

SYMPOSIUM U

Mechanical Properties Derived from Nanostructuring Materials

April 22 – 25, 2003

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SESSION U1: BULK AND STRUCTURAL
NANOMATERIALS

Chair: David F. Bahr
Tuesday Morning, April 22, 2003
Metropolitan I (Argent)

8:30 AM *U1.1

RECENT RESULTS ON THE DUCTILITY OF NANOCRYSTALLINE METALS. Carl Koch, North Carolina State University, Dept of Materials Science and Engineering, Raleigh, NC.

While the hardness and strength of nanocrystalline metals is found to be significantly increased over those of their conventional (micron or larger) grain size counterparts, ductility values have been typically low. For many pure metals prepared by "two-step" processes which require the consolidation of powders or particulates, the artifacts associated with processing can mask the inherent ductility behavior. More recently, there are now several examples of samples prepared by "one-step" processes such as electrodeposition or severe plastic deformation in which consolidation is not necessary and therefore the possible artifacts associated with it such as porosity or incomplete particle bonding are eliminated. In some materials made by "one-step" processing, significant ductility has been observed. This talk will review the evidence for ductility results for nanostructured metals and alloys and suggest reasons for the large variability observed for this property. Examples from the authors laboratory and from the literature will be presented.

9:00 AM U1.2

SUPERPLASTIC BEHAVIOUR IN NANOCRYSTALLINE ELECTRODEPOSITED Ni AT 600K? F. Dalla Torre and H. Van Swygenhoven, Paul Scherrer Institut, Villigen-PSI, SWITZERLAND; M. Victoria, Fusion Technology-CRPP-EPFL, Villigen-PSI, SWITZERLAND.

Tensile properties of nanocrystalline electrodeposited Ni with a mean grain size of 20nm are measured at different temperatures ranging from room temperature up to 600K. The mechanical properties are accompanied by careful structural analysis by means of XRD and TEM. At room temperature a limited amount of plasticity is obtained. Measurements of activation volume and strain rate sensitivity indicate that, compared to values obtained for coarse grained Ni, dislocation activity is very limited but grain boundary accommodation mechanism are not fully operative neither. At 600K however, the material behaves superplastically. It will be shown that this can be attributed to the presence of a second Ni-S phase in the grain boundaries that is forming in-situ during annealing and deformation. The second phase has a low melting temperature and therefore plays a lubricating role for the intergranular processes at play (Acta Mater. 2002).

9:15 AM U1.3

STRUCTURAL EVOLUTION OF NANOLAMINATES DURING SEVERE PLASTIC DEFORMATION: MOLECULAR SIMULATIONS IN THE Cu-Zr SYSTEM. Alan C. Lund and Christopher A. Schuh, Department of Materials Science and Engineering, Massachusetts Institute of Technology.

Plastic deformation is commonly used to prepare unique nano-scale structures with exemplary mechanical properties, for example by ball milling, equal-channel angular extrusion, or high-pressure torsion. One such method, employing repeated folding and rolling of elemental foils, can produce laminate structures with layer thicknesses on the nano-scale. Further plastic straining of such nanolaminates has also been shown to produce amorphous alloys, although there is little understanding of the atomic-scale mechanisms behind this amorphization. In the present work, we explore the final stages of such a mechanical alloying process via molecular simulations. Initial Cu-Zr nanolaminates are sequentially strained and consolidated, and the amorphization process is followed through the evolution of the atomic radial distribution functions. The results are in qualitative agreement with existing experimental data, and provide insight into experimentally inaccessible features of the structural evolution.

9:30 AM U1.4

NANOINDENTATION TESTS ON HIGHLY ORIENTED PYROLYTIC GRAPHITE (HOPG). Wei-Hua Xu and Tong-Yi Zhang, Hong Kong University of Science and Technology, Department of Mechanical Engineering, Clear Water Bay, Kowloon, HONG KONG.

Nanoindentation Tests were conducted on Highly Oriented Pyrolytic Graphite and the morphology of the impression was examined by scanning electron microscopy. The nanoindentation loading-unloading curves reveal single pop-in and multiple pop-in phenomena, which is induced by fracture of the graphite layers and/or by delamination between the layers. From the load at pop-in, we can estimate the fracture strength of the layers and/or the bonding strength between

the layers. Lateral force microscopy pictures show that the nanoindentation tests result in steps at the atomic flat surface and the step density near the impression caused by large indentation loads is obviously higher than the density with small loads. It was observed that the nanoindentation tests cause the formation of carbon tubes, which are rolled up by the delaminated graphite layers.

10:15 AM U1.5

NANOMECHANICS OF CERAMIC-BASED MATERIALS ISSUES OF SCALE. Brian R. Lawn, Antonia Pajares, Herzl Chai, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

The role of characteristic dimension in the mechanical response of ceramic-based materials is addressed, in special relation to small-scale contact events. Specific issues considered include: contact dimension, flaw size and microstructural scale (monolithic materials); and coating thickness (layer structures). Fundamental brittle-quasiplastic transitions in behavior as these characteristic dimensions diminish through the microscale toward the nanoscale will be examined. Implications of these transitions in relation to strength, toughness, brittleness, fatigue and wear will be discussed.

