

SYMPOSIUM N

Interfacial Engineering for Optimized Properties III

April 13 - 15, 2004

Chairs

Christopher Schuh

Dept of Materials Science & Engr
Massachusetts Institute of Technology
Cambridge, MA 02139
617-452-2659

Mukul Kumar

Chem & Matls Science Directorate
Lawrence Livermore National Laboratory
Livermore, CA 94550
925-422-0600

Valerie Randle

Materials Res Centre School of Engr
University of Wales at Swansea
Swansea, SA2 8PP United Kingdom
44-1792-295-841

C. Barry Carter

Dept of Chem Engr & Materials Science
University of Minnesota
Minneapolis, MN 55455-0132
612-625-8805

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Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 819
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

8:30 AM *N1.1

On the Role of Grain-Boundary Films in Optimizing the Mechanical Properties (Strength, Toughness, Creep, Fatigue and Wear Resistance) of Silicon Carbide Ceramics.

Robert O. Ritchie^{1,2}, Xiaofeng Zhang² and Lutgard C. De Jonghe^{1,2};

¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The development and microstructural optimization of a high-toughness silicon carbide ceramic is described, based on the notion of *in situ* toughening through the presence of nanoscale grain-boundary films and the growth of plate-like, elongated grains, induced by sintering element additions of Al, B and C, during hot pressing. The fully controllable microstructure and phase composition allows for development of optimized recipes for different mechanical requirements. Specifically, although the use of commercial SiC has been severely limited to date by its very poor fracture toughness, the current family of ceramics, termed ABC-SiCs, is shown to have significantly higher fracture toughness at ambient temperatures than commercial material (by a factor of three). One principal feature of these ceramics is that above approximately 1100°C, *in situ* crystallization of the amorphous grain-boundary films is seen to occur, with a concomitant increase in resistance to creep damage. Consequently, these materials combine good lower temperature toughness with excellent elevated-temperature strength and creep resistance, a highly desirable but unusual feature of most structural ceramics. The mechanisms of crack-growth resistance, associated with fracture, creep and fatigue, and the abrasive wear resistance, are discussed in light of microstructural and compositional control, and specifically in terms of the role of the grain-boundary films. Sponsored by the Office of Science (Basic Energy Sciences) of the U.S. Department of Energy.

9:00 AM *N1.2

Effect of Recalcitrant Grain Boundaries in Cleavage Cracking Across a Field of Grains. Yu Qiao and Xinguo Kong; Department of Civil Engineering, University of Akron, Akron, Ohio.

In a recent research on the cleavage cracking across a field of randomly oriented grains at low temperature in a coarse-grained Fe-2wt%Si alloy, the detailed chronology of percolation of the cleavage front was observed. When the crack front encounters an array of grain boundaries, the boundaries with relatively low fracture resistance and high local stress intensity will be broken through first, and the recalcitrant boundaries will be left behind the verge of propagating and bridge across the crack flanks. As the overall stress intensity rises, the recalcitrant grain boundaries will eventually be sheared apart. The fracture resistance consists of the work of separation of the fracture surfaces and the work to overcome the crack trapping effect of the recalcitrant boundaries, which will be discussed through an energy analysis in this paper. It is found that the global resistance to cracking is function of the volume fraction of the recalcitrant boundaries, the roughness of the fracture surface, and the initial crack length. The factor of crack length comes in by affecting the rate of the energy release rate.

9:30 AM N1.3

Failure Modes and Grain-Boundary Effects in Polycrystalline Materials. W. M. Ashmawi and M. A. Zikry; Mechanical and Aerospace Engineering, NC State University, Raleigh, North Carolina.

A multiple-slip dislocation-density based constitutive formulation and specialized computational schemes have been developed to characterize material failure on the appropriate physical scales needed for the accurate prediction of physical mechanisms that control failure initiation, growth, and coalescence. Dislocation-density transmission and blockage interfacial conditions and local stress fields have been obtained for grain-boundary distributions associated with random and tilt orientations. These evolving local stress fields are used as failure criteria to track the initiation and evolution of intergranular and transgranular fracture. The interrelated effects of grain boundary orientation, dislocation density pile-ups and evolution, geometrical and thermal softening, void distribution and geometry, and hydrostatic stresses on failure paths in cubic crystalline materials have been studied. Based on the present analysis and on comparison with experimental observations, it is shown transgranular and intergranular failure can be characterized in terms of the competition between the strengthening and the softening mechanisms of the crystalline structure.

10:15 AM N1.4

Scaling of Fracture Surfaces in Polycrystalline Materials.

Eira T. Seppala, Bryan W. Reed, Mukul Kumar, Roger W. Minich and Robert E. Rudd; Lawrence Livermore National Laboratory, Livermore, California.

In statistical mechanics fracture surfaces of random media have attracted considerable interest due to their scaling properties [1,2,3]. We study fracture surfaces of polycrystalline materials, such as pure aluminum and bismuth-embrittled copper, both computationally and experimentally, proposing that the roughness follows a self-affine scaling with a characteristic exponent ζ . First we computationally construct grain boundary networks matching empirical special boundary fractions (e.g. of $\Sigma 3$, $\Sigma 9$, or random types) and triple junction distributions which have been obtained from electron backscatter diffraction (EBSD) data using scanning electron microscopy (SEM) [4]. Then we search the minimum energy paths through the dual networks of the grain boundary structures, where the edges of the networks are assigned with strength values depending on the type of the grain boundary. These minimum energy paths serve as predicted cracks through the samples [5]. Finally our aim is to compare such properties as roughness, special boundaries belonging to the cracks, etc., of the surfaces of the simulated networks with the properties from actual fracture surfaces in polycrystalline materials. Acknowledgment: This work was performed under the auspices of the US Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48. [1] *Statistical Models for the Fracture in Disordered Media*, eds. H. J. Hermann and S. Roux (North-Holland, Amsterdam, 1990). [2] E. Bouchaud, J. Phys. Cond. Matt. **9**, 4319 (1997). [3] R. H. Dauskardt, F. Haubensak, and R. O. Ritchie, Acta Metall. Mater. **38**, 143 (1990). [4] R. W. Minich, C. A. Schuh, and M. Kumar, Phys. Rev. B **66**, 052101 (2002). [5] V. I. Räisänen, E. T. Seppälä, M. J. Alava, and P. M. Duxbury, Phys. Rev. Lett. **80**, 329 (1998).

10:30 AM *N1.5

Resolving Orientation Correlations in Deformation Structures by EBSD. Wolfgang Pantleon, Materials Research Department, Risoe National Laboratory, Roskilde, Denmark.

During plastic deformation dislocations are trapped and aggregate into dislocation boundaries. The emerging deformation-induced boundaries subdivide the grains of initially homogeneous orientation in subgrains of slightly deviating orientation. Electron back-scattering diffraction (EBSD) can resolve the spatial arrangement of the orientations. Identification of original grain boundaries in an orientation imaging map by a simple threshold for the disorientation angle might be misleading, as the disorientations within a single grain increase with proceeding deformation and some of the initial orientation differences between grains in the polycrystal are rather small. In order to gain information on the grain scale, statistical methods must be employed. Investigation of the dependence of the disorientation angle on the sampling distance resembles orientation correlations within the deformed grains and allows evaluation of the grain size (chord length) distribution. Such an indirect approach of determining the grain size from losing any orientation correlation can be applied even in heavily deformed material where grain boundaries and deformation-induced boundaries cannot be distinguished by the disorientation angle any longer. On the lower hierarchical level of subgrains a new method is proposed to reveal orientation correlations more directly. From the quaternions describing the orientation difference between the local orientation of a subgrain and the average orientation of the grain a tensorial measure of the disorientation within a single grain is constructed. This measure of orientation spread allows an unambiguous determination of the pre-dominant rotation axis in a grain and the definition of a sign for the disorientation angles. The sign-carrying angles resolve different levels of organization in the deformation structure: long-range orientation gradients over the entire grain and alternating orientation changes on a smaller scale are revealed; the later reflecting deformation-induced boundaries with alternating disorientations. The new evaluation scheme for orientation imaging maps from EBSD allows spatial characterization of the orientation spread within individual grains.

11:00 AM *N1.6

Plastic Anisotropy, Tension/Compression Asymmetry and Size Effects in the Plastic Deformation of Ti-6242 Single Colonies. Michael John Mills¹, Michael D. Uchic² and David M.

Norfleet¹; ¹Materials Science and Engineering, The Ohio State University, Columbus, Ohio; ²Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH, Ohio.

The constant strain rate deformation behavior of individual alpha-beta colonies of the titanium aeroengine alloy Ti-6Al-2Sn-4Zr-2Mo-0.1Si is being studied over a range of size scales in both tension and compression. Single colonies, with a near-Burgers orientation relationship between alpha and beta phases, exhibit

significant anisotropy depending on the active alpha-phase slip system. This asymmetry can be understood by considering the effect of the alpha-beta interfaces and the relative orientation of the slip systems in the two phases. In addition, a significant tension-compression asymmetry has been found for both single colony and polycrystals. Previous work has demonstrated these effects using samples having millimeter-sized dimensions. More recently, we have employed focused ion beam methods to micromachine cylindrical compression samples having diameters in the range from 5 to 40 microns to establish the effects of sample size on the plastic response. Mechanical testing was performed using an MTS Nano Indenter XP fitted with a flat tip to apply uniaxial compression at a constant strain rate. The effect of sample size on the flow properties will be discussed. The importance of plastic anisotropy, tension-compression asymmetry and size effects for modeling the creep and fatigue response of polycrystalline structural components will also be addressed.

SESSION N2: Chemical and Environmental Effects
Chairs: Ian Baker and Robert Ritchie
Tuesday Afternoon, April 13, 2004
Room 3004 (Moscone West)

1:30 PM *N2.1

Role of Coincident Site Lattice Boundaries in the Creep, Corrosion and Stress Corrosion Cracking of Austenitic Alloys.

Gary S Was¹, Bogdan Alexandrescu², Brent Capell¹, Peter Andresen³ and Mukul Kumar⁴; ¹Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, Michigan; ²Argonne National Laboratory, Argonne, Illinois; ³General Electric Global Research, Schenectady, New York; ⁴Lawrence Livermore National Laboratory, Livermore, California.

Interfaces control many properties in engineering materials, several of which are critical to the integrity of the engineering structure. In single phase, solid solution, austenitic alloys, grain boundaries are often the weak link, displaying susceptibility to creep, corrosion and stress corrosion cracking. As such, grain boundary structure control affords the opportunity to improve the overall performance of alloys in a variety of applications. This paper will focus on the role of coincident site lattice boundary (CSLB) enhancement and grain boundary connectivity in the creep, grain boundary sliding, intergranular stress corrosion cracking, irradiation assisted stress corrosion cracking and intergranular corrosion in austenitic nickel-base (high purity Ni-Cr-Fe and alloy 600) and iron-base (high purity Fe-Cr-Ni and 304 stainless steel) alloys. Results will focus on the role of CSL boundaries in the improvement of grain boundary properties as measured by their response to stress and the environment.

2:00 PM *N2.2

Grain Boundary Structure, Segregation and Precipitation on Environment-Induced Cracking.

Stephen Bruemmer, Materials Science, Pacific Northwest National Laboratory, Richland, Washington.

Intergranular degradation continues to be a common failure mode for a wide variety of corrosion-resistant metallic alloys. The more routine use of advanced characterization tools has helped explore and define controlling metallurgical features often related to the grain boundary structure and composition. This paper will highlight examples of beneficial and detrimental segregation of alloying and impurity elements as well as the influence of grain boundary character and second-phase precipitation on environment-induced cracking. High-resolution analytical transmission electron microscopy observations of crack-tip corrosion reactions will be used to illustrate complex effects of interfacial structure, composition and precipitate phases on the mechanisms of crack advance.

2:30 PM N2.3

Tailoring grain boundary properties by selective doping: First-principles study of solute segregation and its impact on boundary cohesion. Donald Siegel and John Hamilton; Materials Physics, Sandia National Laboratories, Livermore, California.

It is well known that the mechanical properties of a solid are highly sensitive to the presence of solute atoms at internal interfaces, such as grain boundaries (GB). Since different solutes have varying effects on interfacial cohesion—in Ni, for example, S (B) is a GB embrittler (cohesion enhancer)—one could imagine the possibility of tailoring interfacial properties via selective doping. To realize this possibility it is essential to understand (1) whether a given solute will segregate to GB's, and (2) how that solute impacts GB cohesion upon its arrival. Here we address these issues for a Ni Sigma 3 {112} tilt GB in the context of first-principles simulations. (This specific GB is a common microstructural feature in electrodeposited Ni MEMS.) For solutes, we select the light interstitial elements H, B, C, N, and O, but also

consider S and Mn. Curiously, the most strongly segregating elements, O and B, exhibit opposing effects on boundary cohesion. Ni ferromagnetism is found to impact the segregation energies of all solutes, and acts as an additional driving force favoring segregation. We discuss additional factors controlling GB segregation, such as solute-solute interactions in multicomponent alloys.

3:15 PM *N2.4

Oxygen-Induced Dynamic Embrittlement in Nickel-Base Superalloys. Charles J. McMahon¹, William Kane¹, XinYu Liu¹ and Ulrich Krupp²; ¹Matls. Sci. & Eng., Univ. of Pennsylvania, Philadelphia, Pennsylvania; ²Institut fuer Werkstofftechnik, Universitaet Siegen, Siegen, Germany.

