ADSORPTION, ION EXCHANGE, AND SOLVENT EXTRACTION: General Hydrometallurgy

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

Thursday AM Room: Plaza Room C
February 19, 1998 Location: Convention Center

Session Chair: R. G. Robins, Lindfield, New South Wales 2076, C. A. Young, Montana Tech, Metallurgical Engineering, Butte, MT 59701

8:30 AM INVITED
REMEDIATION OF AMD: THE GREEN PRECIPITATE PROCESS: R. M. Taylor[1]; *R. G. Robins*[2]; R. Arthur[2]; [1]Geo2 Limited, Melbourne, Victoria 3000 Australia; [2]AquaMin Science Consortium, Lindfield, New South Wales 2076 Australia

Lime addition to acid mine drainage (AMD) leads to the precipitation of metal hydroxides with calcium sulfate, and is the benchmark for remediation by chemical precipitation. Geo2 Ltd. (Melbourne, Australia) has developed an alternative precipitation methodology designated as the Green Precipitate Process. This novel process is based on the precipitation of double cation [M(II)-M(III)], hydroxy sulfate salts. When the composition of AMD is appropriate, the Green Precipitate Process provides a useful and more effective alternative to conventional liming. The characteristics and utility of the Green Precipitate Process will be described in terms of (1) the underlying theory, (2) a case study in which the Green Precipitate Process outperforms conventional liming, (3) a case study in which conventional liming remains the method of choice, and (4) a description of a mobile pilot pipe reactor rig which has been built by Geo2 to demonstrate the process.

8:55 AM INVITED
THE INFLUENCE OF ADSORPTION DENSITIES ON THE ION FLOTATION OF CU2+ WITH ALKYL SULFATES: *Fiona M. Doyle*[1]; Mr. John T. Newberg[1]; Dr. Kandipati Sreenivasarao[2]; [1]University of California at Berkeley, Department of Materials Science and Mineral Engineering, Berkeley, CA 94720-1760 USA; [2]Argonne National Laboratory, Energy Systems Division, Argonne, IL 60439 USA

Ion flotation is a process in which metal ions are removed from solution by interaction with dissolved, surface active organic collectors that adsorb preferentially at solution-air interfaces, and hence can be removed by bubbling air through the solution, then separating the resulting foam. This process has great potential in environmental and process engineering. We have used surface tension measurements of aqueous solutions of copper dodecylsulfate, tetradecylsulfate and hexadecylsulfate, to estimate the adsorption densities of copper as a function of concentration of surfactant. Ion flotation tests with these surfactants show that the copper removal rates and the minimum collector concentration attainable are consistent with the adsorption densities. As expected from Traube's rule, lower concentrations can be attained with longer chain length. Our findings suggest that collector selection for specific separations can be guided by thermodynamic principles, supplemented by straightforward surface tension measurements.

9:20 AM INVITED
THE HYDROGEN REDUCTION OF NICKEL - ELECTROCHEMICAL INTERPRETATION OF LITERATURE RESULTS: *I. M. Ritchie*[1]; S. G. Robertson[1]; [1]A J Parker Cooperative Research Centre for Hydrometallurgy, Murdoch, Western Australia 6150 Australia

At the present time, there is considerable activity in nickel processing. It seems certain that a number of new nickel plants will come on stream in the next few years. It also seems certain that some novel methods of extracting the nickel will feature in the new plants. For example, it has been demonstrated in Australia that nickel can be extracted from a sulphide ore using a combination of fine grinding and pressure leaching. It may also be possible to use bioleaching to bring the nickel into solution. However, choices for recovering the nickel from solution appear to be limited to electrowinning or hydrogen reduction. Although both processes are widely used, our understanding of the hydrogen reduction reaction is very limited. Most of the studies published so far focus on the kinetics of the reaction and the morphology of the product. In this paper, an attempt is made to synthesize the existing knowledge using an electrochemical approach. Evans-type diagrams are used to discuss the possible rate determining steps in the hydrogen reduction of nickel. It is concluded that much of the existing knowledge can be interpreted on this basis.

9:45 AM
LOW-LEAD NICKEL PRODUCTION BY ELECTROWINNING OF LEAD-CONTAMINATED NICKEL CHLORIDE SOLUTION IN A MEMBRANE-EQUIPPED ELECTROLYTIC CELL: *L. Liao*[1]; A. van Sandwijk[2]; *G. Van Weert*[3]; [1]University of British Columbia, Metals and Materials Engineering, Vancouver, BC V6T 1Z4 Canada; [2]Delft University of Technology, Raw Materials Technology, Delft 2628 RX The Netherlands; [3]Oretome Limited, Caledon East, ON L0N 1E0 Canada

Lead removal has been problematic in nickel production by electrowinning from chloride solutions, as developed by Falconbridge. The Cl2 leach liquor needs to be diluted by electrolyte to allow precipitation of the lead prior to electrowinning. This results in higher solution purification costs and an aversion to consider lead contaminated (secondary) feeds. In this paper, the electrowinning of nickel chloride is carried out in a membrane equipped electrolytic cell. When lead containing nickel chloride solutions are fed into the anode compartment and the anolyte is separated from the catholyte with a cation exchange membrane, lead remains in the anolyte due to the presence of a negatively charged chloride complex. The positive nickel ions migrate preferentially through the membrane to the catholyte, allowing a low-lead nickel cathode to be produced. Lead contamination in the catholyte and the cathode product has been tested as a function of lead concentration in the anolyte. Results are presented and discussed.

10:10 AM Break

10:25 AM INVITED
THE ELECTROCHEMICAL BEHAVIOR OF Zn-Pb(1.7%) IN GALVANIC STRIPPING: Chi-Ming Chang[1]; Thomas J. O'Keefe[1]; [1]University of Missouri - Rolla, Materials Research Center, Rolla, MO 65409

Alloy powders are commonly used in the purification of zinc sulfate solutions for use in standard electrowinning practice. The primary goal of this research is to study the use of zinc-lead alloys in the galvanic stripping reactions from organic solutions. The effects of various parameters on the electrochemical behavior of commercially produced zinc-lead allot powders were determined. A qualitative evaluation and summary of the influence of the more pertinent parameters on iron removal from di-(2-ethylhexyl) phosphoric acid (D2EHPA) by galvanic stripping is given. Water concentration, oxygen content and reaction temperature were the principal factors in affecting the reaction time and process efficiency. Activation energies were also calculated and indicate that the reaction changes from chemical to diffusion

control with increasing temperature in the rang of 35C to 45C. The results showed that zinc-lead alloy exhibited faster reaction rates and less sensitivity to process variables than SHG zinc as a reducing agent for galvanic stripping. The role of lead could be as cathodic sites for the reaction which enhances the zinc dissolution or anodic half reaction. The morphology of the zinc-lead alloy surfaces, before and after the reactions, supports this assumption.

10:50 AM INVITED
AUTOCLAVE TESTING A HIGH-ARSENIC, HIGH-CARBONATE GOLD ORE AT THE GETCHELL MINE, NEVADA: *Dave Tahija*[1]; John B. Ackerman[2]; [1]Gehenna Corporation, Butte, MT 59701; [2]Getchell Gold, Golconda, NV 89414

The Getchell Mine produces gold from a geologically complex ore bearing high concentrations of arsenic and carbonate minerals. The mill treats the ore using high temperature aqueous oxidation in autoclaves, followed by conventional carbon-in-leach gold recovery. We laboratory tested a variety of Getchell ores to determine the effects on gold recovery of conventional factors such as grind size and retention time, as well as the influence of factors such as ore variability and preliminary carbonate destruction. Because the mill is currently operating, we were able to directly compare certain laboratory predictions with operational results.

11:15 AM INVITED
MECHANISM FOR THE PHOTOCATALYTIC DESTRUCTION OF METAL-COMPLEXED CYANIDES: *C. A. Young*[1]; [1]Montana Tech, Metallurgical Engineering, Butte, MT 59701

The destruction of various cyanide species by several photolytic techniques has been investigated for the past few years. Process variables such as pH, Oxygen, and photolytic reagent type and amount have been examined. Literature surveys suggest heterogenous photocatalysis with anatase (TiO2) should behave similarly to homogeneous photolysis with hydrogen peroxide (H2O2). However, experimental evidence suggests otherwise. A new mechanism for the photocatalytic destruction of metal-complexed cyanides is therefore proposed.

11:40 AM CLOSING REMARKS

ALUMINA & BAUXITE: Alumina Properties

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

Thursday AM Room: Fiesta A
February 19, 1998 Location: Convention Center

Session Chair: T. J. Sivakumar, Jamalco, Kingston Jamaica

8:30 AM
IMPROVEMENT OF CHEMICAL QUALITY ALUMINA IN C.V.G. BAUXILUM WITH DOUBLE FILTRATION HIDRATE: *Mr. Juan Carlos Rojas*[1]; [1]CVG Bauxilum Alumina Plant, Edo Bolivar-Venezuela, Pto. Ordaz Venezuela

With the increasing of its annual production of metal grade alumina to 2 MMTM., CVG BAUXILUM included new process improvements into the production line. Knowing the high requirement from the international market, in regard to the chemical quality of alumina, specially the contents of total sodium (Na2O), C.V.G. BAUXILUM adapted part of the infrastructure installed with the purpose of reducing the contents of total sodium in the alumina, from a level of 0.45-0.55 to 0.30-0.40, concentrating basically on the reduction of soluble soda. This paper describes how with few changes in piping arrangement and using one third of the capacity installed for seed filtration, C.V.G. BAUXILUM obtained a significantly decrease of total sodium in the alumina, adopting a process of double filtration of hidrate product, previous to the calcination area.

8:55 AM
SEDIMENTATION AND SEGREGATION EFFECTS WHEN FILTERING COARSE ALUMINA FRACTIONS IN TOP-FEED FILTERS: *Mr. Jose Angel Sorrentino*[1]; [1]Laboratorio de Separaciones Macanicas, Universidad Central de Venezuela, Caracas 1015-A Venezuela

In the alumina industry, alumina suspensions are commonly filtered in a variety of vacuum filters, like drum, disc and horizontal filters. Coarse fractions are usually filtered, washed and dewatered on horizontal filters at the end of the Bayer process, just before the calciners. As both the high particle size and the high density of such particles give them fast settling velocities, the filtration process take really place due to a superposition of filtration and sedimentation, being the usual filtration theory unable to predict the time needed to achieve a liquid-free surface. Experiments were conducted in a transparent laboratory filter for both gravitational and gas pressure filtration. The time profile for the cake surface, the slurry-clear liquid interface and the liquid-air interface were recorded. Independent measurements of settling rates at different concentrations and cake permeability were also done. Good agreement was found between experimental and calculated profiles when using a model which include the sedimentation effect but underestimation of the cake formation (liquid-free surface) time up to 50% was found when using the typical filtration equation.

9:20 AM
THERMAL PROPERTIES OF ALUMINA POWDERS AND SYNTHETIC HALL-HEROULT CRUSTS: *Mr. Miguel A. Liavona*[1]; [1]Universisdad de Oviedo, Dept. Materials Science Reinerio Garcia s/n 33600, Mieres Spain

The procedures for evaluating water content and some properties of smelting grade aluminas were investigated. Thermal conductivities of commercial aluminas and density, hardness and thermal conductivity of synthetic crusts made from some of these aluminas have been determined by the hot wire and hot strip methods. A linear relation between thermal conductivity and density was observed at any temperature. An increase in thermal conductivity with increasing temperature in the temperature range 25-600^{o}C was observed for all the aluminas investigated while a constant to slight decrease was observed for the crusts studied in the temperature range of 25-800^{o}C.

9:45 AM Break

10:00 AM
FLUID-DYNAMIC CONTINUOUS MIXING OF FINE FREE FLOWING POWDERS: *Mr. Olaf Eichstadt*[1]; [1]ETH Zurich, Institute of Process Engineering and Cryogenics, Zurich Switzerland

Modern fine particle processes more frequently call for continuous mixers fully integrated into the process itself. Mixing in bulk solids at high solids concentrations using conventional mixing equipment requires high energy input and may cause breakdown of fragile powders. Novel fluid-dynamic mixers with time constant feed streams operating in a state of high expansion at low solids concentrations under conditions of high mobility allow for intense mixing within short periods of time. The mixing process is driven by the potential energy inherent in the feed streams it requires little energy input. In experiments, between 36 and 360 kg/h of Al(OH)3 (d50.3 between 30 and 110 microns m) were mixed with 0.18 to 1.8 kg/h of a black tracer materials (d50.3 approx. 10 micron m) in fluid-dynamic mixers differing in cross-sectional area. For the mixtures, the coefficient of variation STD(x).x-1 as a simple measure of mixture quality was in the vicinity.

10:25 AM
ATH TYPES AS FLAME RETARDANTS: THEY ARE STILL ALIVE: *Dr. Ruediger Schmidt*[1]; [1]Martinswerk GmbH, D-50127 Bergheim Germany

This paper will focus on the excellent flame retardant properties of aluminium hydroxide (ATH) being the flame retardant worldwide. ATH has the biggest market share by volume due to the fact that it offers the most cost effective and environmentally safe flame retardant solution

today and which in case of a real fire scenario produces low smoke, low carbon monoxide and low toxicity of the combustion gases. Thermoplastic, elastomers and thermosets flame retarded with pure ATH or combinations of ATH with further additives will be presented and the level of expertise reached with such materials will be shown. The product portfolio for top applications such as in the electronics industry (cabling), public transportation (parts for trains in tunnels, metros), public buildings (airports), automotive (wiring) as well as the corresponding manufacturing processes being in use for different types of ATH will be briefly presented.