10:30 AM U1.6

CREED BEHAVIOUR OF A CRYSTALLIZED Si-B-C-N CERAMIC OBTAINED FROM THE POLYMER PRECURSOR T2-1 ($\{B[C_2H_4Si(CH_3)NH]_3\}_n$). Ravi Kumar N.V., Andre Zimmermann, Fritz Aldinger, Max-Planck-Institut für Metallforschung and Institute für Nichtmetallische Anorganische Materialien, Universität Stuttgart, Pulvermetallurgisches Laboratorium, Stuttgart, GERMANY.

Boron modified silicon carbonitrides, hereafter referred to as Si-B-C-N ceramics, are a new class of high temperature materials which offer very interesting properties at elevated temperatures. In applications such as gas turbine industries and in nuclear power applications such as reactors, where a combination of high temperature and low stresses can cause the material to irreversibly deform as a function of time, materials having good creep resistance are required. With respect to this, Si-B-C-N ceramics offer a great potential.

Amorphous Si-B-C-N ceramics obtained from the solid state thermolysis of organic precursors have been investigated earlier. They exhibited very good creep resistance, oxidation resistance and thermal stability at elevated temperatures compared to conventionally sintered materials due to the lack of low melting point oxidic grain boundary phases. Since amorphous materials are metastable, devitrification takes place at high temperatures and nano-crystallites of SiC and Si₃N₄ are formed in situ in the amorphous material beyond 1700°C. It seemed therefore interesting to investigate whether the creep rate would be further reduced by devitrification of the amorphous state.

The polymer precursor boron modified poly(vinyl)silzanes denoted as T2-1 with the chemical composition ($\{B[C_2H_4Si(CH_3)NH]_3\}_n$) was milled and sieved. The polymer particles from different size fractions were compacted using a graphite die in a uni-axial warm pressing machine at a pressure of 48 MPa and in the temperature range 250°C to 330°C. The green bodies were pyrolysed in an argon atmosphere at a temperature of 1300°C where the organic polymer converts into an inorganic amorphous ceramics. These amorphous ceramics were annealed under various conditions of temperature, nitrogen overpressure and holding times and nano-crystalline Si-B-C-N ceramics were produced.

Compression creep experiments were carried out in atmospheric ambience on nano-crystalline Si-B-C-N ceramics at loads varying from 5-100 MPa and in the temperature range 1350°C -1500°C to investigate the high temperature deformation behavior of the material. The interest is to understand the mechanisms of deformation in these nano-crystalline Si-B-C-N ceramics at elevated temperatures and to compare the results with that of amorphous ceramics. The investigation also includes the determination of viscosity of the material at high temperatures and also comments on the anelastic behavior.

10:45 AM U1.7

FRACTURE TOUGHNESS OF NANOCRYSTALLINE L1₂ (Al₃+Xat.% Mn)₃Ti PREPARED BY MECHANICAL ALLOYING AND CONSOLIDATED BY SPS. Hee Sup Jang, Hwan Gyun Moon, Sung Hoon Lee, Seon Jin Kim, Division of Materials Science and Engineering, Hanyang University, Seoul, SOUTH KOREA.

The modification of the chemical composition of trialuminides by alloying with substitutional elements such as Cr, Mn, Fe, Co, Ni, Cu and Zn may result in higher ductility and fracture toughness. Mechanical alloying was conducted with (Al+Xat.%Mn)₃Ti (X=0~12) powders and the L1₂ structure was formed only in the Mn concentration of 8~12at.%. The SPS (spark plasma sintering) process was used to sinter nanocrystalline L1₂ (Al+Xat.%Mn)₃Ti. When it was achieved to 99% of relative density, sintering was stopped. In binary Al₃Ti, the final sintering temperature was 864°C, which was

further reduced to 658°C by the addition of 12at.%Mn. The micro-hardness test, grain size measurements, and fracture toughness test were conducted as a function of Mn content. With increasing temperature, micro-hardness decreased by heterogeneous segregations of Al₄C₃, Al₂O₃, and TiC, while fracture toughness increased. The Vickers indentation fracture toughness of compacts was also investigated. Fracture toughness decreased as Mn content increased. The lowest fracture toughness (1.15MPa m^{1/2} under 1kg load) was measured at 12at.%Mn. According to the results obtained from the microstructure, fracture toughness and grain size studies of (Al+Xat.%Mn)₃Ti intermetallic compounds, it may be considered as adequate for high temperature structural applications.

11:00 AM U1.8

EXFOLIATED GRAPHITE NANOPATELETS AS REINFORCEMENTS FOR POLYMERS. Lawrence T. Drzal and Hiroyuki Fukushima, Department of Chemical Engineering and Materials Science and Composite Materials and Structures Center, Michigan State University, East Lansing, MI.