Both static and slow dynamic loading of Ni-base superalloys in an oxygen-containing environment at elevated temperatures can produce brittle intergranular cracking at rates near one micrometer per second. This is believed to be the result of stress-induced diffusion of oxygen into the core of sharp cracks. The susceptibility to this kind of cracking has been shown to depend on the grain-boundary structure (i.e., grain-boundary diffusivity), and it can be reduced by increasing the content of special boundaries in the material (i.e., by grain-boundary engineering). In very-high-strength alloys it can produce quench cracking during rapid cooling from heat treatments done in air.

3:45 PM *N2.5

Characterization of Elemental Segregation in Alloys by Quantitative STEM X-ray Mapping and TEM Orientation Imaging.

Masashi Watanabe¹, David B. Williams¹ and Chunfei Li²; ¹Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania; ²Physics, Portland State University, Portland, Oregon.

X-ray mapping in a scanning transmission electron microscope is one of the most useful approaches to characterize boundary segregation with high (nanometer-level) spatial resolution. However, the quantified segregant composition is not always reliable, because the measurement is influenced by the specimen thickness, boundary inclination and other experimental conditions. The boundary excess coverage, which is less sensitive to the specimen and experimental conditions, is a better measure of segregation, but requires knowledge of the specimen thickness. In this study, the local thickness was determined via the χ -factor method, which simultaneously provides specimen composition and thickness at the analysis point, using X-ray mapping, and hence the boundary excess is determined locally. This approach was applied to a low-alloy steel in which Ni, Cr and Mo co-segregate on a prior austenite boundary. The boundary excesses of Cr and Mo vary locally, even on the same boundary. In addition, orientation imaging can also be performed for thin-foil specimens in a transmission electron microscope (TEM) using a technique named automated crystallography for TEM (ACT), which was stimulated by the success of electron backscattering diffraction (EBSD) in a scanning electron microscope (SEM). One of the major advantages of using the ACT technique instead of SEM-EBSD is that the same grain boundary in the same thin specimen can be characterized by STEM X-ray mapping and orientation imaging. Therefore, the measured values of the local boundary excess can be directly linked to the crystallographic misorientation across the boundary, thus permitting unique structure-chemistry-property correlations. This research was supported by Bechtel Bettis Laboratories and NSF DMR-0304738.

4:15 PM N2.6

Interface nanochemistry in Mg-doped Al₂O₃. Georgette Petot-Ervas¹, Gianguido Baldinozzi¹, Claude Petot¹, Daniel Monceau¹, Mike J Graham², Irwin G Sproule² and Jean-Marc Raulot¹; ¹SPMS, CNRS-Ecole Centrale Paris, Chatenay-Malabry, Hauts de Seine, France; ²Institute for microstructural sciences, NRC, Ottawa, Ontario, Canada.

In this experimental paper we will focus on the influence of the grain size, the thermal history and the nominal composition on the nanochemistry of the interfaces in α -alumina submicronic powders. The consequences on the physical and chemical properties will also be discussed. Nanocrystalline Mg-doped α -alumina powders (550 and 1650 ppm by wt MgO) were prepared by the alum process. These powders (10-400 nm) were characterized by X-ray diffraction, SEM, TEM, XPS and surface area measurements (BET). In agreement with BET analysis, SEM observations show that the grain size increases with annealing time and annealing temperature. This effect is less pronounced in the highly doped samples. The less doped samples are also less aggregated and sintering bridges between the grains are still observed. XPS shows that Mg segregates at the periphery of the grains on a depth ≤ 0.5 nm. The dopant segregation is stronger when the nominal amount of Mg increases, leading eventually to the formation of MgAl₂O₄ precipitates near the grain surface. At low Mg concentrations it is possible to observe an increase of the dopant segregation with grain size. Other impurities like Si or higher cooling

rates also favour this Mg segregation. However, the rate of cooling is so effective that it can overshadow all the other parameters (grain size, impurities, ...) and we have shown this is certainly the key parameter for obtaining a perfect sintering of these ceramics.

4:30 PM N2.7

Intergranular Segregation in Magnetic Recording Media Characterized by Analytical Electron Microscopy.

James Bentley¹, Neal D Evans¹, James E Wittig² and Jafar F Al-Sharab²; ¹Metals and Ceramics Div, Oak Ridge National Lab, Oak Ridge, Tennessee; ²Vanderbilt University, Nashville, Tennessee.

Longitudinal and perpendicular recording media for computer hard disks rely on strong segregation to produce paramagnetic intergranular layers that magnetically isolate the grains. In the development of improved media for recording data at high-densities, characterization of these intergranular layers (and intragranular compositions) is critical for understanding structure-property-processing correlations and for micromagnetic modeling. Quantitative compositional mapping at nanometer resolution by energy-filtered transmission electron microscopy (EFTEM) has been extensively applied to sputtered CoCr(TaPt) thin-film longitudinal media, where intergranular Cr segregation is primarily responsible for magnetic isolation. Optimized procedures and special data acquisition/processing schemes developed over a period of several years ensure the composition maps are reliable. Spectrum imaging with simultaneous electron energy-loss spectroscopy (EELS) and energy-dispersive x-ray spectroscopy (EDS), again at nanometer resolution, is an important complementary technique that shows Ta and Pt (elements difficult to analyze by EELS/EFTEM) are uniformly distributed. A comprehensive and systematic study of the effects of composition and deposition conditions on segregation and magnetic properties has recently been completed for a set of CoCr(TaPt) alloys. On the basis of high-resolution TEM imaging and EFTEM composition mapping of identical areas, the growth mode of CoCrPt has been identified as different from that of CoCrTa. The EFTEM and spectrum imaging experimental methods have been extended to address the more challenging problem of boron segregation in CoCrPtB sputtered thin films. Spectrum imaging is proving to have some advantages over EFTEM for mapping boron, especially with regard to the reliability of background subtraction at low boron concentrations. The dependence of intergranular segregation on crystallographic misorientation, again measured with combined high-resolution TEM and EFTEM, has revealed pronounced minima at 0, 30, 60 and 90° misorientation of the basal planes in a (longitudinal) CoCrTa alloy, but no detectable orientation dependence for a (perpendicular) [0001]-textured CoCrPt alloy. Research at the ORNL SHaRE User Center was sponsored by the Division of Materials Science and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Support from an IBM Faculty Partnership and the National Storage Industry Consortium is also gratefully acknowledged.

***N2.8 TRANSFERRED TO *N1.6**

SESSION N3: Poster Session
Chairs: C. Barry Carter, Mukul Kumar, Valerie Randle
and Christopher Schuh
Tuesday Evening, April 13, 2004
8:00 PM
Salons 8-9 (Marriott)

N3.1

Self-assembled monolayers of alkylsiloxane on MgO for protection against hydration. Jeong O. Lee, Jung W. Lee and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

MgO thin film has been used as a protective layer for dielectrics in AC-plasma display panel (AC-PDP) to improve discharge characteristics and panel life time. These properties are originated from high secondary electron emission coefficient, high transparency, and low sputtering rate of MgO. Hydration, however, is one of the serious problems of MgO layer because the MgO reacts easily with moisture in the air, forming Mg(OH)₂. The purpose of this study is molecular-level modification of MgO surfaces with alkylsilane-based self-assembled monolayers (SAMs) for protection of MgO against hydration. Alkylsiloxane SAMs were deposited on MgO surface from a gas phase. The protection ability of SAMs on MgO against hydration has been estimated by x-ray photoelectron spectroscopy (XPS) and contact angle analysis. The results show that the SAMs have sufficiently high protection ability against hydration.

N3.2

Oxidation behavior of TiN with a Ti interlayer on stainless steel. Ming Hua Shiao¹, Ching Chiun Wang², Chien-Ying Su¹ and Fuh Sheng Shieu²; ¹Precision Instrument Development Center,

National Science Council, Hsinchu, Taiwan; ²Department of Materials Engineering, National Chung Hsing University, Taichung, Taiwan.

Characterization of the TiN coatings oxidized in air at temperatures at 600 and 700°C in air for 30 min was carried out by X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), and Auger electron spectroscopy (AES). TiN thin films with a Ti interlayer were prepared by hollow cathode discharge ion plating on AISI 304 stainless steel. XRD and TEM results show that the TiN coatings and Ti interlayer have columnar structure with (111) and (0002) preferred orientations, respectively. AFM results show that the surface roughness (Ra) changes from 3.5 nm for the as-deposited specimen to 11.6 nm after oxidation at 700°C, and there exist pinholes on the surface of specimens due to electropolishing of the steel substrate. After oxidation, the TiO₂ oxide layer formed on the specimen surface was porous and retained the columnar structure as the original TiN coating. The microstructure of the Ti interlayer gradually changed from columnar to polycrystalline structure due to grain growth. The Auger elemental depth profiling found that interdiffusion of the Ti interlayer with steel substrate was occurred.

N3.3

Direct Measurement of Impurity Segregation Concentration at Grain Boundaries for Polycrystalline Materials using EBSD and 3D Reconstruction of SEM images of Etch Grooves. Rene Le Gall and Marilyne Cornen; Laboratoire Genie des Materiaux, Polytech Nantes, Nantes cedex 03, France.

It is well known that, on the one hand impurity segregation in metallic alloys depends on grain boundaries (GB) misorientation, and on the other hand that GB mobility depends on segregation due to the impurity drag mechanism. So one can imagine to influence GB orientation distribution function using trace impurities alloying and controlled thermal treatments. But, it is firstly needed to improve experimental data on GB segregation in polycrystalline alloys. The aim of this paper is to measure segregation-misorientation dependence on polycrystalline Ni-S alloys using both EBSD and 3D reconstruction of etch grooves. Samples of Ni-S alloys (1.6 and 7.2 ppm at) were annealed at different temperatures to get equilibrium segregation at grain boundaries. They were then etched near the transpassive potential in 1M sulfuric acid in order to form etch grooves at grain boundaries. It was previously shown by Beaunier et al.[1] that the geometry of these grooves depends on the sulphur concentration, XS, in the GB. Thus, having the angle measurement and the depth of the groove allow us to calculate XS. The geometrical parameters were obtained thanks to 3D reconstruction of a stereographic pair of SEM images using Mex[®] software from Alicona[®]. To calibrate the electrochemical technique, Auger spectroscopy experiments were performed on in-situ cold fractured samples. The grain boundary misorientations were measured using EBSD on the electrochemically-etched samples. The combination of EBSD and 3D reconstruction technique allows us to get in a relatively short time the temperature-segregation-misorientation function for a polycrystalline alloy. [1] L. Beaunier, M. Froment, C. Vignaud A kinetic model for the electrochemical grooving of grain boundaries Electrochim. Acta, 25(1980) 1239-1246

N3.4

Manipulation of magnetic anisotropy Cu/Ni/Cu(001) films by using ion irradiation. Sangwon Shin¹, Jong-Han Lee³, Taegon Kim², Hyunmi Hwang¹, In-Hoon Choi³, Jaeyoung Lee¹, Chungnam Whang¹ and Jonghan Song²; ¹Physics, Yonsei University, Seoul, South Korea; ²Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, South Korea; ³Materials Science and Engineering, Korea University, Seoul, South Korea.

The epitaxial magnetic thin-film Cu/Ni/Cu(001) structure is well known as possessing perpendicular magnetic anisotropy (PMA) properties over a wide range of Ni layer thickness (t), about 15-140 Å and it is generally agreed that the observed PMA in this system is closely related to the strain in the Ni layer due to the lattice mismatch with the Cu(001) substrate. Recently, ion irradiation into magnetic thin films has been used to modify extrinsic magnetic properties such as magnetic anisotropy, coercivity, and magnetic exchange field. In this study, we suggest that the magnetic anisotropy of Cu/Ni/Cu(001) film can be controlled to in-plane or perpendicular direction by ion irradiation and post-annealing process. Epitaxial Cu/Ni(45 Å)/Cu film that has perpendicular magnetic anisotropy was irradiated by 1 MeV C⁺ with dose of 2×10¹⁶ ions/cm². After 1MeV C⁺ irradiation, the spin reorientation transition from perpendicular to in-plane direction is caused by the relaxation of the strain in Ni layer. To measure the strain of Ni layer and hysteresis loop, grazing incidence X-ray diffraction (GID) and magneto-optical Kerr effects (MOKE) were used. In order to change magnetic anisotropy from in-plane to perpendicular direction again, 95 keV Cu⁻ irradiation and

post annealing at 300 °C for 1 min were subsequently performed into previous 1 MeV C⁺ irradiated Cu/Ni(45 Å)/Cu sample. It is found from MOKE measurements that the recovery of perpendicular magnetic anisotropy was observed from 95 keV Cu⁻ irradiated and post-annealed sample. It is believed that Cu/Ni/Cu film is amorphized by damage induced by 95 keV Cu ion irradiation and amorphous Cu/Ni/Cu film becomes epitaxial because regrowth take place during the post-annealing. The regrowth cause recovery of strain in Ni layer that result in change of magnetic anisotropy form in-plane to perpendicular direction.

N3.5

Effects of 1 MeV C⁺ irradiation on the magnetic properties of Ni(60Å)/Cu/Si(100). Jong-Han Lee², In-Hoon Choi², Sangwon Shin¹, Chungnam Whang¹, Jonghan Song³ and Teagon Kim³; ¹Physics, Yonsei University, Seoul, South Korea; ²materials science and engineering, korea university, seoul, South Korea; ³Advanced analysis center, korea institute of science and technology, seoul, South Korea.

