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

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 AM Room: Plaza Room C
February 18, 1998 Location: Convention Center

Session Chair: Ron Neuman, Auburn University, Chemical Engineering, Auburn, AL 36849, Kathryn Sole, Mineralogy and Precious Metals Division, Mintek, Randburg, 2125 South Africa

8:30 AM INVITED
THE EXTRACTION KINETICS IN A NEW SOLVENT EXTRACTION PROCESS WITH BOTTOM GAS INJECTION WITHOUT MECHANICAL MOVING PARTS: *H. Y. Sohn*[1]; D. Doungdeethaveeratana[1]; [1]University of Utah, Metallurgical Engineering and Chemical and Fuels Engineering, Salt Lake City, UT 84112-0114

The extraction kinetics in a novel solvent extraction process have been investigated. In this process, the liquid-liquid emulsion is generated by bottom gas injection into countercurrently flowing aqueous and organic phases. This process has a number of advantages over the mixer-settler unit or the spray column in terms of simple equipment configuration without any mechanical moving parts and the ease of cleaning and process control, while providing a sufficiently large interfacial area for rapid mass transfer. The overall rate increased with increasing gas injection rate and height of the aqueous phase but decreased with increasing injector diameter at the same gas injection rate. The variation of the overall rate constant was correlated against a set of dimensionless numbers, representing the operating conditions. Extraction rates and efficiencies comparable to those in a mechanically generated emulsion were attained in this new process.

8:55 AM INVITED
MASS TRANSFER CORRELATION COEFFICIENTS FOR TWO-PHASE SYSTEMS: A REVIEW FOR LIQUID-LIQUID EXTRACTION SYSTEMS: *Renato G. Bautista*[1]; Victor Vasquez[1]; [1]Mackay School of Mines, Chemical and Metallurgical Engineering, Reno, NV 89557-0136

The mass transfer in two-phase systems can be achieved in many different ways. Once the two phases are in contact, the transfer or movement of a specific component from one phase to the other is governed by very complex processes involving mixing conditions, concentration, rheology, chemical reactions, temperatures, pressures, interfacial area, etc. For physical purposes, all the effects of the variables involved, with the exception of concentration and interfacial area, are lumped together using mass transfer coefficients. Therefore, the modeling and prediction of mass transfer essentially rely on the appropriate estimation of these mass transfer coefficients. A general review of the mass transfer correlation coefficients involved for two-phase systems in continuous operations, in particular the case for liquid-liquid systems, is presented. More work has to be done in order to establish more general models that permit reporting only their parameters for a given system and/or equipment.

9:20 AM INVITED
MOLECULAR MODELLING OF REVERSED MICELLES IN SOLVENT EXTRACTION SYSTEMS: *Ronald D. Neuman*[1]; Taleb H. Ibrahim[1]; [1]Auburn University, Department of Chemical Engineering, Auburn, AL 36849 USA

Molecular modelling is a powerful tool that can be used to study the aggregation of extractant molecules which in turn aids in understanding the solvent extraction of metal ions from aqueous to nonpolar organic phases. In this presentation we will show how molecular simulation of the structure and dynamics of metal-extractant species correlates with extractability and selectivity in cobalt-nickel separation by acidic organophosphorus extractants. The nature of metal-extractant aggregates can be better understood by observing how the individual metal-extractant complexes are organized, the type of forces holding them together and the orientation and location of the different molecules which are present. The effects of solvent, metal, water, temperature and extractant structure on the aggregate structure will be shown. In addition, a new structural model which we have designated the "open water-channel" model, where the solubilized water does not exist in the aqueous core as classically assumed for reversed micelles but rather it is in channels along the outer surface of the reversed micellar aggregates, will be discussed from the perspective of its unique application to metal extraction processes.

9:45 AM INVITED
DIRECT SOLVENT EXTRACTION OF COBALT AND NICKEL FROM LATERITE - PRESSURE ACID LEACH LIQUORS: *Karin Helene Soldenhoff*[1]; Mr. Noel Hayward[2]; [1]Australian Nuclear Science Organisation ANSTO, Sydney, NSW 2234 Australia; [2]Resolute Limited, Perth, WA Australia

The Bulong deposit situated near Kalgoorlie in Western Australia and owned by Resolute Limited, is a lateritic deposit containing on average 1.1% nickel and 0.09% cobalt. The process developed for this ore involves crushing and grinding followed by high pressure sulphuric acid leaching, neutralisation and sequential solvent extraction of cobalt and nickel from the leach liquor. The loaded strip solution produced from the first SX circuit is enriched in Co and a product of intermediate purity is produced. This is further refined into high purity cobalt cathodes. The loaded strip solution produced from the second SX circuit is sufficiently pure for electrowinning of nickel. The innovative feature of this flowsheet is the use of solvent extraction for direct separation of cobalt and nickel from a leach liquor containing high levels of impurities. To date, reported industrial applications and pilot plant studies have included a primary separation stage (e.g. precipitation), before solvent extraction. This paper describes mini-pilot plant. solvent extraction trials, run at ANSTO. The separation of cobalt, using Cyanex 272, and nickel using Versatic 10 is discussed. The selectivity of the solvents with respect to the major impurities such as Mn, Mg, Ca, Cu, Zn and Fe is also presented. The pilot plant trials successfully integrated the electrowinning of nickel with the solvent extraction circuits and produced suitable nickel cathodes. Construction of the commercial plant is being fast tracked and start up is planned for the first half of 1998.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM
USE OF EXTRACTANTS IN ZINC SOLVENT EXTRACTION FROM IMPURE SOLUTIONS: *C. Lupi*[1]; D. Pilone[1]; [1]Universita degli Studi di Roma, ICMMPM, Roma 18 - 00184 Italy

Zinc impure solutions as spent electrolytes, i.e., leach liquors coming from aqueous treatment of both minerals and solid waste, need to be purified before undergoing the treatment to obtain the final product. Solvent extraction is one of the most selective operations particularly when many metallic ions are present in solution. Zinc pure solutions are frequently obtained using D2EHPA as extractant. In this work, a comparative investigation on zinc extraction effectiveness of various

extractants was carried out. The tested extractants were D2EHPA, naftenic acid, and TBP. For each extractant, the partition coefficient was determined as a function of temperature, equilibrium pH and zinc concentration. In some cases, the extractant concentration and various diluents were also taken into account. Experimental results show that all the examined extractants are very effective in zinc extraction if the process conditions are appropriately selected. In order to avoid an impure solution pretreatment and in order to obtain the maximum extraction yield, the appropriate solvent can be chosen. Some examples are reported.

10:50 AM

COMMERCIALIZATION OF THE MINATAUR PROCESS: COMMISSIONING OF HARMONY GOLD REFINERY: *Kathryn C. Sole*[1]; Leslie J. Bryson[1]; James Watt[2]; Angus Feather[1]; Paul Sorensen[1]; [1]Mintek, Randburg 2125 South Africa; [2]Harmony Gold Mining Company, Ltd., Glen Harmony 9435 South Africa

A novel solvent-extraction process for the refining of gold was recently commercialized, with the commissioning of a 24 tpa refinery at Randgold's Harmony Gold Mine in Virginia, South Africa, in May 1997. The MinataurTM Process (Mintek Alternative Technology for Au Refining) employs solvent-extraction technology to produce gold of 99.99% purity from the gold-containing cathode sludge arising from a conventional carbon-in-pulp/electrowinning circuit. Implementation of this process introduces significant cost benefits compared with the conventional toll-refining route previously followed, and a saving of production costs in excess of US$30 per lilogram of gold has been estimated. This presentation will outline the process, present selected results from the Harmony Refinery obtained during the first few months of operation, and discuss some of the associated techno-economic advantages.

11:15 AM INVITED

SOLVENT EXTRACTION OF RHODIUM FROM BROMIDE MEDIA: *T. M. Dreher*[1]; S. N. Asrafizadeh[1]; G. P. Demopoulos[1]; [1]McGill University, Mining and Metallurgical Engineering, Montreal, Quebec H3A 2B2 Canada

The difficulties associated with the operation of a classical rhodium refining process have prompted many attempts to develop a viable solvent extraction flowsheet for rhodium. Recent investigations at McGill University have involved the activation of rhodium prior to its solvent extraction. The role of activation is to convert the aquochlorocomplexes of rhodium to a form extractable by conventional solvent extraction reagents. In the novel separation scheme identified, chloro complexes of rhodium are converted to bromo complexes, which undergo aquation to a lesser extent, making them more easily extracted. Rhodium is then extracted using Kelex 100, and stripping is achieved by use of a concentrated chloride based solution. Separation of rhodium from iridium is achieved by either prior reduction of Ir(IV) to Ir(III), as the latter is not extracted, or via coextraction and differential stripping. The modified flowsheet for the refining of rhodium using this method is discussed, along with its advantages and disadvantages over tradition refining methods.

11:40 AM

SOLVENT EXTRACTION IN THE PHOSPHATE FERTILIZER INDUSTRY: *Fathi Habashi*[1]; [1]Laval University, Mining and Metallurgy, Quebec City, Quebec G1K 7P4 Canada

The recovery of uranium from wet process phosphoric acid was applied on an industrial scale in the 1940's with octylpyrophosphoric acid. Later, more efficient reagents were used, e.g., di(2-ethylhexyl) phosphoric acid and actyl phenyl phosphoric acid. In the 1970's, the rare earths in Kola phosphate were recovered in Finland and recently (1997) in Norway using HNO3 as a leaching agent and di(2-ethylhexyl) phosphoric acid as solvent. It was demonstrated later, on a laboratory scale, that both uranium and rare earths could be extracted from the rock by tributyl phosphate but at different pH values provided that the rock is leached with nitric or hydrochloric acids instead of the commonly used sulfuric. This new concept opens the way to the possibility of treating phosphate rock by in-situ, dump, or vat leaching for the recovery of phosphate values as well as uranium and the rare earths. Another solvent extraction process is used industrially for the purification of phosphoric acid with butyl and amyl alcohols.

ALUMINA & BAUXITE: Alumina precipitation

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Jean Doucet, Alcan International, PO Box 6090, Montreal, Quebec H3C 3A7 Canada

Wednesday AM Room: Fiesta A
February 18, 1998 Location: Convention Center

Session Chair: Joseph L. Anjier, Gramercy, Louisiana 70052 USA

8:30 AM

A MODEL FOR ALUMINIUM TRIHYDROXIDE CRYSTALLIZATION FROM PURE AND IMPURE SOLUTIONS: *Dr. Mark S. Wainwright*[1]; [1]The University of New South Wales, Department of Chemical Engineering, Sydney, 2052, New South Wales Australia

Mannitol has been used as a model hydroxy organic compound to simulate the influence of organic compounds on the growth, nucleation and agglomeration mechanisms of aluminium trihydroxide precipitation. Organic free seed hydrate (60 g/L) with a geometric surface area of 0.2 m2/g was used in an isothermal batch system to seed sodium aluminate liquor containing levels of mannitol from 0 to 13 mmol/L (mM). The population density of particles was measured by sampling during the precipitation process and analyzing particle size distributions using a Coulter Multisizer particle size analyzer. As little as 151.6 mg mannitol/m2 of seed (0.17 mmol/g seed) was sufficient to completely suppress the precipitation. A population balance equation (PBE) including terms for nucleation, growth and agglomeration, coupled with a mass balance equation forms the basis of a mechanistic model for batch crystallization of aluminium trihydroxide. By fixing the exponent parameters at values reported in the literature, the coefficient parameters were determined by minimizing the difference between the values predicted using the model and the experimental values. The presence of mannitol at a level as low as 92.2 mg mannitol/m2 of seed (6.21 mM) reduced the growth rate coefficient by an order of magnitude and the nucelation rate coefficient by two orders of magnitude. This low mannitol concentration also increased the agglomeration parameter. Four different kernels of shear flow, turbulent flow, size independent, and an empirical kernel were checked for best fit in the present study. Precipitation in the absence of mannitol was best fitted with no agglomeration term in the model. In the presence of mannitol precipitation was found to be fitted best with the empirical kernel of KuS4(u-113yv-113)3.

8:55 AM

CONTRIBUTION OF LIQUOR COMPOSITION ON BOUND SODA: *Mr. Philippe Clérin*[1]; [1]Aluminium Pechiney, Centre de Recherche, 13541 Gardanne Cedex France

The influence of caustic soda and temperature on the coefficient of the equation linking bound soda and alumina supersaturation has been established for a range of plant liquors. It has been confirmed that temperature has no direct effect on the coefficient value. Coefficients calculated from laboratory precipitation tests are in good agreement with industrial results. For a given caustic concentration, the influence of liquor impurities has been evaluated. It appears that digestion conditions is the main factor, likely due to different degradation process of bauxite organics. Additional work with additives, including humate removal, has been performed.

9:20 AM

ALUMINA AND SODIUM LOSSES DURING THE BAYER PROCESS: *Mr. J.M. Lamerant*[1]; [1]Aluminium Péchiney, Centre de recherche, 13541 Gardanne Cedex France

Industrial Bayer digestions have been performed in industrial conditions on bauxites from three different origins: Greece (Delphes and Parnasse), Australia (Weipa) and Guinea (Boké). Compositions and weight fractions of all crystalline phases contained in bauxites and associated red muds have been analyzed by Rietveld refinement of X-ray diffraction patterns. Of main interest: - Hematite is not altered by the digestion but newly formed goethite can incorporate large amounts of Al substituted to Fe. A significant loss of alumina in Boké bauxite arise from this substitution. - A new phase containing Ca, Ti, Al and Fe has been found in the muds from Weipa bauxite and tentative cell parameters have been determined. The proportions of Na and Ca in cancrinite structure vary according to the origin of the bauxite and parameters of the Bayer process. - The Fe/Al ratio as well as the Si content in hdyrogarnet are also highly variable depending on the origin of the bauxite and parameters of the Bayer process. These results show that a detailed distribution of cations from bauxites to red mud can be obtained through Rietveld analysis of X-ray powder diffraction patterns if proper care is taken of cationic substitutions in the structure of hematite, goethite, cancrinite and hydrogarnet. In particular, they provide an explanation for the higher than expected losses of alumina and sodium observed during the processing of the Boké bauxites.

9:45 AM

GIBBSITE GROWTH HISTORY - REVELATIONS OF A NEW SCANNING ELECTRON MICROSCOPE TECHNIQUE: *Dr. Gerald I. Roach*[1]; [1]Alcoa of Australia Limited, Research and Development, Kwinana, Western Australia, 6167 Australia

A new scanning electron microscope technique has been developed which enables the growth history of gibbsite particles from the Bayer process to be studied. The technique called trapped charge contrast enables the growth of hydrate on different crystal faces to be directly measured and can differentiate between the seed hydrate and new growth enabling information on agglomeration to be unambiguously obtained. The technique readily differentiates batch and continuously grown hydrates as growth rings associated with each pass through precipitation are readily distinguished. This enables the complete growth history of a particle to be ascertained which includes its residence time for each pass through precipitation. The technique can also indicate if secondary nucleation has occurred. The data obtained via this technique has been confirmed using specially prepared laboratory samples and examples of images and the information that can be obtained are presented. The technique is now finding wider application in areas such as medicine (examination of kidney stones), geology and ceramics.

10:10 AM Coffee Break in Exhibit Hall

10:25 AM

INTERACTIONS OF PARTICLES IN GIBBSITE - SODIUM ALUMINATE SOLUTIONS AND GIBBSITE - AQUEOUS DISPERSIONS: *Mr. Jonas Addai-Mensah*[1]; [1]Ian Wark Research Institute, University of South Australia, Adelaide 5095 South Australia

The atomic force microscopy, rheology, zeta potential measurement and semi-empirical quantum mechanical molecular modelling techniques have been employed to investigate the inter-particulate forces and interfacial structures occurring at the interface of gibbsite - Bayer liquor or gibbsite - aqueous media dispersions. The results show that a weak, long range and strong short range, non-DLVO repulsive forces exist between colloidal size gibbsite particles in the background of aqueous solutions of high ionic strength at pH >10, saturated and supersaturated sodium aluminate solutions. It was observed that on slurry aging, considerable increase in viscosity occurs as a result of gibbsite - Bayer liquor interfacial structuring. Zeta potential measurements using electro acoustics and phase analysis light scattering identified a specific intraction of sodium ions from aqueous solutions with the gibbsite surface. Potassium ions did not show such specific interaction. The preference for sodium ion adsorption over potassium is supported by molecular modelling.

10:50 AM

IMPROVING THE FILTRATION OF ALUMINA TRIHYDRATE AT EURALLUMINA: *Dr. John T. Malito*[1]; [1]Nalco Chemical Company, Naperville, Illinois 60536-1198 U.S.A.

Prior to calcination, alumina trihydrate must be washed and dewatered to reduce the energy required for removing residual moisture and to produce alumina having the lowest possible leachable soda. At Eurallumina this is accomplished using Dorr-Oliver multi-stage table vacuum filters operating in the countercurrent mode. During the past few years, a chemical drainage aid, Nalco N7846 has been extensively evaluated on the hydrate filters. The addition of low levels of this product into the wash water circuit resulted in significant reductions in cake moisture and soda. In addition, beneficial improvements in other operating parameters, such as better control of filter vacuum, were also observed. Details for the optimal application of the drainage aid and the resulting improvements in product quality and filter operability are presented.

10:50 AM

THE NUCLEATION MECHANISM OF GIBBSITE FROM BAYER LIQUORS: *Mr. Jonas Addai-Mensah*[1]; [1]Ian Wark Research Institute, University of South Australia, Adelaide 5095 South Australia

A considerable number of experimental techniques have been employed to elucidate the mechanism of gibbsite nucleation in Bayer liquors. These techniques include small angle x-ray scattering (SAXS), small angle neutron scattering (SANS), dynamic light scattering (DLS), cryovitrification transmission electron microscopy (Cryo-TEM), semi-empirical quantum mechanical molecular modelling and in situ x-ray adsorption fine structure spectroscopy (XAFS). These techniques indicate that gibbsite nuclei are initially highly diffuse and that growth is accompanied progressive densification. Below a radius of approximately 100 nm, particles are invisible to techniques that rely on phase contrast (SAXS, SAMS and DLS). By estimating the contrast required for observation, it is possible to estimate the density of the growing nuclei and hence derive an approximate stoichiometry.

11:40 AM

GRAIN SIZE DISTRIBUTION AND CRYSTAL GROWTH IN ALUMINA HYDRATE PRECIPITATION PROCESS: *Dr. P. Vidyasagar*[1]; [1]National Aluminium Co. Ltd., R&D Centre, Koraput, Orissa 763 008 India

In alumina hydrate precipitation process, caustic concentration and super saturation of input aluminate liquor, temperature, seed charge and precipitation retention period are the key parameters which determine the yield and quality of precipitated hydrate. Out of many properties, the grain size is the most important characteristic which determines its acceptability and value in the market. In this present investigation, studies have been made on effect of these variables with respect to particle size distribution of the precipitate product. Batch precipitation experiments were carried out on laboratory scale using aluminate liquor and seed hydrate from operating plant. Rate of crystal growth, population of fine particles, surface area and yield of the products after precipitation have been examined.

ALUMINUM ALLOYS FOR PACKAGING III: Session II - Developmental Studies

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

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

Session Chair: John Adams, Metal Container Corporation, St. Louis, MO 63127-1218

8:30 AM

DEVELOPMENT AND PERFORMANCE OF A NEW WATERBORNE COIL COATING FOR BEVERAGE END STOCK: *Lynn Murr Spataro*[1]; Gary E. Hendrickson[1]; [1]The Valspar Corporation, 2000 Tracu Street. Pittsburgh, PA 15233

Waterborne coil coatable beverage end coatings have been under development at several laboratories for many years. The key forces driving this development are environmental protection and improved performance. The demands on a coating for this end use are severe. The coating is coil applied at high line speeds, it must fabricate while maintaining coating integrity and provide corrosion protection against a wide variety of beverages. This paper describes the development of a waterborne, retortable beverage end coating with performance equal to commercial solvent based options. Film properties and application characteristics will be discussed.

9:00 AM

THE FRACTURE MECHANICS OF ALUMINUM BEVERAGE CONTAINERS: AN EXPERIMENTAL INVESTIGATION: *Mr. Matthew R. Hackworth*[1]; Dr. John M. Henshaw[1]; [1]University of Tulsa, Department of Mechanical Engineering, Tulsa, OK 74104 USA

The fracture mechanics behavior of 355 ml aluminum beverage containers (both 0.0039" and 0.0044" minimum wall thicknesses) was investigated by two general types of experiments. First, cracked center panel thinwall specimens were cut such that the crack was either parallel or perpendicular to the container axis at the mid-height position. These two specimen orientations were repeated at 0, 45, and 90 degrees to the roll direction, making for a total of six different specimen orientations. These six orientations yielded average fracture toughness values ranging from 16.0 to 19.1 ksi(in)^.5. The lowest fracture toughness orientation from the center cracked panel tests was selected for the second experiment. This involved containers machined with an external crack of known length and depth, filled with 355 ml of water, and pressurized to failure. At a constant crack depth, an increasing crack length gave a decreasing failure pressure. For a constant crack length, an increasing crack depth gave a decreasing failure pressure. In both cases a transition from a leaking to a rupturing failure is seen, with longer and shallower cracks resulting in ruptures. These results are compared to accepted leak-before-break fracture mechanics theory.

9:30 AM

THE RECRYSTALLIZATION OF STRIP CAST AA5182 ALLOY AND A COMPARISON WITH DC CAST AA5182 ALLOY: L. Liu[1]; S. Ding[1]; *J. G. Morris*[1]; [1]University of Kentucky, Light Metal Research Laboratories, Lexington, KY 40506

The aluminum alloy AA5182 has been used as a packaging material for more than twenty years, and has been the automotive material of choice. The microstructure of the alloy can be controlled to provide the properties required for particular applications. The grain structure, crystallographic texture, insoluble intermetallics and dispersoids, etc., have great influence on the mechanical properties and formability of the alloy. These factors are influenced by the heat treatment applied prior to cold work. In this study, various heat treatments prior to cold work have been performed and their influence on the microstructure and mechanical properties of the alloy are examined in detail. Age Softening behavior of this alloy will be measured and considered in terms of the final properties, structure and formability of the material.

10:00 AM Coffee Break in Exhibit Hall

10:30 AM

THE EFFECT OF ANNEALING AND COLD ROLLING CONDITIONS ON THE FORMABILITY AND EARING OF CAN BODY STOCK: *Hans-Erik Ekström*[1]; [1]Griänges Technology, Finspång Sweden

High quality aluminum can body stock is characterized by a low frequency of fractured cans during can forming, a low level of earing and a high strength of the finished can body. The formability in the can plant is controlled by alloy composition and homogenizing heating conditions but also cold rolling conditions have a considerable influence. The latter have also an effect on strength of the can. The earing level is dependent on alloy composition, homogenizing and hot rolling conditions and heating rate during annealing of the hot band. In this paper some new results are shown regarding the influence of the heating rate during annealing and the cold rolling conditions.

11:00 AM

MODELING STATIC RECRYSTALLIZATION OF 3003 ALLOY DURING MULTIPASS HOT ROLLING: *P. L. Orsetti Rossi*[1]; [1]C.V.G. Industria Venezolana de Aluminio, C.A., Zona Industrial Matanzas, Guayana Venezuela

This paper reports on an approach to modelling the static recrystallization behavior of Al-1Mn(AA3003) during multipass hot rolling, as a tool for optimizing industrial schedules. The experimental observations in Al-1Mg have been used to establish, reasonable assumptions for modelling fraction recrystallized and recrystallized grain size during multipass hot rolling considering the three different situations when the material is unrecrystallized, partially and completely recrystallized prior to a subsequent pass, whereas developed quantitative relationships for the kinetics and recrystallized grain size along with a commercial hot rolling schedule are used to predict the recrystallization behavior. The through-thickness gradients in recrystallization are also computed using the deformation history distribution and compared with measurements.

ALUMINUM REDUCTION TECHNOLOGY: Modeling

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

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

Session Chair: Jay Bruggeman, Aluminum Company of America, Alcoa Center, PA 15069

8:30 AM

NUMERICAL SIMULATION, TOOLS TO DESIGN AND OPTIMIZE SMELTING TECHNOLOGY: J. Bos[1]; G. Bouzat[1]; J. Colln de Verdlere[1]; *B. Feve*[1]; J. C. Rofger[1]; [1]Aluminium Pechiney, 73300 Saint Jean de Maurienne, Cedex France

For many years, Aluminum Pechiney has been developing an extensive know-how in process modeling for smelting technology. The wide range of models developed has been valuable in designing equipment and facilities for new projects or for retrofitting as well as in evaluating the performance of various process technologies. Thermo-electrical and magneto-hydro-dynamic analyses of the pot are well known by aluminium producers. The purpose of the paper is to present some other examples of numerical simulation addressing various and less known fields. We first summarize the fundamental goals of numerical simulation and the main stages leading to efficient numerical models. Then, with the help of powerful software, we present animated results of numerical simulation. The first example deals with cathode rodding operation and illustrates the strong interaction between cathode bars and cathode blocks. The second example deals with the potroom ventilation and illustrates the aeraullic balance of the various flows which convey heat fluxes around the pots. The last example illustrates the use of numerical simulation to optimize the flue-wall design in an anode baking furnace regarding flow distribution.

8:55 AM

ADAPTATION OF AN ELECTROLYTIC CELL MODEL IN STATIC AND DYNAMIC MODES: *Abdelhamid Meghlaoui*[1]; Laszlo Tikasz[1]; Yousef Ali Mohammed[2]; [1]Dubai Aluminium Company Ltd., Dubai United Arab Emirates; Universite du Quebec, Chicoutimi, Quebec, Canada G7H 2B1

Dubai has developed a simulator to mimic the operational states of an aluminium reduction cell. In order to enable the soft cell to better approach the behavior of the live one, the cell model was adapted in both static and dynamic modes using plant data, and then controlled by real algorithms. Model validation in static mode was done by comparing the simulated voltage breakdown and energy balance to actual measured values. Conclusions drawn facilitated decisions relating to the acceptance or further refinements of the model parts. The real control program was embedded into the simulator and the validity of the model in dynamic mode was then tested over a selected period of operation. A plant experiment was carried out on a live cell to gain information about the process dynamics. This scenario was repeated by superimposing the real material balance and the specific operations undertaken during the period onto the cell simulator. For demonstration purposes, measured and simulated data was presented and remarks on model adaptation outlined to help in fine-tuning model to a particular cell.

9:20 AM

COMPUTATION OF ALUMINUM REDUCTION CELL ENERGY BALANCE USING ANSYS FINITE ELEMENT MODELS: *Marc Dupuis*[1]; [1]GeniSim, Jonquiere, Quebec G7S 2M9 Canada

Over the last 10 years, the industry standard for modeling the aluminum reduction cell energy balance went gradually from 2D "in-house" codes to 3D commercial codes, mainly using the ANSYS finite element code. In this transition, many different modeling tools have been developed: 3D cathode slice, half anode, full cell slice, cathode corner/ quarter and full cell corner models. In this paper, advantages and disadvantages of each of those 3D models basic assumptions are reviewed and the classic 2D model is revisited to introduce a new improved approach.

9:45 AM

IMPROVED 2-DIMENSIONAL MODEL FOR MAGNETOHYDRODYNAMIC STABILITY ANALYSIS IN REDUCTION CELLS: *Ch. Droste*[1]; M. Segatz[1]; D. Vogelsang[1]; [1]VAW Aluminium-Technologic, 53117 Bonn Germany

Comparison of magnetohydrodynamic (MHD) instabilities calculated by means of a newly developed depth-averaged 2D model and a general 3D modelling tool demonstrates the range of validity of the shallow water approach. Good agreement was found for instabilities driven by vertical magnetic fields. The contribution of the horizontal magnetic field, however, can be significant and is only covered fully by the 3D model. The 2D model is based on a consistent mathematical description of the fluctuating magnetic fields and currents including the effect of individual anode resistances. A solution procedure in the real space domain facilitates the proper treatment of the boundary conditions and avoids restrictions of the Fourier spectra approach. Examples of industrial applications illustrate the impact of parameters like anode size or gap dimension on MHD stability and cell performance.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM

HEAT TRANSFER ON A SURFACE AFFECTED BY AN AIR/WATER INTERFACE UNDERGOING WAVE MOTION: *Z. D. Chen*[1]; J.J.J. Chen[1]; Mark P Taylor[2]; [1]The University of Auckland, Chemical & Materials Engineering Department, Auckland New Zealand; [2]Comalco Aluminium, Tiwwai Point New Zealand

In an attempt to provide some understanding of the high local sidewall heat/mass transfer rate near the electrolyte/metal interface in an aluminium reduction cell, experiments were conducted to investigate the heat transfer from a discrete area on a vertical wall and on a concave wall affected by an air/water interface undergoing wave motion caused by a mechanical wave-maker. The local heat transfer rate near the interface is much higher than that for a steady uni-directional flow over a flat plate at the same mean velocity. In addition, the heat transfer rate reaches a maximum when the frequency of the mechanical wave-maker is the same as the fundamental frequency of the experimental system. The experiments also showed that for a given wave amplitude and frequency, the local heat transfer rate is greater when the vertical wall is changed to one which is concave, and furthermore, the heat transfer rate increases as the concave angle is decreased. Visualization studies showed that the local heat transfer enhancement is related to the periodic renewal of the wall boundary layer. For concave walls, the direct impingement of the liquid near the wall further enhances the local heat transfer.

10:45 AM

INSTABILITY MECHANISMS IN ALUMINIUM REDUCTION CELLS: *P. A. Davidson*[1]; [1]University of Cambridge, Dept. Engineering, Cambridge CB2 1PZ United Kingdom

We have developed a simple model of reduction cell instabilities which highlights the critical role played by the single grouping $J_O B_Z$ / hH, where J_O is the current density in the cell, B_Z is the vertical component of the background magnetic field and h and H are the depths of electrolyte and aluminium. We discuss the implications of this model for the stability of real cells and suggest means of increasing the stability threshold of cells without reducing their performance.