Nanocomposites composed of polymers reinforced with reinforcements of less than 100 nm in size, are being considered for applications such as interior and exterior accessories for automobiles, structural components for portable electronic devices, and films for food packaging. While most nanocomposite research has focused on exfoliated clay platelets, the same nanoreinforcement concept can be applied to another layered material, graphite, to produce nanoplatelets and nanocomposites. Graphite is the stiffest material found in nature (Youngs Modulus = 1060 MPa), having a modulus several times that of clay, but also having excellent electrical and thermal conductivity. With the appropriate surface treatment, exfoliation and dispersion in a polymer matrix results in a composite with excellent mechanical properties as well as electrical properties, opening up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements as well. In this paper, the mechanical properties of an exfoliated graphite reinforced epoxy composite will be presented, including modulus, strength, coefficient of thermal expansion, as well as electrical and thermal properties. The results will be compared and contrasted with the same epoxy matrix reinforced with nanoclay, vapor grown carbon fibers and particulate graphite. The results show that nanocomposite materials made with these nanographite platelets have three times the modulus of nanoclay platelet reinforced composites. With the proper surface treatment of the nanographite, little reduction in composite tensile strength was detected compared to the neat matrix. Impedance measurements have shown that these platelets percolate at below 3 volume percent and exhibit a ~10 order of magnitude reduction in impedance at these concentrations.

11:15 AM U1.9

SHEAR-INDUCED MESOSTRUCTURE IN POLYMER-NANOCCLAY NETWORKS. Sheng Lin-Gibson, Charles C. Han, Erik K. Hobbie, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD; Gudrun Schmidt, Louisiana State University, Department of Chemistry, Baton Rouge, LA; Hong Doo Kim, Kyunghee University, Department of Chemistry, Yongin, Kyungkido, KOREA.

The mesoscale shear response of a model polymer-nanoclay gel is measured using small-angle neutron scattering, shear light scattering, optical microscopy, and rheometry. When combined in solution with the adsorbing polymer, poly(ethylene oxide), reversible short-range-attractive polymer-clay interactions create a dynamic network with ideal clay dispersion that is homogeneous on a macroscopic scale but heterogeneous on the nanometer scale. As the shear distorts the nanoscale structure and ruptures the network, coupling between composition and stress leads to macroscopic phase separation, reminiscent of other shear-induced structural transitions. On much smaller length scales, the platelets exhibit a shear-induced nematic phase with their surface normal parallel to the direction of vorticity. We examine similarities with flow-induced transitions in other complex fluids, and we suggest that the clay might orient in response to a biaxial stress arising from viscous and elastic forces within clay-rich macrodomains, where these domains represent intact remnant "droplets" of the equilibrium gel.

11:30 AM U1.10

DEFORMATION AND FRACTURE IN COLD-ROLLED NANOSCALE MULTILAYERS. A. Misra, R.G. Hoagland, D.L. Hammon, X. Zhang, J.D. Embury, and J.P. Hirth, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM; H. Kung, Division of Materials Sciences & Engineering, U.S. Department of Energy, Germantown, MD.

Nanolayered metallic composites, synthesized by physical vapor deposition, exhibit extremely high hardness when the bilayer periods are on the order of a few to a few tens of nanometers. However, limited

work has been done so far to characterize the deformation behavior of these vapor deposited nanolayered composites when subject to large plastic strains. In this presentation, we report on recent work on deformation behavior during cold rolling of sputter deposited Cu-Nb multilayered foils. The development of dislocation substructures, work hardening and eventual fracture of these nanoscale composites is studied as the bilayer thickness varies from micrometers to nanometers. The presentation will highlight how the nanostructured length scales lead to new regimes of plasticity in metals not observed in micro-scale materials. The nanoscale multilayers exhibit extraordinary stability upon room temperature rolling undergoing uniform reduction in layer thickness to high levels of plastic strain. Large reduction in thickness is accomplished without the formation of the classical dislocation cell structures. Furthermore, no out-of-plane lattice rotations are observed. These results suggest that the deformation occurs via a coordinated slip mechanism, in which the interface plays a critical role in the homogeneous distribution of slip. The mechanisms of work hardening, in the absence of the dislocation cell structures, are discussed. Limited deformability is observed at bilayer thicknesses of a few nanometers or less. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

11:45 AM U1.11

INVESTIGATION OF THE SURFACE STRESS IN SiC AND DIAMOND NANOCRYSTALS BY IN-SITU HIGH PRESSURE POWDER DIFFRACTION TECHNIQUE. B. Palosz, S. Stelmakh, E. Grzanka, S. Gierlotka, High Pressure Center UNIPRESS, Warsaw, POLAND; Y. Zhao, Los Alamos National Laboratory, Los Alamos, NM; W. Palosz, USRA/NASA-MSFC, Huntsville, AL.

The real atomic structure of nanocrystals determines key properties of the materials. For such materials the serious experimental problem lies in obtaining sufficiently accurate measurements of the structural parameters of the crystals, since very small crystals constitute rather a two-phase than a uniform crystallographic phase system. As a result, elastic properties of nanograins may be expected to reflect a dual nature of their structure, with a corresponding set of different elastic property parameters. We studied those properties by in-situ high-pressure powder diffraction technique. For nanocrystalline, even one-phase materials such measurements are particularly difficult to make since determination of the lattice parameters of very small crystals presents a challenge due to inherent limitations of standard elaboration of powder diffractograms. In this investigation we used our methodology of the structural analysis, the "apparent lattice parameter" (alp) concept. The methodology allowed us to avoid the traps (if applied to nanocrystals) of standard powder diffraction evaluation techniques. The experiments were performed for nanocrystalline SiC and GaN powders using synchrotron sources. We applied both hydrostatic and isostatic pressures in the range of up to 40 GPa. Elastic properties of the samples were examined based on the measurements of a change of the lattice parameters with pressure. The results show a dual nature of the mechanical properties (compressibilities) of the materials, indicating a complex, core-shell structure of the grains.

