The validity of extending constitutive relationships established under uniaxial condition to biaxial forming is important from both basic and applied interests. Titanium alloy under superplastic condition is studied under both uniaxial and biaxial states to understand the relationships. Ti-6Al-4V alloy is tested at uniaxial condition to establish the mechanical constitutive equation and also study the evolution of certain metallurgical parameters (e.g., grain size, grain shape, phase distribution, and grain size distribution). The same material is then subjected to biaxial condition in a multi-cone testing setup. In this testing, the sheet is subjected to a balanced biaxial state with varying levels of strain-rate. Comparison between the mechanical and metallurgical states of the specimen under the two types of loading is made.

2:45 PM

IMPROVED MEASUREMENT OF SUPERPLASTIC FLOW BEHAVIOR AND MODELING OF CAVITATION: *A. K. Ghosh*[1]; D-H. Bae[1]; [1]University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109-2136

Due to the difficulty of direct sample strain measurement in a precise manner during superplastic tensile test, considerable effort has been directed toward developing a crosshead schedule for conducting constant strain rate tests. The improved method now allows the establishment of precise strain rate history so that dynamic changes such as grain growth, cavitation, etc. as a function of strain can be determined with much greater confidence than previously possible. Thus, flow hardening, cavity initiation and growth characteristics have been determined carefully in an Al-4.7%Mg-0.8%Mn-0.4%Cu alloy as a function of strain rate and strain state. Cavities appear to nucleate at particles during flow; the density of cavity nuclei being a strong function of stress. However, a plasticity-based constrained cavity growth model captures all essential microscopic features of observed cavitation behavior. From the viewpoint of applications of the forming technology, an iso-cavitation diagram as a forming limit is developed based on the present biaxial deformation model. (Work supported by USDoE, Grant No. DE-FG02-96ER45608.A000)

3:05 PM

RADIAL RETURN EXTENSION FOR THE NUMERICAL SIMULATION OF THE SUPERPLASTIC PROCESS: *J. P. Ponthot*[1]; [1]University of Liége 21, LTAS-Thermomécanique, Liége B4000 Belgium

In numerical simulation of superplastic processes by the finite element method, viscous effects have to be taken into account. Therefore, we use an elastic-viscoplastic law depending on different parameters, including elasticity, viscosity, hardening and grain size. This constitutive equation is integrated in time by using a newly developed hypoelastic algorithm which is an extension of the classical radial return algorithm for elasto-plasticity with an extended von-Mises criterion. The resulting implicit algorithm is both efficient and very inexpensive, even in the presence of very large strains. In addition, in the rate-independent case, the presented algorithm degenerates exactly into the classical radial return algorithm for elasto-plasticity. In a similar way, frictional contact between die and material is also introduced in the simulation.

3:25 PM Break

3:40 PM

CHARACTERIZATION OF LASER-WELDED Ti-6-22-22/Ti-6-4 SUPERPLASTICALLY-FORMED PANELS: *J. D. Will*[1]; M. G. Kistner[1]; J. D. Cotton[1]; [1]Boeing Defense & Space Group, Seattle, WA 98124

While single sheet superplastically-formed (SPF) components have been utilized in structural applications for some time, multisheet structures have not been fully exploited. Part of the reason is the scarcity of data describing mechanical behavior of multisheet structural elements. In this paper, we describe the design, fabrication and mechanical properties of two four-sheet titanium alloy panels produced by laser welding/SPF/diffusion bonding. The panels were constructed of Ti-6-22-22 face sheets with Ti-6-4 core sheets in a sine-wave geometry. Testing consisted of face sheet tension, panel edgewise compression, and panel fatigue. The mechanical properties, microstructures and failure modes of the panels were characterized.