11:10 AM

THE INFLUENCE ON THE CURRENT DISTRIBUTION BY THE INITIAL SHAPE AND POSITION OF AN ANODE AND BY THE CURVATURE OF THE METAL IN PREBAKE ALUMINIUM CELLS: *J. Zoric*[1]; J. Thonstad[2]; T. Haarberg[2]; [1]Norwegian University of Science, Dept. of Electrochemistry, N-7034 Trondheim Norway; [3]Norwegian University of Science and Technology, Dept. of Electrochemistry , N-7034 Trondheim Norway; [2]SINTEF Materials Technology, Process Metallurgy and Ceramics, N-7034 Trondheim Norway

Mathematical modeling of the secondary current distribution in prebake aluminium cells was used to study the influence of (1) a modified anode shape, (2) curvature of the metal, and (3) an anode being set too high or too low. The calculations show that if the lower corners of a new anode are cut off by 5 cm (diagonally), the steady state shape of the anode is reached after 3 days, as against 6-8 days for rectangular corners. If the metal curvature corresponds to a 3 cm difference in height per 100 cm length, and the skewed metal is facing a newly set horizontal anode, the current density varies across the anode with a maximum of 125% of the normal value (0,75 A cm-2), and it takes 4 days until the anode is aligned with the metal. If a new anode is set 1 cm too low or too high, the initial current through that anode after heat-up is 124% and 85% respectively, compared to the normal value, and it takes 4.2 and 7.7 days respectively, until the interpolar distance is correct (45mm +/- 1mm).

11:35 AM

SEDIMENT TRANSPORT AND DISSOLUTION IN HALL-HEROULT CELLS: *K. Kalgraf*[1]; K. Torklep[1]; [1]Elkem Research, N-4602 Kristiansand Norway

We propose that soft sludge is governed by the general laws of sediment transport, which appear never to have been applied to aluminium cells before. Sludge particles exposed to the moving metal are then - in accordance with elementary fluid dynamics - transported along the cathode bottom by a saltation process caused by a combined lift and drag. In the presence of turbulence, the particles may even reach the bath and dissolve there, thus providing a mechanism for back feeding. Sludge movements are simulated in a physical model using nylon particles exposed to water moving at velocities comparable to metal flow in actual cells. Recordings show that horizontal transport occurs through saltation at close to theoretical rates. When turbulence is introduced, the amount of simulated sludge creeping along the supporting surface rapidly diminishes as the particles are whirled into the bulk of water.

CAST SHOP TECHNOLOGY: Session IIIA - DC Casting

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

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

Session Chair: Wolfgang Schneider

8:30 AM
COMPUTATIONAL MODELING OF D.C. CASTING OF ALUMINUM ALLOY USING FINITE ELEMENT METHOD: *J. Du*[1]; K. M. Chang[1]; J. Harris[2]; B. S-J. Kang[1]; [1]West Virginia University, Dept. of Mechanical and Aerospace Eng., Morgantown, WV 26506; [2]Ravenswood Aluminum Corporation, Ravenswood, WV 26164

A pertinent simulation model of transient D.C. casting of Aluminum alloy is developed based on the theories of heat transfer and continuum mechanics. This model is then implemented in a general purpose finite element code ABAQUS to determine the time dependent temperature field and the induced thermal stress field in the ingot during solidification. The objective of this investigation is to find the temperature gradient and associated thermal stresses which may be the cause of the ingot cracking during solidification. In this study, both two dimensional and three dimensional finite element models are developed. In the transient analysis, fully coupled temperature and displacement elements are used and latent heat of the alloy is also included in the analysis. The solidus part of the ingot is assumed to be uniform, isotropic and obeys the elastic-plastic constitutive law with isotropic hardening. The liquidus part of the ingot is assumed to be an ideal fluid without viscosity as well as stress free. The temperature dependent thermal properties of the alloy used in the finite element model are obtained from literature and the mechanical properties are directly measured in as-cast conditions. In order to simulate the water cooling process, a novel heat flow model is developed based on the measured temperature data. The bottom block is also modeled including heat transfer through the interface between the ingot and bottom block. Regions of high temperature gradient and peak stresses are analyzed. From the numerical simulation, mechanism of the cracking occurrence during D.C. casting in established. The predicted location of the maximum effective stress coincides with the observed crack path. The butt curl deformation of the ingot during the start-up phase of the casting is also predicted and the result is in good agreement with the measured data. Finally the simulation model is used to optimize the cooling water flow rate and water flow pattern to minimize stress accumulation during D.C. casting of the aluminum alloy.

8:50 AM
PECHINEY'S GLOBAL AUTOMATION CONCEPT FOR DC CASTING: *Jacques Charpentier*[1]; Jean-Marie Chateau[1]; [1]Pechiney Aluminium Engineering, Voreppe France

Pechiney Aluminium Engineering has continuously developed for over 10 years an automatic casting process for use in its own production facilities which fully integrates the control of all functions for automatic DC slab casting. This paper reviews the developments that have enabled us to adapt this proven process to customers's specific environments and guarantee rapid implementation on site. It details in particular the different mechanical parts, the sensors, the actuators, the supervision system and the automation package.

9:10 AM
FLUID FLOW AND HEAT TRANSFER IN A BILLET HOT TOP CASTING DISTRIBUTION PAN: *Soizic Blais*[1]; J. Alexandre[1]; J. V. Opbergen[2]; [1]Pechiney Centre de Recherches de Voreppe, Voreppe France; [2]Pechiney Nederland N.V., Flessingue Netherlands

The number of molds on billet hot top casting tables becomes more and more important. So it is difficult to get reliable start-up conditions and good metallurgical quality of the billets. The design of the distribution pan requires therefore to take into account some thermo-hydrodynamic specifications: uniform filling time for all molds during the start-up phase and both homogeneous velocity field of the molten metal into the mold and low thermal gradient from the front to the back of the pan during the stationary phase. Instrumented experimental casting and 3D numerical simulations of fluid flow and heat transfer have been carried out to optimize the distribution pan design, The new design has been validated on a multi-strand casting unit in the casthouse of Pechiney Nederland.

9:30 AM
ANALYSIS OF THE FLUID MECHANICS IN DISTRIBUTOR BAGS USED IN DC AND EM CASTING OF ALUMINUM: *W. K. Jones, Jr.*[1]; D. Xu[1]; J. W. Evans[1]; [1]; [1]University of California, Dept of Materials Science and Mineral Engineering, Berkeley, CA 23261 USA

The inflow of liquid aluminum into the melt pool in aluminum casters is generally controlled using a distributor bag. A properly designed bag has the ability to control both the temperature and the degree of turbulence in the melt. The control of these parameters can only be optimizing by understanding the flow phenomena developed from the bag. As the flow profile changes it can significantly affect the developing solid front and hence the final properties of the as-cast microstructure. "Combo" and "channel" bags are widely used in DC and EM casting of aluminum because of the extreme modification they can make to the inflow. This study will focus on the flow behavior in the sump, as well as in the bag. The analysis will consist of computational modeling using the finite element package FIDAP; results will be compared to velocities measured in a physical model using particle image velocimetry. Two different sized combo bags, as well as channel bag, will be treated. Furthermore, the influence of the vertical nozzle placement will be presented.

9:50 AM
PHYSICAL MODELING OF THE EFFECTS OF NON-SYMMETRIC PLACEMENT AND BLOCKAGE OF FLOW CONTROL BAGS USED IN SEMI-CONTINUOUS CASTING OF ALUMINUM : *W. K. Jones, Jr.*[1]; D. Xu[1]; J. W. Evans[1]; [1]University of California, Dept. of Materials Science and Mineral Eng., Berkeley, CA 94720

The nature of the convection in molten aluminum during the DC casting process has been shown to control the as-cast microstructure and subsequently the final physical properties of the alloy. Many research endeavors have been focused on physical and mathematical modeling of the complex interaction between the fluid motion, heat and mass transfer and the developing crystal structures. However, the open literature shows far less work on the same topics with addition of flow control devices such as "combo" and "channel" bags. These types of bags are widely used by the aluminum industry to control the distribution of superheated liquid aluminum as it enters the mold region. It is therefore the intent of this study to show, using an innovative physical modeling technique, how critical the proper employment of flow control devices is in the development of desired flow patterns in the liquid pool. More specifically, two main classes of operational defects will be simulated namely, non-symmetric placement and partial blockage of the flow bags. The secondary aim of this study is to evaluate the effects of these difficiency on the generated flow patterns which will give insight into the heat and mass transfer occurring in the liquid. This will therefore allow for better prediction of hazardous casting defects, such as shell breakout, which has been shown to occur when areas of the solidifying alloy are deprived of liquid aluminum. Comparison with results calculated in the commercial finite element package FIDAP will be presented.

10:10 AM Coffee Break in Exhibit Hall

10:30 AM

IMPACT OF WATER HEAT EXTRACTION AND CASTING CONDITIONS ON INGOT THERMAL RESPONSE DURING D.C. CASTING START-UP PHASE: *Andre Larouche*[1]; Yves Caron[1]; Duygu Kocaefe[2]; [1]Alcan International Limited, Arvida Research and Development Centre, Jonquiere, Quebec Canada; [2]Univeriste du Quebec a Chicoutimi, Department des sciences appliquees, Chicoutimi, Quebec G7H2B1 Canada

Water cooling during the cast start-up phase is one of the major parameters affecting the casting performance, along with the heat input (casting speed, metal temperature), primary and bottom block cooling. Water cooling depends on the ingot (surface roughness and temperature), casting parameters (water flow rate and temperature, mould technology) and water quenching ability. This paper describes the method used to determine the heat transfer coefficients for some of the above parameters (surface temperature, water flow rate and temperature, pulsation characteristics). The influence of casting parameters on ingot thermal response is then predicted using the ALCAN 3-D finite volume transient casting model, in a context of a better understanding and control of the D.C. casting process.

10:50 AM

AS-CAST MECHANICAL PROPERTIES OF HIGH STRENGTH ALUMINUM ALLOY: *Keh-Minn Chang*[1]; Jian Wan[1]; Hwei-Min Lu[2]; Jerry Harris[2]; [1]West Virginia University, Mechanical & Aerospace Eng., Morgantown, WV 26506 USA; [2]Century Aluminum, Ravenswood, WV 26164 USA

Many attempts of numerical simulations have been performed on direct-chill (DC) Casting of high-strength aluminum alloys. One of important factors, which involves the microstructural variations from location to location in the large ingots, is seldom implemented in the simulation. Different cooling profiles are observed at different locations: the solidification rate through liquidus-solidus determines the as-cast structure, and the secondary cooling rate after solidification allows the precipitation reaction to occur. New experimental approaches were used to measure the representative mechanical properties for the constitutive modeling of cast ingots. The results suggest that thermomechanical properties of castings are remarkably different from those of wrought products. The microstructural consideration of constitutive modeling provide a much more accurate numerical simulation.

11:10 AM

GROWTH MECHANISMS OF INTERMETALLIC PHASES: *X. G. Chen*[1]; [1]Alcan International Limited, Arvida Research and Development Centre, Jonquiere Canada

In DC cast AA1xxx series alloys, the presence of a "fir tree zone" has long been recognized to be detrimental to the surface quality of critical sheet products. The fir tree zone in DC cast ingots in mainly caused by a macroscopical transition between intermetallic phases. In this paper, the formation of the major intermetallic phases commonly occurred in DC ingot structure, such as Al_3Fe_2, Al_6Fe_2, Al_mFe and alpha-AlFeSi, is investigated by using a deep etching and Sem technique. The three-dimensional morphologies of intermetallic particles revealed by deep etching are presented. Based on the morphological aspects and the cooling conditions of the DC ingot, the growth mechanisms of different intermetallics observed under SEM are also demonstrated.

11:30 AM

A THERMODYNAMIC STUDY OF METASTABLE Al-Fe PHASE FORMATION IN DIRECT-CHILL (DC)-CAST ALUMINUM ALLOY INGOTS (ABSTRACT ONLY): C. A. Alirauci, J.E. Gruzelski, M.O. Pekguleryuz

Abstract not available.

DEFECTS IN CRYSTALS: A SYMPOSIUM HONORING THE CONTRIBUTIONS OF JOHN P. HIRTH: Mechanical Behavior

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 AM Room: 102
February 18, 1998 Location: Convention Center

Session Chair: James C.M. Li, University of Rochester, Department of Mechanical Eng., Rochester, NY 14627-0133

8:30 AM INVITED

SOLUTION SOFTENING IN SPINEL: *Prof Terence E Mitchell*[1]; Dr. William T. Donlon[1]; Prof. Arthur H. Heuer[1]; [1]Los Alamos National Laboratory, Center for Materials Science, Los Alamos , NM 87545 USA

The critical resolved shears stress of magnesium aluminate spinel ($MgO.nAl_2O_3$) decreases by almost orders of magnitude as n increases from 1 (stoichiometric spinel) to 3.5; at the same time the minimum temperature for compression ductility decreases from ~1800°C to ~1300°C. The temperature dependence of the CRSS is such that it decreases logarithmically with temperature. Deviations from stoichiometry are compensated by the introduction of cation vacancies with a concentration given by [Vc]=(n-1)/3(3n+1). The solution softening effect resulting from increasing values of n and [Vc] is found to be such that the CRSS is proportional to $1/[Vc]^2$. The temperature dependence and the concentration dependence suggest that the CRSS is controlled by a Peierls stress which is decreased by kink nucleation at cation vacancies. In addition both {111}<110> and {110}<110> slip systems are observed; the latter has a lower CRSS at lower temperatures and for non-stoichiometric crystals because of its higher activation energy. These effects are discussed in terms of the crystal structure of spinel.

9:00 AM INVITED

MODELING STRESS-TEMPERATURE HYSTERESIS CURVES FOR THIN METAL FILMS ON SUBSTRATES : *Prof. William D. Nix*[1]; [1]Stanford University, Dept. Matls. Sci. & Engr., Stanford, CA 94305-2205 USA

Plastic deformation occurs in thin metal films on substrates during thermal cycling due to differences in thermal expansion. The problem is of particular importance for interconnect metals used in microelectronic devices. Here we study the mechanisms of dislocation motion and interaction in thin single crystal films on substrates in an effort to provide a microscopic picture of the factors that control the observed stress-temperature relations. Following the methods of Matthews and Blakeslee and Freund, we describe plastic deformation by the motion of ≈threading″ dislocations that move in the crystalline film and leave ≈misfit dislocations″ at the film/substrate as they move. Strain hardening is taken into account by considering the elastic interactions of the moving dislocations with pre-existing misfit dislocations. We show that the thickness dependence of the strength of metal films can be accounted for by this channeling mechanism. We also show that the elastic interactions between the dislocations leads to strong strain hardening and also to the pronounced Bauschinger effects that have been

observed in thermal cycling experiments. This kind of modeling will be used to explain the shapes of stress-temperature plots for thin metal films on substrates.

9:30 AM

STRUCTURE/PROPERTY RELATIONSHIPS IN NANO-LAYERED COMPOSITES: *Dr. Harriet Kung*[1]; Y-C. Lu[1]; A. Misra[1]; M. Nastasi[1]; J. D. Embury[1]; T. E. Mitchell[1]; [1]Los Alamos National Laboratory, Center for Materials Science, Los Alamos, New Mexico 87545 USA

The development of thin film multilayers has been the focus of extensive study due to enhanced properties and the broad range of applications. The structural constraints in multilayered geometry may also stabilize metastable phases with unique properties, which are not available by conventional processing routes. In this study, the effect of composition wavelength on the microstructure, interfacial structure, and mechanical properties of Cu/Nb, Cu/Cr, and Cu/Ni nanolayered composites was evaluated by transmission electron microscopy and nano-indentation. The as-sputtered Cu/Nb multilayers, with layer thickness varying between 25Å and 1000Å, exhibit a strong Kurdjumov-Sachs orientation relationship: <110>{111}Cu || <111>{110}Nb. As the layer thickness decreases to 12Å, Cu is constrained to grow pseudomorphically as a slightly distorted b.c.c. structure on the b.c.c. Nb template. The hardness of the Cu/Nb multilayers increases with decreasing layer thickness, while the modulus stays constant. Cu/Cr multilayers, grown by sputtering technique, shows the same Kurdjumov-Sachs textured growth but a higher hardness than Cu/Nb at the same layer thickness. In addition, Cu/Ni multilayers have been grown epitaxially on NaCl and Cu single crystal substrates by using electron beam evaporation technique. The multilayers are single crystalline in nature but contain a high density of dislocations. The deformation structure was monitored to determine the effect of interfaces on the dislocation movement and slip propagation in multilayers. The mechanical behavior and the deformation structure of the three nanolayered composites will be discussed based on the modulus difference, microstructure, and the crystal structure discontinuity at the interfaces.

9:50 AM

DAMAGE ACCUMULATION DURING SLIDING OF METALS: *David A. Rigney*[1]; T. Kasai[1]; A. Zharin[1]; [1]The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210-1179 U.S.A.

Sliding contact causes dramatic changes near the interface in metals. These include the development of large plastic strains and strain rates, with associated changes in defect concentration, microstructure and crystallographic texture, and sometimes phase transformations. In addition, there are commonly interactions with the counterface material and with the environment, and also mechanical mixing processes which can modify the material on both sliding surfaces. Structural and chemical characterization techniques have provided some insight into friction and wear processes, but many questions remain concerning mechanisms. A non-contact probe which detects changes in electronic work function offers a useful tool for monitoring damage accumulation associated with wear. Results suggest that wear rate can vary with a well defined period. Acknowledgments: This work is supported in part by The National Science Foundation, Surface Engineering and Tribology, under Grant No. CMS-9509624 and by the U.S. Civilian Research and Development Foundation under Award No. BE2-109.

10:10 AM

A DISLOCATION POLE MECHANISM FOR DEFORMATION TWINNING IN THE $L1_0$ STRUCTURE: *Man H. Yoo*[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6115 U.S.A.

A dislocation model is proposed for twin formation in the $L1_0$ structure on the basis of dissociation of a jog on an ordinary [110]/2 dislocation into a Shockley and a Frank partial. Under a compressive stress along the c-axis, a pile-up of [101] superdislocations assists a Shockley loop to spiral around two sessile nodes and, by means of climb expansion, the Frank partial mitigates the high repulsion between two Shockley partials. Available data on the apparent CRSS for twinning in Ti-56 at. % Al single crystals are explained in terms of a local stress concentration and a vacancy supersaturation at elevated temperatures. The so-called radiation-induced ductility reported in Ti-47 at. % Al alloys is discussed from a viewpoint based on the proposed pole mechanism. *Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract number DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

10:30 AM

RELATING ALLOY CHEMISTRY, DISLOCATION CORES AND MECHANICAL PROPERTIES IN THE (NiX Fe1-X)3Ge SYSTEM: *Mr. T. John Balk, II*[1]; Dr. Mukul Kumar[1]; Prof. Kevin J. Hemker[1]; [1]Johns Hopkins University, Dept. of Mechanical Engineering, Baltimore, MD 21218 USA

Intermetallic alloys are excellent materials for bridging the gap between atomic level processes and macroscopic properties, as the mechanical behavior of these alloys can be closely related to their dislocation structures. Ni_3Ge and Fe_3Ge are ordered $L1_2$ alloys that show complete solubility across the composition range. However, the yield strength anomaly that is observed in Ni_3Ge gradually disappears with increasing Fe content, and it will be shown that this change in mechanical behavior is related to modifications of the core geometry of dissociated superdislocations. Weak-beam TEM observations of deformation structures have been obtained for six different alloys and will be presented along with detailed measurements of superdislocation dissociation widths. The yielding behavior will be discussed in the light of these dissociations and the effect that they have on the governing deformation mechanisms.

10:50 AM

CORE STRUCTURE OF GRAIN BOUNDARY DISLOCATIONS IN THE Al INCOHERENT TWIN BOUNDARY: *Dr. Stephen M. Foiles*[1]; Dr. Douglas L. Medlin[2]; [1]Sandia National Laboratories, Comp. Mat. Sci. Dept., Livermore, CA 94551-0969 USA; [2]Sandia National Laboratories, Surface and Microstructure Research Dept., Livermore, CA 94551-0969 USA

It is known that the (a/3)[111] grain boundary dislocation in the Al incoherent twin boundary separates into two partial dislocations. In this talk, the core structure of these partials is determined from atomic scale calculations. Embedded atom method calculations show that the dislocation cores are very broad consistent with high resolution electron microscopy observations. The width of the dislocation cores is related to the energy barrier for sliding to two grains across each other through a modified Peierls-Nabaro model. This model gives results consistent with the detailed simulations. Finally, electronic structure calculations of the energetics of critical relative displacements of the grains are performed to check the predictions of the embedded atom method calculations.

11:10 AM

THE TEXTURE AND ANISOTROPY OF A HOT ROLLED 7050 ALUMINUM ALLOY: *Professor Shih-Chin Chang*[1]; Q. D. Jiang[1]; F. R. Chen[1]; [1]National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu, Taiwan ROC

The microstructure and compressive deformation behavior of a 7050-T7451 aluminum alloy were studied. When compressed in the short transverse direction, the macroscopic shear bands formed are more visible on T plane than on L plane, and the tendency of forming shear bands is higher in the center portion of the plate than in the outer portion. It was also found that when compressed in the short transverse direction, the strain in the longitudinal direction is at least 50% larger than that in the transverse direction. On T plane, two sets of slip bands which make an angle of about 70 degrees with each other and having the longitudinal direction as their bisector were observed in many grains. On L plane, two sets of parallel slip traces which make an angle of about 40 degrees with each other and having the transverse direction as their bisector were observed in some grains. When cold rolled, slip band formation is more evident in the specimens cold rolled in the longitudinal direction than in the specimens cold rolled in the transverse direction. It is found that the macroscopic shear bands and the microscopic slip bands are closely related to each other. By X-ray diffraction and pole figure study, a duplex texture of two superimposed components, namely the {110}<001> Goss texture and the {110}<1 -

1 2> Brass texture, were found in the 7050-T7451 aluminum alloy. An explanation of the phenomena described above is proposed on the base of the textures of the material.

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

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 AM Room: 103
February 18, 1998 Location: Convention Center

Session Chair: TBA

8:30 AM INVITED
REFRAMING OUR VIEWS OF TEACHING AND LEARNING: *Dr. Susan A. Ambrose*[1]; [1]Carnegie Mellon University, Eberly Center for Teaching Excellence, Pittsburgh, PA 15213-3890 USA

Common metaphors for learning such as students as sponges absorbing material or as containers into which we pour knowledge reveal how our intuitions or assumptions about learning can be misleading. Years of cognitive psychology and educational research now help us to understand the limitations of those metaphors, and can help us to reframe our teaching based on what we know about learning. For example, we now understand the importance of things like connecting to prior knowledge, creating effective organizing schemes, promoting active engagement in learning, and using multiple representations. We also know what differentiates experts from novices across a variety of domains and how to help students develop proficiency in key skills like problem solving. Finally, we have vast amounts of research on the first year undergraduate experience, particularly what students find most difficult in making the transition into college life. Faculty members can use all of this information to help create and implement effective courses to help students not only survive their first year in college but flourish in a competitive and constantly changing world. This talk will address all of these issues as they impact engineering education.

9:10 AM INVITED
TEACHING FRESHMAN CHEMISTRY AND MATERIALS SCIENCE IN AN INTERACTIVE STUDIO MODE: *Dr. John B. Hudson*[1]; Dr. Linda S. Schadler[1]; Dr. Mark A. Palmer[1]; Dr. James A. Moore[2]; [1]Rensselaer Polytechnic Institute, Materials Science and Engineering Department, Troy, NY 12180 USA; [2]Rensselaer Polytechnic Institute, Chemistry Department, Troy, NY 12180 USA

About ten years ago, Rensselaer developed a first-year course sequence combining traditional Freshman Chemistry and beginning Materials Science. Over the past two years we have been transitioning this sequence from the traditional lecture-recitation format to an interactive studio format, in which lecture, student team problem solving, classroom demonstrations and laboratory work are integrated into each class session. We will describe the resulting format in detail, and discuss the results of this change in format on student performance and student satisfaction with the course sequence.

9:50 AM INVITED
MULTIMEDIA TUTORIALS FOR INTRODUCTORY MATERIALS SCIENCE: *Dr. Charles J. McMahon, Jr.*[1]; [1]Univ. of Penn., Mat. Sci. & Eng., Philadelphia, PA 19104 USA

We are in the process of constructing a one-semester set of interactive multimedia tutorials for a course in introductory materials science that are being disseminated to our students on CD-ROM and a local network. The topics to be available in the Fall of 1997 will include dislocations and plastic deformation, phase diagrams, magnetic materials, and electronic materials. They will be linked to the interactive glossary that is currently available on CD-ROM. Our goal is to replace the lecture part of the course with studio exercises, for which the tutorials will be required preparation. As they are produced, the tutorials will be made available at no cost to instructors for use on local networks so that they can be evaluated. This work is being supported by the NSF under grant no. DUE 94-55333.

10:30 AM Coffee Break in Exhibit Hall

10:40 AM INVITED
PUBLISHERS IN THE NEW EDUCATIONAL RUBRICK: *Ms. Leslie G. Bondaryk*[1]; [1]PWS Publishing, Boston, MA 02116 USA

Publishers are project managers. They are responsible for bringing together the pieces of a complex educational project - author's vision and content, pedagogical quality, visual design and usability, and market focus - developing them into a coherent, effective, and saleable project. With the advent of the new media, a new kind of management skill is now required of publishers. Publishers have become technology consultants in the age of interactive media. When the skills required are analyzed, it's interesting to note that they are really extensions of what publishers have always done well, which is to help authors communicate effectively. We'll explore the relationship of the professional publisher to the author, the professor using the product, and, in the modern age of the Web, to the student. We'll also explore the prerequisites for authoring published media in this context, and discover what makes a successful publishing proposal.

11:20 AM
WEB-BASED INSTRUCTIONAL TOOLS FOR MATERIALS EDUCATION: *Dr. Darcy J.M. Clark*[1]; [1]University of Michigan, Materials Science and Engineering, Ann Arbor, Michigan 48109-2136 USA

As the World Wide Web matures, multimedia and programming technologies are evolving to enable development of instructional software containing significant depth and interactivity. We will discuss the development and integration of web-based software to support introductory materials science courses.

11:40 AM
IMPLEMENTING SIMULATION SOFTWARE INTO THE UNDERGRADUATE CURRICULUM: *Dr. Laraba Parfitt Kendig*[1]; Dr. Darcy J. M. Clark[1]; [1]University of Michigan, Materials Science and Engineering, Ann Arbor, MI 48109-2136 USA

Simulation software has been used to study topics in both industrial and academic settings. With the advent of readily available computers, it is now possible to incorporate simulation work into undergraduate courses. Through simulation, students are able to study scientific phenomena by controlling vital parameters. Students also gain experience in using simulations, which is advantageous for many career paths. We will discuss some of the programs currently being tested in University of Michigan courses. These include relatively elementary simulations which introduce basic concepts, as well as complex industrial programs which allow students to examine the interplay of many variables.

GENERAL ABSTRACTS: V - Fracture

Sponsored by: TMS

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

Session Chair: Jill Wright, Idaho National Engineering and Environmental Laboratory

8:30 AM

THE BRITTLE-TO-DUCTILE TRANSITION IN ICE: *S. Qi*[1]; E. M. Schulson[1]; [1]Dartmouth College, Thayer School of Engineering, Hanover, NH 03755

Ice exhibits two kinds of behavior. When rapidly loaded under compression, it breaks into fragments; when slowly loaded, it flows. The transition from brittle to ductile behavior is important because it marks the point at which the load-bearing ability (ships, off-shore platforms, etc.) that serve within ice-infested waters. This paper will describe a quantitative physically-based model of the transition. Attention is placed upon the competing processes of stress build-up and stress relaxation at the tips of cracks. New results show that the transition strain rate remains constant from near zero C to -20 C, and then decreases with decreasing temperature. The effect is explained in terms of a variable apparent activation energy for creep. Sponsored by Office of Naval Research

8:50 AM

CORROSION FATIGUE CRACK INITIATION IN AL 7075-T7351 ALLOY: *P S Pao*[1]; C R Feng[1]; S J Gill[1]; R A Bayles[1]; [1]Naval Research Laboratory, Code 6312, Washington, DC 20375

The mechanisms of corrosion-fatigue crack initiation by pitting in a high-strength aluminum alloy were studied. The model alloy was an overaged 7075-T7351 alloy. In 3.5% NaCl solution, the corrosion-fatigue cracks initiate from pits which are formed by the electrochemical reaction between the constituent particles and the surrounding matrix. Depending on whether these particles are cathodic or anodic relative to the alloy matrix, the pits form as a consequence of matrix (for cathodic particles) or particle (for anodic particles) dissolution. Because these particles tend to cluster parallel to the rolling plane in the rolling direction, significant pit growth from pit coalescence is anticipated following prolonged exposure in a salt water environment. Preliminary results indicate that the presence of these corrosion pits can significantly decrease the fatigue crack initiation life and the threshold stress intensity of the alloy. The identification of the constituent particles, the mechanism of pit formation and growth, and the fatigue crack initiation kinetics will be discussed.

9:10 AM

STUDY ON HIGH-STRENGTH-TENACITY AND WEAR-RESISTING ALLOY OF HIGH ALUMINIUM ZINC BASE: *Lu Huimin*[1]; Zhang Yufei[1]; [1]Northeastern University, College of Resources Engineering, Shenyang, Liaoning 110006 China

The authors of this paper have developed successfully a novel high-strength-tenacity and wear-resisting alloy of high aluminium zinc base, named as ZA303. The excellent mechanical properties (σ_b=400~440MPa,δ =14~20%,BH-124) were obtained by the optimum design of alloying elements and contents and study of grain refiners. The experimental results have shown that the mechanical properties of ZA303 are superior to those of thin bronze ZQSn6-6-3. This kind of new alloy is promising in metallurgical industry, machine-building industry, light industry and so on for manufacturing bush, gear, worm wheel, nut, slide block and sliding guide.

9:30 AM

INFLUENCE OF GRAIN BOUNDARY MISORIENTATION ON THE GALLIUM PENETRATION OF ALUMINUM: *Richard Charles Hugo*[1]; Richard G. Hoagland[1]; [1]Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99164-2920 U.S.A.

