

# SYMPOSIUM M

## Interfacial Engineering for Optimized Properties II

December 1 – 2, 1999

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Proceedings published as Volume 586  
of the Materials Research Society  
Symposium Proceedings Series.

\* Invited paper

SESSION M1: GENERAL CONCEPTS AND  
MODELING

Chair: C. Barry Carter  
Wednesday Morning, December 1, 1999  
Salon C/D (M)

**8:30 AM \*M1.1**

**INTERFACIAL ENGINEERING IN NANOCOMPOSITES.** Brian Cantor, Department of Materials, University of Oxford, Oxford, ENGLAND.

This paper will present details of Interfacial design, structure and properties in a variety of different nanocomposites. The materials discussed include co-sputtered nanoscale Ag/SiO<sub>2</sub> and Ag/Si thin films which exhibit novel optoelectronic behaviour, and melt spun nanoscale Pb/Al and Sn/Al sheets which exhibit novel mechanical behaviour. The relationships between processing, structure and properties are discussed for these unusual materials systems.

**9:00 AM \*M1.2**

**INFLUENCE OF PROCESSING METHOD ON THE GRAIN BOUNDARY CHARACTER DISTRIBUTION.** Adam J. Schwartz, Mukul Kumar and Wayne E. King, Lawrence Livermore National Laboratory, Livermore, CA.

There now exists a large body of literature that correlates the fractions of special and random boundaries as described by the Coincident Site Lattice Model to improvements in properties such as corrosion resistance, stress corrosion cracking, creep, etc. Such results suggest that precise control over the grain boundary character distribution (GBCD) can be exerted through thermomechanical processing. This investigation evaluates the influence of specific thermomechanical processing methods on the resulting GBCD. Samples of oxygen-free-electronic Cu were subjected to five separate deformation-annealing treatments. The first series of comparisons focuses on compression deformation to 20% strain followed by annealing at 400, 560 and 800°C. A second processing treatment was sequential in nature: 20% deformation followed by annealing repeated for three iterations. The third comparison was a one pass 67% compression followed by the same heat treatments. To examine the influence of rolling versus compression on GBCD and texture, one sample was rolled 82% and a second compressed to 82% in one pass. The results of orientation imaging microscopy characterization of the GBCD and texture will be discussed in terms of the heat treatment temperature and processing method. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48.

**9:30 AM M1.3**

**LOCAL POTENTIAL AT ATOMICALLY ABRUPT OXIDE INTERFACES.** Dawn A. Bonnell, B. Huey, S. Kalinin, The Univ. of Pennsylvania, Dept. of Mat. Sci. Phil., PA; G. Duscher, Vanderbilt University, Nashville TN.

Local field variations near oxide interfaces and grain boundaries are the basis of many electronic ceramic devices as well as chemical nano sensors. We compare scanning probe based Kelvin measurements and finite element calculations of model geometries that allow unambiguous quantification of nm scale field variation. In the case of interfaces intersecting a surface, a procedure for determining interface charge, potential, and density of states will be presented. The force-distance relation with realistic tip geometry and lateral sample variations can not be described as the simple power law often used in AFM analysis. Comparisons are made of potential at interfaces in donor and acceptor doped SrTiO<sub>3</sub> with several different nominal grain boundary structures. Interface potentials differ by an order of magnitude and are found to be either positive or negative depending on structure. The interface potentials are related to the actual atomic structure determined by atom column resolved Z contrast transmission electron microscopy. Generalizations in terms of interface cation coordination will be presented.

**9:45 AM M1.4**

**THE MECHANISM OF MIXED-MODE PHASE TRANSFORMATIONS.** R.C. Pond<sup>1</sup>, P. Shang<sup>2</sup>, T.T. Cheng<sup>3</sup> and M. Aindow<sup>2,3</sup>; <sup>1</sup>Materials Science and Engineering, Department of Engineering, The University of Liverpool, Brownlow Hill, Liverpool, UNITED KINGDOM; <sup>2</sup>School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham, UNITED KINGDOM; <sup>3</sup>IRC in Materials for High Performance Applications, The University of Birmingham, Edgbaston, Birmingham, UNITED KINGDOM.

Recent advances in the understanding of interfacial line defects are enabling mechanistic models of phase transformations to be developed. In particular, the coupling between the deformation produced and the attendant diffusional flux of material arising due to

the motion and interaction of defects in interfaces has been clarified. Such deformations and fluxes can now be predicted using an equation relating the atomic-scale topological parameters of defects (Burgers vectors and step heights) to macroscopic quantities (densities of the constituent chemical species in the two crystals). Using this framework, it can be shown that mechanisms of phase nucleation and growth in terms of interfacial defects which are diffusionless overall, such as martensitic processes, require very special crystallographic circumstances. The particular object of the present paper is to discuss mixed-mode transformations where the crystallographic features exhibited are martensitic, but where diffusion is involved. Using the present approach, it is seen that mixed-mode cases arise when the number of substitutional sites is conserved during transformation because compensating fluxes of the various chemical species present arise. As an illustration, experimental observations of the decomposition of hcp solid solutions of Ti(Al) into  $\gamma$ -TiAl and  $\alpha_2$ -Ti<sub>3</sub>Al lamellae will be presented.

**10:30 AM \*M1.5**

**STRUCTURE AND PROPERTIES OF POLYCRYSTALLINE MATERIALS FROM SIMULATION: AN INTERFACIAL PERSPECTIVE.** S.R. Phillpot<sup>1</sup>, P. Keblinski<sup>1,2</sup>, D. Wolf<sup>1</sup> and F. Cleri<sup>1,3</sup>; <sup>1</sup>Materials Science Division, Argonne National Laboratory, Argonne IL; <sup>2</sup>Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY; <sup>3</sup>Divisioni Materiali Avanzati, ENEA, Rome, ITALY.

We have recently developed a novel molecular-dynamics simulation method to grow polycrystals from a melt containing randomly oriented crystalline seeds. The resulting microstructures contain only randomly oriented (i.e., high-energy) grain boundaries (GBs). We find that these GBs, which are highly constrained by their close proximity to grain junctions, are highly disordered in fcc metals and amorphous in silicon. From simulations of infinitely extended high-energy GBs in bicrystals, we find that such highly disordered and amorphous GBs are actually the thermodynamic ground state; by contrast, low-energy GBs are crystalline. High-energy GBs in diamond, however, are structurally ordered at the expense of a significant amount of graphite-like bonding. We show that these complex GB structures have important effects on properties including GB diffusion (fcc metals and silicon), GB diffusion creep (silicon) and GB electrical activity and strength (diamond). The implications for engineering materials with prescribed properties are discussed. Work supported by U. S. Department of Energy, BES-Materials Science under Contract No. W-31-109-Eng-38.

**11:00 AM \*M1.6**

**ULTRATHIN ALUMINA FILMS ON METALLIC SUBSTRATES: STRUCTURE AND METAL ADSORPTION.** Dwight R. Jennison and Alexander Bogicevic, Surface and Interface Sciences Dept., Sandia National Laboratories, Albuquerque, NM.

First principles density functional calculations are used to study the structure and properties of ultrathin films of alumina on Al(111) and Ru(0001) substrates. We focus on  $\sim 5\text{\AA}$  two O-layer films, naturally produced by oxidizing NiAl, Ni<sub>3</sub>Al, and Al deposited on Ru(0001). The interface consists of chemisorbed 1x1 oxygen on the underlying metal [1], with a nearly coplanar layer of Al<sub>2</sub>O<sub>3</sub> above. The lowest energy structure of the Al-sublattice is found to consist of zig-zag rows of octahedral and tetrahedral Al ions, resembling the bulk  $\kappa$ -phase. Eleven different adsorbed metals, spanning the periodic table, have been studied [2]. At low coverage the bond is purely ionic; at high coverage most metals bind principally by polarization. Contrary to speculations, isolated vacancies are found on MgO(100) not to directly promote metal nucleation [3], and we suggest this behavior is general. However, ad-OH is found not only to promote island nucleation, but can also in high concentrations produce wetting of alumina by Cu [4]. [1] D.R. Jennison, et al., Phys. Rev. B 59, R15605 (1999). [2] A. Bogicevic and D.R. Jennison, PRL 82, 4050 (1999). [3] A. Bogicevic and D.R. Jennison, Surf. Sci. (submitted). [4] J. A. Kelber et al., Surf. Sci. (submitted). Work at Sandia National Laboratories is supported by the U.S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

**11:30 AM M1.7**

**THERMODYNAMICS AND KINETICS OF INTERFACIAL DECOHESION.** Y. Mishin, Dept of Materials Science and Engineering, Virginia Polytechnic Inst., Blacksburg, VA; C.J. McMahon, Dept of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA; J.L. Bassani, Dept of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA; P. Sofronis, Dept of Theoretical and Applied Mechanics, University of Illinois, Urbana, IL.

We analyze thermodynamic aspects and diffusion-controlled kinetics of interfacial decohesion. We consider a uniform separation along an interface, caused by a uniform tensile stress applied normal to the interface. During the separation process, a low-melting embrittling solute can penetrate into the interface either directly from the surface or atmosphere, or through the bulk. This solute reduces the cohesive strength of the interface. Thermodynamic foundations of this process were laid by Hirth and Rice (1980), who considered two extreme cases: fast separation (constant solute concentration) and slow separation (constant chemical potential of the solute). Our work extends the Hirth and Rice analysis to intermediate, time-dependent situations, which correspond to the problem at hand. In order to address such situations at a quantitative level, we introduce a phenomenological model describing the free energy of the interfacial "solid solution" and the stress-separation curve as functions of the solute concentration. A stress-driven diffusion equation, which governs the solute supply, is also derived. The observed separation kinetics, as well as the work of decohesion, depend on the interrelation between the strain rate and the solute diffusion rate. The obtained strain-rate dependencies of the work of separation and the solute concentration at the separated surfaces are analyzed in detail. Our results verify Hirth and Rice's predictions in the respective extreme cases.

#### 11:45 AM M1.8

AB-INITIO CALCULATIONS ON GRAIN BOUNDARIES OF SrTiO<sub>3</sub>. Miyoung Kim, Oak Ridge National Laboratory, Oak Ridge, TN, and Department of Physics, University of Illinois at Chicago, Chicago, IL; N. D. Browning, Department of Physics, University of Illinois at Chicago, Chicago, IL; S.J. Pennycook, K. Sohlberg, Oak Ridge National Laboratory, Oak Ridge, TN; S.T. Pantelides, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN.

The understanding of electrical properties of grain boundaries in perovskites is essential for their application to capacitors, varistors and positive-temperature coefficient resistors. The origin of the electrical activity is ubiquitously attributed to the existence of grain boundary donors, usually assumed to be impurities, which set up a double Schottky barrier as they are screened by dopants in the adjacent bulk crystal. But microscopic understanding of the origin of the grain boundary charge has not been provided. It is not known yet if the grain boundary structure itself is the intrinsic origin of the so-called grain boundary donors or whether non-stoichiometry is essential. The relation between atomic structure and electronic properties is studied by combining experiment and ab-initio calculations. The starting structures for theoretical calculations were obtained from Z-contrast images combined with electron energy loss spectroscopy to resolve the dislocation core structures comprising the boundary. Dislocation core reconstructions are typical of all grain boundaries so far observed in this material. They avoid like-ion repulsion, and provide alternative sites for cation occupation in the grain boundaries. Optimized atomic positions are found by total energy calculations. The density of states of each atom at the grain boundaries and in the bulk are compared with experimentally obtained spectra, and the total charge density is used to determine electrical barriers. Calculated differences in vacancy formation energies between the grain boundaries and the bulk determine if vacancy segregation can account for the postulated grain boundary charge. \*This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

#### SESSION M2: REACTIONS AND WETTING

Chair: Steven R. Nutt  
Wednesday Afternoon, December 1, 1999  
Salon C/D (M)

#### 1:30 PM \*M2.1

OXIDATION RESISTANT CERAMIC COMPOSITES: HOW WEAK INTERFACES BECAME DESIGNED FAILURE PROCESSES.

Ronald J. Kerans, Air Force Research Laboratory, Materials and Manufacturing Directorate AFRL/MLLN, Wright-Patterson AFB, OH.

