MONDAY AM

10TH INTERNATIONAL SYMPOSIUM ON EXPERIMENTAL METHODS FOR MICROGRAVITY MATERIALS SCIENCE: Session I

Sponsored by: ASM International: Materials Science Critical Technology Sector, Thermodynamics & Phase Equilibria Committee, Jt. Electronic, Magnetic and Photonic Materials Division/Structural Materials Division, Alloy Phases Committee, NASA Microgravity Sciences

Program Organizers: Robert Schiffman, R.S. Research Inc., Crystal Lake, Barton, VT 05822; Carlo Patuelli, Universita di Bologna, Depatrmento di Fisica, Bologna I-40126 Italy

Monday AM Room: Plaza Room A
February 16, 1998 Location: Convention Center

Session Chair: Carlo Patuelli, University of Bologna, Departimento di Fisica, Bolonga I-40126 Italy

8:30 AM Introduction and Welcome

8:40 AM
EUTECTIC GROWTH AND THE INFLUENCE OF GRAVITY: *R. W. Smith*[1]; [1]Queen's University at Kingston, Department of Materials and Metallurgical Engineering, Ontario, K7L 3N6 Canada

The physical properties of eutectics tend to be microstructure-sensitive, i.e. as the microstructural scale is reduced (refined), the demand property increases, e.g. mechanical properties (Al-Si), opto-magnetic properties (Bi-Mn). In view of this, terrestrial processing is often directed towards the production of microstructural refinement. Similarly, it has been reasoned that microstructural refinement could result from freezing in reduced gravity. It is recognized that the interphase spacing in a binary eutectic is controlled by liquid diffusion and that, on earth, buoyancy-driven convection enhances solute transport. Hence it is presumed that the interphase spacing ought to decrease when an eutectic alloy is frozen under conditions of much-reduced gravity, where buoyancy effects would be largely absent. The result of such speculation is that many eutectics have been frozen under reduced gravity and it has been reported that, whilst some eutectics did become finer, others showed no change and some even became coarser. This varied behavior prompted the author to conduct well-controlled Bridgman growth studies in two eutectic systems: Bi-MnBi and Sb-MnSb. In both eases, no statistically significant change in spacing occurred under microgravity conditions. The author will present these results and others concerned to determine whether a consistent, reproducible reduction in interphase spacing may be obtained by controlled convection at the solid / liquid interface.

9:00 AM
SEGREGATION IN MICROGRAVITY PROCESSED IMMISCIBLE ALLOYS: *La Shawnda Little*[1]; J. B. Andrews[1]; [1]University of Alabama at Birmingham, Department of Materials and Mechanical Engineering, Birmingham, AL 35294

Early microgravity experiments with immiscible alloys were usually carried out with the intent of forming dispersed microstructures. By processing under microgravity conditions, the main mechanism leading to gross phase separation would be eliminated. However, analysis of flight samples revealed a separated structure where the minor phase was present along the outer surface, while the major phase was present in the center. The Wetting Characteristics of Immiscibles project, scheduled to fly aboard the USMP-4 mission in November of 1997, is designed to gain insight into the mechanisms causing segregation of these alloys. This investigation will utilize an immiscible transparent organic alloy system and a transparent container in order to facilitate direct observation of the separation process. A range of immiscible alloy compositions will be utilized in order to obtain variations in the minor and major phases present and observe the influence on the segregation processes. This presentation will describe the investigation and the results obtained during microgravity processing.

9:20 AM
PROPERTIES OF InSb SOLIDIFIED THROUGH SUPERCOOLING STATE DURING MICROGRAVITY CONDITION: *Dr. Hideki Minagawa*[1]; Mr. Katsuyoshi Shimokawa[1]; Mr. Yoshinobu Ueda[1]; Mr. Jiro Nagao[1]; Dr. Yoshikazu Suzuki[1]; [1]Hokkaido National Industrial Research Institute, Agency of Industry and Science Technology, Ministry of International Trade and Industry, Japan., Materials Division, Sapporo, Hokkaido Prefecture Japan

Supercooling state is usually observed under molten material under containerless system. Furthermore this phenomenon is found to be appeared under microgravity condition because the noncontact conditions is attained. Microgravity experiment has been performed by 1.3 sec drop tower facility in Hokkaido National Industrial Research Institute (HNIR). The grain size which corresponds to solidification speed under microgravity and the properties of indium antimonide (InSb), such as band gap energy and optical absorbance have been investigated. The optical absorbance of InSb in near infrared radiation region, which had been solidified under supercooling state during microgravity condition, were found to be about 10 - 30 % higher than that of single crystal InSb. Moreover, the properties of impurity type semiconductor was observed on InSb alloy with non-stoichiometric composition. The comparison of energy gap between InSb single crystal and InSb solidified through supercooling state during microgravity will be described.

9:40 AM
METASTABLE DEMIXING OF SUPERCOOLED Cu-Co AND Cu-Fe ALLOYS IN AN OXIDE FLUX: *Dr. Delin Li*[1]; T. J. Rathz[2] and G. Williams[2] [1]NASA Marshall Space Flight Center, ES71, Huntsville, Alabama 35803 USA; [2]University of Alabama, Huntsville, Alabama 35899

The metastable liquid-separation in the Cu-Co and Cu-Fe systems has been studied using a melt fluxing method. When these alloys at compositions ranging from 10 to 80 wt pct Co (or Fe) were supercooled below a critical temperature, dependent on the composition, liquid-separation was observed. The metastable liquid miscibility gap has been directly determined through the measured temperature-time profiles. Al phase-separated samples exhibited droplet-shaped morphologies, despite a variety of droplet distributions. It was found that uniformly dispersed microstructures were obtained as the minority component was less than 20 vol.%; while beyond this volume fraction, serious coarsening was incurred. One of the differences between supercooled Cu-Co and Cu-Fe alloys is that Fe-rich droplets obviously moved upwards due to a low specific gravity of Fe. Calculations of the miscibility

gap and the maximum droplet radius were made to analyze the experimental results.

10:00 AM

CONTAINERLESS PROCESSING OF $NdBa_2CU_3O_{7-X}$ SUPERCONDUCTING OXIDE BY AERO-ACOUSTIC LEVITATION TECHNIQUE: *Dr. Yuzuru Takamura*[1]; Mr. Kosuke Nagashio[1]; Mr. Tomotsugu Aoyama[1]; Dr. Kazuhiko Kuribayashi[1]; [1]The Institute of Space and Astronautical Science, Sagamihara-shi, Kanagawa 229 Japan

Containerless processing of $NdBa_2Cu_3O_{7-x}$ superconducting oxide was performed using an aero-acoustic levitation (AAL). Solidification behavior from deeply undercooled liquid state was investigated to study the direct formation of tetragonal $NdBa_2Cu_3O_{7-x}$ (Nd123). Pre-sintered $NdBa_2Cu_3O_{7-x}$ spheres of size 2.7 mm diameter were levitated by AAL and heated by CO_2 laser to be completely melted. Then, the samples were cooled down to be spontaneously nucleated and solidified. Sample temperature was monitored by high-speed two-color pyrometer. In addition, the melted samples were also dropped on a Cu chill plate to trigger the nucleation of solidification at a given temperature of 1000, 1050, 1100, and 1200°C. The processed samples were characterized by an optical microscope, XRD, SEM, and EDS. Strong peaks of Nd123 phase were observed in the XRD pattern of processed samples. The peak intensity of Nd123, which shows the typical dendrite structure, increases with the undercooling, and almost single phase Nd123 was obtained in the most deeply undercooled sample, which nucleated spontaneously at 950°C. No $Nd_4Ba_2Cu_2O_{10}$ phase was observed in it. This shows evidently that the Nd123 phase was formed congruently from the melt.

10:20 AM Break

10:40 AM

MICROGRAVITY GROWTH OF GaSb SINGLE CRYSTALS BY THE LIQUID ENCAPSULATED MELT ZONE (LEMZ) TECHNIQUE: J. Mileham[1]; C. Lopez[1]; *R. Abbaschian*[1]; [1]University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32607 USA

Single crystals of <100> GaSb, encapsulated in KCl-NaCl, were grown by the Liquid Encapsulated Melt Zone (LEMZ) technique in the SPACEHAB-04 Module, aboard the Shuttle Endeavor, as part of the STS-77 shuttle mission launched on May 19, 1996. Three samples were regrown from single crystals which were initially 16 mm in diameter and 65 mm in length at translation speeds ranging from 1 to 6 mm/hr and at a constant rotation speed of 1 rpm in the ELLI-FM mirror furnace by Dornier Inc. Their resulting dislocation density, dopant distribution, and Hall effect data was characterized and related to processing conditions, and a comparison was made to data yielded by ground-processed samples which were grown under similar conditions in the ELLI-EM furnace. The microgravity processed samples were all found to be single crystal after regrowth with reduced defects and dopant striations in comparison to both the as-received crystals and the ground-grown crystals.

11:00 AM

LIQUID DIFFUSION MEASUREMENT OF COMPOUND SEMICONDUCTOR LEAD-TIN-TELLURIDE USING ROCKET AND SPACE SHUTTLE: *M. Uchida*[1]; M. Kaneko[2]; T. Itami[3]; S. Yoda[4]; T. Masaki[4]; [1]Research Institute, IHI, Materials Technology Department, Tokyo 135 Japan; [2]Ishikawajima Jet Service Co., Ltd., Space Department, Tokyo 135 Japan; [3]Hokkaido University, Department of Chemistry, Faculty of Science, Hokkaido 060 Japan; [4]National Space Development Agency of Japan, Tsukuba-shi Ibaragi 305 Japan

In order to obtain the "true" diffusion coefficient of liquid lead-tin-telluride, a microgravity experiment was conducted using German sounding rockets TEXUS, a Japanese sounding rocket TR-1A and a space shuttle Columbia. A diffusion couple was composed of two different chemical composition columns; the one column contained 20 mole % of tin-telluride and 80 mole % of lead-telluride, and the other one contained 30 mole % of tin-telluride and 70 mole % of lead-telluride. The diffusion samples of 2 mm in diameter were kept at diffusion temperatures and quenched by injecting helium gas. All processes were realized under micro-gravity. Cooling was controlled so as to avoid axial directional solidification, which might spoil the diffusion experiments due to a large degree of segregation. The diffusion during the heating and cooling periods was included in the analysis, based on an analytical solution of Fick's second law. The rocket and the space shuttle experiments will be compared and discussed.

11:20 AM

OPTICAL IMAGE FORMATION OF A TRANSPARENT SOLID-LIQUID INTERFACE DURING THE MOMO EXPERIMENT ON BOARD STS -84: T. Fuhrmeister[1]; G. Zimmermann[1]; *S. Rex*[1]; B. Kauerauf[1]; L. Murmann[1]; [1]ACCESS e.V., Aachen D-52072 Germany

Transparent model substances are a common tool for investigations on solidification processes in metallic alloys. Within the experiment MOMO the transparent alloy contained in a cylindrical ampoule was directional solidified using a Bridgman furnace to observe quantitatively the dynamic of cellular growth patterns on an extended solidification interface. The paper describes the design and performance of the optical set-up which was used to generate the desired images of the solidification morphology in a top view. Since the cellular pattern to be observed is only a phase object dark field illumination has to be used despite of the strongly limited available electrical power. The imaging was achieved by using a rod lens endoscope with smal apparture and a modified astro-CCD camera with a high tolerance against varying illumination intensity.

11:40 AM

DIFFUSION IN LIQUID BINARY SYSTEMS: *R. W. Smith*[1]; [1]Queen's University at Kingston, Department of Materials and Metallurgical Engineering, Ontario K7L 3N6 Canada

It is found that the reproducibility of liquid diffusion coefficients measured at lg is poor, due to the intrinsic diffusive transport being enhanced by uncontrolled buoyancy convection. However, is has been reported that if the diffusion capillary is less than about lmm in diameter, the intrinsic rate of diffusion is reduced. Thus it is conventional to write: D(measured)=D(intrinsic)+D(buoyancy)+D(wall effect)+D(thermal). If a long capillary diffusion couple is isothermally processed in microgravity, D(buoyancy) and D(thermal) will be absent and so only D(intrinsic) and D(wall effect) should contribute. Choosing capillaries of different diameters should provide an estimate of D(wall effect) and hence permit an accurate value of D(intrinsic) to be obtained. This can provide clues to the mechanism(s) by which diffusion occurs. Long-capillary liquid diffusion experiments have been conducted with a number of metal and semi-metal alloy systems, in order to obtain precise values for D(measured) and to evaluate the influence of g-jitter vibrations on these values. The results will be presented.

ADSORPTION, ION EXCHANGE, AND SOLVENT EXTRACTION: Adsorption I

Sponsored by: Extraction & Processing Division, Aqueous Processing Committee

Program Organizer: Courtney Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

Monday AM Room: Plaza Room C
February 16, 1998 Location: Convention Center

Session Chair: Rajendra Mehta, University of Nevada, Reno, NV 89557, James Navratil, Lockheed Martin Idaho Technologies Co., Idaho Falls, ID 83415

8:25 AM OPENING REMARKS

8:30 AM INVITED
BIOSORPTION OF HEAVY METALS ONTO PLANT BIOMASS: EXCHANGE, ADSORPTION OR SURFACE PRECIPITATION?:
R. W. Smith[1]; [1]Mackay School of Mines, Chemical and Metallurgical Engineering, Reno, NV 89557

Heavy metal ions readily adsorb onto the nonliving biomass of many aquaphytes. Further, in many cases, the metal ions can be readily desorbed from the biomass by use of a suitable eluting agent. It has been shown in certain cases, at least, that the biomass can be subjected to a number of loading and elution cycles without the biomass losing its adsorption capacity. It has been widely reported that adsorption occurs through an ion exchange mechanism and a number of researchers have shown experimental evidence supporting such a mechanism. However, there is also evidence that the adsorption is through simple surface precipitation of metal hydroxide species. The present study examines some of the existing data on adsorption of metal ions onto aquaphyte biomass and attempts to evaluate which mechanism is the more likely.

8:55 AM INVITED
ADSORPTIVE SEPARATION OF LEAD BY CHEMICALLY MODIFIED POLYSACCHARIDES PRODUCED FROM BIOMASS:
Katsutoshi Inoue[1]; Masayuki Yano[1]; Keisuke Ohto[1]; Kazuharu Yoshizuka[1]; [1]Saga University, Applied Chemistry, Saga 840 Japan

Novel types of adsorbents for metals were prepared from two kinds of polysaccharides: chitosan, polysaccharide-containing primary amino groups; and pectic and alginic acids, polysaccharide-containing carboxylic acid groups. Chitosan, produced by deacetylation from chitin contained in shell of Crutacea such as crab, shrimp, prawn, various insects, etc., was chemically modified by introducing functional groups of EDTA or DTPA which resulted in a drastic enhancement of adsorption and selectivity of some metals. The pH at which lead adsorption takes place was greatly shifted to low pH and accompanied with enhanced adsorption, which allows for its selective separation from zinc. The adsorptive power of these chemically modified chitosan was found to be much stronger than a commercial aminophophonic type of chelating resin. Small amounts of lead were successfully separated from large excesses of zinc by using a column packed with the chemically-modified chitosan. Similarly, pectic and alginic acid, produced from oranges, apples, brown seaweeds, etc. were found to have a high affinity for lead. However, since these acids are water soluble, they were also cross-linked or chemically modified by slightly converting into amide groups thereby avoiding dissolution. Very high selectivity to lead over zinc was observed.

9:20 AM INVITED
BIOSORPTION OF TOXIC PRECIOUS HEAVY METAL BY THE AZOLLA FILTER: *Elisha Tel-Or*[1]; [1]Hebrew University of Jerusalem, Dept. Agricultural Botany, Rehovot 76100 Israel

The Azolla biofilter was developed for the removal of toxic heavy metals from industrial waste water, protect drinking water and reclaim precious metals. We have reclaimed gold from ornamental industries in Jerusalem, and obtained 4% gold in the ashes of the Azolla biofilter. Platinum and Paladium recovery in heterogenous mixtures of metals was successful and the recovered ashes contained 4-6% of these metals. A bench scale experiment of Berkeley Pit water in Butte, Montana was conducted aiming to explore effective removal of copper, cadmium and lead from metal rich mixture containing 3.5 gram metal per liter, at low pH. The Azolla biofilter removed the three toxic metals, to low levels, below the desired standards. Azolla biofilter was proven most effective in polishing Pb to single ppb levels, improving toxic metals from heterogenous industrial wastes in Israel. The Azolla dry biomass is a cheap product, easy to grow and store and pilot plant experiments demonstrate its future industrial application.

9:45 AM INVITED
STUDY OF MAGNETIC DOMAIN STRUCTURE AND FERRITE COMPOSITION IN MAGNETOTACTIC BACTERIA: Charles I. Richman[1]; *Rajendra K. Mehta*[1]; Robert Karlin[2]; [1]Mackay School of Mines, Chemical and Metallurgical Engineering, Reno, NV 89557; [2]Mackay School of Mines, Geology, Reno, NV 89557

Magnetotactic bacteria are gram-negative heterotrophs that have an ecological niche in marine marsh and freshwater swamp sediments. Magnetosomes are cellular bodies that accumulate magnetite under micro-aerobic conditions. Magnetosomes convey to the bacteria a net magnetic moment that allows alignment in the earth's magnetic field. Their small size suggests a single domain magnetosome structure that could be used for magnetic recording media. The Atomic Force Microscope, equipped with a magnetic tip was used to map out the magnetic domain walls of separated and fixed magnetosomes. Results showed the magnetosome's applicability for magnetic recording material. Energy Dispersive Analysis, with the aid of a Scanning Electron Microscope, quantified the elemental content of the magnetotactic microbes. These microbes were grown with chelated ferric quinate and with substitutions of Mn+2, Ni+2, Cu+2 and Ba+1 ions. Further substitutions of Hg+2 and Pb+2 ions showed the reaction of magnetotactic microbes to toxic met al pollution. The crystal structure of the formed magnetosomes were evaluated by viewing the electron diffraction patterns with a Tunneling Electron Microscope.

10:10 AM Break

10:25 AM INVITED
MAGNETIC FIELDS AND IRON OXIDE ADSORBENTS FOR WATER TREATMENT: *James D. Navratil*[1]; [1]Idaho National Engineering Laboratory, Lockheed Martin Idaho Technologies Company, Idaho Falls, ID 83415-3921

Magnetite ($FeO.Fe_2O_3$) has been used to separate a wide variety of substances such as dissolved metal species, particulate matter, and organic and biological materials. In the absence of an external magnetic field, activated magnetite readily adsorbs numerous metal species including Cu, Ni, Co, Pb and Zn. In an external magnetic field, a synergistic effect is observed in using supported magnetite in a fixed-bed for removal of plutonium and americium from waste water. Using a magnetite-containing, nonporous polyamine-epichlorohydrin (MPE) resin bead, we observed that, in the presence of a relatively weak magnetic field (0.3 Tesla), the capacity of the resin for both plutonium and americium increased by a factor of five compared to data that was obtained with unsupported magnetite particles in the absence of a magnetic field. These observations may be explained by a nanolevel HGMS effect, as plutonium and americium are known to form colloidal particles at elevated pHs. The pores of the MPE resin are large enough to permit the free displacement of the colloidal particles. When the field of the magnet is turned on, the magnetic particles are magnetically induced, creating a field that contributes to the net field sensed by the colloidal particles. In the absence of convection and when the magnetic force is sufficiently greater than the force associated with Brownian (thermal) motion, the magnetic force created by the field can be attractive and large enough to allow the magnetite to adsorb the colloidal particles. When the field is turned off, the nanoparticles are released and dispersed in solution by thermal motion (the metal ions would still be adsorbed, however). This process could be referred to as magnetic swing adsorption.

10:50 AM INVITED
THE USE OF STABCAL FOR MODELING ADSORPTION PROCESSES AT HYDROXIDE AND OXIDE SURFACES: H. H. Huang[1]; *C. A. Young*[1]; [1]Montana Tech, Metallurgical Engineering, Butte, MT 59701

Thermodynamic modeling of hydrometallurgical systems has been successfully accomplished via the calculation of various diagrams: EH-pH, I-pH, logai-pH and logai-logaj. However, in many cases, resulting models do not agree with actual applications. Reasons for the disagreement can be attributed to, for example, the use of inaccurate or unavailable thermodynamic data, the consideration of inappropriate species, the presence of nonequilibrium or metastable conditions (i.e., kinetics), and/or the inability to account for adsorption processes. Simple actions can be taken to overcome the three former problems; however, to solve the adsorption problem, specialized programming is required. In this regard, the STABCAL program has been modified with the assumption that adsorption is predominated by coulombic interactions due to electric double-layer phenomenon. In this presentation, the modification and use of the STABCAL program is described. In order to run the new version, pertinent information must first be determined including the surface area and the iso-electric point (iep) of the adsor-

bent. Examples from the literature are cited and compared to thermodynamic calculations before and after consideration for adsorption. Excellent results have been obtained.

11:15 AM INVITED

REMOVAL OF SELENIUM AND ARSENIC FROM PROCESS WATER BY ADSORPTION ON TO LANTHANUM OXIDE BASED ADSORBENT: *M. Misra*[1]; A. Rawat[1]; B. C. Jena[1]; K. Keltner[2]; [1]Mackay School of Mines, Chemical and Metallurgical Engineering, Reno, NV 89557; [2]Clear Water Filters Corporation, Reno, NV 89512

Stringent regulatory limits have been imposed on the maximum contamination levels (MCL) of selenium and arsenic in water due to their toxicity. Currently available water treatment methods are inadequate in meeting the new regulatory limits. A newly patented lanthanum oxide based adsorbent developed at the University of Nevada - Reno is capable of lowering the arsenic and selenium levels in water to below 50 ppb, the MCL set by EPA. This new adsorbent can selectively adsorb selenium and arsenic from water without affecting other ions present and has been tested in water samples from various sources. The results of batch and column adsorption tests will be presented and adsorption mechanism will be discussed.

11:40 AM INVITED

RECOVERY OF HARMFUL SELENIUM AND ARSENIC USING AQUEOUS PROCESSING FOR ENVIRONMENT CONSCIOUS PROCESS: *Mikio Kobayashi*[1]; Kazuya Koyama[1]; [1]National Institute for Resources, Materials Processing Department, Tsukuba-shi 305 Japan

Extraction of valuable metals from sulfide ores continues to be a very important process and so the strict control of discharge of harmful metals in effluents from refineries becomes more important in the future. The recovery methods for heavy metals have been developed. Some metals such as Se and As are still difficult to be removed to very low concentration, although the techniques for recovery and removal for many kinds of metals have already been developed. Especially, in case of Se the recovery system from water with low concentration has not been developed yet, although the WHO decided Se to be harmful for human beings and then the discharge control is under obligation now. In general Se exists as selenite ion and/or selenate ion in aqueous phase and selenite ion is able to be recovered by coprecipitation with ferric hydroxide or by reduction to solid selenium by general reductants. Selenate ion, however, has a strong resistance to conventional treatments. Therefore the new technique for the recovery of Se from water including selenate ion has to be developed. In this presentation the new approach for removal of selenate ion using the reaction in which ferrous ion is oxidized to ferric ion is presented. Selenate ion is reduced to selenite ion during the reaction and then to solid selenium. The coexistence of activated carbon is very useful to increase the reaction rate. The use of iron powder is also effective and very useful for reducing gel-like precipitates mainly consisted of ferric hydroxide. The concentration of the residual selenate ion is probably under 0.1 ppm after recovering Se by the mentioned-above approach. In addition to the mechanisms of these reactions, the effects of pH, coexistent positive and negative ions, and reaction temperature are also presented. Furthermore the investigation of the behavior of selenosulfate is presented.

ALUMINUM REDUCTION TECHNOLOGY: Smelter Technology

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

Monday AM — Room: Fiesta D
February 16, 1998 — Location: Convention Center

Session Chair: Erik Jensen, Reynolds Metals Company, Richmond, VA23230

8:30 AM

ON THE ROAD TO 325 KA: *Pierre Lapointe*[1]; Jacques Caissy[1]; Gilles Dufour[1]; Claude Fradet[1]; Jean-Pierre Gilardeau[1]; Louis-Regis Tremblay[1]; [1]Aluminerie Lauralco Inc., Deschambault, Quebec G0A 1S0 Canada

In 1992, Lauralco started up as a greenfield project a 215000 MT Al plant capacity using the AP-30 pot technology with 30% graphite content cathode blocks. At the same time, a decision was taken to test semi-graphitized blocks in a group of 10 pots having the possibility to run 25 kA higher than the pot line. Fortunately, the decision was taken. The unsatisfactory results of the original generation of pots (tap out, high instability...), and the outstanding results of the test group led Lauralco to convert the entire line to semi-graphitized blocks. This paper will present Lauralco's performance after six years of operation. It discusses our global approach and philosophy on plant operation. It presents semi-graphitized pot results and how the cohesion between technical and management practices lead us to establish new standards of the industry and take us along the road to 325 kA.

8:55 AM

RESULTS FROM IMPLEMENTATION OF POINT FEEDERS AND COMPLETE HOODING ON VS SODERBERG POTS: *T. B. Pedersen*[1]; H. J. Bentzen[1]; M. Jensen[1]; W. Larsen[1]; A. T. Olsen[1]; R. Pedersen[1]; A. K. Syrdal[1]; [1]Elkem Alumiknium Lista, 4551 Farsund Norway

Elkem Aluminium Lista has reduced the emissions of tar fumes, fluorides and perfluorinated carbons substantially by introducing point feeders and complete hooding of the Soderberg pots. The pot productivity has increased. A conversion to PB-technology to meet environmental challenges, requires heavy capital expenditure. Therefore, the company decided in 1986, to further develop the Soderberg technology. The technology comprises two unique modules capturing both the anode baking and pot gases: The Anode Top Hood system and the Closed Point Feeding. The Anode Top Hood system collects all the tar fumes from the anode top. The fumes are cleaned in a dry scrubber. The Closed Point Feeding system replaces the traditional side working, ensuring a very high hooding efficiency and improved pot operation. The results, as well as fundamental design and operation from one upgraded pot line at Elkem Aluminium Lista are presented.

9:20 AM

RESULTS OF CONVERSION TO DRY ANODE TECHNOLOGY AT KRASNOYARSK: *Mr. Doug Hewgill*[1]; Dr. Victor Yurievitch Buzunov[1]; [1]Kaiser Aluminum Technical Services Inc., Pleasanton, California CA 94566-7769 USA

In 1989, Kaiser Aluminum Technical Services Inc. (KATSI), and several other Western aluminum producers submitted proposals for the modernization of the Krasnoyarsk Aluminum Smelter AO (KrAZ) to prebake anodes. After some consideration, KATSI also submitted a proposal for an interim step, following a route that many other Vertical Stud Soderberg Smelters have used, and that is to convert to Dry Anode Soderberg Technology. Also, the use of Kaiser's Celtrol system allowed the use of other control strategies and automatic systems that were not previously available. In order to meet better environmental standards,

a Dry Scrubber was installed. Installation of the Dry Scrubber allowed the use of a more acid electrolyte, with no impact on emissions, which in turn, increased production efficiencies. This report will cover the progress and the results of this test in Potroom 19 of KrAZ.

9:45 AM

REMOVING IMPURITIES FROM THE ALUMINIUM ELECTROLYSIS PROCESS: *Dr. Elmar Sturm*[1]; Geir Wedde[1]; [1]Hamburger Aluminium Werk GmbH, 21111 Hamburg Germany

Modern dry scrubbing technologies for aluminium reduction cells lead to less emissions from pot rooms and scrubbing plant. The closed loop combination of the cells and the scrubber enrich the impurity content of the alumina and metal quality and current efficiency may be lowered. A mass balance of the impurities shows the need of removing part of them for better production conditions. There is a strong correlation between the fine fraction of the enriched secondary alumina and the impurity content. ABB Miljo in collaboration with HAW has found an economic solution to remove the impurities from the alumina. Demonstration plant results and the effect on pot operation with regard to the economic aspects are presented.

10:10 AM Break

10:20 AM

CURRENT REDISTRIBUTION BETWEEN INDIVIDUAL ANODE CARBONS IN A HALL-HEROULT PREBAKE CELL AT LOW ALUMINA CONCENTRATIONS: *Ketil A. Rye*[1]; Margit Konigsson[1]; Injar Solberg[1]; [1]Elkem Aluminium ANS, N-8650 Mosjeen Norway

The carbon anode of a modern cell for electrolysis of aluminium metal consists of a number of smaller anode carbon blocks. It has been observed that when the alumina concentration in the cell becomes very low, and the cell is close to an anode effect, a redistribution of the electrical current between the anode blocks takes place. The anode blocks located in areas where the concentration of dissolved alumina in the electrolyte is very low take less current. In a more advanced cell controller the observed effect can be used as an early warning of an oncoming anode effect, or to detect an uneven alumina distribution in the cell.