10:50 AM

TECHNOLOGICAL INNOVATION IN AN ULTRA FINE GRINDING OF SPECIAL ALUMINA IN THE ROTARY-VIBRATION MILL WITH LOW FREQUENCY OF VIBRATION: *Dr. Jan Sidor*[1]; [1]Academy of Mining and Metallurgy Technical University, Faculty of Materials Science and Ceramics - Dept. of Building Materials, A-3, 30-059 Krakow Poland

Results of investigations of the ultra-fine grinding of special alumina were presented in this paper. The main part of work was study of the grinding kinetic and possibility of the obtainment of ground corundum material with the maximum contents of grains under 1 micron. Tests were carried out in the innovated laboratory rotary-vibration mill with a low frequency of vibration below 15 Hz or two sets of work. In the first one, the mill chamber had the motion collected with the rotary and vibration movements while in the second one, the mill chamber had only the vibration movement such as in the case of a classic vibration mill. Results show that it is possible to obtain ultra-fine corundum material with simultaneous high purity as well as low energy consumption of grinding process.

11:15 AM

HIGH TEMPERATURE MODIFICATION OF THE MORPHOLOGY OF CORUNDUM PRIMARY CRYSTALS OF SPECIAL ALUMINA DURING CALCINATION OF ALUMINIUM TRYHYDRATE WITH MINERALIZERS: *Dr. Mariusz A. Wojcik*[1]; [1]Academy of Mining and Metallurgy Technical University, Faculty of Materials Science and Ceramics - Dept. of Building Materials, A-3, 30-059 Krakow Poland

The properties of special alumina ceramics are very strongly influenced by the raw material alumina powder. The calcination has the most significant effect on the properties of alumina as alpha Al2O3, density, certain size and morphology of primary crystals and grains. The aim of investigations presented in this paper were to recognize the influence of temperature, time and mineralizers on the morphology of primary crystals of calcined special alumina obtained from slovakian aluminium trihydrate SH-4/B with different addition of boron and fluorine compounds. Cilas technic, sedimentary and microscopy methods were used for characterization of the morphology of grains and grain size distribution of calcined alumina. Results showed that only fluorine had the main effect on the shape and size of special alumina and were found that the primary crystals vary from 1 to 6 microns.

ALUMINUM REDUCTION TECHNOLOGY: Fundamental Studies

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

Thursday AM Room: Fiesta D
February 19, 1998 Location: Convention Center

Session Chair: Michel Reverdy, Aluminium Pechiney, Paris France

8:30 AM

THE DYNAMICS OF COMPONENTS OF THE ANODIC OVERVOLTAGE IN THE ALUMINA REDUCTION CELL: *Dr. Nolan E. Richards*[1]; [1]Consultant, Florence, AL 35630 USA

Of all the components of the voltage across an aluminum electrolytic cell, that over the diffusion or double layer between the carbon anode and the electrolyte has the greatest range in value. The reasons for these variations are explained and the quantitative accountability presented in terms of the variation in alumina concentration and to some extent, anode quality. When observed anodic overpotentials under operating conditions are analyzed in terms of basic principles, there are discrepancies. These can be rationalized by correlation with changes in actual current density from which inferences on the dynamics of useful anode area can be drawn. Both the trend and numerical values for "anode screening" derived from these considerations concur with physical models that have been published and the projections made from available physicochemical data presented over the years.

8:55 AM

INTERPRETING CELL VOLTAGE: *Warren Haupin*[1]; [1]Consultant, Lower Burrell, PA 15068 USA

The reason why Vext, the voltage intercept of cell volts extrapolated from a small change in current to zero current, is consistently lower than the true cemf, the counter electromotive force or back emf, is explained. The explanation requires a review of the components of cell voltage, how each component is determined, the time constant of each and how each component varies with current, anode to cathode spacing, bath composition (particularly alumina concentration) and bath temperature. The basis of and typical techniques for the use of Vext and pseudo resistance (or normalized cell voltage) to control alumina concentration, make anode adjustments and detect problem conditions is described.

9:20 AM

SPECTRUM ANALYSIS OF THE ANODE BUBBLING SOUND FROM ALUMINUM REDUCTION CELLS: *Jilai Xue*[1]; Harald A. Oye[1]; Per Utne[1]; Oystein Lindheim[1]; Odd A. Borset[1]; [1]The Norwegian University of Science and Technology, Institute of Inorganic Chemistry, N-7034 Trondheim Norway

The anode bubbling is closely related to anode performance and cell behaviors. However, the high temperature and corrosive conditions in industrial cells make a direct observation on the bubbling process difficult. This paper will present an alternative approach to investigate the in situ bubbling behaviors during the cell operations. A portable computer system with on-line data acquisition and spectrum analysis functions has been developed for use in industrial environment. The correlation between the sound signals and the anode bubbling was observed in both lab simulating tests and industrial processes. The signal patterns on normal anodes in a cell were obtained as reference. The variations in the signals patterns with abnormal anodes such as anode spike and deformation, anode cracking and anode effect were also investigated.

9:45 AM Break

9:55 AM

REVERSIBLE HEAT EFFECTS IN THE ALUMINIUM ELECTROLYSIS: *Dr. Qian Xu*[1]; Prof. Dr. Signe Kjelstrup[1]; [1]Norwegian University of Science and Technology, Division of Physical Chemistry, N-7034 Trondheim Norway

The thermoelectric power of cells relevant to the aluminium electrolysis was measured. The electrodes were oxygen on Pt, and the electrolyte was a mixture of NaF, AlF_3 saturated with Al_2O_3. The mole fraction of NaF varied from 0.69 to 0.75 (cryolite). The temperature of the reference electrode was held constant at a temperature around 1285 K, while the temperature of the other electrode was varied from this level up to 30 K. The Peltier heat of the electrode was surprisingly constant. At technical composition (molar ratio NaF/AlF_3=2.2) the Peltier heat was 241 kJ/mol. This confirms the prediction of Flem et al. (Light Metals 1996), that the reversible cooling effect at the anode, and the reversible heat production at the cathode are both significant during electrolysis of aluminium.

10:20 AM

LITHIUM IN ANODES AND CATHODES OF ALUMINIUM ELECTROLYSIS CELLS: *Rudolf P. Pawlek*[1]; [1]Technical Info Services and Consulting, Le Forum des Alpes, CH - 3960 Sierre Switzerland

The benefits of lithium salt additions to the electrolyte of aluminium electrolysis cells are well known and there are several ways to add lithium salts to the electrolyte in order to keep the lithium level in the electrolyte as constant as possible. One way is to mix lithium salts with green anode paste. Especially the catalytic effects of lithium salts in anodes and the influence of lithium salt additions in the electrolyte on the potlife will be discussed.

10:45AM

ELF CHARACTERIZATION OF IONO-COVALENT BONDINGS IN ALUMINUM(III) CHLORIDE-FLUORIDE COMPLEXES: Mr. Franck Fuster[1]; Pr. Bernard Silvi [1]; *Dr. Gérard Picard*[1]; Mr. Laurent Joubert[1]; [1]Laboratoire de Chimie Théorique (UMR 7616), Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cédex 05 France; [2]Laboratoire d'Electrochimie et de Chimie Analytique (UMR) 7575), ENSCP, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

A conformational study of the complex species relevant to the industrial electrorefining process of aluminum [1] has been performed. The four-fold coordinated aluminum(III) complexes involving chloride and fluoride anions have been investigated. Each bond of aluminum(III) with a particular chloride or fluoride anion has been characterized using the topological analysis of the electron localization function (ELF) gradient field [2]. This theoretical approach has been used to interpret the chloro-fluoride exchange reactions and the relative stabilities of these complexes. The effect of the calcium cation (formation of bimetallic complexes) has also been examined. Results have been compared with the existing equilibrium formation constants of these complexes [3]. References [1]G. S. Picard, V. A. Villard, D. M. Ferry, J.-M. H. Hicter and Y. Bertaud, in « Proceedings of the Seventh International Symposium on Molten Salts », C. C. Hussey, J. S. Wilkes, S. N. Flengas and Y. Ito, eds. « The Electrochemical Soc., Inc., Pennington, NJ, 90-17 (1990), 580. [2] B. Silvi and A. Savin, Nature 371 (1994), 683. [3] G. S. Picard, F. Bouyer, P. Hébant, A. Hemery, C. Bessada, Y. Castrillejo, L.Mouron and J.-J. Legendre, To be Published.

11:10 AM

PREPARATION OF Al-Si ALLOYS VIA SODIUM FLUOSILICATE: *Abd-elnasser Omran*[1]; I. H. Mahmoud[1]; A. A. Nofal[1]; F. M. Ahmed[1]; [1]Aluminium Company of Egypt, R&D Department, Nag-Hammady Egypt

Al-Si alloys and sodium aluminium fluorides were obtained by reacting molten pure aluminium with sodium fluosilifate. Sodium fluosilicate (Na_2SiF_6) had been produced in Egyptian super-phosphate fertilizer plants as a by-product from air pollution gaseous. The obtained products can be easily separated and used directly in casting shops or aluminium reduction cells in aluminum smelters. The produced Al-Si alloy is a high quality, containing up to 20% silicon and less than 0.12% iron. The factors affecting the composition of the produced Al-Si alloys were studied. These factors are: temperature, mixing speed, sodium fluosilicate to aluminium ratio, feeding rate and particle size. The results obtained were correlated to establish some imperical formulas representing the silicon content in the produced alloy with each factor. Microstructure examination and X-ray diffraction for the produced alloys and fluorine salts were examined.

ALUMINUM REDUCTION TECHNOLOGY: Material Studies

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

Thursday AM Room: Fiesta E
February 19, 1998 Location: Convention Center

Session Chair: James Ivey, Norton Refractories, MA

8:30 AM

STABILITY OF ANORTHITE-BASED DRY-BARRIER MIXES IN ALUMINUM REDUCTION CELLS' POTLINING: *C. Allaire*[1]; S. Afshar[1]; D. A. McIntyre[2]; [1]CIREP-CRNF, Ecole Polytechnique, Metallurgy and Materials Engineering Department, Montreal, Quebec H2M 2N9 Canada; [2]A. P. Green Industries, Inc., Mexico, MI 65265 USA

In aluminum reduction cells, potlining refractories are deteriorated in service by the action of cryolitic bath chemicals which migrate through the carbon cathode. In previous work, it was shown that the corrosion of aluminosilicate refractories by such chemicals is related to their alumina:silica ratio. However, the effect of other compounds, such as lime, which may be present in large amounts in such materials was not extensively treated in these works. In this paper, the effect of lime on the corrosion of aluminosilicate refractories submitted to the above conditions was studied on anorthite-based dry-barrier mixes having an alumina:silica ratio higher than 0.85 (in weight). Physical simulation testing as well as thermodynamic calculations showed that such materials gain higher corrosion resistance when their anorthite content is increased. Moreover, such materials made of 100% anorthite not only resist to corrosion by cell chemicals but also prevent the penetration of their fluoride components.

8:55 AM

EXPERIENCES WITH DRY BARRIER POWDER MATERIALS FOR ALUMINIUM REDUCTION CELLS: *Ole-Jacob Siljan*[1]; Kjell Thovsen[1]; Ole J. Junge[1]; Trygve B. Svendsen[1]; [1]Norsk Hydro ASA, Research Centre Porsgrunn, N-3901 Porsgrunn Norway

For more than 13 years Hydro Aluminium has conducted plant tests with Dry Barrier Powder Materials both in prebake and Soderberg cells. A total number of more than 60 cells have been started with Dry Barrier Powders. The presented paper reports results from a comprehensive measurement program for monitoring cell performance, and in addition autopsies have been performed on shut down cell to elaborate the deterioration mechanisms of Dry Barrier powders. The investigations have shown that Dry Barrier Powder materials have advantages compared to standard brick linings, giving rise to productivity increase of the installation. In most cases the operational results of cells lined with Dry Barrier Powders Materials are comparable to that of standard brick lined cells. However, there are clear indications that Dry Barrier Powder Materials results in poorer cell performance.

9:20 AM

RESULTS OF DRY GRANULAR BARRIER REFRACTORIES USED IN ALUMINUM CELL CATHODES: *Ms. Mary A. Windfeld*[1]; [1]REBL - Refractories Evaluations Laboratory Ltd., Surrey, B.C. V4N 1N1 Canada

A study was carried out involving a number of aluminum smelters worldwide that are currently or have previously used dry granular refractories as the barrier layer in their electrolytic cells. Many different dry granular barrier products have been installed and are currently in service in various cell designs. This paper discusses their performance to date with regard to various parameters including original criteria for installation, method of installation and makes comparisons to each smelter's standard design in terms of bath usage, effects on isotherms,

shell bottom temperatures, etc. A comparison of these results versus laboratory testing of this type of product is also included.

9:45 AM Break

9:55 AM

MOLTEN FLUORIDE ATTACK ON ANORTHITE BASED POWDER BARRIER MATERIALS IN ALUMINIUM ELECTROLYSIS CELLS: *Jorn Rutlin*[1]; Tor Grande[1]; [1]Norwegian University of Science and Technology, Department of Inorganic Chemistry, N-7034 Trondheim Norway

In order to evaluate the chemistry of the deterioration of anorthite based powder barrier materials, the phase relations in the system sodium fluoride - cryolite - anorthite are of most importance. Previously, the phase relations in the system sodium fluoride - anorthite have been reported. In the present paper, solid-solid and solid-liquid phase equilibria in the system cryolite - anorthite have been investigated by means of differential thermal analysis and powder X-ray diffraction. At excess amount of cryolite, nepheline is formed in addition to Na_3AlF_6-$NaCaAlF_6$ solid solutions. At higher anorthite concentrations $NaCaAlF_6$ is formed. Due to the low thermal stability of $NaCaAlF_6$, the solidus temperature is observed at as low temperature as 715 plus or minus 5 degrees C, which is considerably lower compared to the solidus along the sodium fluoride - anorthite composition line. A deterioration mechanism of anorthite refractory linings is presented based on these findings. Comparison to the deterioration of traditional fire clay linings is also given.