The penetration of liquid gallium into aluminum grain boundaries is observable in the transmission electron microscope (TEM). In-situ TEM studies show that the speeds of the penetration fronts can differ by two orders of magnitude between different grain boundaries. We use this phenomenon to study the nature of general grain boundaries in aluminum. From misorientation data obtained during TEM experiments, atomistic grain boundary models are constructed based on Embedded Atom Method potentials. Properties such as grain boundary energy and excess volume are calculated and correlated with the observed gallium penetration speeds. We find that boundaries with higher energy and excess volume are penetrated more rapidly; however, the variation in these calculated properties is smaller than the variation in penetration speeds. Other factors that may explain the large variation in penetration speed, such as channels of high excess volume, are discussed. This research is supported by the US Dept. of Energy under grant DE-FG06-87ER45287

9:50 AM

TIME-DEPENDENCE OF ENVIRONMENTAL FATIGUE CRACK PROPAGATION IN AA7075: *Zuhair M. Gasem*[1]; Richard P. Gangloff[1]; [1]University of Virginia, Department of Materials Science and Engineering, Charlottesville, VA 22903

Environmental fatigue crack propagation is influenced by time-dependent processes localized at the crack-tip including the intrinsic effects of mass transport, chemical and electrochemical reactions, and stress corrosion cracking; as well as the extrinsic effect of corrosion-product induced closure. Corrosion fatigue crack propagation tests were performed to understand these processes in peak and overaged AA7075 with S-L oriented cracks immersed in pure 3.5% NaCl. Testing was at constant DK to emphasize steady state behavior. Results indicate that a closure contribution dominates Paris-regime fatigue crack response at low loading frequencies and overshadows stress corrosion cracking superposition. The extent of closure-induced retardation depends on localized corrosion debris which is promoted by overaging. When closure is minimal, da/dN increases as loading frequency decreases until a saturation growth rate is reached. Da/dN at saturation for different DK levels depends on the square root of the reciprocal of frequency. The kinetics of saturation are different, but saturation growth rates are similar, for the two aging conditions investigated. The rate-limiting step at saturation is described by a simple process-zone hydrogen diffusion and embrittlement model. Chromate addition eliminates the environmental acceleration of crack growth and reduces corrosion-product induced closure. The frequency dependence of crack growth in inhibited chloride is unique; crack tip strain rate appears to govern the rupture frequency of the protective surface film.

10:10 AM

FRACTURE SURFACE INTERFERENCE DURING SHEAR LOADING: EFFECT OF CRACK LENGTH ON CRACK FACE TRACTION DISTRIBUTION AND CRACK TIP SHIELDING : *Todd S. Gross*[1]; Christopher M. Prindle[1]; Daniel A. Mendelsohn[2]; [1]University of New Hampshire, Mechanical Engineering, Durham, NH 03824-3591 U.S.A.; [2]The Ohio State University, Aeronautical Engineering, Applied Mechanics, and Aviation, Columbus, OH 43210 U.S.A.

Fracture surface interference during shear loading shields the crack tip from the applied driving force for crack growth. We have used phase shifted speckle interferometry to measure the displacement field around Mode II and mixed Mode II/Mode I cracks as a function of applied Mode II for 6 mm and 12 mm long cracks in quenched and tempered 4340 steel. The displacement fields were fitted to near tip expressions for Mode II and Mode I cracks to determine the effective Mode II stress intensity factor and the induced Mode I stress intensity factor. The crack face displacement profiles were used as displacement boundary conditions in a boundary element model of the specimen to determine the crack face shear and normal tractions. The general trend is that the crack faces are locked until some critical load is reached and then the resistance is roughly constant but the induced opening continues to increase. The crack faces are in contact between 1 and 4 mm from the tip and are lifted off for the rest of the crack. This work was supported by the Department of Energy, Basic Energy Science, Division of Materials Science under grant number DE-FG02-90ER45433

GENERAL ABSTRACTS: X - Iron and Refractory Metal Alloys

Sponsored by: TMS

Wednesday AM Room: Patio B
February 18, 1998 Location: Convention Center

Session Chair: Oswald N. C. Uwakweh, University of Cincinnati, Cincinnati, Ohio 45221-0012

8:30 AM

THE EFFECT OF COMPOSITION AND PROCESS VARIABLES ON THE MICROSTRUCTURE OF RAPIDLY SOLIDIFIED AND HEAT TREATED ULTRA-HIGH CARBON STEELS: *Dr. Khershed P. Cooper*[1]; Dr. Jack D. Ayers[1]; Mr. Harry N. Jones, III[1]; [1]Naval Research Laboratory, Materials Science and Technology, Washington, DC 20375-5343 USA

Superplastic forming offers a promising approach for achieving the constantly increasing need for reducing the cost of fabricating high performance metal components having complex shapes. One method employed for producing the very fine-scale microstructure needed to permit superplastic forming at economically viable rates is through severe thermomechanical processing accompanied by cyclic phase transformations. This technique was successfully applied to ultra-high carbon steels (UHCS) by Sherby and co-workers[1]. We generated similar microstructures by producing a metastable crystalline structure through rapid solidification and then employing cyclic heat treatment at modest temperatures to transform and refine the structure. Melt spun ribbons were made from several UHCS alloys containing varying amounts of C, Al and Cr. The rapidly solidified ribbons had a columnar structure, 0.5 μm across, made up of austenite cells decorated with a very fine carbide film. Across the cells were found elongated, but narrow martensite plates, the volume fraction of which depended upon the alloy composition. After thermal cycling treatments involving an initial tempering, an austenitization and quench cycle, and a final tempering, a fine-scale microstructure was produced consisting of 1-2 μm ferrite grains and 0.1-0.4 μm spheroidal carbide. An extensively dimpled tensile fractured surface suggested a high degree of ductility in this material. While C and Al influenced carbide size, Cr content and the heat treat temperatures had little effect. In this paper, the processing technique and the resulting microstructures will be described and microstructure formation mechanisms will be proposed. 1. D. R. Lesuer, C. K. Syn, A Goldberg, J. Wadsworth, and O. D. Sherby, JOM, 45, (8), 1993, pp. 40-46.

8:50 AM

REPAIR OF STAINLESS STEEL STRUCTURES USING POLYMER MATRIX COMPOSITE MATERIALS: *Maryam Eslamloo-Grami*[1]; Beckry Abdel-Magid[1]; Jason L. Allie[1]; [1]Winona State University, Winona, MN 55987 USA

A number of exposed components in existing stainless steel structures fail at welded connections. This failure is due to sensitization and intergranular stress corrosion in the welded areas. More welding to repair these failures creates more corrosion sensitive areas, which in turn produce unsafe conditions in these components. In this study, polymer matrix composite materials are used to repair welded connections in stainless steel structures. The advantage of using these composite materials are many: they are corrosion resistant, they can be applied on the site at ambient temperature, and they can be designed to provide the required strength and stiffness. The study included: (i) selection and design of the best composite materials for the repair of stainless steel structures, which included fibers, matrix and adhesive materials, (ii) preparation and testing of stainless steel specimens repaired with the selected composite materials for strength and stiffness, (iii) investigation of the long term effects of ultraviolet light, humidity and temperature fluctuations on the composite repaired specimens. The result of the study show that while the strength of the connection of the repaired samples are comparable to the original strength, the stiffness at the connection is reduced and may need further improvement. These results in addition to the long term environmental effects will be presented and discussed.

9:10 AM

INCLUSION CHARACTERISTICS IN BEARING STEEL BEFORE AND DURING CASTING: *Erica Fuchs*[1]; Pär Jönsson[2]; [1]Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139 USA; [2]Ovako Steel AB (An SKF Group Company), TM-313, Hofors 82 SWEDEN

Size, distribution, and composition of inclusions were studied during secondary refining and casting for application to carbon chromium bearing steel production. Samples were collected in the ladle, tapping stream and mold. Total oxygen content, number of inclusions and composition of inclusions were then determined using melt extraction, optical microscopy, and scanning electron microscopy, respectively. The results indicated that the inclusion characteristics do not change significantly during the final treatment in the ladle. A future change in stirring conditions may therefore be necessary. The analyses of the samples taken in the tapping stream and in the mold showed an increase in the oxidic inclusion content. This increase is most likely due to reoxidation during sampling. Based on these results, a future study is recommended to further the present knowledge on inclusion characteristics before and during casting.

9:30 AM

GRAIN SUBDIVISION IN HOT DEFORMED STAINLESS STEEL: *D. A. Hughes*[1]; D. A. Mosher[1]; B. C. Odegard[1]; [1]Sandia National Laboratories, Center for Materials & Engrg. Sciences, Livermore, CA 94550 USA

Compression tests were performed on 304L stainless steel samples at three temperatures: 600, 800, 1000°C. The dislocation microstructures that developed were observed using transmission electron microscopy (TEM) and Kikuchi analysis of local orientations and dislocation boundary misorientations. The high temperature deformation microstructures that developed were characterized by grain subdivision at two size scales similar to that of high stacking fault energy metals at low temperatures: widely spaced long dislocation boundaries with a higher misorientation angle separated groups of equiaxed cells with smaller boundary misorientation angles. Significantly, like pure aluminum, the probability distributions of misorientation angles in 304L scaled with the average angle. This work supported by the U.S. DOE, under contract no. DE-AC04-94AL85000.

9:50 AM Coffee Break in Exhibit Hall

10:00 AM

MÖSSBAUER EFFECT STUDY OF PHASE TRANSFORMATION CHARACTERISTICS OF MECHANICALLY ALLOYED Fe-Zn CUBIC MATERIALS: *O. N. C. Uwakweh*[1]; A. Jordan[1]; Z. Liu[1]; [1]University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, Ohio 45221-0012

The Mössbauer Effect measurement of $Fe_{25}Zn_{75}$ alloy corresponding to the mixed phase $\Gamma + \Gamma_1$ cubic phase reveals the presence of four distinct Fe-sites with quadrupole splitting (QS) of 1.10, 0.241, 0.0773 and 0.0772 mm/s. After aging at 130°C for 30 min., a new site with QS of 1.5 mm/s, and relative abundance of 5% is observed. At stable equilibrium following aging at 400°C for 1 hr, Fe-sites corresponding to the single phases of Γ and Γ are observed, with their total abundance in line with equilibrium compositions as determined by the lever rule. Comparison with the single phases show that this transient stage at 130°C aging is unique in the mixed phase composition and is detected for the first time in this system. X-ray diffraction (XRD) measurements confirm the existence of this stage.

10:20 AM

KINETICS & PHASE TRANSFORMATION OF MECHANICALLY ALLOYED Fe-Zn-Al MATERIALS: *Oswald N. C. Uwakweh*[1]; Zhentong Liu[1]; [1]University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH 45221-0012

Fixed ratios of Fe and Zn corresponding to Γ-(Fe_3Zn_{10}), Γ_1-(Fe_5Zn_{21}), δ-($FeZn_7$) and ζ-($FeZn_{13}$) with the addition of 5% Al (wt.) were ball milled in an argon gas atmosphere. Non-isothermal kinetic analyses of the mechanically alloyed materials, based on DSC measurements revealed two diffusion controlled processes during the evolution of the δ + 5% Al and ζ + 5% Al compositions with activation energies of 227^{+2} kJ/mole, and 159^{+} kJ/mole respectively. Also endothermic and exothermic reactions detected are consistent with respect to the formation of the Fe_3Al, Fe_2Al_5, and δ-$FeAn_7$ phases. Based on $FeAl_2$ formation at 440°C for the ζ + 5% Al, the revision/re-evaluation of the Fe-Zn Al equilibrium phase diagrams is proposed. The Γ + 5% Al, and Γ_1 + 5% Al materials evolved similarly, except at 400°C the former consisted of α-FE + Γ +δ, while the later was without the Γ phase.

10:40 AM

AIR-OXIDATION KINETICS AND MICROSTRUCTURE OF VANADIUM-CHROMIUM-TITANIUM ALLOYS AT 300-600°C*: *M. Uz*[1]; K. Natesan[2]; T. Ulie[3]; [1]Lafayette College, Dept. of Chemical Engineering, Easton, PA 18042-1775; [2]212, Argonne National Laboratory, Argonne, IL 60439; [3]Purdue University, Dept. of Engineering Management, West Lafayette, IN 47906

We assessed and compared the air-oxidation behavior of V and its alloys V-4Cr-4Ti, V-5Cr-5Ti, V-10Cr-5Ti, and V-15Cr-5Ti (all in wt.%) in the temperature range of =300-650°C. The samples were =10x10 x 1-mm coupons made from cold-rolled sheet stock and annealed at 1050°C for 1 h. Oxidation experiments were performed in dry air in a thermogravimetric apparatus and the results were used to model the oxidation kinetcs. Cross-sectional area across the thickness of each sample was examined by both optical and scanning electron microscopy for microstructural characteristics, including grain size and scale thickness. A microhardness profile across the sample thickness was used to determine depth of penetration and parameters of diffusion of oxygen in each alloy. The results will be presented with emphasis on oxidation kinetics and microstructure as they are affected by alloy composition and temperature. *Work supported by the U.S. Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38.

11:00 AM

METASTABLE TRANSFORMATION OF BALL-MILLED Fe-Zn-Si ALLOYS IN EQUILIBRIUM PHASE EVALUATION: *O. Uwakweh*[1]; A. Jordan[1]; [1]University of Cincinnati, Materials Science & Engineering Department, Cincinnati, OH 45221-0012

Fe-Zn intermetallics with the addition of 0.12 wt % Si corresponding to an isocomposition line in the ternary system is investigated with respect to FeSi formation. The mechanically alloyed Γ (Fe_3Zn_{10}) + 0.12% Si; Γ_1(Fe_5Zn_{21}) + 0.12 % Si; δ ($FeZn_7$) + 0.12% Si; and ζ ($FeZn_{13}$) + 0.12 % Si, and the intermediate compositions (i.e., mixed phase alloys) yield metastable crystalline materials through ball-milling of pure elemental powders. DSC measurements in the 200-600°C temperature range indicate the presence of characteristic stages during their structural change. An invariant reaction occurring at 420-423°C is identified in the ζ ($FeZn_7$) + 0.12% Si and ζ + δ + 0.12% Si composition range. This reaction explains the phenomenon associated with the Zn coating of Si bearing steels, otherwise known as the Sandelin Effect. 2-D representation of the domain of FeSi boundaries is constructed from DSC and XRD measurements.

11:20 AM

THE STUDY OF METASTABLE TO STABLE EQUILIBRIUM TRANSFORMATION OF MECHANICALLY ALLOYED Fe-Zn-Si MATERIALS: *O. Uwakweh*[1]; A. Jordan[1]; P. Maziasz[2]; [1]University of Cincinnati, Materials Science and Engineering Department, Cincinnati, OH 45221-0012; [2]Oak Ridge Lab, Metals & Ceramics Divison, Oak Ridge, TN

The ball-milling of elemental powders corresponding to Γ(Fe_3Zn_{10}) + 0.12 Si; Γ_1 (Fe_5Zn_{21}) + 0.12 Si; δ ($FeZn_7$) + 0.12 Si; and ζ ($FeZn_{13}$) + 0.12 Si mechanically alloy to crystalline states. Differential scanning calorimetry (DSC) measurements show that they evolve through characteristic stages. The activation energies for these stages are 120^{+} 0.32 kj/mole, and 130^{+} 0.99 kj/mole (Γ + 0.12 Si); 161^{+} 0.16 kJ/mole (Γ_1 + 0.12 Si) respectively. Three stages with activation energies of 131 kJ/mole, 167^{+} 0.2 kJ/mole and 244^{+} kJ/mole are observed for the δ + 0.12 Si alloy. Evolution of the ζ + 0.12 Si alloy, exhibits two stages with activation energies of 96^{+} 2.08 kJ/mole and 641^{+} 0.45 kJ/mole, while the peak at 420^{+} 3°C depicts the eutectic reaction in Zn-Si, and the melting of Zn in Fe-Zn binary systems.

GENERAL RECYCLING OF NON-FERROUS METALS: General Recycling III - Physical 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 AM Room: Plaza Room B
February 18, 1998 Location: Convention Center

Session Chair: Drew Sinha, Mitsubishi Silicon America, Salem, OR 97303, Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

8:30 AM INVITED

INNOVATIVE GAS-SOLID TORBED REACTOR FOR RECYCLING INDUSTRIES: *V. I. Lakshmanan*[1]; C. Dodson[2]; [1]ORTECH Corporation, Environmental & Materials Processing, Mississauga, ON L5K 1B3 Canada; [2]Torftech Ltd. , Mississauga, ON L5K 1B3 Canada

The Torbed Process is a novel but well proven generic method of processing materials. The process provides unique benefits in precise, rapid, smaller scale and lower cost solutions to industrial materials processing problems. During the process, the feed material is fed into the ring shaped Torbed Chamber which has a fixed ring of angled blades near its base. An appropriate gas or vapour at a suitable temperature is passed through the blades at high velocity to force the particles into swirling or toroidal motion and provide very efficient heat and mass transfer. The paper will discuss application of this technology in oil and metallurgical industries.

8:55 AM INVITED

RECYCLE AND REUSE OF WASTE SILICON IN WAFER MANUFACTURING PROCESS: *Drew Sinha*[1]; [1]Mitsubishi Silicon America, Salem, OR 97303

Success of environmentally benign semiconductor manufacturing depends on the cost-effective integration of the principles of reduce, recover, reuse and recycle from source material to final product disposal. Increasing demand combined with current shortage of polysilicon provide unique opportunities to recover the silicon waste caused by various defects in wafer manufacturing process. Current practices relating to recovery and reuse of waste silicon produced from crystal growth process to finally polished and epitaxially deposited silicon wafer at Mitsubishi Silicon America is presented. Future plan to recycle the process generated silicon fines produced during the intermediate steps of the wafer manufacturing process such as grinding, slicing, lapping and polishing is also discussed.

9:20 AM INVITED

REVIEW OF MINERAL PROCESSING TECHNIQUES FOR RECYCLING APPLICATIONS: *Jan E. Martin*[1]; Robert M. Carver[1]; [1]Carpco, Inc., Jacksonville, FL 32206

The fundamental challenge of recycling is to find an economical and practical method whereby material resources can recovered by both economical and environmentally safe methods. With raw material prices increasing and new regulatory legislation being implemented

around the globe, industry is taking on the challenge to capitalize on this trend. Utilizing the fundamental separation techniques from the mineral processing and mining industries, recycling methods have evolved over that past few years to enhance the recoverability of such recyclable materials. Notably from both post-consumer and post-industrial recycling markets, a wealth of recoverable materials are available. Carpco, Inc. in Jacksonville, Florida, has recently implemented and improved many of the existing techniques and applied them directly to industry.

9:45 AM Coffee Break in Exhibit Hall

10:00 AM INVITED
COPPER RECYCLING FROM ELECTRIC AND ELECTRONIC SCRAP BY PHYSICAL SEPARATION TECHNOLOGIES: *Shunli Zhang*[1]; Dr. Bo Bjorkman[2]; Dr. Eric Forssberg[1]; Dr. Nourredine Menad[2]; [1]Lulea University, Division of Mineral Processing, Lulea s-971 87 Sweden; [2]Lulea University, Process Metallurgical

Copper recovery from electric and electronic scrap by means of physical separation may provide an alternative to the current recycling approach, through which halogenated flame retardants can result in dibenzo-p-dioxins and dibenzo-furans. In addition, a diminishing amount of copper and precious metals present in electronic scrap prompts a pretreatment and upgrading process in order to sustain this particular recycling industry in an economically viable way. In this paper, a sink-float analysis using a series of heavy liquids and a theoretical and practical consideration of air table and high tension separators has been revealed. It has been shown that density-based separation techniques, particularly, air table and high tension (electrodynamic) separation techniques are applicable to this specific waste stream for copper and precious metals recovery. Key words: Electric and electronic scrap, Sink-float analysis, Air table separator, High tension separator

10:25 AM INVITED
MAXIMIZING THE RECOVERY OF NON-FERROUS METAL SCRAP FROM SHREDDED AUTOMOBILES: *Adam J. Gesing*[1]; Ron Dalton[1]; Richard Grisier[1]; Dennis Reno[1]; Richard Wolanski[1]; [1]Huron Valley Steel Corporation, Belleville, MI 48111

End-of-life automobiles are partially dismantled for spare and rebuilt parts. The remaining hulks are shredded to <4" in size, and the steel is removed magnetically from the shreds. The remaining mixture of plastic, rubber and non-ferrous metals is separated by air and eddy current separation. Since this mixture contains only ~10% metal by weight, small residual concentration of metals in the landfill-bound residue can represent large losses as percentage of the metal weight. This paper discusses the practical aspects of eddy current separation as applied to the automotive shredder operation, shows the effect of the metal losses to the landfill residue on the metal balance of the shredder, discusses the concept of Grade-Recovery curves, and applies them to provide practical strategies for minimizing the metal losses.

10:50 AM
NEW RECYCLING APPROACH - GENERATION OF ALUMINUM WROUGHT ALLOY SCRAP OF OLD CARS: *Hartmut Rossel*[1]; [1]VAW Aluminum AG, Research & Development Department, Bonn D-53014 Germany

The recycling of car scrap is an important source of metals and materials for the secondary materials processing industry. In Europe more than 90% of the aluminum used in automobiles is recycled. The driving force behind this excellent recycling rate is the inherent value of aluminum. Traditionally the processing of scrap cars starts with size reduction by a shredder. Second step various sorting procedures follow to generate different material fractions. The metallic fractions are recycled and the residual "fluff," a mixture of plastic, cloth, rubber and glass, is currently landfilled. Aluminum is being used in a multitude of applications in cars and casting alloys as well as wrought alloys. Therefore, the recovered aluminum fractions consist of a mixture of different alloys. Most of this mixed aluminum scrap is returned into the production of new cast automotive aluminum parts. Wrought alloys are produced only on a virgin metal basis due to their tight impurity tolerances. The production of wrought alloys on aluminum car scrap basis requires an upgrading technology, which is able to sort alloys by grade or segregate alloys during dismantling. Future concepts of aluminum intensive vehicles have to fulfill technical and economic as well as ecological aspects. Terms like green manufacturing, life cycle analysis, recyclability, and closed loop recycling are used to evaluate new concepts. Consequently, there exists a certain demand to investigate the parameter for closed loop recycling procedures of automotive aluminum parts. The paper presents technical possibilities for dismantled aluminum intensive automotive parts to generate wrought alloy scraps by using conventional processing techniques.

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

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 AM Room: Centro Room C
February 18, 1998 Location: Convention Center

Session Chair: J. M. Rigsbee, University of Alabama at Birmingham, Department of Materials and Mechanical Engineering, Birmingham, AL 35294, F. Richter, Institüt für Physik, Technische Universität Chemnitz Germany

8:30 AM INVITED
HYPERTHERMAL PARTICLE ENHANCED DEPOSITION OF MATERIALS: *J. W. Rabalais*[1]; [1]University of Houston , Department of Chemistry, Houston, TX 77204

The use of hyperthermal particles in the growth of metastable materials and enhancement of epitaxy will be described. A UHV, mass-selected, low energy, dual ion beam instrument is used to deposit films and modify surfaces. The results of deposition of carbon nitride films by direct impingement of 5-100 eV C^- and N^+ or $N2^-$ ions upon solid surfaces as well as by 5 - 350 eV N^+ bombardment of graphite surfaces will be described. Synergistic effects of the combined ion energy and substrate temperature will be described for (1) growth of carbon nitride and (2) promoting the removal of impurities form silicon surfaces while maintaining good crystalline order. It is proposed that a portion of the kinetic energy is a general phenomenon that is responsible for the enhancement effects of the hyperthermal particles. A generalized epitaxial phase diagram in energy-temperature space can be constructed which provides an understanding of the effects of the hyperthermal particles on surfaces.

9:00 AM
DIFFRACTION AND ELECTRON ENERGY LOSS EVIDENCE FOR THE EXISTENCE OF CRYSTALLINE CARBON NITRIDE IN CN_X/ZRN MULTILAYERS: Mei-Ling Wu[1]; Xi-Wei Lin[1]; Vinayak P. Dravid [1]; *Yip-Wah Chung*[1]; [1]Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208

We demonstrated that when alternating layers of CN_x and ZrN are deposited onto a silicon (100) substrate at 450K in a magnetron sputter-deposition system, the CN_x layers become crystalline when two conditions are satisfied. First, the ZrN should have a strong 111 texture. Second, the CNx layer thickness is one nm, Electron diffraction of such CN_x/ZrN multilayer coatings gives rise to features that cannot be attributed to ZrN, but can be accounted for by either diamond,

graphite, α- or β-C_3N_4. Auger sputter-profiling showed nitrogen concentrations in the CNx layers ~ 50%. It is unlikely that diamond can incorporate this amount of nitrogen and be still crystalline. Therefore, diamond can be excluded. The carbon 1s loss features clearly indicate the predominant presence of sp^3 carbon. Taken together, these experimental data provide strong evidence for the existence of crystalline carbon nitride (α or β) in these CN_x/ZrN multilayers.

9:20 AM

BONDING STRUCTURE IN CN_X FILMS: VARIATION WITH NITROGEN CONTENT AND ANNEALING TEMPERATURE: *A. K. M. S. Chowdhury*[1]; D. C. Cameron[1]; M. S. J. Hashmi[1]; [1]Dublin City University, Materials Processing Research Center and School of Electronic Engineering, Dublin 9 Ireland

The variation in the bonding structure in CN_x films measured by IR spectroscopy was recently described [1]. It was shown that as nitrogen content increased, an increasing proportion of the nitrogen is incorporated with IR-invisible bonding, postulated to be nitrogen-nitrogen bonding. As temperature was increased it was shown that the degradation of the carbon-nitrogen bonds was dependent on their level of saturation with C N bonds being the least stable as expected for their chemical bond strength. These carbon-nitrogen stretching bands are also studied by Raman spectroscopy. The Raman shifts due to inorganic carbon (D and G peak) under different deposition conditions are explained in terms of structural changes of these films. This paper extends these results and also relates them to changes in the local chemical environment of the carbon and nitrogen atoms as determined by XPS measurements. The evolution of the XPS peaks due to the various carbon-nitrogen bonding states is reported as they alter with changing nitrogen content in the films and with increasing annealing temperature. Clarification of the structural changes which occur in the film under these conditions is given. 1 A.K.M.S. Chowdhury, M. Monclus, D.C. Cameron, M.J. Murphy, N.P Barradas, J. Gilvarry, and M.S.J. Hashmi, presented in the Int. Conf. on Metall. Coatings and Thin Films, San Diego, 21st-25th April 1997 and accepted for publication in the Journal of Thin Solid Films.

9:40 AM

NANOINDENTATION AND SCRATCH RESISTANCE PROPERTIES OF AMORPHOUS CARBON COATINGS: *Ashok V. Kulkarni*[1]; Zhenghong Qian[2]; John M. Siversten[2]; Jack Judy[2]; [1]Hysitron Inc., Minnesota, MN 55413; [2]University of Minnesota , Department of Electrical Engineering, Minneapolis, MN 55455

In this paper we present results of nanomechanical properties of amorphous C:N films deposited on Si (100) substrates. Amorphous C:N films of various thickness were deposited by facing target Sputtering (FTS) technique. The elemental composition and chemical bond characteristics of the C:N films have been determined by X-ray Photoelectron spectroscopy (XPS) and Auger electron Spectroscopy (AES). Nanoindentation experiments were performed using Hysitron Triboscope in the load range of 10-500 mN, using a 90° 3-sided pyramidal diamond tip. The surface morphology of the coating were examined by Atomic Force Microscopy (AFM). The film replicated the surface with rms roughness less than 1 nm. Hardness and Young's modulus of elasticity were determined from the load-displacement data. Comparison of the hardness values with carbon coating deposited by different techniques is made. Scratch test were performed on coatings less than 20-nm and the critical loads at which the film debonds the surface was used to determine the adhesion and the yield strength of the film. Nanowear measurements suggests that C:N film have excellent resistance as compared to Si(100). The improved performance is attributed to the high hardness and yield strength of the coating.

10:00 AM

CARBON NITRIDE THIN FILMS SYNTHESIZED FROM THE GAS-PHASE BY LASER-INDUCED REACTIONS: A PARAMETRIC STUDY: *R. Alexandrescu*[1]; A. Crunteanu [1]; R. Cireasa[1]; I. Morjan[1]; [1]National Institute for Lasers, Plasma and Radiation Physics, Bucharest Romania

The possibility of a new ultrahard phase of carbon nitride, with hardness comparable to or greater than that of diamond was first suggested by Liu and Cohen. The presence of α- and -β C_3N_4 phases has been suggested on the basis of electron and X-ray diffraction studies but the overall composition in most experiments was not stoichiometric. In this case study, we focused on the chemical composition and morphology of CN_x thin films deposited from the gas phase (ternary gas mixtures of $C_2H_4/N_2O/NH_3$) by laser-induced chemical vapor deposition (LCVD), in connection with some important experimental parameters: i) laser wavelength, ii) gas phase composition and iii) nature of the substrate. Alternatively, the radiation at 10.6 μm (cw CO_2 laser) and the radiation at 248 nm (Kr excimer laser) were used, perpendicularly irradiating the substrates (alumina, quartz, sapphire). During irradiation, the gaseous composition was monitored by IR specrophotometry. X-ray photoelectron spectroscopy (XPS), transmission electron diffraction (TED) and scanning electron microscopy (SEM) were used in order to analyze the chemical content and the morphology of the deposited films. SEM and TED analysis showed that there were polycrystalline grains in the deposited film. Part of this research was supported by NRC Twining Program.

10:20 AM Coffee Break in Exhibit Hall

10:35 AM INVITED

NITROGENATED CARBON FOR MAGNETIC HARD DISK OVERCOAT: *Ming M. Yang*[1]; Eugene Anoikin[1]; Jim Chao[1]; Mike Russak[1]; [1]HMT Technology Corporation, Fremont, CA 94538 USA

Sputtered thin carbon films are used as the overcoat for hard magnetic recording disks. They provide wear protection against head sliders repeatedly dragging and slapping on the disks surface during start and stop cycles as well as providing protection for the magnetic medium against environmental corrosion. To enhance the wear and friction properties of the carbon overcoat, one or two of the following gases: hydrogen, methane, or nitrogen can be introduced into the sputter chamber and mixed with the argon working gas. In this study, we investigated nitrogenated carbon films prepared in a DC-magnetron sputtering system. The film properties including deposition rate, nitrogen content, nanohardness and thin film stress of the nitrogenated carbon as a function of deposition conditions, i.e. sputter power, substrate bias, substrate temperature, and sputter pressure, are reported. The corrosion resistance of nitrogenated carbon will also be discussed.

11:05 AM

PROPERTIES AND PROCESS OF CARBON OVERCOAT FOR MAGNETIC THIN-FILM DISK APPLICATIONS: *Zunde Yang*[1]; Xi Chu[1]; Jifeng Ying[1]; [1]MaxMedia Hyundai Electronics America, San Jose, CA 95131

Nitrogenated and hydrogenated carbon overcoats were sputtered onto magnetic thin-film disks under different conditions. The composition film structure and surface topography were measured using XPS, Raman spectroscopy and AFM. The mechanical properties including contact start-stop (css) test, ball-on-disk wear test, nanoindentation and thin stress were investigated and correlated with the sputter process. It was shown that the gas flow ratio of N2/Ar during sputtering plays a predominant role on ball-on-disk dry wear performance. However, the css test performance appears to be insensitive to the nitrogen concentration in the sputter gas. Other potential materials and deposition techniques will also be reviewed.