10:45 AM

HOW TO OBTAIN OPEN FEEDER HOLES BY INSTALLING ANODES WITH TRACKS: *Bjorn P. Moxnes*[1]; Jorn H. Skaar[1]; Bjorn E. Aga[1]; [1]Hydro Aluminium, Technology Centre Ardal, N-5870 Ovre Ardal Norway

A study was made on how to keep the feeder holes in a prebaked cell open. A feeder hole is defined as open when it is possible to see the liquid bath at any time, except for the first 5-10s after a new addition of alumina has been made. An open feeder hole increases the solubility of alumina by reducing the size and amount of alumina agglomerates. The conclusion of the experimental work involving different shapes of breakers, different amounts of alumina fed into the holes, different size of alumina dumps, etc. is that the amount of anode gas released into the feeder holes is the significantly most important parameter in keeping the holes open. The amount of anode gas fed into the feeder hole is controlled by the bath flow, location of the feeder hole compared to the anodes and centre channel, and the size of the anodes. By making tracks underneath the anodes it is possible to direct more anode gas into the feeder holes and keep the holes open more than 90% of the time.

11:10 AM

THE OPERATIONAL PERFORMANCE OF 70 kA PREBAKE CELLS RETROFITTED WITH TiB_2-G CATHODE ELEMENTS: *Dr. Alton T. Tabereaux*[1]; Mr. Jim H. Brown[1]; Mr. Ivan J. Eldridge[1]; Mr. William R. Morgan[1]; Mr. Douglas V. Stewart[1]; Mr. Curtis J. McMinn[2]; Mr. Tom Alcorn[1]; Vern W. Rozelle[4]; Dan Thorson[4]; Barry Hullett[4]; Richard C. Jeltsch[4]; Chuck Bronkhorst[4]; Mark Strecher[4]; ; [1]Reynolds Metals Company, Manufacturing Technology Laboratory, Muscle Shoals, AL 35661 USA; [2]Consultant, Florence, AL; [3]Monsanto Corporation, Decatur, AL USA; [4]Kaiser Aluminum Company, Spokane, WA USA

Two 70 kA prebake aluminum cells at the Kaiser Mead Smelter were retrofitted with "mushroom" shaped TiB_2-G cathode elements and operated for test periods to develop the modified cell operations (engineering packages), evaluate the cell operational performance, and test the endurance of the newly developed TiB_2-G cathode materials in an industrial cell as part of a joint cost-shared research program with the U.S. Department of Energy (DOE). Initial results of the test program indicate that the retrofitted TiB_2-G cell can be operated at substantial lower cell voltage and lower energy consumption due to closer A-C distance operation. The current efficiency, or metal production, for the TiB_2-G cathode coverage was close to the design coverage. Actual energy savings would have been greater but were not realized due to significant numbers of broken TiB_2-G cathode elements during test periods resulting in cell operation at higher "effective" A-C distance than the design and consequently higher voltage.

11:35 AM

A PROCESS CONCEPT FOR THE TREATMENT OF ALUMINUM CELL HOT BATH CRUST: *Dr. Arthur Plumpton*[1]; Dr. Jules Thibault[2]; [1]Lakefield Research Ltd., Lakefield, Ontario K0L 2H0 Canada; [2]Laval University, Department of Chemical Engineering, Sainte-Foy, Quebec G1K 7P4 Canada

Many aluminum smelters manage withdrawn anode cover by slow cooling within the parked hot bath crust transfer vessels or by depositing the material on a surface and mixing the material with a front end loader during its cooling. Following a retention period of a day to several days, the partially cooled material is crushed to desired dimensions and recycled. The operations generate corrosive gas and dust emissions and require considerable plant space. Several advantages would accrue with an improved process of crust cooling. The present study followed upon initial work proposed by and undertaken for a Quebec aluminum smelter. It considers the potential application of processes which include initial partial crushing of the hot bath crust followed by its cooling in one of three types of forced air convection cooling systems: inclined rotary cylinder, traveling grate; vertical shaft. A heat transfer model was developed for the grate cooler and experimentally validated in a pilot scale simulator. The model was then applied, with simplifying assumptions, to determine the crust cooling performance and configurations of the other cooling systems. Small scale crushing and attrition tests enabled a preliminary evaluation of probable crushing plant requirements. The advantages and limitations of the processing options are presented in the context of pre-crushing strategy, cooling performance of the systems, gas handling limitations and the feasibility of potential applications within a typical smelter environment.

ATOMIC-LEVEL SIMULATION OF MATERIALS: NEW METHODS & NOVEL APPLICATIONS: Electronic Structure

Sponsored by: ASM International: Materials Science Critical Technology Sector, Computer Simulation Committee

Program Organizers: Jim Adams, Arizona State University, Dept. of Chemical Bio and Materials Dept., Tempe, AZ 85287-6006; Vaclav Vitek, University of Pennsylvania, Dept. of Materials Science & Eng., Philadelphia, PA 19104

Monday AM Room: 203
February 16, 1998 Location: Convention Center

Session Chair: Sokrates Pantelides, Vanderbilt University, Nashville, TN 37064

8:30 AM

REAL-SPACE MULTIGRID CALCULATIONS FOR SURFACES, NANOTUBES AND PROTEINS: *Dr. Jerry Bernholc*[1]; Dr. E. L. Briggs[1]; Dr. C. Bungaro[1]; Dr. M. Buongiorno Nardelli[1]; Dr. M. Ramamoorthy[1];

Dr. K. Rapcewicz[1]; Dr. C. Roland[1]; Dr. M. G. Wensell[1]; Dr. B. I. Yakobson[1]; Dr. C. J. Brabec[1]; Dr. D. J. Sullivan[1]; [1]NC State University, Physics, Raleigh, NC 27695-8202 USA

We describe the results of large-scale electronic structure calculations, made possible by advances in theoretical methods and massively parallel computers. The specific examples include melting and incorporation of defects and impurities at the Si (100) surface, the reconstructions of GaN surfaces, the strength of nanotubes, and the electronic structure of biomolecules. In melting of the Si surface, the disordering proceeds from the outermost surface layer and results in the formation of a well-defined liquid-solid interface; a liquid only a few layers thick is already metallic. The mechanisms of melting will be elucidated with a movie, which shows its progression with time. Turning to defects on surfaces, their formation energies are significantly lower than in the bulk, but a vacancy on a third layer from the surface already has its formation energy close to the bulk value. The proximity of a surface leads to changes in the diffusion mechanisms of dopants, and may also result in ordering of impurities in the subsurface layers. We have also studied the technologically important wurtzite GaN (0001) surfaces, and found that adatom reconstructions are the lowest in energy, and that the presence of hydrogen leads to significant stabilization of the growth surface. For Mg on GaN (0001), the most stable adsorption site depends on the surface coverage, and a relatively low coverage is preferable for doping. Turning to nanotubes, they may be the strongest materials known. We will describe the results of extensive ab initio and classical simulations aimed at the determination of their failure mechanisms and strength. If time permits, initial studies of large protein structures will also be described.

9:05 AM

ATOMIC AND ELECTRONIC STRUCTURE FOR A MODEL CERAMIC/METAL INTERFACE: {222}MgO/Cu : *Dr. Roy Benedek*[1]; Dr. David N. Seidman[1]; Dr. Lin H. Yang[2]; [1]Northwestern University, Materials Sci. and Engr., Evanston, Illinois 60208-3108 USA; [2]Lawrence Livermore National Laboratory, Condensed Matter Physics Div., Livermore, California 94551 USA

Atomistic simulations are less developed for ceramic-metal interfaces than for other solid state interfaces. Existing work, based either on ab initio local density functional theory (LDFT) calculations or the classical image interaction picture, have primarily addressed neutral, nearly lattice-matched interfaces; polar interfaces and the misfit-induced dislocation structure have been treated only via ad hoc interatomic potential models or continuum elasticity theory. Polar interfaces, however, deserve greater theoretical attention in view of their strong adhesion, and an atomistic treatment of misfit dislocations would be desirable. In this work we apply local density functional theory and classical molecular statics simulation to a model ceramic-metal interface, {222}MgO/Cu, which has been the subject of several high-resolution experimental observations by HREM, Z-contrast STEM, spatially resolved EELS, and atom-probe field ion microscopy. A phenomenological short-range interatomic potential is proposed that accurately reproduces LDFT total energy calculations as a function of the translation state of the interface. The potential includes an attractive contribution, parametrized in terms of the Universal Binding Energy function, and a repulsive Born-Mayer contribution. The prefactor of the attractive term depends on the atomic density of Cu in the interface layer. Molecular statics calculations with this model potential, complemented by an embedded-atom-method potential for bulk Cu (the ceramic atomic positions are frozen, in initial calculations) predict a misfit dislocation network with trigonal symmetry and no standoff dislocations. Electronic spectra at the interface exhibit metal-induced states in the MgO gap, for which evidence also appears in EELS experiments. This work is supported by the U. S. Department of Energy.

9:40 AM

ATOMIC SPELUNKING — AN ATOM'S VIEW INSIDE EXPANDED PHASES OF MATERIALS.: *Otto F. Sankey*[1]; Alexander A. Demkov[2]; [1]Arizona State University, Department of Physics, Tempe, AZ 85287-1504 USA; [2]Motorola, Inc, Semiconductor Products Sector, AZ 85202 USA

We discuss an electronic structure method based on "Fireball" orbitals and an approximate local density energy functional for use on complex systems. We use this method to investigate expanded phases of semiconductors and zeolites which contain "tunnels", cages, and "caverns" into which guest atoms may reside. Examples to be discussed are: (1) Silisils, zeolites without ozygen, a class of expanded silicon phases which includes hydrate I and hydrate II structures that are formed with (usually) a templating alkali metal atom. (2) Hypothetical expanded phases of compound semiconductors and their prospects for synthesis. (3) Model clusters and chalcogenide clusters inside the caverns of zeolites. (4) The possible anti-ferromagnetic insulating transition in the charge transfer encapsulated black sodalite system.

10:15 AM Break

10:20 AM

ATOMIC-LEVEL SIMULATION OF SILICON USING AN ENVIRONMENT-DEPENDENT TIGHT-BINDING POTENTIAL: *Dr. Cai-Zhuang Wang*[1]; [1]Iowa State University, Ames Lab - USDOE & Dept of Physics, Ames, Iowa 50011 USA

We have developed a new tight-binding potential for silicon which goes beyond traditional two-center approximation and allows the tight-binding parameters and the repulsive potential to be dependent on the bonding environment. Molecular dynamics simulations using this new tight-binding potentail have been performed to study the structures of silicon clusters and silicon surfaces as well as the properties of bulk phases. The simulation results indicate that the new potential is much more accurate and transferable in comparison with the previous tight-binding potentials based on the two-center approximations.* Work done in collaboration with B. C. Pan, G. D. Lee and K. M. Ho.

10:55 AM

SLATER-KOSTER PARAMETRIZATION USING ENVIRONMENTALLY SENSITIVE PARAMETERS — ROW III AND IV ELEMENTS, AND INTERMETALLIC ALLOYS: *Dr. Michael J Mehl*[1]; Dr. Dimitrios A. Papaconstantopoulos[1]; Dr. Sang H. Yang[2]; [1]Naval Research Laboratory, Complex System Theory Branch, Washington, DC 20375-5345 USA; [2]NRC Postdoctoral Fellow, CSTB Naval Research Laboratory, Washington, DC 20375-5345 USA

First-principles calculations of electronic structure related properties of metallic systems are limited to rather small systems, since the computer time involved scales as the cube of the number of atoms in the system and there is a rather large overhead arising from the large basis set, the setup of the Hamiltonian, and the requirement of self-consistency. This limits the usefulness of these calculations in the study of the properties of real materials, including vacancies, impurities, and defects, because these imperfections typically interact over long ranges and hence require large unit cells. A Slater-Koster parametrized tight-binding Hamiltonian can study much larger systems, since there the basis set is typically much smaller than the first-principles basis set, setup of the Hamiltonian is fast, and there is no self-consistency requirement. The difficulty is in the determination and transferability of the Slater-Koster parameters. Our method [1] requires that the parameters reproduce the electronic structure and total energy of a limited database of first-principles results. We find that a good fit is obtained only if the on-site tight-binding parameters are allowed to change with the local crystal environment. We have applied this method to all of the transition and noble metals. While the first-principles database for these elements contains only fcc and bcc structures, we are able to correctly predict the ground state structure for all of the metals, including hcp and other non-cubic structures. In addition, elastic constants, vacancy formation energies, and surface energies are in good agreement with experimental results. We have now extended our Slater-Koster database to include elements from rows III and IV of the periodic table (Al, Ga, In, C, and Si), and intermetallic alloys (PdH, NiH, CoAl, TiAl, NbC, and CuAu). We will discuss the database needed to determine reliable parameters for these systems, the modification of the formalism [1] needed for binary systems, and the transferability of the parameters. We test the reliability of these parameters by using them to calculate elastic constants, selected optical and zone boundary phonon frequencies, and the relative energies of various structural phases of each system.

11:30 AM

ATOMISTIC SIMULATION IN METALS AND ALLOYS WITH FIRST-PRINCIPLES INTERATOMIC POTENTIALS : *Dr. John A. Moriarty*[1]; [1]Lawrence Livermore National Laboratory, Livermore, CA 94551 USA

Rigorous many-body interatomic potentials, suitable for atomistic simulations on both simple and transition-metal systems, have been developed from LDA quantum mechanics via first-principles generalized pseudopotential theory (GPT). A mixed basis is used to expand the GPT electron density and total energy in terms of weak pseudopotential and d-state matrix elements, yielding a bulk total-energy functional consisting of a volume term plus sums over structure-independent, transferable potentials up to four-ion interactions. Successful bulk applications include a wide variety of structural, thermodynamic, and mechanical properties. In the simple metal Mg, a complete and accurate temperature-pressure phase diagram has been obtained, while in the transition-metal aluminides, the structure-composition phase diagram of aluminum-rich CoAl has been predicted, including the appearance of complex, nonstoichiometric phases. In the central bcc transition metals, where the energetics are complicated by multi-ion d-state interactions, atomistic simulations have been greatly facilitated by the development of a complementary model GPT (MGPT), in which the corresponding angular-force three- and four-ion potentials are simplified to entirely analytic forms, using canonical d bands. MGPT potentials for the bcc metals have been successfully applied to obtain high-pressure thermodynamic properties, including the melting curve in Mo, and are currently being used to obtain deformation and defect properties for multiscale modeling, including ideal shear strength, vacancy and self-interstitial formation and migration energies, grain boundary structure, generalized stacking-fault energy surfaces, and the structure and energetics of <111> screw dislocations in Mo and Ta. *This work has been performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

AUTOMOTIVE ALLOYS II: Session I - Fundamental Research

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

Monday AM Room: Fiesta B
February 16, 1998 Location: Convention Center

Session Chair: Mary A. Wells, University of British Columbia, Vancouver, British Columbia V6T 1Z4 Canada

8:30 AM

THE EFFECTS OF PRE-AGING TREATMENTS ON PRECIPITATION IN Al-Mg-Si AND Al-Mg-Si-Cu AUTOMOTIVE BODY SHEET ALLOYS: *J. Daniel Bryant*[1]; Harriet Kung[2]; Amit Misra[2]; [1]Reynolds Metals Company, Corporate Research and Development, Richmond, VA; [2]Center for Materials Science, Los Alamos, New Mexico

The pre-aging of heat treatable aluminum alloys has been shown to affect the subsequent precipitation development during artificial aging. An important application of this phenomenon is the production of sheet products from Al-Mg-Si and Al-Mg-Si-Cu alloys to be used in the fabrication of automotive body panels. In this application, the automotive paint bake cycle is used to impart an artificial aging response, referred to as the paint bake response (PBR), in the alloys following stamping. The pre-aging treatment has been shown to be effective in increasing the paint bake response by up to a factor of four, while at the same time improving the formability of alloys and reducing the natural aging rate. In this research, the mechanism by which this goal is achieved has been studied using atomic resolution microscopy and in-situ aging experiments within the transmission electron microscope. These results have been related to the activation energies associated with the formation of meta-stable variants of Mg2 Si through the use of differential scanning calorimetry. The changes in precipitate structure, size, distribution and kinetics of formation are described for several alloys in the Al-Mg-Si (Cu) system. The impact of the precipitate evolution on mechanical properties will also be discussed.

9:00 AM

TEXTURAL EVOLUTION AND SPATIAL DISTRIBUTION IN 6111-T4(1) AUTOMOTIVE BODY SHEET: R. M. Ramage[1]; *J. D. Bryant*[1]; A. J. Beaudoin[2]; [1]Reynolds Metals Company, Corporate R&D, Chester, Virginia 23836-3122; [2]University of Illinois, Urbana-Champaign, Illinois

A non-isotropic spatial distribution or banding of textural components develops in Al-Mg-Si-(Cu), such as 6111, sheet as it is produced. During subsequent forming operations, the textural banding causes the formation of ridges. ~0.1mm high, in the rolling direction. Despite their small dimension, they are readily visible and result in a defect that is objectionable on exterior automotive components appear as if a paint brush has been drawn across the sheet. These ridges, or "paint brush lines". Eliminating the condition not only results in an improved surface appearance, but also reduces the textural anisotropy of the sheet, which improves formability. The texture evolution in the production of 6111 and the spatial distribution of the textural components, and their effects on sheet formability will be discussed.

9:30 AM

PRECIPITATION IN Al-Mg-Si-Cu ALLOYS AND THE ROLE OF THE Q PHASE AND ITS PRECURSORS: D. J. Chakrabarti[1]; Byungki Cheong[2]; *David E. Laughlin*[3]; [1]Alcoa Technical Center, Alcoa, PA 15069 USA; [1]Carnegie Mellon University, Materials Science and Engineering Dept., Pittsburgh, PA 15213 USA; [2]Korea Institute of Science and Technology, Materials Design Laboratory, Seoul (136-791) Korea; [3]Alcoa Technical Center, Alcoa Center, PA 15069 USA

Alloys from the 6000 series Aluminum alloys are being used as automotive body panels, because of their ability to be strengthened by artificial aging after forming. Two of the hardening phases in 6000 series aluminum alloys are know to be ß" and ß', phases which form prior to the formation of the equilibrium Mg_2Si, ß phase. The ß phase forms as an equilibrium phase in ternary alloys of Al-Mg-Si, as well as in quaternary alloys of Al-Mg-Si-Cu alloys. However in the quaternary alloys another phase, usually denoted the Q phase (Q for Quaternary), also forms as an equilibrium phase. This phase has been reported to exist in alloys that are in the T6 temper and hence may be an important phase in understanding the overall precipitation hardening mechanism in 6000 series aluminum alloys with significant amounts of Cu. In this paper we will discuss the occurrence of the Q phase in commercial 6000 series alloys in some detail. The thermodynamic stability of the phase will be discussed, as will the methods by which the phase forms in the alloys. Its existence in the T6 temper will be documented by TEM micrographs and diffraction patterns and the crystallographic features which distinguish it from the ß' phase will be presented.

10:00 AM

ALLOY INFLUENCE ON FILLING, MACROSHRINKAGE, HOT CRACKING AND PROPERTIES IN ALUMINUM SHAPE CASTINGS: *J. Righi*[1]; J. C. Lin[2]; [1]Aluminum Company of America, Fluid State Process Design Center, Alcoa Technical Center, PA 15069 USA; [2]Aluminum Company of America, Alloy Design Center, Alcoa Technical Center, PA 15069 USA

Shape casting processes such as sand, permanent mold, squeeze, and die casting have been used to produce aluminum parts for automotive applications for many years. Due to a lack of understanding of the alloy solidification behavior, few aluminum alloys were implemented for commercial production. The demands for new alloys to achieve increased properties and higher quality are inevitable in a fast growing market of aluminum cast components in the automotive industry. In the present study, the solidification behavior of aluminum casting alloys was investigated. Combining experimental results and theoretical work, an alloy solidification behavior model was established. Data such as solid fraction, percent eutectic, constituent phases, density, latent

heat, heat capacity, and viscosity were obtained to serve as guidelines for alloy developments to predict product properties. More importantly, the information was used as input for computer process simulations for mold/die filling, macroshrinkage, and hot cracking. The presentation will show the importance of quantitative alloy solidification data for new alloy development and process optimization.

10:30 AM Break

11:00 AM

THE EFFECT OF Cu CONTENT ON PRECIPITATION HARDENING Behavior IN Al-Mg-Si-Cu ALLOYS: *David E. Laughlin*[1]; L. M. Karabin[2]; D. J. Chakrabarti[2]; [1]Carnegie Mellon University, Materials Science and Engineering, Pittsburgh, PA 15213 USA; [2]Consultant, Ruffs Dale, PA 15679

In this talk the basic processes involved in the age hardening of AlMgSi and AlMgSiCu alloys with automotive applications are reviewed. The problem of natural aging will be discussed as will the need to increase the kinetics of precipitation at 350ºF. The effect of process variables such as solution temperature, prior strain as well as the composition of the alloys will be reviewed. Of particular interest is the effect of Cu on the hardening process. Evidence will be presented to show that in 6000 series alloys with Cu contents more than 0.3 w/o, the equilibrium Q phase forms during artificial aging at 350ºF. This phase increases the aging kinetics. It forms as a lath and looks similar to the ß' phase which is the strengthening phase in low Cu 6000 series Aluminum alloys. The reasons behind the increase in kinetics in alloys containing the Q phase will be discussed from the point of view of nucleation theory.

11:30 AM

CREEP AND BOLT-LOAD RETENTION BEHAVIOR OF DIE-CAST MAGNESIUM ALLOYS: *K. Y. Sohn*[1]; J. A. Yurko[1]; F. C. Chen[2]; J. W. Jones[1]; J. E. Allison[3]; [1]The University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI 48109 USA; [2]TRW Space and Electronics Group, Redondo Beach, CA 90278; [3]Ford Motor Co., Ford Research Laboratory, Dearborn, MI 48124-2053

The use of magnesium die-castings in the automotive industry is projected to experience substantial growth in the next decade. However, for elevated temperature powertrain applications such as transmission cases, a major limitation is the inferior creep resistance of magnesium alloys. This can result in substantial stress relaxation at bolted joints leading to reduced joint sealing capability. This study involves the characterization of the creep and bolt-load retention (BLR) characteristics of the die-case magnesium alloys, AE42 and AZ91, and compares them to the BLR characteristics of die-cast 380 aluminum. The effect of temperature and applied stress or pre-load on the creep and BLR behavior of these alloys will be presented and discussed in terms of the influence of exposure time, bolted joint configuration, heat treatment and microstructure.

12:00 NOON

TENSILE AND CREEP PROPERTIES OF AUTOMOTIVE MAGNESIUM ALLOYS: *A. Luo*[1]; [1]IMRA America, Inc., Ann Arbor, MI USA

The automotive weight reduction incentives have resulted in the use of many magnesium die castings in production vehicles. In order for the automotive product engineers to design and adopt more magnesium components, mechanical property databases on automotive magnesium alloys and castings must be provided in great detail. In this article, tensile and creep properties of several commercial magnesium alloys (AZ91D, AM50A, and AE42) have been studied in comparison with a newly developed ZAC8506 alloy (Mg-8%/Zn-5%Al-0.6%Ca). Tensile properties of the above alloys are obtained at room temperature and 150ºC. Creep testing is performed under several temperature and load conditions. Among the alloys tested in this program, the new ZAC8506 alloy (developed by IMRA America) exhibits the best combination of the tensile and creep properties, and offers the greatest potential for automotive powertrain applications.

12:30 PM

MICROSTRUCTURE DEPENDENCE OF FATIGUE FOR A356.2: *Dr. Weinong (Wayne) Chen*[1]; Mr. Que-Tsang Fang[2]; Dr. David R. Poirier[3]; Mr. Tao Wu[1]; Mr. Bin Zhang[1]; [1]The University of Arizona, Aerospace & Mechanical Engineering, Tucson, AZ 85721 USA; [2]ALCOA, Alcoa Technical Center, Alcoa Center, PA 15069-0001 USA; [3]The University of Arizona, Materials Science & Engineering, Tucson, AZ 85721 USA

Fatigue life was measured in specimens of cast aluminum alloy (A356.2), which were removed from ingots with a gradient of microstuctures. The variation of microstructures in a single casting, quantified by the secondary dendrite arm spacings, was controlled by varying the cooling rates along the ingot height during casting. Fatigue tests were performed under both axial and reciprocating bending loading conditions. From the mechanical testing data and microstructural characterization, the relation between the total fatigue life and the secondary dendrite arm spacing was established. The variation of damage initiation as a function of microstructure was also identified.

CARBON TECHNOLOGY: Anode Quality

Sponsored by: Light Metals Division, Aluminum Committee
Program Organizer: Ron Barclay, Alumax, PO Box 1000, Goose Creek, SC 29445

Monday AM Room: Fiesta E
February 16, 1998 Location: Convention Center

Session Chair: Andre Proulx, Alcan International Ltd., Jonquiere, Quebec Canada G7S 4K8

8:30 AM

THE CONVERSION FROM SOUPY TO DRY VSS ANODE OPERATION AT THE POLISH SMELTER HOTA ALUMINIUM "KONIN" SA: *E. Bugzel*[1]; H. Przybylski[1]; J. Galek[1]; I. Skogland[2]; T. B. Svendsen[2]; P. Stokka[3]; [1]Huta Aluminium "Konin", SA, Poland; [2]Hydro Aluminium Karmoy Norway; [3]Norsk Hydro Research Centre Porsgrunn, N-3901 Porsgrunn Norway

Huta Aluminium "Konin" is the only producer of primary Aluminium in Poland, with a yearly capacity of 50 000 mt. The potline consists of 192 VSS pots. The paper describes the conversion from soupy to dry anode operation, a process that was completed in January 1997, one year ahead of schedule. Technical and organizational aspects of implementation of new technology and external supply of anode paste, are discussed together with positive effects of the conversion on the operational results as well as on the internal and external environment.

8:55 AM

GREEN PASTE DENSITY AS AN INDICATOR OF MIXING EFFICIENCY: *Mr. Pascal Clery*[1]; [1]Aluminerie Lauralco, Inc., Deschambault, Quebec G0A 1S0 Canada

The mixing quality is an important objective to look for to obtain a proper green paste homogeneity and an optimum of technical characteristics of the anode. The green paste density is an excellent indicator of mixing quality. The following presentation proposes a method which respects the environmental criteria of Quebec to measure the green paste density. Furthermore, results obtained will be presented with different types of mixer by considering wear.

9:20 AM

CHARACTERIZATION OF MECHANICAL PROPERTIES AND MICROSTRUCTURES OF GREY IRON MELT UTILIZED FOR THE ASSEMBLY OF THE ANODES: *Jesus Rendon*[1]; Dr. Mokka Rao[1]; [1]Universidad Nacional Experimental De Guayana, Puerto Ordaz-8015A, Estado Bolivar Venezuela- S.A.

Samples of grey iron melt with low linear contraction on solidification are used for studying the mechanical properties and microstructures for correlating them with chemical composition through the use of carbon equivalent. The samples of the ring used for the assembly of anodes are prepared for analyzing the chemical elements C, Si, P, Mn and S and realize tests of traction and hardness. The results obtained indicate that the optimum mechanical properties for execution of this work are those which correspond to the carbon equivalent content near the eutectic point. The characterization of the microstructure is realized by applying techniques of optical microscope with the help of image analyzer. The microscopic analysis revealed that the resulting matrices are the types ferritic and ferritic perlatic. The presence of large laminas of grafite is also observed.

9:45 AM

PLANT STATISTICAL EVALUATION OF THE EFFECT OF AGGREGATE COMPOSITION AND PITCH LEVEL ON ANODE DISTORTION AND PREDICTED PERFORMANCE: *Mr. Tony Ross*[1]; Ken Krupinski[2]; Marilou McClung[1]; [1]Century Aluminum of West Virginia, Inc., Ravenswood, WV 26164 USA; [2]Koppers Industries, Inc., Pittsburgh, PA 15238 USA

Century Aluminum, Ravenswood Operations, has experienced episodes of anode distortion, stub hole distortion and packing material compaction in the stub hole. To examine the factors that can affect these conditions at the plant-scale level, a quality team was formed using members from production and technical units. The team devised a two phase testing program. The first phase consisted of varied Ravenswood aggregate and pitching level in an experimental design of 20 runs using one pitch. The second phase of the testing will involve evaluating selected aggregate formulations with various pitches. This paper details the procedure used to develop the experimental program method of plant scale anode preparation, anode evaluation and results.