SESSION U2: THIN FILMS AND MULTILAYERS

Chairs: Carl C. Koch and Amit Misra
Tuesday Afternoon, April 22, 2003
Metropolitan I (Argent)

1:30 PM *U2.1

MECHANICAL BEHAVIOR OF FILMS, NANOSPHERES AND NANOBUMPS. William W. Gerberich, John J. Jungk and William M. Mook, University of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN.

Recent work on Si nanospheres and various thin films has strongly suggested that work hardening of very small volumes allows one to achieve theoretical strengths. Deformation and strength properties of nanostructured films, nanospheres and nanobumps as processed by sputtering, plasma and e-beam lithography will be presented. For FCC, BCC and HCP nanocrystalline structures of Au, Ta and Ti, it will be shown that the length scale appropriate to strengthening is controlled by both microstructure and constraint. Free surface conditions, as modified by atomic layer deposition (ALD) are examined as well. The goal is to understand how image force and evolved dislocation arrangements contribute to the strengthening of processed features in the 20 to 200 nm scale regime. With 2 to 20 nm overlayers of ALD-processed amorphous Alumina, differences in flow strengths on the basis of surface constraint will be examined.

2:00 PM U2.2

SYNTHESIS AND MECHANICAL PROPERTIES OF TiN/AlN THIN FILM HETEROSTRUCTURES. Cindy Waters, Dhananjay Kumar, Sergey Yarmolenko, Zhigang Xu, Jag Sankar, NSF Center For Advanced Materials and Smart Structures North Carolina A&T State University, Greensboro, NC.

There is a growing research interest in TiN and AlN due to their promising mechanical, electronic and optoelectronic properties. Our studies have shown that mechanical properties can be improved significantly by forming thin film heterostructures of the two materials. We report on our pulsed laser deposition assisted synthesis, microstructural characterizations and mechanical properties of TiN/AlN multi-layer structures. The TiN/AlN superlattice structures are fabricated on (100) silicon substrates at different temperatures (400-800°C) and different nitrogen ambient pressures. The nano-mechanical hardness properties of the multi-layered structures were examined as a function of thickness of individual layers keeping the overall thickness of heterostructures constant. Thickness variations of the films are measured with a optical phase-shift interferometer. The improvement in the mechanical properties of TiN/AlN heterostructures has been found to be associated with interfacial interaction between layers. The interfacial interaction, in turn, depends on processing parameters the most important among which is substrate temperature.

2:15 PM U2.3

YIELD OF $\text{In}_x\text{Ga}_{1-x}\text{As}$ SUPERLATTICES UNDER NANOINDENTATION AND BENDING. Stephen Lloyd and Bill Clegg, Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UNITED KINGDOM; Ken P'ng, Andy Bushby, David Dunstan, Centre for Materials Research, Queen Mary, University of London, London, UNITED KINGDOM.

The coherency strain in $\text{In}_x\text{Ga}_{1-x}\text{As}$ superlattices can be continuously varied through control of the In content. Since these structures can be grown with a low defect density, and the elastic and plastic properties of the component layers vary little with In content, they are a model system to investigate the effects of coherency strain on yielding. Previous work has shown that these superlattices display a remarkable resistance to strain relaxation at temperatures up to nine-tenths of their melting point. Under nanoindentation at room temperature the hardness of the superlattices decreases with increasing strain modulation in the layers, while under 3-point bending at 500°C there is a small increase in the yield stress with increasing strain modulation. Here we investigate the contrasting yield behaviour at different temperatures by examining the deformation in each case in the transmission electron microscope. Use of a focused ion beam microscope allows electron transparent sections to be made through specific sites, such as a nanoindentations. In addition, large areas of uniform thickness can be machined which is useful to examine the deformation of the bent specimens. Initial investigations have shown that twinning accommodates the majority of the plastic strain under room temperature indentation, using a spherical indenter. In this paper we discuss how the yield point, size of plastic zone and twin density and size varies with the strain modulation in order to understand the observed changes in hardness in these conditions where the dislocation mobility is low. Under bending at high temperature dislocations are much more mobile, hence dislocation sources can be activated leading to the creation of slip steps on the surface, and local "sawing" of the superlattice. We also discuss the way in which coherency strain can be relieved through the activation of these dislocation sources in superlattices with a high strain modulation.

2:30 PM U2.4

THICKNESS EFFECTS ON MECHANICAL BEHAVIOR OF ALD FILMS. N.R. Moody, Sandia National Laboratories, Livermore, CA; T.E. Buchheit, B.L. Boyce, and T.M. Mayer, Sandia National Laboratories, Albuquerque, NM; S.M. George, University of Colorado, Boulder, CO.