10:20 AM

GRADED NON-CONSUMABLE ANODE MATERIALS: *Professor J. A. Sekhar*[1]; Dr. J. Liu[1]; Mr. H. Deng[1]; Professor V. de Nora[1]; [1]University of Cincinnati, International Center for Micropyretics, Department of Materials Science and Engineering, Cincinnati, Ohio 45221 USA

It has been shown previously that graded materials have significant potential as non-consumable anodes for use in aluminum electrolysis*. The graded anodes also allow the possibility of being used at high current densities during the electrolysis process. The use of such graded materials requires excellent oxidation resistance and stability of the oxide layer under dissolution conditions. The key oxidation requirements and the relationship to chemical dissolution are explored for the Ni-Al-Fe-Cu class of micropyretically synthesized materials with various additives such as Zn, Sn, Si and Ti. * J. A. Sekhar, H. Deng, J. Liu, E. Sum, J. -J. Duruz and V. de Nora, "Micropyretically Synthesized Porous Non-Consumable Anodes in the Ni-Al-Cu-Fe-X System," pp 347-354, Light Metals, 1997.

10:45 AM

TiB_2/COLLOIDAL ALUMINA CARBON CATHODE COATINGS IN HALL-HÉROULT AND DRAINED CELLS: *Professor J. A. Sekhar*[1]; Professor V. de Nora[1]; Dr. J. Liu[1]; Ms. X. Wang[1]; [1]University of Cincinnati,, International Center for Micropyretics, Department of Materials Science and Engineering, Cincinnati, OHIO 45221

Titanium diboride composite coatings have been found to be promising materials for obtaining wettable cathodic coatings in Hall-Héroult cells*. The effect of the titanium diboride particle size and the colloidal alumina concentration and properties on the composite coating properties are examined. The requirements for a thick coating for drained cells is discussed with reference to the coating microstructure and economics. The mechanism of the low temperature sintering of the titanium diboride coating and the bonding between the titanium diboride and the carbon cathode is also discussed. * J. A. Sekhar, V. de Nora, and J. Liu, " Porous Titanium Diboride Composite Cathode Coating for Hall-Héroult Cells: Part 1: (Thin Coatings), to appear in Met. Trans. 1997.

CAST SHOP TECHNOLOGY: Session IVA - Equipment & Handling

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

Thursday AM Room: River Room B
February 19, 1998 Location: Convention Center

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

8:50 AM

DEVELOPMENT OF THE SHEET FOR CANSTOCK AND OTHER APPLICATIONS OF PECHINEY NEUF-BRISACH JUMBO 3CM CASTER: *Pierre-Yves Menet*[1]; Jean-Luc Hoffman[1]; Klaus Maiwald[1]; [1]Pechiney Rhenalu, Voreppe France

The Pechiney Rhenalu Neuf - Brisach Jumbo 3CM caster has been in operation since mid-1996. First of its generation, it was designed as a tool of development for thin strip casting both technology and products. Since its start up, technical improvements have been made and new features have been added. It has been used in the past months to determine casting parameters and conditions for thin strip casting of several alloys that are commonly cast on conventional casters. Production trials of new hard alloys have also been carried out on this machine for canstock applications. This paper reviews the various results obtained to date and future perspectives.

9:10 AM

RECENT INNOVATIONS IN ADVANCED CASTING TECHNOLOGY: *Randy S. Beals*[1]; Rue Duvvuri[1]; S. Hamer[1]; P. Vangala[1]; C. Romanowski[1]; B. Taraglio[2]; [1]Fata Hunter Inc, Riverside, CA 92507; [2]FATA Engineering, Pianezza, Italy

Continuing advancements in twin roll casting technology have required many elements of the casting machine design to be upgraded. In particular, the latest generation of casters have emphasized the need to further develop the molten metal feeding system, the method by which the release agent is applied to the rolls and the control of cast strip profile. This paper updates the progress of three FATA Hunter programs to improve these systems, describing the design evolution and outlining the results at each stage of development.

9:30 AM

INFLUENCE OF DIFFERENT LUBRICANTS APPLIED DURING THE CONTINUOUS CASTING OF ALUMINUM ALLOYS 6063 AND 5182: *Mr. Frank T.H. Doernenburg*[1]; Prof. Siegfried Engler[1]; [1]RWTH Aachen, Foundry-Institute, Aachen 52056 Germany

The production of continuously cast billets without any surface defects is becoming more and more important because the quality of the final products is already determined by the quality of the billets. A very useful aid therefore is the application of lubricants. The DC casting unit allowed the production of billets of 2m length. Different kinds and varying amounts of lubricants were continuously applicated. The bars were macro- and microscopically examined, especially the surface finish and the near-surface structure (segregation zone). To get information about the friction between mold and solidifying shell, three force sensors were installed. Temperature measurements in the mold allowed to get information about the formation of the air-gap. The effect of different kinds and amounts of lubricants were correlated with the results of metallographic analysis.

9:50 AM

NUMERICAL MODELING OF FLUID FLOW PHENOMENA IN THE LAUNDER - INTEGRATED TOOL WITHIN CASTING UNIT DEVELOPMENT -: *Mr. Gerd-Ulrich Grün*[1]; Dr. Wolfgang Schneider[1]; [1]VAW Aluminium AG, Research & Development, Bonn D-53117 Germany

Time-dependent three-dimensional filling simulations of the launder as well as steady-state calculations of fluid flow in the launder and the billets are used at VAW aluminium AG R&D as a standard tool to optimize mold filling in the start-up phase as well as hot metal support during the stationary phase for all level pour casting units with AIRSOL VEIL molds. Following a specified simulation strategy the time-dependent fluid flow calculations are the basis for the development of a launder design that guarantees a smooth and uniform filling for all molds in the start-up phase, while the optimization of the steady-state flow field yields lowest possible temperature differences between single molds during the production phase. The application of this technique is demonstrated by means of selected casting unit examples. The calculated filling patterns in the launder for these different casting unit designs are discussed in dependency of the geometry, the filling strategy and rheological properties of the melt. In case of the steady-state simulations the effects related to variations of casting velocity and inflow conditions are presented in addition to the influence of the geometrical design. In all cases the resulting flow fields and temperatures in the launder show good agreement with casthouse observations and measurements.

10:10 AM

COMPUTER MODELLING AND PRACTICAL EXPERIENCES OF TEMPERATURE LOSS IN PRE-CAST LAUNDER SYSTEMS AND CASTING TABLES: *J. O. Marthinusen*[1]; S. Ray[1]; [1]Foseco International Ltd, England

A temperature model for predicting performance of launder systems has been developed during the last 18 months. The paper describes the factors affecting launder performance with particular reference to the model. The use of the model to optimize launder design is discussed. The paper concludes by comparing practical experience with predicted results.

10:30 AM

CENTRIFUGAL CASTING OF ALUMINUM ALLOY TUBULAR COMPONENTS: *Dr. J. U. Ejiofor*[2]; K. G. Cook[1]; R. G. Reddy[1]; [1]University of Alabama, Dept. of Metallurgical and Material Engineering, Tuscaloosa, Al 35487-0202 USA; [2]Metallurgical Control, Shelco Foundries, Inc.

Tubular Al-Si alloy castings were centrifugally-cast using a horizontal casting machine. The effects of mold rotation speed (450-800rpm) and mold coating on the pickup of the molten alloys were studied. Bentonite, graphite/bentonite powder mix, and boron nitride solution were used to coat the inside of the horizontal low- carbon alloy steel mold. Excellent pick-up of the alloys A380.1 and A413 (pouring temperature, 650 degrees C) was observed at rotation speeds greater than 650 rpm when the graphite/bentonite mixture was used. Below this value, the pick-up of alloys was increasingly poor and resulted in defective castings that were not reproducible of the mold. The use of different coatings resulted in quite different minimum rotation speed needed to yield excellent pick-up.

10:50 AM

AN ADJUSTABLE MOULD FOR SHEET INGOT PRODUCTION: *Clark Wver*[1]; Pierre Marchand[1]; Mike Parsons[2]; Bob Chow[2]; Yves Charbonneau[3]; [1]Alcan Smelters and Chemicals Ltd., Jonquere, Quebec Canada; [2]Kitimat, B.C. Canada; [3]Montreal, Quebec, Canada

The rather high capital cost of sheet ingot moulds and bottom blocks tends to encourage sheet ingot producers to minimize the number of ingot widths that they produce. To overcome this obstacle, some sheet ingot casting plants have developed and use adjustable width moulds. These moulds can be complicated to adjust from one dimension to another and the ingot flatness is lost rapidly as the mould width is changed. This paper describes an adjustable sheet ingot mould that is robust, easily changed from one width to another and that maintains the flattest ingot possible over a wide range of ingot widths.

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

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

Thursday AM Room: 102
February 19, 1998 Location: Convention Center

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

8:30 AM INVITED

ON THE QUESTION OF INTERPHASE BOUNDARY STRUCTURE ASSOCIATED WITH MASSIVE TRANSFORMATIONS: *Hubert L. Aaronson*[1]; [1]Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213 USA

Classically, massive:matrix boundary structure is viewed as incoherent(Massalski, 1958). From nucleation theory, however, it was proposed that these boundaries are partially coherent (Aaronson, Laird and Kinsman, 1968). The latter proposal was supported by nucleation kinetics studies on the $\beta \rightarrow \alpha$ transformation in Ti-Ag and Ti-Au (Plichta et al., 1980) and by TEM showing partial coherency at β:ξ interfaces in a Ag-Al alloy (Mou & Aaronson, 1994). However, current TEM research on the structure of α_2:γ_m, interfaces in near-TiAl alloys (Zhang et al., 1996; Howe, Univ. of Virginia, and Vasudevan, Univ. of Cincinnati, res. in prog.) and on counterpart interfaces in τ MnAl (Hoydick and Soffa, Univ. of Pittsburgh, res. in prog.) shows no such evidence, even though both exhibit large areas of planar facets. In this talk the possibility that the twinning and slip often associated with massive transformations may play a role in misfit compensation will be considered.

9:00 AM INVITED

INTERFACES — COMPATIBLE DEFORMATION AND RECRYSTALLISATION NUCLEI: *M. Niewczas*[1]; O. Engler[2]; J. Bingert[2]; Z. S. Basinski[2]; David M. Embury[2]; [1]McMaster University, Department of Materials Science and Engineering, Hamilton, Ontario L8S 4L7 Canada; [2]Los Alamos National Laboratory, Los Alamos, NM USA

Copper single crystals deformed at 4.2K exhibit a sequence of deformation by slip followed by twinning and a final stage requiring compatible deformation between the matrix and the twin regions, The scale of the twin and matrix regions are such that they can be studied by a combination of E.B.S.P, and detailed T.E.M. The results show how compatible flow occurs in these structures and also how the deformed structure and the nuclei for recrystallisation are related for the deformed structure prior to twinning and after the introduction of the twin-matrix interfaces.

9:30 AM INVITED

DISCONNECTIONS:THEIR ROLE IN INTERFACE STRUCTURE AND PHASE TRANSFORMATIONS: *Robert C. Pond*[1]; T. Nixon[1]; [1]University of Liverpool, Department of Materials Science and Engineering, Liverpool L69 3BX UK

Disconnections, line-defects in interfaces which exhibit both dislocation and step character, were first discussed by Hirth in 1994. In combination with the precise definition of their topological properties(Burgers vectors and step heights), this concept is valuable for modeling interface structure and processes such as phase transformations. An overview of recent applications of this approach is presented. The topological properties of individual disconnections can be derived using symmetry arguments, and is outlined by way of introduction. As an illustration of the description of an interfacial structure, a martensitic interface is discussed in terms of an orthogonal array of disconnections, and the correspondence with the Phenomenological Theory of Martensite Crystallography demonstrated. Motion of disconnections effects phase transformation, and in general requires a diffusive flux of material as described by an equation due to Hirth and Pond (1996). Special circumstances must pertain for diffusionless processes, as discussed here for the case of martensite formation.

10:00 AM

INTERFACIAL STRUCTURE AND DISSOCIATION IN DIAMOND CUBIC MATERIALS: *Professor William A. T. Clark*[1]; Dr. Anita Garg[2]; [1]The Ohio State University, The Graduate School, Columbus, OH 43210; [2]NASA Lewis Research Center, Cleveland, OH 44135

In the technologically important class of diamond cubic materials, recent research indicates that interfacial structure is considerably more complicated than in simple, monotomic, materials. In this account of a study initiated in collaboration with John Hirth, two aspects of boundary structure in Si are described. In the first, the interfaces in a Si polycrystal are analyzed, and it is shown that boundary orientations which can be described by rotations of the two crystals about a common <110> are favored. This dissociation is further shown to be consistent with the constraints imposed by the covalent bonding along the various interfaces. In the second, the interfacial structure of Σ3 boundaries in Si, created by sintering single crystals, was examined. In order to accommodate the sometimes sizable (up to 4°) deviations from the exact twin orientation, a network of screw dislocations is present, on which is superimposed set of edge dislocations, as might be expected. What is unusual, however, is that the screw dislocation network is orthogonal, rather than hexagonal. One set of the screw dislocations and the edge dislocations have Burgers vectors predicted from the DSC lattice, but the second set of screws have crystal lattice dislocation Burgers vectors. This is attributed to the need to minimize the dislocation core energies in dense dislocation networks.