10:10 AM

IMPROVED OXIDATION PROTECTION FOR CARBON ANODES: *Professor J. A. Sekhar*[1]; Dr. J. Liu[1]; Mr. J. Li[1]; Professor V. de Nora[2]; [1]University of Cincinnati, International Center for Micropyretics, Department of Materials Science and Engineering, Cincinnati, Ohio 45221 USA; [2]MOLTECH S.A, Geneva Switzerland

Boric acid is known to impart oxidation resistance to carbon anodes. The optimal anode treatment involves the precipitation of a boron containing salt from dissolved boric acid on to the carbon surface and in the pores*. The precipitation treatment and the mechanism of protection by this method has been studied. The optimal concentration of the dissolved salt is discussed. Methods for influencing the microstructure in order to reduce the amount of precipitated salt while maintaining the high oxidation resistance are demonstrated. * G. Berclaz, V. de Nora, J. J. Duruz and G. Johnston, "Anode Impregnation System for Aluminum Reduction Cells," pp 619-626, Light Metal 1997.

CAST SHOP TECHNOLOGY: Session IA - Molten Metal Processing

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

Monday AM Room: River Room B
February 16, 1998 Location: Convention Center

Session Chair: Raj Mutharasan, Drexel University, Philadelphia, PA 19104

8:30 AM

ALPUR TS, PECHINEY'S NEW GLOBAL CONCEPT FOR MOLTEN ALUMINIUM TREATMENT: *Jean-Claude Terrier*[1]; [1]Pechiney Aluminium Engineering, Sales Manager, Voreppe 38340 France

In collaboration with casthouses in the Pechiney Group and the Voreppe Research Center, Pechiney Aluminium Engineering has recently developed a new generation of ALPUR degassers. This paper describes the different subassemblies of this new equipment, the effects on metal quality and the robustness of the process, and then operation and operating costs are reviewed.

8:50 AM

NEW ENGINEERED SOLUTIONS FOR UPGRADING EXISTING DEGASSING SYSTEMS AT ALUMAX INTALCO: *Nikolas Winjum*[1]; Mark Arnold[2]; Peter Flisakowski[2]; [2]Pyrotec, Inc, Spokane, Washington; [1]INTALCO Aluminum Corporation, Ferndale, WA USA; [2]Pyrotec, Inc, Spokane, WA

Alumax INTALCO in Ferndale, Washington, USA, commissioned a work team to improve the performance of its installed degassing systems. The objectives were to 1) minimize the operating costs associated with the degassing system's injectors, 2) reduce maintenance cost, 3) enhance features for operating and cleaning practices and 4) minimize investment costs associated with making these improvements. Working in conjunction with Pyrotek, Incorporated, and Pechiney Aluminium Engineering, the INTALCO team designed and implemented a new lid and injector system that achieved these objectives. Features of the new design include the use of an Alpur-style injector system, a simplified inert gas injection panel, and lid improvements for vessel access. Actual cost reductions provided payback for the redesign investment within six months, while helping Alumax with its on-going effort to reduce the cost per treated ton of aluminum.

9:10 AM

IMPROVED METALLURGICAL UNDERSTANDING OF THE ALCAN COMPACT DEGASSING PROCESS AFTER TWO YEARS OF INDUSTRIAL IMPLEMENTATION: *Peter Waite*[1]; [1]Alcan International Ltd., Arvida Research & Development Centre, Jonquiere, Quebec G7S 4K8 Canada

Over the past two years, industrial implementation of the Alcan compact degasser has continued, and it is presently being used in more than half a dozen casting facilities. During this period, further quantification of the process metal treatment efficiency has been undertaken for a wide range of alloys and casting conditions. The extensive plant data that has been collected was analyzed using the underlying metallurgical principles as guidelines. This has led to an improved understanding of the ACD specifically, and of multi-stage in-line treatment processes in general. The relationship between the metallurgical principles used for data analysis and the degasser metal treatment performance are discussed, and factors affecting hydrogen and alkali removal performance were identified. Examples illustrating these findings are presented using plant data for the Alcan compact degasser and for conventional in-line degassers.

9:30 AM

COMPUTER SIMULATION OF FLOTATION TREATMENT METHODS USED IN ALUMINUM ALLOY PROCESSING: *M. Maniruzzaman*[1]; M. M. Makhlouf[1]; [1]Worcester Polytechnic Institute, Aluminum Casting Research Laboratory, Worcester, MA 01609 USA

The role of melt treatment is becoming extremely important in the foundry industry because of the ever increasing demand for high quality end-products. Removal of inclusions by flotation is one of the most commonly used treatment methods in the aluminum foundry industry. In order to optimize this process, it is very important to understand the basic mechanisms underlying this process. During flotation, flow behavior in the melt reactor is very complex, mainly due to turbulence in the flow field. Unfortunately with the currently available equipment, it is not possible to visualize the flow pattern inside the metal reactor. In this study, a computer simulation model for the flotation treatment process has been developed based on turbulent flow field calculations. Since in the flotation treatment process more than two phases are present in the computational domain, Eulerian multiphase flow with modified k-e turbulence modeling has been employed to solve the Navier-

Stokes and continuity equations for the various phases. Coupling of the phases is achieved through pressure and inter-phase exchange coefficients. Computer predicted inclusion removal efficiency and bubble streamlines along with the analysis of the governing parameters will be presented.

9:50 AM

CAN ROTOR-BASED REFINING UNITS BE DEVELOPED AND OPTIMIZED BASED ON WATER MODEL EXPERIMENTS?: *Dr. Stein Tore Johansen*[1]; S. Graadahl[1]; P. Tetlie[1]; B. Rasch[1]; E. Myrbostad[1]; R. Anvar[1]; [1]SINTEF, Materials Technology, N-7034 Trondheim Norway

The paper analyses the removal of hydrogen from aluminium using rotor-based refining units. Two different systems are tested in a water model under different running conditions. The results from the water model is then translated to liquid aluminium. The theoretical model is based on accepted descriptions of equilibrium constants and mass transfer theories. Surprisingly, it was found that the scaling to the metallurgical system shows that the most efficient system in water is the less efficient system in liquid metal. This is found to be in good agreement with industrial experience. The reason for this anomaly is discussed and explained.

10:10 AM

THE CAST HOUSE TROUGH REACTOR -- A NEW CONCEPT IN DEGASSING REACTOR DESIGN: *Chris English*[1]; [1]Cast House Technology Ltd., Guelph, Ontario N1G 2A7 Canada

The principles behind a new concept of degassing reactor design using very high bubble population densities and extreme turbulence are described. The results obtained from a degassing reactor with a treatment zone measuring 28" x 9" x 14" high, designed in accordance with these principles are presented. Degassing performance in excess of 60% reduction in hydrogen levels were obtained at a metal throughput of about 900 lbs/min.

10:30 AM

NOTORP HYDROGEN ANALYZER OPERATING PRINCIPLES AND APPLICATION AT COMMONWEALTH ALUMINUM: *Luiz Martins*[1]; C. William Sanderson[1]; Joeseph Tessandori[2]; [1]Commonwealth Aluminum, Lewisport, KY 42351-0480; [1]Selee Corporation, Hendersonville, NC 28792 USA

The NOTORP Hydrogen Analyzer was developed recently to monitor dissolved hydrogen content in molten aluminum alloys. The Analyzer uses an electrochemical cell mounted inside a sampling tube, with one side of the cell exposed to the molten aluminum and the other side in equilibrium with a reference gas of known hydrogen content. The electrochemical potential measured across a solid state proton conducting ceramic element is proportional to the difference in hydrogen activity. The Analyzer was tested at Commonwealth Aluminum, demonstrating ease of use, reliability and rugged design. Test results and comparisons of the "Notorp" Analyzer with other hydrogen measurement techniques are presented. The tests were also used to establish baseline molten metal quality levels and degasser performance. Several tests were conducted measuring hydrogen content via four (4) techniques as well as alkali element content. Observations and efficiencies for hydrogen removal and alkali element removal are discussed.

10:50 AM

ANALYSIS AND THERMODYNAMIC PREDICTION OF HYDROGEN SOLUTION IN SOLID AND LIQUID MULTICOMPONENT ALUMINUM ALLOYS: *P. N. Anyalebechi*[1]; [1]James Madison University, Integrated Science & Technology Program, Harrisonburgy, VA 22807 USA

Reported experimentally determined values of hydrogen solubility in liquid and solid Al-H and Al-H-X (where X = Cu, Si, Zn, Mg, Li, Fe or Ti) systems have been critically reviewed and analyzed in terms of Wagner's interaction parameter. An attempt has been made to use Wagner's interaction parameter and statistic linear regression models derived from reported hydrogen solubility limits for binary aluminum alloys to predict the hydrogen solubility limits in liquid and solid (commercial) multicomponent aluminum alloys. Reasons for the observed poor agreement between the predicted and experimentally determined hydrogen solubility limits are discussed.

11:10 AM

ROTARY FLUX INJECTION: CHLORINE-FREE TECHNIQUE FOR FURNACE PREPARATION: *Guy Beland*[1]; Claude Dupuis[1]; Gaston Riverin[1]; [1]Alcan International Limited, Arvida Research & Development Centre, Jonquiere, Quebec Canada

In order to reduce its chlorine gas use and consequently chlorinated emissions, Alcan developed over the past years a method to replace chlorine fluxing in furnaces. That chlorine-free technique, currently in permanent use in several Alcan installations, is called the Rotary Flux Injection (RFI) technique. The technique has proven to give equivalent or superior metallurgical performance compared to the standard preparation technique of chlorine injection with lances while offering significant reduction in gaseous and particulate emission levels. This paper will present the latest results obtained on alkali removal efficiency, metal cleanliness and dross generation on alloy series AA1XXX, AA3XXX, AA5XXX and AA6XXX along with a description of the RFI equipment concept.

DEFECTS IN CRYSTALS: A SYMPOSIUM HONORING THE CONTRIBUTIONS OF JOHN P. HIRTH: Dislocation Theory

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

Monday AM — Room: 102
February 16, 1998 — Location: Convention Center

Session Chair: Craig S. Hartley, Florida Atlantic University, Dept. of Mechanical Energy, Boca Raton, FL 33486

8:30 AM INVITED

THE NET INTERACTION FORCE BETWEEN TWO SKEW DISLOCATIONS IN AN ELASTICALLY ANISOTROPIC HALF-SPACE: *Professor David M. Barnett*[1]; [1]Stanford University, Materials Science & Engineering, Stanford, CA 94305-2205 USA

It is generally known that the total interaction force between two non-parallel infinitely long straight dislocations in an infinite isotropic linear elastic medium is independent of their separation. Orlov and Indenbom (1969) have shown that this result is valid for arbitrary elastic anisotropy, and that the net interaction force may be computed explicitly without knowing details of the Stroh solution for the field of a straight dislocation in an infinite anisotropic medium. In the present work it is shown that the independence of the total interaction force on separation remains valid for two skew dislocations in an anisotropic half-space (each dislocation being parallel to the traction-free half-space boundary). If we refer to the dislocation closest to the half-space boundary as (1) and to the other dislocation as (2), we find the remarkable result that the total interaction force of (1) on (2) vanishes, while the total interaction force of (2) on (1) is precisely twice the total interaction force which (2) exerts on (1) in an infinite medium. The fact that the two net interaction forces are not equal and opposite

(unless they both vanish) is due to the lack of translational invariance normal to the boundary of a semi-infinite medium. This set of results is called Nix's Theorem, after W. D. Nix, whose numerical computations for isotropic half-spaces suggested that the results might be true for half-spaces of arbitrary anisotropy, thus motivating the present proof. The implications of the theorem and the ease with which the interaction forces can be computed should prove useful in the modeling of dislocated thin films.

9:00 AM INVITED

SHAPES OF HOLLOW DISLOCATION CORES: *Prof. David J. Srolovitz*[1]; Dr. N. Sridhar[1]; Dr. John W. Cahn[1]; Prof. John P. Hirth[1]; [1]University of Michigan, Materials Science & Engineering, Ann Arbor, MI 48109-2136 USA

Dislocations in crystals with large Burgers vectors, low surface energies, and large elastic constants may have hollow cores. A simple stability test, based on a necessary condition for equilibrium, fails for the circular cores that are commonly assumed, except for screw dislocations in isotropic crystals. We calculate the approximate equilibrium shapes for a variety of conditions. Edge dislocation cores, even in isotropic crystals are significantly elongated normal to their Burgers vectors. Additional shape anisotropy factors are introduced by both mild elastic and mild surface energy anisotropies.

9:30 AM INVITED

LINEAR RELATIONS IN THE DISLOCATION STROH VECTOR SYSTEM, DERIVED BY ENERGY CONSIDERATIONS: *Professor Jens Lothe*[1]; Litian Wang[1]; [1]University of Oslo, Institute of Physics, Oslo N-0316 Norway

The linear dependences within the system of the six force components of the six Stroh (1962)vectors of an elastic anisotropic medium take a particularly simple form in the so-called self-orthogonal formalism introduced by Lothe and Wang (1994, 1995) in connection with the problem of reflection of elastic waves at free surfaces. Such linear dependences are also present in the static dislocation Stroh vector system, as can be demonstrated by simple energy considerations. References: A.N. Stroh, J.Math.Phys. 41, 77-103 (1962) J. Lothe and L. Wang, Wave Motion 20, 41-56 (1994) J. Lothe and L. Wang, Wave Motion 21, 163-181 (1995).

10:00 AM INVITED

FINITE SEGMENT METHOD FOR DISLOCATION MECHANICS: *Dr. Xiao Jiang Xin*[1]; Dr. Robert H. Wagoner[1]; Dr. Glenn S. Daehn[1]; [1]The Ohio State University, Materials Science and Engineering, Columbus, Ohio 43210 USA

A numerical technique has been developed for studying the generation, equilibrium, and energy of curved dislocations in a non-uniform stress field. The Finite Segment Method (FSM) involves approximating a dislocation line by a series of straight dislocation segments, similar to the approximation of a continuum or structure by using the Finite Element Method (FEM). Explicit expressions for energy and force terms and the equilibrium equation are derived for numerical implementation which follows typical FEM assembly and solution. The method is applied to several cases of interest, including the Orowan bow-out mechanism and dislocation equilibration at misfitting particles. The results illustrate the usefulness and versatility of FSM.

10:30 AM INVITED

POINT FORCE MODELS OF PRIMITIVE DISLOCATION LOOPS: *Craig S. Hartley*[1]; [1]Florida Atlantic University, Department of Mechanical Engineering, Boca Raton, FL 33486 USA

Continuum models of crystal defects suffer from the disadvantage of containing a mathematical singularity at the defect location. This requires that the elastic solution for the defect displacement field be terminated at some distance from the defect, defining a region where the continuum model does not apply. Typically, information within this region is obtained from calculations based on atomic models. In addition, information relating to the effect of the crystal structure of the lattice on defect properties is also lost in the usual continuum models. A modification of the continuum model of defects in which the defect is created by placing an array of point forces on atoms surrounding the defect partially relieves the limitations of the continuum model by replacing the singularity at the defect itself with singularities at the points of application of the forces. These singularities can be related to interatomic force constants and elastic constants in a straightforward manner. Dislocations can be constructed from the superposition of an array of primitive loops. The primitive loop is a point defect having a long-range displacement field the same as an infinitesimal dislocation loop in the usual continuum model. Two types are defined: prismatic and glide or shear loops. These are created in a particular crystal structure by applying point forces on an array of atoms and adjusting the magnitudes of the forces to yield the correct dipole moment for the defect. Primitive loops in body centered cubic and face centered cubic structures are described, and the process of constructing a dislocation from these is outlined.

11:00 AM

SMALL-ANGLE X-RAY SCATTERING BY DISLOCATIONS IN DEFORMED METALS: *Dr. Robb Thomson*[1]; Dr. L. E. Levine[1]; Dr. G. G. Long[1]; [1]NIST, MSEL, Gaithersburg, MD 20899

In order to interpret the X-ray scattering experiments described in the following abstract, we have developed a theoretical treatment of small angle scattering of X-rays by dislocations organized in walls. The analysis can be applied to neutron scattering, as well, but our initial focus is the ultra small-angle regime accessible in our X-ray experiments. The analysis shows that the scattering by individual dislocations or dislocation dipoles has a unique wave vector dependence, observable in the high-q regime, and that the wall structure determines the low-q scattering. (In our experiments, the boundary between low and high q behavior occurs in the vicinity of q=0.001 per A.) Single dislocations exhibit $1/q^2$ and dipoles a $1/q^4$ dependence, with a unique dislocation and Burgers vector orientation signature for each. Characteristics of the low-q region, such as the power law dependence, peak features, etc. lead to predictions about the net Burgers vector and partial ordering in the wall, and about the wall width. The theoretical treatment is outlined in the talk. Comparisons with our experiments will be given in the following talk.

11:20 AM

AN ATOMISTIC STUDY OF THE EFFECTS OF STRESS AND HYDROGEN ON A DISLOCATION LOCK IN NICKEL: M. I. Baskes[1]; *R. G. Hoagland*[2]; [1]Materials Reliability Department, Sandia National Laboratories, Livermore, CA 94551-0969; [2] School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164-2920

The effects of stress and hydrogen on a dislocation lock consisting of an a/3[100] stair rod on the intersection of two (111) slip planes in nickel was examined by atomistic simulation using Embedded Atom Method (EAM) potentials. In the absence of hydrogen the lock undergoes several transitions under increasing uniaxial and hydrostatic tension. The transitions are characterized by the absorption and reemission of Shockley partial dislocations at the core of the lock. The reemission involves the generation of both intrinsic and extrinsic stacking faults. Monte Carlo calculations at a hydrogen chemical potential equivalent to 190 atm (260 appm) at room temperature suggest that the hydrogen is strongly trapped in and near the cores of the partial dislocations and the lock. In fact, the trapping is so strong that a stoichiometric hydride is formed in these regions. The evolution of the hydrogen-equilibrated lock with increasing stress is quite different than without hydrogen. In uniaxial tension both dislocation absorption and reemission occur at significantly high stress levels than in the absence of hydrogen. In the case of hydrostatic tension, partial dislocations originate from the hydride/nickel interface rather than from the core of the lock. The hydride remains fault free due to its high stacking fault energy. At the stress levels examined in this study the dislocation lock does not act as a crack nucleus either with or without hydrogen. This work is supported by the U.S. Dept. of Energy under contract DE-AC04-94AL85000 and through grant DE-FG-06-87ER45287.

GENERAL ABSTRACTS: Innovations in Aluminum I

Sponsored by: Light Metals Division, Aluminum Committee, U.S. Department of Energy

Monday AM Room: Patio A
February 16, 1998 Location: Convention Center

Session Chair: Sara Dillich, U.S. Department of Energy, Office of Industrial Technologies, Washington, DC 20585

8:30 AM
AN OVERVIEW OF THE DOE - OIT ALUMINUM PROGRAM: *Ms. Sara Dillich*[1]; [1]U.S. Department of Energy, Washington, DC 20585 USA

The Aluminum Industry Technology Roadmap (May, 1997) identified technology needs, priorities and performance targets for the aluminum industry for each of the principle industry segments - Primary Aluminum Production, Semi-Fabricated Products, and Finished Products. The DOE-Office of Industrial Technologies (OIT) Aluminum Program portfolio consists of projects, all with industrial participation and cost-share, addressing these needs. The project partnerships, goals, and anticipated benefits will be described, as will the project solicitation and selection process. Future plans for the program, and the relevance of other federally-funded R&D to the Roadmap goals will also be discussed.

9:00 AM
WETTABILITY OF TITANIUM DIBORIDE-BASED CATHODES IN LOW-TEMPERATURE SLURRY-ELECTROLYTE ALUMINA REDUCTION CELLS: *Dr. Craig Brown*[1]; [1]Brooks Rand, Ltd., Seattle, WA 98107 USA

The concept of a low-temperature slurry-electrolyte cell with non-consumable electrodes is the underlying concept of this project. This project will specifically address the wettability by aluminum of titanium diboride-based cathodes in low-temperature baths. The concept will look at cathode composition, bath composition, and current density with applied polarization.

9:30 AM
APPLICATION OF AN INNOVATIVE AND NOVEL SONOCHEMICAL TECHNOLOGY FOR PROCESSING BAUXITE : *Mr. Larry Farrar*[1]; [1]Montec Associates, Inc., Butte, MT 59702-4182 USA

An innovative and novel technology that uses mechanically induced acoustic energy to cause cavitation and acoustic streaming in liquids and slurries is being investigated for use in aluminum production. The proposed technology produces strong cavitation and acoustic streaming in the range of a few hundred Hertz to a few thousand Hertz. Additionally, transducer deflections of fractions of an inch are typical. Consequently, this technology allows the use of sonochemistry to industrial process applications.

10:00 AM Break

10:30 AM
FLUIDIZED BED HEAT TREATING OF ALUMINUM WITH FLUID BED QUENCHING AS AN ALTERNATIVE TO LIQUID QUENCHING: *Mr. Marc Glasser*[1]; Ms. Karin Bickford[1]; [1]Procedyne Corp, New Brunswick, NJ 08901 USA

Procedyne Corp. is investigating an alternative quenching method that minimizes the distortion typically found in water or polymer quenching of aluminum. The quench rate is lower than liquid quenching, but much faster than air cooling. This project will determine whether fluid bed quenching will produce acceptable properties for alloys from binary, ternary or quarternary aluminum alloys.

11:00 AM
DEVELOPMENT OF A HIGH CAPACITY MELT FURNACE FOR REDUCED ENERGY CONSUMPTION AND ENHANCED PERFORMANCE: *Dr. Ming Fu*[1]; [1]Micropyretics Heaters International, Inc., Cincinnati, OH 45212 USA

This concept is a novel furnace concept design for aluminum melting which utilizes an ultra hot air/gas generator called the Thermoblower as a heat source. This design provides new versatility to the aluminum melting process by working in a predominant convective heat transfer mode, by increasing safety of the melt, by reducing melting equipment capital costs, by allowing for selective gas coverage during melting which prevents low vapor pressure alloying additions from evaporating, and by overcoming aluminum oxidation problems. This novel design is expected to improve energy efficiency by over 90% and also allows for a substantial enhancement in productivity.

HIGH TEMPERATURE SUPERCONDUCTORS: Bi-, Tl-, and Hg-based Superconductors

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/Structural Materials Division, Superconducting Materials Committee

Program Organizers: U.Balu Balachandran, Argonne National Laboratory, 9700 S. Cass Ave. Bldg. 212, Argonne, IL 60439; Pradeep Haldar, Intermagnetics General Corp., 450 Old Niskayuna Rd., Latham, NY 12110; Paul McGinn, University of Notre Dame, Center for Materials Science, Notre Dame, IN 46556

Monday AM Room: Fiesta C
February 16, 1998 Location: Convention Center

Session Chair: S. E. Dorris, Argonne National Laboratory, Argonne, Illinois 60439

8:30 AM INVITED
COMPOSITE POWDER-IN-TUBE APPROACHES TO OXIDE SUPERCONDUCTOR FABRICATION AND UTILIZATION: *Alex Otto*[1]; Elliott Thompson[1]; Derek Daly[1]; Eric Podtburg[1]; Chris Craven[1]; [1]American Superconductor Corporation, Westborough, MA

This paper reports on key developments in Bi-2223 materials science, multifilament powder-in-tube composite tape processing, and performance. Current densities in substantial lengths are now at commercially interesting levels for product development. Texture, grain to grain connectivity, and the chemical state of Bi-2223 within long composite wire must be understood and controlled for adequate current density. The comprehensive superconducting tape performance required for each application has been a major focus of development work since tape current density reached commercially interesting levels. In addition to current density, these include mechanical properties, energy dissipation in varying magnetic fields, and environment-induced degradation. Although performance and long length fabrication is the most advanced for Bi-2223, its complexity continues to provide opportunities for performance improvements at the most basic levels. One such area is in chemical and defect chemistry modulation via low oxygen potential heat treatments after sintering. These can raise transport transition temperature to about 112 K, with 50 % improvements in transport current densities.

8:50 AM INVITED
DEVELOPMENT AND CHARACTERIZATION OF Ag SHEATHED Bi(2223) TAPES FOR POWER APPLICATIONS WITH IMPROVED MICROSTRUCTURE AND HOMOGENEITY: *Dr.*

Giovanni Grasso[1]; Frank Marti[1]; Yibing Huang[1]; [1]University of Geneva, Physics Department, Geneva 1211 Switzerland

The development of the fabrication process of Ag sheathed Bi(2223) tapes has been carried out in order to improve their transport and mechanical properties, as required by the power applications which are so far under study. Critical current density values of 28 kA/cm2 at 77K have been achieved on long multifilamentary Bi(2223) tapes, with a fabrication process that has been successfully employed in the fabrication of samples longer than 50 m. The microstructure and homogeneity of Ag sheathed multifilamentary Bi(2223) tapes has been markedly improved by introducing a new deformation technique. In a substantial part of the fabrication process, swaging, drawing and rolling have been replaced by deformation with a prototype four-rolls machine, which allows the deformation of rectangular shaped wires. At present, critical current densities in excess of 25 kA/cm2 at 77K have been achieved on long samples prepared with this new technique. Moreover, innovative filament configurations have been employed for the fabrication of square and round-shaped Bi(2223) wires, with critical current density at 77K exceeding 20 kA/cm2.

9:10 AM INVITED
EFFECTS OF PRESSING ON THE CURRENT FLOW IN A Ag/Bi-2223 TAPE: *Dr. Gye Won Hong*[1]; Dr. Hee Gyoun Lee[1]; Dr. Weon Ju Kim[1]; Mr. Min Hyung Lee*[1]; Dr. Hyun Soon Park*[1]; [1]Korea Atomic Energy Research Institute, Superconductivity Research Laboratory, TaeJon 305-600 Korea

The effects of compressive deformation on the current flow in a Ag/Bi-2223 tape have been investigated by pressing the tape annealed at 840°C for 50h with various pressure. It was observed that the critical current, Ic, was gradually decreased with pressure and reached to zero at a strain of ~ 6 %. After further annealing the pressed tape at 840°C for 50h, Ic, for the strain less than ~ 2.5%, decreased with strain and reached to zero at ~ 2.5% whereas Ic, for the strain larger than ~ 2.5%, increased with strain. Low Ic of the tape processed with lower pressure was explained by a thermal stress generated during heating. The resistance of Ag/Bi-2223 tape to thermal stress was markedly decreased at the presence of pre-existing cracks. It is considered that the formation of microcracks, the sausaging effect and the hardening of Bi-2223 core were closely related with the fact that the strain of Bi-2223 core with pressure revealed nearly linear increase to a pressure of 600 MPa and then increased fast from a pressure of 800 MPa.

9:30 AM INVITED
CHEMICAL AND MICROSTRUCTURAL ASPECTS OF THE COATED-WIRE-IN-TUBE Ag/Bi-2223 COMPOSITE CONDUCTOR: *Dr. Nazarali N. Merchant*[1]; Dr. Steve E. Dorris[1]; Mr. Thomas G. Truchan[1]; Dr. Victor A. Maroni[1]; Dr. Konrad T. Wu[2]; [1]Argonne National Laboratory, Argonne, IL 60439 USA; [1]Argonne Natl. Lab., Argonne, IL 60439 USA; [2]SUNY/Old Westbury Campus, Old Westbury, NY 11568 USA

There is growing evidence that an increase in the ratio of surface area of silver to volume of ceramic phase (S/V) in silver-clad (Bi,Pb)2Sr2Ca2Cu3Oy (Ag/Bi-2223) composite superconductors leads to a concomitant improvement in the critical current properties. We are also finding evidence that increasing S/V leads to accelerated Bi-2223 formation kinetics during heat treatment. In the oxide-powder-in-tube (OPIT) method of fabricating Ag/Bi-2223 composite filaments, S/V increases with increasing filament count. The recently introduced coated-wire-in-tube (CWIT) approach to the preparation of Ag/Bi-2223 composites produces core architectures that are analogues to those of OPIT multifilaments in terms of increased S/V but offers the advantage of a higher probability of having a fully interconnected superconducting core. This presentation will describe recent results that illustrate the phase formation chemistry and microstructural features of Ag/Bi-2223 composites prepared by the CWIT method.

9:50 AM INVITED
INFLUENCE OF CHEMICAL PREHISTORY ON THE REACTIVITY OF (Bi,Pb)-2223 PRECURSORS : *Dr. Oleg A. Shlyakhtin*[1]; Mr. Anton L. Vinokurov[1]; Prof. Yuri D. Tretyakov[1]; Dr. Anna V. Shlyakhtina[1]; Dr. Larisa G. Mamsurova[1]; [1]Moscow State University, Department of Chemistry, Moscow; 119899 Russia

Along with similarity of (Bi,Pb)-2223 formation mechanism, the rate of 2223 phase formation is rather different for precursor mixtures prepared by various methods. In order to study the reason for such a difference systematic comparison of processes occurred during heat treatment of precursors obtained by freeze-drying, spray-drying and mechanochemical synthesis is performed. Observed diversity of microstructures evolution, formation rates and stability of (Bi,Pb)-2212 and other intermediates is discussed in terms of topochemical approach to (Bi,Pb)-2223 synthesis. Anion composition of primary solution is found to be principal factor determining the evolution pathway and reactivity of precursors prepared by wet chemical methods.