Interest in ceramic composites arises from their potential for dramatically improved damage tolerance, as compared to monolithic ceramics, while delivering similar high temperature properties. The remarkable toughening effect resulting from the proper combination of brittle phases is dependent upon the failure process developing in a particular way; matrix cracks must deflect into fiber debonding cracks that run in or near the fiber/matrix interface and permit some relative displacement. In early composites, the requirements for crack deflection and good composite behavior seem to have been almost fortuitously satisfied by native C layers; however, the most productive uses of ceramic composites are dependent upon the development of

fiber coatings that not only promote the desired interfacial failure, but also satisfy the additional requirement of being oxidation resistant. Though conceptually simple, the management of a failure process - specifically, predetermining the progress of cracks on a very local level - places a very demanding and unprecedented requirement on the materials designer. Historically, the details of fracture events were of interest principally for insight into means of avoiding them. The composite problem imposes the new requirement that we design to promote a special kind of fracture, and control post-fracture friction within a certain range. This truly is a higher level of sophistication than heretofore attained, and its complexities have deterred many investigators from seriously addressing the problem. Nevertheless, there has been progress both in depth of understanding and in actual achievement of viable systems. Moreover, very interesting properties of several families of materials have been uncovered. These issues will be outlined and discussed in more detail with the objective of developing a broad view of the lessons learned and opportunities revealed.

#### 2:00 PM \*M2.2

INTERFACIAL ENGINEERING FOR OPTIMIZED ADHESION IN POLYMERIC COMPOSITE MATERIALS. Lawrence T. Drzal, Department of Chemical Engineering, Composite Materials and Structures Center, Michigan State University, East Lansing, MI.

Fiber-matrix adhesion is a variable to be optimized so that optimum composite mechanical properties can be achieved in polymer matrix composites. The contemporary view of adhesion rests on an interphase model in which not only the actual chemical and physical interactions between fiber and matrix are considered but also the structure and properties of both the fiber and the matrix in the region near the interface. The optimum design methodology starts with the specification of the fiber and matrix from a structural consideration. Once the constituents are selected, the focus is on the creation of a beneficial fiber-matrix interphase. This region where the fiber and matrix interact has to be designed for both processing and performance. Although no quantitative algorithm is available for interphase optimization, various thermodynamic principles coupled with experimental data can be used to qualitatively design the optimum interphase. Examples will be presented to illustrate how this interphase can be engineered with surface treatments and sizings or coatings to insure thorough wetting, protection of the fiber; chemical bonding between fiber and matrix, toughness and desirable failure modes.

#### 2:30 PM M2.3

CONTROL OF GRAIN BOUNDARY MICROSTRUCTURES IN LIQUID-PHASE SINTERED ALUMINA. N. Ravishankar and C. Barry Carter Department of Chemical Engineering and Materials Science, University of Minnesota Minneapolis, MN.

The properties of liquid-phase sintered ceramics are affected strongly by the grain boundary microstructure. The liquid phase which forms at high temperatures usually remains as a continuous intergranular glass layer on cooling the material from the sintering temperature. The presence of this glassy layer may lead to a degradation of the properties of the material. Post-processing treatments can be used either to exude the liquid from the grain boundary or to crystallize the glass present in the boundary. The present work is a study of the factors involved in the expulsion of silicate liquid (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) from grain boundaries in sapphire. Glass-containing bicrystals of known geometry are used in order to understand the influence of crystallography. The bicrystals are engineered by hot-pressing a glass-coated single crystal of sapphire to a blank piece of sapphire. The crystallography is tailored by orienting the sapphire crystals before hot-pressing. The bicrystals are cut using a diamond saw and polished using standard tripod polishing technique. The assembly is annealed at 1650°C for 2h. A field-emission SEM has been used for microstructural investigation. It is shown that the liquid migrates out of the bicrystal boundary to the polished free surface but that the details of the migration depend upon the nature of the free surface. The driving force for migration is the difference in the temperature variation of wetting behavior between the grain boundary and the free surface. The results emphasize the importance of the crystallography of the boundary and the nature of free surfaces (i.e., the surface energies) on the migration behavior.

#### 2:45 PM M2.4

THEORETICAL CALCULATION FOR INTERGRANULAR GLASSY FILM IN Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> CERAMIC. Masato Yoshiya, Hirohiko Adachi, Kyoto University, Department of Materials Science and Engineering, Kyoto, JAPAN; Isao Tanaka, Kyoto University, Department of Energy Science and Technology, Kyoto, JAPAN.

It is well known that intergranular glassy film of about 1nm in thickness is usually present at two grain junctions in sintered Si<sub>3</sub>N<sub>4</sub> ceramics. Investigation for the IGF in Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> ceramic has been done by static energy minimization technique in order to reveal the

role of the IGF at the grain boundary. A model structure used in the present study well agrees with experiments in density of Si and ratio of N/(N+O) inside the IGF. Interface energies of 0° twist boundary and of 180° twist boundary are calculated both when the IGF is present and when the IGF is absent. The interface energy with the IGF is larger than that without the IGF in 0° twist boundary due to the presence of Oxygen at the grain boundary. On the contrary, interface energy with the IGF becomes lower than that without the IGF in 180° twist boundary. By analysis of the structures, it is found that the IGF plays an important role to reduce the strains at the grain boundary when interface energy is high due to misorientation.

#### 3:30 PM \*M2.5

##### WETTING TRANSITIONS OF GRAIN BOUNDARIES.

John Blendell, National Institute of Standards and Technology, Ceramics Division, Gaithersburg MD.

It has been shown that the concepts used to determine the equilibrium shape of crystals can be extended to determine the conditions under which grain boundaries will be fully wetted, partially wetted, or not wetted by a second phase. Recent experimental observations on the equilibrated morphologies of solid or fluid wetting phases along grain boundaries, reveal features that are predicted, and in some cases required, by this construction. Theory distinguishes between cases where surfaces are smoothly curved or where there are facets, edges and corners. In the latter case the conventional comparison of the energy of the original grain boundary with the sum of the surface energy of the two surfaces of the wetting layer leads to erroneous predictions. The correct predictions are obtained by comparing the Wulff shape of the grain boundary (the interfacial energy minimizing shape for a fixed volume of material) with a carefully defined sum of Wulff shapes of the surfaces of the wetting layer. Where orientations that are wetted join with those that are not, there is almost always an abrupt change of orientation. Faceting on two hierarchical levels can occur. Microscopic morphology changes along macroscopically curved surfaces follow well defined rules predicted by theory. The analogy between the thermodynamics of interface faceting and phase transformations allows the well known concepts of phase equilibria to be used to understand the predicted structures. The predictions of the model will be used to identify the nature of the faceting observed in alumina in the presence of a second phase.

#### 4:00 PM \*M2.6

INFLUENCE OF THE INTERFACIAL PROPERTIES ON THE MICROSTRUCTURAL DEVELOPMENT AND PROPERTIES OF SILICON NITRIDE CERAMICS. Michael J. Hoffmann, University of Karlsruhe, GERMANY; Hui Gu, JST Nagoya, Japan; Rowland M. Cannon, Lawrence Berkeley Lab., University of Berkeley, CA.

Silicon nitride ceramics are usually densified by liquid-phase sintering using metal oxides as sintering additives. During densification a phase transformation occurs which leads to a microstructure consisting of elongated grains embedded in a fine-grained matrix of equiaxed silicon nitride grains surrounded by an amorphous or partially devitrified grain boundary phase. The chemical composition of the grain boundary phase controls grain growth anisotropy of the silicon nitride grains as well as the mechanical properties of silicon nitride ceramics. The paper will focus on the effect of additive mixtures of rare earth oxides and alumina. It will be shown that the grain growth anisotropy decreases in presence of smaller rare earth cations such as Yb, whereas it increases for larger ones such as La when the rare earth/alumina ratio is kept constant. Observations of the crack growth reveal furthermore that the interfacial strength increases with a decreasing cation radius of the rare earth oxides resulting in a predominantly transgranular fracture mode for Yb-containing samples in comparison to an more intergranular fracture for the La-containing ones. In order to understand the impact of different rare earth oxides, STEM/EELS-investigations have been performed to analyse the chemical composition of the grain boundary phase in the thin films between two adjacent grains as well as in multi-grain junctions (pockets). The EELS-results clearly show a difference between the chemistry in the film of Yb- and La-containing samples although the composition of the pockets is the same. The analytical results are finally related to the grain growth experiments and mechanical properties to demonstrate the strong influence of the additive system.

#### 4:30 PM M2.7

MODELLING THE EFFECT OF COMPOSITION ON THE STABILITY OF EQUILIBRIUM INTERGRANULAR FILMS WITH DIFFUSE INTERFACES. Catherine M. Bishop and W. Craig Carter, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Current understanding of the equilibrium thickness of interfacial films derives from models which balance a steric repulsion against an attractive force between abutting crystals such as the van der Waals forces [Clarke, 1987]. Recent experimental observations [Pan et al.,

1996] indicate that, 1) film thickness is a non-monotonic function of additions of impurities and 2) impurities are non-uniformly distributed in the interfacial phases and triple junctions. We have developed a model which couples the steric terms which affect the equilibrium thickness with composition for a semi-infinite film in equilibrium with a chemical reservoir at a fixed composition.

#### 4:45 PM M2.8

##### FORMATION OF SPINEL PHASES IN NICKEL-ALUMINA FUNCTIONALLY GRADED MATERIAL SYSTEMS.

William Windes, Idaho National Engineering and Environmental Laboratory, Metals and Ceramics Department, Idaho Falls, ID; Keith Rozenburg, Colorado School of Mines, Department of Metallurgical and Materials Engineering, Golden, CO.

The formation of new phases or structures inside a Functionally Graded Material (FGM) architecture can significantly influence the macroscopic properties of the entire structure. Analyzing the final microstructure through each sequential layer and subsequent interfaces of the FGM is required to determine constitutive changes to the system. For the present study, a nickel-alumina material system has been chosen for a model FGM to study residual stresses in these unique architectures. Alumina and nickel have been selected due to their well known material properties and limited reactions between the constituents, with the formation of spinel phases being a primary exception. It was assumed that with proper processing environments that spinel phases could be eliminated from the joint and thus not influence the macroscopic mechanical responses of these joint structures. However, recent studies indicate this assumption to be incorrect. FGM joints consisting of varying concentrations of nickel powders (~1µm in diameter) and alumina powders (~22µm in diameter) were consolidated by hot pressing at 1350 °C for 90 minutes in either an inert or slightly reducing atmosphere (4% hydrogen). In addition, some of the nickel powder was pre-treated in an oxygen rich atmosphere (30% oxygen) prior to consolidation. In all cases, spinel structures were formed at the interfaces between the nickel/alumina phases and were observed to increase with increasing nickel content through the FGM structure. This increase is attributed to the total oxygen content in the system as a consequence of dissolved oxygen in the nickel powders. The formation of the spinel structures is not strongly influenced by the surrounding atmosphere and thus a graded increase in spinel phase formation occurs through the FGM structure.

SESSION M3: POSTER SESSION:  
INTERFACIAL ENGINEERING  
Chairs: Clyde L. Briant, C. Barry Carter,  
Ernest L. Hall and Steven R. Nutt  
Wednesday Evening, December 1, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### M3.1

AB-INITIO STUDY OF THE LOCAL BONDING AT METAL-CERAMIC HETEROPHASE BOUNDARIES. S. Koestlmeier and C. Elsaesser, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY.

The adhesion geometries of the (100) heterophase boundaries between the metals Al and Ag and spinel (MgAl<sub>2</sub>O<sub>4</sub>) were determined by density-functional calculations employing a mixed-basis pseudopotential method. The results compare well with high-resolution transmission-electron-microscopy studies which were carried out in parallel.

An analysis of the calculated electronic structures shows that the strong adhesion of Al is mediated by directional bonding. The comparatively weak interaction with Ag is dominated by polarization effects which can be classified as image-charge interaction.

Additionally, the effects of changes in stoichiometry and of segregated atoms at the interface were analysed in terms of the chemical potential. The implications for tailoring both the mechanical properties and the Schottky barrier height at the metal-ceramic junctions are discussed.

This work was funded by the Volkswagen Foundation, Germany, through project No. VW I/70502.