11:25 AM

TRIBOLOGICAL AND MECHANICAL PROPERTIES OF CN_X ULTRA-THIN OVERCOAT FILMS AND THEIR INFLUENCE ON MAGNETIC MEDIA: *R. D. Ott* [1]; J. A. Barnard[1]; [1]The University of Alabama, The Center for Materials for Information Technology, Tuscaloosa, AL 35487

Ultra-thin nitrogenated carbon overcoats have attractive tribological properties that make them favorable for protective coatings for rigid magnetic disks. The wear characteristics of the overcoat are clearly influenced by the nitrogen content and thickness of the overcoat.[1] In addition, as the magnetic media thickness is reduced to approximately 10 nm for future extraordinarily high density recording, the influence of the ultra-thin overcoat on media magnetic properties may become important. In this study, the main parameters of interest were the nitrogen content and the overcoat film thickness. These two parameters were systematically varied to evaluate their influence on

both tribological performance of the overcoat and the magnetic behavior of the media. The nitrogenated overcoats, with thicknesses ranging form 2 to 10 nm, were all deposited on a 20 nm thick layer of Co. The tribological and mechanical properties of the overcoats were evaluated with the use of nanoindentation and nanowear test procedures.[2] The vertical resolution, approximately 1 nm, of the NanoIndenter II allowed examination of tribological properties of ultra-thin films on the order of 2 nm in thickness. Several important properties of the overcoats have been determined as a function of nitrogen content and overcoat film thickness. Included among these are the adhesion of the overcoat to the magnetic layer as well as the surface roughness and the coefficient of friction. Hysteretic properties of the under lying magnetic layer have also been evaluated as a function of nitrogen content and overcoat film thickness. [1]T.W. Scharf, H. Deng, and J.A. Barnard, J. Appl. Phys. 81 (8), 5393 (1997) [2]H. Deng, T.W. Scharf, and J. A. Barnard, J. Appl. Phys. 81 (8), 5396 (1997)

11:45 AM

SYNTHESIS OF CARBON NITRIDE FILMS BY LASER ABLATED GRAPHITE UNDER AN INTENSE NITROGEN ATOMIC BEAM: *Yuancheng Du*[1]; Ning Xu[1]; Zhifeng Ying[1]; Zhongmin Ren [1]; Fuming Li[1]; [1]Fudan University, State Key Joint Lab for Material Modification by Laser, Iion and Electron Beams, Shanghai 200433 CHINA

Covalent Carbon Nitride films have been synthesized on Si substrate by laser ablation of graphite under an intense nitrogen atomic beam, An arc- heated mode of DC discharge source in pure N2 operating pressure of 30 -300 Torr has produced an intensity of $10^{+1}9$ atoms/srs nitrogen atomic beam with kinetic energies of 0.4 - 4 eV. As compared with normal glow mode of the discharge source, the results of the analysis show that the nitrogen atom beam processing with laser ablated graphite is beneficial for formation of carbon nitride films. The films are used for Raman and X-ray photoelectron spectroscopy(XPS)measurements. The x-ray diffraction (XRD) data indicate the formation of covalent carbon nitride in the processed films.

HIGH TEMPERATURE ENVIRONMENTAL IMPACT ON PERFORMANCE: Session I

Sponsored by: Structural Materials Division, High Temperature Alloys Committee

Program Organizers: Susan Jones, Allison Engine Co., P.O. Box 420, Indianapolis, IN 46206; Robert Klug, Allegheny Ludlum Steel, 80 Valley St., Wallingford, CT 06492

Wednesday AM Room: 209
February 18, 1998 Location: Convention Center

Session Chair: TBA

8:30 AM

OXIDATION/SULFIDATION/NITRIDATION AND MECHANICAL DEGRADATION OF THERMAL SPRAY COATINGS IN GAS TURBINE BLADES: *Jun Kameda*[1]; T. E. Bloomer[1]; Y. Sugita[2]; A. Ito[2]; S. Sakurai[3]; [1]Iowa State University, Ames Laboratory, Ames, IA 50011; [2]Chuba Electric Power Co., Inc., Electric Power R & D Center, Nagoya 458, Japan; [3]Hitachi Ltd., MERL, Hitachi 317, Japan

This paper examines how in-service environmental attack influences the ductility (22-950°C)of thermal spray coatings over Ni base superalloy substrates in gas turbine blades using a small punch (SP) testing technique and scanning. Auger microprobe analysis. SP tests have shown strong dependence of mechanical coating degradation on the elevated temperature environmental condition. In-service operation under combined fuels of kerosene and liquidfied natural gas (LNG) led to a two-fold increase in the ductile-brittle transition temperature over CoNiCrAlY coatings observed under mainly LNG due to extensive oxidation and gain boundary sulfidation. Mechanical and microstructural degradation of CoCrALY coatings were also found to strongly depend on the location of blades operated for 21000 h under LNG. Extensive formation Al and Ni enriched nitrides and Al enriched oxides was observed in inner (concave) coatings but not in outer (convex) ones. The oxidation and nitridation in the inner coating produced significant ductility loss. The degradation mechanism is discussed in light of the oxidation, sulfidation and nitridation resulting from the environmental attack.

8:55 AM

MODELING OF HIGH TEMPERATURE DEGRADATION MECHANISMS IN OVERLAY COATINGS: *Dr. Kwai S. Chan*[1]; [1]Southwest Research Institute, Materials and Structures Division, San Antonio, TX 78228-0510 USA

Degradation of overlay coatings at elevated temperature includes oxidation, spallation, and the loss of aluminum from the coating by both inward and outward diffusion. These degradation mechanisms are treated in a recent coating life model developed by coupling a spallation model with an existing diffusion model. In this paper, the application of this coating life model to predict the degradation of both coated and uncoated Ni alloys is demonstrated. Model calculations for NiCoAlYTa and CoCrAlY coatings on several Ni alloys are reported and compared against experimental data from the literature. The results will be used to illustrate the relative importance of oxidation, spallation, and diffusion on the integrity of overlay coatings for selected thermal histories of interest to the combustion turbine industry. Work supported by the EPRI Materials Center for Combustion Turbines at SwRI.

9:20 AM

THE EFFECT OF NI-RE INTERLAYERS ON INTERDIFFUSION FROM MCrAlY OVERLAY COATINGS: *Dr. Richard A. Page*[1]; Dr. Gerald R. Leverant[1]; [1]Southwest Research Institute, Power Generation Materials, San Antonio, TX 78228-0510 U.S.A.; [1]Southwest Research Institute, Materials Engineering Department, San Antonio, TX 78228-0510 U.S.A.

For aluminide and MCrAlY coatings, the life of the coating is controlled by maintaining a reservoir of Al that forms a protective alumina surface scale. Loss of Al from the coating occurs by spallation of the alumina due to thermal cycling and, also, by interdiffusion of the coating and substrate. It would be desirable to suppress interdiffusion that leads to loss of Al to the substrate and ingress of Ni from the substrate. This could be accomplished by the presence of a diffusion barrier that locally slows down diffusional processes. Initial measurements performed on MCrAlY coated IN738 specimens have shown that the presence of a thin Ni-Re layer between the MCrAlY and the substrate can lead to a reduction in the growth rate of the inner beta-NiAl depleted layer. These results and those obtained on GTD-111 and CM247 will be presented.

9:45 AM

EFFECT OF CHEMICAL COMPOSITION, COLD WORK, GRAIN SIZE, AND ISOTHERMAL EXPOSURE OF THE PROPERTIES OF ALLOY 800: *S. K. Mannan*[1]; *C. S. Tassen*[1]; [1]INCO Alloys International, Huntington, WV 25705-1771

Alloy 800 and its variants are extensively used industrial heating, power plants, and petrochemical industries due to their good corrosion resistance. Under certain high temperature service conditions $M_{23}C_6$-type carbides and Gamma Prime are formed which affect the microstructure and mechanical properties. This presentation covers microstructural analysis, room temperature properties of as-produced and isothermally exposed laboratory and commercial materials. Further, the effect of composition, grain size, and cold work on the stress rupture and low cycle fatigue properties are also presented.

10:10 AM

OXIDATION BEHAVIOR OF TERNARY Ti_3Al-Ta ALLOY: *Yang Li*[1]; *R. G. Reddy*[1]; [1]University of Alabama, Department of Metallurical and Materials Engineering, Tuscaloosa, AL 35487

The oxidation behavior of ternary Ti_3Al-Ta intermetallics has been studied in pure oxygen over the temperature of 850°C to 1100°C. The experiments were carried out using TGA. The oxidation products were analyzed using X-ray diffraction, SEM and EDS. Parabolic rate con-

straints were calculated. An effective activation energy of 209 kj/mol was deducted. The present results were compared with that of ternary Ti_3Al-Nb and binary Ti_3Al. The oxidation products were mainly a mixture of TiO_2 (rutile) and Al_2O_3 (alumina). The oxidation scale is easy to spalling off compared with that of Ti_3Al-Nb. Although Ta and Nb in Ti-Al alloys decreases the oxygen solubility, oxide of Ta in Ti_3 Al-Ta cannot act as a glue to keep oxidation scale compact like oxide of NB does in Ti_3Al-Nb.

10:35 AM

HIGH TEMPERATURE OXIDATION BEHAVIOR OF CHROMIA-FORMING ALLOYS EXPOSED TO AIR AT 982 AND 1093°C: *Mark A. Harper*[1]; *Brian Gleeson*[2]; [1]Haynes International, Kokomo, IN 46904; [2]The University of New South Wales, School of Materials Science & Engineering, Sydney 2052 Australia

During the exposure of commercial high temperature alloys to oxidizing atmospheres, internal attack (i.e. internal oxidation and void formation) of the substrate underneath an external scale usually occurs. Aluminum oxide and silicon oxide are the typical internal precipitates that form below the external chromia scale, and logically results from oxygen passing through defects in the external scale, diffusing into the alloy substrate, and reacting with the relatively small amounts of aluminum and silicon that are present in commercial alloys. In an effort to gain a better understanding of the internal attack that is experienced during high temperature oxidation, four chromia-forming commercial alloys were oxidized in air at 982 and 1093°C for times ranging from 100 to 17,280 hours. Two of the alloys were iron-base (Fe-32.5wt% Ni-21Cr and Fe-37wt% Ni-25Cr) and two of the alloys were nickel base (Ni-22wt% Cr-14W and Ni-29Co-28Cr-2.75Si). Thermogravimetric analysis, x-ray diffraction, and scanning electron microscopy confirmed that all of the alloys initially formed and maintained a protective external chromium oxide scale (Cr_2O_3). However, each of the alloys exhibited different external scale growth and internal oxidation behavior, thus allowing an investigation of the effect of the alloying elements. At 982°C, approximately 85% of the total metal affected (i.e. metal recession plus internal attack) in all of the alloys corresponded to internal attack, whereas at 1093°C the internal attack of the two iron-base alloys was only 15% of the total metal affected. This reduction in the relative amount of internal attack in the two iron-base alloys was due to an increase in the metal recession. Also, the Ni-29Co-28Cr-2.75Si alloy exhibited almost complete spallation of its external scale during thermal cycling once every 720 hours, yet demonstrated the ability to reform a protective Cr_2O_3 external scale. The Ni-22Cr-14W alloy also spalled most of its external scale during thermal cycling, but did maintain a thin Cr-rich oxide scale at the alloy/scale interface. These results and others will be discussed within the framework of high temperature oxidation theory.

11:00 AM

DISPERSION HARDENED PLATINUM FOR VERY HIGH TEMPERATURE APPLICATIONS: *Professor Dr. Ing Habil B. Fischer*[1]; D. Freund[1]; A. Behrends[1]; D. Lupton[2]; J. Merker[2]; [1]Fachhochschule Jena, University of Applied Science, Jena D-07745 Germany; [2]W. C. Heraeus GmbH, Hanau D-63450 Germany

Materials which can withstand extreme thermal, mechanical and chemical conditions are required for developments in many areas of high technology - for example in space technology applications and in glass melting plants for the production of special high-performance glass for the optical and electronics industries. The paper will report on examinations of the microstructure and properties of dispersion and properties of dispersion hardened (DPH) platinum for these applications. The material is characterized by high levels of strength and low creep rates in the operational temperature range up to 1600 °C. It also has excellent processing characteristics, for example formability and weldability. The microstructures, contents and distribution of oxide dispersoids were determined by means of metallography, chemical analysis, scanning electron microscopy, x-ray diffraction and secondary ion mass spectroscopy. The stress-rupture strength and numerous creep cures were determined on platinum materials with various dispersoid contents and in different experimental conditions.

11:25 AM

THE EFFECT OF LONG TERM ISOTHERMAL EXPOSURE ON THE MICROSTRUCTURE AND PROPERTIES OF INCONEL ALLOY 783: *Sarwan Mannan*[1]; John deBarbadillo[1]; *Stanley Gregory*[1]; [1]INCO Alloys International, Huntington, WV 25705-1771

Recently developed INCONEL (tm) alloy 783 (nominal composition of Ni-34Co-26Fe-5.4Al-3Nb-3Cr) is precipitation strengthened by Ni, Al-type Gamma Prime and NiAl-type Beta phases. Due to its low co-efficient of thermal expansion, high strength, and good oxidation resistance alloy 783 was designed for use in aircraft gas turbine components such as rings, casings, shrouds, and seals and has been considered for use in a number of other critical industrial turbine components. In this study, commercially produced alloys 783, 718, 909, and THERMO-SPAN were annealed and aged following recommended heat treatments. The materials were then isothermally exposed at 1100°F (593°C) for times up to 10,000 hours. After every 1000 hours exposure, specimens of these alloys were subjected to room temperature tensile (RTT) and high temperature tensile (HTT) testing. The microstructure of as-produced and exposed materials was characterized using optical microscopy, Scanning electron Microscopy, and Transmission Electron Microscopy. Variation in tensile properties with isothermal exposure time was correlated with microstructure. Further, exposed specimens were HTT tested in air and in vacuum to evaluate the effect of test environment. For alloy 783, creep crack growth tests were carried in the as-produced and isothermally exposed conditions to determine the effect of exposure on the crack growth. INCONEL is a registered trademark of Inco family of companies. THERMO-SPAN is a registered trademark of Carpenter Technology Corporation.

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

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow & Fracture Committee, Jt. Electronic, Magnetic and Photonic Materials Division/ Structural Materials Division, Alloy Phases Committee, Materials Design and Manufacturing Division, Powder Metallurgy 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 AM Room: 108
February 18, 1998 Location: Convention Center

Session Chairs: D. G. Morris, University of Neuchatel, Institute of Metallurgy, CH-2000 Neuchatel Switzerland; C. R. Scorey, AMETEK, Wallingford, CT 06492

8:30 AM INVITED

MECHANICAL PROPERTIES OF Fe70Al30 SINGLE CRYSTALS INVESTIGATED BY IN SITU STRAINING EXPERIMENTS IN A TEM: *Guy Molénat*[1]; Harald Rösner[2]; Daniel Caillard[1]; [1]CEMES-CNRS, 31055 Toulouse Cedex 4 France; [2]University of Münster, Institut für Metallforschung, D-48149 Münster Germany

The mechanical properties of Fe-30 at. % Al single crystals are studied by in situ straining experiments in a transmission electron microscope. These experiments are conducted in two temperature ranges:

below and within the temperature range of the yield stress anomaly (YSA). The dislocations involved are identified as superpartials dislocations with a a/2<111> Burgers vector dissociated into two superpartials separated by an APB ribbon. They have a dominant screw character which is explained in terms of a frictional force. Their motion in the {110} plane is controlled by a Peierls type mechanism with two different average velocities at a given strain rate: a slow and continuous one below and a fast and discontinuous one within the temperature range of the YSA. The latter is believed to correspond to microscopic plastic instabilities. The YSA and the associated instabilities and macroscopic small strain rate sensitivity are discussed in terms of dynamic strain aging which involves diffusional processes and collective behavior of dislocations.

9:00 AM

YIELDING, HARDENING, AND CREEP BEHAVIOR OF FeAl ALLOY*: S. C. Deevi[1]; *R. W. Swindeman*[2]; [1]Phillip Morris USA, Richmond, VA 23234 USA; [2]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA

High-temperature deformation behavior of FeAl is needed for the design and structural analysis of components subjected to thermomechanical loading. Design and analysis of FeAl alloy components by finite element analysis require rules for yielding, hardening, and creep in the temperature range of interest. In our work, we carried out tensile, creep, cyclic, and relaxation tests from room temperature to 750°C on foil and bar product of FeAl alloy. The results indicate that FeAl alloy exhibits yield point phenomenon, high strain rate dependency, and rapid recovery of flow stress with little or no hardening in creep. The general features of the inelastic behavior of FeAl alloy conform to those observed for low alloy steels. Application of the data for design of structural components will be discussed. *Research was carried out under Work For Others contract ERD94-1207 at the Oak Ridge National Laboratory.

9:20 AM INVITED

FATIGUE AND CYCLIC DEFORMATION BEHAVIOR OF IRON ALUMINIDE: *C. E. Jaske*[1]; S. C. Deevi[2]; S. S. Shademan[1]; [1]CC Technologies Laboratories, Inc., Dublin, OH 43016-8761 USA; [2]Philip Morris U.S.A., Research and Development, Richmond, VA 23234 USA

When iron aluminide (FeAl) is used at elevated temperature, it may be subject to cyclic loading that can cause failure by fatigue cracking or by cyclic creep rupture. For engineering design considerations, the fatigue and cyclic creep behavior must be characterized. In the current research, fatigue experiments were performed on specimens made from FeAl material. The specimens were tested under constant amplitude cyclic loading in air at temperatures from 400 to 750°C. The frequency was 0.5 Hz and the stress ratio (R) was 0.1. Fatigue life and cyclic creep behavior were determined as a function of stress amplitude. Stress-versus-fatigue-life (S-N) curves and stress-versus-cyclic-creep-rate curves were developed at each test temperature. In some cases, significant variations in fatigue and cyclic creep behavior were observed. Based on these observations, specimens were selected for examination by means of scanning electron microscopy (SEM) and metallography. Application of the data to design and reasons for variations in material behavior are discussed.

9:50 AM INVITED

HIGH-TEMPERATURE DEFORMATION - SUPERPLASTICITY AND CREEP - OF INTERMETALLIC FeAl (CR) ALLOYS: *G. Frommeyer*[1]; J. A. Jimenez[1]; [1]Centro National de Investigaciones Metalurgicas CENIM, Madrid Spain; [1]Max-Planck-Institut für Eisenforschung, D-40237 Düsseldorf Germany

High-temperature plasticity of Fe_3Al-base alloys with addition of chromium have been investigated in a wide strain rate range (10^{-5} and $<\varepsilon<10^{-2}s^{-1}$) at test temperatures between 700 and 1100°C. The fine-grained Fe_3Al (Cr) alloys with small amounts of titanium show superplasticity with maximum strain rate exponents of about m = 0.45 and at strain rates of $\varepsilon = 10^{-4}s^{-1}$. Maximum elongations to failure 300% and more were achieved. Activation energies of 265 kJ mol^{-1} were measured which are lower than the determined creep activation energy described below. From activation analysis and TEM investigations, it is concluded that dynamic recrystallization is the dominant mechanism for superplastic flow. The creep behavior of this material is characterized by power law equation. The determined stress exponent for the plain aluminides is about n = 3. The activation energy is ranging from 360 to 395 kJ mol^{-1}. From the result, it is deduced that creep is controlled by viscous glide of dislocations. The chromium-containing aluminides exhibit higher stress exponents of 4 to 5. The activation energy of about 500 kJ mol^{-1} is much higher than that of the unalloyed iron aluminides. The creep of Fe_3Al (Cr) and of hyperstoichimetric compounds with chromium is controlled by dislocation climb.

10:20 AM Coffee Break in Exhibit Hall

10:40 AM INVITED

PROCESSING OF IRON ALUMINIDES: R. S. Sundar[1]; R. G. Baligidad[2]; Y. V.R.K. Prasad[1]; *D. H. Sastry*[1]; [1]Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India; [2]Defence Metallurgical Research Laboratory, Hyderabad 500 058 India

Successful commercialization of any new material critically depends on the economy and ease of processing. This paper deals with research efforts under way in India towards understanding the processing of iron aluminide Fe_3Al. The first part of the paper deals with a melting procedure for air-induction melting (AIM) of Fe_3Al containing 0.02 to 1.1 wt % carbon. The use of a protective flux cover during AIM results in the minimization of hydrogen gas porosity and a significant reduction in the impurity levels (S3O and N). Attempts have been made to further improve the ductility and hot workability through electroslag remelting. The hot deformation studies on vacuum-induction melted Fe3Al-based alloys were investigated. Hot compression tests were carried out over the temperature range of 750 to 1050°C and over the strain rate range of 10^{-3} to $10s^{-1}$. The results are analyzed by employing the Dynamic Materials Model, and processing maps have been developed. The dominant deformation mechanism in each domain is identified with the help of metallographic studies on the deformed samples. Optimum conditions for processing within the safe deformation domain are established.

11:10 AM

MELTING AND CASTING OF FeAl-BASED CAST ALLOYS: *V. K. Sikka*[1]; D. Wilkening[2]; J. Liebetrau[3]; B. Mackey[3]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA; [2]Columbia Falls Aluminium Company, Columbia Falls, Montana 59912 U.S.A.; [3]Anaconda Foundry Fabrication Company, Anaconda, Montana 59711 USA

The FeAl-based alloys are highly desirable for cast applications because of: (1) their lower density (approximately 25%) as opposed to commercial cast irons, and (2) resistant to corrosive environments such as sulfidation, carburization, oxidation, and molten salts. This paper will identify various applications of FeAl castings, melting and casting trials, properties, and microstructures. 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 Lockheed Martin Energy Research Corp.

11:30 AM

SUPERPLASTIC DEFORMATION IN COARSE-GRAINED FeAl-BASED ALLOYS: *Professor Jinn P. Chu*[1]; Mr. I. M. Liu[1]; Mr. J. H. Wu[1]; Professor W. Kai[1]; Professor K. Inoue[2]; [1]National Taiwan Ocean University, Institute of Materials Engineering, Keelung 202 Taiwan; [2]University of Washington, Dept. of Materials Sci. And Eng., Seattle, WA 98195 USA

Some intermetallics, such as Ni_3Si, Ni_3Al, Ti_3Al and TiAl, have been demonstrated to show superplasticity when they have fine grained structures. In contrast to that, we have recently found that coarse-grained iron aluminides also show similar superplastic behavior. This study is thus directed toward fundamental understanding of superplasticity in iron aluminides. Alloys under investigation include binary [Fe-17at.%Al, Fe-27at.%Al and Fe-35at.%Al] and ternary systems with additions of Cr, Zr, Si and Nb. Grain sizes of these alloys are found to change with the composition in a range between 50 and 850 microm. Results obtained have shown that the Fe-27Al sample can have a superplastic elongation of 180% at 1073 K and exhibits a sharp pinpoint

necking fracture. Microscopic cavitation is observed in fractured samples, revealing an important characteristic of superplasticity. In addition, a number of small recrystallized grains are also seen, which presumably is indicative of a dynamic recrystallization occurring during the tensile test. This paper will present detail observations and discuss the superplastic behavior of iron aluminides in light of such results obtained.

11:50 AM

HIGH-TEMPERATURE DEFORMATION BEHAVIOR OF Fe_3Al: *B. Voyzelle*[1]; J. D. Boyd[2]; [1]CANMET, Materials Technology Laboratories, Ottawa Canada; [2]Queen's University, Kingston, Ontario Canada

The high-temperature deformation behavior and workability have been determined for a single phase, ordered Fe_3Al alloy. The composition of the alloy (Fe-16.5Al-5.5Cr-2.0Mo-1.0Nb-0.005C) was one developed at the Oak Ridge National Laboratory. This alloy was tested in the as-cast condition and in the form of hot-rolled plus annealed plate. Compression tests were carried out over a range of temperatures (900 to 1200°C) and strain rates (10^{-3} to 10 s^{-1}). The flow stress data were analyzed to yield values of the following parameters over the range of processing conditions: (1) strain-rate sensitivity m, (2) true activation energy, and (3) instability parameter. The results are presented as deformation maps and workability maps to compare the two starting materials.

INTERNATIONAL SYMPOSIUM ON SULFIDE SMELTING '98: CURRENT AND FUTURE PRACTICES: Session V - Gas Handling and Sulfur Fixation

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 AM Room: 207
February 18, 1998 Location: Convention Center

Session Chairs: Tony Eltringham, BHP Copper, San Francisco, CA 94104-1020; Theo Lehner, Boliden Mineral AB, Rönnskär Smelter, Skelleftehamn S93281 Sweden

8:30 AM

PROCESS OFF-GAS COOLING DESIGN CONSIDERATIONS: *Paykan Safe*[1]; [1]Goodfellows Consultants Texas, Inc., Irving, TX 75062

This paper intends to discuss various process off-gas cooling options available for sulfide smelting processes. Advantages and disadvantages of each alternative are discussed along with the selection criteria for a reliable and cost effective system. Several case studies are presented to demonstrate typical problems with smelter off-gas handling systems and to outline the approach for the system upgrade.

8:55 AM

GAS FLOW AND COOLING IN WASTE-HEAT BOILERS IN THE OUTOKUMPU FLASH SMELTING PROCESS: *Y. Yang*[1]; A. Jokilaakso[1]; J. Järvi[1]; P. Mäkelä[1]; [1]Helsinki University of Technology, Laboratory of Materials Processing and Powder Metallurgy, HUT FIN-02015 Finland

Gas flow and heat transfer phenomena in two industrial-scale waste-heat boilers of the Outokumpu copper flash smelting process were analyzed with a commercial computational fluid-dynamics package Phoenics. Various operating conditions were simulated for the first boiler and particularly for the second boiler. The gas flow pattern was compared qualitatively with the laboratory physical models, and the general flow pattern was consistent with the laboratory visualization. The heat transfer simulation was validated with temperature measurements for both boilers, and good agreement was reached between the computed temperature profiles and the measured data. The computational results indicate that gas flow in both boilers is of three dimensional and re-circulating nature. Radiative heat transfer accounts for 80-95% of the total heat transported in the radiation sections of both boilers under different operating conditions. The CFD modeling proved to be a useful tool for numerical experiments and analysis of boiler dynamic performance for process optimization.

9:20 AM

DESIGN AND OPERATION OF A NOVEL GAS COOLER FOR REFIMET COPPER SMELTER, LA NEGRA, CHILE: *Tim. J. A. Smith*[1]; Rolando Campos[2]; Sergio Miranda M.[2]; Sergio Jara[2]; [1]Kilborn SNC-Lavalin Europe Limited , Melrose House, Croydon, Surrey CR0 2NE United Kingdom; [2]Fundicion Refimet S.A., Antofagasta Chile

Fundicion Refrimet S.A. have operated a custom copper smelter near Antofagasta in Northern Chile since 1993. Based initially on reverbatory furnace smelting and Peirce-Smith converting, the plant was expanded from 90,000 tones per year to 160,000 tones per year copper production in early 1997 by conversion to oxy-fuel smelting and use of concentrate injection. As part of this expansion, a novel gas cooling and cleaning system was developed and designed by Kilborn SNC-Lavalin Europe, the London, United Kingdom based mining and metals office of Canada's SNC-Lavalin Group. The reverbatory smelting furnace gas cooler needed to satisfy several very specific requirements including low cost, flexibility, robustness, and simplicity of operation. Of particular importance was the requirement to cool and clean the oxy-fuel reverbatory furnace gases and render them suitable for subsequent treatment in a conventional sulfuric acid plant. Of particular importance was the avoidance of accretions or dust handling problems. This paper describes the key design features and subsequent successful installation, commissioning, and operation of the unit.

9:45 AM Coffee Break in Exhibit Hall

9:55 AM

WET SULFURIC ACID - PROFITING FROM AN ENVIRONMENTAL SOLUTION: *Mike Brahan*[1]; [1]Haldor Topsoe, Inc., Houston, TX 77058

With the new SO2 emissions regulations for smelting operations imminent, all metal production operations have to take another look at their sulfur handling. The Haldor Topsoe Wet Sulfuric Acid Process provides a simple way to handle a wide variety of gas strengths with low labor requirements. The production of clean sulfuric acid at usable (or salable) strengths offers smelters an opportunity for a good return on investment for cleaning up an environmental problem. Our paper will review a typical WSA process flow scheme in metallurgical use and discuss expected economics.

10:20 AM

A REVIEW OF RECENT DEVELOPMENTS IN PARTICULATE CONTROL IN THE COPPER AND NICKEL INDUSTRY: *E. Sampath (Sam) Kumar*[1]; Adel Mansour[1]; [1]FLS miljø, Inc., Houston, TX 77067-3611

In this paper, we review the modern particulate emission requirements in copper and nickel industries and the technologies used to achieve them. Particulate control technologies such as dry electrostatic precipitators and baghouses will be reviewed for smelter applica-

tions. Also discussed will be the use of wet ESPs for sulfuric acid mist collection from acid plants. The evolution of wet ESP designs over the past two decades will also be presented. Case studies of operating experience with these technologies will be discussed in addition to the implications for potentially tight future control requirements.

10:45 AM

POLLUTION TO POWER: A CASE STUDY OF THE KENNECOTT SULFURIC ACID PLANT: *R. Michael Fries*[1]; David L. Randolph[1]; Robert W. Grendel[1]; Steven M. Puricelli[1]; [1]Monsanto Enviro-Chem Systems, Chesterfield, MO 63017

Sulphuric acid plants associated with smelters, have historically been an overworked and often neglected pollution control device. It could do little more than manage the wide fluctuations in gas flow and SO2 strength from the smelter. With the introduction of flash smelting, the picture began to change, but the fluctuating batch converters continued to dictate acid plant design. More recently, the commercial use of continuous converting processes has dramatically upgraded the SO2 strength and stabilized the gas flow to the acid plant. The SO2 gas now issues continuously and at concentrations that allow for compact and cost effective acid plants. Relieved of the burden of excessive dilution air, the heats of reaction can also be recovered as medium pressure steam and used to drive a generator, making the acid plant a net producer of power and a valuable asset to the balance sheets. This concept was put into practice at the Kennecott Utah Copper Corporation smelter, located in Salt Lake City, Utah. The accompanying acid plant, which was commissioned in May of 1995, is a sophisticated, low environmental impact, energy producing plant, worthy of review. This paper will examine the unique features of this acid plant, such as controlling its tail gas, by catalysis alone, to an environmentally-friendly 100 ppm of SO2 while feeding the converter with an efficient 14% SO2. The acid plant is also a prudent steward of energy resources, recovering 220.000 lb/hr of 140 psig steam from process heat, which is used to generate a substantial 20 MW of gross power. Also discussed will be some of the ongoing issues, such as handling of selenium and fluorine in the gas cleaning sections as well as a report on the findings following the first major plant turnaround in May of 1997. Today's modern acid plants, by necessity, are becoming a producer of quality, valuable products, making the acid plant an asset and not a liability. Plants like Kennecott are already gaining wider acceptance and are expected to be the vision of the future.