4:00 PM

MANUFACTURING OF 315 MM DIA. X 8 MM THICK PRESSURE VESSEL OF TI-6AL-4V ALLOY BY SUPERPLASTIC FORMING: *N. C. Birla*[1]; [1]Defence Metallurgical Research Laboratory, Hyderabad 500058 India

The total technology package for producing 315 mm diameter, 8 mm thick spherical pressure vessel of Ti-6Al-4V alloy for use in missiles has been developed. It involves controlled microstructure and composition of starting titanium alloy plate, control of pressure-time cycle so as to minimize thickness variation during superplastic forming, and machining and joining of hemispheres by electron beam welding so as to meet the stringent specification requirements of the pressure vessel. The effect of superplastic deformation on microstructure and mechanical properties of the vessel was also studied to meet burst pressure, cyclic loading, and strength and fracture toughness requirements. The above technological aspects along with economics and reliability of the process compared with other conventional methods like forging or hot pressing developed in India will also be discussed in this presentation.

TRANSIENT THERMAL PROCESSING OF MATERIALS II: Session II

Sponsored by: Jt. ASM International: Materials Science Critical Technology Sector/Electronic, Magnetic & Photonic Materials Divison, Thin Films & Interfaces Committee

Program Organizers: N.M. Ravindra, New Jersey Inst. of Tech., Dept. of Physics, Newark, NJ 07102; R.K. Singh, University of Florida, Dept. of Materials Science & Eng., Gainesville, FL 32061; B. Sopori, National Renewable Energy Lab, 1617 Cole Blvd., Golden, CO 80401

Wednesday PM Room: Fiesta C
February 18, 1998 Location: Convention Center

Session Chair: Steven D. Marcus, Steag AST-electroniks, Dornstadt, Germany 89160

2:00 PM

PHASE-FIELD MODELING FOR THE SOLIDIFICATION OF REAL ALLOY SYSTEM: *Seong Gyoon Kim*[1]; Won Tae Kim[2]; [1]Kunsan National University, Department of Materials Science and Engineering, Kunsan, Korea 573-360; [2]Chongju University, Department of Physics, Chongju, Korea 360-764

Recently Wheeler et. al. extended the phase field model for the solidification of a binary alloy by assuming solid and liquid phases to be either ideal or regular solutions in real binary alloy systems, however, there are few alloy systems showing such simple thermodynamic behavior. For the application of the model, it was extended to the solidification behavior of real alloy system by using published thermodynamic data on solid and liquid phases. It was shown that the sharp interface limit of the phase field equation gave the generalized Gibbs-Thomson equation. The relation between the parameters in phase field and the physical parameters were derived from the sharp interface limit conditions. The model was applied to predict the microstructure of rapidly solidified Al-Si alloys by assuming Newtonian cooling conditions. The effect of initial nucleation temperature and heat transfer coefficient on the microstructure evolution during gas atomization will be discussed.

2:20 PM

EFFECTS OF RAPID THERMAL PROCESSING ON THE PROPERTIES OF Al-Si STRUCTURES: *N. M. Ravindra*[1]; O. H. Gokce[1]; S. Abedrabbo[1]; D. Ivanov[1]; [1]New Jersey Institute of Technology, Newark, New Jersey 07102

Abstract not available.

2:40 PM

MODELING EMISSIVITY AND TIME-DEPENDENT TEMPERATURE PROFILES OF ROUGH AND TEXTURED WAFERS: *B. L. Sopori*[1]; W. Chen[1]; S. Abedrabbo[2]; N. M. Ravindra[2]; [1]National Renewable Energy Laboratory, Golden, CO 80401; [2]New Jersey Institute of Technology, Dept. of Physics, Newark, NJ 07102

The emissivity of a wafer is an important parameter for a variety of applications including pyrometry. In RTP applications, the information about emissivity is needed both for the furnace control and process monitoring. It is known that emissivity depends on temperature as well as wafer characteristics such as thickness and its surface morphology. In most cases, emissivity is determined experimentally. Such measurements can be quite tedious and lack generality. There is however, very little effort on theoretical analysis of emissivity dependence on the surface characteristics and the sample thickness. In some cases, such as double side polished wafers, it is rather straight forward to perform optical calculations to determine emissivity. However, if the wafer has one or both non-planar surfaces (e.g rough or textured), the calculations can be quite difficult. Difficulties also arise because of the temperature dependence of refractive index (n) and extinction coefficient (k) are not known. This paper describes the methodology and results of our calculations of emissivity for samples that may have one or both sides rough, textured or polished. A software package has been developed that can perform these calculations. This package is also applicable to such samples of dielectric or metallic layers. To verify these results, the emissivity of various samples of different surface morphologies and different thicknesses were measured by using the spectral emissometer at NJIT. The calculated results agree well with the experimental data. Because our model allows calculation of the absorption in the sample for a given incident spectrum, we can use it to determine the temperature rise in the sample. We have developed the software program to calculate time-dependent temperature proprofiles.