10:20 AM

CONTROL OF CRYSTALLINE ORIENTATION AND GRAIN ISOLATION IN MAGNETIC THIN FILMS FOR ULTRA HIGH DENSITY STORAGE MEDIA: *Sivaraman Guruswamy*[1]; [1]The University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112 USA

The nucleation and growth of Co-Cr and Co-Cr-Pt-Ta films on super-smooth (<5 Angstrom RMS) and textured NiP/Al substrates (~50 Angstrom RMS) for longitudinal and perpendicular recording media is examined. In the current efforts underway in achieving storage densities beyond 10 Gbits/in^2 the control of c distribution and the grain isolation by dopant segregation is critical in achieving high signal to noise ratios. The paper will present an overview of the current understanding of the different microstructural factors that influence the signal and noise and how these ideas have been used in the processing of the perpendicular and longitudinal media examined in this work. The magnetic and underlayer films in the media were prepared by DC magnetron sputtering in an UHV sputtering system. The magnetic properties were characterized by VSM and AGM. The orientation distribution in these nanocrystalline films are evaluated using high resolution X-ray diffraction and by using lattice imaging and orientation imaging in TEM and this information is correlated with magnetic and recording properties.

10:40 AM

COMPUTER SIMULATION OF THE SLIDING RESISTANCE OF A SIGMA 11 <101> {323} GRAIN BOUNDARY IN ALUMINUM: *Dr. Richard J Kurtz*[1]; Dr. Richard G. Hoagland[8]; [1]Pacific Northwest National Laboratory, Materials Science, Richland, WA 99352; [8]Washington State University, Dept. of Mechanical and Materials Engineering, Pullman, WA 99164

Grain boundary (GB) sliding, which involves the relative translation of two adjacent grains by a shear parallel to the boundary plane, is an important mode of deformation in elevated temperature processes such as creep and superplasticity. It is generally accepted that GB sliding occurs by the motion of dislocations rather than the simultaneous shear of the entire boundary. Only limited information has been obtained on the atomic-scale mechanisms by which GB sliding occurs and, in particular, about accommodation mechanisms. High-resolution transmission electron microscopy has been able to provide some details on GB structure, but little information on the dynamic processes of GB sliding. This problem is ideal for study via molecular dynamics simulation techniques since atomic-scale processes can be conveniently modeled. A computer simulation has been performed to determine the effect of extrinsic GB defects on the sliding resistance of a Sigma 11 <101> {323} symmetric tilt boundary in aluminum by means of an embedded atom method potential. The sliding resistance of the equilibrium GB was determined by computing the low-temperature boundary energy as a function of in-plane rigid body translation of the two grains within the cell of nonidentical displacements. Extrinsic GB dislocations were introduced into the models by t he imposition of the exact anisotropic elastic displacement field for a bicrystal interface. Some GB dislocations must be accompanied by geometrically necessary steps (in which case the pair form a disconnection) to avoid the formation of GB faults. Elastic band methods were utilized to determine the energetics and stresses required to move these defects and thereby promote GB sliding and migration.

11:00 AM

ROLE OF GRAIN BOUNDARY DEFECTS IN THE FCC TO 9R TRANSFORMATION AT AN INCOHERENT TWIN BOUNDARY IN COPPER: *Dr. Douglas Lloyd Medlin*[1]; Dr. Geoffrey H. Campbell[1]; C. Barry Carter[1]; [1]Sandia National Laboratories, Surface and Microstructure Research Dept., Livermore, California 94550 USA

Small volumes of metastable 9R stacked material are known to form at incoherent twin boundaries in low stacking fault energy FCC metals. The 9R stacking sequence (ABC/BCA/CAB) is a close-packed arrangement that is equivalent to an FCC stacking of {111} planes with an intrinsic stacking fault inserted at every third plane. In this paper, we present high resolution transmission electron microscopy observations showing the dynamic transformation from FCC to 9R stacking occurring at an incoherent twin boundary in copper. This growth of the 9R phase accompanies the shear of the bicrystal parallel to the plane of the boundary, which results in an increase in the rigid body displacement in the [111] direction. The transformation can be understood in terms of shear processes that are controlled by the arrays of Shockley partial dislocations comprising the two FCC/9R interfaces. Defects in the periodic arrangement of these dislocations result in 9R stacking errors that propagate as the 9R slab grows. This work is supported by USDOE Office of Basic Energy Sciences, Division of Materials Science, under contracts DE-AC04-94AL85000 (Sandia) and W-7405-Eng-48 (LLNL).

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

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

Thursday AM Room: Centro Room C
February 19, 1998 Location: Convention Center

Session Chair: Bruce MacDonald, National Science Foundation, Division of Materials Research, Arlington, VA 22230, Stephen Muhl, Universidad Nacional Autonoma de Mexico, Coyoacan Mexico

8:30 AM INVITED
LASER PROCESSING AND PROPERTIES OF NITRIDES: *J. Narayan*[1]; [1]North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC 27695-7916

This paper reviews laser processing of aluminum nitride, titanium nitride, cubic boron nitride and carbon nitride films for applications ranging from optoelectronics and electronics packaging to superhard protective coatings. The epitaxial films of aluminum nitride and titanium nitride on substrate such as sapphire have been grown via domain matching epitaxy where integral multiples of lattice constants or major planes match across the interface. The cubic boron nitride and carbon nitride films are formed by ion- assisted pulsed deposition. We discuss the details of processing and properties of these novel thin film heterostructures.

9:00 AM
GROWTH AND CHARACTERIZATION OF CRYSTALLINE HARD COATINGS PREPARED BY PULSED LASER DEPOSITION METHOD: *Ashok Kumar*[1]; H. L. Chan[1]; M. Shamsuzzoha[2]; J. A. Barnard[2]; [1]University of South Alabama, Department of Electrical Engineering, Mobile, AL 36688; [2]The University of Alabama, Department of Metallurgical and Materials Engineering, Tuscaloosa, AL 35487

Hard coatings of carbides and nitrides of metal have a large number of applications in modern technology owing to their interesting, and in some ways unique, physical and chemical properties. Thin film coatings of carbides (titanium carbide, silicon carbide and boron carbide), nitrides (titanium nitride, silicon nitride, and aluminum nitride) and also multilayered titanium nitride/titanium carbide were deposited on Si (100) substrates using pulsed laser deposition (PLD) method. The structural and microstructural properties of these films have been characterized using x-ray diffraction, scanning and transmission electron microscope techniques. The mechanical properties of the films were evaluated to measure the hardness and modulus values. It has been shown that the films deposited at higher temperature have the best crystalline quality structures and also have higher hardness and modulus values compared to films deposited at lower temperature. The mechanical properties of the carbides, nitrides and multi layered coatings will be discussed with reference to other ultrahard thin films such as diamond and diamond-like carbon. The research was supported by Alabama NASA EPSCoR, NSF ARI (DMR # 9512324), and NRC Twinning grants.

9:20 AM
PULSED LASER DEPOSITION OF MIXED METAL CARBIDE COATINGS: ALLOYS AND MULTILAYERS: *Robert Leuchtner*[1]; J. Krzanowski[2]; W. Brock[2]; [1]University of New Hampshire, Department of Physics , Durham, NH 03824; [2]University of New Hampshire, Department of Mechanical Engineering

The development of coatings with high levels of hardness, wear resistance and toughness is an important area of research with numerous military and commercial applications. Our research is focused on the development of multi-component and multi-phase carbide coatings deposited by pulsed-laser deposition (PLD). PLD is a vapor deposition process that combines near atomic-level control of the surface composition with the high kinetic energies of the condensing vapor produced by the laser ablation. We are exploiting the PLD process to routinely deposit single and multi-phase transition metal carbide coatings. In addition, we have a unique facility for performing in-situ plume diagnostics using mass spectrometry and have conducted experiments on the energetics of the deposition process. Typically, the laser ablation process produces ions with kinetic energies ranging from ~5-100 eV while the neutral atoms have kinetic energies on the order of 1-5 eV. Coatings have been deposited from TiC, VC, ZrC targets, as well as a ZrC/VC alloy target. The coatings have been evaluated using nano-indentation testing, x-ray diffraction, electron microscopy, x-ray photoelectron spectrometry, and pin-on-disk friction and wear testing. While the single-component films are typically polycrystalline with a preferred (111) orientation, the ZrC/VC alloy films are (110) oriented. The ZrC/VC alloy films also performed far better in the friction and wear test than either the ZrC or VC films. The crystallographic structure and properties of the metal carbide films will be discussed in light of the energetics of the depositing vapor.

9:40 AM
A TEM STUDY OF EPITAXIAL (100) TIC FILM GROWN ON SI (100) SUBSTRATES BY PULSED LASER DEPOSITION METHOD: *M. Shamsuzzoha* [1]; Ashok Kumar [2]; [1]The University of Alabama, School of Mines and Energy Development and Dept. of Metallurgical & Materials Engineering,, Tuscaloosa, AL 35487; [2]University of South Alabama, Department of Electrical Engineering, Mobile, AL 36688

Titanium Carbide (TiC) thin film deposited on Si (100) substrate by Pulsed Laser Deposition (PLD) method has been investigated by transmission electron microscopy. The film appears single crystal but contains a high density of defects such as dislocation, stacking fault, etc. It grows epitaxially on the substrate with a simple but unusual parallel axes orientational relationship. Interface between film and substrate is smooth with substrate showing no sign of any elastic strain associated with misfitting of lattices across the interface. The observed structural features are explained using a geometrical model based on long range lattice matching.

9:50 AM INVITED
LASER ENGINEERED NET SHAPING (LENS): BEYOND RAPID PROTOTYPING TO DIRECT FABRICATION:: *D. M. Keicher*[1]; W. D. Miller[1]; J. E. Smugeresky[2]; J. A. Romero[3]; [1]Optomec Design Company, Albuquerque, New Mexico 87123; [2]Sandia National Laboratories, Livermore, California 87185; [3]Sandia National Laboratories, Albuquerque, New Mexico

The laser Engineered Net Shaping (LENS) technology, using a laser-assisted material deposition process coupled with existing Rapid Prototyping (RP) techniques, has demonstrated the feasibility to fabricate geometrically complex shapes in functional materials directly from a CAD solid model. The LENS process starts with an .STL faceted representation of a CAD solid model to generate a layered pattern representation of the object to be fabricated in a fashion similar to existing RP techniques. However, unlike these existing RP techniques, the material properties of the LENS fabricated structures can be made to be as good, or better than conventionally processed materials. Hardware has been fabricated using a variety of materials including 316 stainless steel, Inconel 625 and H-13 tool steel. Due to the localized heating properties of the laser, a fine grain structure can be achieved which exhibits improved strength and ductility. Additional studies have shown that very good dimensional repeatability and a moderately good surface finish can be achieved directly from the LENSTM process.

Results from studies aimed at improving these properties will be reported on. Additional results from experiments performed to identify methods to create a multiple material systems including functionally graded and step function transitional characteristics will also be discussed.

10:20 AM Break

10:35 AM INVITED
THE GROWTH AND CHARACTERIZATION OF BORON NITRIDE COATINGS: *Gary L. Doll*[1]; [1]Timken Research, Materials Science Department, Canton, OH 44706

Deposition parameters greatly affect the phase, microstructure, and chemical bonding of boron nitride coatings grown by ion-assisted PVD processes. BN coatings which have been grown by an ion-assisted pulsed laser deposition process have been examined by many characterization techniques, including infrared absorption, Auger electron spectroscopy, NEXAFS, and transmission electron microscopy. Elemental bonding and the crystallinity of BN coatings grown in three nitrogen ion energy regimes: high (2500 eV), low (700 eV), and without ions (0 eV) are examined, and the results interpreted within the framework of a compressive stress mechanism for cBN film growth. In addition, recent results are reported in which post-deposition ion implantation into sp^2-bonded BN coatings which are under compression, is found to result in amorphous, sp^3-bonded BN.

11:05 AM
SYNTHESIS AND PROPERTIES OF CUBIC BORON NITRIDE THIN FILMS: *H. Felderman*[1]; M. Sebastian[1]; R. Merk[1]; M. Ceste[1]; C. Ronning[1]; H. Hofsass[1]; [1]Universität Konstanz, Falkutät für Physik, Konstanz D-78457 Germany

The high thermal stability in air and the chemical inertness against iron-containing materials makes cubic boron nitride (c-BN) an interesting hard coating material. To date, the growth of c-BN thin films has only been achieved with methods utilizing energetic particles, such as ion assisted PVD and CVD or pure ion beam deposition. Much progress was made to grow films with high c-BN content, good adhesion and a thickness exceeding 1 μm. Unsolved problems are related to the high compression stress and film growth mechanism itself, which is still poorly understood. The growth mechanism of c-BN can be studied using mass selected ion beam deposition. We have investigated the role of ion energy and substrate temperature on the phase formation and the evolution of compressive stress. Threshold values for the ion energy and substrate temperature exist, above which c-BN growth takes place. The thermal stability of c-BN films and possibilities to minimize compressive stress will be discussed.

11:25 AM INVITED
DEPOSITION OF CUBIC BORON NITRIDE BY MAGNETRON SPUTTERING: PROCESS DIAGNOSTICS AND FILM CHARACTERIZATION: *F. Richter*[1]; R. Pintaske[1]; J. Hahn[1]; Th. Welzel[1]; [1]Technische Universität Chemnitz, Institüt für Physik, Chemnitz D-09107 Germany

Three different magnetron sputtering processes for cubic boron nitride (c-BN) deposition have been investigated, considering both r.f. and d.c. excitation as well as h-BN and pure boron as the target materials. The processes have been characterized in situ mainly using Langmuir probes under laser induced fluorescence. From those measurements together with data of the deposited films, a quantitative analysis of the deposition process has been performed and conclusions concerning critical deposition conditions for c-BN formation have been drawn. Among others, we calculated the total incorporated momentum per deposited boron atom, p_{tot}/B, and found that a critical value of this quantity has to be exceeded in order to nucleate c-BN in the films. Within the error of measurement, these critical values were found to be one and the same for the three processes under investigation, despite the distinct peculiarities of those processes. After nucleation of c-BN growth has been completed, p_{tot}/B may be reduced significantly without interruption of the c-BN growth. The critical value of ptot/B for maintaining c-BN growth is only about 25% of the value for c-BN nucleation. This finding offers the possibility to grow c-BN thin films under reduced ion impact.