#### M3.2

MOLECULAR SIMULATION OF TILTED CHAIN CRYSTAL-AMORPHOUS INTERFACES IN POLYMERS. Sumit Gautam, Dept of Materials Science and Engineering; S. Balijepalli, G.C. Rutledge, Dept of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Semi-crystalline polymeric materials exhibit metastable interfaces which must simultaneously accommodate molecular connectivity through chain bonding and disorder across the interface. To address

this, off-lattice molecular simulations of these crystal-amorphous interfaces have been constructed to capture the structure and properties of materials like polyethylene. Monte-Carlo simulations were carried out on systems having fold surfaces along the {001} planes (orthogonal lateral growth face and fold surface), {201} planes (chains tilted to the lamellar normal by 34°) and {502} planes (chain tilt of 41°) the latter two being the most generally observed in experimental studies. The simulations were performed on the freely rotating chain model, phantom chain model, hindered rotation model and variable bond lengths and bond angles model. Results of the simulations reveal the effect of chain tilt on the structural and thermodynamic properties of crystal-amorphous interfaces. The local structure changes as the tilt angle is increased. The degree of tight folding diminishes with chain tilt, corresponding to an increase in the populations of loops along the higher index fold directions namely (200) and (310) versus a preponderance of (110) directed loops in the untilted {001} interface. The topology shifts towards an increase in loosely folded loops and bridges (which span from one lamellar crystallite to another). The results also compare well with a Gaussian chain length distribution model. Thermodynamic properties and interfacial energy have also been studied. The results are in good agreement with experimental data and suggest that by providing an alternative to tight folding for dissipation of chain flux at the crystal-amorphous interface, tilted chain crystals exhibit increased populations of loose loops and bridges which can entangle with the amorphous phase.

### M3.3

#### GROWTH OF X-RAY OPTICAL Ni-C MULTILAYER FILMS.

Christine Borchers, Univ Gottingen, Institute of Materials Physics, Gottingen, GERMANY; Paulo Ricardo, Carsten Michaelsen, GKSS Research Center, Institute of Materials Research, Geesthacht, GERMANY.

Magnetron sputtered Ni-C multilayer films with periods in the range 3 - 5 nm that are developed for x-ray optical applications, were studied by in-situ resistivity measurements, Cu-K $\alpha$  x-ray reflectometry, and cross-sectional transmission electron microscopy. The multilayers consisted of amorphous carbon layers and hcp nickel layers. A percolation threshold of 2 nm was observed below which Ni did not form contiguous layers. This percolation threshold is the result of island growth of Ni on C, and can be explained by the high surface energy of Ni that makes Ni surfaces unfavorable. The percolation threshold can be seen by an onset of electrical conductivity, and by a rapid increase of x-ray reflectivity for Ni layers thicker than 2 nm. Changes in the sputtering conditions lead to only minor changes in the percolation limit. However, a replacement of C by B $_4$ C leads to amorphous Ni layers with improved interfacial wetting so that thinner contiguous layers are obtained. The correlation between interface quality and enthalpy of mixing of the constituents will be discussed.

### M3.4

#### OBSERVATION OF LOCALIZED CORROSION PROPERTIES OF Ni AND Ni-BASED ALLOYS USING COUPLED ATOMIC FORCE MICROSCOPY AND ORIENTATION IMAGING MICROSCOPY.

Peter J. Bedrossian, Adam J. Schwartz, Mukul Kumar and Wayne E. King, Chemistry and Materials Science Directorate, University of California, Lawrence Livermore National Laboratory, Livermore, CA.

We have observed a strong and systematic correlation between the crystallographic misorientation across individual grain boundaries and the nature of local attack at grain boundaries and triple junctions on Ni-based alloys exposed to specific brine and acidic chloride solutions. Orientation Imaging Microscopy (OIM) provides the misorientation across each grain boundary, and Atomic Force Microscopy (AFM) reveals the nature and extent of localized attack at the microstructural features identified in the OIM. The alloys under consideration include commercially pure nickel, N201, as well as Alloys 600, 625, and C-22. Boundaries are chaotic while the special grain boundaries show little or no attack on nickel, the random boundaries are susceptible to localized attack, and the degree of attack can be correlated with the nature of the grain boundary at which it occurs. In C-22, a highly corrosion-resistant alloy, pits are observed consistently at triple junctions of random grain boundaries. General corrosion of C-22 reveals carbide precipitates at random grain boundaries. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48 and was partially supported by the Yucca Mountain Program.

### M3.5

#### ON DEWETTING OF REACTIVE SILICATE GLASS FILMS ON SINGLE-CRYSTAL CERAMIC SUBSTRATES. Svetlana V. Yanina, C. Barry Carter, University of Minnesota, Minneapolis, MN.

The mechanical and microstructural properties of liquid-sintered ceramics are determined by processes that take place at the interface between a silicate phase and a ceramic substrate. In order to

understand these processes, experiments that employ well-defined reaction geometries, such as thin silicate films deposited on single-crystal ceramic surfaces of known orientation, are needed. By monitoring changes in composition and morphology of a selected area of a system through a series of short annealing-quenching cycles, it is possible to gain useful information on mechanism of silicate-ceramic interactions. The aim of this work is to study early stages of dewetting of ceramic surface by reactive silicate glass and to investigate subsequent secondary interactions between dewet phase and underlying ceramic substrate, such as heterophase reactions at the interface, dissolution/reprecipitation of substrate, evaporation, etc. Thin films of monticellite (CaMgSiO $_4$ ) on cleaved MgO(100) were chosen as a model system for present study. In this paper, observation of several selected areas of the specimens through a series of heat-treatment cycles is performed by Atomic Force Microscopy (AFM) and chemical composition is monitored by X-Ray Energy Dispersive Spectroscopy (XEDS). Research supported by the U. S. Department of Energy under Grant No DE-FG02-92ER45465.

### M3.6

#### INTERFACIAL REACTIONS IN Ti-6Al-4V WITH LASER-EMBEDDED SiC PARTICLES. B.J.Kooi, J.Th.M. De Hosson, Dept Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Groningen, THE NETHERLANDS.

The interfacial exothermic reaction between Ti and SiC is beneficial for obtaining well-bonded Ti-SiC composite materials. Ti has several excellent properties such as high-strength-to-weight ratio and excellent corrosion resistance, but its tribological properties are relatively poor. To improve the wear resistance of Ti, SiC particles were embedded in a 600 nm top layer of Ti-6Al-4V employing a high power Nd-YAG laser. The wear rate for abrasive wear diminished by a factor 7 due to the embedding of SiC particles. Apparently the SiC particles are bonded well to the Ti matrix contributing to the improved wear resistance. The interfacial reaction between Ti and SiC has been studied in detail using FEG-SEM, CTEM, AEM and HRTEM. Particularly the role of Si released during the reaction Ti+SiC $\rightarrow$ TiC+Si has been scrutinized; e.g. Ti $_3$ SiC $_2$  plates develop in enclosed volumes in-between TiC grains and Ti $_5$ Si $_3$  precipitates nucleate on stacking faults in Si saturated TiC grains of the TiC reaction layer around the SiC particles.

### M3.7

#### ARXPS STUDIES OF INTERFACIAL BONDING STATES IN SILICON OXYNITRIDES FABRICATED USING DIFFERENT METHODOLOGIES. Christos G. Takoudis and Sanjit Singh Dang, Advanced Materials Research Laboratory, Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL.

Silicon dioxide has been the main gate dielectric material used in integrated circuits till now. But its properties appear to be far less attractive in the ultra-thin regime (less than about 5nm). Thus, other dielectric materials are being sought after for Ultra Large Scale Integration applications. In this regard, silicon oxynitride has been attracting attention for over a decade now. Compared to the oxide, the silicon oxynitride exhibits better properties such as enhanced radiation hardness, higher barrier properties to boron penetration from the p $^+$  gate layer during the subsequent high temperature processing step, increased stress stability, lesser charge trapping, larger charge to breakdown ratio, and substantial growth rate retardation with time that facilitates the fabrication of ultra-thin films. Since it is N incorporation, which results in these advantageous properties of oxynitrides when compared to oxides, the amount and concentration profile of nitrogen in the film appear to be of critical importance. In this study, silicon oxynitrides were fabricated in a horizontal furnace at 900°C and 1atm for varying times using different methodologies, i.e. growth on bare Si and annealing a pre-grown oxide in N $_2$ O or NO. Depth profiling of N and O was done using Secondary Ion Mass Spectrometry (SIMS). Film thickness and refractive index were measured using spectroscopic ellipsometry. Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) was used for probing the interfacial chemical states of N in these films. Results obtained suggest that silicon forms interfacial Si $_3$ N $_4$ -like bonding with nitrogen for all the oxynitrides. But the presence of any additional bonding state of N at or above the interface depends upon the processing employed. Such an additional bonding appears to contain O alongwith Si and N. Since silicon oxynitrides have been seen to function differently as compared to a stacked dielectric (SiO $_2$  over Si $_3$ N $_4$  grown on Si), it is important to engineer the presence of the bonding configurations other than that of Si $_3$ N $_4$  in these oxynitrides. Such findings may help to understand why the presence of N at the interface improves the chemical, physical, and electrical properties of these dielectric films.

### M3.8

#### INTERFACIAL REACTIONS AND GLASS FORMING ABILITY OF CARBON PHASE/BULK METALLIC GLASS COMPOSITES.

Frigyes Szuëcs, Jan Schroers, William L. Johnson, Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, CA; Hans J. Fecht, Dept. Materials Science, University of Ulm, GERMANY.

Graphite, diamond and amorphous carbon powders are melt infiltrated with bulk metallic glass forming Zr-based alloys of the composition  $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$  and related. The glass forming ability is investigated for different processing times by a setup similar to a DTA method. The interface between the carbon phases and the Zr-alloy matrix is analyzed by scanning electron microscopy, transmission electron microscopy, electron probe and X-ray diffraction. The reinforcement materials form an ZrC-interface with the Zr-containing matrix. The absence of heterogeneous nucleation at this interface suggests carbon phases as promising reinforcements for bulk metallic glass matrix composites. The thickness of the reaction layer presumably controls the mechanical properties of composite materials. Preliminary results of the mechanical properties of different melt infiltrated carbon/bulk metallic glass composites will be presented and compared to the properties of the unreinforced matrix material.

### **M3.9**

#### **OPTIMIZATION OF THE BROADBAND REFLECTANCE OF GRADED MULTILAYERS FOR HARD X-RAY MIRRORS.**

**Adrian Ivan**<sup>a,b</sup>, **Ricardo Bruni**<sup>a</sup>, **Kyung Byun**<sup>a,c</sup>, **Paul Gorenstein**<sup>a</sup>, **Suzanne Romaine**<sup>a</sup>; <sup>a</sup>Smithsonian Astrophysical Observatory, Cambridge, MA, <sup>b</sup>Massachusetts Institute of Technology, <sup>c</sup>Harvard University.

Multilayer structures with graded spacing can present a high reflectivity in a broad energy bandpass for hard X-rays ( $>10$  keV), if critical parameters like interface roughness/diffuseness can be controlled and optimized. We present an optimization study of several multilayer systems deposited by DC magnetron sputtering on smooth, flat substrates. The material combinations studied were: W/Si, W/C,  $WSi_2/Si$ , Pt/C, Ni/C, Cu/Si, and Mo/Si. The main characterization methods used for the interface and surface roughness were X-ray reflectivity (XRR) scans ( $\theta-2\theta$ ) and Atomic Force Microscopy (AFM) in tapping mode. Additional information was obtained from stylus profilometry, Rutherford backscattering, cross sectional TEM and stress measurement. Preliminary single layer coatings were used to calibrate the deposition rates and investigate the surface roughness dependence with the deposition parameters (argon backpressure, target-substrate distance, cathode current, etc.). In the next stage of the study, constant spacing multilayers were produced and their interface roughness improved by selecting optimal process parameter values. The analysis showed uniformity of the spacing within 0.2 Å and interface roughness around 3 Å r.m.s. for the best multilayers. The final step included depositing and measuring the X ray reflectivity for graded spacing multilayers, designed and fabricated using the optimal process parameters. The mirror coatings showed the broadening of the reflection passband and their XRR scans could be fit well by the models.

### **M3.10**

#### **INTERFACIAL PHASE TRANSFORMATION DURING INTERDIFFUSION: KINETICS AND ATOMIC MECHANISMS.**

**L.N. Paritskaya**, Dept. of Crystal Physics, Kharkov State University, Kharkov, UKRAINE; **Yu.S. Kaganovskii**, Dept. of Physics, Bar-Ilan University, Ramat-Gan, ISRAEL.