11:10 AM

BIOPROCESS TECHNOLOGY FOR THE TREATMENT OF ACID PLANT BLOW DOWN STREAMS: *André L. de Vegt*[1]; Cees J. Buisman[2]; [1]Paques, Inc., Exton, PA ; [2]Paques Bio Systems B.V., 8560 AB Balk, The Netherlands

Paques has developed and installed metal and sulfate removal systems. A Paques biological treatment system has been in operation at a zinc refinery since May 1992 treating a ground water flow of 5000 m3/d (1.3 MGD). Sulfate is reduced to below 200 mg/l, while metal removals exceed 99%. Using the same principles, acid plant blow down streams and off-gases can be treated by converting sulfates and SO2 to metal sulfides and/or elemental sulfur. The principle of the biotechnological methods, full scale experience and results of on site test programs will be presented.

11:35 AM

METALLURGICAL GAS CLEANING EFFLUENT DECONTAMINATION AND ACID RECOVERY: *D. W. Lawler*[1]; C. M. Evans[1]; E. G. C. Lyne[1]; J. Thompson[1]; [1]Kvaerner Chemetics, Inc., Vancouver B. C. Canada

Prior to the manufacture of sulphuric acid in metallurgical or regeneration plants, the SO2-rich gas from the smelter, roaster, or furnace must be cleaned to remove particulates, volatile contaminants, SO3, and water. Cleaning is accomplished by contacting the gas with cooled weak acid. The system is designed so that all the contaminants originally in the gas report to the weak acid, which then becomes an effluent from the plant. Historically, the entire weak acid effluent stream has been treated for disposal, with no attempt to recycle or recover any part of it. This is becoming increasingly environmentally unacceptable, and operators must consider better methods of treatment and recovery. In this paper, Kvaerner Chemetics will discuss a number of options that allow the contaminants to be separated from the acid value. This will result in an acid byproduct that can be sold or used elsewhere, and will minimize the volume of hazardous byproducts that must be discharged.

INTERNATIONAL SYMPOSIUM ON VALUE ADDITION METALLURGY: Session V - Powders

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee

Program Organizers: W.D. Cho, University of Utah, Dept. of Metallurgical Eng., Salt Lake City, UT 84112; H.Y. Sohn, University of Utah, Dept. of Metallurgical Eng., Salt Lake City, UT 84112

Wednesday AM Room: 208
February 18, 1998 Location: Convention Center

Session Chairs: W. D. Cho, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA, P. R. Taylor, University of Idaho, Metallurgical and Mining Engineering, Moscow, ID 83844 USA

8:30 AM

THE METAL INJECTION MOLDING OF THE NANOSTRUCTURED W-CU POWDER PREPARED BY MECHANICAL ALLOYING: *I. H. Moon*[1]; J. C. Kim[1]; S. S. Ryu[1]; H. Lee[1]; Y. D. Kim[1]; [1]; [1]Hanyang University, Department of Materials Eng., Seoul 133-791 Korea

Recently, W-Cu alloy becomes one of the very important candiate materials for heat sink and packaging in the field of microelectronics due to its good thermal properties. The metal injection molding of W-Cu powder can satisfy the requirement for mass production of complex shaped parts in semiconductor devices. In the present study, an investigation was carried out on the possibility whether the MIM could be applied to the compacting process of nanostructured W-Cu powder prepared by mechanical alloying. The multi component binder system of 45PW+15BW+30PE+10SA was proven to be suitable one for the MIM of the W-Cu composite powders by adopting the debinding cycles of multi stage in N_20 and H_2 atmospheres. The other process conditions for the MIM of this nanostructured W W-Cu composite powder were also studied. The MIM debinding part of W-30wt%Cu was sintered to the relative density more than 96% by sintering at 1200°C for 1 hour in H_2 atmosphere. Some properties of W-Cu sintered part was analyzed in order to evaluate its performance for the microelectronic device material.

9:00 AM

PLASMA SYNTHESIS OF NANO-SIZED METALLIC POWDERS USING A DE-LAVAL NOZZLE FOR QUENCH: *Patrick R. Taylor*[1]; Wenxian Zhu [1]; [1]University of Idaho, Laboratory Metallurgical & Mining Engineering Department , Moscow, ID 83844

The small dimensions of nano-sized materials leads to novel and enhanced mechanical and physical properties. For the formation of nanometer sized metal particulates, a thermal plasma reactor has been developed in this plasma laboratory. In the reactor system, a supersonic nozzle and a powder filter were designed and used. By vaporizing coarse metal powders in the plasma flame, and quenching the metal vapors in the nozzle at the rate of 107 K/sec, nanometric sized powders have been produced. The powders were collected in the secondary quench and air-tight filter system. The particle size of the product power is 5 ~ 20 nanometers, obtained through TEM analysis. The XRD analysis showed that the powder had no air contamination after the filter was

handled in an inert atmosphere glove box. The product powder recovery was improved by using the quench nozzle and the newly designed powder filter. For the supersonic nozzle flow, a mathematical model has been developed in order to describe the velocity and temperature fields, to understand the condensation process and to estimate the quench rates.

9:30 AM

PRODUCTION OF SINGLE-PHASE Nd2Fe14B ALLOY POWDER BY REDUCTION-DIFFUSION PROCESS AND APPLICATION TO PRODUCTION OF Nd-Fe-B SINTERED MAGNETS: *Mr. Kaname Takeya*[1]; Mr. Katsuya Kase[1]; Yoshiyuki Asakawa[2]; Kenji Ohmori[2]; [1]Sumitomo Matal Mining Co., Niihama Research Laboratories , Niihama, Ehime 792 Japan; [2]Sumitomo Metal Mining Co., Central Research Lab., Chiba 272 Japan

The Reduction-Diffusion Process (the R-D process) using Ca as a reducing agent, has been practiced in industry in the production of the SmCo5 type, the Nd-Fe-B type and the Tb-Fe-Co type magnetic materials. The advantages of the R-D process are the generally high yield of rare earth metals and the single-stage conversion of a mixture of oxides and metal powders into a product of rare earth alloy powders. On the other hand, one of its disadvantages is the slightly high content of oxygen and calcium. This disadvantage is remarkable in the Nd-Fe-B type. Singe-phase Nd2Fe14B alloy powder of low content of oxygen and calcium, is obtained by choosing appropriate raw materials and performing the R-D process in a controlled way. And this alloy powder is useful for the application to the production of Nd-Fe-B sintered magnets.

10:00 AM Coffee Break in Exhibit Hall

10:10 AM

ULTRA FINE BORON NITRIDE (BN) POWDER SYNTHESIS IN A NON-TRANSFERRED ARC PLASMA REACTOR: *Patrick R. Taylor*[1]; Xuema Li[1]; Wenxian Zhu[1]; [1]University of Idaho, Department of Metallurgical & Mining Engineering, Moscow, Idaho 83844-3024

Experiments were performed in a non-transferred arc, thermal plasma flow reactor to investigate the synthesis of ultra fine boron nitride (BN) powder from the reaction system of boron oxide (B203), methane (CH4), ammonia (NH3) and hydrogen (H2). Argon (Ar) and nitrogen (N2) were used as plasma gas. The thermodynamics and kinetics of the synthesis reactions were examined and a chemical reaction mechanism was proposed. The powders produced under certain operationing conditions had high purity and good conversions. All the products were extremely fine powders (< 30nm) and were uniform in size distribution. The powder products were analyzed by chemical and physical characterization. The effects of the reaction variables on the conversions from B203 to BN and the purity of the products were investigated.

10:40 AM

SYNTHESIS OF Al203-SiC-TIC COMPOSITE POWDER FROM SILICA BY SELF PROPAGATING HIGH TEMPERATURE OF SYNTHESIS METHOD: *Won Chang Whan*[1]; Cho Seong Seog[1]; Lee Hong Ro[1]; Chun Byong Sun[1]; [1]Chungnam National University, Rapidly Solidified Material Research Center, Taejon City 305-764 Korea

Al203-SiC-TiC powder was made by Self Propagating High Temperature of Synthesis in the system of SiO2/TiO2/Al/C reaction. The combustion reaction of SiO2/Al/C system is not possible due to the low exorthermic reaction. TiO2 was added in this system for the combustion reaction. The experimental results for the synthesis of Al203-SiC-TiO2 composite powder by SHS are summarized as follows; 1) Optimum mole ratio for the synthesis of Al203-SiC-TiC composite powder is SiO2;TiO2;Al;C=3.0;2.0;8.0;6.0 mole ratio. 2) Combustion temperature is increased with increasing of TiO2 and alumnium mole ratio and compaction pressure. On the other hand, propagation rate is increased with increasing of TiO2 and alumnium mole ratio and decreasing of compaction pressure. Combustion temperature and propagation rate are not affected by the addition of carbon. 3) The synthesized Al203-SiC-TiC composite powder have an spherical shape and the size of particle having submicrometer is increased with increasing of compaction pressure. 4) Al203-SiC-TiC composite powder produced is higher purity than reactants due to the evaporation of impurities during exorthermic reaction of SHS.

11:10 AM

SYNTHESIS OF MULTICOMPONENT POWDERS CONTAINING RARE EARTHS USING AQUEOUS PROCESSING: *Mikio Kobayashi*[1]; Yoshihiro Nishisu[1]; Kazuya Koyama[1]; Mikiya Tanaka[1]; [1]National Institute for Resources and Environment, Materials Processing Department, Tsukuba-shi 305 Japan

Preparation of multicomponent powders are very useful and important for producing the materials with complicated and homogeneous structure. Therefore multicomponent powders have a lot of attention in the field of advanced value-added materials. The aqueous processing in hydrometallurgy has a broad potential for producing multicomponent homogeneous precipitates. Furthermore the aqueous processing has a future potential for integrating the separation, precipitation and synthesis processes. In this presentation the precipitation from homogeneous solution including rare-earths and/or common metals is presented. These precipitates probably consist of almost monodispersed, multicomponent and spherical particles by precisely controlling several reaction factors, reaction temperature, concentrations of starting materials, pH and so on. The separation of the nucleation stage and the growth stage of the particles is very important and how to control the reaction factors to realize enough separation is discussed. In this presentation the systems of Y-Eu-O, Y-Fe-O and Y-Al-O are mainly presented. In addition the precipitation-stripping method from organic phase is presented focusing the synthesis of multicomponent powders of Ni-La-O system. These precipitates have multicomponents homogeneously and so they are converted to multicomponent ceramic powders by calcination. They are important compounds as phospor, optomagnetic materials, optical materials, hydrogen storage alloy or as the related precursors. In this presentation some characterization of these particulate materials is included.

MATERIALS ISSUES IN MICROELECTRONICS: INTERFACIAL REACTIONS, SOLID STATE TRANSFORMATIONS & THERMAL MANAGEMENT: INTERFACIAL REACTIONS AND THERMAL MANAGEMENT III

Sponsored by: Electronic, Magnetic & Photonic Materials Division, Electronic Packaging and Interconnection Materials Committee

Program Organizers: Michael R. Notis, Lehigh University, Dept of Materials Science, Bethlehem, PA 18015; Gautam Ghosh, Northwestern University, Dept. of Materials Science, Evanston, IL 60208-3108; Sung Kang, IBM, TJ Watson Research Center, Yorktown Heights, NY 10598

Wednesday AM Room: Centro D
February 18, 1998 Location: Convention Center

Session Chair: Gautam Ghosh, Northwestern University, Dept. Mater. Sci. Eng., Evanston, IL 60208-3108

8:30 AM INVITED

SILICIDE INTERFACES IN SILICON TECHNOLOGY: *Dr. Francois M. d'Heurle*[1]; [1]IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598 USA

There are many different types of interfaces in the silicides that are used or might be used in integrated circuit technology. They are important both from metallurgical and an electrical point of view. The purpose of the first silicide used in silicon technology, PtSi, was the formation of ohmic and rectifying contacts, where the silicide-silicon

interface plays a fundamental role. That interface plays also a major role in the fabrication of some devices where the desired single crystal silicides, e.g. β-$FeSi_2$, are obtained via epitaxy with underlying silicon. Epitaxy with (111) Si causes thin layers of NiSi to assume a metastable form. In some silicides that undergo allotropic transformations as in cobalt, the density of twins and stacking faults tend towards infinity, which strongly affects the resistivity of the compound, as in WSi_2. Grain boundaries play a dominant role in the growth of silicide layers formed by solid state reactions; and they provide unwanted short circuit paths for dopant diffusion along silicide conductors. As in all thin films exposed to high temperature, surface and interface tension cause silicide films to agglomerate. For the widely used $TiSi_2$, that can be nearly fatal, since nucleating its low resistivity phase requires increasingly high temperatures as the dimensions get reduced. Luckily, in the very recent past, it has been found that slight changes in composition and the resulting epitaxy of the low resistivity phase on another phase considerably reduces its "nucleation temperature".

9:00 AM INVITED

EFFECT OF RIPENING ON INTERMETALLIC COMPOUND FORMATION IN SOLDERING REACTIONS: *Dr. King-Ning Tu*[1]; Dr. H K Kim[2]; Dr. P. A. Totta[3]; [1]UCLA, Dept. Mater. Sci. Eng., Los Angeles, CA 90024-1595; [2]Samsung Corporation, Seoul Korea; [3]IBM, East Fishkill Facility, Hopewell Junction, NY 12533

During soldering reactions in electronic packaging, the Cu_6Sn_5 intermetallic compound formed between molten eutectic SnPb solder and the Cu film in the under-bump-metallization is not layer-like, rather it is scallop-like. The growth of these scallops is accompanied by ripening. The ripening can lead to spalling of the compound grains when the entire Cu film is consumed. The spalling weakens the solder interface and is a serious device reliability issue. In this talk, the morphology and kinetics of reactive ripening on Cu and Ni surfaces will be presented.

9:30 AM INVITED

METASTABLE AND EQUILIBRIUM WETTING STATES IN THE Bi-Sn SYSTEM: Dr. F. G. Yost[1]; Dr. E. J. O'Toole[1] [1]Sandia National Labs, Albuquerque, NM 187185-1411

Sessile drop experiments involving a variety of Bi-Sn alloys on solid Bi substrates were performed. Substrates prepared from small and large-grained polycrystals and single crystals were used to measure equilibrium and metastable contact angles and estimate the surface tension and equilibrium contact angle of the solid-liquid interface. The substrates were also used to investigate the coupling of the dissolution and wetting processes and to investigate the effect of substrate grain size on wetting. It was determined that the equilibrium wetting geometry is independent of linear scale and that grain size has little influence on wetting or dissolution in the Bi-Sn system.

10:00 AM Coffee Break in Exhibit Hall

10:10 AM

WETTING RECATION ON FLAT AND GROOVED Cu SURFACES OF SnPb SOLDERS AS A FUNCTION OF LOW Sn CONCENTRATION: *Mr. C. Y. Liu*[1]; Dr. King-Ning Tu[1]; [1]UCLA, Mater. Sci. Eng., Los Angeles, CA 90095-1595

While pure Pb does not react with Cu to form compounds, it nevertheless wets a flat Cu surface with a wetting angle of 115°. Upon addition of 1 at.% Sn, 2 at.% Sn and so on into Pb, the wetting angle decreases dramatically with increasing Sn concentration in the solder. On a grooved Si surface coated with Cu film, the capillary force pulls the molten solder to wet the grooves, and the length of solder in the grooves again increases dramatically with Sn concentration in the solder. Morphology of the wetted grooves will be presented. A discussion on the driving force of wetting, whether it includes the free energy of compound formation or not, will be given.

10:30 AM INVITED

MODELING THE SOLID-STATE REACTIONS BETWEEN Sn-Pb SOLDER AND A POROUS SUBSTRATE COATING: *Dr. Paul T. Vianco*[1]; Dr. K. L. Erickson[1]; Dr. P. L. Hopkins[1]; [1]Sandia National Labs, Dept. 1831, Albuquerque, NM 87185-1411

Solder Joints in hybrid microelectronic circuit (HMC) electronics are formed between the solder alloy and the thick film conductor that has been printed and fired onto the ceramic. Although the noble metal conductors provide excellent solderability at the time of manufacture, they are susceptible to solid-state reactions with the Sn and/or In components of the solder. The reaction by-product is one or more intermetallic compounds (IMC). The formation of the IMC layer(s) can jeopardize the integrity of the joint as a consequence of their brittleness as well as by the consumption of the conductor layer in the course of the interaction. Unfortunately, IMC development in thick film conductors cannot be well predicted by simply applying the growth kinetics to an assumed one-dimensional layer geometry, because of the inherent porosity of such conductor films. A model was developed which predicts the consumption of a porous thick film conduction, based upon empirically derived reaction kinetics and the two-dimensional geometry of the porous substrate region. The model was applied to reaction couples formed between 63Sn-37Pb solder/100Au and 63Sn-37Pb/76Au-21Pt-3Pd. IMC growth kinetics expressions were derived from laboratory, isothermal aging experiments; the diffusion coefficients were derived from that data and served as input parameters for the model. Thick film consumption as a function of overall porosity as well as the pore size distribution were computed. Comparisons will be illustrate that will compare the extent of conductor loss under the more accurate two-dimensional model versus the simpler one-dimensional approximation. [1]Sandia is a multiprogram laboratory operated by Sandia Corporation, A Lockheed Martin Company, for the United States Dept. of Energy under contract DE-AC04-94AL85000.

11:00 AM INVITED

INTERMETALLIC COMPOUND GROWTH OF Sn/Pb, Sn/Ag, AND Sn SOLDERS ON Ni. Ni/Au, AND Ni/Pd SUBSTRATES: *Dr. Tsung-Yu Pan*[1]; Dr. Howard D. Blair[1]; Dr. John M. Nicholson[1]; Dr. Sung-Won Oh[1]; [1]Ford Motor Company, Ford Research Laboratory, Dearborn, MI 48121-2053

Intermetallic compounds formed at the interface between solder and substrate are natural products of good wetting. The formation of these intermetallics, although an inevitable result of the solder wetting mechanism, may cause mechanical problem at the solder joints because of the brittle nature of these intermetallics. This problem will be more pronounced when high-Sn Pb-free solders are applied because of higher processing temperatures than that required for typical eutectic Sn/Pb. The growth mechanism of the Ni_3Sn_4 intermetallic compound (IMC) during solid state aging for three different solders: 100Sn, 96.5Sn-3.5Ag, and 63Sn-37Pb solders on Ni, Ni/Au, and Ni/Pd substrates were examined in this study. Aging were conducted at 75, 100, 125 and 160°C for up to 36 days to study the IMC growth. The microstructure was studied by scanning electron microscopy. A mechanism to explain the process of the intermetallic compound growth will be discussed. At the end of the 36 day aging test, the metallographic examination revealed cracks and separation in the Ni_3Sn_4 IMC layer, which may account for the mechanical degradation of solder joints often encountered after thermal cycling.

11:30 AM INVITED

MODELING INTERMEDIATE PHASE GROWTH IN SOLID-LIQUID INTERDIFFUSION COUPLES: Dr. M. Schaefer[1]; *Dr. R. A. Fournelle*[1]; Dr. Jin Liang[2]; [1]Marquette University, Materials Science Program, Milwaukee, WI 53201; [2]Rockwell Automation, Milwaukee, WI 53204-2496

Kinetics of phase formation during interdiffusion in solid-liquid diffusion couples are influenced by the morphology of the intermediate compound layer. In some cases an intermediate compound layer is formed which has very fine grain size. This condition favors grain boundary diffusion as the predominant mechanism for transport through the layer. In systems where grain coarsening occurs the coarsening kinetics will influence the interdiffusion kinetics. In addition, for some solid-liquid systems, a grain boundary wetting effect is observed which leads to a highly non-uniform layer thickness; the layer is thinner where the liquid phase wets the grain boundaries. As a consequence of the wetting effects the diffusion path through the layer is shorter along the grain boundaries. This differs from standard interdiffusion models, which assume that the diffusion distance is equal to the average layer

thickness. A model for growth kinetics of an intermediate compound layer is presented for the case where grain boundary diffusion is the predominant transport mechanism. The model includes the geometric effects caused by grain boundary wetting. Two limiting cases are considered: first, when the relevant grain size is constant and second, when the grain size coarsens with increasing layer growth. Comparison between experimental data and model predictions are included for molten tin-lead solder on copper.

MATERIALS SCIENCE OF CHEMICAL-MECHANICAL PLANARIZATION: Session I

Sponsored by: Jt. Electronic, Magnetic and Photonic Materials Division, ASM International: Materials Science Critical Technology Sector, 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 AM Room: 104
February 18, 1998 Location: Convention Center

Session Chairs: Krishna Rajan, Rensselaer Polytechnic Inst., Troy, NY 12180-3590; T. Bibby, IPEC Planar, Phoenix, AZ 85034

8:30 AM Welcome and Introductory Remarks

8:35 AM
UTILIZATION OF CHEMICAL MECHANICAL PLANARIZATION IN DRAM MANUFACTURING: *John H. Givens*[1]; K. M. Robinson[1]; S. Meikle[1]; [1]Micron Technology, Inc., M/S 306, Boise, ID 83707-0006

The scaling of integrated circuit technology has required continual advancements in materials, processes and applied methodologies. As device critical dimensions approach sub-0.25 mm, the challenges associated with the minimization of surface topology and its integrated effects on photolithography and dry etch technologies has become increasingly apparent. To this end, chemical mechanical planarization has become process of choice. Since 1985, CMOS manufacturing has been exploiting Chemical Mechanical Polishing (CMP) for its local and global planarization capability. CMP has been shown to have the ability to minimize topography, reduce surface defects, minimize prior-level effects, and provide process enablement due to its material removal selectivity, among other advantages. The art and now science of CMP has evolved such that it is pervasive in both the manufacturing of the silicon devices (FEOL) and their subsequent wiring circuitry (BEOL). This paper will present several applications of CMP in DRAM manufacturing and discuss problematic difficulties associated with current CMP process technology.

9:05 AM
PROPERTIES AND CHARACTERIZATION OF OXIDE FILMS: IMPLICATIONS FOR CHEM-MECHANICAL PLANARIZATION: *Krishna Rajan*[1]; Rajiv Singh[2]; [1]Rensselaer Polytechnic Institute, Materials Science & Engineering Dept., Troy, NY 12180-3590; [2]University of Florida, Department of Materials Science & Engineering, Gainesville, FL 32611-2066

In this paper we outline a critical review of the mechanical behavior of oxide films and the response of oxide films and surfaces to chemical and mechanical forces. The behavior is discussed in the context of FTIR studies of chem-mechanically polished oxide films. Issues such as hydration effects, plasticity and crack growth are explored in the unique context of chemical-mechanical planarization.

9:25 AM
ANALYSIS OF FLOW BETWEEN WAFER AND PAD DURING CMP PROCESSES: C. Rogers[1]; L. Racz[1]; *Jonathan Coppeta*[1]; C. Duska[1]; *D. Bramono*[1]; [1]Tufts University, Department of Mechanical Engineering, Medford, MA 02155

In this paper we will apply several diagnostics techniques on a modified table top polisher to characterize the flow between the wafer and pad during CMP processes. The diagnostic techniques include dual emission laser induced florescence (DELIF), numerical simulation, as well as standard polishing diagnostics such as removal rates and non-uniformity. DELIF is used (with a glass wafer) to quantify parameters such as slurry transport beneath the wafer, pad slurry carrying capacity, fluid film thickness beneath the wafer, and thermal gradients across the wafer. A numerical model of the CMP processes will be developed to corroborate the experimental results and provide additional insight and data on the fluid physics. Finally, both the experimental and numerical simulation results are used to predict optimum polishing conditions and these conditions are implemented to compare predicted and actual removal rate and non-uniformity trends.

9:55 AM
SURFACE INTERACTION FORCES IN METAL AND OXIDE CMP: J. Adler[1]; U. Mahajan[1]; Y. Rabinovich[1]; R. Singh[1]; B. Moudgil[1]; V. Bucknell[2]; Y. -C. Chen[2]; *Krishna Rajan*[2]; [1]University of Florida, Department of Materials Science & Engineering, Gainesville, FL 32611-2066; [2]Rensselare Polytechnic Institute, Materials Science & Engineering Dept., Troy, NY 12180-3590

Atomic force microscopy provides a powerful means of understanding and monitoring surface forces in solids. In this presentation, we present results of a study examining the effect of surface fluid chemistry on the particle-surface interactions. The relative effects of molality and pH are studied both for oxide/oxide interactions as well as metal/oxide interactions. The results are examined in the context of silica and tungsten polishing.

10:15 AM
NEW SYNTHESIS APPROACHES OF SUSPENSIONS, SLURRIES AND POWDERS FOR CHEM-MECHANICAL PLANARIZATION: *John G. Darab*[1]; [1]Pacific Northwest National Laboratory, Richland, WA 99352

A wide range of ultra-fine, nano-crystalline, single and multi-component oxide/oxyhydroxide powders have been produced using a novel, continuous, flow-through hydrothermal technology developed at the Pacific Northwest National Laboratory. The process, termed Rapid Thermal Decomposition of precursors in Solution (RTDS), converts aqueous feedstock solutions containing, for example, metal nitrate salts and other thermally activated reactants into suspensions or slurries of nano-crystals (diameters of generally less than 10-nm) by continuous flow through a heated, high pressure reaction pipe (typically, 250-350°C, 6000-8000 psi). Flow at pressure is maintained using a nozzle at the down-stream end of the reaction pipe. Crystallite formation occurs during the solution's brief residence time (<30 seconds) in the reaction pipe, not during pressure/temperature let down as it passes through the nozzle. Control of crystalline phase, degree of nano-crystal aggregation, and in some cases, particle morphology can be tailored by selecting the appropriate feed chemistry and processing conditions. The RTDS processing and characterization of nano-crystalline zirconium-, and titanium based oxide and oxhydroxide particulates will be presented. *Pacific Northwest National Laboratory is operated for the United States Department of Energy by the Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

10:45 AM
IN-PROCESS DETECTION OF MICRO-SCRATCHING DURING CMP USING ACOUSTIC EMISSION SENSING TECHNOLOGY: Jianshe Tang[1]; *David Dornfeld*[1]; Suzette K. Pangrle[2]; Alvin Dangca[2]; [1]University of California at Berkeley, Department of Mechanical Engineering, Berkeley, CA 94720-1740, CA 94720-1740; [2]Advanced Micro Devices, Inc., Integrated Technology Division, Sunnyvale, CA 94086

By microelectronic fabrication standards, CMP is an inherently dirty process and leaves micro defects, such as residual slurry, particles,

pits and micro-scratches on the polished wafer surface. Some of the defects can be removed by post CMP cleaning. But defects like micro-scratches, can not be recovered by simply cleaning the wafer and therefore should be especially addressed for the purpose of increasing chip yields. The micro-scratch generation mechanisms are very complex. Both CMP process parameters and slurry contamination can have significant influences on micro-scratch occurring. Another scratch source is due to large particles dislodged from the conditioning wheel during pad conditioning. Micro-scratches can fill with metal and cause puddles and slivers that lead to circuit shorts. Therefore prediction or early detection of a micro-scratch is an important research topic from the viewpoint of industry application of CMP technology in IC fabrication. An experimental investigation of the correlation between the micro-scratches and the signal characteristics of acoustic emission generated during chemical mechanical planarization (CMP) has been performed. We have found that AE signals are sensitive to microscratching. The implications of these results for the development of an in-process scratch detection technique for CMP planarization is discussed.

11:15 AM

ABSTRACT TITLE NOT AVAILABLE: *M. A. Fury*[1]; [1]Allied Signal, Abstract not available.

MICROSTRUCTURE AND ITS EFFECTS ON AMORPHOUS NANOPHASE & NANOCRYSTALLINE MATERIALS: Session V - Performance at Elevated Temperatures

Sponsored by: ASM International: Materials Science Critical Technology Sector, Flow and Fracture Committee, Jt. Electronic, Magnetic and Photonic Materials Division/Structural Materials Division, Alloy Phases Committee, Chemistry and Physics of Materials Committee, Structural Materials Division, Physical Metallurgical 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 AM Room: 205
February 18, 1998 Location: Convention Center

Session Chairs: Derek O. Northwood, Ryerson Polytechnic University, Faculty of Engineering and Applied Science, Toronto, Ontario M5B 2K3 Canada; Helena Van Swygenhoven, Paul Scherrer Institute, Villigen Ch-5232 Switzerland

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8:30 AM Opening Remarks

8:40 AM INVITED

OXIDATION OF NANOCRYSTALLINE ALUMINUM: VARIABLE CHARGE MOLECULAR DYNAMICS ON PARALLEL COMPUTERS: *Shuji Ogata*[1]; Timothy J. Campbell[2]; [1]Yamaguchi University, Department of Applied Sciences, 2557 Tokiwadai Ube 755 JAPAN; [2]Louisiana State University, Concurrent Computing Laboratory for Materials Simulations, Department of Physics and Astronomy, Department of Computer Science, Baton Rouge, LA 70803-4001

Oxidation of Al nanoclusters placed in gaseous oxygen is investigated by performing molecular-dynamics simulations on parallel computers. The simulations take into account the effect of dynamic charge-transfer between Al and O using the electronegativity equalization scheme. The resulting long-range Coulomb interaction is calculated efficiently with the fast-multipole method. In the case of relatively small Al cluster (N_Al - 2000), we find that the oxygen atoms diffuse toward the center of the Al cluster with the final cluster configuration showing faceting. The oxidation of a 250,000-particle aluminum cluster in the presence of 550,000 oxygen atoms is also examined. Results for temperature and charge distributions, bond lengths and bond angles, and diffusivities of Al and O will be presented. The oxidation of nanocrystalline Al will be elucidated through a video. This work is supported by NSF, DOE, AFOSR, ARO, PRF, and Louisiana LEQSF.

9:20 AM

HIGH TEMPERATURE MECHANICAL BEHAVIOR OF NANOCRYSTALLINE MATERIALS: *R. S. Mishra*[1]; A. K. Mukherjee[1]; [1]University of California, Department of Chemical Engineering and Materials Science, Davis, CA 95616

Nanocrystalline materials provide an opportunity to extend the understanding of grain size dependent phenomenon to a much finer scale. At some critical grain size the defect generation and movement are likely to change fundamentally. The question is; "How small is small?" In this study we have addressed this question for superplasticity and creep. Some new results of intermediate temperature tensile tests of nanocrystalline metals, alloys and intermetallics indicate that dislocation plasticity in these materials are quite different from microcrystalline materials. These results are compared with theoretical expectations. This investigation is supported by NSF-DMR-9630881.