The effects of 1 MeV C ion irradiation with various ion dose and flux on epitaxial Ni(60Å)/Cu/Si(100) which possessing perpendicular magnetic anisotropy (PMA). After ion irradiation, the magnetic and structural properties were analyzed by the magneto-optical Kerr effect (MOKE) and grazing incident diffraction (GID). 1 MeV C ion irradiation was performed into Ni/Cu thin films with various ion doses ranged from 1 to 7.5×10¹⁵ ions/cm². As increasing ion dose, the coercivity of Ni/Cu thin film decreased from 16.2 % (1×10¹⁵ ions/cm²) to 72.1 % (7.5×10¹⁵ ions/cm²). It means that the spin reorientation toward in-plane magnetization induced by ion irradiation depends on the ion dose. It is known that the magnetic anisotropy of Ni/Cu is closely related to the magnetoelastic anisotropy of strained Ni film due to the lattice mismatch with the Cu(001) layer. From the GID measurement, as increasing ion dose, the peak position of Ni moves gradually toward the bulk Ni(200) peak position and the half width of the Cu(200) peak is getting narrow. It implies the fact that the relaxation of the strain and grain growth induced by ion irradiation is a function of ion dose. In order to investigate ion flux effect, 1 MeV C⁺ irradiation with a dose of 1×10¹⁶/cm² was carried out by varying ion flux (100, 380 nA/cm²). As increase of ion flux, the coercivity of Ni/Cu thin film decreased and spin orientation more rapidly changed from PMA to in-plane. It is concluded that ion dose and flux plays an important role of modification of the magnetic properties of Ni/Cu thin film.

N3.6

The Role of Thermal Boundary Resistance at GaN/Substrate Interface in Self-heating of GaN Field-Effect Transistors.

Valentin O. Turin and Alexander A. Balandin; Nano-Device Laboratory (<http://ndl.ee.ucr.edu/>), Department of Electrical Engineering, University of California - Riverside, Riverside, California.

Due to the absence of native substrate, most of GaN devices are fabricated on SiC or sapphire substrates. The interface between the substrate and GaN layer contributes to the overall thermal resistance of the devices structure. In this paper, we calculate the temperature dependence of the thermal boundary resistance (TBR) for GaN/SiC or GaN/sapphire interfaces using the diffuse mismatch model. This dependence is than used to investigate the effect of TBR on current-voltage characteristics of GaN field-effect transistors. Specifically, we simulate the dependence of the breakdown voltage and transconductance on TBR values. It has been established that the breakdown voltage is very sensitive to the TBR value for transistors with typical parameters. For example, at zero gate bias, it decreases from more than 250 V to about 100 V as TBR increases from Rth=0.001 Kcm²/W to Rth=0.005 Kcm²/W. Corresponding decrease of the transconductance is about 40%. The results of modeling suggest that the thermal breakdown in GaN MESFETs is caused not only by the gate breakdown but also by the avalanche breakdown under the drain. The negative slope region in the saturation current for zero gate biases is observed. This negative slope increases with increasing thermal boundary resistance due to degradation of the carrier mobility in the active layer as the temperature of the hot spot about drain rises. This work has been supported by the ONR project N00014-02-1-0352. [1]. V.O. Turin and A.A. Balandin, Electronics Letters, submitted, 2003.

N3.7

Modification of magnetic properties by ion-irradiation on Ni/Pd multilayer film. Jun-Sik Lee¹, K.-B. Lee¹, D.-H. Kim², J. Y. Jeong², S.-C. Shin², T. G. Kim³ and J. H. Song³; ¹Physics, POSTECH, Pohang, South Korea; ²Physics, KAIST, Taejeon, South Korea; ³Advance Analysis Center, KIST, Seoul, South Korea.

Various measurements are carried out to understand the correlations between magnetic and structural properties on magnetic [Ni(0.6nm)/Pd(0.7nm)]₃₀ multilayer films. The Ni/Pd multilayer films

have been irradiated by 100 keV low energy deuterium ions (D⁻) with various dose fluence to modify the structures without significant damage on the whole film. X-ray scattering measurements show that the interfacial structures including intermixing widths strongly depend on ion-dose fluence. Also TRIM simulation shows that the damage on the whole film can be ignored, and in-elastic energy transfer to the film during ion-irradiation may modify local atomic rearrangements at the interface. With initial fluence (1×10¹⁵ ions/cm²), the direction of magnetic easy axis rotated toward the perpendicular direction and saturated magnetization is increased by 53% compared with those of as-grown film. Values of structural and magnetic parameters are recovered to their initial ones with excessive dose fluence, implying that the optimum ion-dose condition exists. Our results propose that magnetic properties of the Ni/Pd multilayer films sensitively depend on the structures at Ni/Pd interface.

N3.8

Growth of p-ZnSe_{1-x}Te_x epitaxial films on lattice-matched InGaAs/InP by Photoassisted Metal Organic Vapor Deposition (MOCVD). Bhanu Prakash Venkata Yarlagadda, Angel Rodriguez, Peng Li, John E Ayers and Faquir Jain; Electrical and Computer Engineering, University of connecticut, Storrs, Connecticut.

We report the growth of compositionally controlled ZnSe_{1-x}Te_x (0 < x < 0.6) epitaxial layers using photoassisted Metal-Organic Chemical Vapor Deposition (MOCVD) on lattice-matched InGaAs/InP substrates. High quality ZnSe_{0.53}Te_{0.47} epitaxial layers were grown in a vertical Emcore Reactor at 360 °C with an UV intensity of 12 mW/cm² using dimethyl zinc (DmZn) at 100 μmoles/min, dimethyl selenide (DmSe) at 100 μmoles/minute, and diisopropyl telluride (DipTe) at 135 μmoles/min. Nitrogen doping was obtained using Tertiary Butyl Amine (TBA) at 100 μmoles/min. We have studied the telluride composition as well as incorporation of nitrogen as a function of gas phase mole fraction of telluride, UV intensity (12 mW/cm² - 48mW/cm²) and growth temperature (360 °C to 400 °C). P-type doping of 5×10¹⁶ to 1.3×10¹⁷ cm⁻³ was measured using AC Hall Effect method. The compositional and structural data was extracted from DCXRD from 004 and 044 reflections. The role of III-V and II-VI integration will be discussed in terms of improvement in electronic as well as optoelectronic devices.

N3.9

Boundary Migration in Alumina Bicrystals.

Jessica L. Riesterer¹, Shelley R Gilliss¹, N Ravishanker^{2,1} and C Barry Carter¹; ¹Department of Chemical Engineering and Materials Science, University of Minnesota-Twin Cities, Minneapolis, Minnesota; ²Indian Institute of Science, Bangalore, India.

Liquid-phase sintering is a process which enables the processing of dense ceramics at a lower temperature. In this process, a low-melting-temperature additive forms a liquid phase at the processing temperature and wets the powder compact, increasing the densification rate of the ceramic powder compact. Model geometries of two alumina single-crystals of known orientation with an amorphous thin film at the boundary were used to investigate the driving force for boundary migration in the presence of a liquid phase. The single grain-boundary was constructed with an initially flat interface so free-energy differences across the boundary due to curvature effects are not present. Pulsed-laser deposition (PLD) was used to deposit approximately 100 nm of glass on single crystal alumina. Another crystal of a different known orientation was then hot-pressed to the film/substrate assemblage in a vacuum furnace. After bicrystal fabrication, a surface was prepared perpendicular to the interface by polishing with successive grits of diamond lapping films to a 0.5 μm finish. The bicrystal was then heat treated in air at 1650°C to induce migration. The extent of migration was monitored with scanning electron microscopy (SEM). The orientation and degree of misorientation of the boundary was determined by electron backscattered diffraction (EBSD). A focused-ion beam (FIB) tool was used to prepare specimens for transmission electron microscopy (TEM) analysis. The use of FIB and TEM enables the behavior of the boundary sub-surface to be monitored.

N3.10

TEM Investigations of Interfacial Misfit Dislocations in p/p+ Silicon. Rong Yu and Xiao Feng Zhang; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Lightly boron-doped Si film on heavily boron-doped Si substrate (referred to as p/p+ Si) is popular in ultra-large-scale-integration fabrication. On the one hand, the heavily doped boron in the substrate reduces minority carrier diffusion and junction leakage. On the other hand, it also reduces the lattice parameters of the substrate and induces the formation of misfit dislocations in this homoepitaxial system. Here we report the transmission electron microscopy (TEM) investigations on the detailed structure of the misfit dislocations at high spatial resolution, especially the evolution of the dislocations

upon in-situ heating, which is crucial for both film growth and post-growth device processing. The p/p+ silicon wafers used in this study were prepared via chemical vapor deposition. The cross-section and plan-view TEM samples were prepared using both conventional methods and the lift-out FIB method. The results indicate that the misfit dislocations are in the substrate, instead of the epitaxial layer. High-resolution images show that the misfit dislocations are dissociated into a 90° and a 30° Shockley partial dislocations, with an intrinsic stacking fault (ISF) lying in a (111) plane. The distance between two partial dislocations is about 7 nm. The results of in-situ investigations are also included.

N3.11

A Systematic Study of Monitoring the Changes on the Surfaces and Interfaces in α -Alumina after Chemical and Thermal Treatments. B. Deb, Arzu Altay, Shelley Gilliss and C. Barry Carter; Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Effects of chemical and thermal treatments on the grains and grain boundaries of the polycrystalline α -Al₂O₃ have been examined using a combination of microscopy techniques. Samples were prepared by using high-purity alumina powders by compacting them prior to sintering. Both these samples and commercially available material were chemically etched in phosphoric acid at various temperatures and times. Thermal treatments were carried out at temperatures between 1400°C and 1650°C before and after chemical treatments on the same samples. Using visible-light microscope (VLM) maps as a guide, the same regions were re-examined using atomic force microscope (AFM) after subsequent treatments. The difference in the dissolution rates of different grains and grain boundaries could then be studied using AFM. The geometry of the grain boundary grooves were compared after chemical and thermal treatments. Electron backscattered diffraction (EBSD) patterns in the SEM were used to obtain crystallographic orientations of the grains. The differences in the etching rates of the grains and grain boundaries of different orientations will be discussed and considered in terms of surface energies.

N3.12

Characterization of Twinning In Electroplated Ni-Mn Alloys. Gene Lucadamo¹, Nancy YC Yang¹, Douglas L Medlin², James J Kelly³ and Alec A Talin⁴; ¹Analytical Materials Science, Sandia National Laboratories, Livermore, California; ²Materials Physics, Sandia National Laboratories, Livermore, California; ³Microsystems Processing, Sandia National Laboratories, Livermore, California; ⁴Advanced Lithography, Sandia National Laboratories, Livermore, California.

Interfaces often play a critical role in controlling material properties such as mechanical strength. Twins are well-studied, low energy interfaces formed during annealing or plastic deformation. Here, we characterize twinning introduced during electroplating of Ni-Mn alloys. Previous work found that the twin boundaries effectively refine the grain size, which enhances hardness. This observation is supported by our quantitative measurements from transmission electron microscopy (TEM) images showing that the relative boundary length is comprised predominantly of twin interfaces. Further TEM characterization of as-plated microstructures reveals a range of length scales associated with twinning that ranges from colonies (~1000 nm) down to the width of individual twins, which is typically 100 nm. The crystallographic texture of the electrodeposit also has important implications on the orientation of the twin planes. As-plated Ni-Mn specimens typically have a {110} fiber texture, as measured by X-ray diffraction and electron backscatter diffraction patterns (EBSD). While twinning can occur on {111} planes either perpendicular or oblique to the substrate in {110} oriented grains, planview TEM images show that twins formed during electroplating are primarily on the {111} planes parallel to the plating direction. Another important consequence of a high twinning density is the formation of a large numbers of twin junctions. Measurements show that the area density of twin junctions is comparable to the density of dislocations in a heavily cold-worked metal. Strain fields associated with these junctions can interact with dislocations and act as pinning sites. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

N3.13

Study of Percolation in PMMA-Indium Tin Oxide Composites*. Charles J. Cappozzi^{2,1}, Sandra M. Shackelford¹ and Rosario Gerhardt¹; ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, Georgia; ²Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, Georgia.

Knowledge of percolation in binary composites is critical to the development of new materials with specific electrical and optical properties. So far, carbon black remains a featured filler material in the study of percolation in polymer composites. However, a distinguishable feature of carbon black is that it does not coincide with the transparency associated with some polymers. This provokes interest concerning alternate fillers for polymer-based matrices. Detection of percolation is reported with novel two-phase composites consisting of poly[methyl methacrylate] (PMMA) and indium tin oxide (ITO). ITO is a particular filler of interest primarily for possessing optical clarity consistent with PMMA in the visible light range. For specimens with varying concentrations of filler, a Solartron Impedance Analyzer was used to acquire AC Impedance data between frequencies of 1 x 10⁷ and 0.01 Hz at 0.1 Vrms. The existence of a conducting network amongst ITO particles in the PMMA was detected by a significant enhancement of the electrical conductivity in the composite. This fundamental detection method was applied to study the effect of particle size on the percolation threshold by replacing coarse-sized ITO with nano-sized particles. Connectivity was achieved by coarse-sized ITO particles with a 7-8 vol. % concentration present in the composite. This threshold appeared significantly reduced with substitution by nano-sized ITO particles, where a sharper transition towards percolation was observed to occur with only a 2-3 vol. % concentration. However, it is speculated that minor agglomerates, which may exist in the bulk of the specimens, could be preventing percolation from occurring at an even lower filler concentration. Microstructural analysis of the composites is ongoing and should help to enhance the scientific understanding of percolation and its relationship to the microstructure in two-phase composites. *Work funded by NSF under DMR-0076153 and SURF program at Georgia Tech

N3.14

Expressions for the Effective Diffusivity in Materials with Interphase Boundaries. Irina V Belova and Graeme E Murch; School of Engineering, The University of Newcastle, Callaghan, New South Wales, Australia.