Strength, friction, and wear are dominant factors in the performance and reliability of materials and devices fabricated using microsystem technologies. While adequate for some applications, as-fabricated strength and wear properties severely restrict use of these devices in many dynamic applications. Applying coatings and films is one method to enhance their performance and reliability. This study characterizes films using Atomic Layer Deposition (ALD) as it is ideally suited for applying highly conformal, thin nm-scale films with monolayer precision, necessary for coating microsystems devices. Results focus on the mechanical performance of tungsten and aluminum oxide ALD films. The films were deposited to thicknesses ranging from 1 to 200 nm to highlight the evolution of film and substrate contributions. Nanoindentation was then used to measure elastic and plastic properties. These tests showed that the measured modulus of both film systems increased with film thickness. In contrast, hardness of the tungsten films increased significantly with film thickness while hardness of the aluminum oxide decreased just as dramatically. These results will be discussed in terms of composition and structure of the ALD films and their impact on potential applications. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

2:45 PM U2.5

MATERIALS AND GEOMETRY OPTIMIZATION FOR THE DEVELOPMENT OF ULTRA-HIGH SENSITIVE NANO-MECHANICAL RESONATORS. Kyung-ah Son, Robert W. Fathauer, Thomas George, Jet Propulsion Laboratory, MEMS Technology Group, Pasadena, CA; Brian H. Houston, Naval Research Laboratory, Washington, DC.

Due to their ultra-small volumes, high sensitivity, and high operating frequencies, nano-mechanical resonators have numerous applications including mass sensing, chemical or biological molecule detection, RF communication and in precision time standards. Among fundamental unresolved scientific issues are the factors that control the intrinsic quality factor (Q) of these resonators, which determines the sensitivity of the ultimate devices. Several factors have been reported to influence the Q of resonators including the thermoelastic properties of the resonator material, surface properties, point/line defect movement etc. However, the dominant loss mechanisms influencing the Q are very poorly understood and subject to considerable debate in the literature. Design at the nanometer scale poses new challenges because some of the continuum assumptions used in conventional models break down and the role of surfaces becomes increasingly important. To this end, we are pursuing a two-pronged effort, with modeling and experimental work going hand-in-hand to develop high Q nano-mechanical resonator. We have optimized the geometry of a particular type of resonator known as the "double-paddle oscillator" and are currently studying the behavior of micrometer-scale structures. Performance comparisons will be made to micrometer and nanometer-scale resonators with other geometries. Novel materials choices as well as fabrication methods are also key factors for high Q. We have fabricated nano-mechanical resonators using single crystalline materials with very different mechanical and chemical properties, namely Si, AlN and GaN. Electron-beam lithography and micromachining techniques are used to fabricate the resonators. Evaluation of resonator designs has been carried out by measuring the frequencies and quality factors of the various resonance modes using a laser Doppler vibrometer and a network analyzer. Additional detailed optical, AFM and SEM characterization of the fabricated structures has been carried out, in order to elucidate some of the fundamental energy dissipation mechanisms within these nano-mechanical resonator structures.

3:30 PM *U2.6

INVESTIGATIONS OF THE MECHANICAL PROPERTIES OF NANOSTRUCTURED MATERIALS FOR INTEGRATED NANOTECHNOLOGIES. J.C. Barbour, Sandia National Laboratories, Albuquerque, NM; A. Misra, Los Alamos National Laboratory, Los Alamos, NM; D.M. Follstaedt, J.A. Knapp, T.A. Friedmann, J.P. Sullivan, Sandia National Laboratories, Albuquerque, NM; and H. Kung[†], Los Alamos National Laboratory, Los Alamos, NM. [†]present address Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, Germantown, MD.

Future technologies will rely on a complex integration of materials and functionality that bridges several length scales to connect nanometer-scale architectures to the real world of man. Part of this vision will be the ability to produce mechanical work at the nanoscale and the transduction of energy and information from nano- to microscale systems. Since many architectures of the future will be constructed from nanostructured materials, it is essential to understand the mechanisms and limits of mechanical deformation and stability, as well as the unique properties of materials at the nanoscale. At this size, internal interfaces comprise a significant portion of the material's volume and may have a dominant influence on the material's mechanical properties. This talk will review the development of new materials to achieve novel mechanical properties based upon tailored nanostructures and discuss the current understanding of the mechanisms that govern their mechanical response. Through collaborations within the Center for Integrated Nanotechnologies, our institutions have developed the ability to tailor nanostructures for testing the limits of classical strengthening and toughening mechanisms, such as the nano-dispersion or grain-size strengthening of metals and strength modification in metal multi-layered composites. We have found grain-size strengthening in homogeneous Ni follows the classical behavior down to ~15 nm in size, while the strength drops in layered metals below layer thicknesses of ~5 nm for miscible (e.g., Cu-Ni) and below ~1 nm for immiscible systems (e.g., Cu-Nb). Also, we have investigated the effect of variations in density and bonding on the mechanical properties of amorphous systems, such as alumina and tetrahedrally-bonded carbon, and of energy dissipation in small-scale structures. This work is partially supported by the DOE Office of Basic Energy Sciences. Sandia and Los Alamos are multiprogram DOE laboratories operated by Sandia Corporation under contract DE-AC04-94AL85000 and the University of California, respectively.