9:40 AM

SUPERPLASTIC NET-SHAPE FORMING OF NANOCRYSTALLINE ZIRCONIA TOUGHENED ALUMINA (ZTA): *J. Wittenauer*[1]; F. Batllo[2]; J. Romano[2]; [1]Lockheed Martin Missiles & Spaces Co., Palo Alto, CA 94304-1191; [2]Nanophase Technologies Corporation, Burr Ridge, IL 60521

Advances in the field of ceramic superplastic forming in conjunction with the availability of low cost nanocrystalline powders in the past decade have allowed to consider an adaptation of the technique from a research operation to an economically viable commercial production tool. Superplastic forming exploits the ability of nanometer size ceramic grains to physically slide past each other when the material is submitted to mechanical constraint at high temperature. In selected applications, superplastic forming offers an attractive alternative to conventional ceramic processing. Advantages of the technique include: lower capital investment cost and higher throughput. A description of the superplastic forming process and results obtained with the technique are presented.

10:00 AM

RELATING MECHANICAL MILLING TO AMORPHIZATION IN A BULK TITANIUM SOLID SOLUTION : *Dr. Dongjian Li*[1]; Mr. Kevin J. Doherty[1]; Dr. Joseph Poon[1]; Dr. Gary J. Shiflet[1]; [1]University of Virginia, Department of Physics, Charlottesville, VA 22903 USA

Large ingots of partially amorphous titanium alloys were developed via annealing of a bcc supersaturated solid solution (beta). TEM observation of the annealed alloy showed nanoscale amorphous regions coexisting with a modulated structure which was identified as resulting from a spinodal transformation. In order to understand the effect of the alloy composition on the relative stability of the beta phase, mechanical milling (MM) was employed to determine the relationship between the critical time for complete amorphization and the composition. The MM critical time is believed to be related to the free energy difference between the two phases. A minimum is found in the milling time to amorphization versus composition of the alloy which corresponds to the composition for destabilization and partial amorphization of the beta phase by annealing. Thus, MM supplies an experimental criterion for spontaneous amorphization of solid solutions.

10:20 AM

DYNAMIC MECHANICAL PROPERTIES OF NEAR NANO ALUMINUM ALLOY PROCESSED BY EQUAL CHANNEL ANGULAR EXTRUSION: *T. Mukai*[1]; M. Kawazoe[2]; K. Higashi[3]; [1]Osaka Municipal Technical Research Institute, Osaka 536 Japan; [2]YKK Corporation, Sendai Institute of Material Science and Technology, Tomiya, Miyagi, 981-33 Japan; [3]Osaka Prefecture University, College of Engi-

neering, Department of Mechanical Systems Engineering, Sakai, Osaka 593 Japan

Recently a method for preparing materials with suitably homogeneous microstructure is the new technology of equal-channel-angular-extrusion (ECAE) process. This new technology has some possibilities to permit important contributions to be made for homogenization and process optimization of the common materials produced from the ingot metallurgy. It may provide the same type of mechanical mixing as in mechanical alloying, but without the difficulties associated with powder handling and consolidation and also high production costs. In this technique, a submicron-grained structure can be easily obtained by heavy shear strains at low operated temperatures. Microstructure of 5056 Al-Mg alloy is refined dramatically by ECAE process. Tensile properties at room temperature in the ECAE processed 5056 Al-Mg alloy (5056-ECAE) are characterized as a function of strain rate. Total elongation of 5056-ECAE increases with strain rate as well as some fully annealed Al-Mg alloys. Yield stress (YS) and ultimate tensile strength (UTS) of 5056-ECAE exhibit remarkably higher value than those of fully annealed 5056 alloy (5056-O). UTS of 5056-ECAE is a weak function of strain rate comparing with 5056-O. Change in the strain rate sensitivity is caused by the mobility of dislocations in the grains.

10:40 AM

AQUEOUS CORROSION STUDY OF MELT-SPUN NdFeB RIBBONS WITH TiC ADDITIONS: *M. Arenas*[1]; G. W. Warren[1]; C. P. Li[2]; K. W. Dennis[2]; R. W. McCallum[2]; [1]University of Alabama, Dept. of Metallurgical & Materials Engineering, Tuscaloosa, AL 35487; [2]Iowa State University, Dept. of Materials Sci. & Engineering, Ames, IA 50011

A corrosion study of NdFeB ribbons produced by melt spinning with and without titanium carbide additions has been undertaken. Such material is used for the production of bonded NdFeB permanent magnets. The samples tested were ribbons of different compositions and wheel speed. A microstructural study showed differences in grain size across the thickness of the ribbon. For instance, at a wheel speed of 12 m/s grain size ranges between 80 nm on the wheel surface to 500 nm on the free surface. Upon addition of TiC, the formation of amorphous and/or nanocrystalline material is enhanced resulting in (a) a partially crystalline microstructure with a much smaller grain size, - 50 nm at the wheel surface, and (b) a much smaller difference in grain size across the thickness. Since corrosion properties are dependent on microstructure, the corrosion behavior of the free surface and the wheel surface of the ribbons were measured and compared with those of near stoichometric, unalloyed NdFeB. Anodic polarization techniques in 0.9M Na2SO4 were used to determine the corrosion potential (Ecorr) and the corrosion current (icorr) which showed a much improved corrosion resistance for samples with TiC. Results indicate that the improved corrosion resistance is likely due to changes in microstructure resulting from the refined grain size and the presence of amorphous nanophase material.

11:00 AM INVITED

STRUCTURE, STRENGTH, AND PLASTICITY OF ALLOYS IN AMORPHOUS AND NANOCRYSTALLINE STATES: *N. I. Noskova*[1]; [1]Russian Academy of Sciences, Institute of Metal Physics, Ural Division, Ekaterinburg 620219 Russia

Ribbon samples of Fe, Co and Pd-based alloys in nanocrystalline(nanophase) state was obtained by crystallization of amorphous states at various temperatures (625 - 923 K) after holding for various times. The microstructure of the nanocrystalline alloys was studied “in situ” at different stages of crystallization of the amorphous ribbons in the column of an electron microscope. High-resolution trans-mission electron microscopy was used to study the structure of nanophase crystals and their interfaces in multiphase nanocrystalline alloys. Ribbon samples of alloys in amorphous and nanocrystalline states were tested for strength and plasticity under conditions of high-rate stretching and for creep behavior (at 293-823 K). The temperature variation of strength and plasticity was studied. Analyses of the mechanical properties of nanocrystalline alloys are tested of the suitable dislocation, disclination and diffusion concepts.

11:40 AM

EFFECTS OF ANNEALING TREATMENTS ON THE DEFORMATION AND FRACTURE OF BULK METALLIC GLASS: *L. Ludrosky*[1]; A. Peker[2]; J. J. Lewandowski[1]; [1]Case Western Reserve University, Dept. Matl’s Sci. and Eng., Cleveland, OH 44106; [2]ATI, Inc., Laguna Niguel, CA

Bulk metallic glass materials based on the Zr-Ti-Cu-Ni-Be system have been tested after various annealing treatments in order to determine the effects of such heat treatments on the strength and toughness of such materials. Microhardness testing was additionally conducted over a range of test temperatures on the as-received amorphous materials, while x-ray diffraction was conducted to determine the effects of changes in structure on the resulting properties. SEM fractography was utilized in order to characterize the operative fracture mechanisms. Support was provided by AFOSR AASERT Grant F49620-96-1-0228. Supply of materials by ATI, Inc. and interactions with W.L. Johnson, California Institute of Technology, are gratefully acknowledged.

MODELING THE MECHANICAL RESPONSE OF STRUCTURAL MATERIALS: Session III: Creep Deformation

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 AM Room: 202
February 18, 1998 Location: Convention Center

Session Chairs: E. M. Taleff, Aerospace Engineering Mechanics, Austin, TX 78712-1085; K. L. Murty, North Carolina State University, Raleigh, NC 27695

8:30 AM INVITED

A NEW MODEL FOR CREEP OF DISPERSION-STRENGTHENED METALS BASED ON STRESS CHANGE TEST RESULTS: *Dr. Jeffery C. Gibeling*[1]; Dr. Stuart E. Broyles[1]; [1]University of California, Materials Science and Engineering, Davis, CA 95616 USA

The results of constant structure, stress reduction creep experiments on dispersion-strengthened copper and aluminum are described. The data reveal that the creep transients are similar in appearance to those for solid solution alloys rather than pure metals. This observation illustrates clearly the important contribution of mobile dislocation density to the creep of these materials. A new model is developed to describe creep of dispersion strengthened metals based on the kinetics of thermally activated dislocation glide, and incorporating the influence of applied stress on dislocation density. The thermal activation event is assumed to involve detachment of the dislocation line from the particle-matrix interface. The steady state and constant structure creep behavior of dispersion-strengthened materials is characterized by an athermal flow stress representing the microstructural strength, and a Helmholtz free energy of activation. The constant structure results are used to determine these two parameters. As expected, the values of these parameters are in the range appropriate for dislocation motion controlled by strong obstacles. The model is shown to provide a satisfactory description of the steady state and constant structure creep behavior of dispersion strengthened copper and aluminum alloys. In contrast to other approaches, this model does not rely on threshold stresses or non-physical activation energies for creep.

9:00 AM

MODELING OF THRESHOLD STRESS FOR DISLOCATION CREEP OF DISPERSION STRENGTHENED MATERIALS: *R. S. Mishra*[1]; [1]University of California, Department of Chemical Engineering and Materials Science, Davis, CA 95616 USA

Most of the high temperature structural materials contain second phase particles. Dislocation-particle interaction becomes rate controlling during high temperature creep. In the last fifteen years, the modeling of dislocation-particle interaction has gone through a remarkable change and a new concept of 'attractive dislocation-particle interaction' has emerged. This concept can account for several features of dislocation creep in dispersion strengthened materials. One of these features is the presence of a threshold stress. So far, none of the existing models predict the experimentally observed 'temperature-dependent threshold stress.' The merits of a threshold stress based approach are discussed. A new model is proposed to explain the origin of a temperature dependent threshold stress.

9:20 AM

A MICROSTRUCTURAL MODEL FOR PRIMARY AND STEADY-STATE CREEP OF PARTICLE-STRENGTHENED NICKEL-BASE SUPERALLOYS: *Dr. Martin Christian Heilmaier*[1]; [1]Institute of Solid State and Materials Research Dresden, Institute of Metallic Materials, Dresden D-01171 Dresden Germany

The Haasen-Alexander-Ilschner theory of internal and effective stresses is combined with the modified threshold stress (σ_p -) concept in order to describe steady-state as well as transient creep of particle-strengthened nickel-base superalloys under constant stress conditions. In single-phase material the classical Taylor approach of a homogeneous dislocation distribution enables the prediction of the measured creep behavior via the long-range back stress sr. Thus, the dislocation density ρ and its microstructural evolution during creep plays the major role in the model. Second-phase particles influence creep in a 2-fold manner via reducing $_{eff}$, namely directly by the stress for particle overcoming, and indirectly by increasing ρ. The proposed approach is exemplified with Nimonic 90, IN 738 LC, MA 754 and MA 6000, which represent typical nickel-base superalloys strengthened by coherent γ'-precipitates and incoherent oxide dispe rsoids, respectively. The model accounts for the observed pronounced normal primary creep as well as it correctly reflects the steady-state relationship of ε and σ at large strains.

9:40 AM Coffee Break in Exhibit Hall

9:50 AM

DEFORMATION CHARACTERISTICS OF Sn5%Sb SOLDER USING ABI-TECHNIQUE UNDER CONSTANT STRAIN-RATE, AND STRESS RELAXATION: *K. Linga Murty*[1]; M. D. Mathew[1]; Y. Wang[1]; F. M. Haggag[2]; [1]North Carolina State, Raleigh, NC 27695 USA; [2]Advanced Technology Corporation, Oak Ridge, TN

We applied the recently developed automated ball indentation (ABI) technique to investigate the deformation characteristics of Sn5%Sb alloy at varied temperatures from ambient to 423 K using a cylindrical punch. The strain-rate dependence of the true tensile strength was investigated using constant strain-rate tests from which the stress exponent and the activation energy for deformation were derived. Power-law stress dependence n (5) is noted at low stresses or strain-rates and high temperatures while exponential stress variation is observed at high stresses. The activation energy derived from the power-law region data was low (13 kCal/mole) but in agreement with both creep and tensile data reported earlier. Underlying deformation micromechanisms will be discussed. The stress relaxation studies are now in progress, and the data to-date will be presented. The utility of ABI technique in solder joint life prediction is clearly pointed out.

10:10 AM

CONSTITUTIVE EQUATIONS FOR SUPERPLASTIC FLOW IN ALUMINUM MATRIX COMPOSITES: *Mamoru Mabuchi*[1]; K. Higashi[2]; [1]National Industrial Research Institue of Nagoya, Nagoya 462, Japan; [2]Osaka Prefecture University, Department of Mechanical Systems Engineering, College of Engineering, Osaka 593, Japan

Superplastic behavior is investigated by tensile tests for aluminum matrix composites with discontinuous reinforcements, and constitutive equations for superplastic flow are analyzed through the threshold stress concept. The analysis showed that a rate-controlling mechanism of the superplastic flow is related to dislocation movement controlled by lattice self-diffusion. In addition, the strengthening due to the presence of reinforcements was retained during superplastic flow and the mechanical properties of superplastic flow were affected by the reinforcement characteristics.

10:30 AM

PREDICTING HIGH-STRAIN-RATE SUPERPLASTICITY FROM THE PHENOMENOLOGICAL EQUATIONS FOR CREEP: *Eric M. Taleff*[1]; Woo-Jin Kim[2]; O. D. Sherby[3]; [1]The University of Texas at Austin, Aerospace Engineering and Engineering Mechanics, C0600, Austin, TX 78712-1085 USA; [2]Hong Ik University, Materials Science and Metallurgy, Seoul, Korea; [3]Stanford University, Materials Science and Engineering, Stanford, CA 94305

Recent studies by different investigators have produced high-strain-rate superplasticity in numerous materials. These materials have in common ultra-fine grain sizes 1 (m and less) and maximum ductilities at high strain rates (0.1 1/s and greater) when deformed at elevated temperatures. One model proposed for high-strain-rate superplasticity utilizes grain boundary sliding accommodated by dislocation glide across subgrains with a rate-controlling contribution from dislocation-pipe diffusion to explain observed behavior. Phenomenological equations for this and other mechanisms are used to construct deformation mechanisms maps to predict high strain rate superplasticity. Data from an ultrahigh-carbon steel are compared to predictions. It is found that at temperatures well below the melting temperature, where incipient melting is not expected, the high-strain-rate superplastic behavior of this material can be explained.

MOLYBDENUM & MOLYBDENUM ALLOYS: Development and Fabrication

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 AM Room: 203
February 18, 1998 Location: Convention Center

Session Chair: Mahesh C. Jha, Entech Molybdenum, Inc., Golden, CO 80401

8:30 AM

PRODUCTION OF PURE MOLYBDIC OXIDE FOR MOLYBDENUM METAL AND ALLOY APPLICATIONS: *Dr. Mahesh C. Jha*[1]; Dr. William A. May[1]; [1]Entech Molybdenum Inc., Golden, CO 80401 USA

Molybdenum metal and alloys are used in many applications in the aerospace, electronics, energy and environmental industries. The presence of even small amounts of certain impurities in molybdenum could be disastrous in these applications. Therefore, only high purity molybdic oxide is used to produce molybdenum metal. Currently, sublimation or wet chemical processing is used to pure oxide starting with technical-grade molybdenum oxide obtained by multiple-hearth roasting of high-quality primary molybdenite concentrates. Entech has developed an innovative process for converting lower-grade by-product molybdenite

concentrates to pure molybdic oxide with the potential to produce a higher-quality product at a lower cost. The process flowsheet includes a novel fluidized-bed roasting step followed by a three-step chemical purification process. The results from the pilot plant operations will be presented.

9:00 AM

RECENT DEVELOPMENT OF MOLYBDENUM INDUSTRY IN CHINA: *Dr. Chu You-Yi*[1]; Dr. Ma Bao-Ping[2]; [1]The Nonferrous Metals Society of China, Beijing 100814 China; [2]Jinduicheng Molybdenum Mining Co, Husxian, Shanxi Province 714102 China

China is endowed with rich molybdenum resources. The molybdenum reserves in the mines widely distributed in the country are estimated to be 3.5 million tons. Recently, the production of molybdenum concentrates mainly from primary ores increased rapidly from 14,00 tones in 190 to 26,000 tones in 1996. Mo Oxide is produced from the roasting of concentrates in air furnaces or rotating furnaces and ammonium molybdate produced by leaching-precipitation method. Molybdenum is used in China mainly in the metallurgical industry and in chemical products such as for catalysts, lubricants, and pigments. Jinduicheng Molybdenum Mining Company in Shanxi Province is the most important molybdenum base for mining, metallurgy and fabrication as well as one of the main R&D centers in China. Domestic consumption accounts for around one-third of the total molybdenum production with the balance being exported in the form of industrial Mo oxide and ferroalloys. These developments are described and discussed in detail.

9:20 AM

RHENIUM AND MOLYBDENUM/TUNGSTEN BASED ALLOYS: AN OVERVIEW OF THE DATABASE: *Dr. Boris D. Bryskin*[1]; Mr. Jan C. Carlén[1]; [1]Rhenium Alloys, Inc., Elyria, OH 44036-0245 USA

The technological applications and processing methods for rhenium are growing with increasing vigor, a development that could hardly be foreseen when the metal was first discovered 72 years ago. In many branches of modern industry, alloys in the Mo - Re and W - Re systems have long been recognized to have practical advantages in fabricateability and performance, simultaneously being much more affordable than pure rhenium. This paper constitutes an in-depth review of the physical, electrical, thermal, and some mechanical properties of rhenium and its common alloys with molybdenum and tungsten. Numerous publications were screened to generate the background information. The need for up-dated information on these materials and to create a source for reliable references was the motivation for this comprehensive comparative study.

9:40 AM

ELECTRODEPOSITION OF MOLYBDENUM ALLOYS FROM AQUEOUS SOLUTIONS: *Dr. E. J. Podlaha*[1]; Dr. D. Landolt[1]; [1]Laboratoire de métallurgie chimique, Département des matériaux, Lausanne 1015 Switzerland

Molybdenum and its alloys are interesting for their corrosion resistance. They can be fabricated as bulk materials or in the form of coatings. In order to produce the latter, different physical techniques such as sputter deposition can be used. One alternative to these techniques is electrodeposition. The electrodeposition process has many advantages, such as the ability to easily produce thin films cost effectively. The electrodeposition of molybdenum is rather unusual. Although pure molybdenum can be plated from high temperature molten salt solutions it cannot be plated as a single element from aqueous solutions. However, molybdenum can be deposited from aqueous solutions in the form of an alloy with other elements of the iron-group, Ni, Co and Fe. This type of behavior is often referred to as induced codeposition and will be examined here. A parasitic, hydrogen evolution side reaction always accompanies the alloy codeposition which has been shown to be responsible for cracks in the deposits. Minimizing surface cracking by choosing conditions where the side reaction would be low, while maximizing the molybdenum composition in the alloy, is considered. A mechanistic reaction scheme was developed which describes the deposition rates of molybdenum, the iron-group element and the hydrogen side reaction. This model was used to indicate conditions for plating new, molybdenum alloy coatings. Two types of alloys were electrodeposited, (i) those having a high Mo weight percentage and (ii) compositionally modulated multilayers (CMM). The CMMs were successfully deposited with alternating nanometric layers of a high Mo concentration NiMo alloy and a low Mo concentration NiMo alloy. Their microstructure was observed by SEM and X-ray diffraction.

10:00 AM Coffee Break in Exhibit Hall

10:20 AM

THE SYNTHESIS OF $MoSi_2$ AND $MoSi_2$ - COMPOSITES BY FIELD-ACTIVATED COMBUSTION: *Dr. Z. A. Munir*[1]; [1]University of California, Dept. of Chemical Engineering & Materials Science, Davis, CA 95616 USA

Through the use of the field-activated pressure-assisted combustion method, $MoSi_2$ can be synthesized and densified simultaneously. Highly dense samples (up to 99.2 % TD) were produced from elemental powders in one step. Using stoichiometric powder mixtures, the product contained minor amounts of Mo_5Si_3 present at the grain boundaries of MoSi2 in the interior of the samples. Reactants with 2.5 mol % excess amounts of Si resulted in Mo_5Si_3-free, dense $MoSi_2$ samples. The effect of the synthesis parameters of pressure, temperature, and current on the process and on the resulting product were investigated. The kinetic parameters of the self-propagating high-temperature synthesis (SHS) of molybdenum silicide were investigated using the Boddington-Laye mathematical analysis of the temperature profiles associated with the passage of the combustion wave. The effect of the field on the wave propagation velocity and its dependence on the reactants green density was investigated. Furthermore, the imposition of a field during synthesis was found to have an effect on the particle size distribution of the $MoSi_2$ product. The average particle size decreased when moderate fields were used but increased significantly when high fields were used. The use of an electric field to activate SHS reactions was made use of to synthesize molybdenum silicide composites. Composites of $MoSi_2$-SiC, $MoSi_2$-Nb, and $MoSi_2$-ZrO_2were synthesized by this method. In the case of $MoSi_2$-x SiC, composites with x 0.18 cannot be made without the application of a field across the reactants. The minimum (threshold) field required to initiate and sustain an SHS reaction depended on the value of x, reaching a maximum around a value of x 0.5, i.e., for equimolar composite.

10:40 AM

REACTIVE SOLID STATE PROCESSING OF DYNAMICALLY DENSIFIED Mo + Si POWDER COMPACTS: *Kevin S. Vandersall*[1]; Naresh N. Thadhani[1]; [1]Georgia Tech, Materials Science and Engineering, Atlanta, GA 30332-0245 USA

Dynamic densification employing explosive, gas gun, and magnetic implosion techniques was utilized to form the high density (~78-95% dense) powder compacts starting with ~50-55% initial density. The compacts were then thermally treated under controlled conditions to obtain a Mo-Si alloy via solid state reactive processing. The influence of densification parameters including initial packing density, pressure utilized, and loading conditions (which in turn control the compact density, defect concentration, and minimization of macroscopic cracking) on the reaction behavior was investigated using x-ray diffraction (XRD) and optical and scanning electron microscopy (SEM). This paper will review the methods utilized and microstructures obtained from densification as well as outline the fundamental conditions necessary to achieve the most desirable compacts for solid state reactive processing. Microstructural characteristics of the reaction processed Mo-Si Alloy will also be presented. Work supported by ARO/AASERT Grant No. DAAH04-95-1-0235

11:00 AM

COMBUSTION SYNTHESIS OF $Mo(Si,Al)_2$ AND RELATED COMPOSITES: *Dr. Sarit B. Bhaduri*[1]; Mr. J-G. Huang[1]; Mrs. Sutapa Bhaduri[1]; [1]University of Idaho, Dept. of Metallurgical & Mining Eng., Moscow, ID 83844-3024 USA

Recent research has shown that Al can be dissolved into $MoSi_2$ in forming $Mo(Si,Al)_2$ compounds. The addition of Al to $MoSi_2$ structure is expected to enhance the metallic character and improve the oxidation resistance of $MoSi_2$. In this work, both combustion synthesis and

reaction HIPing were carried out with addition of Al up to 16 Wt%. As Al content was increased, composites to predominantly single phase $Mo(Si,Al)_2$ formed. Addition of Al seemed to stabilize the hexagonal structure (C40) as opposed to the original tetragonal (C11b) structure. The samples were characterized using SEM and XRD. However, contrary to the expectations, the toughness values did not increase. Supported by SBOE, Idaho and NSF DMR-9315057.

11:20 AM

COMBUSTION SYNTHESIS AND DENSIFICATION OF MOLY SILICIDES AND THEIR COMPOSITES: *Dr. Seetharama C. Deevi*[1]; [1]Philip Morris, Research Center, Richmond, VA 23112 USA

Among the many alloys and compounds of molybdenum, moly silicides based on $MoSi_2$, and Mo_5Si_3 have gained attention due to their unique properties such as oxidation resistance, strength, hardness, and metallic conductivity. Synthesis of moly silicides and their composites by combustion synthesis offers the ability to obtain pure compounds, alloys, and in-situ composites. For example, hot pressing of a mixture Mo and Si can give rise to dense $MoSi_2$ or Mo_5Si_3 or a mixture of the silicides. A composite of $MoSi_2$ and SiC can be obtained by the addition of C to the Mo and Si mixture. Alternately, oxidation-reduction reactions based on MoO_3, Al, and Si can be employed to obtain in-situ composites of $MoSi_2$,-Al_2O_3. In this paper, synthesis, processing approaches, and fracture toughness of $MoSi_2$, Mo_5Si_3, and the composites of silicides will be presented.

11:40 AM

MECHANICAL PROPERTIES OF OXIDE DISPERSION STRENGTHENED (ODS) MOLYBDENUM ALLOYS: Robert Bianco[1]; R. William Buckman, Jr.[2] [1]Westinghouse Electric Corporation, Bettis Power Laboratory, West Miffin, PA; [2]Refractory Metal & Technology, Pittsburgh, PA

The creep-ruptive life of unalloyed molybdenum up to 0.65 T_m(1600°C or 2910 F) is increased by approximately an order of magnitude with up to 50 weight percent (wt.%) addition of rhenium. A proprietary powder metallurgy process, developed for unalloyed molybdenum, results in an increase in creep-rupture life at 0.65 T_m by 3-4 orders of magnitude and still exhibits ductile fracture behavior at temperatures significantly below room temperature.

NON-AEROSPACE APPLICATIONS OF TITANIUM & ITS ALLOYS: Session V - Fabrication and Processing Technologies

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 AM Room: 101
February 18, 1998 Location: Convention Center

Session Chair: Oleg Senkov, University of Idaho, IMAX, Moscow, ID 83844-3026I

8:30 AM

DEVELOPMENTS IN SOLID STATE JOINING OF TITANIUM ALLOYS: *Mr. P. L. Threadgill*[1]; [1]TWI, Abington, Cambridge CB1 6AL UK

Titanium alloys are often readily joined by solid state processes such as friction welding and diffusion bonding, and as a result such processes are attractive in the development of manufacturing technologies for new titanium products. New solid state joining technologies are also being applied to titanium, leading to the potential for greater flexibility in future manufacturing. A number of cases where joining is critical in the introduction of titanium to new market areas will be considered. These will include joining titanium pipes for the offshore industry, where the application of friction welding can significantly reduce welding times, and the use of the recently developed friction stir welding for joining of sheet materials for many applications. Other challenges which will be considered are joining titanium alloys to other materials, and the opportunities afforded by the use of electron beam diffusion bonding, which can reduce diffusion bonding times to a small fraction of the time required for conventional diffusion bonding.

8:50 AM

ELEMENTAL BLENDED POWDER SEMI-SOLID FORMING ON Ti-Al ALLOY: *Mr. K. Yasue*[1]; [1]National Industrial Research Institute of Nagoya, Nagoya Japan

Semi-solid forming by using COMPASS method was tried on a Ti-6%Al alloy, and the effects of the forming pressure, temperature, pressure holding time and grain size of titanium powder on the density were discussed. The blending powder which were prepared by mixing both powders of titanium and aluminum was filled in a metal mold, and heated to around the melting point of aluminum, and then the forming pressure was loaded and held for the prescribed time. The green compacts were heat-treated for alloying at 1473K. Pores in the green compacts were not observed under all the forming condition, however the pressure holding time has a considerable influence on the density of samples after the heat-treating. The voids and intermetallic compound were observed on the alloyed sample in case of the short pressure holding time, but these faults gradually disappear as the pressure holding time increases.

9:10 AM

PRODUCTION OF LOW-COST TITANIUM: *E. G. Baburaj*[1]; K. Prisbrey[2]; O. N. Senkov[1]; P. McCormick[3]; [1]University of Idaho, Institute for Materials and Advanced Processes (IMAP), Moscow, ID 83844-3026; [2]University of Idaho, Department of Metallurgical and Mining Engineering, Moscow, Idaho 83844-3024; [3]University of Western Australia, Research Centre for Advanced Mineral and Materials Processing, Perth 6907 Western Australia

Expansion of titanium into non-aerospace applications requires lower cost production methods for titanium and its alloys. In this paper recent progress in the synthesis of titanium by displacement reactions induced by mechanical alloying will be reviewed.

9:30 AM

SAT-2041CF ALLOY SUITABLE FOR COLD PROCESSING: *Mr. I. Inagaki*[1]; [1]Sumitomo Metal Industries, LTD., Railway Parts & Forgings Manufacturing Department, Osaka Japan

SAT-2041CF, developed by Sumitomo Metal Industries, Ltd., is high strength β type titanium alloy suitable for cold processing. After β solution treatment, the cold upsetting limit of SAT-2041CF alloy is the same level as the spheroidized 0.45%-carbon steel, and the cold flow stress of this alloy is reduced to the same level as the commercially pure titanium. The cold working of this alloy is easier than the other β type titanium alloys, ex. Ti-15V-3Al-3Sn-3Cr, β-c. Moreover, the tensile strength of this alloy increases greatly by the aging treatment, which induces the precipitation of fine β phase within β phase matrix. By utilizing the cold workability of this alloy satisfactorily, the material-yield of titanium alloy increases and the machining cost decreases. Consequently, the total processing cost will be reduced. The bars, sheets and plates of SAT-2041CF alloy have been mass-produced for the nonaerospace applications such as the parts for the bicycles and golf heads.

9:50 AM

PARTICULATE-REINFORCED TITANIUM COMPOSITES: P/M-BASED PRODUCTION ALTERNATIVES: *Susan M. Abkowitz*[1]; Walter H. Zimmer[1]; Paul F. Weihrauch[1]; Stanley Abkowitz[1]; [1]Dynamet Technology, Inc., Burlington, MA USA

Powder metallurgy (P/M) technology is ideally suited to meet the emerging commercial market demand for custom-designed titanium materials including particulate-reinforced titanium matrix composites. With this approach, design flexibility, competitive production eco-

nomics and tailored product performance can be achieved while bypassing supply-limited mill schedules and its associated price volatility. Composite structures, such as a titanium alloy matrix reinforced with selected loadings of TiC or TiB/TiB2 (CermeTi), have been demonstrated to offer improved wear resistance, stiffness, and elevated temperature strength. Manufacture of novel designs with enhanced properties in prescribed locations are uniquely enabled by the P/M approach. Conventional metalworking processes such as forging and extrusion have been employed to finish the P/M preform to net or near net shape. A more recent development is the successful manufacture of CermeTi and other custom titanium materials by a combination of P/M and investment casting. This PM-based technology offers accelerated introduction of new titanium compositions into economic high volume complex components, meeting the challenges of the dynamic commercial market.