11:55 AM
STRESS ANALYSIS IN C-BN FILMS BY X-RAY DIFFRACTION USING SIN2φ METHOD: *Guanghua Chen*[1]; Hui Yan[1]; Xingwang Zhang [2]; Xiying Ma[2]; [1]Beijing Polytechnic University, Applied Physics Department, Beijing 100022 China; [2]Lanzhou University, Physics Department, Lanzhou 730000 China

The mixed-phase BN thin films have been prepared on Ni substrates by thermal filament assisted RF plasma chemical vapor deposition (CVD). The stress and strain in BN films is determined by X-ray diffraction analysis using the Sin2φ and assuming an effective stress model. The results show that the compressive stress in c-BN phase is much greater than that in h-BN phase for the same film, when both c-BN and h-BN in the same film have similar amount of elastic strain. Effective stresses in the films were compressive and varied from 2.8 GPa to 12 GPa with increase of c-BN content resulting from increasing substrate temperature (700-1200°C). The decrease of strain and the increase of c-BN content resulting from increasing substrate temperature is responsible for the dependence of stress in the films on the substrate temperature. The dependence of the compressive film stress on c-BN content is also given in the present work. The increase of compressive film stress with increasing c-BN content is due to the elastic modulus of c-BN being greater than that of h-BN.

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

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

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

Thursday AM Room: 108
February 19, 1998 Location: Convention Center

Session Chairs: K. Natesan, Argonne National Laboratory, Energy Technology Division, Argonne, IL 60439; C. G. McKamey, Oak Ridge National Laboratory, Oak Ridge, TN 37831

8:30 AM INVITED
PROCESSING AND FRACTURE PROPERTIES OF Fe-40AT%Al MATRIX COMPOSITES REINFORCED BY CERAMIC PARTICLES AND FIBERS: *Masahiro Inoue*[1]; Katsuaki Suganuma[1]; Koichi Niihara[1]; [1]Osaka University, The Institute of Scientific and Industrial Research, Osaka 567 Japan

Synthetic process of Fe-40at%Al alloys and its composites by reactive hot-pressing was investigated. Mechanical properties of the alloy can be controlled by micro-alloying of B and Si using reactive hot-pressing. The doping of 0.1at%B is effective for toughening by suppression of environmental embrittlement. The alloying of 0.5-5at%Si significantly affects improvement of yield strength. The Fe-40at%Al matrix composites containing with various ceramic particles, whiskers and short fibers can be also fabricated successfully by reactive hot-

pressing. The increment of yield strength by the addition of 5-15vol% reinforcements is limited to 1.5 times higher than that of the monolithic alloy. However, the significant strengthening is achieved in the composites with ß-SiC particles and whiskers due to the dissolution of a few at%Si. Fracture properties of the alloys and the composites measured with chevron-notched testing bars will be discussed in detail.

9:00 AM

POWDER METALLURGICAL PROCESSING OF IRON ALUMINIDES: *S. C. Deevi*[1]; [1]Philip Morris, Research and Development Center, Richmond, VA 23234 USA

Iron aluminides are attractive for high temperature applications due to their high melting points and excellent oxidation resistance. Powder processing techniques employing reaction synthesis principles offer a considerable flexibility in exploiting the unique attributes of iron aluminides and their composites. A variety of powder processing techniques such as hot extrusion, hot pressing, and hot isostatic pressing were used to obtain fine grain iron aluminides (FeAl) using Fe and Al powders with Al content ranging from 20 to 30 Wt.%. Composites of iron aluminides were obtained with the addition of ceramic powders, and by in-situ synthesis technique based on thermite reactions. Tensile properties of powder processed aluminides measured at room, and elevated temperatures exhibit higher strengths, and better elongations than the cast materials. Fractured surfaces of powder processed iron aluminides also provide evidence of ductile tearing as opposed to brittle fracture observed with the cast materials. The influence of processing techniques and processing parameters on the microstructures, and on the mechanical properties of iron aluminides and their composites will be discussed in detail.

9:20 AM

MECHANICAL PROPERTIES OF Fe-Al/Al_2O_3: *C. G. McKamey*[1]; R. Subramanian[1]; L. R. Buck[1]; J. H. Schneibel[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6115 USA

The potential of Fe_3Al-based intermetallic alloys has been restricted by low-fracture toughness and a decrease in strength at temperature above 600°C. One avenue for potentially improving the high-temperature strength of the Fe_3Al matrix is by reinforcing it with a ceramic phase. In this research, starting with mixtures of Fe-40 Al (at. %) and iron oxide powders (Fe_2O_3), composites with an intermetallic Fe_3Al matrix reinforced by Al_2O_3 were produced using in situ displacement reactions during sintering or hot-pressing. The resulting phases and microstructures were analyzed using EDS, XRD, SEM, and optical metallography. The evaluation of the mechanical properties of the composites included hardness measurements, bend testing, and the determination of toughness using Chevron-notched specimens in three-point bending. The results indicate that a composite of Fe_3Al reinforced with Al_2O_3 can be produced using this processing technique. The mechanical properties of these composites will be presented and discussed with respect to the potential of this unique processing technique to produce improved strengthening in Fe_3Al-based intermetallics. This research was sponsored by the Laboratory Directed Research and Development Program of the Oak Ridge National Laboratory, and by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. This research was also supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education. L. R. Buck was partially supported through the American Chemical Society's Project Seed at the Oak Ridge National Laboratory.

9:40 AM

IRON-ALUMINIDE-BONDED CARBIDE AND BORIDE CERMETS - MICROSTRUCTURAL SCALE EFFECT: *R. Subramanian*[1]; J. H. Schneibel[1]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831 USA

Iron aluminide (Fe-40 at. % Al) has been demonstrated to be a successful binder in carbide and boride-based cermets. These cermets can be processed to near full density with ceramic volume contents from 30 to 85 vol. %. Using FeAl-TiC as an example, microstructural analysis showed that iron-aluminide ligaments are less than 5 mm in width in cermets containing 70 vol. % ceramic. A systematic evaluation of the fracture surfaces shows that the microstructural scale affects the fracture mode of the ligaments. Ligaments smaller than about 1 mm fail by ductile fracture and those that are larger fail predominantly by cleavage. This is contrary to the typically observed cleavage fracture mode for bulk Fe-40 at. % Al. A simple explanation based on a dislocation pile-up model is discussed. Furthermore, results from slow crack growth experiments indicate that iron aluminide when present as thin ligaments in FeAl-TiC composites (70 vol. % TiC) is less susceptible to environmental embrittlement, in comparison to bulk iron aluminide. Thus, the results presented will clearly demonstrate the effect of the microstructural scale on the fracture behavior of iron aluminide (Fe-40 at. % Al). Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DEAC0596OR22464 with Lockheed Martin Energy Research Corp.
and in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by ORISE and ORNL.

10:00 AM Break

10:20 AM

HIGH-TEMPERATURE ELECTROCHEMICAL TESTING OF SPRAY-ATOMIZED AND DEPOSITED IRON ALUMINIDES ALLOYED WITH BORON AND REINFORCED WITH ALUMINA PARTICULATE: *L. G. Martinez*[1]; M. Amaya[1]; J. Poroayo-Colderon[2]; E. J. Lavernia[3]; [1]UNAM, Instituto de Fisica, 62251, Cuernavaca, Mor. Mexico; [2]Instituto de Investigaciones Electricas, 62490 Temixco, Mor. Mexico; [3]University of California, Chemical Engineering and Materials Science Department, Irvine, CA 92717 USA

The corrosion behavior of FeAl40 at. %, FeAl40 + 0.01 at. % B, and FeAl40 + 0.01 at. % B + 10 at. % Al_2O_3 in a mixture of molten salts of 80% V_2O_5 + 20% Na_2SO_4 (wt %) from 600 to 900°C was studied using a potentiodynamic polarization technique. Experiments were conducted in a typical three-electrode cell immersed in the fused salt. Curves of corrosion current density (1 corr) as a function of molten salt temperature were obtained and discussed in terms of the passive layer and corrosion products formed during the electrochemical tests.

10:40 AM

THE WEAR OF IRON-BASED ALUMINIDES BY HARD PARTICLES: *J. A. Hawk*[1]; D. E. Alman[1]; [1]U.S. Department of Energy, Albany Research Center, Albany, OR 97321-2198 USA

The wear behavior of iron-aluminide-based alloys and composites by hard particles has been investigated at the Albany Research Center. The iron-aluminide alloys and composites were produced using a combination of arc melting and P/M processing techniques. The base alloy composition for the study was Fe_3Al to which the following were done: (1) addition of ternary elements to the base alloy at the 2, 5, and 10 at. % levels (i.e., substituting for iron in the compound alloy); (2) the systematic variation in the Al content in an Fe-Al alloy from 16 to 34 at. % with subsequent heat treatments to affect order changes (i.e., $D0_3$ or B2) within the structure; (3) the substitution of Ti to the base Fe_3Al structure at the 4, 10, and 20 at. % level with subsequent heat treatments to change the structure to either $D0_3$ or B2; and (4) the effect of selected nonmetallic reinforcements and volume fraction on the wear behavior (e.g., SiC whiskers). This paper summarizes the important findings of the research, relating the wear behavior to the microstructural features that result as a consequence of the changes in the Fe3Al alloy structure as a result of ternary element additions and heat treatment and as a direct result of composite strengthening.

11:00 AM

FRICTION WELDING OF $FeAl_{40}$ GRADE 3 MATERIAL: B. J. Inkson[1]; *P. L. Threadgill*[2]; [1]Max-Planck Institut, Stuttgart Germany; [2]TWI, Cambridge UK

Rotary friction welding has been used to join FeAl40 Grade 3 material, which is an ODS alloy manufactured by CEREM in Grenoble, France. Initial studies concentrated on the development of suitable welding parameters and on the effects of heat treatments, applied either before or after welding, on the microstructure and mechanical

properties of the joints. Selected welds were examined in detail at the bond line and in other regions of the joint using transmission electron microscopy. These studies identified several interesting features, including the agglomeration of yttria particles at the weld interface. Despite this, and the other thermal effects such as bond line recrystallization, room-temperature mechanical properties were not substantially reduced. Yttria particles were also strongly faceted on (100) B2 planes. The prospects for the use of friction welding as a method for joining such alloys are reviewed.

11:20 AM

SLIDING WEAR BEHAVIOR OF Fe3Al-BASED ALLOYS: *Professor Yong-Suk Kim*[1]; Mr. Yong-Hwan Kim[1]; Mr. Seung-Hyun Kim[1]; [1]Kookmin University, Metallurgical and Materials Engineering, Seoul 136-702 KOREA

Sliding wear research has been conducted on Fe-23~30 at. % Al iron aluminides at room temperature. Hot-rolled aluminides were heat treated to have different ordered structures (DO3, B2, α+DO_3, and α+B2) and dry pin-on-disk wear tests were performed on them varying applied load, wear distance, and sliding speeds. Wear surfaces and wear debris were examined with optical microscopy and scanning electron microscopy. The wear rates of aluminides increased with the increase of applied load and aluminides with DO_3 structure showed lower wear rates than those of B2 structure. Sliding wear of the aluminides occurred through plastic deformation of the surface. The wear mechanism consisted of microploughing and subsurface deformation by surface fatigue, which was confirmed by the formation of sheet-like wear particles. The depth of the subsurface deformation zone played an important role in determining the wear rates, which was discussed through different deformation behavior of DO_3 and B2 structures.

11:40 AM

FABRIC CUTTING APPLICATION OF FeAl-BASED ALLOY: *V. K. Sikka*[1]; C. A. Blue[1]; S. Sklad[1]; H-R. Shih[2]; [1]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831-6083 USA; [2]Jackson State University, Jackson, MI 39217 USA

Iron-based alloys are commonly used as cutting edges for all type of cutting applications including fabric and paper. The primary reasons for using carbon steels include: (1) they are heat treatable to high hardness levels, and (2) they are inexpensive materials. However, the heat-treated cutting edges lose their performance from the softening that results from the heat generated at the cutting interface. Thus, it is desired to examine an alternate cutting blade material that does not derive its cutting properties from heat-treated microstructures. The purpose of this paper is to describe the use of an FeAl alloy for fabric and paper cutting applications. A cutting blade testing facility and the data from the cutting experiments will be presented in comparison to other possible materials and steels currently used. Research sponsored by the U.S. Department of Energy, Office of Energy Research, Energy Research Laboratory Technology Research Program, under contract DEAC0596OR22464 with LockheedMartin Energy Research Corp.