No work has been done previously on describing the effective or long-time limit atomic diffusivity in two phase material in the presence of a contribution from diffusion along the interphase boundaries. Taking a phenomenological approach along the lines of the mean-field analysis of Maxwell describing the effective electrical conductivity of composites, we develop expressions for the effective diffusivity for various grain geometries and fractions of interphase boundaries. The expressions are tested with Monte Carlo calculations employing lattice-based random walk methods.

N3.15

Computational and Experimental Investigations of Atomistic Structural Order at Solid-Liquid Interfaces. Wayne David Kaplan and Yaron Kauffmann; Materials Engineering, Technion, Haifa, Israel.

As microstructural length-scales are reduced, the role of interfaces in determining the properties of materials becomes more dominant. The importance of the correlation between interface structure and chemistry with interface (and bulk) properties is evident in a range of material systems, and is a topic of intense experimental and theoretical work for solid-solid interfaces. While detailed thermodynamic analysis of solid-liquid interfaces is routinely conducted, and many works include ex-situ microstructural investigations of solid-liquid interfaces after solidification, knowledge of the local structure at solid-liquid interfaces is still incomplete. To be more specific, the correlation between the structure of the solid, and the structure in the liquid near the interface, has not been fully addressed. Some information on structural order in a liquid at the interface with a crystalline solid has been obtained by rather elegant neutron scattering experiments, some electron microscopy observations, and indirectly inferred from wetting experiments. Structural order also plays a role in basic models describing equilibrium amorphous films at grain boundaries. This work is an attempt to combine experimental high resolution transmission electron microscopy of solid-liquid interfaces with molecular dynamics simulations to understand the role of atomistic ordering at solid-liquid interfaces. In this study a model system for a solid-liquid interface is introduced. The solid is assumed to be composed of static atoms positioned in an ideal lattice with various crystallographic symmetries, and liquid Al is introduced adjacent to several different terminating planes of the solid. Both flat ideal substrates, and substrates with predefined geometries are used. Molecular dynamics was applied to study the structural correlations between the liquid metal and the solid. Analysis of the equilibrated structures showed the presence of density oscillations (layers) of liquid atoms parallel to the interface, extending to significant distances within the liquid (1.5-2.0nm). A significant increase in structural order was found for substrates with steps and geometrically confined regions. The results

from the molecular dynamics simulations served as atomistic models for simulated HRTEM images, which were used to define experimental conditions for which observed ordering is an artifact of the optical system. In this way true structural order can be observed and measured directly from HRTEM, as will be demonstrated for the sapphire-glass system. The implications of a significant volume of interfacial atoms with a local structure differing from a crystal and differing from an ideal liquid will be discussed.

N3.16

Ca_{2-x}La_xRuO₄ Thin Films Growth by Pulsed Laser

Deposition. Xu Wang¹, Yan Xin² and Jim P Zheng¹; ¹Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, Florida; ²Magnet Science and Technology, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida.

Bulk Ca₂RuO₄ is an antiferromagnetic Mott insulator with the metal-insulator transition above room temperature, and the Neel temperature at 110K. There is strong coupling between crystal structures and magnetic, electronic phase transitions in this system. It exhibits high sensitivity to chemical doping and pressure that makes it very interesting material to study. We have epitaxially grown Ca₂RuO₄ thin films with different La doping concentration on LaAlO₃ and SrTiO₃ substrates by pulsed laser deposition technique. Growth conditions such as substrate temperature and oxygen pressure were systematically varied in order to achieve good quality single phase film. Crystalline structure and lattice orientation of these films were characterized by X-ray diffraction spectrometer. Microstructure of thin films including film-substrate interface and lattice mismatch and surface morphology was examined by high-resolution transmission electron microscope. The magnetic and transport properties were also measured and compared with that obtained from Ca_{2-x}La_xRuO₄ single crystal. Thin films grown on different lattice mismatched substrates were compared. Particular attention is paid to the effects of growth conditions and strains on the thin film properties.

N3.17

Scaling Micro-Mechanical Properties in Soft Multifase Gels Based on Nanofabrication Methodology and Interfacial Interactions. Phillip J. Cole¹, Joseph L. Lenhart¹, John A.

Emerson¹ and Jeffrey T. Koberstein²; ¹Advanced Manufacturing of Organic Materials, Sandia National Laboratories, Albuquerque, New Mexico; ²Chemical Engineering, Columbia University, New York, New York.

Polymer gels are particularly suited for a variety of emerging technical areas including drug delivery, biomedical implants, membranes, sensors, display devices, fuel cells, electronics, and optical devices, among others. The polymer network or swelling solvent are easily modified or exchanged, resulting in the wide range of applications listed. As a specific example, the stress development in a gel can be tuned such that it is large and responsive to external stimuli (a sensor) or small such that a gel-substrate interface maintains integrity over a broad temperature range (an electronic component). Gel micromechanical response may be controlled through the gel nanostructure, which is in turn determined during gel fabrication, or through network-solvent interactions. To study this effect, a series of crosslinked polybutadiene-based gels were prepared either at different initial solvent contents or swollen with varying percentages of solvent. In addition, solvents were chosen with favorable, neutral, and unfavorable network-solvent interactions. The modulus of each of these gels was determined, both before and after extraction. The results indicate that the preparation method dramatically affects the nanostructure, as well as the modulus. Additionally, the network-solvent interactions impact the nanostructure. Combining these results leads to a scaling relationship between the modulus and gel composition as a function of chemical environment during gel fabrication. Considering the importance of interfacial integrity at the gel-substrate interface, the adhesion of the gel to two model substrates was studied. The phase behavior of the gel altered the network nanostructure, which was further amplified at the gel-substrate interface, severely impacting the integrity of the model interfaces. The results of this work will assist in the design of superior gel composite systems for the many emerging applications.

N3.18

The Dramatic Effect of Oxidation Species on the Oxide and Interfacial structure. Judith Yang, Maja Kisa and Long Li;

Materials Science and Eng., University of Pittsburgh, Pittsburgh, Pennsylvania.

A simple method to create different oxide nanostructures, and, hence, tailor oxide-substrate interfaces, is by oxidation in different oxygen species. We studied the dramatic effect of oxidation in various oxygen species, including atomic oxygen and ozone, on the interface, surface and oxide structures of various metals, Al and Ag, and

semiconductors, Si, by primarily transmission electron microscopy methods. Completely different oxides and interfacial structures formed due to oxidation in ozone or atomic oxygen as compared to molecular oxygen. Aluminum was oxidized in ozone, atomic oxygen and molecular oxygen. Silicon was oxidized in atomic oxygen and molecular oxygen. Both Al and Si form amorphous oxides during oxidation, but the reactive oxygen species created a more ordered and thicker oxide. Electron energy loss spectroscopy and high resolution imaging of cross-sectional specimens revealed a flatter and more uniform interface in Si exposed to atomic oxygen as compared to molecular oxygen.

N3.19

Effect of Crystal Defects on the Properties in Epitaxial Tin Dioxide Thin Films. Xiaoqing Pan and Juan Dominguez; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Epitaxial (101) tin dioxide thin films with thickness ranging from 6 and 100 nm were deposited on the r-cut sapphire substrate by femtosecond pulsed laser ablation. Due to the lattice and thermal expansion mismatch with the substrate, the SnO₂ film shows several types of crystal defects including interfacial misfit dislocations, antiphase boundaries (APBs), and partial dislocations caused by the APBs which terminate in the film. The APBs lie along the (-101) planes with a displacement of 1/2[101]. The densities of APBs and partial dislocations vary with film thickness, whereas the average spacing of misfit dislocations remains constant. Hall effect measurements showed that both electron concentration and mobility decreases with reducing the film thickness, which is ascribed to the scattering of electrons by crystal defects and interfaces and the effect of a native space charge region at the near surface region of the films. The response of the films to reducing gases was found to depend on the electron concentration of the film and the relative fraction, with respect to film thickness, of material that is depleted of electrons.

N3.20

Nanostructural Engineering of Metal Oxide Coatings and Nanolaminates by Atomic Layer Deposition. Gerry Triani¹, Peter Evans², Darren Attard¹, David R.G. Mitchell¹, Kim S. Finnie¹, Bruno A. Latella¹, Christophe J. Barbe¹ and John Bartlett¹;

¹Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia; ²Environment, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia.

Deposition of thin metal oxide films with controlled nanostructures using atomic layer deposition (ALD) involves the use of sequential surface chemical reactions to saturate a surface with a (sub)monolayer of reactive compounds such as metal alkoxides or covalent halides, followed by reaction with a second compound such as water to "grow" coatings layer-by-layer. A judicious choice of reactants and processing conditions ensures that the exchange reactions are self-limiting, resulting in controlled film growth. The self-limiting nature of the interfacial chemistry ensures excellent conformality, even on very convoluted substrates, resulting in exquisite control over the nanostructure of the coatings and their associated properties. Single (TiO₂, Al₂O₃, SiO₂), compositionally-graded and multi-layered coatings composed of alternating TiO₂ and Al₂O₃ layers have been formed via ALD on Si<100> substrates, using covalent halides, metal alkyls, metal alkoxides and water as precursors. Sub-unit configurations of high/low refractive index and low/high refractive index were deposited at 200 °C, to build nanostructured laminates. The effect of processing conditions on the deposition kinetics were investigated using a quartz crystal nanobalance, and optical/structural properties of the coatings were determined using via transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), X-ray reflectometry (XRR), spectroscopic ellipsometry (SE) at multiple angles and in-situ tensile testing. TEM and SIMS revealed that the nanolaminates consisted of chemically homogeneous layers of thickness 20±1 nm, with excellent compositional uniformity within the layers and distinct interfaces between individual layers. The chemical and structural uniformity of the coatings over longer length scales was evident from the XRR data obtained with a beam "footprint" of ca. 7 cm, which revealed the typical oscillatory reflectance behaviour associated with highly uniform and chemically homogeneous layers, with sharp inter-layer interfaces in the nanolaminates. The influence of processing conditions on the growth kinetics, key optical properties (refractive indices) and mechanical properties (adhesion and Young's modulus) will also be discussed. These results highlight the precise control of film thickness and composition attainable using atomic layer deposition for producing single and multi-layer coatings with controlled nanostructures, opening new opportunities for the design and deposition of optical coatings.

N3.21

Brazing Joining of Al₂O₃-SUS304 with Improved Interface Microstructure by Using IBAD. Kyu-Yong Lee, In-Su Jung, Sang-Joon Kim and Chul-Ho Ok; School of Mechanical Engineering, Pukyong National University, Busan, South Korea.

Joining of ceramics to metal materials has been studied by many researchers but still difficulties exist due to the dissimilar properties of two materials. Successful joining of ceramics to metals are related to the topics of filler metal that reacts with the ceramic, metallizing process that modify the wettability of ceramic surface and thermal expansion mismatch during the cooling process. The active metal brazing is simple compare to the traditional Mo-Mn method. However, it is known that additions of reactive elements such as Ti in filler metal raise the melting point, reduce fluidity and form the brittle phase in the interface. Recently, new approaches for the metallization of ceramic materials are presented to introduce the reactive element directly into the ceramic surface by using the implantation of metal vapour or multi-layer metallization, etc. Moreover, in Mo-Mn method, Invar was used successfully as low expansion material for the solution of thermal mismatch. In this paper, brazing joining of Al₂O₃-SUS304 with conventional Ag-Cu eutectic filler metal was performed by applying the surface modification technique of IBAD for the metallization of ceramics with active material of Ti and low expansion coefficient material by co-deposition. This new approach has been developed to reduce the thermal mismatch problem in terms of interface microstructure. Al₂O₃ ceramic surfaces were modified with Ar ion beam bombardment prior to deposition for the cleaning purpose. IBAD was used for the reactive Ti and low thermal expansion materials coating to provide the wetting capability on the ceramic and to reduce the thermal mismatch problem by forming a graded interlayer structure of low thermal expansion. The effects of reaction products on the rupture strength of the brazement on the process parameters such as brazing temperature, brazing time and the surface modification effects were observed based on the microstructure of the interlayer. The interlayer of these specimens were analyzed by the analytical devices such as atomic force microscope (AFM), energy dispersive analysis by X-Ray (EDAX), scanning electron microscope (SEM), X-Ray diffraction analyzer (XRD) and electron probe micro analyzer (EPMA). The obtained results will be discussed in detail.

N3.22

Interphase Coatings for Oxidation and Fracture-resistant SiC composites. Ramanathan Krishnamurthy, Princeton Materials Institute and Dept. of Mech. and Aerospace Engg., Princeton University, Princeton, New Jersey.