10:10 AM

THERMOHYDROGEN PROCESSING TO IMPROVE TITANIUM ALLOY PERFORMANCE: *O. N. Senkov*[1]; J. J. Jonas[2]; F. H. (Sam) Froes[1]; [1]University of Idaho, Institute for Materials and Advanced Processes, Moscow, ID 83844-3026; [2]McGill University, Department of Metallurgical Engineering, Montreal H3A 2B2 Canada

Thermohydrogen processing (THP) of titanium and its alloys leads to easier processing and enhanced properties in the final product. The status of THP will be reviewed and related to products which could see use in non-aerospace applications.

10:30 AM

PRODUCTION, CHARACTERIZATION AND APPLICATIONS OF LOW COST TITANIUM POWDER PRODUCTS: *V. Moxson*[1]; *V. Moxson*[1]; O. N. Senkov[2]; F. H. Froes[2]; [1]ADMA Products, Inc., Twinsburg, OH 44087; [2]University of Idaho, Institute for Materials and Advanced Processes, Moscow, ID 83844

This paper describes production, characteristics, and applications of a new high quality powder produced from titanium dioxide using a metal hydride reduction (MHR) method. The powder does not contain remnant salt and as such is suitable for demanding applications. A number of uses of this powder for environmental, medical and other applications are discussed.

10:50 AM

THERMOMECHANICAL PROCESSING OF TITANIUM ALLOYS-AN OVERVIEW: *I. Weiss*[1]; S. L. Semiatin[1]; V. Seetharaman[1]; [1]Wright State University, Department of Mechanical and Materials Engineering, Dayton, Ohio 45435 USA

The main objectives of thermomechanical processing (TMP) are to produce usable shapes through primary working (Ingot breakdown) and secondary mill operation (hot rolling or forging), and to optimize mechanical properties through microstructure control during the different stages of the thermomechanical process. This paper reviews the thermomechanical processing of alpha, alpha/beta, and beta titanium alloy in general, and the high temperature deformation, the breakdown of lamellar microstructure, the occurrence of cavitation/wedge cracking, and the development of crystallographic texture during TMP in particular.

PROCESSING-STRUCTURE-PROPERTY RELATIONSHIPS OF COMPOSITE INTERFACES: SESSION IV: INTERFACE ENGINEERING AND CHARACTERIZATION

Sponsored by: Jt. ASM International: Materials Science Critical Technology Society/Structural Materials Division, Composite Materials Committee, Materials Design and Manufacturing Division, Powder Metallurgy 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 AM Room: Centro A
February 18, 1998 Location: Convention Center

Session Chairs: Benji Maruyama, Wright Laboratory Materials Directorate, Wright-Patterson AFB, OH 45433; Awadh B. Pandey, Systran Corporation, 4122 Linden Avenue, Dayton, OH 45432

8:30 AM INVITED

DEVELOPMENT OF SiC-C FUNCTIONALLY GRADIENT COATINGS FOR OXIDATION PROTECTION OF GRAPHITE AND CARBON-CARBON COMPOSITES: *F. C. Ohuchi*[1]; [1]University of Washington, Department of Materials Science and Engineering, Seattle, WA 98195

Functionally Graded Coating (FGC) represents a new class of composite materials that have been intentionally graded compositionally and/or structurally. For some applications, coatings must be made homogeneously over the entire three-dimensional surface of the materials without creating uncoated "dead" areas. We have developed an innovative CVD method specifically designed for this purpose. A key feature of the design is to adopt an electromagnetic levitation to simultaneously float and heat a substance of interest. We have applied this technique to fabricate SiC-C functionally graded coatings on graphite materials. Thermo-mechanical and chemical properties of the SiC-C FGC's are characterized in order to assess the questions as to oxidation resistance coatings for graphite materials at high temperature environment.

9:15 AM

EVALUATION OF INTERFACIAL PROPERTIES IN HIGH-PERFORMANCE SiC/SiC-BASED COMPOSITES: *Dr. Ian Jeffrey Davies*[1]; Dr. Masaki Shibuya[2]; Mr. Tetsuro Hirokawa[3]; Dr. Takashi Ishikawa[1]; [1]National Aerospace Laboratory, Airframe Division, Tokyo 181 Japan; [2]Ube Industries Ltd., Corporate Research and Development, Yamaguchi, 755 Japan; [3]Shikibo Ltd., Industrial Textile Division, Shiga, 527 Japan

The present work is concerned with evaluation of fibre/matrix interface properties for a 3-D woven SiC/SiC-based composite tensile tested up to 1380°C in vacuum and air. The composite contained surface-modified Tyranno Si-Ti-C-O fibres which resulted in excellent mechanical properties at room temperature and 1200°C in vacuum (strength ~400 MPa; strain to failure >1%), but were significantly reduced upon testing at elevated temperature in air. In order to sustain high-temperature mechanical properties in an oxidising atmosphere, the composite was impregnated with a proprietary glass-based system. Mechanical properties for the oxidation-protected specimens measured in air at elevated temperature were similar to those of unprotected specimens tested in vacuum. The status of the fibre/matrix interface was evaluated for both unprotected and oxidation-protected speci-

mens through microstructural observation of composite fracture surfaces including measurement of fibre pull-out lengths and in situ fibre strength. Interfacial properties inferred from these results correlated well with observed mechanical properties.

9:40 AM

ROLE OF FIBER/MATRIX INTERFACE IN ENVIRONMENTAL ENHANCED CRACK GROWTH OF SiC/SiC: *R. H. Jones*[1]; C. H. Henager, Jr.[1]; C. A. Lewinsohn[1]; [1]Pacific Northwest National Laboratory, Richland, WA 99352

The failure mechanisms of CFCCs at elevated temperatures when oxidation processes occur during deformation are presented and discussed in the framework of a "failure Mechanism Map" that includes an oxidation embrittlement mechanism (OEM) and interphase removal mechanism (IRM). In particular, the transition between OEM and IRM is discussed with respect to oxygen concentration, exposure temperature, and carbon interphase thickness. Data and modeling from subcritical crack growth studies at PNNL is flexure showing IRM operating from 800°C to 1200°C is combined with observations of OEM, reported by others, to produce the map.

10:05 AM Coffee Break in Exhibit Hall

10:20 AM

BaZrO3 AND SnO2 AS INTERPHASE MATERIALS FOR TOUGH ALUMINA-BASED COMPOSITES: *G. M. Gladsyz*[1]; M. Schücker[2]; K. K. Chawla[1]; H. Schneider[2]; M. K. Ferber[3]; D. L. Joslin[3]; [1]New Mexico Institute of Mining and Technology, Department of Materials Engineering, Socorro, NM 87801; [2]Materials Research Institute, German Aerospace Establishment (DLR), Köln Germany; [3]Oak Ridge National Lab, Oak Ridge, TN 37831

There has been a growing interest in oxide/oxide composite systems due to their stability at high temperatures in oxidizing environments. To control the degree of interfacial bonding and increase fracture toughness, an interphase material must be added. We present work on the development of SnO_2 and $BaZrO_3$ as an interphase in alumina-based laminated composites. We used Al_2O_3/$BaZrO_3$ laminates as a model system to illustrate the in-situ formation of multiple interfaces. It made use of $BaZrO_3$ as a "pre-interface" material with Al_2O_3 and the resulting reaction layers (ZrO_2, $BaO?Al_2O_3$, and $BaO?6Al_2O_3$) were formed as thermodynamically predicted. $Al_2O_3SnO_2$ composites are difficult to produce because of the tendency of SnO_2 to decompose to SnO (m.p.=1125°C) in reducing environments. The fabrication of this com posite was achieved by hot pressing in air. Characterization techniques used included SEM, TEM, WDS, and three-point bend tests. Results showed that the presence of these interphase materials was effective in increasing fracture toughness.

10:45 AM

IMPURITY EFFECTS ON THE ADHESION OF TEXTURED ALUMINUM THIN FILMS ON SAPPHIRE SUBSTRATES: *J. A. Schneider*[1]; S. E. Guthrie[1]; N. R. Moody[1]; [1]Sandia National Labs, Livermore, CA 94551-0969

Differences in the adhesion of textured aluminum thin films on single crystal sapphire due to the presence of controlled contaminants are being investigated. Adhesion is evaluated by use of nanoindentation and continuous scratch tests. Properties were compared for varying thickness of aluminum films (100 to 2000nm) that were vapor deposited onto (0001) oriented sapphire substrates. Thin (< 1 nm) layers of carbon were deposited on selected sapphire substrates prior to vapor deposition of aluminum films. Spalling was observed during continuous scratch testing in specimens with carbon at the interface but not in specimens without carbon at the interface. This work was supported by the U.S. Department of Energy under Contract #DE-AC04-94AL85000.

11:10 AM

STRUCTURE AND FRACTURE RESISTANCE OF INTERFACES IN NiAl/Mo MODEL LAMINATES: *M. R. Fox*[1]; A. K. Ghosh[1]; [1]University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109

Intermetallic matrix composites with ductile phase reinforcement are being considered for high temperature structural applications. Increases in room temperature toughness over that of monolithic NiAl have been achieved in solid-state processed and directionally-solidified NiAl/Mo eutectic composites. The nature of interface fracture is critical to the understanding of toughening effects in these composites. Thus NiAl/Mo laminates, which were selected as model systems, were fabricated by diffusion bonding under various conditions for structural examination and mechanical testing. Interfaces have revealed the presence of a reaction layer which varies in thickness with bonding conditions. Fracture occurred between the reaction layer and Mo. Fracture surfaces reveal a replicated structure with some evidence of plastic deformation, particularly for crack initiation. Mechanical response of the interfaces was studied under mixed loading conditions using a novel technique in which one of the adjoining phases was loaded in compression, producing a stable interface crack. Interface fracture resistances were determined by using FEM analysis to model the experimental tests which provides insight into the toughening process in these composites. This research supported by the Air Force Office of Scientific Research, Grant #DOD-G-49620-93-1-0283.

11:35 AM

MICROSTRUCTURAL STABILITY AND STRENGTHENING OF Cu-Ag FILAMENTARY MICROCOMPOSITES: *Sun Ig Hong*[1]; Mary Ann Hill[2]; [1]Chungnam National University, Department of Metallurgical Engineering and RASMO, Taejon 305-764 Korea; [2]Los Alamos National Laboratory, Materials Science Division, Los Alamos, NM 87545

One of the most important features in two phase Cu-Ag microcomposites is the abundance of interfaces compared to conventional Cu-based alloys. Although the nature of interfaces between silver filaments and the Cu matrix may have pronounced effects on the physical properties of Cu-Ag microcomposites, little is known about these interfaces. In this study, the microstructural and mechanical stability of Ag filaments and their effect on the mechanical properties in Cu-24 wt.% Ag microcomposites heat treated at various temperatures were investigated. The microstructural scale observed in this study using T.E.M. was found to be much finer than that reported previously by other investigators. In heavily drawn Cu-Ag microcomposites, the microstructure is too fine and the interfacial area is too large to maintain a stable internal dislocation structure because of closely spaced filaments. Rather, most dislocations are thought to be gradually absorbed at the interfaces as the draw ratio increases. The stress-strain responses and fracture behavior of Cu-Ag microcomposite wires were also examined and correlated with the microstructural change caused by thermomechanical treatments. The strength of Cu-24 wt.% Ag microcomposites of the present study was predicted by a modified rule of mixtures in which the strength of each of the three regions observed by T.E.M. was evaluated based on the available data. The predictions of the model are in good agreement with experimental data.

SOLIDIFICATION AND DEPOSITION OF MOLTEN METAL DROPLETS: Session II

Sponsored by: Materials Design and Manufacturing Division, Solidification Committee

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

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

Session Chair: Enrique J. Lavernia, University of California, Department of Chemical Engineering and Materials Science, Irvine, CA 92717 - 2575

8:30 AM

A PROBE TO MEASURE THE PARTICLE ENTHALPY AT THE IMPACT DURING THE SPRAY FORMING PROCESS: *Dr. Robert L. Kozarek*[1]; Mr. Joern E. Fischer[2]; [1]Alcoa Technical Center, Fluid State Processing Center, Alcoa Center, PA 15069 USA; [2]University of Bremen, Institute for Materials Science, Bremen 28359 Germany

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. For an economical application of the spray forming process it is necessary to optimize the product microstructure (grain size, porosity) and to maximize yield (deposit shape and overspray). Process models have been developed to gain a better understanding of the factors influencing the process and product quality. In these models the average solid fraction of the droplets in the spray is an important parameter which has been strongly correlated to porosity, particle sticking efficiency, overspray and product microstructure. Unfortunately, there is very little experimental data available on the solid fraction of the spray to validate the model calculations. This study reports on our efforts to develop a probe to experimentally measure the enthalpy of a collection of particles in the spray from which the solid fraction can be computed. The probe is based on a calorimetric technique. Multiple probes are used to determine the influence of nozzle design and operating parameters on the spatial distribution of average liquid fraction of the spray. Details of the probe design considerations and methodology will be presented.

8:50 AM

CHARACTERIZATION OF THE IN-FLIGHT SOLIDIFICATION OF Sn-Pb UNIFORM DROPLETS: *Mr. Charles David Tuffile*[1]; Dr. Teiichi Ando[1]; Dr. Jung-Hoon Chun[2]; [1]Northeastern University, Department of Mechanical, Industrial and Manufacturing Engineering, Boston, MA 02115 USA; [2]Massachusetts Institute of Technology, Laboratory for Manufacturing and Productivity/Department of Mechanical Engineering, Cambridge, MA 02139 USA

The in-flight solidification of uniform-droplet sprays of Sn-Pb alloys was characterized as a function of flight distance. Metal droplets in a spray experience varying degrees of undercooling prior to solidification, depending on the metal purity, cooling rate, droplet size, surface oxidation, and droplet collisions/merging. A systematic study of the in-flight droplet solidification thus requires a spray consisting of mono-disperse droplets having identical thermal history. Using a recently developed calorimetric droplet enthalpy measurement technique augmented by microscopy, X-ray diffraction and differential scanning calorimetry, it was possible to determine the prior undercooling, the microstructural evolution, and the degree of metastability in 180-micron Sn-Pb alloy droplets. The results provide critical information required to improve microstructural control in both controlled spray forming and powder production.

9:10 AM INVITED

OBSERVATION OF THERMAL PROFILES DURING IMPACT AND SOLIDIFICATION OF NICKEL DROPS: *Dr. William Hofmeister*[1]; Dr. R. J. Bayuzick[1]; Dr. Douglas M. Matson[2]; Dr. Gerardo Trapaga[2]; [1]Vanderbilt University, Materials Science, Nashville, TN 37235 USA; [2]MIT, Dept. of Materials Science and Engineering, Cambridge, MA 02139

A 3.5 meter drop tube was used to accelerate molten nickel droplets and observe spreading and solidification at the bottom of the drop tube. The impact and solidification of the droplets on a quartz plate was observed through the plate with high speed thermal imaging systems such that the temperature distribution at the spat interface was recorded spatially and temporally. Drops superheated at impact solidified from the outer radius of the splat to the center with only slight undercooling. Undercooled splats solidified immediately on impact with no additional undercooling. These results are not predicted by classical nucleation theory and raise some interesting questions on the physics of nucleation and solidification in droplet impacts.

9:35 AM

IMPINGMENT BEHAVIOR OF A SPRAY CAST ALUMINUM ALLOY: Mr. Matthieu Rolland[1]; *Dr. Douglas M. Matson*[1]; Prof. Merton C. Flemings[1]; [1]Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139 USA

The deposition behavior of Al-4.5% Cu (wt.) was observed for several conditions (warm and cold substrate, droplets with various fraction solid). A variety of impact categories were observed using high speed video imaging: thick pancake, thin pancake, spherical pancake, spherical, bilaminate, rigid. These categories were found to occupy the same domain on a plot of Weber number versus a dimensionless "freezing number"; the former relates to the tendency to spread in absence of solidification, and the later relates to the amount of solidification. Experimental results from other investigators on other materials indicate the breadth of applicability of the correlation.

9:55 AM INVITED

THE STICKING EFFICIENCY IN DEPENDENCE ON AFFECTING PARAMETERS: Christoph Kramer[1]; Dr. Volker Uhlenwinkel[1]; Klaus Bauckhage[1]; [1]University of Bremen, Institute for Materials Science, Bremen, Deutschland 28359 Germany

In general, the spray forming process is characterized by the atomization of a molten metal stream and the deposition of the spray onto a substrate. Due to the specific conditions of the spray cone and the substrate or later the deposit, just a part of the hitting mass of the spray cone sticks onto the surface. This is called overspray and it's minimization is a very important factor from the economic point of view. In contrast to the overspray the sticking efficiency defines the ratio of the sticking mass flux to the hitting mass flux. Thus, it is a measure for the effectiveness of the compaction process. With the knowledge of this ratio the prediction of the growing of the deposit and therefore its shape is possible. In this investigation the sticking efficiency is determined experimentally for Gaussian-shaped deposits. The local and time depending sticking mass flux is calculated from the contour of the growing deposit and the hitting mass flux is measured with the help of collecting probes mounted into one or several planes of the spray cone. Furthermore, different affecting parameters (particle size, particle velocity, fraction liquid of the particles, deposit surface temperature and angle of impact) are measured or modeled and thus could be set into dependence on the sticking efficiency. The results show that the thermal condition of the deposit surface is the most critical factor influencing the sticking efficiency. The fraction of liquid of the particles and

the particles momentum are less important. The angle of impact has no effect. From the data a first attempt was taken to predict the sticking efficiency by an empirical equation. The investigation so far was done using a low carbon steel, further work will focus on different materials.

10:20 AM Coffee Break in Exhibit Hall

10:30 AM INVITED
SOLID/LIQUID COARSENING BEHAVIOR OF SPRAY FORMED IN 718: Ms. Estelle D. Manson-Whitton[1]; *Dr. Ian C Stone*[1]; Dr. Patrick S Grant[1]; Prof. Brian Cantor[1]; Ms. Sarah Blackham[2]; [1]Oxford University, Department of Materials, Oxford OX1 3PH U.K.; [2]Rolls-Royce plc, Derby DE24 8BJ U.K.

The grain size in spray formed Ni superalloys is important in controlling subsequent workability. Currently, there is little understanding of the factors controlling the as spray formed grain size. This paper presents: (1) A numerical investigation of the factors determining the equiaxed grain size immediately after deposition of the spray, based on a geometrical consideration of droplet size distribution and the relative amounts of liquid and solid in the spray; and (2) An experimental study of the subsequent coarsening kinetics of the equiaxed grains at low (<0.4) and decreasing billet liquid fraction. By combining experimental and numerical data, the final as spray formed grain size has been predicted, and is shown to be in reasonable agreement with measured grain sizes from spray formed billets.

10:55 AM INVITED
MICROSTRUCTURE EVOLUTION DURING MULTIPHASE DROPLET DEPOSITION: *Dr. C. G. Levi*[1]; Dr. J. P. A. Lofvander[1]; Dr. J. Mayer[2]; Dr. J. Marien[2]; Dr. G. Soyez[2]; [1]University of California, Materials Department, Santa Barbara, CA 93106-5050 USA; [2]Max-Planx-Institut fur Metallforschung, Stuttgart Germany

Iron-base coatings produced by thermal spray processes are of interest for improving wear resistance in automotive applications. The processing conditions can lead to a metal-oxide composite coating whose mechanical performance depends, among other factors, on the relative amounts and distributions of the constituent phases. A peculiar feature of the Fe-O system is a large miscibility gap in the liquid phase between ~1 and ~50 at.%O. This suggests that, under the conditions anticipated for the deposition of these coatings, the liquid would tend to separate into two phases with widely different oxygen contents. The implications of this phase separation on the solidification behavior and subsequent microstructure evolution are explored. The discussion is based on wire-fed HVOF coatings with sufficient oxygen to place then in the liquid miscibility gap. The coatings were analyzed by X-ray, SEM and TEM, including HRTEM and advanced microchemistry performed by energy filtering techniques.

11:20 AM INVITED
MICROSTRUCTURE TRANSFORMATION DURING DEPOSITION AND HEAT TREATMENT OF SPRAY FORMED TOOLING ALLOYS: *Dr. Kevin M. McHugh*[1]; [1]INEEL/Lockheed Martin, Idaho Falls, ID 83415-2050 USA

Spray forming is an advanced materials processing technology which converts a bulk liquid to fine droplets and deposits them onto a suitably shaped substrate or pattern to produce a coherent solid deposit. The evolution of microstructural features of the deposit, and resultant product properties, reflect the interplay of characteristics of the spray plume (droplet size distribution, velocity, heat content, flux, and flow pattern) with those of the substrate (material properties, surface finish, and temperature). This paper describes solidification behavior of spray-formed commercial tooling alloys, and material response to artificial aging and conventional heat treatment.

11:45 AM
EFFECT OF SUBSTRATE TEMPERATURE ON SPLAT FORMATION AND MICROSTRUCTURE DEVELOPMENT DURING THERMAL SPRAY DEPOSITION: *Dr. S. Sampath*[1]; X. Jiang[1]; A. Vardelle[2]; M. Vardelle[2]; [1]State University Of New York, Center for Thermal Spray Research, Stony Brook, NY 11794-2275 USA; [2]University of Limoges, LMCTS, Limoges, France

It is widely appreciated that thermal spraying is a highly dynamic process resulting from rapid heating/melting/accelerating of powder particles or wire in a flame, followed by impact and rapid solidification of the droplet (splat). A splat resulting from the flattening of an individual droplet is the basic building block ("unit cell") of the thermal spray microstructure. The phase and microstructure of the splats (intrinsic) and the integration of the splats (extrinsic) are both affected by processing. Recent results have shown that deposition temperature plays an important role in the formation of the thermal spray deposit microstructure. For many material - substrate systems there exists a characteristic temperature regime above which the morphology of the splat changes from a fragmented to a more cylindrical morphology. This has important implications on microstructure development, porosity and properties. In this investigation, single splats and deposits of Mo, Al2O3 and partially stabilized zirconia have been produced by plasma spraying onto stainless steel substrates at various temperatures. The splat cooling and flattening behavior have been monitored using high speed pyrometric methods and the microstructure development has been analyzed using a variety of analytical techniques. The results indicate that the interface temperature and contact area play a key role in modifying the splat morphology and consequent microstructure development. This work was supported by the MRSEC program of the National Science Foundation under award number DMR-9632570 and by the NSF-CNRS International Cooperation Program INT 9415888

STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS: STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS V: Gamma Titanium Aluminides 2

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 AM Room: 107
February 18, 1998 Location: Convention Center

Session Chairs: Chain T. Liu, Oak Ridge National Laboratory, Metals and Ceramic Division, Oak Ridge, TN 37831; Wole O. Soboyejo, Ohio State University, Dept. of Materials and Science and Engr., Columbus OH 43210-1179

8:30 AM
STRENGTHENING OF GAMMA TiAl: PROS AND CONS: Dr. Curt M. Austin[1]; *Dr. James C. Williams*[1]; [1]GE Aircraft Engines, Cincinnati, OH 45215-6301 USA

Intermetallic compounds such as TiAl plastically deform by planar slip and twinning. These deformation modes often lead to internal stress concentrations at slip barriers at low macroscopic strains and can initiate brittle fracture. TiAl is intended for use at elevated temperature. Therefore, the traditional solution to mitigating brittle fracture by shortening the slip length is of limited value because of the attendant reductions in creep strength. As a result, the prognosis for increased yield strength is mixed. The high cycle fatigue strength scales with the yield strength, but the balance between flow and fracture, which affects low temperature ductility, typically is adversely affected. In this talk, the available means of strengthening gamma will be outlined and reasons for the resulting property trades will be examined. The prospect of increasing the yield strength without a negative effect on creep

strength or ductility will be discussed and some suggestions for next steps will be offered.

9:00 AM

STRENGTH AND DUCTILITY OF NOTCHED GAMMA TITANIUM ALUMINIDES: *Prof. Jack L. Beuth*[1]; David A. Knaul[1]; [1]Carnegie Mellon University, Department of Mechanical Engineering, Pittsburgh, PA 15213 USA

Due to their low density and high high-temperature strength retention, gamma titanium aluminides are emerging as viable engineering for gas-turbine engine applications. A concern for the applications, however, is their low ductility, which may limit the useful strength levels in the components containing stress concentrators. In this study, the notched strength of cast 48Al-2Cr-2Nb gamma TiAl is considered under monotonic tensile loading. Efforts are further focused on behavior under conditions of plane stress and on cases where notch radii are large relative to grain size. The key issues considered in this work are, first, how much ductility is needed in gamma. More specifically, the amount of plastic deformation needed in gamma to sufficiently reduce stress concentrations is quantified. Second, the effects of material property variability in specimens machined from gamma castings are considered. Finally, the applicability of approximate design rules to the analysis of notched gamma components is addressed. Finite element predictions are described for notched tensile specimens. Results from the testing of two specimen geometries are presented and the numerical models are used to interpret the test results. Use of the Neuber criterion to relate gamma ductility to notched component strength is also assessed.

9:20 AM

IMPACT RESISTANCE OF Ti-48Al-2Nb-2Cr (AT.%): *Dr. Susan L. Draper*[1]; J. M. Pereira[1]; B. A. Lerch[1]; Dr. Michael V. Nathal[1]; [1]NASA-Lewis Research Center, Cleveland, OH 44135 USA

One of the risks of implementing Gamma TiAl low pressure turbine blades (LPTB) is the poor impact resistance of gamma in comparison to the current blade material, Rene 77. The objective of the current program is to determine the influence of impact damage on the fatigue life of Ti-48Al-2Nb-2Cr (at.%). Specimens have been cast to size to simulate the leading edge geometry of LPTB's. To minimize the quantity of high cycle fatigue tests required, a design of experiments (DOE) has been conducted with impact variables consisting of leading edge thickness, projectile hardness, and impact energy. Additionally, a side experiment studying the effect of temperature has been performed. The quantity of cracking on the front and back sides of the impacts has been measured for each impact condition. The experimental impact conditions produced a spectrum of damage from minor denting to major cracking. The degree of cracking was related to the impact conditions by DOE models. In terms of the results of this study, LPT blades should be as thick as possible for improved impact resistance. With thickness held constant, the initial selection of impact variables can be down-selected to energy for the follow-on fatigue study. The results of some preliminary fatigue tests will be correlated to impact conditions and degree of cracking.

9:40 AM

DISLOCATION DYNAMICS IN SOLID SOLUTION AND PRECIPITATION HARDENED TITANIUM ALUMINIDE ALLOYS: *Dr. Fritz Appel*[1]; Dr. J. Paul[1]; U. Christoph[1]; Prof. Richard Wagner[1]; [1]GKSS Research Center, Institute for Materials Research, Geesthàcht D-21502 Germany

Solution and precipitation hardening were investigated in two-phase titanium aluminide alloys with the base-line compositions Ti-(45-48)Al+Nb and Ti-48Al+C. Significantly enhanced strengths can be achieved through Nb-solid solution effects and carbon precipitates of perovskite type. The effects of the doping elements on the dislocation dynamics were characterized by activation parameters of thermally activated glide processes and TEM observations. Accordingly, the strengthening effects of Nb-solid solutions should be attributed to the related refinement of the lamellar microstructure. It is argued that Nb occupies only Ti-sites and that strength is primarily determined by the $\alpha 2$ content. The hardening achieved via carbon precipitates arises from their strong interaction with gliding dislocations. The analysis qualifies the precipitates as athermal glide obstacles whose glide resistance is maintained up to relatively high deformation temperatures. The mechanism significantly enhances the creep resistance and allows the high temperature capability of the titanium aluminides to be extended. The alloys were subjected to thermomechanical treatments using forging or extrusion. In this way, balanced mechanical properties involving low temperature ductility and high temperature strength have been achieved.

10:10 AM

THE INFLUENCE OF LAMELLAE STATISTICS ON THE HALL-PETCH TYPE STRENGTHENING IN FULLY-LAMELLAR TiAl ALLOYS: *Dr. Seshagiri Sriram*[1]; Dr. Dennis M. Dimiduk[2]; Dr. Peter M. Hazzledine[3]; [1]SYSTRAN Corporation, Dayton, OH 45432 USA; [2]Wright-Laboratory, Materials Directorate (WL/MLLM), Wright-Patterson AFB, OH 45433 USA; [3]UES, Inc., Dayton, OH 45432 USA

Fully-lamellar (FL) two-phase ($\alpha 2+\gamma$) TiAl alloys, subjected to variable cooling-rate controlled heat treatments exhibit a wide range (50-115nm) of mean $\alpha 2$ and γ/γ variant thicknesses, and $\alpha 2$-$\alpha 2$ spacings (50-400nm), and typically follow a log-normal distribution. Room temperature (RT) compressive yield-strength, as a function of the mean lamellae thickness (λ) exhibit a linear Hall-Petch (HP) type relationship. RT compressive yield strength obtained from the same alloys following a thermal treatment in the ($\alpha 2+\gamma$) two-phase field, on the other hand, exhibit a deviation from HP linearity with respect to l. Changes in the microstructure in terms of $\alpha 2$ and g thickness, $\alpha 2$-$\alpha 2$ spacing, and volume fraction of $\alpha 2$, between the two sets of alloys have been quantified by employing statistical methods to data obtained from several grains in TEM thin foils, corresponding to each alloy. Attempts to explain the deviation from linearity using these statistical results will be outlined. The necessity for rigorous statistical sampling to obtain meaningful microstructural parameters from a population of such fine-scale microstructures, will be highlighted.