MICROSTRUCTURE AND ITS EFFECTS ON AMORPHOUS NANOPHASE & NANOCRYSTALLINE MATERIALS: Session VII - Sintering Mechanisms and Atomistic Simulation

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

Thursday AM Room: 205
February 19, 1998 Location: Convention Center

Session Chairs: Ram B. Bhagat, The Pennsylvania State University, University Park, PA 16802; K. Higashi, Osaka Prefecture University, Department of Mechanical Systems Engineering, Sakai 593 Japan

8:30 AM Opening Remarks

8:40 AM INVITED

MULTIMILLION ATOM MOLECULAR DYNAMICS SIMULATIONS OF NANOPHASE CERAMICS ON PARALLEL COMPUTERS: *Rajiv K. Kalia*[1]; Aiichiro Nakano[1]; Shuji Ogata[1]; Andrey Omeltchenko[2]; Kenji Tsuruta[1]; Priya Vashishta[1]; [1]Louisiana State University, Computing Laboratory for Materials Simulations, Department of Physics and Astronomy, Department of Computer Science, Baton Rouge, LA 70803-4001; [2](Permanent Address:)Yamaguchi University, Department of Applied Science Japan

Large-scale molecular dynamics (MD) simulations are performed to investigate properties and processes in nanophase silica and silicon nitride. The simulations are based on reliable interatomic interactions, and they are executed with highly efficient, portable and scalable, multiresolution algorithms on massively parallel machines. Structural correlations and their effect on vibrational densities-of-states of nanophase silica and silicon nitride are determined. Effects of porosity and grain size on mechanical properties are also investigated. Results for dynamic fracture in the nanophase systems will be illustrated with a video. This work is supported by DOE (Grant No. DE-FG05-92ER45477), NSF (Grant No. DMR-9412965), AFOSR (Grant No. F 49620-94-1-0444), USC-LSU Multidisciplinary University Research Initiative (Grant No. F 49620-95-1-0452), Army Research Office (Grant No. DAAH04-96-1-0393), and Louisiana Education Quality Support Fund (LEQSF) (Grant No. LEQSF(96-99)-RD-A-10).

9:20 AM

SINTERING MECHANISMS OF ALUMINUM NANOCRYSTALS - A MOLECULAR DYNAMICS STUDY: *Janhavi Rautl*[1]; Kristen A. Fichthornl[1]; Ram B. Bhagat[2]; [1]The Pennsylvania State University, Department of Chemical Engineering, PA 16802; [2]The Pennsylvania State University, Engineering Science and Mechanics Department

A major concern for consolidating nanocrystalline metal powders into useful shapes is the difficulty of retaining nanograined structure in the consolidated materials. The nanocrystals invariably consist of a crystalline core surrounded by an amorphous or disordered surface re-

gion having atoms at a relatively higher energy level than the core atoms. Such atomic structures allow the nanocrystals to sinter rapidly at temperatures significantly lower than that required for the sintering of the micrometer-size particles. Excessive grain growth is generally observed in obtaining full densification. In this investigation we use molecular dynamics (MD) simulations to study the sintering behavior of two and three particles of aluminum. Interatomic forces are obtained from a MD/MC-GEM (corrected effective medium theory) many-body potential model. Simulations have been done for temperatures ranging from 300 to 1000 K for nanocrystals consisting of 1000 to 3375 atoms. The influences on the sintering process of temperature, particle size, as well as initial particle separation and orientation have all been studied. The simulations provide new insight into sintering mechanisms for nanometer-size particles. Practical ramifications of the simulation results will be discussed.

9:40 AM

CHEMICAL SYNTHESIS AND PROPERTIES OF NANOCRYSTALLINE Cu-Fe-Ni ALLOYS: *Jonathan Douglas Stolk*[1]; Arumugam Manthiram[1]; [1]The University of Texas at Austin, Center for Materials Science and Engineering, Austin, TX 78712 USA

During the past century, low coefficient of thermal expansion Fe-Ni alloys such as Invar have been developed and used in a variety of applications. The use of Invar in the electronics industry, however, has been limited by its poor thermal and electrical conductivity. It should be possible to produce composite structures having low thermal expansion and improved thermal and electrical conductivity by the addition of copper to the Fe-Ni system and proper control of composition and microstructure. This study involves the synthesis of nanocomposites consisting of copper, iron, and nickel by ambient temperature chemical reduction of Cu^{2+}, Fe^{3+}, and Ni^{2+} ions with sodium borohydride in aqueous solution. The as-prepared powders are compacted and subjected to sintering heat treatments between 400 and 1000ºC. Sintering at intermediate temperatures in H_2 led to the formation of a stable copper-rich phase and a metastable FCC (Fe,Ni) phase. The growth and stability of the (Fe,Ni) phase and its effects on the microstructure and properties of Cu-Fe-Ni alloys of varying composition are investigated. The samples are characterized by X-ray diffraction, optical microscopy, scanning and transmission electron microscopies, and energy dispersive X-ray spectroscopy. Thermal and mechanical properties are evaluated by dilatometry and microhardness.

10:00 AM

LARGE-SCALE, LONG-TIME BEHAVIOR OF NANOPHASE CERAMICS: MULTILEVEL ALGORITHMS FOR PARALLEL MOLECULAR DYNAMICS SIMULATIONS: *Aiichiro Nakano*[1]; [1]Louisiana State University, Concurrent Computing Laboratory for Materials Simulations, Department of Computer Science, Baton Rouge LA

Large-scale, long-time phenomena such as fracture and sintering are studied for nanophase ceramics (silicon nitride) by molecular dynamics (MD) simulations on parallel computers. For realistic modeling of nanostructured materials, the scope of simulations must be extended to large system sizes, long simulated times, and complex realism. New multilevel algorithms and physical models encompassing multiple levels of abstraction are developed: 1) space-time multiresolution schemes; 2) fuzzy clustering approach to hierarchical dynamics; 3) wavelet-based load balancing in curvilinear space; 4) variable-valence MD based on electronegativity equalization; and 5) multilevel preconditioned conjugate gradient method. Work supported by NSF CAREER Program, ARO, PRF, DOE, and Louisiana LEQSF.

10:20 AM

SINTERING OF NANOPARTICLES: NEW MECHANISMS OR SCALING DOWN?: *J. R. Groza*[1]; [1]UC Davis, Chemical Engineering/ Materials Science Department, Davis, CA 95616

The desire to take advantage of the unique properties of nanocrystalline materials requires the fabrication of bulk parts that retain a small grain size. Numerous processes have been developed to consolidate nanopowders ranging from pressureless sintering to very complex ones involving high pressure or electric field application. The densification of nanocrystalline powders is analyzed in order to understand the similarities with conventional powder sintering behavior and detect the specifics. Examples of these analyses include early sintering stages, Herring scaling law, deformation mechanisms, contamination issues. The final goal is to identify the sintering mechanisms and establish whether or not new mechanisms come into play.

10:40 AM

STRUCTURE, MECHANICAL BEHAVIOR, AND INTERFACIAL PHONONS IN NANOPHASE SILICON CARBIDE VIA PARALLEL MOLECULAR DYNAMICS*: *Kenji Tsuruta*[1]; Alok Chatterjee[1]; [1]Louisiana State University, Computing Laboratory for Materials Simulation, Department of Physics & Astronomy, Department of Computer Science, Baton Rouge, LA 70803

Using large-scale molecular dynamics (MD) simulations on parallel computers, we investigate sintering, structural correlations, mechanical behavior, and vibrational properties of nanophase silicon carbide. Sintering rates of nanophase systems as a function of temperature are determined through constant pressure MD method. Structural correlations inside the clusters and intercluster regions are analyzed and compared with those in the bulk SiC. The static structure factor and the vibrational density-of-states of nanophase SiC are compared with recent neutron-scattering measurements. Results for the effect of the grain-size and porosity on elastic moduli will be discussed. A video of these MD simulations will also be presented.*Work supported by AFOSR, DOE, NSF, USC-LSU MURI from DARPA, and LEQSF

11:00 AM INVITED

THE INFLUENCE OF GRAIN STRUCTURE AND MORPHOLOGY IN NANOPHASE Ni ON ITS MECHANICAL PROPERTIES: A MOLECULAR DYNAMICS COMPUTER SIMULATION: *H. Van Swygenhoven*[1]; M. Spaczer[1]; R. Robin[2]; A. Caro[3]; [1]Paul Scherrer Institute, Villigen CH-5232 Switzerland; [2]R. Schaublin,CRPP-EPFL, Materials Group, Villigen CH-5232 Switzerland; [3]Centro Atomico Bariloche, Bariloche 8400 Argentina

Molecular dynamics computer simulations of large nanophase samples of pure Ni have been performed on a massively parallel computer. Samples containing up to 50 grains in the range of 2 to 8 nm have been constructed by filling a volume with a polycrystal nucleated from different seeds chosen stochastically. In some samples orientations are chosen at random, resulting in samples with mainly high energy grain boundaries, in others a restriction on the orientation is imposed in order to obtain samples with a lot of low energy grain boundaries. All samples are relaxed to stable configurations with final density close to bulk values. The structure of the grain boundaries is studied by means of pair distribution functions, coordination and energy contour plots, simulated electron diffraction patterns, and visual inspection of slices. The relaxed samples are then loaded and sequentially unloaded with several levels of uniaxial stress at different deformation temperatures. The mechanism of plastic deformation in these nanophase samples is studied and related to the morphology, the interior grain structure and the grain boundary structure of the samples. . .

11:40 AM

MECHANICAL PROPERTIES OF NANOCRYSTALLINE NiAl: *M. Choudry*[1]; M. Dollar[1]; J. Eastman[1]; [1]Argonne National Laboratory, Materials Science Div., Argonne, IL; [1]Illinois Institute of Technology, Materials & Aerospace Energy Dept., Chicago, IL 60616

Nanocrystalline intermetallic NiAl (n-NiAl) powders were synthesized from pre-cast NiAl and nickel using an electron beam inert gas condensation system, transported under high vacuum to a compaction unit, and compacted under vacuum conditions at temperatures ranging from 100 to 275°C. As-consolidated samples (9mm diameter, 1 - 3 mm thick discs) - showed density values from 78 to 93% of the theoretical density and grain sizes in the range of 3 to 11 nm. Some of the consolidated samples were annealed at temperatures ranging from 200 - 1000°C. Chemical composition and microstructures of as-consolidated and annealed samples were characterized.

MODELING THE MECHANICAL RESPONSE OF STRUCTURAL MATERIALS: Session V: Fracture Processes

Sponsored by: Structural Materials Division, Structural Materials Committee

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

Thursday AM Room: 202
February 19, 1998 Location: Convention Center

Session Chairs: A. K. Vasudevan, Naval Research Laboratory, Arlington, VA 22217; K. S. Chan, Southwest Research Institute, San Antonio, TX 78238-5100

8:30 AM INVITED

EXTENSION OF THE UNIFIED APPROACH TO CORROSION FATIGUE CRACK GROWTH: I BASIC CONCEPTS: *Dr. K. Sadananda*[1]; Dr. A. K. Vasudevan[1]; [1]Naval Research Laboratory, Washington, DC 20375-5343

The unified approach involves quantification of fatigue crack growth in terms of two load parameters, K_{max} and ΔK, with the corresponding two thresholds that must be simultaneously satisfied before crack growth can occur. We have shown that acceleration of short cracks and the retardation due to overloads can be explained, without invoking crack closure. Of the two, K_{max} is related to the fracture process in terms of breaking the bonds, and ΔK is related to cyclic work-hardening ahead of the crack tip required to facilitate that breaking. Environment can significantly affect the Kmax, for example by reducing the surface energy. Based on the extensive analysis of the literature data, we show how the two parametric approach provides a systematic classification of corrosion fatigue behavior. We present the basis of classification and its implication in terms of the governing mechanisms.

9:00 AM

EXTENSION OF THE UNIFIED APPROACH TO CORROSION FATIGUE CRACK GROWTH: II EXPERIMENTAL ANALYSIS: *K. Sandananda*[1]; A. K. Vasudevan[2]; [1]Naval Research Laboratory, Code 6323, Washington, DC 20375 USA; [2]Office of Naval Research, Code 332, Arlington, VA 22217 USA

Extensive analysis of the corrosion fatigue data in the literature is done. It is shown that the data cannot be adequately analyzed without the consideration of second variable, Kmax, in addition to K. Corrosion being a time, temperature, and Kmax dependent process, its influence is most significant in the regime of fatigue crack growth where fatigue crack growth is Kmax controlled. In the intermediate Paris regime, where fatigue crack growth is mostly cycle-dependent, the environmental effects are minimum. Effect of corrosion on the dislocation nucleation versus dislocation mobility will be examined to explain the differences in behaviors in different systems. Experimental data is presented in support of the various types of the corrosion fatigue behavior and the associated governing mechanisms will be discussed.

9:20 AM

AN ASSESSMENT OF SMALL CRACK BEHAVIOR ON FATIGUE LIFE: *Dr. Kwai S. Chan*[1]; [1]Southwest Research Institute, Materials and Structures Division, San Antonio, TX 78228-0510 USA

The phenomenon of fast propagating small fatigue cracks at stress intensity ranges below the large crack threshold is well known, but a general methodology for treating these small fatigue cracks has not been established. In this paper, recent results on the growth of microcracks in structural alloys such as TiAl alloys and steels are highlighted. Various methods proposed for treating small fatigue cracks are evaluated against experimental data. Both the experimental and modeling results are used to determine the extent that small cracks affects the fatigue life of a structure. Based on these results, a fatigue map is proposed for depicting the stress range and crack size regimes where the growth of small cracks control the fatigue life. Potential applications of the fatigue map for fatigue lifetime estimation is illustrated.

9:40 AM

ROLE OF CRACK MORPHOLOGY ON THE FAILURE BEHAVIOR OF LAMINATED COMPOSITES: *S. B. Biner*[1]; [1]Iowa State University, Ames Laboratory, Ames, IA 50011

In this study, the failure of the ductile layers from collinear, multiple and delaminating cracks that occur in laminated composite systems was studied using a constitutive relationship that accounts for strength degradation resulting from the nucleation and growth of voids. The results indicate that in laminated composites, void nucleation and growth ahead of the cracks occur at a much faster rate due to evolution of much higher stress values at the interface region. Except for short crack extensions, collinear and multiple cracks develop crack resistance curves similar to that seen for a crack in the ductile layer material as homogenous isotropic case. The results also show that if the crack tip is at the interface, similar maximum stress values develop in the ductile layers as in the fracture test of the same ductile material; suggesting that ductile/brittle fracture transition behavior of the ductile layers is dependent upon the extent of the cracks in the brittle layers and fracture characteristics of the brittle layers. This work was supported by USDOE, Office of Basic Energy Sciences, Div. of Materials Science under contract no. W-7405-ENG-82.