4:00 PM U2.7

MISFIT DISLOCATIONS IN Ni-Cu NANO-LAYER COMPOSITES. David Mitlin, Amit Misra, Mike Nastasi, and Terence E. Mitchell.

Understanding bilayer behavior is a critical step in the successful development of ultra-high hardness nano-layer composites. We have analyzed misfit dislocations at the interface of Ni/Cu bilayers using plan-view and cross-sectional transmission electron microscopy (TEM). The bilayers consisted of varying thickness of Ni (25-200 angstroms) deposited on 1500 angstroms of Cu. Conventional g/b analysis was used to determine the types of dislocations present at the interface, while high-resolution TEM performed on cross-sectional samples was used to analyze the interface in more detail. It is demonstrated that there is minimum Ni thickness below which interface dislocations do not nucleate. As the Ni layer thickness is increased, the dislocations spacing decreases. Agreements and discrepancies of the experimental results with the existing interface dislocation theory are discussed.

4:15 PM U2.8

THICKNESS AND TEMPERATURE EFFECTS ON CREEP BEHAVIOR OF METAL THIN FILMS. Seungmin Hyun, Walter L. Brown and Richard P. Vinci, Lehigh Univ, Dept of Materials Science and Engineering, Bethlehem, PA.

Thin metal films such as Al and Au often play an important role as structural elements or reflective surfaces in MEMS applications. Residual stresses present in metal layers and changes in those stresses with time cause undesired curvature and curvature changes in films on substrates. The long-term stress stability of the thin metal films is thus a major concern. In order to gain a better understanding of creep mechanisms we have studied the creep (stress relaxation) of metal thin films as a function of thickness and temperature. Thin films with thicknesses between 50 and 200 nm were prepared by DC magnetron sputtering and by evaporation onto a silicon nitride membrane spanning a 2mm x 12 mm rectangular window etched through a Si wafer. Creep behavior (stress relaxation) was investigated using the frequency of normal resonance modes of the composite membrane to determine the stress. This method has very high sensitivity to stress changes in even very thin metal films. Thermal cycling to temperatures up to 300°C was used to establish a stress, and the time dependence of the stress was examined at temperatures between 20 and 100°C. In some cases the time dependence follows a logarithmic expression based on dislocation motion. Results will be presented for Al, Cu, and Au.

4:30 PM U2.9

FULLY REVERSIBLE DISLOCATION-BASED DEFORMATION IN A NANOLAYERED CARBIDE: Ti₃SiC₂. Michel W. Barsoum, Tiejun Zhen, Surya R. Kalidindi, Anand Murugaiah, Drexel Univ, Dept of Materials Engineering, Philadelphia, PA; Miladin Radovic, Oak Ridge National Laboratory, Oak Ridge, TN.

Without exception, all known crystalline solids exhibit a fairly linear elastic stress-strain response at low stresses. In the elastic regime, the response is reversible and non-dissipative. Once the elastic regime is exceeded, the response is plastic and non-reversible (i.e. the hysteretic loops formed on cycling are open). In fact, the only known materials that exhibit fairly large regimes of nonlinear elastic response with significant levels of energy dissipation in fully reversible hysteresis loops are rubbers (which are lightly cross-linked and non-crystalline). In this work, we show that macroscopic polycrystalline Ti₃SiC₂ cylinders can be compressed, at room temperature, to stresses of up to 1 GPa, and fully recover upon the removal of the load. The stress-strain curves are non-linear, outline fully reversible, reproducible closed loops whose size and shape depend on grain size, but not strain rate. We believe, the energy dissipated when cycling to 1 GPa, viz. 0.7 MJ/m³, is a record for crystalline solids. At temperatures higher than 1000°C, the stress-strain loops are open and the response becomes strain rate dependent. Cyclic hardening is observed at 1200°C, for both fine and coarse-grained samples. This hitherto unreported phenomenon is attributed to the fully reversible formation and annihilation of incipient kink bands at room temperature deformation. At higher temperatures, the incipient kink bands dissociate and coalesce to form regular kink bands that are no longer reversible. The technological implications of having a lightweight, inexpensive, elastically stiff solid, (with a specific stiffness almost 3 times that of Ti) that can be machined with a manual hack saw, with compressive strengths of 1 GPa, that can also damp a significant portion (25% at 1 GPa) of the mechanical energy will be discerned.

4:45 PM U2.10

MICRO-SCALE MEASUREMENTS OF THE MECHANICAL PROPERTIES OF ULTRANANOCRYSTALLINE -DIAMOND THIN FILMS. B. Peng, B.C. Prorok, K.-H. Kim, H.D. Espinosa, Department of Mechanical Engineering, Northwestern University

Evanston, IL; O. Auciello, J.A. Carlisle, D.M. Gruen, and D.C. Mancini, Materials Science and Experimental Facilities Divisions, Argonne National Laboratory, Argonne, IL.