Interface engineering is an integral component of the design strategy necessary to fabricate fracture-resistant and oxidation-resistant SiC composites for high-temperature applications. Thin interphase coatings for the fiber (or laminae in a laminated composite) are often employed to achieve desirable crack deflection behavior at the fiber / matrix interface. A dense oxide layer can function as an effective passivation layer. In this study, a uniformly porous thin alumina layer deposited by an aerosol spray vapor deposition process is used to create the necessary 'weak' interfaces in a SiC laminated composite. Since SiC oxidizes at high temperatures, the oxide product thus formed can fill up the porosity of the interphase coating and alter its fracture resistance. In order to directly measure the effect of such an oxide layer on interfacial fracture resistance, oxidation conditions under which a thin persistent oxide layer is formed are identified using both mathematical modeling of SiC oxidation / porous structure evolution and pertinent oxidation experiments. The mathematical model for porous diffusion / reaction kinetics in this system employs two different representations of the interphase pore structure, namely the pore model, wherein the porous interphase is modeled as an effective pore / channel and the grain model in which the porous interphase is represented in terms of its constituent grains. Microscopic observations after oxidation at 800°C reveal that pore closure at the laminate ends occurs before the oxidation front can penetrate through to its interior. The grain model successfully reproduces this observation. Furthermore, numerical calculations and post-oxidation microscopic examination indicate that a thin uniform oxide layer is formed at 500°C. Experimental measurements of interfacial fracture resistance using a standard four point bend test procedure show a decrease in its value with increasing duration of oxidation at 500°C. Microscopic examination of the fracture surface shows a complex multi-phase microstructure, and indicates that crack deflection occurs at a 'weak' interface within the oxidized interphase coating. These experimental results indicate that a thin persistent oxide layer can produce desirable crack deflection behavior. In contrast, rapid pore closure enhances the oxidation resistance of these composites. As a possible solution to these seemingly contrasting requirements, the effect of a two-phase SiC/porous alumina interphase coating on pore closure and oxidation layer persistence is examined through the numerical model and is found to accelerate pore closure considerably. The implications of these results with regard to the

design of high-temperature SiC composites is discussed.

N3.23

Localized vibrational modes in metallic nanocrystalline interfaces. Peter Michael Derlet, Steven Van Petegem and Helena Van Swygenhoven; Paul Scherrer Institute, PSI-Villigen, Switzerland.

The high frequency phonon properties of a computer generated nanocrystalline (nc) fcc Ni with a mean grain size of 5nm are investigated by directly calculating the onsite phonon Greens function using a recursion technique based on a continued fraction representation. It is found that the high frequency tail, observed in both experiment and previous simulation work, arises primarily from localized vibrational modes forming within the nc grain boundary regions. The location of such modes is found to correlate well with free volume within the grain boundary that has been identified by theoretical positron lifetime calculations. The vibrational modes and the corresponding thermal properties such as the Debye-Waller factor and heat capacity will be discussed in terms of grain boundary structures.

N3.24

Influence of Interfacial Energy on the Phase Stability in Metallic Multilayers. Rajarshi Banerjee¹, Arda Genc¹, Gregory B Thompson² and Hamish L Fraser¹; ¹Materials Science and Engineering, The Ohio State University, Columbus, Ohio; ²Materials Science and Engineering, University of Alabama, Tuscaloosa, Alabama.

Phase stability in thin film multilayers can be described in a simple yet elegant manner based on classical thermodynamics involving the competition between volume and interfacial energies of the constituent phases. Often, when the layer thickness in a multilayer is reduced to the nanometer scale, the layers transform from their bulk stable structure to a pseudomorphic form. Stabilization of such pseudomorphic phases is considered to be driven by marked reductions in the total interfacial energy resulting from the transformation. We have recently proposed a new type of phase diagram, the biphasic diagram, in which concurrent phase stabilities are mapped as a function of two degrees of freedom, the volume fraction and the size scale of the multilayers. The model was initially applied for rationalizing phase stability in Co/Cr multilayers. Subsequently, the model has been employed for rationalizing the stabilization of bcc Zr and bcc Ti and also for predicting the novel pseudomorphic hcp Nb phase in Zr/Nb and Ti/Nb multilayers. The existence of this novel hcp Nb phase, stabilized by the reduction in the Zr/Nb interfacial energy, has been experimentally confirmed. The energy differences between the interfaces involving the metastable pseudomorphic phases and those involving the stable phases have been estimated based on the experimental results. These experimental values compare well with assessments of the interfacial energy based on models involving the misfit dislocation network and bonding at the interface.

N3.25

Electronic properties and band alignments at the Metal-Oxide-Silicon interface. Ragesh Puthenkovilakam and Jane P Chang; Chemical Engineering, University of California, Los Angeles, California.

Ultra thin HfO₂ and ZrO₂ thin films are being considered for possibly replacing SiO₂ gate oxide in silicon based metal-oxide-semiconductor (MOS) transistors. In this thickness regime of the dielectric layers, transport properties of the MOS device will be greatly influenced by the interface atomic and electronic structures and band discontinuities. Electronic and material properties of ZrO₂ and HfO₂ films on silicon were investigated using first principles simulations using density functional theory, x-ray photoelectron spectroscopy (XPS), and extended x-ray absorption fine structure analysis (EXAFS). The electronic structure of HfO₂/Si interface showed dangling bond states at the interface due to the reduced coordination of Hf caused by the intrinsic bond constraints at the HfO₂/Si interface. However, our calculations indicate that these dangling bonds could be passivated by hydrogen or oxygen, which can appropriately change the coordination numbers at the interface thereby removing the dangling bond states. Barrier heights or band offsets at the HfO₂/Si interface were theoretically calculated using the band lineup procedure proposed by van de Walle and Martin and showed that the conduction band offsets at the HfO₂/Si interface ranged from 1.9-2.1 eV much larger than at the ZrO₂/Si interface (0.7-1.0 eV). Band offsets were experimentally determined by measuring the core-level to valence-band maximum binding energy differences of both HfO₂ and Si and referencing them with respect to the core-level to core-level separation, at a HfO₂/Si junction. To accurately determine the valence band maximum, we modeled the XPS valence band spectra near the band maximum with the ab initio calculated density of states by fitting the leading edge of the valence band with an instrumentally broadened theoretical valence band density of states. The experimentally measured conduction band offset

at the HfO_2/Si interface was 1.5 eV while that at the ZrO_2/Si interface was 0.9 eV indicating that HfO_2 provides adequate tunneling barriers to holes and electrons while ZrO_2 will need additional interface preparation to have sufficient barrier heights. We also investigated the effect of interfacial silicate layer and found that HfSiO_4/Si and ZrSiO_4/Si interfaces do not show dangling bonds arising from the Hf d states and provided sufficient conduction band offsets (2.2 and 1.9 eV respectively).

N3.26

Energy and processing gas effects on interfacial structure of Spin-valve multilayer. Junjie Quan¹, Xiaowang Zhou¹ and Haydn

N.G. Wadley¹; ¹Intelligent Processing of Materials Laboratory, University of Virginia, Charlottesville, Virginia; ²4Wave Inc., Sterling, Virginia.

A variety of sputtering deposition techniques has been used to deposit GMR spin valves in recent years. Successful approaches include magnetron sputtering and ion beam sputter deposition. Detailed analysis using both atomistic simulations and experiments indicated that conventional ion beam deposition has a number of shortcomings. First, the use of high-energy focused ion source can cause overspill contamination and non-uniform deposition. Secondly, the oblique ion incident angle causes high-energy reflected neutrals, resulting in damage on films. Thirdly, it does not allow the control of adatom energy. Recent atomistic simulations indicate that control of the energy of the depositing atoms (and assisting ion fluxes) provides a powerful means for controlling interfacial structures in multilayer systems. A new biased target ion beam deposition (BTIBD) approach has been developed to overcome all these problems. Here, we describe this new deposition method, and the deposition energy and processing gas effects on interfacial structures of preliminary spin valves deposited using this new technology.

N3.27

Grain Boundary Engineering of Copper Shaped-Charge

Liners. Kerri J.M. Blobaum¹, James Stolken² and Mukul Kumar¹;

¹Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; ²Department of Mechanical Engineering, Lawrence Livermore National Laboratory, Livermore, California.

Shaped-charge liners are thin metallic cones that are explosively driven to high pressures and strain rates for use as penetrators in industries such as defense, mining, and oil drilling. Using a combination of experiments and modeling, we are developing processing methods for engineering the microstructure of copper shaped-charge liner cones in order to improve their performance. The performance of shaped-charge liners is measured by the break-up time of the explosively-driven jet, and it is known that this is influenced by factors such as grain size, morphology, and texture. The deformation experienced during the expansion of the shaped-charge liner jet is akin to superplastic forming, where the strain rate sensitivity and strain hardening characteristics greatly influence the uniform stretching of the material by delaying the onset of plastic instability. The onset of failure could also be influenced by reducing the total interfacial area for void nucleation by increasing the fraction of special boundaries. With this in mind, we are systematically processing materials to obtain specific microstructures. Using finite element analysis, a multi-step back-extrusion/annealing process was developed to form the liners. The effectiveness of this processing will be evaluated by testing the strain rate sensitivity of the materials. Strain rate sensitivity is a good indicator of how the material uniformly elongates before the onset of instability. Tensile strain rate jump tests in the range of 10^{-4} sec^{-1} to 10^1 sec^{-1} and at temperatures ranging from 25C to 500C will be used to evaluate samples with engineered microstructures, as well as conventionally processed samples. The relationship between processing, microstructure, and mechanical properties of copper will be discussed in the context of shaped-charge liner performance. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

SESSION N4/P4: Joint Session: Grain Boundaries and

Interfaces in Nanoscale Materials

Chairs: Peter Anderson and Valerie Randle

Wednesday Morning, April 14, 2004

Room 3002 (Moscone West)

8:15 AM N4.1/P4.1

Interaction of Extrinsic Dislocations with a Geometrically Necessary Dislocation Boundary using Dislocation Dynamics Simulations. Shafique Khan¹, Hussein M Zbib¹ and Darcy A

Hughes²; ¹School of Mechanical and Materials Engineering,

Washington State University, Pullman, Washington; ²Center for Materials and Engineering Sciences, Sandia National Laboratories, Livermore, California.

Different types of dislocation structures are produced during deformation of metals, which are important in terms of their effect on the mechanical properties. One of these deformation dislocations structures are nearly planar geometrically necessary boundaries (GNBs), which accommodate the mismatch in lattice rotation caused by regions of different slip on either side. The internal dislocation structure of a planar dislocation boundary is characterized by the boundary misorientation axis and the boundary normal. In the present studies, the misorientation axis and boundary normal, as determined from experiments, are used to obtain the internal dislocation structure of the GNB. This information is then used to construct a GNB for 3D dislocation dynamics (DD) simulations. Then an extrinsic dislocation moving in the simulation cell under applied stress is allowed to have an interaction with the GNB. These interactions of an extrinsic dislocation with the GNB may include accommodation of the extrinsic dislocation in the GNB and ejection of an intrinsic dislocation from the GNB. Comprehensive results of these interactions will be presented for extrinsic dislocations of different Burgers vectors and character.

8:30 AM *N4.2/P4.2

Deformation mechanism in nanocrystalline fcc metals: bridging experiments with simulations.

Helena Van Swygenhoven, Peter Michael Derlet, Zeljka Budrovic, Abdellatif Hasnaoui and Anders Froseth; Paul Scherrer Institute, PSI-Villigen, Switzerland.

Atomistic simulations have provided unprecedented insight into the structural and mechanical properties of nanocrystalline materials, highlighting the role of the non-equilibrium grain boundary structure in both inter- and intra-deformation processes. One of the most important results is the capability of the nanosized grain boundary to act as source and sink for dislocations. However the extrapolation of this knowledge to the experimental regime requires a clear understanding of the temporal and spatial scales of the modelling technique and a detailed structural characterisation of the simulated samples. In this contribution the dislocation activity suggested by molecular dynamics for three different nc-fcc metals, Al, Cu, Ni and Au are discussed in terms of the inherent restrictions of the technique, in terms of material properties such as the generalized stacking fault energy, in terms of grain boundary structures and last but not least in terms of experimental observations including efforts to bridge simulations to experiments by means of diffraction pattern calculations.

9:00 AM N4.3/P4.3

Structure of dissociated grain boundaries in nanocrystalline gold. Douglas L. Medlin¹, D. Cohen¹, G. Lucadamo¹ and S. M.

Foiles²; ¹Materials Physics Department, Sandia National Laboratories, Livermore, California; ²Materials and Process Modeling Department, Sandia National Laboratories, Albuquerque, NM, New Mexico.

Grain boundaries in low stacking-fault-energy metals can spread, or dissociate, into a three dimensional configuration by the emission of partial dislocations. This phenomenon is of particular importance in nanocrystalline materials because it increases the volume fraction of material associated with interfacial sites and because the constraints of geometric compatibility in such small-grained systems can locally promote the dissociation. Here, through HRTEM observations and atomistic simulations, we consider the structure of dissociated boundaries in nanocrystalline, [110]-textured Au films. In particular, we address the question of how the ordering of stacking fault arrays at dissociated boundaries is related to the crystallographic orientations of the abutting grains. We focus on experimental observation of two important limiting cases: (1) the formation of 9R stacking, corresponding to a stacking every three close-packed planes, and (2) the formation of HCP stacking, which, possessing a "fault" every other close packed plane, possesses the highest possible density of stacking faults. From an analysis of the topological defects required to connect these intergranular layers to the neighboring FCC crystals, we show how these observations, as well as the dissociated boundary structures found at other misorientations, can be understood and predicted from relatively simple geometric considerations. Finally, we analyze how the constraints that arise at boundary junctions affects the separation of the interfacial dislocations. This work is supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000 by the Office of Basic Energy Science, Division of Materials Science.