10:00 AM

CREEP CAVITATION AND CRACK GROWTH BEHAVIOR OF BRIDGED CRACKS: *S. B. Biner*[1]; [1]Iowa State University, Ames Laboratory, Ames, IA 50011 USA

In this study, the growth behavior of bridged cracks in the creep regime is investigated numerically. In the analysis, crack growth resulting from the growth of prenucleated creep cavities with diffusional and dislocation assisted mechanisms are fully accounted for. The results indicate that the bridging tractions significantly relax even with the creep deformation of the composite alone. While the rate of this relaxation is not influenced by the rate of crack growth, the rate of change in the bridging zone length or the density of the bridging elements in the bridging zone; all these variables strongly affected both the maximum value and the distribution of the tractions in the bridging zone. A much weaker stress singularity than the ones described by K or C* occurs ahead of the bridged cracks in the creep regime. In this weak singularity region the cavities grow at comparably high rates to each other. This work was supported by USDOE, Office of Basic Energy Sciences, Div. of Materials Science under contract no. W-7405-ENG-82.

10:20 AM Break

10:30 AM

MODELING OF CRACKING AND CAVITATION DURING HOT WORKING OF GAMMA TITANIUM ALUMINIDES: *V. Seetharaman*[1]; S. L. Semiatin[2]; [1]UES Inc., Materials and Processes Division, Dayton, OH 45432-1984 USA; [2]Wright Laboratory, WL/MLLM, Materials Directorate, Wright-Patterson AFB, OH 45433-7817

Hot workability of gamma titanium aluminides was assessed using hot compression and hot tension tests. A simple model for the brittle intergranular failure of these alloys during hot working was developed to seek correlations between flow properties, microstructural characteristics, and the propensity for cracking. The onset of wedge cracking was predicted using a criterion based on a critical value of the product of the peak flow stress and the square root of the grain size. In contrast, the occurrence of ductile fracture of the workpiece in regions subject to secondary tensile stresses is controlled by the kinetics of nucleation, growth, and coalescence of cavities. This type of cavitation damage could be predicted using the maximum tensile work criterion proposed originally by Cockroft and Latham. The applicability of the preceding

criteria for the onset of brittle and ductile fracture in gamma titanium aluminide alloys is demonstrated.

10:50 AM
INFLUENCE OF PLASTIC DEFORMATION ON FRACTURE TOUGHNESS OF THE BCC METALS WITH A DIFFERENT COHESION ALONG INTERFACES: *A. D. Vasilev*[1]; S. A. Fistov[1]; [1]Francevich Institute for Problems of Materials Science, Kyiv, Ukraine

Dr. Alexander D. Vasilev Francevich Institute for Problems of Materials Science 3, Krjijanovskoho Str. Fracture toughness as well as fracture mechanisms at liquid nitrogen and room temperatures of molybdenum and chromium alloys deformed with rolling for different degree (up to 95%) were studied. As a measure of cohesion along interfaces the inclination to intergranular and intercellular fracture was chosen. In molybdenum that is strongly inclined to intergranular as well as to intercellular fracture deformation leads in fracture mechanisms change from cleavage to pores coalescence and partially to intercellular fracture at room temperature loading. Fracture toughness also strongly and non-monotonously depends on deformation degree being increased more than in four times in comparison with initial state at 60% deformation even. The measurement of fracture toughness of 75 and 95% deformed molybdenum is problematic due to high plasticity of these sites. At low temperature loading the fracture mechanism is cleavage at all deformation degrees with a weak dependence of fracture toughness on deformation. In chromium that is practically not inclined to intergranular fracture the fracture mechanisms change that might be resulted from deformation was not observed at both low and room temperatures. Mechanism fracture was cleavage. Fracture toughness at liquid nitrogen temperature does not practically depend on deformation. At room temperature testing fracture toughness also practically does not depend on deformation in interval 0-90%. But room temperature fracture toughness of deformed for 95% Cr increases in about three times in comparison with initial state. The comparative structural, with transmission electron microscopy and Auger-electron microanalysis, and thermodynamic analysis shows that the differences in mechanical behaviours of molybdenum and chromium may be resulted from different cohesion of structural elements due to segregation of additives mainly oxygen, carbon and nitrogen along inner interfaces as well as formation of new intercellular boundaries like intergranular ones with deformation.

11:10 AM
ON THE TEMPERATURE DEPENDENCE OF FRACTURE TOUGHNESS OF DEFORMED AND RECRYSTALLIZED LOW-ALLOYED CHROMIUM: A. V. Sameljuk[1]; *A. D. Vasilev*[1]; S. A. Firstov[1]; [1]Frantsevich Institute for Problem Of Materials Science, Kiev, Ukraine 252680

The temperature dependencies of fracture toughness as well as sequences of fracture mechanisms changes of deformed and recrystallized low-alloyed chromium were studied in a wide temperature range. Big samples of 16 mm diameter with ring sharp notch were tested under uni-axial tension. It was found that brittle fracture occurs by cleavage in temperature ranges 293K - 793K for deformed material and 293K - 893K for recrystallized material. Cleavage fracture toughness of both materials increases monotonously with temperature. Change of fracture mechanism from cleavage to pores coalescence leads to additional increasing of fracture toughness of deformed material at temperatures above 793K. An appearance of brittle intergranular fracture of recrystallized material leads to decreasing of fracture toughness at temperatures above 893K. The area of intergranular fracture increases with temperature. It was also found that appearance of this fracture mechanism is due to impurities redistribution during annealing. The difference in courses of fracture toughness dependencies of deformed and recryctallized materials with temperature is explained with different fracture mechanisms sequences of these materials.

11:30 AM
ANISOTROPY OF STRUCTURE AND FRACTURE TOUGHNESS OF ROLLED BCC-METALS: Mykola Danilenko[1]; [1]Frantsevich Institute for Problems of Materials Science, Kiev, Ukraine 252180

Effect of dislocation structure on fracture toughness, yield stress and mechanism of fracture of Mo-, Cr-, and Fe-based alloys have been studied. Fracture toughness was determined by bending of specimens with cracks introduced into the plane perpendicular (direction 1) and parallel (direction 2) to the plane of rolling. Tests were carried out at a range of temperatures below ductile-brittle transition temperature. Non-monotonic dependence of fracture toughness against strain is connected with instability of dislocation cell structure for low prestrained materials (for both directions). The increasing of fracture toughness in direction 1 and decreasing of fracture toughness in direction 2 for highly strained materials is connected with changing of the fracture mechanism. On the basis of this investigations the explanation of some phenomena which take place during tension of samples are presented.

MOLYBDENUM & MOLYBDENUM ALLOYS: Materials Testing and Applications

Sponsored by: Structural Materials Division, Refractory Metals Committee

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

Thursday AM Room: 203
February 19, 1998 Location: Convention Center

Session Chair: E. L. Baker, Picatinny Arsenal, NJ 07806-5000

8:30 AM
APPLICATIONS OF Mo AND Mo ALLOYS AS THERMAL SPRAY COATINGS: *Dr. S. Sampath*[1]; Dr. S. Usmani[1]; Dr. David L. Houck[2]; [1]SUNY at Stony Brook, Dept. of Materials Science and Engineering, Stony Brook, NY 11794 USA; [2]Osram Sylvania Inc., Chemical and Metallurgical Products, Towanda, PA 18848

Refractory metal based alloys, particularly molybdenum alloys and tungsten carbides find wide spread applications in tribology related environments in industry. The desirable tribological characteristics of molybdenum alloys are their excellent low friction and sliding wear resistance during adhesive contact with most ferrous alloys. They find extensive applications as coatings in the automotive industry on sliding contact surfaces such as piston rings, synchronizer rings, gears etc. In addition, they are used as protective coatings on rolls in the paper industry to provide good thermal conductivity as well as sliding wear resistance. Considerable developments have taken place in materials development based on Molybdenum compounds for thermal spray coating applications. This presentation will review the key tribological characteristics of Mo coatings and the associated developments in materials and processes. These results will be compared with that of the sintered materials of similar compositions in order to distinguish the wear behavior of the coatings with that of the bulk compositions. The tribological behavior will be discussed in the context of their microstructural characteristics in an effort to develop a structure-property relationships.

9:00 AM
MECHANICAL PROPERTIES AND CONSTITUTIVE RELATIONS FOR MOLYBDENUM UNDER HIGH-STRAIN-RATE DEFORMATION: *Dr. Shuh Rong Chen*[1]; Dr. G. T. Gray, III[1]; [1]Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM 87545 USA

Molybdenum and its alloys have received increased interest for ballistic applications. The stress-strain behavior of several molybdenums varied in compositions, manufacturing sources, and the degree of

pre-straining were investigated as a function of temperature from 77 to 1273K, and strain rate from 10-3s-1 to 8000s-1. The yield stress was found to be sensitive to the test temperature and strain rate; however, the strain hardening remained rate-insensitive. The constitutive response of a powder-metallurgy molybdenum was investigated. Similar mechanical properties compared to conventionally processed molybdenums were achieved. The frequently observed inhomogeneity in mechanical behavior of molybdenum inherited from conventional processes therefore can be levitated. Constitutive relations based upon the Johnson-Cook, the Zerilli-Armstrong and the Mechanical Threshold Stress (MTS) models were evaluated. Parameters for fitting these models to various molybdenums were derived. The capabilities and limitations of each model for large-strain applications will be examined. Work supported by the U.S. Department of Energy.

9:20 AM

DEVELOPMENT OF MOLYBDENUM SHAPED CHARGE LINERS: *Dr. E. L. Baker*[1]; Dr. A. Daniels[1]; Dr. G. P. Voorhis[1]; Dr. T. Vuong[1]; [1]U.S. Army Armament Research Development and Engineering Center, Picatinny Arsenal, NJ 07806-5000 USA

The development of molybdenum lined shaped charges is a relatively new area of investigation, with recent emphasis placed in producing increased jet ductility. Excellent jet ductility has now been successfully produced from a variety of molybdenum shaped charge liners. Conventional forging and high energy rate forming (HERF) have been used to produce a variety molybdenum shaped charge liner preforms including hemispheres, cones and trumpets. Most liner forgings exhibited good formability using both conventional forging and HERF processing. Liner forgings have been fabricated from arc cast and powder metallurgy molybdenum, as well as one from a single crystal. Grain size and geometry have been investigated using scanning electron microscopy. Neutron diffraction has been used to investigate material texture through samples taken from the base and apex regions for some of the liner forgings. Tensile tests have been used to investigate low rate material strength and ductility. Hopkinson bar testing has been used to develop Johnson-Cook, Zerilli-Armstrong and MTS material models. Long standoff triple flash radiography was used to evaluate overall jet ductility. All the designs produce experimental jet tip velocities in close agreement with modeling, typically near 12.0 Km/s. Experimental trends of jet ductility were observed with proper material selection and thermomechanical conditioning.

9:40 AM

SHOCK AND SHEAR INDUCED CHEMICAL REACTIONS IN Mo-Si, Nb-Si, AND Ti-Si SYSTEMS: *Dr. V. F. Nesterenko*[1]; Dr. S. S. Batsanov[4]; Dr. K. S. Vecchio[2]; Dr. M. A. Meyers[2]; [1]University of California, La Jolla, CA 92037 USA; [2]National Institute of Standards, Mendeleevo, Moscow Region Russia

Chemical reactions between metal (Mo, Nb, or Ti) and metalloid (Si) powder mixtures were produced by subjecting them to shock compression and high strain, high strain rate plastic deformation. It was confirmed that a threshold energy is required for the initiation of shock-induced chemical reactions. This threshold was originally proposed by Krueger and Vreeland and corresponds to the energy required to melt a fraction of the silicon. The threshold energy is a function of the exothermicity of the reaction as well as of the porosity of the powder mixture. For a 35% metal porosity of the mixture, and powder size of ~ 44 mm, the threshold values were 12 and 2 GPa for the synthesis of $MoSi_2$ and Ti_5Si_3, respectively. Under high strain, high strain rate deformation with superimposed pressures that are significantly below the threshold for shock initiation, chemical reaction can be initiated at a sufficiently large plastic strain. Such is the case within shear bands, where the engineering shear strains can be as high as 50. For Nb-Si and Mo-Si mixtures, the reaction occurred only inside the shear bands and for Ti-Si it initiated inside the bands and propagated throughout the entire specimen at a sufficient strain. Mechanisms for the initiation and propagation of shock and shear induced reaction are proposed. This research was supported by the U.S. Army Research Office Contracts DAAH04-93-G-0261, DAAH04-94-G-0314, the Office of Naval Research Contract N000 14-94-1-1040, and by the National Science Foundation Grant DMR 9396132.

10:00 AM Break

10:20 AM

PROCESSING OF MOLYBDENUM FOR USE AS A SHAPED CHARGE LINER MATERIAL: *Dr. K. J.A. Mawella*[1]; Dr. K. G. Cowen[2]; Dr. J. S. Jones[2]; Dr. D. J. Standing[1]; [1]Defense Research and Evaluation Agency, Structural Materials Centre, Farnborough, Hampshire GU14 OLX UK; [2]Defense Research and Evaluation Agency, Weapons Systems Sector, Fort Halstead, Kent TN14 7BP UK

Molybdenum is an attractive material for shaped charge application due to it's high bulk sound speed (5055.5m/s) This property is important in relation to the ability to drive the jet tip with a higher velocity without it becoming incoherent and radially dispersed, so that the armour penetration capacity could be increased. The density of the molybdenum liner depends on the consolidating process used whilst the performance depends on various factors including microstructure. DERA has been investigating various processing routes for producing molybdenum shape charge liners in order to achieve dense SCLs with a suitable fine grained microstructure so as to obtain a coherent and ductile jet. This paper summarizes the microstructural characteristics and the performance of Mo SCLs produced by three processes namely, flow forming, pressing and sintering, and by extruding the material and machining. A suite of computer models has been used to predict the jet characteristics and where possible, the modeling and experimental results are compared.