Interfacial diffusion in materials controls various mass transfer processes useful for technological applications, including phase transformation at relatively low temperatures, when bulk diffusion is practically frozen. At such conditions we have experimentally studied kinetic regularities of two processes: decomposition of supersaturated solid solution into equilibrium phases and formation of solid solution from two separate components. Experiments were carried out at  $T=(0.3-0.5)T_m$  ( $T_m$  is the melting temperature of the basic alloy component). The objects of investigations were binary alloys Ni-7.5at%In and Ni-9at%Sn, and diffusion couples Ni-Cr, Ni-Cu, Ni-Au. Analyzing the obtained results we have found both processes to be provided by diffusion-induced grain boundary migration (DIGM). We have proposed theoretical model of the diffusion-induced growth of solid solution over free surface regarded as one of the banks of open interface. The growth occurs due to surface interdiffusion of diffusant and substrate atoms captured by moving elementary steps. Step motion leads to layer-by-layer growth of solid solution. The theoretical model has been developed also for interfaces accounting atomic jumps across the interface. The migration rate of the interface has been calculated in dependence on atomic structure of the interface and interfacial diffusion characteristics. The special attention has been paid to the interdiffusion process with unequal partial diffusion coefficients. The atomic mechanisms have been confirmed experimentally.

### **M3.11**

#### **LIQUID PHASE DIFFUSION BONDING FOR THERMOELECTRIC MATERIAL Pb-Sn-Te.** **Y. Shinohara**, **Y. Imai**, **Y. Isoda**, **I.A. Nishida**, National Research Institute for Metals, 4<sup>th</sup> Research Group, Tsukuba, JAPAN.

Liquid phase diffusion bonding was applied to development of the 2-segmented thermoelectric material Pb-Sn-Te superior to the monolithic Pb-Sn-Te. A Sn sheet 50 $\mu$ m thick was used for soldering material. The sheet was sandwiched between Pb-Sn-Te solidified ingots with different hole concentrations, and subsequently the bonding was performed under 2MPa at 700K for 15 min in Ar. The Sn sheet was changed to an interfacial layer of Sn and Te in main composition and less than 10 $\mu$ m in thickness. The interfacial layer showed good bonding and ohmic contact up to 550K. Liquid phase diffusion bonding was an excellent technique for segmentation of thermoelectric material Pb-Sn-Te.

### **M3.12**

#### **TRIPLE JUNCTION ENGINEERING: THE OCCURENCE OF COINCIDENCE BOUNDARIES AT TRIPLE JUNCTIONS IN POLYCRYSTALLINE GOLD THIN FILMS.** **Kwame Owusu-Boahen**, **Alexander H. King**, SUNY Stony Brook, Dept. of Materials Science & Engineering, Stony Brook, NY.

We have investigated compliance with the sigma-product rule at triple junctions with a common [111] axis using computer simulations and in real thin films, using transmission electron microscopy. Large discrepancies exist between the simulations, which assume randomly distributed misorientations, and the experiments. Although for both cases the rule fails at most triple junctions, the real material shows a much higher than expected occurrence of compliance. This result can be explained in two distinct ways: first, there might be a preference for triple junctions that obey the rule (implying a distinct influence of the triple junction itself). Alternatively, the misorientations in the real crystal might not be randomly distributed: if there is a preference for boundaries that have only small deviations from coincidence, there will be an increase in compliance with the rule. We seek to distinguish between these two possibilities in this paper. Acknowledgement: This work is supported by the National Science Foundation, grant number DMR 9530314.

### **M3.13**

#### **ATOMIC-LEVEL STRESSES AT INTERFACES AND THEIR EFFECT ON SOLUTE SEGREGATION.** **Olof C. Hellman** and **David N. Seidman**, Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL.

Segregation of a solute species to a grain boundary is known to be dependent on many factors, including strain, chemistry and crystal structure. We attempt to make general statements about the relationship of segregation at the grain boundary to the stress calculated at each site near the boundary on an atomic scale. We not only find a relationship between local stress and segregation, but also show that the traditional definition for stress at an atomic site is only part of the influence of stress on segregation phenomena. The goal of this work is to tie together two different aspects of atomistic calculations concerning grain boundaries. The first is the calculation of stress on a site-by-site basis for each atomic site near a grain boundary. The second is the calculation of preferential segregation of one atomic species to a grain boundary. We will show results of static calculations of atomic stresses for a number of grain boundary structures based on the Embedded Atom Method for interatomic potentials, and the results of Monte Carlo calculations of segregation, showing how best to fit these calculations together.

### **M3.14**

#### **MECHANISMS OF IMPROVING HIGH TEMPERATURE OXIDATION RESISTANCE OF Ni-Al-Mo-B ALLOY IC6 BY ADDING YTTRIUM.** **Xiao Chengbo**, **Yafang Han**, Cast Superalloys Lab., Beijing Institute of Aeronautical Materials, Beijing, CHINA.

The directionally solidified alloy IC6 with the chemical composition of Ni-(7.5-8.5)Al-(13.0-15.0)Mo-(0.02-0.1)B wt% has been recently developed as a high-temperature structural material used for advanced jet-engine blades and vanes operating in the temperature range of 1050-1100°C. The alloy not only has high yield strength and fairly good ductility from room temperature to 1100°C but also has high creep resistance in the temperature range of 760-1100°C. Alloy IC6 has low density(7.9g/cm<sup>3</sup>), low cost, high melting temperature(1300°C). Its high temperature oxidation resistance is substantially improved by adding proper amounts of yttrium. The mechanisms of improving the high temperature oxidation resistance of alloy IC6 by adding yttrium are investigated with scanning electron microscopy, x-ray line scan for elements of electron probe micro-analyzer (EPMA) and X-ray diffraction technique. The beneficial effects of yttrium on high temperature oxidation resistance

include: (a) inhibiting of segregation of sulfur to the scale/substrate interface and hence improving the adhesion of scale to the substrate; (b) inhibiting the cationic transportation and decreasing the depth of the diffusion layer; (c) promoting the selective oxidation of aluminum; (d) decreasing the easily spalled NiO region in the surface scale and promoting the formation of a fine close packed oxide grain structure; (e) migrating to the oxide grain boundary and improving the mechanical strength of the grain boundary, changing the oxide scale spallation cracks of the yttrium modified alloy from intergranular to be transgranular.

### **M3.15**

**ADHESION PROPERTIES OF CELLULOSE FILMS.** Xiujuan Zhang, Raymond A. Young, University of Wisconsin-Madison, Materials Science Program, Madison, WI.

Lignocellulosic fibers are being used in new biobased composite materials. The applications of these composites could be greatly expanded by property enhancement through improved bonding and adhesion of the lignocellulosic and thermoplastic polymeric materials. In this study, adhesion was evaluated by atomic force microscopy (AFM) force curves in untreated and modified cellulose (cellophane) films. Several functional groups were introduced at the film surfaces by plasma based treatments. All the films were characterized by AFM, electron spectroscopy for chemical analysis (ESCA) and scanning electron microscopy (SEM). AFM was employed to study the adhesion properties using both standard silicon nitride tips as well as self-assembled monolayer (SAM) modified gold coated tips containing a variety of specific functional groups. The acetone extracted cellulose films were used as substrates, which are rich in -OH groups, the adhesion force of -COOH terminated AFM tips ( $\sim 25$  nN) was much larger than that of -CH<sub>3</sub> terminated AFM tips ( $\sim 10$  nN), which was attributed to the hydrogen bonding between -COOH and -OH. The adhesion force of -NH<sub>2</sub> terminated AFM tip on the acetone extracted cellulose film was 23.5 nN. However, after surface modification of cellulose film with oxygen base plasma treatment, the adhesion force was increased to 37 nN. The enhanced adhesion force between -NH<sub>2</sub> and the -CHO/-COOH groups introduced by the oxygen plasma to the cellulose films is due to much stronger acid-base interaction. Hydrazine plasma treatment also was used to introduce -NH<sub>2</sub> groups on the film surfaces, and similar adhesion behavior was observed with AFM tips terminated with -COOH groups. The Argon plasma treatment greatly increased the surface roughness, resulting in poor adhesion properties. Both surface roughness and chemical modification of the cellophane films affected the adhesion properties as measured by AFM force curves.

### **M3.16**

**IMPACT OF GRAIN BOUNDARY CHARACTER ON ELECTRICAL PROPERTY IN POLYCRYSTALLINE SILICON.** Shu Hamada, Koichi Kawahara, Sadahiro Tsurekawa, Tadao Watanabe, Tohoku Univ, Dept of Machine Intelligence and Systems Engineering, Sendai, JAPAN; Takashi Sekiguchi, Tohoku Univ, Institute for Materials Research, Sendai, JAPAN.

Grain boundaries in polycrystalline silicon are most likely to make localized states in band gap. The localized states sometimes play a dominant role in determining the performance of solar cells by acting as traps or recombination center of carriers. In the present investigation, the SEM-ECP (Scanning Electron Microscope -Electron Channeling Pattern) method was applied to characterize the grain boundaries in p-type polycrystalline silicon with 99.999% in purity. Thereafter, temperature dependence of electrical properties of individual grain boundaries was measured by an EBIC (Electron Beam Induced Current) technique.

It has been found that temperature dependence of EBIC contrast at grain boundaries varies not only with the misorientation but also with the boundary plane. The results can be explained by the difference in the position of the localized state within the band gap on the basis of the Shockley-Read-Hall statistics. The  $\{111\} \Sigma 3$  symmetrical tilt boundary has shallow states, whereas high  $\Sigma$  boundaries have deep states. Also, low angle boundaries reveal high electrical activities. The EBIC contrast at low angle boundaries was found to increase with increasing misorientation angle up to 2 degrees, followed by an almost constant value. High electrical activity at low angle grain boundaries is probably attributed to a stress field of primary dislocations forming low angle boundaries.

### **M3.17**

**OBSERVATIONS OF INTERACTION BETWEEN MAGNETIC DOMAIN WALL AND GRAIN BOUNDARIES IN Fe-3wt%Si ALLOY BY KERR MICROSCOPY.** Koichi Kawahara, Yukinori Yagyu, Sadahiro Tsurekawa, Tadao Watanabe, Tohoku Univ, Dept of Machine Intelligence and Systems Engineering, Sendai, JAPAN.

The magnetic properties of ferromagnetic materials are closely related to magnetic domain structures. The domain structure is known to be

affected by various kinds of defects such as voids, cracks and grain boundaries. Therefore, it is of great importance to understand the interaction between the domain wall and those defects for control of magnetic properties in polycrystalline materials. In this study, we have examined the effect of grain boundaries on the arrangement of domain patterns in Fe-3wt%Si alloys. In particular, much attention has been paid to grain boundary character on the development of the domain structures. Individual grain boundaries were characterized by an SEM/ECP and/or an SEM/EBSD techniques, then domain structures were observed by a magneto-optical Kerr microscopy. It was found that the observed domain patterns depended strongly not only on the misorientation angle, but also on the inclination of boundary planes. For small misorientation angle of the grain boundary, the stripe domain structure was not disturbed by grain boundaries and the continuity of the domain was kept. As the misorientation angle increased, the domain was found to incline at the grain boundary by the misorientation angle, but the domains were still continuous at grain boundaries. On the other hand, for large misorientation angle, the domain structure was largely disturbed by grain boundaries, resulted in the discontinuous domain structure. The magnetic domain wall favored to orient parallel to such an easy magnetization axis whose perpendicular component was the largest to the grain boundary.

### **M3.18**

**INTERFACE RELATED STRENGTH PHENOMENA IN TWO-PHASE TITANIUM ALUMINIDES.** Ulrich Christoph, Michael Oehring, Fritz Appel, GKSS Research Centre, Institute for Materials Research, Geesthacht, GERMANY.

Titanium aluminides with compositions slightly lean in Al are presently being considered for engineering applications. Phase equilibria and transformation in these alloys lead to the formation of a lamellar microstructure comprising of the intermetallic phases  $\alpha_2$ (Ti<sub>3</sub>Al) and  $\gamma$ (TiAl). This morphology has received much attention since nearly all mechanical properties of  $\gamma$ -base alloys are improved when the materials contain a significant volume fraction of lamellar colonies. Several aspects of the deformation behaviour might be associated with mismatch structures and coherency stresses of lamellar interfaces. In the present study these structural features will be examined by detailed transmission electron microscopy observations involving in situ heating studies and high resolution imaging techniques. The implications of interface related processes will be discussed with respect to strengthen phenomena and the structural stability of lamellar materials.

### **M3.19**

**THE STRUCTURE AND DEFECTS OF THE INTERFACES IN YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/BaTbO<sub>3</sub> AND PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/BaTbO<sub>3</sub> HETEROSTRUCTURE THIN FILMS.** C.L. Jia, R. Hojczyk, M. Faley, U. Poppe and K. Urban, Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

The interfaces in c-axis oriented YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/BaTbO<sub>3</sub> and PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/BaTbO<sub>3</sub> heterostructure thin films are investigated by high-resolution transmission electron microscopy. It is found that the BaTbO<sub>3</sub> layers terminate at the interfaces by either the TbO<sub>2</sub> or the BaO plane, depending on the deposition temperature. The two types of terminating planes does not only result in two types of interface structure with facing the Cu-O chain plane of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> or PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> layers, but also lead to different defect configurations at the interfaces.