9:15 AM N4.4/P4.4

Interactions between Lattice Dislocations and sigma3 Boundaries in Gold. Emmanuelle A Marquis and Douglas L

Grain boundary engineered materials are typically processes to contain high densities of first and higher order twin boundaries, which play important roles in improving the material behavior. It is therefore important to understand their behavior during material deformation, and in particular their interactions with gliding lattice dislocations. In this study, we focus on the interactions between $1/2 \langle 110 \rangle$ lattice dislocations and the $1/6 \langle 112 \rangle$ Shockley partial dislocations at σ_3 boundaries. The resulting defects are dislocations with a Burgers vector equal to $1/3 \langle 111 \rangle$ observed along $\sigma_3 \{111\}$ boundaries and at junctions between $\sigma_3 \{111\}$ and $\sigma_3 \{112\}$ boundaries. Using high-resolution transmission electron microscopy, we characterized these defects in gold thin films with a $\langle 101 \rangle$ texture and containing high densities of $\sigma_3 \{111\}$ and $\{112\}$ twin boundaries. The frequency of observations of these defects suggests their crucial role in the formation and deformation of twin structures. We present a series of micrographs illustrating possible locking mechanisms of twin boundaries involving lattice dislocations. In particular, one mechanism, by which parallel $\{112\}$ boundaries interact, involves the interplay between the rigid-body translation state across the $\{112\}$ boundaries and lattice dislocations. This work is supported by the U.S. Department of Energy, in part by the Office of Basic Energy Sciences, Division of Material Sciences, under contract DE-AC04-94AL85000.

9:30 AM *N4.5/P4.5

Slip Transfer across Hetero-Interfaces in two-phase Titanium Aluminum Intermetallics. Jorg M.K. Wiezorek¹, Xiao-Dong Zhang² and Hamish L. Fraser³; ¹Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Center for Materials Science, Bose Corporation, Framingham, Massachusetts; ³Department of Materials Science & Engineering, The Ohio State University, Columbus, Ohio.

Two-phase TiAl based intermetallics with microstructures comprising large volume fractions of lamellar grains are promising candidate materials for applications in advanced gas-turbine-engines. The anisotropic mechanical properties associated with the lamellar microstructure are very well documented in the literature. So-called "soft" and "hard" deformation modes can be distinguished. The interfaces between neighboring lamellae of the two constituent phases, tetragonal ordered gamma-TiAl and hexagonal ordered alpha-2 Ti3Al, have been proposed as efficient obstacles for dislocation motion during "hard" mode deformation. Supposedly, the interactions of slip accommodating defects with these hetero-interfaces play an important role in strengthening of lamellar TiAl. The present experimental study used mechanical tests of oriented lamellar grains and detailed transmission electron microscopy to investigate interactions of slip-accommodating defects with these lamellar interfaces. The details of slip transfer across the lamellar hetero-interfaces have been identified, which could provide a basis for modeling the strength of lamellar two-phase TiAl alloys. Thus the role of defect-interactions on the strength and ductility of two-phase TiAl has been elucidated. Support for this work by a grant from the National Science Foundation with Dr. Bruce MacDonald as program manager and from the Office of Research, University of Pittsburgh are gratefully acknowledged.

10:30 AM *N4.6/P4.6

Shear of weak interfaces as a strengthening mechanism in nanoscale layered composites. Richard G Hoagland and John P Hirth; Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico.

Resistance to slip through interfaces can take on a variety of forms often involving the internal stresses associated with coherency. But in composites with incoherent interfaces, such as those formed from metals with dissimilar crystal structure or large lattice parameter mismatch, coherent stresses are unlikely although such materials, e.g., Cu/Nb, are still found to achieve very high strength levels. Atomistic simulations of an fcc/bcc system containing incoherent interfaces, reveals that such interfaces shear in response to the stress fields of nearby dislocations. We present these results and show their implications that: 1) a dislocation near an interface is attracted to it, and 2) once in the interface the dislocation core spreads. Both consequences make it difficult for slip to pass through the interface and we suggest that this behavior can explain the origins of strength in systems with incoherent interfaces. We also present a linear elastic model that generalizes the results to enable predictions of the relation of interfacial shear strength to the overall strength of this type of composite. This work was supported by the Office of Basic Energy Sciences, U. S. Dept. of Energy.

11:00 AM N4.7/P4.7

Atomistic Study of Dislocation-Coherent Precipitate Interaction in Cu-Co Alloys. Jae-Hyeok Shim and Brian D Wirth; Department of Nuclear Engineering, University of California, Berkeley, Berkeley, California.

Introducing precipitates in a metal matrix is an effective means of increasing strength at low and at high temperatures, and of improving high temperature creep behavior. While the general features of precipitate strengthening that results from coherency strain hardening, chemical hardening and dispersion hardening are well known, many of the detailed interaction mechanisms remain to be determined at the atomic scale. In particular, consider the case of Cu-Co alloys. In these alloys, small ($d < 5$ nm) fcc Co precipitates form which have very strong coherency with the Cu matrix. At larger sizes ($d > 10$ nm), the precipitates transform to the equilibrium hcp structure. Yet, at sizes where the precipitates are believed to all be coherent, anomalous temperature dependence of the yield strength has been observed in Cu-Co alloys [1]. In this work, we use molecular dynamics simulations to investigate the detailed atomistic dislocation-precipitate interactions in Cu-Co alloys. In particular, we report the dislocation bypass mechanism from the precipitates as a function of Co precipitate size, interface coherency and temperature. The simulations have been performed using different parameterizations of the Cu-Co alloy system within the Embedded Atom Method (EAM). The results reveal the effect of the precipitate shear modulus, lattice stability and interface type on the dislocation interactions. 1. N. Buttner and E. Nembach: Z. Metallkd., 76 (1985) 82.

11:15 AM N4.8/P4.8

Dislocation-Twin Interactions in Monazite. Randall Hay, USAF, WPAFB, Ohio.

Monazite (LaPO₄) is monoclinic with lattice parameters $a = 0.683$ nm, $b = 0.706$ nm, $c = 0.648$ nm, and $\beta = 103.2$ degrees. It is refractory (mp 2072C), relatively soft (5 GPa), machinable, and stable with many common oxides. The mechanical properties of monazite promote distributive damage mechanisms in ceramic composites. Dislocation-twin interactions were identified by TEM in monazite that was spherically indented at room temperature. Emissary lattice dislocations in front of twin tips were observed. Shear of twin lamellae by slip was also observed. Where possible, slip systems were identified. Three types of climb-dissociated partial dislocations were observed. Two types were found on twin boundaries, and a third in the lattice. Formation mechanisms are discussed. Glide of climb dissociated partial dislocations allowed by stacking fault migration is considered. Monazite recovers easily from radiation-induced amorphization at low temperatures. Room-temperature wear of monazite forms fine-grained microstructures that suggest recrystallization. These observations, as well as those presented here for climb-dissociation, suggest that some low-temperature diffusion mechanisms may be faster in monazite than in other refractory oxides.

11:30 AM N4.9/P4.9

The Mechanical Properties in the vicinity of Grain Boundaries in ultrafine-grained and polycrystalline materials studied by Nanoindentations. Elmar Schweitzer and Mathias Goeken; Materials Science, University Erlangen-Nuremberg, Erlangen, Germany.

The strength of structural materials strongly depends on the structure and properties of grain boundaries. Interfaces usually act as barriers to dislocation motion and therefore strengthen materials with decreasing grain size, quantitatively described by the well-known Hall-Petch relation. However, interfaces in nanocrystalline materials are often covered with impurities or second phases, which may influence the mechanical properties. With nanoindentation testing it is now possible to probe the strength of interfaces like grain boundaries directly on a nanometer scale. Therefore this method was used to investigate the properties around grain boundaries in polycrystalline materials with conventional grain sizes and in ultrafine-grained metals prepared by equal channel angular pressing (ECAP), where no impurities are introduced during processing. The results show that strengthening effects of grain boundaries strongly depend on the alloy composition in the vicinity of the boundary. Measurements on an austenitic steel clearly show a decreasing hardness close to the interface in opposite to the general expected behaviour of strengthening. In this case segregation effects strongly influence the mechanical properties around the boundaries. In strongly ordered intermetallics like NiAl no softening or strengthening influence around boundaries was found. The influence of interfaces on the mechanical properties was investigated in materials with grain sizes down to 100 nm and will be discussed in the paper.

11:45 AM N4.10/P4.10

Interfacial properties of a computer generated nanostructured alloy as influenced by the thermodynamics of the classic model used for the interactions. Alfredo Caro, Babak Sadigh and Eduardo Bringa; CMS, LLNL, Livermore, California.

We study the interfacial properties of a computer-generated nano-structured alloy, as influenced by the thermodynamics implicit in the classic model used for the interactions. Metallic alloys are difficult to model with the present level of complexity of empirical potentials because basic thermodynamic properties are absent from the formulation of these potentials and can only be incorporated in an empirical way, thus introducing uncertainty in the reliability of the predictions. Due to the complexity involved in the calculation of accurate phase diagrams, in most cases the thermodynamics that emerges from these empirical models is unknown. In this work we use our calculated phase diagram of EAM Au-Ni alloys and its interesting property that the excess enthalpy of mixing in the liquid phase is negative, while in the solid solution is positive. We show that the interfacial disordered region of an EAM Au-Ni bulk nano-phase made up of nano grains of pure Au and pure Ni, stabilizes the structure, opening the way to super-plasticity by increasing the energy needed for inter-granular fracture.

SESSION N5: Functional Materials

Chairs: Brent Adams and Narayanan Ravishankar
Wednesday Afternoon, April 14, 2004
Room 3004 (Moscone West)

1:30 PM *N5.1

Interfacial Engineering of Superconductors. David Larbalestier, Dmitri Abramov, Matt Feldmann, Alex Gurevich, Sang-Il Kim, Anatoly Polyanski and Xueyan Song; Applied Superconductivity Center and Department of MS&E, University of Wisconsin-Madison, Madison, Wisconsin.

Almost immediately after the most unexpected discovery of superconductivity operating at liquid nitrogen temperatures came the bad news: only small grain-to-grain misorientations of about 5 degrees or less would be permitted if strong superconducting properties were required. Wires useful for cables, magnets or other large devices are inevitably polycrystalline and would thus require quasi-single crystal texture over kilometer lengths. Amazingly this requirement is now close to fulfillment. The so-called coated conductor of $\text{YBa}_2\text{Cu}_3\text{O}_7$ can now be made by continuous processes with a grain-to-grain spread of as little as 5 degrees FWHM. Moreover the scientific understanding of why grain boundaries become obstructive to current has advanced to the level at which it is possible to do some useful grain boundary engineering. At this point understanding the detailed distribution of grain-to-grain misorientations, the way in which dissipation occurs at some boundaries rather than others such that the percolation geometry of current through large networks of low angle grain boundaries can be predicted is important and within view. We will describe recent work studying the current flow by magneto-optical imaging, identification of locations of dissipation by low temperature scanning laser microscopy (LTSLM*) and microstructural analyses of such networks using orientation imaging and electron microscopies.

*LTSLM work carried out in collaboration with the group of Professor Alexey Ustinov, University of Erlangen. Work supported by the AFOSR-MURI on fundamental science of coated conductors.

2:00 PM N5.2

Effect of Nano-Scale Compositional Fluctuations in Sm-Ba-Cu-O Materials. Shih-Yun Chen¹, Chuan-Pu Liu¹, In-Gann Chen¹ and Maw-Kuen Wu², ¹Materials Science and Engineering, National Cheng Kung University, Tainai, Taiwan; ²Institute of Physics, Academia Sinica, Taipei, Taiwan.

It has been reported [1] that the superconductivity of top-seeded melt-textured (TSMT) Sm-Ba-Cu-O materials (SmBCO) exhibit J_c enhancement in samples with nano-particle addition compared with that of control sample (no nano-particle additives). The scaling theory analysis of volume pinning force $F_p(H)$ of these two types of samples show different pinning mechanisms. A superconducting phase with lower T_c was observed in samples with nano particle additions by the direct current transport R-T analysis, which can be attributed to the origin of $\Delta\kappa$ pinning centers and related to the improvement of critical current density (J_c) at high field regions. In this study, TSMT SmBCO materials with two types of nano-sized particles, $\text{Sm}_2\text{BaCuO}_5$ (Sm211) and $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ (nm422) additions had been studied to reveal the effect of nano-scale compositional fluctuation on the pinning mechanism as well as J_c enhancement. It was found that different types of nano-particle addition will result in different anisotropic factor, γ ($\gamma = J_c // c / J_c // a-b$), J_c -H relationship. The microstructure of the nano-scale compositional fluctuations found

in the matrix was investigated by TEM and the optima nano-particle addition will be discussed. Supported by NSC-92-2112-M-006-022, TAIWAN Reference: [1] S-Y.Chen, I-G. Chen, P-C. Hsieh, and M-K. Wu, accepted for publication in JMR.

2:15 PM *N5.3

Self-assembled Multifunctional Oxide Nanostructures. Ramamoorthy Ramesh, Materials / Physics, University of Maryland, College Park, College Park, Maryland.

There is currently considerable interest in the design of multifunctional materials, i.e., materials with multiple order parameters (ferromagnetism, ferroelectricity, etc). We have been working on two families of multifunctional materials, namely single phase multiferroics such as BiFeO_3 and self-assembled multifunctional nanostructures, such as BaTiO_3 - CoFe_2O_4 . In this talk, I wish to discuss such nanostructures. We have found that the deposition of films from a composite target consisting of BaTiO_3 and CoFe_2O_4 on single crystal perovskite substrates leads to the spontaneous formation of almost ordered arrays of nanopillars of the ferromagnetic CoFe_2O_4 phase embedded in the ferroelectric BaTiO_3 matrix. The interfaces between the substrate and these two phases as well as between these two phases are heteroepitaxial, thus being one of the first examples of 3-d heteroepitaxy. These nanostructures exhibit a strong magnetoelectric effect. I will present the details of the structure and properties of such novel nanostructures.