10:10 AM Break

10:20 AM INVITED
EFFECTS OF LEAD-CONTENT ON MICROSTRUCTURE DEVELOPMENT AND PROPERTIES OF Bi-2223 POWDER-IN-TUBE CONDUCTORS: *Dr. S. E. Dorris*[1]; Ms. N. Ashcom[1]; Mr. T. Truchan[1]; Dr. N. Merchant[1]; Dr. V. A. Maroni[1]; [1]Argonne National Laboratory, Argonne, IL 60439 USA

We have investigated the influence of Pb content on the microstructure and properties of Bi-2223. Processing conditions depend strongly on total Pb content, with significantly higher temperatures required to maximize critical current density (Jc) in samples with low Pb content ($<Pb_{0.25}$). In optimizing the processing conditions for low Pb samples, we demonstrated that Bi-2223 may be processed at significantly higher temperatures than previously believed. X-ray and acoustic velocity measurements suggest that Bi-2223 can be processed in 8% O2 up to 844-850°C, rather than the typical processing temperature range of 820-825°C. Jc increased by a factor of 10 for Pb0.20 and Pb0.25 as the processing temperature was raised from 825 to 845°C. The higher processing temperatures also increased Jc in samples with Pb0.30 and Pb0.35, but not as dramatically. Microstructural and X-ray analysis suggested that the Jc increase resulted from more complete Bi-2223 formation, higher density, and better grain alignment. Second phases did not grow significantly larger during processing at the higher temperatures, but tended to spread along the 2223 grain boundaries rather than remain as isolated blocky particles. With such a second phase morphology, control of second phase content is crucial to maximizing Jc in samples processed at the higher temperatures. Work supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, under Contract W-31-109-Eng-38.

10:40 AM INVITED
THEORY OF DIFFUSION KINETICS IN CUPRATE SUPERCONDUCTORS: *Dr. David O. Welch*[1]; [1]Brookhaven National Lab., Dept. of Applied Science, Upton, NY 11973-5000

Atomic diffusion plays a crucial role in several aspects of the processing of cuprate superconductors. For example, oxygen diffusion is of critical importance in many aspects of cuprate processing, including radiation damage and annealing in both thin films and bulk superconductors, while cation diffusion is central to the intercalation mechanism of (Bi,Pb)-2212 to -2223 conversion and in the controlled precipitation of second phases, for improved flux pinning, during the processing of (Bi,Pb)-2223 ceramics. In this paper I will discuss the theory of diffusion kinetics in these materials and processes, with emphasis on the role of the quasi-two-dimensional nature of cuprates and the important role played by elastic stresses in diffusion kinetics in cuprates. This work was supported by the of the Division of Materials Sciences, Office of Basic Sciences and the Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

11:00 AM INVITED
MAGNETOTRANSPORT STUDIES OF Bi-BASED 2212 AND 2223 HIGH CRITICAL TEMPERATURE SUPERCONDUCTORS: *Dr. M. Ausloos*[1]; Dr. R. Cloots[2]; Dr. M. Pekala[3]; [1]SUPRAS, Institute of Physics, University of Liege, B-4000 Liege Belgium; [2]SUPRAS, Institute of Chemistry, University of Liege, B-4000 Liege Belgium; [3]University of Warsaw, Dept. of Chemistry, PL-02-089 Warsaw Poland

The electrical resistivity, thermoelectric power and thermal conductivity probe the charge and heat currents caused by the electric and temperature gradients. A magnetic field additionally superimposed on the superconducting sample with an orientation perpendicular to the electric or temperature gradient allows to observe phenomena called excess electrical resistivity, excess thermoelectric power, Nernst effect, magneto-resistivity and magneto-thermal conductivity. These parameters together supply interesting consistent information on the kinetics of vortices and of quasi particle scatterings in the mixed state. For illustration we examine the case of Bi-based 2212 and 2223 superconducting ceramics, discussed with emphasis on the layered structure of such perovskites.

11:20 AM INVITED
PROCESSING OF DOPED Hg-1223 SUPERCONDUCTORS: *Dr. P.V.P.S.S. Sastry*[1]; Dr. K. M. Amm[1]; Dr. D. C. Knoll[1]; Dr. J. Schwartz[1]; [1]National High Magnetic Field Lab., Florida State University, Tallahassee, FL 32310 USA

The $Hg_1Ba_2Ca_2Cu_3O_y$ (Hg-1223) superconductor has the highest T_c (135 K) among all the high temperature superconducting cuprates. It has been shown that the stability and superconducting properties of Hg-1223 are greatly improved by partial substitution of Hg by Re, Bi, and Pb. It is necessary to develop processing techniques for grain growth and texture, which are essential to make this material suitable for practical applications. We have undertaken a detailed study on doped Hg-1223 materials to evaluate the relative merits of various dopants and their suitability for using them in powder-in-tube or other forms of conductors. Both Bi and Pb-doping allowed the formation of significant amounts of liquid phase during the reaction and yielded very dense superconducting phase with some degree of texture among the grains. Further, the reaction temperature for (Hg,Bi)- and (Hg,Pb)-1223 are around 850°C, which is suitable for growth of these materials on metals. Samples were characterized for phase purity, microstructure and interfacial reactions using XRD, SEM, and high field magnetization measurements. Details of the measurements and the optimized processing schedules will be discussed.

11:40 AM INVITED
THE INFLUENCE OF Bi-DOPING ON THE IN SITU GROWTH OF $TiBa_2Ca_2Cu_3O_9$ HIGH TC FILMS: *Norbert Reschauer*[1]; Horst H. Wagner[1]; Wolfgang Brozio[1]; Uli Spreitzer[1]; Thomas Schauer[1]; Karl F. Renk[1]; [1]Universität Regensburg, Institut für Experimentelle und Angewandte Physik, Regensburg 93040 Germany

The in situ deposition process - laser ablation in the presence of Tl_2O vapor - has turned out to be a preparation method for single phase and epitaxial $TlBa_2Ca_2Cu_3O_9$ (1223) thin films with T_c values up to 109 K. It was found by several groups that a partial substitution of Tl by Bi simplifies the phase development of the 1223 compound. We have investigated the influence of Bi-doping on the in situ growth. X ray measurements show that the films consisted mainly of the Tl-1223 compound. In 300 nm thin films there was no evidence of a Bi amount in the crystal structure, but thinner films show a small amount of Bi. We concluded that Bi-doping supports the development of the 1223 compound only in an early stage of film growth. The Bi-doped films have high T_v values up to 114 K, high j_c values up to $6*10^5$ A/cm^2 and low surface resistances of 56 mΩ (77 K, 87 GHz), respectively 740γ Ω K, 10 GHz).

HUME ROTHERY AWARD FOR PROF. RYOICHI KIKUCHI: Hume-Rothery Symposium I

Sponsored by: Jt. Electronic, Magnetic & Photonic Materials Division/ Structural Materials Division, Alloy Phases Committee
Program Organizers: Juan M. Sanchez, The University of Texas, Center for Materials Science, Austin, TX 78712; Lawrence Anthony, The University of Toledo, Dept. of Physics and Astronomy, Toledo, OH 43606

Monday AM Room: 104
February 16, 1998 Location: Convention Center

Session Chair: Lawrence Anthony, University of Toledo, Dept. of Physics and Astronomy, Toledo, OH 43606-3390

8:30 AM KEYNOTE
SPACE IS CONTINUOUS: *Dr. Ryoichi Kikuchi*[1]; [1]U. C. Berkeley, Materials Science & Mineral Engr, Berkeley, CA 94720-1760

In theories of phase diagram calculations, the conventional way is to distribute atoms over lattice points and permute them to find the minimum free energy state. Now need is arising to allow atoms move away from lattice points. Two approaches will be presented as extensions of the Cluster Variation Method (CVM). One is to decrease the lattice constant to infinitesimal. The other is to let atoms move away from the assigned lattice points. In the first, Liquid-CVM, all shapes and sizes of the basic cluster are used in the theory. This leads to the liquid state, and related to the Percus-Yevic and the hyper-netted chain theories. The second method, Continuous Displacement CVM, takes into account local elastic deformation of the lattice, caused by the thermal origin, composition of alloys of different size species, and external deforming forces. These origins lead to thermal expansion, alloy phase diagrams, and elastic constants. Computational results and future expectations will be presented.

9:00 AM INVITED
MULTI-ATOM INTERACTIONS IN THE ORDERING OF CLOSE-PACKED STRUCTURES: *Dr. John W. Cahn*[1]; [1]NIST, Materials Science and Engineering Laboratory, Gaithersburg, MD 20899

The theory of ordering on binary face-centered-cubic (FCC) (or hexagonal close packed (HCP)) crystal structures using the point approximation is reexamined. The Shockley diagram with its multiphase critical point is robust for pair-wise interactions stretching to higher neighbors. Conditions for obtaining realistic diagrams can be exactly described in the point approximation with multi-atom interaction (or composition dependent pair-wise) energies. The multiphase critical point remains and can be used for a Landau expansion, but becomes metastable and submerged under the $L1_0$ (or B19) first-order transitions. Its effects are seen in the two-phase regions of disordered A1 (or A3) with ordered $L1_2$ (or DO19) regions as they approach the middle of the phase diagram: the narrowing of the two-phase region, the reduction in latent heat, the reduction in computed interfacial energies. There is also a predicted continuity between the extrapolations of the order-disorder transitions of the two wings of the $L1_2$ (or DO19) parts of the diagrams. These results lead to an understanding of why it was possible to predict the realistic diagram with CVM.

9:30 AM INVITED
CLUSTER METHODS FOR DISORDERED-SYSTEM THERMODYNAMICS: *Dr. Didier de Fontaine*[1]; [1]U.C. Berkeley, Materials Science, Berkeley, CA 94720-1760 USA

The Cluster Variation Method was proposed in 1950 by Ryoichi Kikuchi as a hierarchy of approximations to obtain improved solutions for the Ising model. Then, in 1973, Kees van Baal of Delft, following earlier work by Lee, showed how one could use the CVM to calculate

prototype phase diagrams. This important development started a veritable cottage industry of phase diagram calculations, one of the earliest (for fcc crystal, 1977) being a "fitted" phase diagram produced by Ryo and myself for the popular Cu-Au system. After "prototype" and "fitted" came "first principles" calculations for which a new tool was required: that of Cluster Expansion, the key paper in this field being that of Sanchez, Ducastelle and Gratias (1984). In a sense, the CVM gave rise to a very general "cluster algebra" method of calculating thermodynamic properties of disordered (or partially ordered) systems. The ultimate goal of the enterprise is of course the lofty one of calculating phase diagrams from the knowledge of only the atomic numbers of the constituents. The historical aspect of this quest will be briefly reviewed and some recent examples of applications presented.

10:00 AM Break

10:10 AM INVITED
FIRST-PRINCIPLES CALCULATION OF PHASE STABILITY IN METAL, SEMICONDUCTOR, AND OXIDE ALLOYS: *Dr. Christopher Wolverton*[1]; [1]NREL, Golden, CO 80401 USA

The groundbreaking work of R. Kikuchi in the statistical thermodynamics of alloy phase stability has been subsequently followed by a new field which combines first-principles total energy calculations with statistical techniques and provides a method to theoretically predict alloy phase stability without the use of any experimental data. We discuss a recently proposed advance in this field which extends the predictions of alloy phase stability to "state-of-the-art" first-principles LDA calculations including the effects of atomic relaxation: A small set of first-principles total energies of atomically relaxed configurations are mapped onto a generalized (mixed-basis, extended pair, many-body) Ising-like Hamiltonian, followed by statistical mechanical treatment of this Hamiltonian by Monte Carlo simulation. With this technique, we are able to provide prediction of unsuspected ground state structures, short-range order in disordered solid solutions, order-disorder transitions, free energies and entropies, and bond length distributions. This technique effectively extends the "state-of-the-art" in first-principles calculations (i.e., full potential, atomically relaxed, total energy) to 10,000-atom alloy systems at finite temperature. Furthermore, this technique is not restricted to a single class of materials, but can be used to study the thermodynamics of alloys composed of metals, semiconductors, or ceramics. Applications will be shown for a variety of alloy systems (e.g., Cu-Au, Cu-Ag, Ni-Au, Al-Mg, GaP-InP, LiO-CoO, etc.). Supported by BES/OER under contract no. DE-AC02-83CH10093. Work performed in collaboration with Alex Zunger and V. Ozolins.

10:40 AM INVITED
ORDER/DISORDER TRANSITIONS IN OXIDES: *Prof. Gerbrand Ceder*[1]; [1]MIT, Dept. of Materials Science and Engineering, Cambridge, MA 02139 USA

The general approach to calculate phase diagrams in materials with substitutional disorder from first-principles is now well established: It involves a quantum mechanical part to determine the effective cluster interactions in a lattice-model Hamiltonian, and a statistical mechanical method to obtain the free energy and state of order for the system. Very good results have been obtained with this approach in metallic systems. Oxide materials present some new challenges to this model: In alio-valent oxide mixtures, configurational disorder can occur on multiple sublattices. These sublattice can undergo separate or simultaneous order/disorder transitions, depending on the strength of the coupling interaction and the level of symmetry coupling. We will show applications for β-Al_2O_3, Li_xCoO_2 and Gd_2O_3-ZrO_2. Diffusion in β-Al_2O_3 was previously studied by Professor Kikuchi with the Path Probability Method.

11:10 AM INVITED
VIBRATIONAL MODES AND CONFIGURATIONAL DISORDER IN THE Ni-Cr SYSTEM: *Dr. J. M. Sanchez*[1]; Dr. P. J. Craievich[1]; [1]The University of Texas, Center for Materials Science and Engineering, Austin, TX 78712 USA

We develop a method to calculate the free energy of alloys that includes the coupling between vibrational and configurational degrees of freedom in the classical limit. The approach resolves the long standing issue of how to determine the vibrational free energy of alloys that are mechanically unstable for many configurations with long-range atomic order and, thus, for which the cluster expansion of the vibrational free energy in the harmonic or quasi-harmonic approximation cannot be applied. The theory is used to calculate the solid state portion of the Ni-Cr phase diagram.

11:40 AM
Cu-Au, Ag-Au, Cu-Ag AND Ni-Au INTERMETALLICS: FIRST-PRINCIPLES STUDY OF PHASE DIAGRAMS AND STRUCTURES: *Dr. Vidvuds Ozolins*[1]; Dr. Alex Zunger[1]; Dr. Christopher M. Wolverton[1]; [1]National Renewable Energy Laboratory, Golden, CO 80401 USA

The classic metallurgical systems — noble metal alloys — that have formed the benchmark for various alloy theories, are revisited. First-principles fully relaxed general potential LAPW total energies of a few ordered structures are used as input to a mixed-space cluster expansion calculation to study the phase stability and thermodynamic properties and of Cu-Au, Ag-Au, Cu-Ag and Ni-Au alloys. We find: (i) the size-mismatched systems Cu-Au (12%), Cu-Ag (12%) and Ni-Au (15%) possess large multibody and long-ranged pair interactions, which makes it impossible to describe them in terms of the classical Ising model with a few near-neighbor pair interactions. (ii) Our theoretical calculations correctly reproduce the tendencies of Ag-Au and Cu-Au to form compounds and Ni-Au and Cu-Ag to phase separate at T=0 K. (iii) Cu_3Au ($L1_2$) and CuAu ($L1_0$) are found to be the stable low-temperature phases of $Cu_{1-x}Au_x$ with transition temperatures of 530 K and 660 K, respectively, compared to the experimental values 663 K and approx 670 K. The significant improvement over previous first-principles studies is attributed to the more accurate treatment of atomic relaxations in the present work. (iv) LAPW formation enthalpies demonstrate that $L1_2$, the commonly assumed stable phase of $CuAu_3$, is not the LDA ground state for Au-rich alloys, but rather that ordered (100) superlattices are stabilized. (v) We extract the non-configurational (e.g., vibrational) entropies of formation and obtain large values for the size mismatched systems: 0.48 k_B/atom in $Ni_{0.5}Au_{0.5}$ (T=1100 K), 0.37 k_B/atom in $Cu_{0.141}Ag_{0.859}$ (T=1052 K), and 0.16 k_B/atom in $Cu_{0.5}Au_{0.5}$ (T=800 K).

INTERNATIONAL SYMPOSIUM ON IRON ALUMINIDES: ALLOY DESIGN, PROCESSING, PROPERTIES & APPLICATIONS: Alloy Design and Dislocation Behavior

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, Phillip 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

Monday AM Room: 108
February 16, 1998 Location: Convention Center

Session Chairs: S. C. Deevi, Phillip Morris USA, Research and Development, Richmond, VA 23234; L.L. Horton, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831

8:30 AM Introductory Remarks - S.C. Deevi

8:35 AM KEYNOTE
IRON ALUMINIDES, PRESENT STATUS, AND FUTURE PROSPECTS: *N. S. Stoloff*[1]; [1]Rensselaer Polytechnic Institute, Troy, NY 12180-3590

This keynote lecture will summarize the current status of our understanding of the mechanical properties, alloy design, and processing of the iron aluminides FeAl and Fe_3Al. The attractive physical properties and excellent corrosion resistance of iron aluminides have been known for many years, but commercial exploitation of these interesting compounds have been hindered by serious deficiencies in their mechanical properties. The most notable of these have been poor ductility and impact toughness at low temperatures, coupled with inadequate creep resistance at elevated temperatures. Nevertheless, considerable progress has been made in determining the causes of these problems and alleviating them. Of particular importance was the discovery that both Fe3Al and FeAl, while apparently brittle when tested in air, actually are quite ductile when moisture and other sources of hydrogen are excluded from the environment. Creep resistance in these aluminides has been improved by a combination of alloying and heat treatment. Considerable progress also has been made in melting and powder metallurgical techniques. Consequently, commercial viability of these compounds may be expected in the near future.

9:20 AM
TEM INVESTIGATIONS ON THE STRUCTURE OF ANTIPHASE BOUNDARIES IN $D0_3$-ORDERED Fe_3Al: *Dr. W. Liu*[1]; Dr. H. Rösner[1]; Dr. A. Gemperle[1]; Dr. J. Gemperlova[2]; Prof. Dr. E. Nembach[1]; [1]Universität Münster, Institut für Metallforschung, D-48149 Münster Germany; [2]Academy of Science, Institute of Physics, CZ 180 40 Prague 8 Czech Republic

Antiphase boundaries (APBs) in $D0_3$ long-range ordered Fe_3Al were studied by transmission electron microscopy. It was found that the APBs gave rise to diffraction contrast not only in superlattice reflections but also in fundamental ones. This indicates that the total displacement R across the APBs does not equal the basic displacement R_0 but involves an additional one r so that $R = R_0 + r$. The basic displacement R_0 is either $R_0 = 1/4<111>$ for the first nearest-neighbor APBs or $R_0 = 1/2<111>$ for the second nearest-neighbor APBs. R_0 is responsible for the normal, strong APB diffraction contrast, when superlattice reflections are excited. Anomalous APB contrast observed by exciting fundamental reflections can be attributed to the additional displacement r. The APB contrast caused by r was generally weak and asymmetric. While the first nearest-neighbor APBs were clearly visible when imaged with fundamental reflections, the second nearest-neighbor APBs gave hardly any anomalous contrast. The additional displacement r is therefore dependent on R_0. Its magnitude is much smaller for $R_0 = 1/2<111>$ than for $R_0 = 1/4<111>$. Furthermore, both the direction and the magnitude of the additional displacement r vary with the orientation of the domain boundaries. By comparing the contrast images with the simulated ones, the fault vector r as well as its relation to R_0 and the orientation of the domain boundaries were determined.

9:40 AM
THE USE OF ATOMIC SIZE EFFECTS TO TUNE PHASE STABILITY IN IRON ALUMINIDES: *Prof. L. Anthony*[1]; [1]University of Toledo, Dept. of Physics and Astronomy, Toledo, OH 43606-3390 USA

It has been known for some time that the addition of certain ternary elements such as Ti and Si can result in huge increases in the $D0_3$-B2 transition temperature [$T_c(D0_3\text{-}B2)$] of Fe_3Al. Recent high-temperature calorimetry work by Anthony and Fultz [Acta. Metall. Mater., in press] has shown that the varying efficacies of early transition metal solutes in raising $T_c(D0_3\text{-}B2)$ in Fe_3Al is related to their metallic radii. This size-effect phenomenon may prove useful in extending the stability range of other $D0_3$-ordered intermetallics. In this talk, I shall present results of such an attempt at controlling the stability range of the $D0_3$-ordered pseudobinary alloy $Fe_3Al_ySi_x$. By adjusting the relative concentrations of Al and Si in $Fe_3Al_ySi_x$, it should be possible to tune the size matching to a particular early transition metal, and there by optimize the stability of the $D0_3$ structure in this alloy system. I shall discuss the relevance of my results for alloy design and engineering in these and other intermetallic systems.

10:00 AM Break

10:20 AM INVITED
DISLOCATION PROCESSES AND DEFORMATION BEHAVIOR IN B2 INTERMETALLIC COMPOUNDS OF THE (Fe,Ni)-Al PSEUDOBINARY SYSTEM: Michael F Savage[1]; R Srinivasan[1]; M S Daw[2]; *M J Mills*[1]; [1]The Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210-1178 USA; [2]Clemson University, Department of Physics and Astronomy, Clemson, SC 29634 USA

The mechanical properties and the dislocation microstructure of single crystals with a range of compositions within the (Fe,Ni)-Al pseudobinary system are being investigated, with the purpose of bridging the behavior from FeAl to NiAl. Initial experiments are focused on compression testing of <001> oriented single crystals with a family of compositions of the form $Fe_x\text{-}Ni_{60\text{-}x}\text{-}Al_{40}$ (where x=60, 50 and 10 at %). Measurements of critical resolved shear stress and work hardening rates are being correlated with slip activity as a function of temperature. Of particular interest is the effect of composition on APB energy, and the resulting influence on mechanical behavior and dislocation activity, including slip transitions at high temperatures. The results of this investigation will be discussed in light of deformation models for the B2 compounds. This research supported by the U.S. Department of Energy under contract no. DE-FG02-96ER45550 (for MFS, RS and MJM) and by the National Science Foundation under grant no. 95-10259 (for MSD).

10:50 AM
DISLOCATION CORE STRUCTURES IN FeAl: *Dr. Diana Farkas*[1]; Dr. Cristophe Vailhe[1]; [1]Virginia Tech, Materials Science and Engineering, Blacksburg, VA 24061

Embedded atom potentials were developed for the Fe-Al system reproducing lattice and elastic properties of B2 FeAl. The structure and energy of vacancies, antisites and anti phase boundaries (APB's) were studied. A significant decrease in the APB energy was obtained for Fe rich B2 alloys. Shear fault energies along the {110} and {112} type

planes were computed showing stable planar faults deviated from the exact APB fault. Core structures and critical Peierls stress values were simulated for the <100> and <111> dislocations. The superpartials created in dissociation reactions were not of the 1/2<111> type but 1/8<334> in accordance with the stable planar fault in the {110} planes. The results obtained for these simulations are discussed in terms of mechanical behavior of FeAl and in comparison with B2 NiAl.

11:10 AM

DISLOCATION PROCESSES IN Fe_3Al INVESTIGATED BY TRANSMISSION ELECTRON, SCANNING FORCE, AND OPTICAL MICROSCOPY: E. Nembach[1]; A. Brinck[2]; C. Engelke[2]; G. Molénat[3]; *H. Neuhäuser*[2]; H. Rösner[1]; [1]Institut für Metallforschung der Universität, D-48149 Münster Germany; [2]Inst. für Metallphys. u. Nukleare Festkörperphys. der Technischen Universität, D-38106 Braunschweig Germany; [3]CEMESLOE/CNRS, 31055 Toulouse Cedex France

The mobility of dislocations in Fe_3Al has been investigated by the following complementary methods: (1) in-situ TEM observation of dislocation motion in thin single crystal foils, (2) postmortem TEM study of dislocation configurations in single crystal deformed in the bulk, (3) postmortem SFM of slip traces on deformed bulk single crystals, and (4) in-situ optical microscopy of slip traces on bulk single crystals during plastic deformation. The temperatures ranged from 300 to 973 K. These investigations yield information on activated glide planes, direction, and magnitude of the Burgers vectors of the dislocations; mode of glide (concentrated versus finely distributed, smooth versus jerky); and specific energy of antiphase boundaries.

11:30 AM

QUANTITATIVE ASSESSMENT OF SLIP LINE STRUCTURE IN Fe_3Al SINGLE CRYSTALS AFTER DEFORMATION AT VARIOUS TEMPERATURES: *A. Brinck*[1]; C. Engelke[1]; H. Neuhäuser[1]; [1]Inst. für Metallphys. u. Nukleare Festkörperphys. der Technischen Universität, D-38106 Braunschweig Germany

The fine structure of slip lines produced during the first stages of compressive deformation of Fe_3Al single crystals in the temperature range of 300 to 900 K has been examined by scanning force microscopy (AFM). A special evaluation scheme has been developed to obtain the distribution of local shear which yields quantitative information on the clustering of slip. This permits conclusions on the distribution and activity of dislocation sources as well as on the transition of slip to neighboring planes. Characteristic differences of the results obtained at different temperatures will be discussed.

INTERNATIONAL SYMPOSIUM ON PROCESSING OF METALS & ADVANCED MATERIALS: Modeling and Design

Sponsored by: Extraction & Processing Division, Synthesis, Control, and Analysis in Materials Processing Committee

Program Organizer: Ben Q. Li, Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99164-2920

Monday AM Room: 201
February 16, 1998 Location: Convention Center

Session Chair: Ralph E. Napolitano, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA, Yu M. Gelfgat, Latvian Academy of Sciences, Salaspils, Latvia LV-2169

8:30 AM

PIV AND PHYSICAL MODELING OF FLUID FLOW FLOW IN THE MOLD OF CONTINUOUS CASTING OF STEEL: *D. Xu*[1]; W. K. Jones, Jr.[1]; J. W. Evans[1]; [1]University Of California, Berkeley, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720 USA

A physical (water) model based on particle image velocimetry (PIV) has been constructed at UC Berkeley. The PIV technique enables the use of water modeling to quantitatively characterize the fluid flow behavior in the mold during the simulated continuous casting of steel, in a whole field sense, i.e. section by section. A method to obtain the time-average-velocity (TAV) vector maps was developed by averaging 40 instantaneous vector plots revealing the time average features of the flow. Another benefit of TAV vector maps is the ability to compare with present mathematical models, which are mostly based on time-averaged velocities. Bifurcated submerged entry nozzles (SEN) with ports inclined at various angles to the horizontal have been used in the model to study their effects on the flow inside the caster. Argon was also introduced into the model to simulate the influence of argon-injection on the metal delivery from the tundish into the caster. The bubble sizes and distribution (in specific sections) of argon were characterized by the imaging system of the PIV. This will allow for validation of current mathematical models developed to simulate argon injection in SEN's. Comparison with results calculated in the commercial finite element package FIDAP will be presented.

8:50 AM

MHD METHODS FOR CONTROLLING HYDRODYNAMICS AND HEAT/MASS TRANSFER IN THE PROCESSES OF BULK SEMICONDUCTOR SINGLE CRYSTAL GROWTH (A REVIEW): *Yu. M. Gelfgat*[1]; [1]Latvian Academy of Sciences, Institute of Physics, Salaspils, LV-2169 Latvia

The quality of bulk semiconductor single crystals grown from the melt is determined by the conditions of heat/mass transfer in the vessel and at the crystallization front. Considering the enlargement of diameters of single crystals produced and the increased requirements to their perfection, uniform distribution of dopants and impurities, etc., at present traditional means providing optimal growth conditions do not meet the practical requirements. That is why nowadays MHD methods influencing the hydrodynamic characteristics of initial melt and allowing to actively and expediently control the parameters of heat/mass transfer in growth processes play a much more important role. These MHD methods can be classified considering the electromagnetic fields in use (steady, alternating, traveling, combined magnetic fields), and for a certain growth technology to offer the optimal type of electromagnetic influence. The report presents the review of different MHD methods applied for controlling the characteristics of growth processes proceeded with the analysis of their specific characteristics. Beside the steady magnetic field mostly investigated today, the influence of alternating, rotating and other combined magnetic fields on the melt and crystallization front is also considered. The report discusses the results of theoretical and experimental investigation of the electromagnetic fields influence on stationary and non-stationary hydrodynamic characteristics in the melt and at phase interface and analyzes the conditions contributing to the effective control of transfer phenomena. The following methods of crystal growth and their characteristics are considered in the report: the methods of Czochralski, Bridgman-Stockbarger, zone melting and THM.