### **M3.20**

**ENHANCEMENT OF THE ADHESION OF CORDIERITE GLASS-CERAMIC COATINGS ON MOLYBDENUM BY THE DEPOSITION OF METALLIC INTERLAYERS ON THE SUBSTRATE.** Jesus Noel Calata, Guo-Quan Lu, Thomas Kuhr, Virginia Polytechnic Inst and State Univ, Dept of Materials Science and Engineering, Blacksburg, VA.

Sintered coatings of cordierite-base glass-ceramic do not adhere readily on bare molybdenum substrates. This is due to the absence of a stable metal oxide film on the substrate that serves as a suitable transition layer between the glass-ceramic and the substrate. To address this problem, dual layers of either chromium/nickel or chromium/copper were deposited by electroplating on the molybdenum substrates. Glass powder in slurry form was then cast on the substrates using a doctor blade and sintered in a helium-hydrogen atmosphere at 950°C. The metallic interlayer structure was found to produce an excellent bond between the coating and the substrate. The adhesion of the coatings was observed to be sensitive to the thickness of the deposited metal layers. Quantitative chemical analysis of the interface region was performed to explain the difference in adhesion quality. In all instances, the fracture surface was found to occur at the chromium oxide/chromium boundary providing a clear indication that the chromium oxide layer plays an important role in enhancing the

adhesion. The superior adhesion in samples with the Cr-Cu interface was attributed to Cu acting as an effective diffusion barrier to Mo. Cr however, was able to diffuse through the Cu layer enhancing the bond between Mo and Cu by alloying with the Mo. Ni was not as effective as Cu in preventing the diffusion of Mo towards the glass-ceramic coating but a thicker Cr layer still produced a strong bond. In samples where the distinct Cr layer was either too thin or non-existent, adhesion was poor possibly because the Cr oxide does not bond well to the Ni-Cr alloy layer that formed after firing.

### **M3.21**

**IMPROVEMENT OF THE ADHESION OF BOROSILICATE GLASS ON STAINLESS STEEL BY A PREOXIDATION TREATMENT OF THE SUBSTRATE.** Jesus Noel Calata, Guo-Quan Lu, Xingsheng Liu, Virginia Polytechnic Inst and State Univ, Dept of Materials Science and Engineering, Blacksburg, VA.

Sintering of glass on metal substrate is an inexpensive method of producing protective coatings and insulation on metal surfaces such as plates and tubes. Sintered coatings of borosilicate glass (BSG) generally adhere to stainless steel substrates. The coatings are typically produced by casting glass slurry on the substrates using a doctor blade. The coated steel substrates can then be fired in air at or in the vicinity of the softening point of the glass (710°C). The adhesion is enhanced by the presence of an adherent and stable oxide layer on the metal surface. However, the bond quality on a clean stainless steel surface is spotty and inconsistent. The coating had a tendency to spall over a prolonged period of time. Spalling occurred faster when thick substrates were used. The difference in the thermal expansion coefficients of the coating and the substrate induces a residual in-plane stress upon cooling and accelerates the debonding of the glass coating. A simple preoxidation of the substrate surface by heating at elevated temperature was found to significantly improve the adhesion and stability of the sintered glass coating on the substrate. The coating is able to withstand mechanical handling and polishing without delamination. Preoxidation temperatures between 600 to 700° generally produced satisfactory adhesion between the glass and substrate.

### **M3.22**

**THE EFFECT OF FRICTION ON SCRATCH ADHESION TESTING; APPLICATION TO A SOL-GEL COATING ON POLYPROPYLENE.** M.H. Brees, A.R. Balkenende, J.M.J. den Toonder, Philips Research Laboratories Eindhoven, THE NETHERLANDS; G.B. Winkelman, Cooperative Research Centre for Alloy and Solidification Technology (CAST), CSIRO Manufacturing Science and Technology, Preston, Victoria, AUSTRALIA.

A detailed study on the effect of friction on scratch adhesion testing is described. The scratch test was applied to a model system consisting of a (hybrid) sol-gel coating deposited on polypropylene. The friction coefficient between indenter and coating was varied by a short plasma modification of the surface of the coating, while all other relevant parameters (i.e., interfacial adhesion, layer thickness, E-modulus of the coating, etc.) remained constant. The critical load (normal to the surface) showed a pronounced decrease of more than an order of magnitude with increasing friction coefficient. Several models are discussed and compared to the experimental data. In addition, the effect of substrate pretreatment on coating adhesion was studied. The adhesion of the sol-gel coating induced by microwave oxygen plasma modification of polypropylene, is considerably better than the adhesion obtained by wet-chemical modification in chromosulfuric acid at room temperature. The adhesion induced by immersion in chromosulfuric acid is shown to be independent of the immersion time between 1 and 10 min.

### **M3.23**

**BIAXIAL ZERO CREEP MEASUREMENTS OF INTERFACE ENERGIES IN Ni/Ag MULTILAYERS.** A.B. Mann, A.C. Lewis, T.P. Weihs, The Johns Hopkins University, Materials Science & Engineering Department, Baltimore, MD; D. Josell, NIST, Metallurgy Division, Gaithersburg, MD; J. Tapson, University of Cape Town, Department. of Electrical Engineering, Rondebosch, SOUTH AFRICA.

A new experimental setup combining wafer curvature measurements with a vacuum furnace has been used to perform zero creep measurements on Ni/Ag multilayer films on sapphire substrates. These experiments have been explicitly designed to measure the free energies of solid-solid interfaces and to investigate their effect on the structural stability of multilayered materials. Two distinct types of interfaces are characterized for the multilayer samples: the grain boundaries within the individual layers and the interfaces between the alternate layers. Grain boundary free energies ( $\gamma_{gb}$ ) have been measured for many elements and alloys, but only a few free energies ( $\gamma_{int}$ ) have been quantified for interfaces between dissimilar solid phases. Current understanding suggests that the ratio of the free

energies for these two interfaces ( $\gamma_{gb}/\gamma_{int}$ ) controls the stability of nanoscale and microscale multilayer materials; when the ratio  $\gamma_{gb}/\gamma_{int}$  is large, significant grooving occurs where grain boundaries meet the interfaces between layers. In this case, grooves can extend through layers and the microstructure is unstable. When  $\gamma_{gb}/\gamma_{int}$  is small, there is little grooving at grain boundary-interface junctions and the layering is stable. For the Ni/Ag multilayers studied, significant plastic straining, followed by constant strain (equilibrium), is observed using the wafer curvature system when the multilayers are at temperatures of approximately 400C and above. Combining the wafer curvature data with subsequent scanning electron microscopy of the grain boundary grooves in the specimen permits equilibrium measurements of  $\gamma_{gb}$  and  $\gamma_{int}$ . This distinguishes the biaxial technique from the uniaxial zero creep techniques which are kinetic in their nature, and hence, dependent on the dominant deformation mechanism. The results for Ni/Ag obtained with the biaxial technique are compared to those obtained previously with the uniaxial method.

### **M3.24**

**INDENTATION-INDUCED DUCTILE FILM INTERFACIAL DEBONDING.** Alex A. Volinsky<sup>1</sup>, W. Miles Clift<sup>2</sup>, Neville R.

Moody<sup>2</sup> and William W. Gerberich<sup>2</sup>; <sup>1</sup>University of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; <sup>2</sup>Sandia National Laboratories, Livermore, CA.

Thin film adhesion can be measured by means of the nanoindentation technique [1]. In the case of a ductile film (Cu, Al, Au, etc.) well adhered to a brittle substrate, plastic deformation in the film acts as an energy dissipation mechanism, preventing film debonding. Depositing a brittle layer of W (about 1 micron thick) on top of the film of interest increases the driving force for delamination, thus solving the problem. Indentation produces circular delaminations (blisters), sometimes two orders of magnitude bigger than the indenter contact radius. Thin film adhesion was shown to scale with the film thickness, approaching the true work of adhesion of 0.4 J/m<sup>2</sup> for Cu films under 100 nm thick [2]. Conceptually it is important to know along what interface the fracture occurs during the blister formation. Auger electron spectroscopy (AES) has been used to determine where fracture occurs for different film systems. Cu films on SiO<sub>2</sub> failed along the Cu/SiO<sub>2</sub> interface. Fracture of Cu films with a 10 nm adhesion-promoting Ti underlayer occurred along the Ti/Cu interface. Ti increased the thin Cu film adhesion by a factor of ten. Blisters were removed from the substrate, and the fracture surface was analyzed. In the case of thin Cu films, crack arrest marks were found upon blister removal, and represent the shape of the crack tip [3]. AFM has been used to determine the geometry of the marks. The main component of a mark is carbon, which comes from the hydrocarbons adsorbed on the newly formed surfaces in the indentation process. I. D.B. Marshall and A.G. Evans, J. Appl. Phys., 1984, 56, pp. 2632-38 2. A.A. Volinsky, N.I. Tymiak, M.D. Kriese, W.W. Gerberich and J.W. Hutchinson, Mater. Res. Soc. Proc. 539, 1998 3. A.A. Volinsky and W.W. Gerberich, Mater. Res. Soc. Proc. 553, 1999

### **M3.25**

**INTERFACIAL EFFECTS IN Nb/Nb<sub>5</sub>Si<sub>3</sub> MICROLAMINATES FOR HIGH TEMPERATURE APPLICATIONS.** David Van Heerden, Andrew J. Gavens, Tim P. Weihs, Johns Hopkins University, Dept Materials Science and Engineering, Baltimore, MD; Tim Foecke, National Institute of Standards and Technology, Gaithersburg, MD.

New microlaminate composites are now being developed to serve as the outer walls in future high-temperature turbine blades. These composites consist of a refractory metal that imparts room temperature toughness and an intermetallic phase that instills high temperature creep resistance. Here we consider Nb/Nb<sub>5</sub>Si<sub>3</sub> microlaminates that are vapor deposited and possess strong and stable interfaces between the Nb and Nb<sub>5</sub>Si<sub>3</sub> layers. We demonstrate that the strength and stability of these interfaces is critical in determining the mechanical properties of these materials both at room temperature and at high temperature. At room temperature the microlaminates fail in tension by cracking of the brittle silicide layers and plastic straining of Nb ligaments that bridge the crack faces. Because the Nb/Nb<sub>5</sub>Si<sub>3</sub> interfaces are strong, the edge cracks that tunnel through the silicide layers do not extend up along these interfaces. Thus, the bridging Nb ligaments are highly constrained and their plasticity and ductility are some what limited, at least compared to metal/silicide composites with weak interfaces. At high temperatures above 1200°C the Nb/Nb<sub>5</sub>Si<sub>3</sub> interfaces are very stable with limited grooving or signs of breakdown. However, we will show that the creep rates of the microlaminates are dependent upon the number of interfaces and increase as interface density increases. In addition we will show that metastable phases form at the Nb/Nb<sub>5</sub>Si<sub>3</sub> interfaces above 1400°C and these phases act to degrade the mechanical properties of the samples.



### **M3.26**

**MICROSTRUCTURAL EVOLUTION IN FCC MATERIALS DURING SEQUENTIAL THERMOMECHANICAL PROCESSING IMPLICATIONS FOR GRAIN BOUNDARY ENGINEERING.** Mukul Kumar, Adam J. Schwartz and Wayne E. King, Lawrence Livermore National Laboratory, University of California, Livermore, CA.

Manipulation of the relative fractions of special and random boundaries in the microstructure in order to improve materials properties like corrosion, creep resistance, and weldability has received increased attention in recent years. Sequential thermomechanical processing consisting of moderate strains and annealing at high temperatures for short periods of time has been employed to systematically modify the topology of the microstructure. The optimization treatments performed on fcc metals and alloys with low to medium stacking fault energies have resulted in microstructures with high fractions of  $\Sigma 3^n$  and other special boundaries, as defined by the CSL model. These modifications in the grain boundary network have been correlated with OIM and TEM observations of the deformed and annealed states of the material. The evolution of the microstructure, with a high fraction of  $\Sigma 3^n$  boundaries, has been correlated with the decomposition of immobile boundaries during annealing. This has been evidenced by TEM observations of relatively immobile boundaries decomposing into two components, one with very low energy and thus immobile, and the other a highly mobile boundary that migrates into neighboring areas of higher strain levels to produce a relatively strain free microstructure. These results will be discussed within the context of existing theories for the formation of annealing twins in fcc materials. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48.