2:45 PM N5.4

The Dynamic Formation of Metal-Oxides by In situ Oxidation of Cu Thin Films. Judith Yang, Guangwen Zhou and Liang Wang; Materials Science and Eng., University of Pittsburgh, Pittsburgh, Pennsylvania.

Fundamental understanding of the oxidation mechanisms provides information needed for the control of oxide-metal interfaces, which is essential for a wide range of applications, including catalysis, fuel cells, engineered nanocomposites, and passivation. We studied copper oxidation by in situ and ex situ electron microscopy methods. Surface orientations altered the oxide nanostructures from island to nearly layer-by-layer growth. Temperature had a dramatic effect on the oxide nanostructure, where domes, nanorods, and hollow pyramids are created by altering only the oxidation temperature. The dynamically forming oxide-metal interface was noted to be irregular with possible different oxidation states across the interface. Interfacial strain plays a key role in the cornucopia of microstructures observed by electron microscopy and atomic force microscopy.

3:30 PM *N5.5

Role of Grain Boundaries and Grain Misorientation in the Electrical and Electromechanical Properties of Ferroelectrics. Susan Trolier-McKinstry, Michael Biegalski, Cihangir Duran, Edward Sabolsky and Gary L. Messing; MRI, Penn State, University Park, Pennsylvania.

Grain boundaries can have a profound impact on the properties of ferroelectric ceramics. Many bulk ceramic preparation techniques result in the development of thin intergranular layers, often of PbO or Bi_2O_3 . As the thickness of the grain boundary layer grows, the dielectric permittivity is suppressed substantially, especially at its peak value. The high field properties such as the remanent polarization are affected less strongly. Examples will be given of the impact of grain boundaries on the processing and properties of textured $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 ceramics, as well as growth of BaTiO_3 single crystals by surface templated grain growth. The role of texture development on the properties will also be described. Despite the importance of grain boundaries, comparatively little is known about how the ferroelectric polarization propagates across a boundary. To try and probe this more systematically, epitaxial BaTiO_3 films have been grown on bi-crystal substrates, and the switching behavior across the boundary has been studied. In general, it is found that the boundary exerts relatively little impact on the amount of in-plane switchable polarization for bicrystals where the boundary acts as a mirror plane.

4:00 PM N5.6

Piezoelectric - Ferromagnetic Interface Engineering for Voltage Driven Magnetic Assessment. Wouter Eyckmans, Gustaaf Borghs and Jo De Boeck; MCP/MN, IMEC, Leuven, Belgium.

Assessing magnetic materials and its properties has always implied using external magnetic fields. These fields are most commonly generated by sending currents through on-chip dedicated lines. The disadvantages of this approach urge for a solution. The stress sensitivity of magnetic materials opens possibilities for using piezoelectric layers as an alternative assessment technique. Since the interface between the piezoelectric and the ferromagnetic materials acts as stress transducer, controlling its properties cannot be

overemphasized. Ferromagnetic thin film properties are influenced by the roughness of the substrate. The high roughness of piezoelectric single crystals and ceramics makes this the key issue determining the feasibility of the combination. The PZT ceramics we used were chemically mechanically polished from an initial 1micron rms roughness to 0.7nm rms roughness (AFM scanning area 1*1micron). Thin (10-20nm) magnetic films of Ni and Co50Fe50 were deposited on polished ceramics with roughnesses between 3nm rms and 0.7nm rms. MOKE measurements showed a decrease of coercivity from 7kA/m down to 3kA/m, which is comparable to the inherent coercivity of these materials. The importance of reaching this low coercivity lies in the fact that the stress effect has to compete with the anisotropy (in first order proportional to the coercivity), and hence a lower anisotropy implies a larger stress effect. The CMP step, however, has the disadvantage of leaving slurry particles. These jeopardize magnetic component operation, and complicate magnetic characterization significantly. An ammonia based wet etch proved to remove the particles. Since stress is used as magnetic excitation means, not only the dynamically used stress plays a role, but the initial stress state also determines the operation. The piezoelectric ceramics exhibit a large thermal expansion, so changing the temperature can severely alter the substrate-magnetic thin film stress conditions. This initial substrate-film interfacial stress can also be used to its benefit. Controlling substrate temperature during deposition and annealing the composite shows a linear dependence of coercivity on temperature. An alternative manner for setting the initial stress conditions was obtained by applying a bias voltage to the piezoelectric ceramic during deposition. This provides an even more accurate tuning method for interfacial stress engineering. Finally, using buffer layers was examined. Using SiO₂ between the PZT and a Ni film lowered the effect of the stress. For a film of 50nm SiO₂, no measurable stress effect on magnetic properties could be detected. This can be used to buffer stress between different magnetic layers. Another possibility lies in using a Ni80Fe20 buffer layer. When used with a Co50Fe50 thin film, the Co50Fe50 layer exhibits a reduction of coercivity by 35%. The absolute stress dependence remains unaltered, consequently increasing its relative importance.

4:15 PM N5.7

Effect of strain and growth morphology on the evolution of the domain structure of ferromagnetic manganites near their curie temperature. Holly Miller¹, Amlan Biswas², Joshua Higgins³,

Richard Greene³ and Yakov Mukovskii⁴; ¹Department of Natural Sciences, Longwood University, Farmville, Virginia; ²Department of Physics, University of Florida, Gainesville, Florida; ³Department of Physics, University of Maryland, College Park, Maryland; ⁴Moscow State Steel and Alloys Institute, Moscow, Russian Federation.

Hole-doped perovskite manganese oxides (manganites) are ferromagnetic metals below their curie temperature (T_C). They also exhibit perfect spin-polarization near the fermi level i.e. the charge carriers have the same spin orientation. Hence it is expected that magnetic tunnel junctions (MTJ) using manganites such as La_{0.7}Sr_{0.3}MnO₃ (LSMO, T_C 360 K) as electrodes should display an enhanced tunneling magnetoresistance (TMR), below the curie temperature of the material. Such effects have been demonstrated at low temperatures. However, the magnitude of the TMR decreases rapidly as the temperature is increased even if one remains well below the T_C . Although, mechanisms such as surface dead layers and poor epitaxy of the multilayers have been suggested as reasons for such behavior, it is not clear how these mechanisms modify the properties of manganites leading to poor performance of devices at room temperature. We have used temperature dependent Magnetic Force Microscopy (MFM), to study the evolution of the magnetic domain structure of single crystals and thin films of LSMO as the temperature is increased up to T_C . Our results show that even in the single crystal form, the surface magnetism starts changing drastically about 10 K below the bulk T_C . In compressively strained thin films, the domains are affected by the surface morphology of the thin films which leads to smaller domain sizes (50 nm) and the surface magnetism starts changing 20-30 K below the bulk T_C . As the strain is reduced, behavior similar to single crystals is observed. Using these results we will explain the performance of manganite based devices. We will discuss how phenomena such as multiphase coexistence and percolation of the metallic phase in manganites, lead to the observed behavior of these devices and suggest methods of improving and modifying these properties.

4:30 PM N5.8

Nanopatterning on Reconstructed Ceramic Surfaces. Shwetha Shetty¹, Vijay B Shenoy¹, Barry C Carter² and Ravishankar Narayanan¹; ¹Materials Research Centre, Indian Institute of Science, Bangalore, India; ²Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Ordered arrays of metal nanoparticles on oxide substrates find diverse applications ranging from catalysis to magnetic recording and hence

patterning to produce such arrays is an area of considerable technical importance and active research. A novel method to produce ordered arrays of metal nanoparticles based on heterogeneous nucleation of a liquid phase from an undersaturated vapour will be demonstrated. The m-plane of alumina is used as a template for producing the arrays. The m-plane, an unstable plane reconstructs into a hill-and-valley structure on annealing at high temperature. The length scale of annealing is in the nanometric scale making it an ideal template for nanopatterning. It is shown that the nucleation process is assisted by electric-field singularities on the crests/hills of the reconstructed ceramic surface. Regular arrays of Pt nanoparticles ranging from 30-50 nm with spacing ranging from 50-120 nm have been produced by this electric field assisted nanopatterning technique. Preliminary studies to extend this technique to nucleation of a solid phase from an undersaturated liquid will also be presented.

4:45 PM N5.9

Dewetting on the Surface of Rutile. Shelley Gilliss¹, N.

Ravishankar² and C. Barry Carter¹; ¹Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; ²Indian Institute of Science, Bangalore, India.

The wetting of a ceramic surface by a secondary phase is a technologically relevant problem that is encountered under many situations. Processing of ceramics using liquid-phase sintering relies on the wetting of the ceramic powder compact by a lower melting-point additive. The additive may be a non-metallic glassy phase, as in oxide ceramics, or can be a liquid metal as in the case of Co additives for WC ceramics. The wetting of ceramics by liquid metals is also encountered in joining applications, such as active-metal brazing. The role of chemistry and kinetics on the wetting behavior will be discussed. The manner in which the secondary phase wets the crystalline ceramic at processing temperatures dictates the microstructure and therefore the properties of the material. Model systems of silica and rutile and tungsten oxide and rutile will be emphasized. Thin films (100 nm) of SiO₂ or WO₃ are deposited onto a single-crystal substrate rutile by pulsed-laser deposition. The specimens are then heat-treated in air at high temperature (1100°C-1650°C). At high-temperature and during cooling steps and facets form on the oxide surface and the secondary-phase may dewet or continue to wet the surface. Atomic-force microscopy coupled with electron-backscattered diffraction analysis in the scanning electron microscope has been used to study the dewetting behavior. Due to the nature of the WO₃/TiO₂ and SiO₂/TiO₂ systems, an instability arises at the periphery of the droplet during the dewetting process. This leads to a final patterned morphology. The instability at the periphery of the droplet is a result of excess TiO₂ dissolved in the system precipitating out during cooling. This change in composition changes the surface/liquid interfacial energy and this leads to a Marangoni-type instability. Pinning at the periphery, coupled with the Marangoni flow, amplifies the instability and a pattern is formed. The roughness of the surface, in this case, the faceting of the surface can modify the morphology of the patterns formed, therefore the morphology of the dewet droplets are different for the (001) and (110) surfaces of rutile. The degree of dissolution and reprecipitation of the substrate material within the secondary phase has been monitored by X-ray energy dispersive spectroscopy and electron energy-loss spectroscopy.

SESSION N6: Interfacial Structure and Migration

Chairs: C. Barry Carter and Valerie Randle

Thursday Morning, April 15, 2004

Room 3004 (Moscone West)

8:30 AM *N6.1

Dynamics of grain boundary motion at the atomic level.

Karl L. Merkle¹, Loren J. Thompson¹ and Fritz Phillipp²; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany.

Grain boundaries (GBs) play a pivotal role in controlling mechanical and physical behavior in polycrystalline materials. Thermally activated GB migration in Au and Al is studied in this work by in-situ high-resolution electron microscopy (HREM) at elevated temperatures ($T > 0.5 T_m$). Suitable grain and interfacial geometries are manufactured by epitaxial templating. These techniques allow us to observe not only tilt, but also twist and general GBs at atomic resolution. Surface-energy driven GB migration is observed in the latter, whereas tilt GB motion is curvature driven. Digital analysis of HREM video recordings have given considerable insight regarding the dependence of GB migration mechanisms on interfacial geometry and structure. For example, spatio-temporal GB fluctuations involving hundreds of atoms have been observed in Au at high temperature. Such collective phenomena will be discussed along with other aspects of atomic-scale GB migration mechanisms. This work was supported

9:00 AM *N6.2

Grain Boundary Mechanics - Influence of Mechanical Stress Fields on Grain Boundaries. Myrjam Winning, Institute of Physical Metallurgy and Metal Physics, RWTH Aachen, Aachen, Germany.

The reaction of grain boundaries to mechanical stresses is reviewed. It was found that the motion of low angle grain boundaries as well as of high angle grain boundaries can be induced by the imposed external stress. The experiments were carried out on planar tilt and also planar twist grain boundaries in aluminium with different rotation axes and misorientation angles. The observed activation enthalpies allow conclusions on the migration mechanism of the stress induced grain boundary motion. The motion of planar low and high angle grain boundaries under the influence of a mechanical stress field can be attributed to the movement of the grain boundary dislocations which comprise the structure of the boundary. For the investigated tilt boundaries a sharp transition between low and high angle grain boundaries was observed for different tilt axes. Also the investigated twist grain boundaries show a difference in the dynamical behaviour between low and high angle grain boundaries. The motion of planar grain boundaries under the influence of an external driving force presents the possibility to determine the absolute grain boundary mobility. Therefore the motion and the mobilities of planar and curved grain boundaries with the same tilt axes and misorientation angles can be compared. The fact that boundaries can also be moved by mechanical forces sheds new light on microstructure evolution during elevated temperature deformation and dynamic recrystallization.

9:30 AM *N6.3

In-situ measurements of growth in the bulk of deformed single crystals at the 3DXRD microscope. Soeren Schmidt and Dorte Juul Jensen; Center For Fundamental Research: Metal Structures In Four Dimensions, Risoe National Laboratory, Roskilde, Denmark.

The Three Dimensional X-ray Diffraction microscope (3DXRD) situated at the European Synchrotron Radiation Facility (ESRF) has now been in commission for 4 years. Lately, and for the first time ever, complete 4D maps (3 spatial dimensions + time dimension) of interface migration during recrystallization of the individual grains have been achieved by annealing of deformed aluminum single crystals. The nature of the growth of the recrystallizing grains has been shown to have a so-called jerky nature, i.e. alternating periods of surface expansions and pauses within local regions of the grain. Since it is possible to measure the boundary migration rate locally the overall goal is to clarify to what extend the local migration rate is correlated to the local deformed microstructure. The talk will give an overview of the current state of the analysis.