9:10 AM

EXPERIMENTAL STUDY OF MELT FLOW AND TURBULENCE DURING ELECTROMAGNETIC STIRRING ELECTROMAGNETIC STIRRING: *Dr. K. Wang*[1]; *Dr. Ben Q. Li*[3]; Mr. Terrence Johnson[2]; [1]Washington State University, Dept of Mechanical Engineering, Pullman, WA 99163 USA; [2]Louisiana State University, Mechanical Engineering, Baton Rouge, LA 70803; [3]Washington State University, Dept. of Mechanical Engineering, Pullman, WA 99163 USA

Electromagnetic stirring has found a wide application in metals processing for the benefit of obtaining refined solidification microstructures. The paper presents an experimental study on the melt flow and turbulent behavior in an electromagnetically stirred Woods metal pool. The experimental setup consists of metal bath unit equipped with temperature control to allow both cooling and heating, velocity probe positioning unit and data and signal acquisition and processing unit. The whole measuring system is under the control of an IBM personal

computer. Velocity measurements are made using the incorporated magnet probes, which are calibrated using a turnable. The measured results on the effect of the coil positions, coil arrangements and the applied currents on the melt flow are presented. Both mean flow and turbulence quantities are discussed.

9:30 AM

MHD METHOD APPLIED FOR PRODUCTION OF COMPOSITE MATERIALS OF "FROZEN EMULSION" TYPE: THEORY, EXPERIMENT AND APPLICATIONS: *Yu. M. Gelfgat*[1]; [1]Latvian Academy of Sciences, Institute of Physics, Salaspils LV-2169 Latvia

The report presents the results of theoretical and experimental investigations of the MHD method used for production of composites from immiscible metals, e.g., Al-Pb, Zn-Pb, Bi-Ga, etc., which, when solidified, can be presumed as "frozen emulsions". This method rests upon the idea of quasiweightlessness implementation by volume electromagnetic forces under the terrestrial conditions, when all the components of a composite alloy have a similar "effective density" and are in indifferent equilibrium with regard to each other. There is no gravitational sedimentation under such conditions, and it seems possible to produce a composite material with a uniform and fine-disperse distribution of every phase as that under weightlessness at realistic cooling rates. The report considers the regimes needed for implementing quasiweightlessness conditions for metal electromagnetic processing as well as different factors either contributing to or preventing the formation of fine-disperse homogeneous crystal patterns. The theoretical data are compared to the experimental results obtained, and then the dependencies for definition of rational parameters of technological processes are plotted. Certain possibilities for practical implementation of the MHD method offered for producing composites from metals with a wide range of immiscibility and that advantages are shown on the example of production of an antifriction alloy on the base of Al-Pb system. The experimental facility for semi-continuous casting has been manufactured and used for producing the above antifriction alloy. This facility allowed to obtain the casting up to 2m long with the cross-section 10x15 mm^2. Plain bearings made of this material for car engines had been tested (i.e., their antifrictional and mechanical characteristics) and have shown rather high operational properties. The obtained results evidence that the proposed MHD method for implementing the physical conditions of space and orbital flights under the terrestrial conditions allows to apply it as for modeling certain phenomena occurring in microgravity as for developing terrestrial technologies similar to the space ones.

9:50 AM Break

10:10 AM

DYNAMIC INTERFACIAL PHENOMENA IN POLYMER-MATRIX COMPOSITES: *Livia M. Racz*[1]; Behrouz Abedian[1]; [1]; [1]Tufts University, Mechanical Engineering Department, Medford, MA 02155 USA

We address dynamic interactions between high-energy, reactive surfaces of polymer-matrix composites and solid surfaces. A common characteristic of this interfaces is that bonding occurs readily upon contact. In many industrial and biomedical applications, it is desirable to suppress this bonding phenomenon. This interfacial effect is discussed in light of the development of our new method of handling polymer-matrix composites in dental applications. This method involves vibration of the solid-polymer interface at different frequencies. For each material, there is a critical frequency at which the sum of the viscoelastic and inertial energies of the fluid at the surface exceeds the energy available for bonding. When the polymer is vibrated at or beyond this frequency, it does not adhere to solid surfaces. An important aspect of the developed process is that it can be used to characterize surface and interfacial properties of polymers under dynamic conditions, whereas existing techniques are restricted to the study of bulk dynamic properties.

10:30 AM

CELLULAR AUTOMATON FINITE DIFFERENCE MODELING OF MORPHOLOGICAL EVOLUTION DURING ALLOY SOLIDIFICATION: *Dr. Ralph E. Napolitano, Jr.*[1]; Dr. Thomas H. Sanders, Jr.[1]; [1]National Institute of Standards and Technology, Metallurgy Division, Gaithersburg 20899 Maryland; [2]Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA USA

Morphological evolution of a dendritic growth front in a binary alloy is simulated using a cellular automaton approach to establish the feasibility of modeling such growth with a local rule-based scheme. The motivation for this work is derived from the need to understand and predict the development of solidification structures within components of complex geometry, where significant constraint of the thermal and solutal fields may exist. In these cases, local transients and anomalies may preclude the effective use of more conventional methods of microstructural prediction. The model utilizes a two-dimensional alternate-direction-implicit finite-difference technique for calculation of the solute field. A uniform temperature gradient and a constant isotherm velocity are assumed, describing the conditions within a small representative volume element of a casting. Local temperature, composition, and interface curvature are incorporated into a growth function which is utilized by the automaton in a probabilistic fashion, allowing the interface to evolve. Alloy solidification is simulated over a range of experimental conditions, giving rise to planar, cellular, and dendritic growth, and comparisons with analytical solutions are made where possible. The model is shown to predict growth modetransitions, thermal and solutal interfacial conditions, and microsegregation.

10:50 AM

THERMODYNAMIC ANALYSIS OF COPPER SMELTING PROCESS: *Pengfu Tan*[1]; Chuanfu Chang[1]; [1]Central South University of Technology, Department of Nonferro Metallurgy, Changsha, Hunan 410083 People's Republic of China

A thermodynamic model is developed to predict the distribution of Ni, Co, Sn, Pb, Zn, As Sb, Bi, Au and Ag in copper smelting processes such as Mitsubishi and/or Noranda process. In this model, as many as 21 elements (Cu, S, Fe, Ni, Co, Sn, As, Sb, Bi, Pb, Zn, Au, Ag, O, N, C, H, Ca, Mg, Al, and Si) and 72 compounds (in fayalite-stag-making system) or 74 compounds (in ferrite-slag-making system) are considered. The allowance is also made to account for physical entrainment in the melts. Accessory-element behavior is studied for two types of slag , fayalite and ferrite, and two levels of oxidation. Model simulations are carried out to study the effects of controllable process parameters such as oxygen enrichment, matte grade, smelting temperature, and types of slag on accessory-element behavior in matte, slag and gaseous phases. The predictions by the present computer model are compared with the known experimental measurements from Gui Xi Smelter in China, Horne Smelter in Canada and Naoshima Smelter in Japan and excellent agreement between calculations and measurements is obtained.

11:10 AM

THERMODYNAMIC MODELING FOR NICKEL FLASH SMELTING PROCESS: *Pengfu Tan*[1]; Chuanfu Zhang[1]; [1]Central South University of Technology, Department of Nonferro Metallurgy, Changsha, Hunan 410083 People's Republic of China

A thermodynamic model is developed to simulate nickel flash smelting process in which oxidation of concentrate occurs at one end, and reduction of slag at the other. The model makes use of two zones, namely the reaction shaft/settler zone and the appendage zone and accounts for 6 phases (matte, slag, silica magnetite, Cu-Ni alloy and gaseous phase), 13 elements (Ni, Co, Cu, Fe, S, O, N, C, H, Si, Al, M g and Ca) and 33 chemical components in nickel flash smelting system. The compositions of matte, slag and gaseous phases in equilibrium are calculated using the data of free energies of formation and activity coefficients of components. Two nickel sulfide species are used to allow for the modeling of sulfur-deficient mattes. The distribution of Ni, Co, Cu, Fe, S and O in the nickel smelting furnace depends on the process parameters such as smelting temperature, volumes of air, the content of the elements in charge and oil. The model predictions are compared with the known data from Kalgoorlie Nickel Smelter, and excellent agreement is obtained. The model can be a very useful tool for monitoring and optimizing the actual industrial operations of nickel smelting process.

11:30 AM

USING TECHNOLOGIES OF POWDER SURFACE MODIFICATION TO INCREASE DENSITY AND UNIFORMITY OF GREEN PARTS AND REPEATABILITY OF CERAMICS WITH FINE CHARACTERS: Professor Boyi Chu[1]; Dr. Guodong Li[2]; Professor Bolin Wu[2]; [1]Wuhan Univ. of Technology, National Laboratory, Shezhen, Rm 1-508, Jintiancun, Gongxia, Shenzhen, Guongdong 518026 China; [2]Wuhan Univ. of Technology, National Laboratory, Wuhan, Lushi Rd, Wuhan, Hubei 430070 China

By properly choosing multi-etherxy, multi-hydroxy and multi-carboxyl dispersing agents to process Alfa-Alumina powder with 0.6mu average particle size, the green parts were obtained with relative density up to a 55-61% solid content and highly uniformed microstructure. The density and uniformity of green parts was higher than that obtained by iso-static pressing (400 Mpa) forming with no surface modification. The later only had density up to 54%. After Alfa-Alumina powder surface modification by palmitic acid it was found that the esterify reaction happened between organic acid and the hydroxy on Alfa-Alumina surfaces, which was similar as that between acid and alcohol, forming single molecular film on particle surfaces. This modified powder avoided from particle agglomeration, improved powder fluxibility and dispersity so the pressing forming ability was increased obviously. Experiment results showed that the density and uniformity of green parts obtained by one-end uniaxial pressing and surface modified powder was higher than the parts obtained by iso-static pressing at the same pressure above with no surface modified powder. The ceramic strength and repeatability improved obviously.

INTERNATIONAL SYMPOSIUM ON SULFIDE SMELTING '98: CURRENT AND FUTURE PRACTICES: Session I - Opening, Plenary, and Nickel Smelting

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

Monday AM Room: 207
February 16, 1998 Location: Convention Center

Session Chairs: Jussi Asteljoki, Outokumpu Oy, Espoo FIN-02101 Finland; Norbert Piret, Piret & Stolberg Partners, Duisburg D-47279 Germany

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8:30 AM Plenary Address: H.Y. Sohn, Univ of Utah, Dept of Met Engrg, Salt Lake City, UT 84112-1183

9:15 AM

COMPARISONS BETWEEN COPPER, LEAD AND NICKEL SMELTING PROCESSES FROM THERMODYNAMIC VIEWPOINTS: *Akira Yazawa*[1]; Shigeatsu Nakazawa[1]; [1]Tohoku University, Department of Metallurgy, Graduate School of Engineering, Sendai 981 Japan

The similarities and differences in the sulfide smelting processes for copper, lead and nickel concentrates are discussed based on the sulfur-oxygen chemical potential diagrams. The prominent features of copper smelting are ascribable to the fact that copper has strong affinity for sulfur, while weak for oxygen, and the liquid phase immiscibility between Cu and Cu2S. During oxidation of sulfides, metallic leads looks stable as like copper, but Pb and PbS are much more miscible. Nickel metal is miscible also with sulfide, and increases its stability above the melting point. Taking account of recent smelting practice, oxidation procedures of each sulfide concentrate are simulated by use of thermodynamic package. Vaporization of lead and impurities during smelting is also discussed. Reducing smelting stages of copper, nickel and lead are discussed based on thermodynamic and experimental data. Due to the immiscible nature between Pb and Fe, high-grade lead bullion is easily obtained, and lead is tolerant of impurities. The effects of oxygen potential and temperature on the copper content of slag are not significant due to the monovalent character of copper, and the reduction of copper content of slag is not easy in practice. The effect of slag composition on the metal contents of slag is more significant for lead than copper or nickel.

9:45 AM

HSC CHEMISTRY 3.0 IN METALLURGICAL APPLICATIONS: *Antti Roine*[1]; [1]Outokumpu Research Oy, Pori FIN-28101 Finland

HSC Chemistry is a widely used thermochemical tool in the chemical and metallurgical industries and in universities. The main reasons for this popularity is the easy user interface and the large integrated thermochemical database. This paper summarizes the main properties of the new HSC Chemistry version 3.0 and gives a short review of the new features. Some metallurgical applications with the new features are also presented. HSC Chemistry 3.0 contains seven calculation modules and a thermochemical database with more than 11000 chemical compounds. The new spreadsheet type table editor gives more control to the user, the new graphics routines have fewer limitations and more formatting properties. The capabilities and speed of the calculation routines have also been improved.

10:15 AM Break

10:25 AM

PHYSICAL CHEMISTRY OF DIRECT NICKEL MATTE SMELTING: *Tuula Mäkinen*[1]; Pekka Taskinen[2]; [1]Outokumpu Engineering Contractors Oy, Espoo FIN-02201; [2]Outokumpu Research Oy, Pori FIN-28101 Finland

One of the latest innovations in the Outokumpu Flash Smelting Technology is the direct smelting of nickel concentrates to metallised low-iron nickel mattes resulting in considerable economic and environmental benefits compared to the conventional nickel smelting units. Fundamentals and the thermodynamic background of smelting nickel concentrates in one stage to low-iron mattes are presented. Properties of nickel smelting slags with an emphasis on the slag fluidity at high MgO levels are also discussed. Conditions prevailing in nickel mattes at high oxidation degrees are presented as well as their influence on the behavior of such mattes in the settler and on tapping the furnace. Distributions of elements in the direct smelting and the electric slag cleaning furnace are presented and compared with the conventional process at the Harjavalta Smelter. A further comparison is made with pilot plant and industrial scale data, as well as with the compositions of the slags and matte produced.

10:55 AM

THE LIQUIDUS SURFACE AND TIE-LINES IN THE NICKEL-COBALT-SULPHUR TERNARY SYSTEM BETWEEN 1273-1573K: *M. Soltanieh*[1]; J. M. Toguri[1]; R. Sridhar[1]; [1]University of Toronto, Department of Metallurgy & Materials Science, Toronto, Ontario M5S 3E4

The liquidus surface and tie-lines in the nickel-cobalt-sulphur ternary system has been determined between 1273-1573K. The experiments were conducted by equilibrating the liquid sulphide with the metallic alloy phase. The liquid was analyzed by electron microprobe. Combining the present results with the available literature data, the thermodynamic properties of this system were calculated.

11:25 AM

ON THE REACTION MECHANISMS OF SULFIDIC NICKEL PARTICLES IN SUSPENSION SMELTING CONDITIONS: *S. Jyrkönen*[1]; S. Strömberg[1]; J. Sjöblom[1]; A. Jokilaakso[1]; [1]Helsinki University of Technology, Laboratory of Materials Processing and Powder Metallurgy, HUT FIN-02015 Finland

A single particle laminar-flow technique was used to study reactions of sulfidic nickel particles. The studied materials were four natural nickel concentrates and four synthesized nickel mattes. The variables of the experiments were the gas preheating temperature (500-1300ºC), the compositions of the reaction gas (N2 + O - 75 vol -% 02) and the particle size of the feed. Chemical analysis of the particles was used to determine the oxidation degree of the materials, and optical and scanning electron microscopy was used to detect alteration in their morphology, internal composition and structure. General reactivity of the materials was monitored by the extent of sulfur removal. The reaction mechanism of the studied materials was found to depend primarily on the materials composition as well as oxygen content of the reaction gas.

11:55 AM

KALGOORLIE NICKLE SMELTER ENVIRONMENTAL PROJECT: *Paul Phillips*[1], Mark Tjerkstra[1]; [1]Kalgoorlie Nickel Smelters, Kalgoorlie, WA 6930 Australia

An acid plant was commissioned at Kalgoorlie Nickel Smelter in September 1996 for the treatment of flash furnace waste gas. The impact of the commissioning and subsequent operation of the acid plant on gas emission and air quality is reviewed. In addition the approach and issues related to effluent treatment are described. Benefits for smelter availability has occurred and operation performance is briefly reviewed. The acid plant flow sheet is described.

INTERNATIONAL SYMPOSIUM ON VALUE ADDITION METALLURGY: Session I - Preparation of Intermetallic Compounds

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

Monday AM Room: 208
February 16, 1998 Location: Convention Center

Session Chairs: W. D. Cho, University of Utah, Dept. of Metallurgical Engineering, Salt Lake City, Utah 84112-0114 USA and H. Y. Sohn, University of Utah, Dept. of Metallurgical Engineering, Salt Lake City, Utah 84112-0114 USA

8:30 AM Opening Remarks

8:40 AM

ADHESION IMPROVEMENT OF ALUMINA SCALE FORMED ON Y-ADDED Fe_3Al DURING HIGH TEMPERATURE OXIDATION: *I. Kim*[1]; W. D. Cho[1]; J. C. Choi[2]; [1]Univ. of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112; [2]Ajou University, Department of Materials Engineering, Suwon Korea

Investigation on the oxidation behavior of Fe_3Al with and without yttrium addition was carried out at 800, 900, and 1000°C to study the effect of yttrium addition in terms of oxidation rate and adhesion. The oxidation rate of the both alloys was nearly same at all temperatures employed. The general equation for the parabolic rate constant as a function of temperature is Kp=5128 exp[-39506(cal/mol)/RT] mg^2/cm^4 hr. Thermal cycling and ultrasonic tests were performed to examine the alumina scale adhesion. While the oxide layer (Al_2O_3) formed on the Fe-Al alloy without Y was found to be very poor and spelled easily during the tests, the scale formed on the Fe-Al alloy containing Y (0.31 wt%) was much m ore protective, dense, and adhesive. The formation of second phase enriched with yttrium was observed along the grain boundary of alumina scale formed on the Y-doped alloy. Based on microstructural and compositional analysis by XRD, SEM, TEM, EDS, EPMA, and optical microscope, a model was proposed to explain the improvement of scale properties in the Y- containing iron aluminide.

9:10 AM

FORMATION MECHANISM OF LIGHT RARE EARTH - IRON INTERMETALLIC COMPOUNDS IN REDUCTION-DIFFUSION PROCESS: *Teruo Tanabe*[1]; Zenjiro Asaki[1]; [1]Kyoto University, Dept. of Materials Science and Engineering, Kyoto Japan

The rate and mechanisms of the formation of rare earth (R = Ce, Pr, Nd or Sm) - Fe intermetallic compounds by the reduction-diffusion (RD) process were examined. Two kinds of experiments were carried out; (1) reduction of briquettes composed of it-oxide powder mixed with CaH_2 and (2) RD reaction for briquettes consisting of R-oxide, CaH_2 and Fe (powder or wire). The formation rate of compound R_2Fe_{17} was compared with the results obtained in the reaction of Fe with R-Fe melts of which composition was on the Fe-side liquidus line of R-Fe binary phase diagram.

9:40 AM

SYNTHESIS OF ULTRAFINE PARTICLES OF TITANIUM ALUMINIDES AND NICKEL ALUMINIDES BY THE VAPOR-PHASE MAGNESIUM REDUCTION OF CHLORIDE MIXTURES*: *H. Y. Sohn*[1]; S. PalDey[1]; [1]University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114

Intermetallic compounds were synthesized by the vapor-phase reduction of mixtures of constituent metal chlorides by magnesium vapor. The advantages of the process include (a) the use of inexpensive raw materials, (b) low reaction temperatures, and (c) products in the form of fine particles. The effect of $AlCl_3/TiCl_3$ partial pressure ratio on the formation of different titanium aluminides was studied. A two-phase mixture containing 80 mol% of TiAl + 20 mol% of $TiAl_3$ were obtained at an $AlCl_3$ /$TiCl_3$ ratio of 10. The amount of $TiAl_3$ was maximized at 72 mol% at an $AlCl_3$ /$TiCl_3$ ratio of 16. In the case of nickel aluminides, NiAl, $NiAl_3$, and Ni_2Al_3 were formed by reducing mixtures of $NiCl_2$ + $AlCl_3$ vapors. The maximum content of NiAl obtained was 98 mol%. At the $AlCl_3/NiCl_2$ ratio of 19, a phase mixture of 17 mol% of NiAl + 83 mol% of $NiAl_3$ was produced. The product particles were very fine in the size range of 50 to 200µm. *Work supported by the U.S. Department of Interior's Mineral Institutes Program.

10:05 AM

SYNTHESIS OF ULTRAFINE INTERMETALLIC PARTICLES BY THE VAPOR-PHASE COREDUCTION OF METAL CHLORIDES WITH HYDROGEN: *S. PalDey*[1]; H. Y. Sohn[1]; [1]University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114

Fine particles of nickel aluminides and Ni_4Mo were synthesized by reducing mixtures of, respectively, $AlCl_3$+$NiCl_2$ and $NiCl_2$+$MoCl_5$ vapors with hydrogen. Though thermodynamically favorable, the coreduction of $NiCl_2$ and $AlCl_3$ by H_2 to form Ni_3Al did not readily happen experimentally. The addition of a small amount of aluminum vapor was needed to initiate the coreduction reaction. The product particles as observed by TEM were very fine but usually agglomerated. The electron diffraction pattern of particles identified NiAl and $NiAl_3$ along with Ni_3Al and metallic Ni. The content of Ni_3Al was maximized at 52 mol% at 1050°C and the partial pressures of H_2, $AlCl_3$, and $NiCl_2$ = 57, 1.4, and 0.5 kPa, respectively. When a mixture of $NiCl_2$ + $MoCl_5$ was reduced by hydrogen, Ni_4Mo with some Ni or Mo was obtained, the maximum content of Ni_4Mo obtained being 93 mol%. The particle size was in the range of 100 to 200 nm. An Ni_4Mo coating of 700 nm thickness on an Ni substrate was also prepared.

10:30 AM

SYNTHESIS OF TITANIUM ALUMINIDE BASED COMPOUNDS AND COMPOSITES WITH NANOCRYSTALLINE AND BIMODAL STRUCTURES: *N. Srisukhumbowornchai*[1]; O. N. Senkov[1]; F. H. Froes[1]; [1]University of Idaho, Institute for Materials and Advanced Processes, Moscow, ID 83844-3026

Mechanical alloying (MA) and thermohydrogen processing (THP) approaches were used to synthesize amorphous or nanocrystalline powders of the titanium-aluminide-based alloys and composites. Fully dense samples with nanocrystalline and bimodal structures were produced from these powders by hot isostatic pressing Stability of the microstructures during continuous heating at high temperatures was studied. Characterization techniques including X-ray diffraction, scanning and transmission electron microscopy, energy dispersive spectroscopy, and differential thermal analysis were used in this work.

LITHIUM: Extraction Technology and Market Forecasting

Sponsored by: Light Metals Division, Refractory Metals Committee
Program Organizers: Donald R. Sadoway, MIT 8-109, Cambridge, MA 02139-4307; G. J. Kipouros, University of Nova Scotia, Dept. of Mining & Met. Eng., Halifax, NS B3J2X4 Canada

Monday AM Room: 209
February 16, 1998 Location: Convention Center

Session Chairs: Donald R. Sadoway, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139-4307; George J. Kipouros, University of Nova Scotia, Department of Mining & Met. Eng., Halifax, NS B3J2X4 Canada

8:30 AM Opening Remarks

8:35 AM

THE CHEMISTRY AND ELECTROCHEMISTRY OF LITHIUM PRODUCTION: *Prof. Donald R. Sadoway*[1]; Prof. G. J. Kipouros[2]; [1]MIT, Dept. of Materials Science & Engineering, Cambridge, MA 02139-4307 USA; [2]DalTech, Dept. of Mining & Metallurgical Engineering, Halifax, NS B3J 2X4 Canada

New developments in batteries, fuel cells, and light structural alloys are poised to cause radical changes in the demand for lithium metal. Most notably, the industry which today treats lithium as a chemical reagent will undergo a transformation in which lithium is treated as a structural material, i.e., both primary metal and alloying element. This could have a major effect on the price which in turn may open up new markets. To satisfy the performance requirements of new applications traditional production methods will have to be improved and new extraction processes will have to be developed. Existing and proposed extraction technologies will be reviewed and research opportunities will be identified.

9:05 AM

NEW DIRECTIONS FOR LITHIUM?: *Mr. Piers Nicholson*[1]; [1]Roskill Information Services, Ltd., London England

While most metals are selling at substantially less than 1973 prices, the price of lithium carbonate, the major product of the lithium industry has held up remarkably well. This "orderly market" reflects both the small number of producers and their belief that lower prices would not result in higher revenues. Both are now under challenge. Two US companies have held a very large share of the lithium chemicals and metal market for forty years or more. As new sources of lithium, mainly from brines in South America, have become available, the two leading producers have made arrangements to maintain their dominant market share. Their high price, high margin policy has been founded on the belief that demand for lithium is broadly inelastic and has been supported by the fact that barriers to entry into the lithium market are high. The entry of SQM into the lithium market is set to challenge all these assumptions. SQM have a very large by-product source of lithium, so their production costs are very low, and they have announced that they intend to sell lithium carbonate at 30% or so below ruling prices. They believe that lower lithium prices will lead to the development of new uses, and to the expansion of existing ones. This paper will look at the impact of these changes on the lithium market.

9:35 AM

THE GLOBAL LITHIUM INDUSTRY: A PORTRAIT OF RAPID FLUX: *Mr. Peter W. Harben*[1]; [1]Peter W. Harben Inc., Morris, NY 13808 USA

The global lithium industry is in a state of rapid flux with radical changes in the supply pattern likely to shake up a hitherto tranquil market. By the end of the century the bulk of commercial lithium will be extracted from salt-lake brines rather than from hard-rock mining, Chile will supplant the United States as the world's largest lithium producer, and Argentina will emerge from nowhere to become the third largest player. It is expected that prices will fall to half their 1996 levels, and, if all goes well, these new price levels will stimulate the growth of new and larger markets.

10:05 AM Break

10:25 AM

NEW RESOURCES AND PURIFICATION TECHNOLOGIES FOR THE LITHIUM INDUSTRY: *Dr. Paul J. Pickering*[1]; Mr. Kin-wai Mok[1]; [1]Pacific Lithium Limited, Auckland Mail Centre New Zealand

Many of the world's lithium resources and purification technologies have been exploited for over forty years. However, the recent rapid expansion of the markets for lithium, particularly the primary and secondary battery industry, has placed new demands on lithium producers in terms of the lithium resources available for utilization and the purification technologies used to meet the exacting impurity specifications of these new users. This paper will present details of Pacific Lithium's work on the areas of both extraction of lithium from recycled lithium battery materials and novel purification technologies developed to produce extremely high purity lithium salts specifically designed for use in lithium ion battery component manufacture.

10:55 AM

IMPROVING THE ENERGY EFFICIENCY OF ELECTROWINNING OF LITHIUM: *Prof. Derek J. Fray*[1]; Mr. A. R. Cox[1]; [1]University of Cambridge, Department of Materials Science and Metallurgy, Cambridge CB2 3Q2 United Kingdom

The centrifugal separation of lithium in a novel fused salt electrolysis cell, incorporating horizontal rotating electrodes, is presented. In order to prevent molten lithium rising to the anode and reacting with the chlorine, a lower steel cathode is used, which is wetted by the lithium. A maximum current efficiency of 83% was achieved at a cell voltage of 4.8 V, compared to a reversible potential of 3.7 V, at an inter-electrode spacing of 10 mm using co-planar electrodes rotating at 40 rpm. This resulted in a significant reduction in the resistive contribution to the cell voltage. An energy consumption of 22.3 kWh kg-1 was obtained for current densities of the order of 7800 A m-2 which can be compared with values of 40 kWh kg-1 obtained in conventional cells.

11:25 AM

ELECTROCHEMICAL PRODUCTION OF LITHIUM METAL FROM LITHIUM OXIDE IN MOLTEN LITHIUM CHLORIDE: *Dr. James L. Smith*[1]; [1]Argonne National Laboratory, Chemical Technology Division, Argonne, IL 60439 USA

Argonne National Laboratory (ANL) has developed a process for conditioning U.S. Department of Energy (DOE) spent oxide nuclear fuel for long-term storage or disposal. The first step involves the chemical reduction of the oxide fuel to metals. This is done in a

lithium-saturated lithium chloride bath at 650°C. A product of the chemical reduction step is lithium chloride with dissolved lithium oxide. The lithium oxide must be converted back to lithium metal in order to continue the process without creation of additional waste. A process has been developed in which the lithium oxide is electrochemically converted to lithium metal and collected in a porous cathode for transport back to the reduction process. Details of the process and the cell performance will be discussed. Key features that will be highlighted include the materials work for the anode, cathode, and containment, the cell design, and cell operation.