### **M3.27**

**EFFECT OF SELF ASSEMBLING MONOLAYERS ON ICE ADHESION TO METALS.** Shuling Peng, Victor F. Petrenko, Dartmouth College, Thayer School of Engineer, Hanover, NH; Masahiko Arakawa, Hokkaido University, Sapporo, JAPAN.

Strong adhesion of ice to almost all known solids is a serious engineering problem that has not been solved yet because physical mechanisms of ice adhesion are not understood. In this research we used an original method to study the role of hydrogen bonding in ice adhesion and to minimize the effect of this mechanism on ice adhesion. For this purpose, we coated metals (Au and Pt) with a mono-molecular layers of specific organic molecules that had either strong hydrophobic properties (CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH) or strong hydrophilic properties (OH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH). To determine the contribution of hydrogen bonding to ice adhesion SAMs of varying hydrophobia/hydrophilia were made by mixing the hydrophobic and hydrophilic components. All the films were built of similar molecules that differed only in their outermost groups, OH- and CH<sub>3</sub>. Thus, when the films were grown on the same substrate (almost atomically smooth metal films) any difference in their adhesion to ice were due to the difference in the hydrogen bonding between the ice and SAM's. The films structure and quality were examined with SPM and the degree of SAM's hydrophobia/hydrophilia was characterize with a contact angle of water on the films. We have then frozen water on the films and measured shear strength of ice/SAM/metal interfaces. Possible damage to the interfaces was examined with SPM after the ice was melted. We found a correlation between the contact angle of water and the ice adhesion strength even though the hydrogen bonding was found neither single nor major mechanism contributing in ice adhesion.

### **M3.28**

**MODIFICATION OF STRUCTURAL AND PHYSICAL PROPERTIES IN OXIDES BY EPITAXIAL LATTICE DEFORMATION.** J.W. Seo<sup>1,2</sup>, J. Perret<sup>1,2</sup>, J. Fompeyrine<sup>2</sup>, H. Siegwart<sup>2</sup> and J.-P. Locquet<sup>2</sup>, <sup>1</sup>Université de Neuchâtel, Institut de Physique, Neuchâtel, SWITZERLAND, <sup>2</sup>IBM Zurich Research Laboratory, Rüschlikon, SWITZERLAND.

The transition metal oxides exhibit a large variety of electrical & magnetic properties and can be grown by MBE with a high structural perfection. However, the thin film phase diagram shifts away from the bulk compound, beyond what is feasible under high pressure and novel properties appear. As a film grows on a substrate, strain is induced due to their mismatch yielding a lattice deformation that can stabilize novel phases. This applies to structural, electrical (metal-insulator; ferroelectric-paraelectric) and magnetic (antiferromagnet - paramagnet) phases. It allows first to shed light on the fundamental microscopic interactions responsible for the physical properties observed and second, to modify the lattice, going beyond what nature allows us. Examples relate to superconductors (doubling of  $T_c$  in La<sub>1.9</sub>Sr<sub>0.1</sub>CuO<sub>4</sub>), dielectrics ( $\epsilon$  in Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub>), ferroelectrics (in-plane polarization in LaTiO<sub>3.5</sub>) and

antiferromagnets ( $T_N$  and exchange bias in La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub>). Attention is paid to correlate the observed changes in properties with the precise lattice deformation. We explore how different substrates or defects change the lattice deformation and consequently the physical properties. Finally, the mechanisms linking microstructure with physical properties and their use to modify a given lattice are studied.

### **M3.29**

**FRACTURE AND OXIDATION OF POROUS CERAMIC INTERFACIAL LAYERS.** Ramanathan Krishnamurthy, Franco M. Capaldi and Brian W. Sheldon, Division of Engineering, Brown University, Providence, RI.

Thin porous ceramic layers were formed by aerosol spray deposition of nanosized alumina powders, followed by hot-pressing. These materials have previously been used to produce laminated ceramics with enhanced toughness. In the current work, model sandwich specimens of these materials were used to explore fundamental questions about crack deflection and interfacial fracture resistance. Crack deflection was observed to occur in cases where the measured interfacial fracture resistance far exceeds the upper bound predicted by He and Hutchinson. In cases where the porous alumina was sandwiched between bulk SiC bars, interfacial oxidation reactions typically reduced the interfacial fracture resistance. In addition to these experimental results, possible explanations for the observed behavior will also be analyzed and discussed.

### **M3.30**

**EVOLUTION OF THE TRIPLE JUNCTION DISTRIBUTION IN POLYCRYSTALS WITH SEQUENTIAL THERMOMECHANICAL PROCESSING.** Wayne E. King, Mukul Kumar and Adam J. Schwartz, Lawrence Livermore Laboratory, Livermore, CA.

Recently, it has been demonstrated that grain boundary engineering, i.e., systematic modifications in the topology of the microstructure, can enhance some material properties. Observations of the improvements in properties have been correlated with enhancements in the special fraction of the grain boundary character distribution (GBCD). It has been suggested, however, that improvements in the GBCD are a necessary condition but not fully sufficient to cause property improvements. For example, it has been observed that cracks propagating along interconnected networks of random grain boundaries can be arrested when intersecting a triple junction where the remaining two pathways are special boundaries. Therefore, it is of interest to characterize microstructures in terms of the distributions of triple junction types. A simple description of a triple junction is in terms of the types of grain boundaries intersecting at that junction (special vs. random). The distribution of 0-CSL, 1-CSL, 2-CSL and 3-CSL triple junctions in the microstructure can then be plotted as a function of the fraction of special boundaries. Such data has been collected using orientation imaging microscopy for oxygen-free electronic (ofe) Cu and Inconel 600 over a range of GBCD. These results have been compared with theoretical models considering isolated triple junctions and invoking the S-product rule where S is the inverse density of coincident lattice sites. This work is performed under the auspices of U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

### **M3.31**

**THE CRITICAL STRESS FOR TRANSMISSION OF A DISLOCATION ACROSS AN INTERFACE: RESULTS FROM PEIERLS AND EMBEDDED ATOM MODELS.** Peter M. Anderson, Yaogeng Cheng, Dept. MSE, Ohio State University, Columbus, OH; Satish Rao, Peter Hazzledine, UES Inc, Dayton, OH.

The critical stress for dislocation transmission across interfaces is a fundamental interfacial quantity. Our understanding of Hall-Petch slope, for example, and the maximum possible plastic strength achievable in nanocomposites depends on the magnitude of such a critical stress. Earlier models have viewed the transmission process using both Volterra (Head) and Peierls (Pacheco and Mura) descriptions of the transmitting dislocation. This paper extends those models by allowing the interface to slip, so that it can store and supply dislocation content during the transmission process. One approach uses the Peierls approach to model the elastic mismatch and relative sliding of the interface during transmission. A second approach uses the embedded atom approach to simultaneously account for the mismatches in elastic constants, lattice parameters and stacking fault energies across an interface of a layered material. Results show that interfacial slip can dramatically change the process of interfacial transmission and the corresponding critical stress. Interfaces which are compliant to shear appear to readily attract a dislocation, so that the critical stress to transmit is associated with that to extract the dislocation from the interface. The results of the EAM and Peierls approaches will be compared and contrasted with previous models.

### **M3.32**

**BONDING AND INTERFACE CHARACTERIZATION OF THE IMMISCIBLE Cu-Ta SYSTEM.** M.E. Reiss, Johns Hopkins University, Dept of Materials Science and Engineering, Baltimore, MD; S.E. Shoenfeld, G. Boyce, Army Research Labs, Aberdeen, MD.

The mechanism by which mechanically robust bonds can be formed between two immiscible materials is not well understood, but is of considerable interest for joining applications. In this paper we investigate the nature of the bond between two such systems, namely Cu and Ta, as well as the factors that influence its mechanical integrity. The samples examined in this work were varying sizes of Cu and Ta plate. The bonding of the plates was achieved using isothermal anneals as well as vacuum induction heating. The sample geometries and bonding conditions were varied in order to investigate the influence of surface roughness and existence of oxides on the bond strength. Using the induction press method we examined the effect of temperature profiles across the interface on the mechanical properties of the interface. The mechanical properties of the interfaces were determined using double lap shear tests. For both processes mentioned we show that there is extensive interfacial adhesion with shear strengths exceeding those of the Cu constituent. The observed mechanical properties of the interfaces will be discussed on the basis of the structure and bonding of the interfaces.

### **M3.33**

**STRUCTURAL DESIGN OF GEOMETRICAL SHAPE OF INTERFACE IN BONDED DISSIMILAR MATERIALS BASED ON INDEX OF STRESS SINGULARITY.** Masayoshi Tateno, Kogakuin University, Dept of Mechanical Engineering, Tokyo, JAPAN; Yasushi Fukuzawa, Shigeru Nagasawa, Nagaoka University of Technology, Dept of Mechanical Engineering, Niigata, JAPAN; and Hiroshi Sakuta, Aoyama Gakuin University, Dept of Mechanical Engineering, Tokyo, JAPAN.

In order to evaluate practical strength of bonded dissimilar materials and fracture mode of one, it is an important to notice stress distribution near edge of interface by analysis of strength and fracture. A factor of strength evaluation which indicates feature of the stress distribution, is index of stress singularity based on theoretical elastic analysis. In this paper, thermal stress analysis and evaluation of experimental practical strength of bonded dissimilar materials are carried out to clarify a possibility of simplified evaluation of the practical strength based on index of stress singularity. Applicability of secant stiffness module to evaluation of the practical strength, is evaluated by elastoplastic FEM analysis method which is used for the analysis of stress distribution in composite materials. As model materials for FEM analysis, the couple of Ceramics-Metal Joint as  $TiB_2 - Ni$  is applied, which have temperature dependency of physical constants of materials. The geometrical condition of interface shape for the analysis is sphere. It is found that thermoelastic behavior with usage of secant stiffness module is almost compatible to thermal elastoplastic behavior. Relationship between index of stress singularity and practical tensile strength of bonded  $TiB_2 - Ni$  system is investigated by comparing thermoelastic behavior with the practical strength under geometrical edge angle of interface between  $60^\circ$  to  $90^\circ$ . Correlation factor of the relationship between index of stress singularity and the practical strength of bonding is found positive. Thus, practical strength can be evaluated by usage of index of stress singularity based on thermoelastic analysis. This result shows that structural design of high strength bonded dissimilar materials is possible based on index of stress singularity.

### **M3.34**

**NEAR-INTERFACE CRACK INITIATION IN THERMAL BARRIER COATINGS.** Zhehua Zhang, T.E. Bloomer, J. Kameda, Ames Laboratory, Iowa State University, Ames, IA; S. Sakurai, Mechanical Engineering Research Laboratory, Hitachi Ltd, Hitachi, JAPAN.

A protruded four-point bending testing method has been developed to characterize the near-interface crack initiation of thermal barrier coatings (TBC). Two types of protruded TBC specimens, with and without a reinforcement on the top of the protruded TBC, were prepared from in-service used transition ducts made of TBC (8% $Y_2O_3$  stabilized  $ZrO_2$ ) and bond coatings (NiCoCrAlY) plasma-sprayed over a super alloy substrate. In the unreinforced protruded TBC specimen tests, pre-existing TBC cracks extended in the transverse direction while near-interface TBC cracking did not occur. The reinforced protruded TBC specimen hindered the transverse TBC cracking and allowed the formation of TBC cracks adjacent to the oxidized TBC/bond coating interface in a similar mode to in-service TBC spalling. The onset of TBC cracks was identified by a change in the loading rate in the elastic deformation regime. The local stress distribution at the edges of reinforced protruded TBC was analyzed using finite element analysis. The critical local tensile stress for the initiation of TBC cracks near the interface was estimated for the

in-service used transition duct. The near-interface TBC cracking behavior in the protruded TBC tests is discussed in light of the applied and residual stress distribution.