Carbon in its various forms, specifically diamond, may become the material of choice for the fabrication of MEMS/NEMS devices. Ultrananocrystalline diamond (UNCD) films developed at Argonne National Laboratory have unique mechanical, tribological, and biocompatible properties, and may provide the basis for novel and revolutionary devices. However, before full-scale integration can occur, several intrinsic material properties, such as elastic modulus, fracture strength and toughness must be well characterized and correlated to the material microstructure. In this presentation, we will discuss measurements of the elastic modulus and fracture strength of UNCD thin films by two micro-scale techniques; namely micro-cantilever deflection and the membrane deflection experiment developed by the Northwestern University group. We have taken special care to design sample characteristics suitable to each technique in an attempt to minimize spurious effects that could hinder accurate property measurements. Cantilever deflection tests on several freestanding UNCD cantilevers, 0.5 μm thick, 20 μm wide and 80 μm long, yielded elastic modulus values of 940 ± 20 GPa. The tests showed good reproducibility by repeated testing on the same cantilever and by testing several cantilevers of different lengths. The largest source of error in the method is believed to be accurate measurement of film thickness. The membrane deflection experiment was found to yield similar values. This testing scheme differs from the micro-cantilever bending technique by subjecting the specimen to pure tension. The test also provided strength properties, which will be discussed in terms of statistical theory. The mechanical properties of UNCD measured at the scale relevant to microelectromechanical systems (MEMS) will be discussed in view of application to the development of a new MEMS technology based on UNCD. Work at Argonne supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract #W-31-109-ENG-38.

SESSION U3: POSTER SESSION

Chairs: David F. Bahr and Neville R. Moody
Tuesday Evening, April 22, 2003
8:00 PM
Golden Gate (Marriott)

U3.1

Transferred to U1.4

U3.2

MECHANICAL PROPERTIES OF YSZ/Al₂O₃ NANOCOMPOSITE THIN FILMS. Jennifer M. Kirchoff and Renato P. Camata, University of Alabama at Birmingham, Dept of Physics, Birmingham, AL.

Yttria-stabilized zirconia (YSZ) is an important material in many emerging technologies such as solid oxide fuel cells, thermal barrier coatings, and multi-layer superconductor structures. While these applications rely primarily on the electrochemical, thermal, and electronic properties of YSZ, the reliability of actual devices is often limited by the inability of YSZ to withstand high mechanical stresses. Bulk YSZ presents indentation hardness above 10 GPa and Young's modulus ~220 GPa. As most ceramics, it displays low fracture toughness and bending strength. Recent studies have shown that YSZ containing 5-10 vol.% Al₂O₃ microparticles exhibit increased fracture toughness and bending strength with manageable adverse effects in thermal and ionic conductivity. The engineering of YSZ/Al₂O₃ composites at the nanoscale, however, remains largely unexplored. In this study we have used pulsed laser deposition (PLD) to create micron-thick YSZ films containing well-dispersed, uniformly-sized Al₂O₃ nanoparticles with controlled concentration. This was accomplished by alternately ablating cubic 8-mol.% YSZ and amorphous Al₂O₃ targets with the focused beam of a KrF excimer laser (248 nm) and synchronous control over background atmosphere and pressure. Laser fluence on targets was varied in the 3-10 J/cm² range and films were deposited on silicon and Ti-6Al-4V substrates in the 500°C-800°C range. By varying the background pressure, we have been able to control the nanoparticle average size in the 5-40 nm range. By changing the number of pulses during each cycle, films were deposited with different nanoparticle concentrations ranging from ~10¹⁰ to ~10¹² cm⁻² per nanoparticle layer. X-ray diffraction measurements on the films exhibit all reflections of cubic YSZ. Nanoindentation measurements yield values of hardness between 0.5 and 1.0 GPa and elastic modulus between 10 and 29 GPa. These values are significantly lower than those obtained for bulk cubic YSZ. A correlation between these measurements and Al₂O₃ nanoparticle size and concentration in the nanocomposite will be presented. (Funding: NSF-DMR-9987872 (REU-Site), DMR-0116098).

U3.3

ELECTRICAL FIELD MORPHOLOGY CONTROL IN THERMOSET NANOCOMPOSITES: MODEL SYSTEMS FOR STRUCTURE-PROPERTY RELATIONSHIPS. Hilmar Koerner, University of Dayton Research Institute, Dayton, OH; John D. Jacobs, David W. Tomlin, Nathan A. Pearce, Richard Vaia, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Low volume additions (1-5%) of highly anisotropic nanoparticles, such as layered silicates or carbon nanotubes, provide property enhancements with respect to the neat resin that are comparable to that achieved by conventional loadings (15-40%) of traditional fillers. The lower loadings facilitate processing and reduce component weight. Critical to all of these endeavors is establishment of scientifically sound structure-property relationships, not just demonstration of analytical descriptions to experimental data. Developing systems with the simultaneous morphological characterization and control at the nano, micro and millimeter scale necessary for detailed investigation of mechanical response is a challenge. Here in, we use electric fields of modest strength to align nanoparticles in an uncured epoxy matrix and then lock in the orientation by amine crosslinking. The dial-in of nanoparticle orientation opens up new possibilities for investigating mechanical and transport properties at interfaces. We will discuss results on the dynamics of the poling process derived from in-situ X-ray experiments. Additional experiments, including TMA and DMA allow us to evaluate the influence of the reorientation of particle and particle/matrix interface on macroscopic properties, including thermal coefficient of expansion, tensile strength and dynamic mechanical response.