MATERIALS PROCESSING FUNDAMENTALS: Pyrometallurgy

Sponsored by: Extraction & Processing Division, Process Fundamentals Committee

Program Organizers: Patrick R. Taylor, University of Idaho, Dept. of Met & Mining Eng., Moscow, ID 83843-3024; Srinath Viswanathan, Oak Ridge National Lab, PO Box 2008 Bldg. 4508, Oak Ridge, TN 37831-6083

Monday AM Room: 206
February 16, 1998 Location: Convention Center

Session Chair: Ramana G. Reddy, University of Alabama, Tuscaloosa, Alabama 35487-0202

8:30 AM

LOW TEMPERATURE REDUCTION OF CHROMITE ORES WITH CARBON: *Dr. R. G. Reddy*[1]; R. B. Intutri[1]; M. V. Klein[1]; [1]University of Alabama, Dept of Met & Matls Engrg, Tuscaloosa, AL 35487-0202 USA

Reduction of different chromite ores with graphite was studied as a function of C/FeO ratio and temperature in the range 700°C to 1100°C by thermogravimetry (TGA) analysis. Powders of chromite ore(-150 mesh) and graphite(-150 mesh) were thoroughly mixed in a desired proportions and were placed in the reaction crucible. The reduction rates of reactions were determined by continuously monitoring the weight loss as a function of time at constant temperature using TGA set up. The analysis of results suggest that FeO present in the chromite ores is reduced to Fe involving gaseous intermediates CO and CO2. The overall rate of FeO reduction is controlled by the oxidation of carbon. A kinetic equation, that of random nucleation, was proposed. The activation energies for the reduction of FeO, present in roast movat and transvaal ores, with graphite were determined to be 55800 and 23000 J/mole, respectively. The results of the present study are compared with the data available in literature. The low activation energy values as determined in this study suggest that the carbon oxidation reaction is catalyzed. It is concluded from the present investigation that the low grade chromite ores can be significantly upgraded to higher value added chromite that can be used as a feed source for economical smelting.

8:55 AM

COMPUTER MODELING FOR KIVCET DIRECT LEAD SMELTING: *Tan Pengfu*[1]; Dr. Zhang Chuanfu[1]; [1]Central South University of Technology, Dept of Non-ferrous Metallurgy, Changsha 410083 China

By using computer-aided techniques of equilibrium calculations for multicomponent and multiphase systems, a computer model has been developed to simulate KIVCET direct lead smelting process. A mathematical description is studied using three zones, namely offtake shaft zone, smelting shaft zone and electric furnace zone. The amount of each component in lead, slag and gaseous phases under equilibrium is calculated by using the data of free energies of formation and activity coefficients. The predictions by the present computer model are compared with the known data from Ust-Kamenogorsk Lead-Zinc Combinat in Kazakhstan. The agreements between the computer predictions and the known data are excellent, so that the present computer model can be used to monitor and optimize the actual industrial operations of KIVCET direct lead smelting. In this paper, the effects of oxygen enrichment, fuels, smelting temperature on behaviors of Pb and Zn among metal, slag and gaseous phases have been discussed.

9:20 AM

RECOVERY OF COPPER AND COBALT FROM INDUSTRIAL SLAGS BY TOP SUBMERGED INJECTION: Xun An[1]; Nan Li[1]; *Eric J. Grimsey*[1]; [1]Curtin University of Technology, Kalgoorie 6340 Western Australia

Industrial copper slags from an electric slag cleaning furnace have been reduced with injection of methane and air mixtures. The effects of methane-to-air ratio, gas flowrate and temperature on the rate of reduction and metal separation have been investigated. The results showed that over 90 percent copper and up to 60 percent cobalt in the slag can be reduced using this method. A thermodynamic simulation showed that the gas utilization was around 70 percent. The use of small nozzle and deep injection improved the gas utilization significantly. Injection of gaseous reductants greatly enhanced the coalescence of the entrained metal droplets and a rapid settling of metal droplets in the turbulent slag bath was observed.

9:45 AM

KINETICS OF CARBOCHLORINATION OF CHROMIUM (III) OXIDE: *I. Gaballah*[1]; N. Kanari[1]; [1]Rue du Doyen Marcel, Mineral Processing & Environmental Engrg, Vandoeuvre, Cedex 54501 France

Carbochlorination kinetics of Cr_2O_3 with $C_{l2+}CO$ was studied between 500 and 900ºC using thermogravimetric analysis. Effects of the gas flow rate, temperature and partial pressure of the reactive gases on the reaction rate were studied in isothermal conditions. The apparent activation energy is 100 kJ/mol. Between 550 and 800ºC, the reaction order with respect to $C_{l2+}CO$ is 1.34. The reaction mechanism is independent of the $C_{l2+}CO$ content or the C_{l2} /($C_{l2+}CO$) ratio of the gas mixture. The reaction rate passes through a maximum of about 0.5.

10:10 AM

REACTIVITY OF MAGNESIUM OXIDE IN DIFFERENT CHLORINATING GAS MIXTURES: *N. Kanari*[1]; I. Gaballah[1]; [1]; [1]Rue du Doyen Marcel Roubault, Mineral Processing & Environmental Engineering, Vandoeuvre, Cedex 54501 France

Reactivity of MgO towards C_{l2+}air, C_{l2+}N2 and $C_{l2+}CO$ gas mixtures was studied up to 1000ºC. Carbonchlorination of MgO occurs at temperatures lower than that of its oxychlorination. Effects of gas flow rate, temperature and partial pressure of the carbochlorinating gas mixture on the reaction rate were investigated. The apparent activation energy of MgO carbochlorination is 49 kJ/mol. The apparent reaction orders with respect to $C_{l2+}CO$, C_{l2} and CO at 550ºC are 2.37, 1.47 and 0.89, respectively. Maximum reaction rate is obtained using a gas mixture having a C_{l2} /CO ratio of 0.6.

10:35 AM

THE ENHANCED So_2 ABSORPTION CAPACITY AND KINETICS DUE TO THE FORMATION OF CaSo4 3MgSo4 PHASE IN THE SULFATION OF CALCINED CMA (CALCIUM MAGNESIUM ACETATE): Dong Hoon Han[1]; *H. Y. Sohn*[1]; [1]University of Utah, Dept of Met Engrg, Salt Lake City, UT 84112-0114 USA

The sulfation rates of magnesium oxide and calcium oxide (molar ratio 7:3) contained in calcined CMA (calcium magnesium acetate) by SO_2 were measured. The experiments were carried out in the temperature range 700 to 1100ºC and under the SO_2 concentrations of 0.3 to 1 mol% (5%O_2). In the low-temperature range below 830ºC the reaction produced $CaSO_4$ $3MgSO_4$ and unreacted MgO, but no $MgSO_4$ phase. The formation of the $CaSO_4$ $3MgSo_4$ phase has a significant implication in that it allows the utilization of MgO for SO_2 removal whereas the sulfation of M90 from conventional sources is so slow that it is of no practical interest. Thus, the calcined CMA can remove SO_2 at lower temperatures than conventional SO2 absorbents and at a greater capacity. Above 950ºC only the CaO reacts with SO_2, but at a much greater

rate than even the calcined Ca(OH)21 which is one of the most reactive SO_2 absorbents.

11:00 AM
COMPUTER MODELING OF A LATERITE PRE-REDUCTION ROTARY KILN: *E. C. Papadopoulos*[1]; [1]National Technical University of Athens, Laboratory of Metallurgy, Athens 157 80 Greece

At the Laboratory of Metallurgy, NTUA, a computer simulation of an industrial rotary kiln, which is used for the pre-reduction of nickeliferrous lateritic ores and plays a key role in the production of Fe-Ni alloy has been developed. The simulation software funds under Win95 and WinNT. It incorporates a steady-state mathematical model, which is based on the results obtained from the systematic analysis of the metallurgical system. The model predicts the temperature profile of the kiln and the temperature of the off-gases and solid product within a very good accuracy.

11:25 AM
MODEL PREDICTIONS OF THE LIQUIDUS SURFACE OF MULTI-COMPONENT IRON SILICATE SMELTING SLAGS CONTAINING MAGNESIA AND CALCIA: *Florian KONGOLI*[1]; Dr. Eric J Grimsey[2]; [1]Ecole Polytechnique, Center for Research in Computational Thermochemistry, Montreal, Quebec H3C 3A7 Canada

Non-ferrous smelting slags can contain magnesia, which substantially increases the liquidus temperature. One option to counter this increase is to flux with calcia. In this work, experimental liquidus measurements including new measurements on industrial slags have been compared with a F*A*C*T-based thermodynamic model, which predicts the liquidus surface of multi-component iron silicate smelting slags containing both magnesia and calcia. The predictions that agree very well with experimental results are summarized in both isothermal and non-isothermal diagrams as a function of possible fluxes compositions in order to give a quantitative description of the liquidus surface. A number of diagrams for seven component iron silicate slags are presented and the fluxing implications discussed.

MICROSTRUCTOLOGY CONNECTING PHASE DIAGRAMS KINETICS & STEREOLOGY TO MICROSTRUCTURAL EVOLUTIONS: F.N. RHINES: Phase Diagrams and their Applications

Sponsored by: ASM International: Materials Science Critical Technology Sector, Atomic Transport Committee
Program Organizers: Robert T. DeHoff, University of Florida, Dept. of Materials Sci & Eng., Gainesville, FL 32611-6400; John Morral, University of Connecticut, Dept. of Metallurgy, Storrs, CT 6260

Monday AM Room: 103
February 16, 1998 Location: Convention Center

Session Chair: Reza Abbaschian, University of Florida, Gainesville, FL 32611-6400

8:30 AM Opening Remarks

8:40 AM INVITED
STRATEGIES FOR THE QUANTITATIVE CALCULATION OF PHASE EQUILIBRIA IN MULTI-COMPONENT ALLOYS : *Dr. Nigel Saunders*[1]; [1]Thermotech Ldt., Surrey Technology Centre, Guilford, Surrey GU2 5YG U.K.

CALPHAD methods have always held the promise of providing predictions for phase equilibria in multi-component alloys. However, until recently and with the exception of steels, calculations have tended to remain firmly at the lower end of the multi-component spectrum often centering around quaternary alloys at best and more usually at the ternary level. 'Real' alloys are, however, truly multi-component in nature usually containing more than 7 or 8 components. In the past few years a number of thermodynamic databases have been developed by the present author for Al, Ni, Ti and TiAl alloys where it can be demonstrated that highly accurate calculations for 'real' multi-component alloys can be achieved. As part of this process new paradigms and strategies have had to be developed. This presentation will discuss these and also critically examine other existing strategies which are currently being used to develop multi-component databases.

9:10 AM INVITED
PRESSURE-TEMPERATURE DIAGRAMS: WHAT BIRD FEET HAVE TO DO WITH MULTIPHASE EQUILIBRIA: *Dr. Richard G Connell, Jr.*[1]; [1]University of Florida, Materials Science and Engineering, Gainesville, FL 32611 USA

In the teaching of phase diagrams a concurrent presentation of pressure-temperature diagrams (PT) provides a foundation for understanding of the various types of commonly used phase diagrams and the interrelations among them. Though composition-blind, PT diagrams lead to a comprehensive understanding of the hierarchy of the various classes of multiphase equilibria. This is where bird feet come into the discussion. PT diagrams are particularly useful for the schematic construction of temperature-composition (TX) and pressure-composition (PX) diagrams for binary and ternary systems. In quaternary systems they guide the schematic construction of sequences of isobaric isotherms and isothermic isobars. For systems of higher order, the PT diagram can be used to construct the flow diagrams that provide a catalogue of the various classes of equilibria within each order and the connectivity among the various classes of orders.

9:40 AM
ON THE SYSTEMATICS OF THE BINARY, R-ME, PHASE DIAGRAMS OF THE RARE EARTH METALS: *Dr. Ricccardo Ferro*[1]; [1]Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica e Metallurgia, via Dodecaneso, Genova Italy

A summary is presented of the general alloying behavior shown by the rare earth metals (R) in their binary R-Me systems. Phase diagram types are described and compound formation capability examined and discussed for selected series of R-Me alloys formed by given R with different partners Me and, on the other hand, for the alloy series formed by the different rare earths with a fixed second component Me. Special attention is given to the R-rich regions of the binary systems where, owing to the solid state polymorphism of several R metals, complex equilibria are often observed corresponding to a number of subsequent transformations (such as peritectic, cutectic, catatectic, or eutectoidal regions). Moreover, a few comments are presented about ternary alloys (and systems) containing R metals and their possible classification. Finally, with particular reference to the work carried out by the author's research group, a few details are given about problems met in the experimental determination of these phase diagrams.

10:00 AM
THE PHASE EQUILIBRIA OF THE Si-Ge-Ti SYSTEM AT 900°C: *Dr. C. R. Kao*[1]; [1]National Central University, Dept. of Chemical Engineering, Chungli 32054 Taiwan

Recently Si-Ge alloys have been investigated for incorporating them into Si-based electronic devices. This potential application has motivated many studies on the metallizations of Si-Ge alloys. The element Ti is an interesting candidate of potential since $TiSi_2$ is currently the most widely used metallization material in Si-based devices. The knowledge of the Si-Ge-Ti ternary phase equilibria will be very helpful for devising a similar Ti metallization scheme for Si-Ge alloys. In this study the Si-Ge-Ti isotherm at 900°C is experimentally determined by metallography, powder X-ray diffraction, and electron microprobe. At 900°C $TiSi_2$ and $TiGe_2$ have the same crystal structure (C54) and very similar lattice constants. These two compounds are found to form continuous solid solution at 900°C. The tie lines between this solid solution and the Si-Ge solid solution are determined. Diffusion couple study between pure $TiSi_2$ and pure $TiGe_2$ is performed to further con-

firm the existence of a continuous solid solution. The Si-Ge-Ti ternary isotherm at 900°C will be presented.

10:20 AM Break

10:30 AM INVITED
IMMISCIBILITY IN COMPOUND SEMICONDUCTORS AND ITS AFFECT ON EPITAXY: *Dr. Tim Anderson*[1]; J. S. Cho[1]; H Shen[1]; [1]University of Florida, Chemical Engineering Department, Gainesville, FL 32611 USA

Group III-V and II-VI solid solutions often show large miscibility gaps, mainly as a result of size differences in atoms on the same sublattice. The epitaxial growth of single-phase multicomponent films with a composition in the 2-phase region, however, is often possible when the lattice parameter of the film and substrate are closely matched. It is believed that the strain energy introduced by the substrate stabilizes the single phase field. This presentation gives the results of calculations of the extent of immiscibility in II-VI and III-V systems by the delta lattice parameter model. The results are then incorporated into a complex chemical equilibrium calculation for CVD of selected systems. In addition a strain energy term is added to the Gibbs energy to predict the phase behavior of the system.

11:00 AM INVITED
THE PHASE DIAGRAM AS A ROADMAP TO UNDERSTANDING MICROSTRUCTURE DEVELOPMENT: *Dr. M. R. Notis*[1]; Dr. J. I. Goldstein[2]; [1]Lehigh University, Bethlehem, PA 18015-3195 USA; [2]University of Massachusetts, Amherst, MA 01003 USA

In 1956, the textbook PHASE DIAGRAMS IN METALLURGY, by Frederick N. Rhines, was published. Although this book was not the first to describe binary or higher order phase equilibria (ex.,TERNARY SYSTEMS by G. Masing in 1932), it became a very significant milestone and a classic text because it presented for the first time a broadly accepted set of conventions for drawing multicomponent diagrams and categorizing invariant reactions in higher order systems; it provided an approach to visualization and space perception through the use of perspective drawings and pull-apart models; it integrated the fields of phase equilibria and physical metallurgy in a way to demonstrate the utility of phase diagrams for the understanding of microstructure development (a prime focus of Rhines' work); and it presented the material in such a manner as to highlight the application of phase diagrams to metallurgical problems. The authors of the present paper, in keeping with the flavor of Rhines' work, will demonstrate recent advances made in graphic presentation of higher order systems (CAD and true 3D display), and their use in understanding microstructure development for applications such as solder joining, aluminiding, galvanizing, sulfidation, and the study of meteorites.

11:30 AM
MAXIMIZING ALLOY SOLUBILITY WITH COMPUTATIONAL THERMODYNAMICS: *Dr. Caian Qiu*[1]; Dr. J. E. Morral[2]; Dr. Hong Du[1]; [1]United Technologies Research Center, E. Hartford, CT 06108 USA; [2]University of Connecticut, Department of Metallurgy and Materials Engineering, Storrs, CT 06269-3136 USA

A strategy for the design of both age hardening and oxidation resistant alloys is to identify an alloy chemistry and heat treating temperature that yields the maximum possible solubility of a critical component. In principle phase diagrams contain the required information to obtain the optimum conditions, but special methods are needed to access the information when dealing with ternary and higher order systems. Here methods of using monovariant lines and phase boundary normals that have been calculated using computational thermodynamics will be described.

MICROSTRUCTURE AND ITS EFFECTS ON AMORPHOUS NANOPHASE & NANOCRYSTALLINE MATERIALS: Session I - Metals, Cermets and Composites

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

Monday AM Room: 205
February 16, 1998 Location: Convention Center

Session Chairs: Robert D. Shull, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA; Larry Kabacoff, ONR, Code 332, Arlington, VA 22217

8:30 AM Opening Remarks

8:40 AM INVITED
SEARCH FOR SUPERHARD MATERIALS: NANOCRYSTALLINE - AMORPHOUS COMPOSITES WITH HARDNESS EXCEEDING 50 GPa: *Stan Veprek*[1]; [1]Inst for Chemistry of Inorganic Matls, Technical University of Munich, Garching b. Munich D-85747 Germany

The recent search for superhard materials with Vickers hardness $H \geq$ 50 GPa (about 5000 kg/mm^2) concentrates mainly on the polycrystalline Diamond, cubic c-BN and C_3N_4. This approach is based on the theoretical strength which is propertional to be bulk modulus. However, the practically achievable strength (and hardness) of engineering materials is two to four orders of magnitude smaller because their failure occurs due to multiplication and movement of dislocations and growth of microcracks, and it is determined by their microstructure which hinders those mechanisms of failure. This is illustrated e.g. by superlattices whose microshardness exceeded 50 GPa or by a turbostratic, graphite-like, substoichiometric CN_x (x=0.25-0.35) with a hardness of about 40-60 GPa. Recently, we have developed a new concept for the design of superhard nanocrystalline composites and verified it on several nc-Me_nN/a-Si_3N_4 systems (Me=Ti, W, V,...). These materials consist of a nanocrystalline hard transition metal nitride embedded into $\leq$ 1nm thin matrix of amorphous silicon nitride. Unlike pure nanocrystalline metals and the heterostructures which show softening when the crystalline size or lattice period decreases below 5-6 nm, the hardness of our composites strongly increases with decreasing crystallite size in that range and approaches the hardness of diamond. These results show the crucial importance of the nature of the nc-Me_nN/a-Si_3N_4 interface and the grain boundaries, and it opens up challenging questions regarding the origin of the superhardness in these composites which clearly differs from that in conventional materials.

9:20 AM INVITED
MICROSTRUCTURE AND MECHANICAL PROPERTIES OF WC/Co NANOCOMPOSITES: *Kang Jia*[1]; Traugott E. Fischer[1]; [1]Stevens Institute of Technology, Materials Science and Engineering, Hoboken, NJ 07030

The microstructure, mechanical properties, abrasion and wear resistance of WC-Co nanocomposites synthesized by the spray conversion

technique by McCandlish, Kear and Kim have been investigated. The binder phase of WC-Co nanocomposites is enriched in W and C, compared to conventional cermets. Small amorphous regions exist in the binder despite the slow cooling after liquid phase sintering. Few dislocations are found in the WC grains. The increased WC content and the amorphous regions modify (i.e. strengthen) the binder phase of the composites. Vickers indentation measurements show a hardness of the nanocomposites reaching 2310 kg/mm2. While the toughness of conventional cermets decreases with increasing hardness, the toughness does not decrease further as the WC grain size decreases from 0.7 to 0.07 um but remains constant at 8 MPaml/2. Scratches caused by a diamond indenter are small, commensurate with their hardness. These scratches are ductile, devoid of the grain fracture that is observed with conventional materials. The abrasions resistance of nanocomposites is about double that of conventional materials, although their hardness is larger by 23% only. This is due to the lack of WC grain fragmentation and removal which takes place in conventional cermets. Sliding wear resistance of WC/Co is proportional to their hardness; no additional benefit of nanostructure is obtained. This results from the very small size of adhesive wear events in even large WC grains.

10:00 AM

CHARACTERIZATION OF A NANOCRYSTALLINE COMPOSITE Ti-47Al-3Cr/30VOL.%Ti_5Si_3: *O. N. Senkov*[1]; M. L. Ovecoglu[2]; N. Srisukbumbowornchai[1]; F. H. Froes[1]; [1]University of Idaho, Moscow, ID 83844-3026; [2]Istanbul Technical University, Istanbul 806 Turkey

A nanocrystalline TiAl-based composite reinforced with nanocrystalline Ti_5Si_3 particles was produced by mechanical alloying and hot isostatic pressing. Microstructure stability of the composite was studied during annealing at 850ϒC to 1100°C with the use of TEM and XRD. As produced composite consisted of a homogeneously distributed mixture of the nanocrystalline gamma-TiAl grains and Ti_5Si_3 particles. During annealing, slow grain growth occurred which was restrained by ceramic particles and was controlled by their coarsening. The microstructure of the composite was much more stable at high temperatures than the microstructure of the Ti-47Al-3Cr alloy produced by using identical conditions. Even after annealing at 1100°C for 100 hours, the grains were less than 1 mm in size. Microhardness measurements were also performed which showed high hardness of this material after compaction as well as following annealing.

10:20 AM

AN ULTRAHARD AND TOUGH NANOCERMET: *R. B. Bhagat*[1]; G. Wright[1]; B. Jones[1]; M. F. Amateau [1]; [1]The Pennsylvania State University, Applied Research Laboratory, State College 16804 PA

This paper deals with the development of an ultrahard and tough nanograined cermet (or nanocermet) for high performance cutting tools. We use nanocrystalline WC-10wt%Co powder and hot press at temperatures significantly lower than the eutectic temperature of 1320°C. The consolidation time is kept low. The fast consolidation leads to fully dense material with nanograined structure. The consolidated nanocermet has hardness reaching 2389 HV and fracture toughness higher than the conventionally consolidated fine-grained cermet of the identical composition.

10:40 AM

MECHANISMS OF FRACTURE AND FATIGUE CRACK-GROWTH IN Zr-Ti-Ni-Cu-Be BULK AMORPHOUS METALS: *Ms. Katharine M. Flores*[1]; [1]Stanford University, Dept. of Materials Science and Engineering, Stanford, CA 94305-2205 USA

The recent development of bulk metallic glasses offers the potential for metallic material systems with dramatically improved mechanical properties. Until recently, little work has been undertaken to study the mechanical properties of the bulk material or to elucidate its failure mechanisms. Our work at Stanford has focused on the fracture and fatigue crack-growth mechanisms of a $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass. Toughness values in excess of 50 MPa $m^{1/2}$ are modeled in terms of the micromechanisms of fracture, which depend on the microstructure and strain localization processes. Similarly, the micromechanics of fatigue crack growth are considered and related to fatigue loading parameters, environment and microstructure.

11:00 AM

BULK NANOPHASE SiC/Al COMPOSITES BY SQUEEZE CASTING: *S. M. Pickard*[1]; J. Y. Yang[2]; C. G. Levi[2]; [1]MER Corporation, Tucson, AZ 85706; [2]University of California, Materials Department, Santa Barbara, CA 93106

High volume fraction SiC/Al composites containing Vf-40-50% of 200-400 nm size SiC particulate have been fabricated by a high pressure squeeze casting technique. The small interspacing of the fine dispersion of SiC, of the order of 80 nm, for a uniform particle array, has potential for dispersion strengthening and Hail-Petch-strengthening in addition to geometric constraint strengthening due to the high Vf of SiC. Tensile strength and toughness tests are conducted on the bulk namophase composite, for comparison with conventional size SiC/Al composites. Microstructure of the composite is scrutinized by SEM,TEM, and electron beam microanalysis, to confirm full infiltration of Al into the SiC, and assess the uniformity of the SiC distribution. The extent of interfacial Sic/Al reaction and changes in the chemistry of the matrix due to the presence of the fine reinforcement particles are examined. The squeeze casting manufacturing process is evaluated for production of thick section near net shape bulk nanophase Sic/Al composites parts.

11:20 AM

A STUDY OF KINETICS AND MICROSTRUCTURE OF NANOCRYSTALLINE WC DURING SINTERING: *G. R. Goren-Muginstein*[1]; S. Berger[1]; A. Rosen[1]; [1]Technion, Department of Materials Engineering, Haifa 3200 Israel

WC/Co materials are widely used in the cutting tool industry. Usually micron-size and recently sub-micron size WC powders with 6-15wt.% Co are sintered at the liquidus temperature of about 1340°C in order to reach full density. There is a need to improve the fracture toughness of the sintered WC/Co products while maintaining or improving the hardness. One approach to reach this goal is to produce fully dense nanocrystalline WC product in which the large density of grain-boundaries improve the fracture toughness while the small grains increase the hardness. We have produced nanocrystalline WC powder with an average size of about 6nm by ball milling of sub-micron size WC powder. Sintering of the nano-WC powder with cobalt resulted in grain-growth to sub-micron size even with grain growth inhibitors. Green compacts of nano-WC (without Co) were sintered up to 1800°C in a dilatometer to a density of about 97%. During sintering volume shrinkage started at about 700°C and two shrinkage rate peaks were observed at 800°C and 1300°C. The kinetics of sintering was studied by monitoring the rate of volume shrinkage as a function of temperature. During sintering only preferred grains grew while many others remained in the nanometer size. The kinetics of sintering as well as the growth of preferred grains are discussed.

11:40 AM

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF COPPER-BASED NANOCOMPOSITES: *V. Provenzano*[1]; L. Kurihara[1]; S. M. Shastry[2]; R. L. Holtz[1]; [1]Naval Research Laboratory, Materials Science and Technology Division, Washington, DC 20375; [2]Washington University, Department of Mechanical Engineering, St Louis, MO

Nanocrystalline copper matrix nanocomposites were synthesized and processed by two different nanocomposite routes. The first route involved the deposition of copper-aluminum amorphous films on a stainless steel substrate (drum) by the inert-gas condensation method. Following the deposition, the films were scraped from the drum and cold compacted into pellets without breaking vacuum. The pellets were then annealed at the appropriate crystallization temperature in order to transform the amorphous structure into a nanocomposite structure consisting of a copper matrix reinforced with nanoscale copper-aluminum intermetallic particulates. In the second method copper-alumina nanocomposite powders were synthesized by polyol process. The powders were then consolidated by cold pressing followed by vacuum hot pressing at 400°C into 1.25 cm diameter thin disks. Following the respective consolidation procedures, the microhardness of both types of nanocomposites was measured. Further, for the case of copper-alumina nanocomposite disks, the tensile strength and ductility at room temperature were also determined. The microstructural evolution be-

fore and after the high temperature treatments and the fracture features of the consolidated samples after the mechanical testing were examined by high resolution scanning electron microscopy (HRSEM). Finally, microstructure-properties correlations were obtained from themicroscopic analysis and the corresponding mechanical data.

MICROSTRUCTURE & PROPERTIES OF DIRECT FABRICATED MATERIALS: Microstructure & Properties of Direct Fabricated Materials I

Sponsored by: Materials Design and Manufacturing Division, Surface Modification & Coatings Technology Committee
Program Organizers: John E. Smugeresky, Sandia National Labs, MS 9403 Bldg. 940-0969, Livermore, CA 94551-0969; Michelle Griffith, Sandia National Labs, Albuquerque, NM 87185; David M. Keicher, Optomec Design Company, Albuquerque, NM 87123

Monday AM Room: Centro Room C
February 16, 1998 Location: Convention Center

Session Chairs: John E. Smugeresky, Sandia National Labs, Livermore, CA 94551; M. Eric Schlienger, Sandia National Labs, Albuquerque, NM 87185-1411

8:30 AM
OVERVIEW OF DIRECT FABRICATION PROCESSES AND MATERIALS: *J. Mazumder*[1]; J. E. Smugeresky[2]; D. M. Keicher[3]; M. L. Griffith[3]; [1]University of Michigan, Ann Arbor, MI 88888; [2]Sandia National Laboratory, Livermore, CA 94551-0969; [3]Optomec Design Company, Albuquerque, NM 87185 USA

Direct fabrication processes are the most recent generation of rapid prototyping technologies whereby prototyping and manufacturing are losing their distinct identities, beginning to become nearly indistinguishable. Starting with CAD software to design and visualize mechanical parts in 3-D renderings on computer monitors, and using slicing algorithms to break up the mechanical component into layered cross-sections, the electronic files are being used to control movements of various types of manufacturing systems to fabricate/build the mechanical parts, layer by layer using additive rather than subtractive material forming processes. In rapid prototyping, surrogate materials have been used to provide full size 3-D model parts to check things like tolerances and fit. In direct fabrication, actual materials of construction are used, and the first part can serve as both prototype and first production unit, especially in cases when low volume production is required. In this presentation, a brief tutorial will be given to describe the variety of direct fabrication processes being developed and the range of materials under investigation.