10:40 AM

MECHANICAL PROPERTIES OF MOLYBDENUM AT HIGH STRAIN RATES: *Dr. Steven J. Savage*[1]; Mrs. Catharina Bratt[1]; Mr. Jan Eriksson[1]; Mr. Svante Karlsson[1]; [1]FOA-Defense Research Establishment, Dept. of Materials, Stockholm SE-172 90 Sweden

The tensile properties of unalloyed molybdenum have been measured at strain rates of 0.01, 1 and 400/s. Using these results, the constants A, B and n in the Johnson and Cook equation have been estimated. These constants may be used to calculate the shape of a deforming object, and this has been done for the case of a simple cylindrical sample under uniaxial compression. The calculated deformation is compared with experimental results derived from high-speed video recordings of the compression tests in a high energy rate forming process (HERF). Metallographic observations of virgin and deformed material are being used to determine the microstructural factors which influence high strain rate ductility in molybdenum.

11:00 AM

A STUDY OF Mo-V AND Mo-V-Fe ALLOYS FOR CONDUCTIVE CERMET APPLICATIONS: *Dr. J. J. Stephens*[1]; Dr. B. K. Damkroger[1]; Dr. K. G. Ewsuk[1]; Dr. S. J. Glass[1]; Dr. S. L. Monroe[1]; Dr. M. Reece[1]; Dr. J. E. Smurgeresky[1]; [1]Sandia National Laboratories, Dept 1833, Albuquerque, NM 87185-0367 USA

Molybdenum/alumina cermets are used for simple geometry, electrical feed-throughs in insulating alumina ceramic bodies. However, with larger and more complex geometries, high residual stresses and cracking of the alumina ceramic occur due to differences in coefficient of thermal expansion (CTE) between the pure Mo in the cermet and the 94% alumina ceramic. A study was conducted at Sandia Labs to develop CTE-matched cermets based on binary Mo-V and ternary Mo-V-X alloy systems. It was found that the CTE of 94% alumina (over the range 1000°C to room temperature) could be precisely matched by a binary Mo-32.5V alloy. However, to address concerns regarding the selective oxidation of V, Mo-V-X alloys with CTE's similar to 94% alumina were made with Fe or Co additions. The ternary additions are limited to about 3 wt.% in order to maintain a single phase BCC alloy, and permit some reduction in the V addition. This talk will discuss alloy development, ingot and powder production, cermet processing and properties, and compatibility test results. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy Contract number DE-AC

11:20 AM
EFFECTS OF ROLLING TEMPERATURE ON MICROSTRUCTURE AND TENSILE PROPERTIES OF THICK PLATE P/M Mo: Zwonitzer; Lewandowski; Rozak
Abstract Not Available

STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS: STRENGTHENING IN HIGH TEMPERATURE INTERMETALLICS VII: Gamma Titanium Aluminides 4

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

Thursday AM Room: 107
February 19, 1998 Location: Convention Center

Session Chairs: Young-Won Kim, UES, Inc., Dayton, OH 45432; Thomas R. Bieler, Michigan State University, Dept. of Materials Science and Mechanics, East Lansing, MI 48824-1226

8:30 AM Opening Remarks

8:35 AM
FACTORS GOVERNING THE STRENGTH OF TiAl-BASED INTERMETALLICS: *Prof. M. H. Loretto*[1]; E. Shelton[1]; T. T. Cheng[1]; A. Godfrey[1]; D. Hu[1]; I. P. Jones[1]; P. A. Blenkinsop[1]; [1]University of Birmingham/IRC, Birmingham B15 2TT United Kingdom

The room temperature and high temperature strength of alloys based on TiAl are strongly influenced by composition, heat treatment and by thermomechanical processing. The wide range of properties which are obtainable for a number of alloys will be reported and an attempt will be made to relate these changes to microstructural observations. The situation is complicated for some alloying additions by strong partitioning of the alloying elements so that the actual composition of the phases as their spatial distribution and the volume fractions are changed for different heat treatments and for different processing routes It is thus very difficult to define, from experiment alone, which variable is responsible for the observed changes in properties. The results of detailed chemical analysis of the various phases present in some of the alloys form an essential part of the microstructural observations and these will be reported together with other microstructural data. Despite the difficulties in isolating the important factors an attempt will be made to define the most important factor(s) in controlling the properties of a number of alloys. This research is sponsored by the EPSRC through the IRC core grant.

9:05 AM
CREEP OF TiAl ALLOYS WITH FINE LAMELLAR STRUCTURE BY A LEDGE MECHANISM: *Prof. Jian Nong Wang*[1]; Prof. Baiyun Huang[1]; [1]Central South University of Technology, Powder Metallurgy Research Institute, Hunan 410083 China

Creep experiments have been conducted on powder metallurgy TiAl alloys with fine grains, fine lamellar structures, and a base composition of Ti-47Al-2Cr-2Nb. Results show that the stress exponent n and the activation energy Q decrease with decreasing stress. Thinning and dissolving of Ti3Al lamellae and continuous coarsening of TiAl lamellae were observed at both low and high stresses with cross-twinning being a microstructure exclusive at high stresses. To under the underlying deformation processes, a ledge creep mechanism is proposed. The mechanism involves bunching and escaping of unit-height ledges into or from multiple-height ledges at interfacial boundaries. It is assumed that the ledge motion, which is diffusion-controlled, causes phase transformation and thus deformation of the sample.

9:25 AM
CREEP MECHANISM AND MICROSTRUCTURAL EVOLUTION IN FULLY LAMELLAR TiAl ALLOYS: *T. G. Nieh*[1]; Dr. L. M. Hsiung[1]; [1]Lawerence Livermore National Laboratory, Livermore, CA 94551-9900 USA

Creep of several TiAl alloys with a fine grain, fine lamellar spacing, and different compositions [Ti-47Al-(Cr, Nb, Ta, W, Si)] were conducted at temperatures from 650 to 815°C and stresses from 35 to 723 MPa. Experimental results indicate that there exists a change in deformation mechanism from high to low stresses. Microstructural examinations using TEM indicated that the deformation strain at low stresses is mainly accommodated by soft lamellar grains through the operations of mobile dislocations in interfaces and the (111)γ slip planes. When the alloys are strained at higher stresses, a deformation substructure associated with mechanical twins is developed within g lamellae. The alloys become more resistant to creep, resulting from the formation of mechanical twinning. It was found that at a given lamellar spacing, the addition of 400 ppm B, or replacing 1% Nb with 1% Ta, or replacing 0.2% Ta with 0.2% W, induced little effect, but the addition of 0.3% Si decreased the creep resistance. The results are explained in terms of solute/dislocation interaction in the lamellar interfaces.

9:55 AM
THE EFFECT OF HIP CONDITIONS AND HEAT TREATMENTS ON CREEP AND TENSILE PROPERTIES IN INVESTMENT CAST Ti-47Al-2Nb-2Mn-XD ALLOYS: *Dr. D. Y. Seo*[1]; Dr. Thomas R. Bieler[1]; Mr. Donald E. Larsen[2]; Mr. Paul A. McQuay[2]; [1]Michigan State University, Dept. of Materials Science and Mechanics, East Lansing, MI 48824-1226 USA; [2]Howmet Corporation, Advanced Technology, Whitehall, MI 49461-1895 USA

Two Hot Isostatic Pressing (HIP) conditions (1260°C or 1185°C for 4 hours at 172 MPa) and heat treatments of various times at 1010°C were developed and applied to investment cast Ti-47Al-2Nb-2Mn-XD alloys to improve primary creep and tensile properties. Data obtained from several alloys indicated that the lamellar spacing distribution was refined by an easy deformation mode during the initial strain below 0.5%, and this refinement process strongly affected the creep time to 0.5%. The alloys HIP'ed at the lower temperature showed slight increases in elongation, and the yield strength and UTS at room temperature and 650°C were lower by 8-10%. In primary creep, the time to 0.5% strain was slightly increased and the variability was significantly decreased by the lower temperature HIP process. The volume fraction of lamellar grains and grain sizes were measured using SEM, TEM, optical microscopy, and image analysis. The microstructure and the changes in lamellar spacing distributions due to heat treatment we re compared in the grip and gage sections of tested creep and tensile specimens and correlated with primary creep and tensile properties.

10:15 AM
CHARACTERIZATION OF A PRECIPITATION STRENGTHENED γ-TITANIUM ALUMINIDE ALLOY: *Dr. Perena Gouma*[1]; Prof. Michael J. Mills[1]; Dr. Young-Won Kim[2]; [1]Ohio State University, Dept. of Mat. Sci. & Eng./CISM, Columbus, OH 43210 USA; [2]UES, Inc., Dayton, OH 45432 USA

The creep properties of a fully-lamellar γ-titanium aluminide alloy reinforced with C and Si additions, have been investigated over a temperature range from 750 to 870°C in aged conditions. Under certain aging conditions, the alloy exhibited remarkable improvements in both the primary and secondary creep resistances. The superior performance is largely attributed to the fine precipitation of H-type carbide particles, which were found to delineate the interlamellar γ/γ phase boundaries. Analytical electron microscopy showed that many of the fine carbide (and silicide) precipitates are present along the dissolving α2 (and B2) laths. The fine details of microstructural changes in the material during aging have also been investigated. From these results, it is suggested that the precipitation process is linked with the dissolution of the α2 phase laths during the high temperature treatment, and

the supersaturation of the boundary area with C given the limited solubility of the latter in the γ-phase.

10:35 AM

INFLUENCE OF TWINNING AND DISLOCATION GLIDE DURING CREEP OF EQUIAXED AND LAMELLAR TiAl ALLOYS: *Prof. Maria Morris*[1]; M. Leboeuf[1]; P. Gindraux[1]; [1]University of Neuchatel, Institute of Structural Metallurgy, Neuchatel CH-2000 Switzerland

It is well established that g-based TiAl alloys with lamellar structures have a better creep resistance than those with equiaxed grains or duplex microstructures. In particular the minimum or secondary creep rate can be two orders of magnitude lower in lamellar alloys while the initial primary stage is rather independent of initial structure. The present study compares the creep behaviour of two different alloys with both equiaxed and lamellar structures. Although the equiaxed alloys have the same fine grain size, the lamellar alloys have different colony size and lamellar spacing. The active deformation mechanisms have been analyzed by TEM and SEM in all cases during the primary stage of creep and at the onset of the minimum creep rate. While mechanical twinning determines the hardening process during primary creep of the equiaxed alloys, the lamellar interfaces are responsible for the more effective hardening stage of the lamellar structures. The thermally activated mechanisms responsible for the different creep rates measured have been interpreted in terms of the active slip systems analyzed.

10:55 AM

PRIMARY CREEP RESISTANCE IN FULLY-LAMELLAR TiAl ALLOYS: *Prof. Soo Woo Nam*[1]; Han Seo Cho[1]; [1]Korea Advanced Institute of Science and Engineering, Department of Material Science and Engineering, Taejon 305-701 Korea

Because the creep resistance of lamellar TiAl alloys is superior to the other microstructures, the creep deformation characteristics in the lamellar TiAl alloys have been investigated actively to utilize the TiAl alloys at high temperature. The size tolerance in the design of engineering components operated under sustained stress at high temperatures, such as a turbine blade, is usually exceeded by the primary creep strain. Therefore, understanding the primary creep deformation characteristics are critically important in designing creep-resistant TiAl alloys. However, reports have been concentrated on the study of the steady state deformation mechanism through the measurement of activation energies and/or stress exponents. In addition, the effects of chemical composition and microstructural variables such as lamellar grain size, grain boundary morphology, lamellar spacing, strengthening particles, and initial dislocation structures, on the deformation behavior in primary creep range, have only just begun to be investigated. In this report, the enhancement of the primary creep resistance in fully-lamellar TiAl alloys will be discussed by analyzing the observations made on the influences of microstructural variables and the development of deformation structure.

11:25 AM

INTERFACE ENHANCED DEFORMATION TWINNING IN LAMELLAR TiAl/Ti_3Al: *Dr. L. M. Hsiung*[1]; Dr. T. G. Nieh[1]; [1]Lawrence Livermore National Laboratory, Livermore, CA 94551-9900 USA

Formation mechanism of deformation twinning in creep deformed lamellar TiAl(γ)/$Ti_3Al(\alpha_2)$ crystals have been investigated. Since the multiplication of lattice dislocations within γ lamellae becomes very limited as a result of refined lamellar spacing, the movement of interfacial dislocations in the γ/α_2 and γ/γ interfaces becomes a dominant deformation mechanism. The mobility of interfacial dislocations at the primary creep stage is mainly impeded by interface ledges and dislocation obstacles formed by the impingement of lattice dislocations to the lamellar interfaces. When the crystals deform into the secondary creep stage, the density of interfacial dislocations continues to increase and deformation twins start to form within the γ lamellae. It is suggested that the deformation twinning in the TiAl/Ti_3Al crystals can be viewed as a stress-relief process due to the pile-up of interfacial dislocations in the lamellar interfaces. The deformation twins are resulted from dislocation reactions based upon a stair-rod cross-slip mechanism. The local stress concentration due to the dislocation pile-up and the resolved shear stresses on both the interfacial and cross-slip planes are considered to be important factors for the formation of deformation twins in lamellar TiAl/Ti_3Al crystals.