## SESSION M4: INTERFACE STRUCTURE/COMPOSITION/CHARACTER

Chair: Ernest L. Hall  
Thursday Morning, December 2, 1999  
Salon C/D (M)

### **8:30 AM \*M4.1**

**TAILORING GRAIN BOUNDARY SEGREGATION TO CONTROL MECHANICAL PROPERTIES.** David B. Williams and Vicki J. Keast\*, Lehigh University, Dept of Materials Science and Engineering, Bethlehem, PA. \*Cambridge University, Department of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

Traditionally, the relationship between microstructure and properties has dominated the field of physical metallurgy. However, there are cases when understanding the structure is not sufficient to comprehend the properties. One example is intergranular brittle fracture, which is often associated with the segregation of an impurity element to grain boundaries (GBs). While the GB structure may indeed affect the amount of segregation, it is still the boundary chemistry rather than the structure that appears to control the failure. GB segregation is associated with such phenomena as temper embrittlement and hot shortness in steels, stress-corrosion cracking, hydrogen embrittlement and liquid-metal embrittlement. Despite the well-known association of segregation with such failures, we still do not know the distribution of segregants on all GBs. Typically, segregants are localized within an atomic monolayer, but variation from boundary to boundary can be significant, e.g. from zero to several mono layers. Recent developments in high spatial resolution X-ray mapping in the analytical electron microscope (AEM) have made it possible to determine the statistical distribution of segregants on large numbers of grain boundaries, without the need to fracture the specimen, which may disturb the boundary chemistry. While GB segregation correlates with brittle fracture, it is still not known *why* a segregant causes failure since, in other cases, (e.g. B in  $Ni_3Al$ ) segregation makes a brittle material become ductile. Similarly electromigration in Al interconnects in semiconductors is reduced by orders of magnitude when a few percent of Cu segregates to the GBs. Electron energy-loss fine structure studies in the AEM can reveal changes in atomic bonding at boundaries containing segregants, which may explain why certain segregants embrittle and others do not. Understanding the role of segregation in bonding changes may permit direct control of mechanical properties and the tailoring of the boundary chemistry to give the desired behavior.

### **9:00 AM \*M4.2**

**INTERFACE CHARACTERIZATION USING THE AUTOMATED-EBSP TECHNIQUE.** John A. Sutliff, GE Corporate Research and Development, Niskayuna, NY.

The use of the Electron BackScattering Pattern (EBSP) technique of electron diffraction (also called EBSD and BKD) to study microstructure continues to gain popularity in the materials characterization community. The techniques ability to rapidly measure lattice orientation with good relative accuracy provides a statistically powerful tool for investigating the misorientation character of interfaces. It is certainly possible to gather basic misorientation data on thousands of interfaces in a only a couple of hours. This paper will discuss the detection and characterization of interfaces in polycrystalline materials using the automated-EBSP technique with specific discussion of sub-grain and twin boundaries in deformed and/or annealed materials. This paper will also attempt to demonstrate with data from  $\gamma/\gamma'$  Ni-base superalloys that the process of acquiring, with high accuracy, all the spatial, orientation, and chemical information associated with boundaries during an extended data acquisition is a substantial experimental challenge. Combining quantitative image analysis of traditional high-resolution scanning electron micrographs with the EBSP data can help correct some of the distortions commonly encountered in EBSP data.

### **9:30 AM M4.3**

**ATOMIC FORCE MICROSCOPE AND TRANSMISSION ELECTRON MICROSCOPE CHARACTERIZATION OF POST ION IMPLANTED CUBIC BORON NITRIDE MULTI-LAYER FILMS FOR CUTTING TOOL APPLICATIONS.** Rui Liu, Changmo Sang, Center for Advanced Materials, Dept. of Chem. & Nuclear Eng., University of Massachusetts, Lowell, MA; E.S. Byon, K.W. Lee, S.W. Lee and S.R. Lee, Korea Institute of Metals and Machinery, Changwon, KOREA.

Cubic boron nitride (c-BN) is a chemically inert, thermally conducting, electrically resistive material with hardness second only

to that of diamond. The major limiting factor of using c-BN thin films is the poor adhesion between the film and substrate due to the strong compressive stress built up during the deposition process as well as the limited thickness (less than 500 nm) for cutting tool applications. Boron nitride thin films were deposited by Magnetically Enhanced Activated Reactive Evaporation technique (ME-ARE) and the plasma immersion ion implantation was repeatedly applied to improve the adhesion and to obtain thicker c-BN multilayer films. Nitrogen was the best ion source for c-BN formation. By changing the ion implantation energy and dose, the optimum conditions were determined for the formation of c-BN films. Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM) were used to characterize the interfacial structures of BN films in a cross-sectional view and the phase distributions by force modulation and phase contrast techniques in a plan-view. Microstructural results will be discussed in relation with processing conditions to achieve thicker and high quality interface in c-BN multilayer films.

#### 9:45 AM M4.4

ENGINEERING THE INTERFACIAL CHEMISTRY IN METAL/OXIDE SYSTEMS. K. Pruessner<sup>1,3</sup>, P.Y. Hou<sup>2</sup>, B.A. Pint<sup>1</sup>, K.B. Alexander<sup>1,4</sup>, and P.F. Tortorelli<sup>1</sup>, <sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, <sup>2</sup>Berkeley National Laboratory, Berkeley, <sup>3</sup>now at: Universität Siegen, GERMANY, <sup>4</sup>now at: Los Alamos National Laboratory.

Alloys for high-temperature applications such as turbine blades depend on the formation and adhesion of a dense, slow-growing oxide scale, e.g. alumina, which protects the material from further deterioration. The adhesion of the scale is usually a problem though, especially under thermal cycling conditions. It has been recognized that the chemistry of the scale/metal interface is of crucial importance for the resistance of the scale to spallation. Both alloying elements and impurities are of importance. In our experiments, the composition of model alloys and commercial materials has been modified. Thermally grown scales were compared to plasma-deposited coatings of similar composition. Microstructure and microchemistry of the resulting alumina scales were characterised by transmission electron microscopy (TEM) techniques. Segregation of alloying elements and impurities at the metal/oxide interfaces was analysed using energy-dispersive x-ray spectroscopy (EDS) with a fine probe in a FEG-TEM. The experiments show that both for model alloys and commercial alloys the composition of the interface plays a critical role in the oxidation performance of the material. Oxygen active elements such as yttrium or zirconium segregate to the interface in systems with a thermally grown interface and in systems with an artificial interface between a coating and the alloy. In both cases also segregation of the reactive element to oxide grain boundaries occurs. In systems without reactive elements, the oxidation performance is determined by minor impurities in the alloy, such as sulfur. Sulfur was found to segregate to the scale/metal interface and result in spallation of the scale or coating.

#### 10:30 AM \*M4.5

ENHANCING OXIDATION PERFORMANCE BY CONTROL OF INTERFACIAL SEGREGATION AND MICROSTRUCTURAL DESIGN. Kathleen B. Alexander\*, Bruce A. Pint and Peter F. Tortorelli, Oak Ridge National Laboratory, Oak Ridge, TN; \*now at Los Alamos National Laboratory, Los Alamos, NM.

Thermally-grown oxide scales on high temperature alloys can provide oxidation protection if they are slow-growing, dense and adherent to the substrate. The factors affecting the integrity of the metal/oxide interface during dynamic oxidation processes are complex and include interfacial segregation, interface morphology, near-interface substrate properties, as well as the development of stresses in the growing oxide scale. Minor additions of reactive elements (RE) to the base metal have been shown to improve the oxidation performance of many high temperature materials. Studies on a variety of alloys have shown that the presence of reactive elements in the alloy affects segregation processes at both the metal/oxide and oxide/oxide interfaces. Whereas segregation to the metal/oxide interface can affect the scale adherence, segregation to the oxide/oxide interfaces in RE-containing systems has been proposed to result in changes in transport mechanisms as well as changes in the scale microstructure itself. High spatial resolution analytical electron microscopy techniques has been used to provide information on the microstructure and microchemistry of the scale and the metal/oxide and oxide/oxide interfaces. In general, in systems which exhibit improved oxidation performance, a consistent set of interfacial segregation phenomena and microstructural features were observed. Examples will be shown from a variety of nickel- and iron-based alumina formers. These kinds of studies, combined with traditional scanning electron microscopy studies of oxide scales can lead the development of a more complete link between RE doping, interfacial segregation, interfacial/scale microstructure, and oxidation performance.

#### 11:00 AM \*M4.6

INTERFACE MULTIPLICATION THROUGH THE COMBINATION OF INTERFACE DIFFUSION-CONTROLLED AND LATTICE DIFFUSION-CONTROLLED PHASE TRANSFORMATIONS IN ALLOYS. J.A. Cohn, R.M. Andrade and I.G. Solorzano, DCMM, PUC-Rio de Janeiro, BRAZIL.

The procedure for obtaining interface and grain boundary multiplication, without externally applied deformation, in alloy systems is described. It is shown that an essential pre-requisite is the occurrence, and the possibility of controlling, discontinuous precipitation (DP) reactions in the alloy. Several alloy systems have been studied and experimentally generated, in a controlled volume fraction, DP lamellar products in the following model alloys: Al - 15at%Ag; Al - 22at%Zn; Cu - 7at%In and Ni - 8at%Sn. The resulting microstructures have been observed in detail through conventional and analytical electron microscopy, confirming that DP is a transformation controlled by solute diffusion along moving grain boundaries. Although the precipitates correspond to the equilibrium phase, the transformation, as a whole, does not reach thermodynamic equilibrium since high resolution microanalysis of aged and quenched microstructures reveal that a significant amount of supersaturation is retained in the depleted lamellar matrix. In addition, TEM observations has revealed that the DP products, besides generating a high density of interfaces, are able to incorporate a significant amount of strain energy in the wake of their growth. On the other hand, the dissolution of the lamellar microstructures has been observed to proceed though both continuous or discontinuous fashions. The former, dominating at high dissolution temperatures, is controlled by volume diffusion and gives rise to the development of new microstructures in the original DP colonies: the generation of dislocations and their dynamic re-arrangement into cellular structure in Al-base alloys; the formation of new grains through nucleation and growth mechanisms, in Cu - In alloys, or due to a topological effect in Ni - Sn alloys. Operating mechanism are proposed and the nature of the driving force for the observed phenomena is discussed in terms of its chemical, interfacial and strain energy components.

#### 11:30 AM M4.7

THE FORMATION OF CARBIDE INTERFACE LAYERS: THE MOLYBDENUM/CARBON AND SILICON/CARBON INTERFACE. P. Reinke, P. Oelhafen, Universität Basel, Institut für Physik, Basel, SWITZERLAND.

With the expansion of the application of carbon films for industrial purposes, the need to understand properties and formation of carbide interfacial layers is rapidly gaining in importance. In the present study we focus on the formation of molybdenum and silicon carbide interfaces in a wide temperature range (ambient to 1100°C), which is of interest for a variety of applications as well as deposition techniques (e.g. diamond deposition at T>600°C). The samples, either molybdenum or silicon, are exposed to a carbon beam created through the electron beam evaporation of graphite. The changes in surface composition and electronic structure are monitored in-situ by photoelectron spectroscopy in the ultraviolet (UPS) and X-ray regime (XPS). The reaction of carbon with the substrate leads to the formation of the stable carbide (SiC, Mo<sub>2</sub>C) prior to the onset of amorphous carbon overlayer growth. In the case of molybdenum the transition from metal to carbide is gradual and allows to study the electronic structure of the carbide and its sub-stoichiometric transitional stages. The growth of the carbide layer is strongly temperature dependent and proceeds even after the formation of an a-C layer (dynamic interface). In contrast, SiC functions as a diffusion barrier and forms a thin (< 1 nm), stable layer for temperatures below 900°C (static interface). The importance of interface dynamics can be illustrated in the deposition of diamond films, a typical high temperature deposition process. The method applied in this study also allows to investigate the electronic structure of contamination-free carbide surfaces of a wide range of materials and can be extended to include the investigation of other parameters decisive for interface quality.

#### 11:45 AM M4.8

ROLE OF INTERFACES ON SPINEL FORMING REACTION UNDER AN APPLIED ELECTRIC FIELD. C. Korte, N. Ravishankar, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; H. Schmalzried, Institut für Physikalische Chemie und Elektrochemie der Universität Hannover, Hannover, GERMANY; and C.B. Carter, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Composite ceramics or coated ceramics are materials of technological importance. The interfacial reactions that take place at elevated temperatures in these materials may lead to a mechanical and/or electrical failure. In many cases where the composite material is used as an insulator, it may also be subjected to high electric fields.