8:50 AM
MICROSTRUCTURE AND MECHANICAL PROPERTIES OF METAL PARTS PRODUCED BY SLS/HIP:: *Suman Das*[1]; Martin Wohlert[1]; Joseph J. Beaman[1]; David L. Bourell[1]; [1]The University of Texas at Austin, Laboratory for Freeform Fabrication, Austin, TX 78712

SLS/HIP is a new direct fabrication method that combines the strengths of selective laser sintering and hot isostatic pressing. Selective laser sintering can produce metal parts of complex geometry with an integral, gas impermeable skin. These parts can then be directly post-processed to full density by containerless HIP. Current research is focused on developing SLS/HIP for Inconel-625 and Ti-6Al-4V. Microstructure and mechanical properties of SLS processed and HIP post-processed specimens will be presented. This research is funded by DARPA/ONR contract N00014-95-C-0139 titled "Low Cost Metal Processing Using SLS/HIP".

9:10 AM
GAS PHASE APPROACHES TO SOLID FREEFORM FABRICATION: SALD AND SALDVI: *James E. Crocker*[1]; Eric Geiss[1]; Shay Harrison[1]; Kevin J. Jakubenas[1]; Lianchao Sun[1]; Leon L. Shaw[1]; Harris L. Marcus[1]; [1]University of Connecticut, Institute of Materials Science, Storrs, Connecticut

Selective Area Laser Deposition (SALD) and Selective Area Laser Deposition Vapor Infiltration (SALDVI) are two gas phase Solid Freeform Fabrication techniques for direct production of metal and ceramic shapes. The effect of processing parameters on the deposit microstructure is discussed. Results are presented for silicon carbide, silicon nitride, and other material systems investigated using these two processes. Applications include the fabrication of embedded devices and ceramic joining. The authors would like to acknowledge the support for this research by DARPA and ONR.

9:30 AM
HIGH-RATE ELECTROTRIBOLOGICAL DEPOSITION OF QUENCHED ALUMINUM ALLOYS: *C. Persad*[1]; R. M. Gee[1]; A. Yeoh[1]; G. Prabhu[2]; D. L. Bourell[2]; [1]University of Texas, Institute for Advanced Technology, Austin, TX 78759 USA; [2]University of Texas, Materials Science and Engineering Program, Austin, TX 78712-1063 USA

Quenched Metal Deposits (QMDs) with controllable features are formed during the operation of novel laminated sliding electrical contacts. When the interface between the sliding conductor and a stationary planar conductor contains a series of fine rectangular channels, a thin deposit of molten aluminum from the sliding conductor is trapped and resolidified. High-speed transit (0 - 1000m/s) of the sliding conductor produces deposits at volumetric rates of 100cm3 to 200cm3 per second. Microstructural evaluation reveals that grains with 200 nm dimensions are formed in QMDs with chemistries such as that of aluminum alloy 7075. Modifications in QMD structure are observed when alternate substrate materials are employed. Experimental results are compared for QMDs of aluminum-on-copper and of aluminum-on-stainless steel (AlSi 304). The experimental apparatus and evaluation offer a method for rapidly screening the melt processing behaviors of new materials over a wide range of power densities. QMD evaluations of alloy chemistry effects show promise for the development of new materials for direct fabrication processing. Research supported by the U.S. Army Research Laboratory, ARL/WMRD.

9:50 AM
SHAPE DEPOSITION MANUFACTURING OF METALS: MICROSTRUCTURES, INTERFACES, AND PROPERTIES: *P. S. Fussell*[1]; J. R. Fessler[2]; L. E. Weiss[3]; F. B. Prinz[2]; [1]Alcoa Technical Center, Alcoa Center, PA 15069; [2]Stanford University, Stanford, CA 94305; [3]Carnegie Mellon University, Pittsburgh, PA 15213

Metals directly fabricated from CAD geometry by the Shape Deposition Manufacturing (sdm) process being developed at Carnegie Mellon and Stanford are characterized in this paper. Of particular interest is the evolved microstructure resulting from the various deposition strategies used in sdm. This work will focus on the interior and surface (last deposited) microstructures in several metals, interfaces between metals of differing compositions (both graded and abrupt internal interfaces), and some property information of the resulting bulk materials. Material classes will include stainless steel, invar, and copper alloys. Limited information on deposited aluminum structures will be presented, as well.

10:10 AM
THERMOMECHANICAL DROPLET INTERACTIONS DURING THE BUILD-UP OF RESIDUAL STRESSES IN LAYERED MANUFACTURING METHODS: *Jack Beuth*[1]; Cristina Amon[1]; Richard Chin[1]; Nathan Klingbeil[1]; John Zinn[1]; [1]Carnegie Mellon University, Department of Mechanical Engineering, Pittsburgh, PA 15213-3890

The build-up of residual stress, which is caused by differential contractions from solidification or curing, is a concern in almost all layered manufacturing processes. The most detrimental effect of residual stresses

is typically part warping, which can lead to unacceptable losses in part tolerance. In this paper, the role of thermal and mechanical interactions between deposited metal droplets in the build-up of residual stresses is considered. The application of primary focus is the microcasting process used within Shape Deposition Manufacturing (SDM), which is a layered manufacturing method currently being pursued at Carnegie Mellon and Stanford. First, experimental results from warping measurements and x-ray diffraction studies are shown to suggest that the droplet-by-droplet nature of the microcasting process is reflected in residual stress distributions in void-free microcasted deposits. Results also suggest that residual stress magnitudes are different in directions parallel to and perpendicular to the direction of droplet deposition. Thermomechanical modeling results are then presented which attempt to quantify thermal and mechanical interactions between deposited droplets. Understanding these interactions can provide insight into some of the experimental observations noted above. Results and insights of this work also have applications to other processes involving deposition of molten materials, such as welding and powder/laser deposition processes used within SDM and the Laser Engineered Net Shaping (LENS) process being pursued at Sandia National Laboratories.

10:30 AM

MICROSTRUCTURE AND PROPERTIES OF CERMET COMPOSITE ABRASIVE BLADE TIPS PRODUCED BY DIRECT LASER PROCESSING: *Suman Das*[1]; Timothy P. Fuesting[2]; Gregory Danyo[1]; Lawrence E. Brown[2]; Joseph J. Beaman[1]; David L. Bourell[1]; Kathleen Sargent[3]; [1]University of Texas at Austin, Laboratory for Freeform Fabrication, Austin, TX; [2]Allison Engine Company, Indianapolis, IN; [3]Wright Laboratories, Wright Patterson AFB, OH

This paper presents development of a new technique for the production of cermet composite abrasive turbine blade tips by direct laser processing. These components form part of the low pressure turbine sealing system in an IHPTET demonstrator engine being developed for the Air Force. The influence of laser processing parameters on resulting solidification microstuctures will be presented. This research is funded by the United States Air Force, contract F33615-94-C-2424 titled "Affordable Turbine Blade Tips".

10:50 AM

SOLID FREE FORM FABRICATION OF METAL AND CERAMIC PARTS USING A MODIFIED POWDER INJECTION MOLDING PROCESS: *Harald Eifert*[1]; Matthias Greul[1]; Donald Kupp[1]; Matthias Kuenstner[1]; Karl Steiner[1]; Dr. Harald H. Eifert[1]; [1]Fraunhofer USA - Resource Center Delaware, Newark, DE

In order to fulfill the requirements for the rapid and direct production of metallic and ceramic components for functional testing and application, the Multiphase Jet Solidification (MJS) process has been developed at the Fraunhofer Institute for Applied Materials Research (IFAM) and the Fraunhofer Resource Center-Delaware (FRC-DE). The MJS process extrudes metal and ceramic based binder systems (such as Al2O3, SiC, stainless steel, and Ti), forming the desired component layer by layer. As in powder injection molding, after a part is formed by MJS, the binder phase is removed chemically or thermally and the remaining powder compact is sintered to final density. Prototype components produce by this method exhibit many of the microstructural features and process artifacts more commonly associated with P/M and more specifically, PIM components. This paper discusses these details and correlates their existence to various steps in the MJS process.

11:10 AM

STAINLESS STEEL ENGINEERING COMPONENTS FABRICATED BY CAM-LEM TECHNOLOGY: *B. Kernan*[1]; T. Ko[1]; J. D. Cawley[1]; A. H. Heuer[1]; [1]Case Western Reserve University, Department of Materials Science and Engineering, Cleveland, OH

Computer-Aided Manufacturing of Laminated Engineering Materials (CAM-LEM) is an emerging Solid Freeform Fabrication (SFF) technology designed for metals, alloys, advanced ceramics, and engineering plastics. It has been reduced to practice for a variety of engineering ceramics and for 316L stainless steel. For the stainless steel case, two different feedstocks have been used. Both are commercial powder injection molded (PIM) formulations which have been compression molded into sheets for the CAM-LEM process. In this SFF technology, each sheet is laser cut into the outline of the computationally sliced 3D component, robotically stacked, laminated to form a monolith, and sintered conventionally. The PIM formulations each contain approximately 64 volume % metal particles in the polymer resin and each requires its own optimized lamination approach. Tensile and impact data comparable to wrought materials have been achieved. Engineering components of complex internal and external geometries have been fabricated and performance tested.

NON-AEROSPACE APPLICATIONS OF TITANIUM & ITS ALLOYS: Session I - Keynote Paper; Fundamental Research

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

Monday AM Room: 101
February 16, 1998 Location: Convention Center

Session Chair: M. Niinomi, Toyohashi University of Technology, Dept. of Production Systems Engineering, Toyohashi Japan

8:30 AM

OVERVIEW NON-AERO APPLICATIONS OF TITANIUM: *F. H. (Sam) Froes*[1]; P. Allen[2]; M. Niinomi[3]; [1]IMAP, University of Idaho, Moscow, ID 83844-3026I; [2]TIMET, Henderson Tachnical Laboratory, Henderson, NV 89015; [3]University of Technology, Toyohashi Japan

Traditionally the majority of titanium usage has been in the aerospace industry. However, with the outbreak of peace in the world, titanium producers and processors have aggressively expanded their horizons into non-aerospace applications. In this overview presentation, the attributes of titanium will be related to this these latter types of use. The emphasis will be on new and developing applications including architecture, use in aggressive environments, armor applications, medical use, navy components, and the "holy grail" family automobile use. Dramatically use of titanium necessitates development of low-cost extraction and processing techniques, particularly for the "cost obsessed" automobile industry. This paper will set the tone for the more detailed papers which follow in this symposium.

9:00 AM

LOW COST SYNTHESIS OF P/M Ti ALLOY AND Ti-BASED PARTICULATE COMPOSITES WITH IMPROVED HIGH CYCLE FATIGUE STRENGTH: *Mr. M. Hagiwara*[1]; Mr. S. Emura[1]; [1]National Research Institute for Metals, Tsukuba 305 Japan

The use of titanium alloys in non-aerospace applications such as automobile industries are still limited due to a high manufacturing cost associated with the expensiveness of raw materials and machining difficulties. Furthermore, lower stiffness and poorer abrasion-related properties compared to iron-made parts also prevent the wide usage of titanium alloys. The synthesis of titanium alloys and titanium-based particulate composites using a blended elemental (BE) powder metallurgy (P/M) method has a potential to overcome these cost and quality problems. Because high cycle fatigue strength is particularly important in various practical application, special emphasis must be paid to improve this property by the modification of matrix microstructure or by the process innovation. This paper summarizes the research work done by the present authors aimed at improving high cycle fatigue strength of BE P/M titanium alloys and particulate composites. The alloys synthesized ranges from near alpha alloy such as IMI829 to beta alloy

such as LCB, and particulate composites include such as Ti-6Al-2Sn-4Zr-2Mo/TiB and Ti-6Al-1.7Fe-0.1Si/TiB.

9:20 AM

FATIGUE BEHAVIOR AND MICROSTRUCTURE OF PURE TITANIUM: *Mr. F. Morito*[1]; [1]National Research Institute for Metals, Tsukuba 305 Japan

Details of fatigue softening behavior have been reported for the materials such as aluminum, copper, silver and iron. However fatigue properties in titanium alloys have scarcely been examined in connection with the characteristics of crystal structures and microstructures. We studied the microstructures after the fatigue softening and hardening phenomena in the worked and the annealed state of the hcp type titanium under the stress ratio (R) between 0.1 and -1. The maximum stress of the worked titanium was higher than that of the annealed one. The maximum stress under R=0.1 was higher than that under R=-1. Dislocation dipoles were often observed after fatigue test of the annealed titanium. Layered substructures due to fatigue deformation were formed more easily under R=-1 than under R=0.1. In the worked titanium, such layered substructures also tended to be formed at the fatigue test under R=-1 with higher stress level.

9:40 AM

SUPERPLASTIC BEHAVIOR OF Ti-Al-Fe ALLOYS: *Mr. J. Koike*[1]; [1]Tohoku University, Department of Materials Science, Graduate School of Engineering, Sendai 980-77 Japan

Ti- 5.4 Al-1.4 Fe alloys were studied for their superplastic behavior. The microstructure was examined by TEM and XRD at high temperatures. The microstructure consists of equiaxed a grains and pockets of the β phase at the a triple grain junctions. The grain size is 3 to 5 mm. Tensile tests were performed in an argon atmosphere at 1100 K. A superplastic elongation of approximately 700% was observed in a wide range of strain rates from 10- 4 and 10- 2 s- 1. Strain-rate sensitivity was found to be 0.5 in the entire range of strain rates, suggesting that a major deformation mechanism is grain boundary sliding with dislocation accommodation. The effects of the βphase at the a triple grain junctions will be discussed.

10:00 AM

THERMAL CONDUCTIVITY OF BETA Ti-V ALLOYS BELOW ROOM TEMPERATURE: *Mr. Masahiko Ikeda*[1]; [1]Kansai University, Department of Materials Science and Engineering, Osaka Japan

Thermal conductivity (k) of six Ti-V alloys was measured at room temperature (RT) and near liquid nitrogen temperature (LN) by laser flash and steady state method, respectively. Apparatus for steady state method was designed by present authors and accuracy of the apparatus was confirmed by measuring of k of a Fe-18Cr-8Ni stainless steel (SUS 304). The k of the Ti-V alloys is one third of k of the SUS 304 at RT and one second of that of the SUS 304 near LN. The k of the Ti-V alloys increases with decrease in resistivity (r) of these alloys. Moreover, relatively good linear relation between the k and reciprocal values of the r was obtained, that is, a similar relation to the Wiedemann-Franz's law was obtained.

10:20 AM

EFFECT OF BETA RECOVERY TREATMENT PRIOR TO AGING ON THE (ALPHA + BETA) MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Ti-15V-3Cr-3Sn-3Al: *Mr. T. Furuhara*[1]; Mr. T. Nagaokal[1]; Mr. T. Maki[1]; [1]Kyoto University, Department of Material Science and Engineering, Kyoto 606-01 Japan

Microstructure developed during various thermo-mechanical processing and their effects on the tensile properties were studied in a Ti-15V-3Cr-3Sn-3Al alloy. Cold rolling and aging after the solution treatment results in the localized precipitation of alpha phase on the dislocations in planar slip bands introduced in the beta matrix by rolling. The crystallographic variants of alpha precipitate are strongly restricted by the nature of dislocations. Controlled short time annealing above the beta transus after cold rolling produces the fully recovered beta matrix structure with fine subgrain sizes smaller that 1mm. By subsequent aging of the recovered specimens, alpha precipitates form preferentially on beta subgrain boundaries. Alpha precipitation within beta subgrains also occurs. More numbers of alpha variants than those in the cold rolled and aged specimens are observed locally. Beta recovery treatment prior to aging clearly improved the strength-ductility balance, as previously reported by Ouchi et al., mostly by the increase of local elongation.

10:40 AM

COMPOSITION OF ω AND α IN Ti-10V-2Fe-3Al ALLOY ANALYSED BY TEM-EDX SYSTEM: *Mr. A Yamamoto*[1]; H. Tsubakino[1]; [1]Himeji Institute of Technology, Department of Materials Science and Engineering, Himeji, Hyogo 671-22 Japan

Compositional analyses of ω and α in Ti-10%V-2%Fe-3%Al (in mass %) alloy have been performed by means of TEM-EDX system equipped with the field emission filament. The specimens were solution heat treated at 1033K for 7.2ks, and then quenched into iced water, which is followed by aging in the temperature range of 473 to 673K. In the early stage of aging at 573K, only the ω phase precipitated, and the EDX analysis of the w showed that all the solute elements, V, Fe and Al, are depleted in ω phase compared with the matrix, β. Fine α precipitates were observed with ω in prolonged aging at 573K. The contents of V and Fe in a were lower than in ω, while that of Al is higher in α than in both ω and β. Size of ω increased during aging and then saturated when the precipitation of a occurred.

11:00 AM

MICROSCOPIC EVALUATION OF FRACTURE PROCESSES IN POWDER BLENDED ELEMENTAL-Ti-10V-2Fe-3Al ALLOY: *Mr. Hisashi Mori*[1]; [1]The University of Birmingham, IRC in Materials for High Performance Applications, Edgbaston, Birmingham B15 2TT U.K.

Fracture processes in a Ti-10V-2Fe-3Al alloy were processed by the powder blended elemental method have been investigated in terms of microscopic analysis. Two microstructures with different morphologies of the aspect ratio of the alpha phase were prepared by the addition of Al2O3 powder to the powder blended elemental process. To understand facet formation mechanisms in this alloy, Acoustic Emission (AE) was applied during fracture toughness tests. The AE signals generated followed different trends in these microstructures. Furthers investigation of the AE behavior together with microscopic fractographic observations indicates that AE generation depends on the details of the stress and strain localization process, which results in deformation and cleavage facet formation. It can be concluded that facet formation is affected by the aspect ratio of alpha phase and particularly in terms of the anisotropy of α / β crystallographic orientation relationships.

RAPID SOLIDIFICATION: MODELING & EXPERIMENTS: Rapid Solidification Fundamentals - Session I

Sponsored by: Materials Design and Manufacturing Division, Solidification Committee

Program Organizers: W. Hofmeister, Vanderbilt University, P.O. Box 1543 Station B, Nashville, TN 37235; R. Trivedi, Iowa State University, 100 Wilhelm Hall, Ames, IA 50011

Monday AM — Room: Plaza Room D
February 16, 1998 — Location: Convention Center

Session Chair: Rohit Trivedi, Ames Laboratory US-DOE and Dept. of Materials Science and Engineering, Ames, IA 50010

8:30 AM Opening Remarks

8:35 AM KEYNOTE
FUNDAMENTAL ASPECTS OF RAPID SOLIDIFICATION: *Dr. William J. Boettinger*[1]; [1]NIST, Metallurgy Division, Gaithersburg, MD 20899 USA

General principles governing the liquid to solid transformation at high rates can provide a unified framework to understand the variety of processing approaches and microstructures developed during rapid solidification. The thermodynamics of metastable and non-equilibrium solidification sets the possible range of solidification product phases. Nucleation and growth kinetics determine the detailed microstructural evolution. Selected topics in these areas will be reviewed, including: T_0 curves, solute trapping, and solidification by cellular, dendritic and eutectic mechanisms.

9:20 AM
DISORDER TRAPPING IN Ni-Al-Ti ALLOYS BY RAPID SOLIDIFICATION: *Dr. O. Hunziker*[1]; Dr. W. Kurz[1]; [1]Swiss Federal Institute of Technology, Department of Materials, Lausanne Switzerland

Rapid solidification of Ni-Al-Ti alloys containing near 25 at% Al and 0 to 6 at% Ti is performed by laser surface modification. In Ni-Al alloys, growth of microstructures containing gamma prime-Ni3Al phase occurs only at low velocities and metastable microstructures containing only gamma-Ni and beta-NiAl phase prevail at higher velocities. This is attributed to the effect of disorder trapping in the gamma prime-Ni3Al phase. The increase of the transition velocities from the stable to the metastable microstructure with increasing Ti content is attributed to the stabilizing effect of Ti on gamma prime-Ni3Al. The experimental results are compared with calculations using models for plane front, cellular, dendritic and eutectic growth, including a recent model for disorder trapping in the gamma prime-Ni3AI phase.

9:55 AM
THE STRUCTURE OF METASTABLE LIQUIDS: *Dr. Shankar Krishnan*[1]; Dr. S. Ansell[2]; Dr. D. L. Price[2]; [1]Containerless Research, Inc., Evanston, IL 60201 USA

We have recently developed the ability to perform structural measurements on high-temperature ceramic and metallic liquids in the normal and metastable (undercooled) states. Our approach employs synchrotron radiation scattering measurements in combination with conical nozzle levitation and laser beam heating and melting of materials. Specimen materials of interest are aerodynamically levitated, heated with a 270 watt laser, positioned in the X-ray synchrotron beam and scattered X-rays are detected with an energy-dispersive detector. Structural measurements have been obtained on molten aluminum oxide, silicon, germanium, boron, a series of metals, metallic alloys, metal fluorides, and in other chemical systems. Our data on aluminum oxide shows that it undergoes a drastic structural change upon melting with the Al coordination changing from octahedral in the solid to tetrahedral in the liquid. Further, as the liquid is supercooled, there is a small increase in the intermediate-range order as expected from the known temperature dependence of viscosity of liquids. Results on liquid Si show that as the liquid is supercooled, a structural change occurs resulting in lowered coordination with a strong tendency towards local tetrahedral order. Supercooled liquid boron is most unusual; our data show that the liquid is composed of B12 icosahedral clusters, very much like solid boron. Structural data will also be presented on supercooled liquid Zr, Ni, and yttrium oxide. Results on pure elements show that there is a strong tendency for supercooled liquids to assume local order that resembles the order in the crystalline phases that nucleate from them. The implications of the structural measurements are discussed in the context of rapid solidification, thermophysical and transport properties of stable and metastable liquids.

10:30 AM Break

10:40 AM INVITED
TIME-DEPENDENT NUCLEATION - GLASS FORMATION AND STABILITY: *Dr. Kenneth F. Kelton*[1]; [1]Washington University, Department of Physics, St. Louis, MO 63130 USA

Glass formation and devitrification data are typically analyzed assuming a steady-state nucleation rate. A time-dependent nucleation rate for crystal phases during quenching, however, can significantly increase the ease of glass formation in some cases. Further, even when no change in glass formation is apparent, glass stability can be enhanced. Experimental and theoretical studies of the crystallization of silicate glasses demonstrate a complicated temperature/time dependence for the nucleation rate, often with the transient nucleation rate rising above the steady state rate. The origin of a time-dependent nucleation rate is discussed in light of the classical theory of nucleation (CNT). Experimental glass formation and crystallization data are compared with theoretical calculations based on that model. A new model is introduced for time-dependent nucleation in liquids and glasses that transform to crystal phases having a different composition. Computed nucleation rates are contrasted with those predicted from the CNT, demonstrating the impact that partitioning during nucleation has on glass formation. The extremely fine microstructures obtained by the devitrification of bulk metallic glasses emerge naturally within this new model.

11:25 AM
DENDRITE GROWTH VELOCITY-UNDERCOOLING RELATIONSHIPS AND MICROSTRUCTURAL EVOLUTION IN HIGHLY UNDERCOOLED DILUTE Cu-Sn ALLOYS: *Dr. Robert F. Cochrane*[1]; Ms. Sharon E. Battersby[1]; Dr. Andrew M. Mullis[1]; [1]University of Leeds, Department of Materials, Leeds LS2 9JT U.K.

A melt encasement (fluxing) technique has been used to systematically investigate the velocity-undercooling relationships in a range of dilute Cu-Sn alloys. A maximum level of undercooling of 220 K was achieved in the Cu-1 wt% Sn alloy. Good agreement was observed between the experimentally determined dendrite growth velocities and those predicted on the basis of the LKT model. At all undercoolings studied, and for all the alloy systems, the microstructures produced were predominantly dendritic although these structures became progressively more fragmented as the initial undercooling increased. Grain refinement was observed at the highest undercoolings (greater than 190 K in Cu-3wt%Sn) but without the spherical sub-structure previously seen to accompany grain refinement in Cu-based alloys. Microstructural analysis using light microscopy, texture analysis, TEM and microhardness measurements reveals that recrystallisation accompanies the grain refinement at high undercoolings. Furthermore, at undercoolings between 110 and 190 K, a high density of sub-grains are seen within the microstructure which indicate the occurence of recovery, a phenomenon previously unreported in samples solidified from highly undercooled melts.

STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS: STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS I: General

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

Monday AM Room: 107
February 16, 1998 Location: Convention Center

Session Chairs: Norman Stoloff, RPI, Materials Science Dept., Troy, NY 12180; John Mundy, Office of Basic Energy Sciences, Division of Materials Sciences, Germantown, MD 20874-1290

8:30 AM Opening Remarks

8:35 AM
CREEP STRENGTHENING MECHANISMS IN INTERMETALLICS: *Priv.-Doz. Dr. Gerhard Sauthoff*[1]; [1]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf D-40074 Germany

Intermetallics for structural applications at high temperatures must show a sufficient high temperature strength which is controlled by creep processes. In the first section the creep behavior of single-phase intermetallic alloys is overviewed with respect to effects of stress, temperature, composition and microstructure on the rate controlling mechanisms which are dislocation creep and diffusion creep in parallel. It is pointed out that the effective diffusion coefficient is a most important materials parameter for creep deformation in any case. The second section refers to multiphase intermetallic alloys, and both particulate and non-particulate alloys are regarded. Data are presented for single-phase and multiphase alloys based on B2 phases and less-common phases and the consequences of diffusion control for alloy design are discussed. Recent results on new NiAl alloys with Laves phase strengthening are reported.

9:05 AM
PERSPECTIVES ON DUCTILE/BRITTLE BEHAVIOR IN HIGH-TEMPERATURE INTERMETALLICS: *Mr. Eli N. Ross*[1]; Dr. Michael J. Kaufman[1]; [1]University of Florida, Materials Science and Engineering, Gainesville, FL 32611 USA

Reduction of the brittle-to-ductile-transition temperature (BDTT) in high-strength intermetallics has been examined as being indicative of improved ductility and damage tolerance. However, in many cases (e.g. NiAl) brittle failure predominates even under conditions which result in significant elongations. Unfortunately, most studies have been conducted without considering the intrinsic and extrinsic factors responsible for this brittle behavior. Thus, the need exists for a thorough analysis and classification of intermetallic materials as to their potential for true ductile behavior, and identification of those materials which should in fact exhibit a real brittle-to-ductile transition. Based on our preliminary analysis, most intermetallics fall into four classes with respect to the number of independent slip mechanisms and the relative flow (σ_0)and fracture stresses (σ_f) within a specific temperature range: Class I - $\sigma_0 < \sigma_f$, > 5 slip systems; Class II - $\sigma_0 < \sigma_f$, < 5 slip systems; Class III - $\sigma_0 > \sigma_f$, > 5 slip systems; and Class IV - $\sigma_0 > \sigma_f$, < 5 slip systems. Class I and III should exhibit a true BDTT whereas Class II and IV should not. Work supported by ONR (Dr. Steven Fishman) and ARPA (Dr. William Coblenz).

9:35 AM
HIGH TEMPERATURE STRENGTHS OF Nb_3Al SHEET PRODUCED BY ELECTRICALLY-HEATED POWER ROLLING: *Mr. Chitoshi Mochizuki*[1]; Mr. Masao Mikami[1]; Mr. Kenji Matsuda[2]; [1]Ishikawajima-Harima Heavy Industries, Research Institute,Yokohama 235 Tokyo 135-91 Japan; [2]Ishikawajima-Harima Heavy Industries Co., Ltd., Machinery and Structure Development Dept.,Tokyo 135-91 Japan

Electrically-heated powder rolling is a suitable method for making sheets of high melting point metals or hard materials. An experimental apparatus of this method was developed for making Nb_3Al intermetallic compound sheets. The plasma-melt-gas-atomized Nb-Al and Nb-Al-Mo powders were prepared. The maximum size of the powder particles was less than 0.1 mm. These powders were heated during powder rolling by applying a direct electric current between horizontally arranged two rolls through each roll shaft and slip-ring. The rolling was carried out in the atmosphere of 10^{-2} Pa for preventing oxidation of powder and rolls. It is verified that the powders have the bcc structure because of the quench effect; however, sheets made by electrically-heated powder rolling have the A15 structure of Nb_3Al. The tensile strength of Nb_3Al sheets made under several conditions were tested at 2073°; K, and the maximum tensile strength was 31 Mpa. The tensile strength was related to the electric current value during rolling, and this will be discussed.