3:00 PM

EFFECTS OF COATINGS ON EMISSIVITY INDEPENDENT TEMPERATURE MEASUREMENTS IN RAPID THERMAL PROCESSING: *S. Abedrabbo*[1]; W. Chen[1]; F. M. Tong[1]; N. M. Ravindra[1]; J. Gelpey[2]; S. Marcus[2]; [1]New Jersey Institute of Technology, Newark, New Jersey 07102; [2]AST Elektronik USA Inc., Lynnfield, Massachussetts 01940

Abstract not available.

3:30 PM Break

3:40 PM

A NOVEL TECHNIQUE FOR THE RTP ANNEALING OF COMPOUND SEMICONDUCTORS: *M. Fu*[1]; R. Singh[1]; C. Abernathy[1]; S. Pearton[1]; J. A. Sekhar[1]; [1]MHI Inc., and University of Florida, Cincinnati, Gainsville, OH, FL 45212, 32611

The ion implantation of GaN and SiC type materials can be expected to significantly reduce power losses by reducing the device access resistance. Several recent studies have shown that RTP processing for annealing at temperatures higher than 1400^{0}C is the preferred processing technique for ion implanted compound semiconductors. A novel Zapper device is described in this article for the RTP processing of materials at such high temperatures. The device allows for the required short time uniform heating up to 1700°C. Temperature profiles and implant damage profiles obtained by processing GaN with the Zapper unit will be described and discussed.

4:10 PM

USE OF EFFECTIVE HEAT FORMATION MODEL TO DETERMINE PHASE FORMATION SEQUENCES OF In-Se,Ga-Se, AND Cu-Se THIN FILMS: *Ms. Hannah J. Moore*[1]; Dr. David L. Olson[1]; Dr. Rommel Noufi[2]; [1]Colorado School Of Mines, Department of Metallurgical and Materials Engineering, Golden, CO 80401; [2]National Renewable Energy Laboratory, Solar Energy Research Facility, Golden, CO 80401

The effective heat of formation (EHF) model has been used to determine the sequences of three of the binary thin film couples comprising the Cu (In,Ga) Se system. These binary systems are Cu-Se, In-Se, and Ga-Se. Each of the films were deposited by means of thermal evaporation. Investigation of the reaction sequences of the films was performed by differential thermal analysis (DTA) and X-ray diffraction (XRD). To predict phase formation of a binary system using EHF model, it is not only important to consider the thermodynamics involved, but the effective concentration of the two reacting species at the growth interface must also be taking into account. The effective concentration is assumed to be the concentration which leads to the highest mobility and is give n by the composition of the liquids minimum of the binary system under consideration. After first phase formation, the EHF model predicts that the next phase to form is that which is richer in unreacted element which has the most negative EHF. The three films that were analyzed were approximately fifty atomic percent each element comprising the binary film. They were multilayer films which were deposited onto 12.7 micrometer molybdenum foil on soda lime glass. The first and final layers of the multilayer films were either Indium, gallium, or copper, depending on the binary system being generated, so that each selenium layer was capped off in an attempt to prevent evaporation of selenium before thermal analysis. For the binary systems of In-Se, Ga-Se and Cu-Se, both the first phase

to form and the subsequent phase formation sequences of these thin film systems were correctly predicted by the EHF model.

4:30 PM
THERMAL STABILITY AND RADIATIVE PROPERTIES OF DIAMOND LIKE CARBON FILMS ON SILICON SUBSTRATES: *S. Amin*[1]; N. M. Ravindra[1]; O. H. Gokce[1]; S. Abedrabbo[1]; [1]New Jersey Institute of Technology, Newark, New Jersey 07102

Abstract not available.