10:30 AM

LOADING-RATE EFFECT ON THE FRACTURE RESISTANCE OF A GAMMA TITANIUM ALUMINIDE ALLOY: *Dr. Kumar V. Jata*[1]; Dr. Young-Won Kim[2]; [1]Wright Laboratory Materials Directorate, Metals Development and Materials Processing Branch, Wright Patterson Air Force Base, OH 45433-7718 USA; [2]EUS, Inc., Dayton, OH 45432 USA

A wrought gamma TiAl alloy, K5S (Ti-47.0Al-1.8Cr-3.0Nb-0.2W-0.2Si-0.2Ox), in fully-lamellar microstructural forms, has been investigated for the loading-rate dependence on its fracture behavior at various temperatures. Compact-tension specimens containing various lamellar-grain sizes (200-800 μm) and lamellar spacing were fatigue-precracked and then toughness-tested at various strain rates in the range 10^{-1} to 10^{-6} mm/sec. Preliminary results show that the sensitivity to loading-rate increases with increasing temperature. The extent to which crack-opening displacement and fracture resistance change with loading rate depends also on the grain size as well as lamellar spacing. These results will be discussed along with fracture modes and analyzed in comparison with those of the creep-crack growth observations made on the same alloy under sustained loading conditions. * UES, Inc., Dayton, OH

10:50 AM

APPLICATION OF TITANIUM ALUMINIDE TO EXHAUST VALVES FOR AUTOMOTIVE ENGINES: *Dr. Mamoru Sayashi*[1]; Mr. Toshiharu Noda[2]; [1]Nissan Motor Co., Ltd., Nissan Research Center Materials Research Laboratory, Kanagawa 238-02 Japan; [2]Daido Steel Co., Ltd., Corrosion/Heat-Resistant Alloys Research & Development Division, Nagoya 457 Japan

In order to apply TiAl alloys to parts used in exhaust systems of automotive engines, their mechanical properties and oxidation resistance over a wide temperature range, from room temperature to over 1150K, had to be improved. Ti-33.5Al-0.5Si-1Nb-0.5Cr(mass%) intermetallic compound, we developed, satisfied these conditions. We also developed a precision casting method for TiAl that provides a low-cost, high-quality process, and a plasma carburizing technique for assuring good wear resistance on the valve stem end, stem and face. By developing these technologies, high-performance TiAl alloy exhaust valves were produced. The TiAl valve can improve power output and

fuel economy by contributing higher engine speeds and a reduction in valvetrain friction.

11:10 AM

MICROMECHANISMS OF CRACK NUCLEATION AND SHORT FATIGUE CRACK GROWTH IN THE TiAl ALLOY 47-XD: *Dr. Donald L. Anton*[1]; Mr. D. DeLuca[2]; [1]United Technologies Research Center, MS 129-22, East Hartford, CT 06108 USA; [2]Pratt & Whitney, Advanced Engineering Operations, West Palm Beach, FL 33410-9600 USA

The important aspects of crack growth as it relates to gas turbine engine application is the relatively low dynamic fracture toughness of 20-25 MPa Ãm and high fatigue crack growth threshold of 7-10 MPa Ãm. In order to study this phenomenon in greater detail, a study was conducted into the short fatigue crack growth characteristics in the TiAl alloy, 47-XD. Tests were conducted on EDM notched axial fatigue specimens in the cast and heat treated condition. Crack growth rates were monitored at stress intensities ranging from 2.5 MPa Ãm through fracture. Crack initiation at the EDM flaw was problematic, with 50% of the specimens nucleating cracks at regions other than the EDM flaw. Many of these nucleation events were in view of the optical imaging system, and data was obtained from 75% of the tested specimens. When nucleation occurred away from the EDM notch, the site of nucleation could be identified with adjacent lamellar colonies which, due to poor geometrical orientation, had limited slip transfer. An assessment of these grain misorientations will be given along with short fatigue crack growth data which was shown to be significantly greater than the large crack data generated previously.

11:40 AM

MECHANICAL PROPERTIES OF Ti48Al-2Nn-2Cr AND Ti-50.7Al ALLOYS AFTER THERMOMECHANICAL PROCESSIING: *V. M. Imayev*[1]; G. A. Salishchev[1]; R. M. Imayev[2]; M. R. Shagiev[1]; A. V. Kuznetsov[1]; Dr. Oleg N. Senkov[2]; F. H. Froes[2]; [1]Russian Academy of Sciences, Ufa, Russia, Institute for Metal Superplastisity Problems Ufa 450001 Russia; [2]University of Idaho, Institute for Materials and Advanced Processes (IMAP), Moscow, Idaho 83844-3026 USA

Room temperature mechanical compression tests were performed on Ti-50.7Al and Ti-48Al-2Nb-2Cr alloys in equiaxed fine-grained, duplex, and fully lamellar microstructural forms. Hall-Petch analysis indicated that the parameters k_y and O_o in fully lamellar materials were much higher than in the equiaxed fine-grained and duplex materials. In fully-lamellar materials k_y and σ_o increased when the lamellar spacing (λ) was decreased. However, k_y became independent of λ if the lamellar boundaries were taken into account. In this case, k_y can be expressed as a function of effective grain size which is defined as $d_{eff} \approx d/(d/\lambda)^{1/3}$. Both of the parameter s (k_y and σ_o) were measured to be higher for Ti-48Al-2Nb-2Cr than for To-50.7Al. The proportions of slip and twinning activities were observed to vary with grain size, resulting in a ductility maximum occurring in the equiaxed fine-grained material. For ultra-fine grain sizes (d<1 μm), the dislocation pile-up length was insufficient to produce deformation twinning, leading to decreases in room temperature ductility.

SUPERPLASTICITY AND SUPERPLASTIC FORMING: Session V - Forming and Joining of Advanced Materials

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

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

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

Session Chair: Dr. S. L. Semiatin, Air Force Materials Lab, MLLM, Wright-Patterson AFB, OH 45433

8:30 AM INVITED

COMPRESSIVE DEFORMATION OF LIQUID-PHASE SINTERED SILICON CARBIDE AT ELEVATED TEMPERATURE: *T. Nagano*[1]; S. Honda[1]; F. Wakai[1]; M. Mitomo[2]; [1]Japan Science and Technology Corporation, Nagoya Japan; [2]National Institute for Research in Inorganic Materials, Tsukuba Japan

Nano-grain sized β-SiC was prepared with the addition of 7 wt% Al2O3, 2 wt% Y2O3 and 1 wt% CaO at 2023 K in argon atmosphere by hot-pressing. The relative density was more than 97%. Phase transformation from β to α was only 4 ~ 5% during sintering. The average grain size was 170 nm. Compressive tests were performed at the strain rate from 3 °° 10-3 to 1 °° 10-5 s-1 at the temperature range from 1973 to 2073 K in argon atmosphere. Superplastic behavior with grain growth was observed at a strain rate of 1 °° 10-3 s-1 at 2023 K. Strain did not contribute to the grain growth during compressive deformation. The additives formed a liquid at elevated temperature and accelerated the sintering and the creep rate.

8:55 AM INVITED

SUPERPLASTICITY IN ZIRCONIA-BASED CERAMICS: *A. H. Chokshi*[1]; [1]Indian Institute of Science, Department of Metallurgy, Bangalore 560 012 India

Following the initial report by Wakai on an elongation of over 100% in a 3 mol% yttria stabilized zirconia (3YTZ), superplasticity has now been demonstrated in a wide range of zirconia containing ceramics, with a maximum elongation of over 1000% in a glass containing ceramic. The presence of trace impurities can have a very significant effect on the mechanical properties of these ceramics. This report will examine data on a wide range of superplastic zirconias to evaluate the role of impurities in these materials. It will be demonstrated that, while trace impurities apparently hinder grain boundary sliding in superplastic metals, these impurities appear to facilitate grain boundary sliding in superplastic zirconia.

9:20 AM

INFLUENCE OF MICROSTRUCTURAL CHANGES DURING SUPERPLASTIC DEFORMATION ON MECHANICAL RESPONSE OF A NEAR-GAMMA TITANIUM ALUMINIDE ALLOY: *C. M. Lombard*[1]; S. L. Semiatin[1]; A. K. Ghosh[2]; [1]Wright Laboratory, WL/MLLM, Materials Directorate, Wright-Patterson AFB, OH 45433-7817; [2]University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109-2136

The uniaxial hot tension behavior of a near-gamma titanium aluminide alloy sheet (Ti-45.5Al-2Cr-2Nb) was determined in the as-rolled condition (initial grain size # 3 to 5 μm) and rolled-and-heat treated (1177°C/4 hours or 1238°C/2 hours) conditions (initial grain size # (10 to 12 μm). Microstructural evolution, cavitation rates, and failure modes were established via isothermal constant strain rate tests conducted at 10-4 s-1 to 10-2 s-1 and test temperatures between 900°C

and 1200°C. Interrupted and strained-to-failure tests were conducted in order to track dynamic microstructural changes with time. Additionally, strain rate sensitivity values as a function of strain were established via strain rate jump tests. The changes in strain rate sensitivity were then correlated with microstructural changes, including grain refinement via dynamic recrystallization and dynamic grain growth.

9:40 AM

THE HOT WORKABILITY AND SUPERPLASTICITY OF TI-48Al-2Nb-2Cr ALLOYS: *G. E. Fuchs*[1]; [1]Lockheed Martin Corporation, Schenectady, NY 12301-1072

The hot compression behavior and microstructure evolution of ingot metallurgy (I/M) and powder metallurgy (P/M) processed samples of the near-γ Ti-aluminide alloy, Ti-48Al-2Nb-2Cr (at%), were determined. Three I/M conditions and two P/M conditions were examined in this study. Hot compression tests were performed in the temperature range of 1100°-1300°C at strain rates ranging from 1.67 °°10-1/sec to 1.67 °° 10-4/sec. P/M materials consolidated by either hot isostatic pressing (HIP'ing) or extrusion exhibited the best hot workability in most cases. The P/M possessed finer, more homogeneous microstructures than the I/M materials. It was also noted that improved workability, and in some cases superplastic behavior, was observed in materials with equiaxed microstructures without any lamellar constituents.

10:00 AM Coffee Break in Exhibit Hall

10:15 AM

SUPERPLASTIC FORMING OF Ti-6Al-4V WITH APPLICATIONS IN DENTISTRY: *R. V. Curtis*[1]; [1]UMDS, Dental Materials Science, London UK

A 20-ton superplastic forming press with a novel design has been developed for use in a dental school in Great Britain. The design incorporates a metal tooling assembly that allows for the insertion of ceramic tools produced from a slurry made from investment powder and water. Forming operations have shown that Ti-6Al-4V sheet with complex shapes can be formed over a period of approximately twenty minutes. For dental applications dies should be readily produced but must be sufficiently strong in compression at temperatures around 900°C to withstand the forming pressures. In addition, good surface detail is important and must be transferred from the die to the alloy sheet during the forming process. Other properties of the die material that are of significance include thermal expansion characteristics on heating and cooling and interactions with the alloy sheet. Applications include the fabrication of denture bases and dental implant superstructures. Both types of dental prosthesis can be produced in a relatively thin section compared with similar structures produced in other materials and both have a high strength to weight ratio.

10:35 AM INVITED

SUPERPLASTIC FORMING AND DIFFUSION BONDING OF AVESTA 2304 DUPLEX STAINLESS STEEL: *J. Pilling*[1]; Z. C. Wang[2]; N. Ridley[2]; [1]Michigan Technological University, Houghton, MI; [2]University of Manchester/UMIST, Materials Science Centre, Manchester, M1 7HS UK

Diffusion bonding (DB) is often combined with superplastic forming (SPF) in the manufacture of complex cellular structures from microduplex alpha/beta titanium alloys. The work described in this paper relates to the strongly emerging interest in the application of DB/SPF in the manufacture of heat exchangers from duplex stainless steels. Previous work has shown that duplex stainless steels can, in fact, be processed to develop the necessary superplastic properties, but little is known of their suitability for diffusion bonding given the highly protective chromium oxide normally present on their surfaces. Alloys such as 3RE60 and Zeron 100 are both superplastic and can be diffusion bonded although the process cycle for diffusion bonding has been difficult to predict. The present work involves the characterization of the superplastic behavior of Avesta 2304, and alpha/gamma stainless steel together with a study of the process of diffusion bonding.

11:00 AM

HIGH RATE SUPERPLASTIC FORGING AND DIFFUSION BONDING: M. Hopper[1]; *T. R. Bieler*[1]; [1]Michigan State University, Department of Materials Science and Mechanics, East Lansing, MI 48824-1226

Samples of high rate superplastic IN90211 mechanically alloyed aluminum have been upset forged in air at strain rates between 0.4-4 s-1. To investigate the possibility of diffusion bonding at these strain rates, two pieces were forged simultaneously that were separated by a distance so that the two pieces would meet during the forging process. Room temperature tensile tests were performed on the specimens after forging to investigate whether the bond line was weaker than a forging of a single piece. The effects of strain rate and temperature on the diffusion bond strength are reported.

11:20 AM

DUCTILITY AND CAVITATION AT ELEVATED TEMPERATURES IN A SUPERPLASTIC ZK60-BASED COMPOSITE: *T. Mukai*[1]; T. G. Nieh[2]; K. Higashi[3]; [1]Osaka Municipal Technical Research Institute, Osaka 536 Japan; [2]Lawrence Livermore National Laboratory, Livermore, CA 94551; [3]Osaka Prefecture University, College of Engineering, Department of Metallurgy and Materials Science, Osaka 593 Japan

An extruded magnesium-based composite, ZK60/SiC/17p, has been studied and shown to be superplastic at high strain rates. The composite has an extrusion ratio of 100:1. This thermomechanical process resulted in a uniform microstructure in the composite and produced a superplastic elongation in excess of 450% at a strain rate of 0.1 s-1. Cavitation behavior was also characterized. Volume fractions of cavity were measured as a function of strain. It was found that the cavity growth rate was relatively slow in this additionally extruded material. Scanning electron micrographs taken from the fracture sample revealed that the cavity mainly nucleated in the matrix (ZK60 alloy) and grew as deformation proceeded. The uniform distribution of the SiCp reinforcement obviously plays an important role on the suppression of cavitation. In the present paper the microstructure-ductility-cavitation relationship will be addressed.

TRANSIENT THERMAL PROCESSING OF MATERIALS II: Session I

Sponsored by: ASM International: Materials Science Critical Technology Sector/Electronic, Magnetic and Photonic Materials Division, 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 AM Room: Fiesta C
February 18, 1998 Location: Convention Center

Session Chairs: B. Sopori, National Renewable Energy Laboratory, Golden Co 80401; Rajiv Singh, University of Florida, Gainesville, FL 32061

8:30 AM

SURVEY OF DEPOSITION UNIFORMITY IN AN EDGE-HEATED RTCVD SYSTEM: *Kevin R. Kimberlin*[1]; J. R. Hauser[1]; William J. Kletcher[1]; [1]North Carolina State University, Electrical and Computer Engineering, Raleigh, NC 27695

The issue of deposition uniformity must be addressed before industry accepts RTCVD applications. The NCSU vertical RTP (VRTP) utilizes a three-zone lamp profile with direct edge heating to compen-

sate for thermal losses associated with the wafer edge. While thermal uniformity moderately controls deposition uniformity, other process conditions have been found to contribute significantly. This paper surveys the uniformity of various process conditions in several RTCVD applications. In previous work, the VRTP has achieved thickness uniformity better than 3.5 %, 1 sigma for polysilicon. However, the across wafer temperature profile require to achieve similar results, 3.7 %, 1 sigma for oxide depositions varied significantly near the wafer edge. The parameters that may influence deposition uniformity include surface conditions, gas composition, local reactant concentrations, gas flow rate, flow orientation, and pressure. Film characterization concentrates on thickness uniformity. Process characterization uses pyrometry, thermocouple wafer, and monitor wafers. The deposition studied are : Polysilicon, epi, thin and thick oxides, and SiGe. The experiments are designed to find open-loop temperature profiles that optimize deposition uniformity and also to determine the film uniformity for uniform temperature profiles. Additionally, parameters such as deposition surfaces and flow rates are varied. Finally, the results of a novel scheme to increase final deposition uniformity is presented.

9:00 AM

GROWTH OF POLYCRYSTALLINE SILICON FILMS BY RAPID THERMAL-CVD PROCESS: *A. Slaoui*[1]; D. Angermeier[1]; S. Boudrais[1]; R. Monna[1]; J. C. Muller[1]; [1]Laboratoire PHASE(CNRS) , Strasbourg cedex 2, France

Here we report on Boron-doped silicon films deposited on various substrates using a rapid thermal-CVD system working at atmospheric or reduced pressure. This is a cold-wall reactor, and employs high temperature hydrogen reduction of dichlorosilane (SiH2Cl2) or trichlorosilane (SiHCl3) for si deposition. Depositions were carried out on commercially available substrates such as SiO2 coated Si, graphite, alumina and mullite. Effects of various parameters, including reactant gas, working pressure, flow rates, deposition temperatures and substrates properties, on the silicon film characteristics (deposition rate, grain size and orientations) were extensively investigated. Surface morphology and minority-carrier lifetime of the deposited films were also studied. High deposition rates in the range of 1-3 micrometers/min were achieved irrespective of the substrate nature. The grain size and preferential orientations, however, were found to be dependent on the deposition temperature, gas pressure and flow rates as well as the substrate of choice. The effective lifetime in our p-type silicon films range between 0.2 and 0.5 microsec. The main purpose of the present work is to comprehend the impact of the experimental parameters on film quality for solar cell applications.

9:20 AM

OPTIMIZATION OF RTP PARAMETERS TO PRODUCE ULTRA-SHALLOW, HIGHLY ACTIVATED AS+, BF2+ AND B+ ION IMPLANTED JUNCTIONS: *Daniel F. Downey*[1]; Steven D. Marcus[2]; Judy W. Chow[2]; [1]Varian Ion Implants systems, Gloucester, MA 01930; [2]AST elektronoiks USA, Tempe, AZ

The effects of time, temperature, ramp-up and ramp down rates with rapid thermal annealing were investigated on 2 keV 75As+, 2.2, 5.0 and 8.9 keV 49BF2+ and 1.0 and 2.0 keV 11B+, 1e15/cm2 ion implanted samples to optimize electrical activation and to minimize sheet resistance values, while simultaneously maintaining ultra-shallow junctions. These annealed samples were analyzed by four point probe, SIMS, spreading resistance profiling (SRP), Hall Effect Measurements, and in select cases by transmission electron microscopy (TEM). Based on the above results, detailed mechanisms of the annealing and electrical characteristics of these layers are developed.

9:40 AM

OPTICAL EFFECTS DURING RAPID THERMAL DIFFUSION: *S. Noel*[1]; L. Ventura[1]; A. Slaoui[1]; J. C. Muller[1]; B. Groh[2]; R. Schindler[2]; B. Froschle[3]; T. Theiler[3]; [1]Laboratorie PHASE, Strasbourg, France 67037; [2]Fhg ISE, Freiburg, Germany 79100; [3]AST-electronik, Dornstadt, Germany 89160

Forming n+ -p or n+ -p-p+ junctions by rapid thermal diffusion of phosphorous or co-diffusion of phosphorous and aluminum into silicon is opening new possibilities for low-cost and environmentally safe solar cell production. Different furnace conceptions involves different lamp radiation spectra, due to difference in applicated lamp power. Diffusion of Phosphorus from doped glass films spun onto crystalline silicon material results in different diffusion profiles for comparable annealing temperatures in different furnaces. Further experiments using additional UV lamps are involved to analyze the impact of the short wave length part of the lamp spectrum on the diffusion mechanisms. Annealing pre-diffused profiles reveals the importance of the oxide presence in the observed enhancements. All results are discussed in terms of sheet - resistance, doping profiles and diffusion coefficients. Diffusing simultaneously phosphorous and aluminum in order to form a n+ -p-p+ structure is known to induce deeper n+ emitter compared to a single phosphorous diffusion. Observing glass densification of Spin-On glass deposited films in absence or presence of evaporated aluminum on the back side reveal temperature consequences in the sample volume for constant lamp power. Systematical thinner oxide thickness are measured. This will be correlated to decrease of the emissivity due to the presence of aluminum.

10:10 AM Coffee Break in Exhibit Hall

10:20 AM

RTP REQUIREMENTS TO YIELD UNIFORM AND REPEATABLE ULTRA-SHALLOW JUNCTION WITH ENERGY BORON AND BF2 ION IMPLANTS: *Steven Marcus*[1]; Wilfried Lerch[2]; Daniel F. Downey[3]; Stanislov Todorov[3]; Judy Chow[3]; [1]Steag AST elktroniks, USA, Tempe, AZ; [2]Steag AST elktroniks GmbH, Dornstadt, Germany; [3]Varian Ion Implant Systems, Gloucester, MA 01930

Ion Implant of 2.0 and 5.0 keV boron and 2.2 and 5.0 keV BF2 at a dose of 1e15/cm2 were investigated. Optimal RTP anneal conditions were developed which produced highly activated yet shallow junctions. The effects of oxygen were studied and found to be an important variable to control in order to produce uniform and rep for each and every anneal to assure repeatable anneals. This paper discusses these optimal anneal conditions and this interlocked purge procedure in detail.

10:40 AM

CONTROLLED THERMAL KINETICS IN RTP: *Z. Nenyei*[1]; J. Nieb[1]; C. Grunwald[1]; [1]Steag AST elektronik, Dornstadt, Germany D-89160

Process control of subhalf micrometer structures require separate optimization of different process components taking place simultaneously during high temperature annealing. In many cases, reaction rate limited and diffusion limited process parts are to be promoted or suppressed in a complementary manner. In case of reaction rate limited process short time "flash" annealing at higher temperature is often more advantageous than the conventional temperature time functions for 10-60s. Linear ramp functions do not give best results in such cases. We are going to show the importance and possibilities of the controlled thermal kinetics processing mode in some RTO and RTA experiments.

11:10 AM

PATTERN FORMATION DURING SURFACE MELTING AND ZONE MELTING RECRYSTALLIZATION OF SILICON THIN FILMS: *Won Tae Kim*[1]; Seong Gyoon Kim[2]; [1]Chongju University, Department of Physics, Chongju, Korea 360-764 ; [2]Kunsan National University, Department of Materials Science and Engineering, Kunsan, Korea 573-360

Solid-liquid (S/L) interface morphology during surface melting and zone melting recrystallization (ZMR) of Si thin film was calculated by using phase-field model in a personal computer. The formation of irregular S/L interface during melting could be interpreted by the difference in reflectivity between solid and liquid Si, which results in the formation of undercooled liquid in front of the interface. The effects of heater scanning rate, radiation intensity and intensity profile during ZMR on S/L interface morphology were calculated for a given interface morphology were calculated for a given interfacial energy anisotropy constant. Dentrite-like pattern was preferred at lower scanning velocity, lower energy intensity and wider radiation zone. Regular cellular spacing S/L morphology can be obtained at a certain range of processing parameters. Cellular spacing increased with increasing either heater scanning velocity or radiation width.

11:30 AM

OPTICAL AND ELECTRONIC PROPERTIES OF Si-Al INTERFACES PRODUCED BY OPTICAL PROCESSING: *Bhushan L. Sopori*[1]; Michael Cudzinovis[1]; Wei Chen[1]; [1]National Renewable Energy Laboratory, Golden, CO 80401

Si-Al interfaces are used extensively in Si solar cells to incorporate such features as the formation of a backsurface field (BSF) that acts as a minority carrier reflector, for impurity gettering, and potentially to serve as an optical reflector for enhancing optical absorption. To meet these requirements the interface characteristics such as the morphology of the interface, the thickness of Al-Si alloy layer, the reflectivity of the interface, and the resistivity of the contact, must be very carefully controlled. The use of conventional furnace annealing can produce excellent gettering and good BSFs. However, such interfaces have undesirable optical properties. We have used optical processing to simultaneously control these parameters. To perform the optical processing, the device, such as solar cell, is deposited with a layer of Al typically > 0.2 micrometer thick. The sample with the Si side facing the light, is then illuminated with lights from a bank of tungsten halogen lamps. The lamps have a spectrum peak about the wavelength of 2 micrometers. The processing conditions can be arranged to produce a controlled thickness of a Si-Al alloy at the interface. The interfacial alloying causes a low resistivity contact to P-type substrate. The optical properties at the Si-Al interface depend on the thickness of such an interface and the gradient in the refractive index. Si-Al interfaces of very low contact resistance can be produced to have a very high reflectivity that is close to an ideal interface. Such an interface is abrupt with an alloyed thickness of less than 100 A units and is free from pits. Because of the preferential nature of the interdiffusion at the interface, the interface can develop a texture leading to pyramid formation in the case of a (100) wafer. Such an interface is effective in light trapping, which enhances the optical absorption and thus improves the cell efficiency.

ZINC-BASED STEEL COATING SYSTEMS: PRODUCTION & PERFORMANCE: Session V - Post Treatments and General Discussion

Sponsored by: Structural Materials Division, Ferrous Metallurgy Committee

Program Organizers: Frank E. Goodwin, Int'l Lead Zinc Research Org., PO Box 12036, Research Triangle Park, NC 27709-2036; Michelle DuBois, Cockerill Sambre, Quai Du Halage 10, Flemalle B-4400 Belgium; Jong-Sang Kim, Pohang Iron & Steel Co. Inc., Kwangyang Research Labs, Chonnam 544 090 Korea; Josef Faderl, Voest Alpine Stahl Linz, Turmstrasse 45, PO Box 3, A-4031 Linz, Austria; Eduardo A. Silva, USS Technical Center C-20, Monroeville, PA 15146

Wednesday AM Room: Centro Room B
February 18, 1998 Location: Convention Center

Session Chair: Michele DuBois, Cockerill Sambre, Quai Du Halage 10, Flemalle B-4400 Belgium

8:30 AM

THE SURFACE COLOR OF CHROMATE FILM ON THE ELECTROGALVANIZED STEEL: *Y. K. Song*[1]; H. J. Kim[1]; [1]POSCO, Coating Technology and Electrical Steel Sheet Research Team, Technical Labs, Pohang 790-785 Korea

A conversion chromate coating is widely used to have a good corrosion resistance in the continuous electrogalvanizing works. The color of chromated film depends on chemical composition of bath as well as Cr coating weight. In this study, in order to find out the relationship between the surface color and the properties of chromated film, which were characterized by ESCA, SAM and XRD technique. The surface color of chromated film mainly depends on the coating weight of chromium and the ratio of Cr(Vl)/Cr(III) in the film. The surface color of chromated film was changed from blue bright to black under high humidity condition. While the ratio of Cr(Vl)/Cr(III) was not directly related to this color changes. The diffusion and oxidation of Zn trapped in the chromated film was the main factor of this color change.

8:50 AM

THE VISUAL APPEARANCE OF PAINTED GALVANNEALED PANELS : *B. C. DeCooman*[1]; C. DeMaré[1]; K. Meseure[1]; [1]OCAN NV, The research center of Sidmar, ARBED Flat Rolled Products Group, Zelzate, 9060 Belgium

OCAS has been involved in research on the visual appearance of painted panels for quite a few years. This was largely due to the development of SIBETEX by the Sidmar Group. Some of the most interesting results have come from the study of the visual appearance of painted galvannealed panels, which showed that thanks to the EBT (electron beam texturing) technology, hot dipped sheet products were now available which had a visual appearance after painting that could rival the appearance of painted electroplated sheet. Both the composition dependence of the visual appearance of painted galvannealed panels on Ti IF steels and the effect of the Electron Beam Textured (EBT) full hard strip texture have been reported at the Galvatech'95 conference. The aim of our presentation is to review the most recent findings on the subject and propose a mechanism which relates inhibition layer breakdown, outburst formation and alloying reaction to the final visual appearance as appreciated by the human eye or as measured by a number of observer-independent methods. The better visual appearance of bare galvannealed sheet in comparison to galvanized sheet is by and large due to the low visibility of surface defects on the sheet. This does not however play an important role when the coated sheet is painted. In that case the amplitude of the longer wavelength components of the galvannealed surface profile is the fundamental variable. The visual appearance of painted galvannealed panels is strongly influenced by the emergence of out-bursts. These outburst generate a large profile waviness due to the flow of the liquid Zn and the profile roughness increases mainly as a result of the ζ phase formation. In fact, the surface profile is determined mainly by the crests of the outbursts. The depth distribution of this surface profile is characterized by a positive skewness in contrast to the depth distribution of the EBT textured full hard substrate which has a clear negative skewness. As the galvannealing proceeds, the ζ crystals forming the outbursts are gradually replaced by a compact δ phase and the positive skewness reverts back to a negative value. At higher Fe contents the visual appearance improves and a visual appearance index of 90%, a value similar to the one obtained on electroplated sheet, can be obtained for coatings with 9-11% Fe after temper rolling, if a low amplitude waviness full hard EBT profile is used. A reconstruction process of the full hard surface profile takes place during galvannealed and it effectively transfers the low amplitude EBT waviness from the coating/steel interface to the coating surface. It is therefore important that any trace of the outbursts features is effectively eliminated during the galvannealing if a high visual rating must be achieved. This effect cannot be exploited for hot dipped galvanized sheet for which the full hard texture pattern on the strip is masked by the Zn coating. The visual appearance of painted galvanized panels can therefore only be improved by temper rolling. Unfiltered 3D surface profiles me asured taken at different coating Fe contents reveal that the circular depressions caused by the EBT crater rim imprints react more slowly than the flat areas on the sheet where the reaction proceeds more evenly. This confirms the model during galvannealing the EBT textured full hard substrate profile is reconstructed on the surface of the coating as soon as the compacteδ phase is the main phase at the surface. Consequently, painted galvannealed panels on Fe-rich coatings with a mainly δ phase surface will result in a better visual appearance.

9:10 AM

HIGH PERFORMANCE THIN ORGANIC COATINGS FOR ZINC-COATED STEEL: *N. Maurus*[1]; [1]Chemetall, Gmbh, Frankfurt Germany

It is well known, that inorganic passivation agents are widely used to enhance the corrosion protection properties of zinc coated steel such as 55%Al-Zn or Hot Dip Galvanized steel. To extent the properties of passivated substrates a new generation of Thin Organic Coatings was developed to provide the following assets: Increased corrosion protection, Anti finger print characteristics, Formability without additional lubrication, Pretreatment for subsequent paint, Applicable on all zinc an zinc alloy coated sheets, One step application. This paper describes the application and the properties of this thin organic film (about 1 µm). Tests methods and results to evaluate corrosion protection morphology, formability and paintability are presented. Sheets coated with a Thin Organic Coating offer many new ways of application in the automotive, appliance, computer and general industry. These translates into significant savings for the customer. Some examples are presented.

1998 Institute of Metals Lecture and Robert F. Mehl Medalist

Lecturer:
Prof. Dr. Paul Shewmon
Prof. Emeritus, Ohio State University

Topic:
Grain Boundary Fracture

Wednesday, February 18
12:00 noon

Location:
Fiesta A, Convention Center

Light Metals Division Luncheon

Speaker:
Norman F. Nieder
Anheuser-Busch, Inc.

Topic:
"Tracing the History of the Beverage Can"

Wednesday, February 18
12:00 noon

Location:
South Banquet Hall, Convention Center