10:05 AM
FLOW STRESS, WORK HARDENING AND STRAIN AGEING EFFECTS IN EQUIAXED Ti-48Al-2Cr: *Dr. Arno Bartels*[1]; Dr. St. Willems[1]; Prof. H. Mecking[1]; [1]Technical University Hamburg-Harburg, Physics and Technology of Materials, Hamburg Germany

In contrast to other intermetallic aluminides Ti-48Al-2Cr with equiaxed microstructure exhibits no pronounced yield stress anomaly between RT and 600°C. But the work hardening increases up to 400°C and therefore a flow stress anomaly is found at higher strains. In this temperature region static and dynamic strain ageing phenomenas have their maximum and it is attempted to explain the flow stress behavior with strain ageing effects. We present measurements of the work hardening, recovery and strain rate sensitivity. By that we can describe the general deformation behavior and additional effects of second order. Between RT and 400°C the work hardening behavior can be characterized by an athermal region II type with no recovery. In this temperature region the validity of the Cottrell-Stokes law is confirmed. From there Ti-48Al-Cr exhibits a similar deformation characteristic like pure fcc metals where as the yield stress seems to be determined by the CRSS for different deformation modes and microstructural parameters like grain or lamellae size. The influence of strain ageing effects on the flow stress is only of second order. Nevertheless strain ageing may be the reason for the suppressed recovery.

10:25 AM
EFFECTS ON STRENGTHENING FROM CONSTITUTIONAL DEFECTS IN LAVES PHASE INTERMETALLICS: *Dr. Katherine C Chen*[1]; Dr. Fuming Chu[1]; Dr. Dan J Thoma[1]; Eric J Peterson[2]; William L Hults[2]; [1]Los Alamos National Laboratory, Materials Science & Technology/Metallurgy, Los Alamos, NM 87545 USA

Laves phase intermetallics (AB_2) have shown potential as high temperature structural materials, especially when incorporated as part of a dual phase alloy. However, further alloy development requires the basic understanding of structure-property relationships of the Laves phase itself. Constitutional defects in off-stoichiometric intermetallics are known to affect mechanical properties. A combination of x-ray diffraction, density measurements, electronic calculations and geometrical modeling were used to help identify non-stoichiometric defect mechanisms (i.e., vacancies or anti-site substitutions). These defects were then correlated with microhardness and fracture toughness measurements from different Laves phases (e.g., $TiCr_2$, $NbCr_2$, $HfCo_2$) and from several different compositions. Elastic constants were also determined by resonant ultrasound spectroscopy (RUS). Contrary to most intermetallic phases, the greatest strength of these materials generally occurred at the stoichiometric composition, which corresponds to the most "perfect" lattice. Departures from stoichiometry resulted in decreases in hardness and increases in toughness values. Thus, constitutional defects may assist the synchroshear deformation mechanism and result in greater deformability found in the off-stoichiometric Laves phase compositions.

10:45 AM
PLASTIC DEFORMATION IN SINGLE CRYSTAL Ti-56Al: *Dr. Q. Feng*[1]; Prof. S. H. Whang[1]; [1]Polytechnic University, Department of Chemical Engineering, Chemistry and Materials Science, Brooklyn, NY 11201 USA

Single crystal Ti-56Al was deformed plastically between 673K and 1073K under single slip of ordinary dislocations. The deformation was carried out in three different compression orientations: [-1 12 7], [-1 6 3], [-1 12 5] to investigate yield stress, critical resolve shear stress (CRSS), work hardening and strain rate sensitivity in single crystal gamma Ti-56Al. The CRSS curves exhibit orientation dependence as well as temperature dependence in these orientations between 673K and 1073K. The work hardening rate decreases with increasing temperature. The CRSS values for a given temperature were correlated with the Schmid factor ratio between potential cross slip planes and the primary slip plane of ordinary dislocations from 673K to 1073K. The deformation below 673K in these orientations were carried out by both ordinary and superdislocations regardless of their Schmid factor advantage. Also, above 1073K, the orientation dependence and the anomalous hardening disappear simultaneously, indicating the close relationship between the two. The dissociation of ordinary dislocations and the

resulting core structures in the specimen deformed at 873K are under investigation using the weak beam technique and HREM. This research has been sponsored by the Division of the Basic Energy Science, U.S. Department of Energy under contract DEFG02-93ER.45499.

11:05 AM

MICROSTRUCTURE AND HIGH TEMPERATURE DEFORMATION BEHAVIOR OF MECHANICALLY-MILLED ODS $L1_2$-$(Al,Cr)_3$ Ti: *Dr. H. Saage*[1]; M. Heilmaier[1]; J. Eckert[1]; L. Schultz[1]; [1]Institute of Solid State and Materials Research Dresden, Dresden D-01096 Germany

High energy ball milling was used to prepare Cr modified $L1_2$-Al_3Ti intermetallic compounds additionally strengthened by different volume fractions of Y_2O_3 dispersoids. X-Ray diffraction and transmission electron microscopy investigations of the powder indicate that the ordered matrix can nearly be amorphizised during milling. Moreover, the Y_2O_3 dispersoids are homogeneously distributed in the matrix with an average diameter of about 10 nm. Using the high driving forces for recrystallization of the nearly amorphous powders different consolidation routes were employed including cold and hot pressing as well as hot extrusion under protective atmosphere, resulting in different grain sizes between 200 nanometers and several micrometers. The high temperature deformation behavior of the resulting ODS intermetallic compound was analyzed for different Y_2O_3 volume fractions and grain sizes, using constant compression rate tests at 1000°C.

11:25 AM

PHASE STABILITY AND FRACTURE RESISTANCE OF Nb(Cr,C0)2 TERNARY LAVES PHASE SYSTEM: J.H. Zhu[1]; P. K. Liaw[1]; C. T. Liu[2]; [1]The University of Tennessee, Knoxville, TN 37996; [2]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115

The phase stability and fracture resistance in ternary Nb-Cr-Co Laves phase alloys were studied. Our previous study in NbCr2-based transition-metal Laves phases has shown that the average electron concentration factor, e/a is the dominating factor in controlling the phase stability of NbCr2-b Laves phases when the atomic size ratios are kept identical. Since Co has more out-shell electrons than Cr, the substitution of Co for Cr in NbCr2 will increase the average electron concentration of the alloy, thus leading to the successive changes of the crystal structures from C15 to C14 to C15. Number of Nb (Cr,Co)2 alloys were prepared and their crystal structures after long heat-treatment at 1000°C as a function of Co content were determined by x-ray diffraction technique. The boundaries of the C15/C14 transitions were determined and the e/a ratios corresponding to the different Laves polytypes were calculated and compared with the previous prediciton. It was found that the electron concentration and phase stability correlation is well obeyed in the Nb-Cr-Co system. The changes in lattice constant, Vickers hardness, fracture toughness were also determined as a function of the Co content, and are discussed in terms of the phase stability. The incorporation of co-based second phase to toughen the Laves alloy via ductile-phase toughening mechanism has been demonstrated. The implications of these results on alloy development will also be discussed.

11:45 AM

MECHANICAL BEHAVIOR OF AN INVESTMENT CAST Ti-25 Al-10Nb-3V-1Mo ALLOY: *C. Cady*[1]; Dr. Zhe Jin[1]; R. U. Vaidya[1]; D. P. Butt[1]; G. T. Gray, III[1]; [1]Los Alamos National Laboratory, Materials Research and Processing Science, Los Alamos, NM 87545 USA

The mechanical behavior of an investment cast Ti-25Al-10Nb-3V-1Mo alloy at strain rates ranging from 0.001 to 3000 s^{-1} and temperatures from -196 to 1000°C was investigated in compression. The anomalous yield stress-temperature dependence was observed to occur at 800°C only for low strain rates below 1 s^{-1}. The work hardening rate also showed an anomalous temperature dependence at 800°C and at strain rates below 1 s^{-1}. No apparent strain rate dependence of the work-hardening rate was observed within the range of strain rate and temperature studied except at 800°C. Both yield and flow stresses were seen to be insensitive to strain rate when the strain rates were below 1 s^{-1} while positive strain rate sensitivity was observed at higher strain rates. The stress-strain response of Ti-25Al-10Nb-3V-1Mo alloy was found to be controlled by the stage-II hardening at low temperatures and by the stage-III hardening at temperatures greater than 1000°C.

SUPERPLASTICITY AND SUPERPLASTIC FORMING: Session I - Microstructural Mechanisms

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

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

Monday AM Room: 106
February 16, 1998 Location: Convention Center

Session Chair: Amit K. Ghosh, University of Michigan, Dept. of Matls., Sci. & Eng., Ann Arbor, MI

8:30 AM INVITED

A SLIDING BAND DESCRIPTION FOR SUPERPLASTICITY: *J. J. Blandin*[1]; R. Dendievel[1]; B. Baudelet[1]; [1]Insitut National Polytechnique de Grenoble, Génie Physique et Mécanique des Matériaux, Université Joseph Fourier, Cedex F-38402 France

Most conventional descriptions of superplasticity are generally based on two main hypotheses. First, they assume that a unique mechanism is activated in the whole superplastic domain (i.e., grain boundary sliding (GBS) accommodated by diffusion or dislocation movements) leading to a sharp transition between optimum superplastic conditions and conventional dislocation creep. Second, they suppose that a representative elementary volume (REV) can be defined (typically several grains) for which the rheology is similar to the macroscopic behavior of the material. However, some experimental work tends to support the idea that GBS may be promoted along particular directions through the sample, which can result in difficulty defining a REV. In this paper, a new description of superplastic deformation at a mesoscopic scale is proposed, assuming that the macroscopic strain results from the contributions of zones (sliding bands) which preferentially slide through the material. Along each band the grains can contribute to the macroscopic deformation by GBS or dislocation creep, depending on the local microstructure and on the experimental conditions. Theoretical predictions will be compared with experimental data.

8:55 AM INVITED

AN INTRINSIC DISLOCATION MODEL FOR GRAIN BOUNDARY SLIDING: *R. I. Todd*[1]; [1]University of Manchester/UMIST, Materials Science Centre, Manchester, M1 7HS UK

It has long been acknowledged that grain boundary sliding plays an important part in superplastic deformation. Many experiments have been conducted to study “pure” grain boundary sliding in bicrystals, but the details of the mechanisms responsible for sliding remain a matter for debate. In this paper, a model for grain boundary sliding based on the movement if intrinsic grain boundary dislocations is developed. The model correctly predicts a number of the experimentally observed trends at low stresses, including the influence of stress, and grain boundary type (e.g., low angle, “special”, “general”). The implications for the nature of grain boundary sliding during superplastic flow of polycrystals and the relationship to other models are discussed.

9:20 AM

THE ROLE OF PHASE BOUNDARY SLIDING IN THE SUPERPLASTIC DEFORMATION OF A Pb-Sn EUTECTIC ALLOY: *T. K. Ha*[1]; Y. W. Chang[1]; [1]Pohang University of Science and Technology, Center for Advanced Aerospace Materials (CAAM), Pohang 790-784 Korea

The superplastic deformation behavior of a Pb-Sn eutectic alloy, known as a representative microduplex superplastic material, was systematically investigated by employing the internal variable theory of structural superplasticity. A series of load relaxation and tensile tests were conducted on Pb-Sn eutectic and its constituent single phase alloys at room temperature. The flow curves obtained from load relaxation tests on superplastic Pb-Sn eutectic alloy were shown to consist of the contributions from boundary sliding (BS) and the accommodating plastic deformation of grains. The boundary sliding behavior could be described as a viscous flow process characterized by the power index value of Mg = 0.5, which is much less than the previously reported value of Mg = 1.0 for grain boundary sliding (GBS) obtained in quasi-single-phase superplastic materials such as 7475 Al and 8090 Al-Li alloys. From a series of surface observations during tensile tests, it was found that the smaller value of Mg was attributed to the onset of intense phase boundary sliding (PBS). An attempt to deduce optimum strain rate, one of the most important parameters in superplastic forming (SPF) process, has been also made.

9:40 AM INVITED
THE EVOLUTION OF GRAIN SIZE DISTRIBUTION AND ITS INFLUENCE ON THE BEHAVIOR OF SUPERPLASTIC MATERIALS: *D. Lesuer*[1]; R. Glaser[1]; C. Syn[1]; [1]Lawrence Livermore National Laboratory, Livermore, CA

It is generally recognized that the behavior of superplastic materials is strongly dependent on grain size. Most studies of this dependence have used some average measure of grain size, such as mean linear intercept. Materials, however, possess a collection of grain sizes which can have a strong influence on deformation behavior. For annealed materials this collection of grains can be represented by a log normal distribution. This paper addresses the evolution of grain size distribution during superplastic deformation and its influence on stress-strain-strain rate behavior and flow stability. This study involved studying three superplastic materials - an ultrahigh-carbon steel (UHCS), Al7475 and a copper alloy (Coronze 638). The evolution of the grain size distributions were studied as a function of strain, strain rate and temperature. The grain size distribution could be specified from the evolution of the mean value and standard deviation. The stress-strain-strain rate behavior was calculated from these distributions using a distributed parameters approach. The results have been used to study the problem of variable strain rate forming and the minimization of forming time.

10:05 AM Break

10:20 AM INVITED
FACTORS AFFECTING SUPERPLASTIC DUCTILITY AND ELONGATION: *C. H. Hamilton*[1]; K. Kannan[1]; [1]Washington State University, School of Mechanical and Materials Engineering, Pullman, WA 99164-2920

High tensile elongations form the basis for commercial use of superplastic forming for a wide range of applications. It is well known and accepted that the strain rate sensitivity, m = (lnσ/ln#), is an important parameter in superplasticity and understanding the rate sensitivity has been the focus of considerable research; however, it is also commonly found the correlation between m and elongation is not a good one. It is further known that superplastic ductility can also be affected by other factors such as cavitation. While there is general knowledge about superplastic ductility, it is nonetheless often found that there is considerable variability in ductility from lot to lot of an alloy, or even among repeated tests of the same lot of an alloy, which provides a challenge for understanding. In this paper, a range of material and deformation parameters are considered with respect to their potential effects on superplastic ductility, and results of predicted elongations are compared to experimental observations for some of these parameters. Included in the discussion are the m value, cavitation and cavitation gradients, stress state effects, temperature gradients, grain size variations, and dynamic recrystallization.

10:45 AM INVITED
STUDY OF SUPERPLASTIC DEFORMATION MECHANISMS USING ATOMISTIC SIMULATION APPROACH: *N. Chandra*[1]; P. Dang[1]; [1]Florida State University, Department of Mechanical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310

A clear knowledge of superplasticity hinges on the understanding of grain boundary structure and deformations. In this work, atomistic simulations are performed on a series of grain boundary structures in aluminum, and the energies associated with each of their equilibrium configurations are computed. Interatomic potentials using Embedded Atom Method (EAM) are used in conjunction with molecular statics and dynamics calculations to predict the structure, energy and mobility of symmetric tilt grain boundaries (STGB) in aluminum. At 0 K, the width of grain boundaries in these STGB are found to be about 10 angstrom and the magnitude of grain boundary energy is proportional to the interplanar spacing normal to grain boundary plane. When grain boundary energies are computed as a function of grain misorientation angle, three low energy configurations (corresponding to three twin structures) are found in the [110] STGB structures. Temperature has more effect on the grain boundary energy than structure. No significant sliding or migration was observed under 500 K without applied stresses. However, grain boundary mobility is promoted under an applied shear stress.

11:10 AM
A TECHNIQUE FOR THE NUMERICAL VALIDATION OF A MECHANISTIC MODEL FOR OPTIMAL STRUCTURAL SUPERPLASTICITY: *S. S. Bhattacharya*[1]; K. A. Padmanabhan[1]; [1]Indian Institute of Technology, Materials Testing Facility, Metal Forming Laboratory, Department of Metallurgical Engineering, Chennai 600 036 India

A mechanistic model for optimal structural superplasticity rate controlled by grain/interphase boundary sliding and based on isoconfigurational flow kinetics has been developed. The sliding process is considered at an atomistic level. The iso-structural strain rate-stress relationship has been derived. The analysis involves five physically meaningful constants, of which three can be derived theoretically. Earlier attempts at the numerical validation of the model either neglected the threshold stress needed to be overcome for mesoscopic sliding or used elaborate computational procedures based on trial and error. In this study, a technique is presented that obtains a unique solution by iteratively arriving at a "best fit" threshold stress value and then determines the activation energy and other deformation parameters in a straightforward manner. Data pertaining to several superplastic materials were analyzed and an excellent agreement between the results of the analysis and the experimental findings is demonstrated.

ZINC-BASED STEEL COATING SYSTEMS: PRODUCTION & PERFORMANCE: Session I - Phenomena in the Galvanizing Bath

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; Edwardo A. Silva, USS Technical Center C-20, Monroeville, PA 15146

Monday AM Room: Centro Room B
February 16, 1998 Location: Convention Center

Session Chair: Frank E. Goodwin, Int'l Lead Zinc Research Org., Research Triangle Park, NC 27009-2036

8:30 AM

THERMODYNAMICS AND KINETICS OF ALLOY FORMATION IN GALVANIZED COATINGS: *Nai-yong Tang*[1]; [1]Cominco Ltd., Product Technology Centre, Sheridan Science and Technology Park, Mississauga Ontario L5K 1B4 Canada

Theoretical analyses as well as experimentations reveal that the activity of iron in the vicinity of the liquid-steel interface is much higher than that in the bulk of a galvanizing bath where a dynamic equilibrium state prevails. Consequently, alloy formations in galvanized coatings are frequently dictated by kinetic factors. Coatings produced in baths containing aluminum marginally higher than the σ - η (Fe_2Al_{L5}) transition composition (0.134%Al at 460°C) may contain mestasable ζ and η crystals along with the η phase in the form of a partial inhibition layer. However, the formation of the inhibition layer in coatings produced in baths containing aluminum below the transition point is shown to be neither thermodynamically nor kinetically feasible. The σ - η transition point is the optimum composition for galvanneal production, and the optimum Al composition for galvanizing in higher than the transition point by only 0.02%.

8:50 AM

THE STRUCTURE OF THE INHIBITION LAYER FORMED DURING HOT DIP GALVANISING ON TiNb IF-DDQ, TiIF-DDQ AND TiNb+P IF-HSS SUBSTRATES: *I. Hertveldt*[1]; J. Craenen[1]; J. Dilewijns[1]; B. Blanpain[2]; C. Xhoffer[3]; B. C. De Cooman[3]; [1]University of Ghent, Laboratory for Iron and Steelmaking, Ghent Belgium; [2]MTM, Katholieke Universiteit Leauven, Heverlee Belgium; [3]OCAS NV, The research center of SIDMAR, ARBED, Zelzate Belgium

The formation of an inhibition layer at the substrate/liquid metal interface is the first stage of most of the hot dipping coating processes. In galvannealing, the inhibition layer must strike the delicate balance between two contradictory requirements. It must be able to prevent all reaction between the substrate and the liquid Zn until the strip has passed the thickness-controlling air knives and it must have extremely short breakdown times during the annealing process. The Zn baths used for producing galvannealing coated sheet steel are therefore generally characterized by a lower effective Al content (Al_{eff} than in the case of galvanising where a strong substrate/liquid Zn reaction inhibition is the only requirement. The bath Al content is known to influence the galvannealing kinetics, the coating adhesion and the powdering. It is believed that the formation and the breakdown of the inhibition layer, of which relatively little is known, are in fact the processes that control the two latter properties. In the present contribution, the morphology, the composition and the thickness of the substrate/liquid metal interface layer formed on TiNb IF-DDQ, TiIF-DDQ and TiNb+P IF-HSS substrates, after hot dip galvanising in Zn baths with Al_{eff} contents varying between 0.1 and 0.2%, will be reported in detail. The structure of the inhibition layer and the epitactic interfacial Zn-Fe-phase crystals formed on the inhibition layer were studied in function of the following process parameters: Al_{eff}, bath temperature and strip temperature. X-ray diffraction, electron microscopy, Auger electron spectroscopy and Rutherford Backscattering were used to fully characterize the substrate/coating interface. The results revealed that the inhibition layers were strongly influenced by the process parameters; it was found that the layer had a submicron thickness and its composition differed considerably from Fe_2Al_5.

9:10 AM

STUDY AND MODELING OF INTERFACIAL Al TAKE-UP IN CONTINUOUS GALVANIZING USING A LAB SIMULATOR: *Patrick Toussaint*[1]; L. Segers[1]; R. Winand[1]; M. Dubois[1]; [1]ULB

A lab scale continuous galvanizing simulator has been designed and used in order to study the effects of control parameters on interfacial Al take-up, with particular emphasis on hydrodynamical effects and very short immersion times, inferior to one second. Effects of Al concentration and process temperatures have also been studied. It was shown that Al take-up is extremely fast at the very early stages of the reaction, leading to the complete coverage of the steel within a tenth of a second, and that the reaction subsequently proceeded at a rate compatible with solid state diffusion through the inhibiting layer. A mathematical model is proposed to describe the take-up curves. Atomic force microscopy was used to analyze the morphology of the inhibition layer and energy dispersive x-ray spectroscopy for thickness measurements.

9:30 AM

Mn IN THE GALVANISED COATING: *Michel Dubois*[1]; [1]Cockerill Sambre, Départment Métallurgique, Flemalle Belgium

The behavior of Mn from the substrate in the continuous hot dip galvanising process is studied. The results are for the majority from industrial products and bathes and from a pilot line for only some of them. Galvanise and Galvannealed are considered. The study is only based on standard chemical analysis of substrates, coatings and melts. The Mn content in the melts is not zero. Variations exist depending mainly upon the substrate dissolution while entering the pot and the average coating weight. Both of them affect the Mn balance of the melt. The Mn content of the coatings can be split in 2 parts: one is coming from the liquid dragged zinc, the other is related to the substrate-coating interdiffusion and is included in the intermetallic. Mn take fully part in the Fe-Zn diffusion when Galvannealing. Its level is very constant along the same sheet as well as Gi as in Ga. Cold Rolled materials exhibit a Mn enrichment at the extreme surface of the sheet whereas Hot Rolled sheets show a depletion. Those enrichment and depletion are probably due to external oxidation during the process prior galvanising. The Mn surface concentration is of course depending upon its content in the substrate.

9:50 AM

INVESTIGATION OF THE INTERACTIONS BETWEEN LIQUID ZINC AND STAINLESS STEELS IN CONTINUOUS GALVANISING: *M. S. Brunnock*[1]; R. D. Jones[1]; G. A. Jenkins[1]; D. T. Llewellyn[1]; [1]British Steel, San Antonio, TX

Immersion tests for 120 hours in liquid zinc at 480°C have been carried out on a variety of iron-chromium and iron-chromium-nickel alloys including some commercial stainless steels. In binary iron-chromium alloys the increased chromium content provided to be detrimental to performance in liquid zinc. However, an addition of 9% nickel to an 18% chromium alloy produced an improved performance. Similar tests were carried out on commercial Types 410, 304, and 316 stainless steel, the latter being generally used as the current material for bath hardware rolls in hot-dip galvanizing lines world-wide. The austenitic stainless steel grads (Types 304 and 316) were more resistant than the martensitic grade (Type 410). A further series of experimental Type 316 stainless steel casts was made with different silicon contents in the ranges 0.1-0.5%. Tests on these samples showed variations in perfor-

mance linked to silicon content similar to that observed in low carbon steels.

10:10 AM
MATERIALS SELECTION FOR CONDUCTOR ROLLS IN ELECTROGALVANIZING PLANTS: *Raul B. Rebak*[1]; [1]Haynes International, Inc., Kokomo, IN 46904-9013

In the production electrogalvanized steel, zinc (Zn) or zinc alloys, mainly with iron (Fe) and nickel (Ni), are electrochemically deposited on the surface of carbon steel coils in a continuous way. The moving steel strip (cathode) is galvanized in a series of cells containing an acid electrolyte of Zn salts and an anode. Current is carried to the steel strip by a conductor roll located above each pair of cells. Since these conductor rolls are exposed to the acidic electrolyte, they may suffer corrosion and corrosion-erosion. Laboratory electrochemical tests have been performed to determine the corrosion rate, oxide film stability and repassivation rate of six different alloys in conditions simulating the operation of electrogalvanizing plants. Results show that alloys containing high amounts of Fe (such as stainless steels) are not recommended for this application. Taking into consideration properties such as corrosion rate, repassivation rate and wear resistance, it has been concluded that the ranking of the alloys for conductor rolls is as follows: ULTIMET<C-2000 <C-22 <G-30 <NAR-A<317L SS

10:30 AM
THE EFFECT OF OVERLAY COATING ON THE COATING PERFORMANCE OF ELECTROGALVANIZED STEEL SHEETS: *Jae-Ryung Lee*[1]; Tae-Yeob Kim[1]; S. K. Chang[1]; [1]POSCO, Coating Technology Research Team, Pohang, 790-785 Korea

The most troublesome defects of electrogalvanized steel sheets produced in CAROSEL type electrogalvanizing line (EGL) was the occurrence of band mark on the bottom surface during passing top coating section. Due to the uneven conductor roll profile, the zinc coating layers previously plated in the bottom coating section could easily be pressed by contacting band edge to produce continuous band marks along the strip moving direction. They could be observed even after painting. To overcome the detrimental effect of the band mark, it was proposed to overlay additional coating layers to shield the band mark. Lab-scale simulations of the overlay electroplating were revealed that the coating weight should be more than 5 g/m_2, and the whiteness of the coating layer were increased without lowering the glossiness.

10:50 AM
INVESTIGATION OF THE AIR KNIFE WIPING USING CFD APPROACH: *V. Laviosa*[1]; A. Milani[1], F. E. Goodwin[1]; [1]CSM, Italy

The uniformity of the coating weight in hot dip galvanizing is an important quality issue for subsequent forming and spot welding by the automotive industry. The final thickness of the coating film is controlled by the variables related to the wiping gas jets impinging on the strip and by process variables such as product quality and line speed, and thermophysical properties of the coating bath. This paper presents an analysis of the jet stripping process and demonstrates how a CFD (Computational Fluid Dynamic) approach to predict the pressure gradient and surface shear stress distribution gives a good estimate of the boundary conditions that determine and control the final coating thickness. A two-dimensional model to predict the final coating thickness is presented together with the major effects that bear an impact on the overall coating consistency. At the state of the art it is still difficult to get rid of overcoating at the strip edges (the "Edge Build-Up" effect, here referred to as EBU). Practical countermeasures have been empirically adopted in industrial air knife equipment, either by the original manufacturer or by subsequent modifications of the process engineers. However, a more general approach based on a fluid-dynamic model of the wiping gas flow pattern at the strip edges was required, in order to investigate the problem from a fundamental point of view. A proposed explanation of the EBU based on this modeling approach will be presented. The generated information can be used to predict the EBU reduction potential of practical designs. The turbulent flow of the air knife is difficult to measure in detail by means of anemometry and flow visualization, owing to very small physical dimensions and to compressibility effects. However, the work has proved that a fundamental approach, based on a suitable mix of both, mathematical and physical models is the best way of tackling the problem and of providing guidelines for design solutions tailored to the particular plant/process.

MDMD/SMD/IMM Luncheon
Sponsored by:
TMS Materials Design & Manufacturing Division, Structural Materials Division and Institute of Mechanics and Materials
Speaker:
Ali S. Argon
Massachusetts Institute of Technology
Topic:
"Contributions to Manufacturing Through the Mechanics/Materials Linkage"
Monday, February 16, 1998
12:00 noon
Location:
South Banquet Hall, Convention Center

TUTORIAL LUNCHEON LECTURES:

"The Role of Minerals In Papermaking and Paper Recycling"
Sponsored by the TMS Young Leaders Committee

Presenter:
John K. Borchardt
Shell Chemical Company

Monday, February 16
12:00 noon - 1:30 p.m.

Location:
Room 102, Convention Center

"Perspectives on Industry - University Cooperative Research Centers"
Sponsored by the TMS Continuing Education Committee

Presenters:
Joseph D. Defilippi, USS Technical Center
David K. Matlock, Colorado School of Mines

Monday, February 16
12:00 noon - 1:30 p.m.

Location:
Centro B, Convention Center

"Advanced Rechargeable Batteries: A Materials Science Perspective"
Sponsored by the TMS Continuing Education Committee

Presenter:
Donald R. Sadoway,
Massachusetts Institute of Technology

Monday, February 16
12:00 noon - 1:30 p.m.

Location:
Patio A, Convention Center