10:30 AM *N6.4

Microstructure control in aluminum alloys by manipulation of grain boundary mobility. Hasso Weiland¹, Sonnwuk Cheong¹, Joe Fridy¹ and Claire Maurice²; ¹Material Science, Alcoa, Alcoa Center, Pennsylvania; ²Ecole Nat. Sup. Des Mines, St. Etienne, France.

Aluminum alloys are processed to obtain recrystallized grain sizes in the 5 to 50 μm range after thermal operations. This is achieved by controlling the deformation structure and the grain boundary mobility. The two dominant mechanisms affecting grain boundary mobility during recrystallization of aluminum alloys are solute drag and particle pinning (Zener drag). The role of second phase particles in exerting a grain boundary drag is well understood for particles larger than about 100 nm, however for smaller particles, the effect is not very clear and is currently a subject of debate. In the past, solute drag was considered to be less effective than particle pinning in controlling grain boundary mobility. Although a systematic study of the drag imposed on a moving boundary by various alloying elements has not yet been carried out, recent experiments reported in this paper show that solute drag is more significant in controlling grain size than has previously been thought. We have constructed a network model to study the role of the deformation structure on the formation of recrystallization nuclei and thus on the formation of mobile large angle grain boundaries. This presentation will review our current understanding and future research needs.

11:00 AM N6.5

Solute Effects On Grain Boundary Mobility and Character in Aluminum Alloys. Mitra L. Taheri¹, Anthony D. Rollett¹ and Hasso Weiland²; ¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Alcoa Technical Center, Alcoa Center, Pennsylvania.

Recent studies have shown that recrystallization in aluminum alloys is strongly influenced by alloy composition. The retardation of

boundaries under the influence of solute is widely accepted, however the understanding of the activity of individual boundaries with respect to their character remains vague. This paper examines the mobility of aluminum alloys under the influence of zirconium during in-situ annealing within a Scanning Electron Microscope under a stored energy driving force. The velocities of recrystallizing grains are measured and their profile exhibits irregular motion, in support of recent theoretical solute drag models. Electron backscattered diffraction is used to study the effect of solute on certain boundary types, and shows an asymmetric mobility maxima at $40^\circ <111>$ misorientation, which is supported by the literature. A preference for $\Sigma 7$ type CSL boundaries to grow rapidly is observed and faceted growth of these particular grains is noted. Serial sectioning was used to examine boundary inclination angles of the recrystallized grains and henceforth grain boundary energy. The segregation of solutes to particular boundary types is studied using Transmission Electron Microscopy. The results are compared to recent in-situ recrystallization experiments and provide new insight within the context of boundary character-specific growth.

11:15 AM *N6.6

Grain Boundary Properties and Grain Growth. Katayun Barmak¹, Wayne Archibald¹, Anthony Rollett¹, Shlomo Ta'asan² and David Kinderlehrer²; ¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Department of Mathematical Sciences, Carnegie Mellon University, Pittsburgh, Pennsylvania.

To tailor the grain structure of materials, it is of interest to develop predictive models of grain growth that incorporate experimentally determined grain boundary properties. To this end, we have made use of 100 micron thick foils of Al and electron back scatter diffraction, in combination a statistical multiscale method, to determine the relative boundary energies and mobilities of 890 boundaries as a function of misorientation angle and misorientation axis. Grain growth has been examined in 100 nm thick films of Al using transmission electron microscopy. For each annealing time, the distribution of grain area, grain size, dihedral angle and the number of sides for between 1100 and 2000 grains has been determined. The experimental grain structures are compared with those obtained in 2-D simulations of grain growth.

11:45 AM N6.7

Anisotropy in Grain Boundary Migration during Recrystallization: A Molecular Dynamics Study. Moneesh Upmanyu^{1,2} and Zachary Trautt¹; ¹Engineering Division, Colorado School of Mines, Golden, Colorado; ²Materials Science Program, Colorado School of Mines, Golden, Colorado.

We have performed atomic-scale simulations of grain boundary motion driven by dislocation density gradients across the grain boundary plane. Molecular dynamics simulation technique has been employed to study motion of individual flat grain boundaries, in both two- and three-dimensions. The simulation cell consists of a dislocation free grain abutting a grain with a periodic array of threading dislocations. Elastic anisotropy induced due to the dislocation array drives the grain boundary, resulting in long-range boundary motion. In this talk, we shall present boundary mobility data for high-angle $<11>$ tilt misorientations in a two-dimensional, Lennard-Jones triangular lattice. The anisotropy in the boundary mobility is compared with existing mobility data for curvature driven grain boundaries. The difference in the anisotropy is discussed. Finally, a model for boundary migration mechanism is presented, and compared with existing migration models.

SESSION N7: Grain Boundary Structure, Networks and Correlations

Chair: Katayun Barmak and Christopher Schuh
Thursday Afternoon, April 15, 2004
Room 3004 (Moscone West)

1:30 PM *N7.1

Recrystallization Processing of Cold-Rolled Nickel. Ian Baker, Hui Chang, Beatrice Iliescu, Jiying Li and Harold J. Frost; Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire.

Polycrystalline nickel was cold-rolled to 90% rolling reduction, followed by either directional annealing at either 643 K or 1273 K, or static annealing at a variety of temperatures from 623 K to 1273 K for 60 min. Similar nickel sheets were cold-rolled to 20% reduction followed by annealing at 773 K for 20 min, with this process repeated up to five times. The resulting microstructures were characterized using both electron back-scattered patterns on a scanning electron microscope and optical microscopy. The statically annealed 90%-rolled nickel showed a $\{100\}<001>$ texture and small grains with a very

high fraction of special boundaries after primary recrystallization at ≤ 700 K, but a $\{124\} \langle 211 \rangle$ texture and large grains after secondary recrystallization at >1000 K. Initial processing of the 20% cold-rolled nickel showed an increase in special boundaries, but this was followed by a reduction, with subsequent processing runs. Directional annealing of the 90%-rolled nickel at 1273 K over a wide range of hot zone velocities produced either columnar grains or a single crystal via secondary recrystallization. Research supported by AFOSR grant F49620-00-1-0076 and NSF DMI grants 9976509 and 0217565.

2:00 PM *N7.2

Crystallographic distribution of internal interfaces in polycrystals.

Gregory S. Rohrer¹, David Saylor², Bassem El Dasher¹, Ying Pang¹, Herbert Miller¹, Paul Wynblatt¹ and Rollett D. Anthony¹; ¹MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²NIST, Gaithersburg, Maryland.

Five parameters are needed to characterize grain boundaries in polycrystalline solids: three can be associated with the lattice misorientation and two with the orientation of the interface plane. Using orientation imaging microscopy, it is possible to measure four of the five parameters from a single section plane. The fifth parameter, the inclination of the boundary with respect to the section plane, can be determined either by serial sectioning or stereological analysis. We have used these techniques to measure the distribution of interfaces in a range of different polycrystals. The results indicate that the boundaries of individual grains in dense polycrystals prefer certain crystallographic habit planes, almost as if they were independent of the neighboring crystals. In MgO, SrTiO₃, MgAl₂O₄, TiO₂, and Al, the specific habit planes within the polycrystal correspond to the same planes that dominate the external growth forms and equilibrium shapes of isolated crystals of the same phase. The observations reduce the apparent complexity of interfacial networks and indicate that a model for grain boundary energy and structure based on grain surface relationships is more appropriate than the widely accepted models based on lattice orientation relationships.

2:30 PM N7.3

Crystallographically-Necessary Constraints at Triple Junctions in Grain Boundary Engineered Alloys.

Valerie Randle, Materials Research Centre, School of Engineering, University of Wales Swansea, Swansea, United Kingdom.

It is well known that a geometrical combination rule governs the constitution of triple junctions which consist of coincidence site lattice boundaries. In typical grain boundary engineered alloys this combination rule refers to twin-related boundaries, i.e. the sigma 3 family. Here we present some new insights into the consequences of triple junction constraints in such alloys, by reference to data from a nickel-based superalloy. Sigma 3 boundaries were classified as twin, off-twin or general. At triple junctions composed of sigma3/sigma3/sigma9 it was shown that a combination of one twin sigma 3 and one off-twin sigma 3 was more likely to occur than two twin sigma 3s or two general sigma 3s. The explanation for the preferred combination is that mobile sigma 9 boundaries with high deviations from the reference misorientation encounter twin sigma 3s, and in consequence regenerate a sigma 3 at the triple junction which must be off-twin according to the crystallographic constraints at the junction. Further analysis of the general sigma 3s indicated that more than half the boundaries in this category could not have $\{211\}\{211\}$, $\{774\}\{855\}$, $\{111\}\{511\}$, $\{001\}\{221\}$ or $\{110\}\{411\}$ planes.

3:15 PM *N7.4

Variance and Connectivity of the Grain Boundary Network.

Brent Larsen Adams, Jay Basinger and Eric Homer; Mechanical Engineering, Brigham Young University, Provo, Utah.

Measures of the connectivity of grain boundaries in 304 stainless steel, that are subject to intergranular failure when sensitized, are described. The primary results pertain to 2-dimensional networks, but extensions to 3-dimensions are discussed. Of particular focus is the variance of these measures. Methodology for relating connectivity at varying length scales to the critical crack size is also described.

3:45 PM *N7.5

The Relationship Between Stochastically Driven Grain Boundary Interfaces and the Global Structure of Grain Boundary Networks.

roger minich¹, james stolken¹ and mukul kumar¹; ¹Lawrence Livermore National Laboratory, Livermore, California; ²Lawrence Livermore National Laboratory, Livermore, California; ³Lawrence Livermore National Laboratory, Livermore, California.

The hierarchical structure of grain boundary networks is treated as a stochastically driven system of connected interfaces. Each interface is driven both by additive thermal fluctuations as well as multiplicative strain fluctuations manifest in the heterogeneous statistical storage of

dislocations. The connectivity of the interfaces must also satisfy fundamental crystallographic constraints resulting in long-range statistical correlations. A nonlinear Langevin equation for the stochastically driven interface results in a stationary probability distribution of interfacial energy and velocity. The derived probability distribution for interface energy in the presence of thermal and strain fluctuations is presented and is shown to exhibit a phase diagram with an order parameter describing the degree of symmetry of the most probable moving interface. The probability distribution for the interface energy is used as input into a computer generated 2-D grain boundary network that includes the crystallographic constraints. Long-range correlations spanning many interfaces are characterized for different temperatures and dislocation microstructures. The results are also discussed in the context of constrained percolation theory and a maximum entropy approach is presented to study the competition between order and disorder in grain boundary networks. The theory reproduces certain universal trends observed in experimental triple junction distributions. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

4:15 PM N7.6

Group Theory, Correlated Microstructures, and Grain Boundary Engineering.

Bryan W Reed, Eira T. Seppala, Robert E. Rudd, Roger W. Minich and Mukul Kumar; Lawrence Livermore National Laboratory, Livermore, California.

The field of grain boundary engineering, which seeks to improve material properties by controlling the topology of the network of grain boundaries, demands a sophisticated understanding of the correlations in boundary character resulting from various processing methods. Some of these correlations are inherently crystallographic, deriving from the structure of the rotation group describing the various "special" boundaries. One example is the Σ product rule, which governs the types of coincident site lattices that may be present at a triple junction, and it is already known that the crystallographic correlations induced by this constraint can significantly alter long-range statistical behavior such as percolation thresholds and calculated brittle fracture properties.[1,2] This seems to be particularly true for systems dominated by annealing twins. However, the Σ product rule is only a necessary, not a sufficient, criterion for the crystallographic compatibility of a grain boundary network. We show some of the additional insights that arise from a more complete consideration of the structure of the coincident site lattice rotation group, and especially of the highly-important twin-related subgroup. For example, the Σ product rule arises naturally as a special case of a general topological mapping problem, and preliminary results suggest that higher-level analogs of the Σ product rule may be operating on all length scales. Working within a new analytical framework (which implicitly accounts for all such constraints), we can efficiently generate empirically realistic grain boundary networks and also make several general observations. These include a new understanding of the very different natures of twin-limited structures in two and three dimensions, the effects of crystallographic correlations on brittle fracture properties, and the manner in which certain commonly-simulated topologies (including the 2-d hexagonal and 3-d tetrakaidecahedral arrays) can produce significantly skewed results. Acknowledgment: This work was performed under the auspices of the US Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48. [1] R. W. Minich, C. A. Schuh, and M. Kumar. Phys. Rev. B 66, 052101 (2002). [2] C. A. Schuh, R. W. Minich, and M. Kumar. Phil. Mag. 83, 711 (2003).

4:30 PM N7.7

Modeling and Simulation of the Percolation Problem in High-T_c Superconductors: Role of Crystallographic Constraints on Grain Boundary Connectivity.

Megan Frary and Christopher A Schuh; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Superconductivity in high-T_c materials is often modeled as a percolation problem in which grain boundaries are classified as strong or weak-links based on their disorientation angle. Using Monte Carlo simulations, we have determined the topology and percolation thresholds for grain boundary networks in orthorhombic and tetragonal polycrystals where the grain boundary disorientations are assigned in a crystallographically consistent manner. We find that the networks are highly nonrandom, and that the percolation thresholds differ from those found with standard percolation theory, both in two and three dimensional microstructures. For biaxially textured substrates, we have also developed an analytical model that illustrates the role of local crystallographic constraint on the observed nonrandom behavior.