Presence of an electric field significantly increases ionic transport, thus leading to higher rate of interfacial reactions. This effect is particularly important along interfaces where the rate of matter transport is much higher than that through the bulk. Therefore, it is important to obtain an understanding of the nature of interfaces and their influence on the solid-state reactions that occur in electric fields. The aim of present research is to study the effect of electric fields on the mechanism of the formation of  $\text{MgIn}_2\text{O}_4$  by the reaction between single-crystal  $\text{MgO}$  substrate and a thin film of  $\text{In}_2\text{O}_3$  by using imaging and back-scattered Kikuchi diffraction in a SEM. The results indicate that the morphology during early stages of growth of the  $\text{MgIn}_2\text{O}_4$  in the electric field is determined by the grain structure of the  $\text{In}_2\text{O}_3$  layer. The reaction front is seen to progress faster at the places where the grain boundaries are present in the  $\text{In}_2\text{O}_3$  layer. Morphological instabilities due to different conductivities in  $\text{MgO}$ ,  $\text{MgIn}_2\text{O}_4$  and  $\text{In}_2\text{O}_3$  are, on the contrary, far less important. In this paper, the influence of the transport of  $\text{In}^{3+}$  and  $\text{Mg}^{2+}$  in the grain boundaries on the shape of the reaction front, will be discussed.

#### SESSION M5: MECHANICAL PROPERTIES

Chair: Clyde L. Briant

Thursday Afternoon, December 2, 1999

Salon C/D (M)

##### 1:30 PM \*M5.1

IMPROVEMENT OF MECHANICAL PROPERTIES OF METAL-OXIDE INTERFACES BY PROCESSING UNDER THE RIGHT OXYGEN PARTIAL PRESSURE. Monika Backhaus, Centre d'Etudes de Chimie Metallurgiques, CNRS, Vitry, FRANCE.

Metal-ceramic interfaces such as  $\text{MgO-Cu}$ ,  $\text{MgO-Fe}$ ,  $\text{Al}_2\text{O}_3\text{-Fe}$  and  $\text{Al}_2\text{O}_3\text{-Cu}$  are elaborated by internal reactions in order to produce flat, chemically clean, well oriented, perfect interfaces, which can serve as model interfaces. These interfaces are then equilibrated at different oxygen partial pressures in their coexistence range. Precipitate equilibrium shape is measured for a large number of precipitates by SEM and TEM for reconstruction of the Wulff shape as a function of  $p\text{O}_2$ . The exact atomic structure of the interfaces at a given  $p\text{O}_2\text{-T}$  condition is determined by HREM combined with image analysis and image simulation. Electronic interfacial states are deduced from interfacial ELNES and its semi-quantification. For all different model systems an evolution of the relative interfacial energies, atomic and electronic structure of the interface with the equilibrium oxygen partial pressure is observed which can be simplified as a preference of the system to form oxide bonds across the interface at high oxygen activity and to form metallic bonds at low oxygen activity. By proper choice of the oxygen activity during processing optimum mechanical properties of the metal-oxide interfaces can be obtained. A detailed thermodynamic analysis is combined with an analysis at an atomistic level.

##### 2:00 PM \*M5.2

ANNEALING EFFECTS ON INTERFACIAL FRACTURE OF GOLD-CHROME FILMS USED IN HYBRID MICROCIRCUITS. N.R. Moody, Sandia National Laboratories, Livermore, CA; A.A. Volinsky, University of Minnesota, Minneapolis, MN; D.P. Adams, Sandia National Laboratories, Albuquerque, NM; M. Kriese, Osmic Inc., Troy, MI; W.W. Gerberich, University of Minnesota, Minneapolis, MN.

Interface structure and composition are two of the most important factors controlling the performance and reliability of thin films. They are particularly important in gold-chrome hybrid microcircuits where the interfaces can change markedly during processing at elevated temperatures through diffusion and segregation. Nevertheless, the effect of these changes on durability is known only by relative comparisons. We have therefore begun a systematic study of how exposure to elevated temperatures during post deposition processing affects susceptibility to fracture using laboratory prepared gold-chrome films on sapphire substrates. We employed nanoindentation to determine film properties and combined nanoindentation with highly compressed overlayers to drive delamination and subsequent blister formation. In all cases, fracture occurred along the film substrate interface. Fracture energies and interfacial toughness values were obtained from the blisters and spalls using the mechanics-based models for circular buckle formation modified for multilayer films. From these results, mode I crack initiation values and interfacial bond strengths were determined assuming slow crack growth conditions for blister formation. In this presentation, the results will be used to show quantitatively that elevated temperature exposure increases resistance to interfacial fracture as does the use of chrome as an adhesive layer. In addition, the crack initiation fracture energies and interfacial bond strengths will be used to explore the processes controlling adhesion in these film systems. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

##### 2:30 PM M5.3

INTERFACE PROPERTIES OF CERAMIC COMPOSITES AT HIGH TEMPERATURE. X. Zhou, C. Marston, and Steven R. Nutt, Center for Composite Materials, University of Southern California, Los Angeles, CA.

The success of ceramic composites in high-temperature applications is strongly dependent on the interface designs, which are intended to provide toughness through debonding while resisting thermal oxidation in aggressive environments. Thus, understanding the temperature dependence of fiber interfaces provides important input to the interface design process, contributing to improved designs and enhanced properties. Interface properties are measured by fiber pushout testing conducted at high temperatures in a conventional SEM equipped with a heating stage and instrumented indenter. Three advanced ceramic composites were selected to perform pushout testing at 20-2000C. Variations in interface designs and effects of thermal history were evaluated with respect to interface failure strength. Interface property measurements were correlated with bulk mechanical response, and in some cases, TEM observations, to evaluate the effectiveness of the interface designs in achieving desired properties.

##### 2:45 PM M5.4

MEASUREMENT OF ADHESION STRENGTH OF Cu/EPOXY INTERFACES. Ho-Young Lee, Jin Yu, KAIST, Dept of Materials Science and Engineering, Taejon, KOREA.

The true interfacial energy between the Cu-based leadframe and epoxy molding compound (EMC) was varied by treating the Cu-based leadframe in alkaline solution and forming brown or black oxides. After oxidation, leadframes were molded with EMC and machined to form sandwiched double cantilever beam (SDCB) and sandwiched Brazil-nut (SBN) specimens. Then, the adhesion strengths between Cu-based leadframe and EMC were measured, and the failure paths were studied. SDCB and SBN specimens were designed to measure the adhesion strength in terms of critical energy release rate ( $G_C$ ) under quasi-Mode I and mixed Mode loadings, respectively. Results showed that oxidation of leadframe in the brown oxide forming solution introduced acicular  $\text{CuO}$  precipitates on the leadframe surface, and the thickness of  $\text{CuO}$  layer saturated  $\sim 0.15 \mu\text{m}$  within two minutes of the oxidation time. Once a continuous layer of oxide passivated the leadframe, no more oxidation occurred. In a similar manner,  $G_{IC}$  of leadframe/epoxy interface increased almost proportionally initially, reached a maximum value of  $\sim 80 \text{ J/m}^2$  at two minutes of the oxidation time, and saturated. On the other hand, oxidation of leadframe in the black oxide forming solution initially introduced pebble-like  $\text{Cu}_2\text{O}$  precipitates with smooth facets on the leadframe surface, and the thickness of  $\text{Cu}_2\text{O}$  layer reached  $\sim 0.2 \mu\text{m}$  within a minute. Then, acicular  $\text{CuO}$  precipitates, much larger than those of the brown oxide, started to nucleate on the  $\text{Cu}_2\text{O}$  layer and thickened up to  $\sim 1.3 \mu\text{m}$  at the 20 minutes of the oxidation time.  $G_{IC}$  was close to nil until the precipitation of  $\text{CuO}$  started after 1 minute, but increased rapidly to the level of  $90 \sim 100 \text{ J/m}^2$  after 3 minutes, and then saturated. The trend was consistent with the thickening kinetics of the  $\text{CuO}$  layer. Overall trends of  $G_C$  under mixed Mode loading secured by the SBN tests coincided well with those of SDCB tests at low phase angles. Fractography analyses based on XRD studies of leadframe and EMC fracture surface indicated that the failure paths were quite different with oxide type, oxide thickness, and the loading condition.

##### 3:30 PM \*M5.5

DYNAMIC EMBRITTLEMENT: QUASI-STATIC INTERFACIAL DECOHESION. C.J. McMahon Jr., Department of Materials Science and Engineering and J.L. Bassani, Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA; Y. Mishin, Department of Materials Science and Engineering, Virginia Polytechnic Institute & State University, Blacksburg, VA.

In a surprising variety of cases, interfaces in normally ductile materials can undergo time-dependent brittle cracking under the influence of a tensile stress, either applied externally or existing as an internal residual stress. The connecting feature in all these cases is the presence of a surface-adsorbed element that is highly mobile in comparison to the constituent elements of the material. As in the phenomena of diffusion creep and diffusive growth of cavities at high temperatures, the driving force for this cracking is the work done by the tensile stress when a surface atom enters the solid. At temperatures below about  $0.5T_m$  of the solid, this occurs mainly along grain boundaries. Examples of systems that have been studied in some detail include cracking of alloy steels by sulfur, Cu-Sn alloys by tin, and nickel-based alloys by oxygen. Because the cracking involves diffusive penetration along grain boundaries, the rate of cracking is highly sensitive to grain-boundary structure and composition, and these variables offer opportunities to control the

problem. We are aiming at a quantitative understanding of the effects of grain-boundary structure, stress, and temperature on this phenomenon by crack-growth experiments on bicrystals, by atomistic modeling of the stress-driven diffusion, and by micro-mechanical modeling of the events occurring at the tip of a growing crack.

**4:00 PM \*M5.6**

**INTERGRANULAR FRACTURE IN ALUMINUM: THE EFFECT OF GRAIN BOUNDARY ORIENTATION AND CRACK GROWTH DIRECTION.** Jeffrey W. Kysar, Clyde L. Briant, Brown University, Division of Engineering, Providence, RI.

Intergranular fracture is a common failure mechanism in materials and many issues remain to be resolved. In this work we discuss the results of a series of fracture tests on several sets of specially oriented symmetric tilt bicrystals of pure aluminum. One item of interest is the effect that grain boundary orientation has on the propagation of an intergranular crack. The second item of interest is the effect of direction of crack propagation within the grain boundary, which gives rise to a directional dependence of fracture. We also present the results of a series of finite element simulations of the experiments taking into account the full elastic-plastic anisotropy of the single crystal constituents. We calculate the asymptotic deformation states for both stationary and quasi-statically growing cracks. Further we model the fracture process with a cohesive-zone model, for which the energy of the grain boundary can be varied.

**4:30 PM M5.7**

**CREEP AND GRAIN BOUNDARY SLIDING IN ALUMINUM.** Clyde Briant, Brown University, Division of Engineering, Providence, RI; David Davidson, Southwest Research Institute, San Antonio, TX.

This paper will report a study of grain boundary sliding in aluminum. The unique feature of this study is that it shows the power of using two techniques in the scanning electron microscope to study this problem. One of these is straining in a hot stage directly in the SEM and following the strain evolution through imaging techniques. The other is the use of EBSP to detect orientation changes. This paper will report on experiments which show that there is general deformation throughout the grains during creep and that the triple point inhibits grain boundary sliding. EBSP shows that there is rotation of the grains during creep. EBSP examination of the grain boundary region showed no evidence of grains of new orientation forming during creep. Any recrystallization that occurred took place by the migration of one existing grain into another.

**4:45 PM M5.8**

**ON THE GRAIN BOUNDARY MICROSTRUCTURE DEPENDENT INTERGRANULAR FRACTURE IN POLYCRYSTALLINE MOLYBDENUM.** Sadahiro Tsurekawa, Tadao Watanabe, Tohoku Univ., Dept. of Machine Intelligence and Systems Engineering, Sendai, JAPAN.

The intergranular brittleness in polycrystalline materials is a serious problem for material processing and for practical applications. To obtain a fundamental knowledge for improvement of the embrittlement, we have examined the relationship between fracture behaviour and grain boundary (GB) microstructures in 2D-polycrystalline molybdenum. Quantitative analyses of GB microstructures were performed by orientation microscopy (OIM), and followed by 4-points bending tests at 77K. Thereafter, crack propagation was analyzed in connection with GB microstructures. We found the fracture stress depends on grain size with similar manner to the Hall-Petch relation. In addition, the Hall-Petch relation also depends on the grain boundary character distribution (GBCD). The fracture stress increases with increasing the frequency of low sigma GBs at constant grain size. Conversely, random GBs seems to act as weak intrinsic defects and the interconnection among them may give rise to premature failure. Therefore, the connectivity of random GBs probably becomes important to suppress the intergranular fracture as well as the GBCD.