U3.4

EVIDENCE FOR NEW MODULUS/DENSITY SCALING RELATIONSHIPS AND FRAMEWORK ARCHITECTURES IN POROUS, SELF-ASSEMBLED NANOSTRUCTURES. Hongyou Fan, Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM; Christopher Hartshorn, Dept of Chemistry, Univ of New Mexico; Thomas Buchheit, David Tallant, Sandia National Laboratories, Albuquerque, NM; Salvatore Torquato, Princeton Univ, Dept of Chemistry and Princeton Materials Inst, Princeton, NJ; C. Jeffrey Brinker, Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM, The Univ of New Mexico/NSF Center for Micro-Engineered Materials and Dept of Chemical and Nuclear Engineering, Albuquerque, NM.

A continuing challenge in the integration of nanostructures into microsystems is their mechanical behavior. However, although much effort has been put on synthesis of nanostructured materials, little attention has focused on the mechanical performance of synthetic nanostructures. In addition, an important issue in mechanical properties that emerges at nanoscopic scales is whether such self-assembled nanostructures can be evaluated by mechanical continuum model or not. In this presentation, we developed a unique synthetic route to produce highly periodic nanostructure with controlled porosity and structures starting with one same recipe. Our results show that these self-assembled nanostructures exhibit structure-specific scaling relationships of modulus and density. For ordered nanostructures (hexagonal and cubic), the relative modulus can exceed the upper bound predicted by continuum mechanics. Detailed results from nanoindentation, Si-NMR, and Raman spectra will be presented to understand the structure-mechanical property relationships and deviations from continuum behavior at molecular level. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000.

U3.5

GRAIN SIZE EFFECTS ON NANOINDENTATION LOADING BEHAVIOR OF Pt THIN FILMS. Seungmin Hyun and Richard P. Vinci, Lehigh Univ, Bethlehem, PA.

Dislocation behaviors exhibited during depth-sensing indentation of thin films are often very different from those associated with traditional large-scale materials because the deformation field size is often in the range of the microstructural feature size. Although size dependent deformation behavior has been heavily investigated, the deformation behaviors particular to thin films are still not fully understood. Recently, it has been shown that microstructure plays a key role in determining the magnitude of the pop-in events in Au thin films. A small-grained film and a large-grained film, defined relative to the indenter tip size, displayed very different loading curves. This effect was attributed largely to easy dislocation nucleation when the indenter tip was near a grain boundary. In the current study, microstructure dependent deformation behavior of Pt films was systematically explored to add to the growing understanding of pop-in behavior of polycrystalline materials. A detailed examination of grain size effects on loading behavior was investigated by preparing three films with different average grain sizes. The deformation behavior was

studied in terms of both grain size and proximity of the indenter tip to a grain boundary. Pop-in behavior of Pt films is affected by the presence of a grain boundary in the indented area. Large discrete deformation behaviors (pop-in events) were observed when a single grain was indented whereas fewer pop-in events were observed if an indentation was performed near or on the grain boundary area.

U3.6

CONTINUUM ANALYSIS OF COOPERATIVE PIT/ISLAND FORMATION AND STABILITY IN Si/Ge ON Si(100). Nitin Singh, Dana Elzey, University of Virginia, Department of Materials Science and Engineering, Charlottesville, VA.

Recent experimental work (J. Gray, R. Hull and J. Floro, App. Phys Lett. Vol 81, No 13, 2002) has investigated the cooperative nucleation and growth of pits and islanding at pit edges in SiGe/Si(100) epitaxial films. The pits, which are observed to form under certain growth conditions, evolve along with the islands until a complete island wall is formed around the pit's periphery. Once formed the pit/island configuration, also called a "Quantum Fortress", exhibits a surprising stability, with no further lateral growth during continued deposition or annealing. The pits comprise of low energy {501} facets (inverted {501} pyramid) and the islands surrounding the pit also exhibit faceting. Elastic finite element analyses of these configurations were carried out to investigate the dependence of strain energy and surface stress on pit/island geometry. In particular, our results provide insight as to the mechanism responsible for the observed size stability of the pit/island structure once it has become fully developed. Surface stress gradients are also found to be responsible for the initial island formation at the center of pit edges rather than at the pit corners during growth.

U3.7

ATOMIC SCALE FRICTION OF AMORPHOUS HYDROGENATED CARBON THIN FILM IN MEMS. Myoung-Gyun Ko and Jong-Wan Park, Department of Nano-structure Semiconductor Engineering, Hanyang University, Seoul, KOREA.

Diamond and diamond related carbon thin film have extensively studied over the past several years due to their unique combination of properties. Especially, amorphous hydrogenated carbon (a-C:H), called diamond like carbon (DLC), film is a promising friction reducing coating material for Microelectromechanical system applications. The film is prepared by electron cyclotron resonance chemical vapor deposition (ECRCVD) employing CH₄ and H₂ gases. It is deposited by the control of CH₄ / H₂ gas flow ratio, deposition working pressure, and In-situ thermal treatment temperature. The atomic scale friction behavior, structure and properties of a-C:H film are dependent on the deposition condition, thermal treatment temperature and chemical bondings in films. Atomic scale friction behavior is analysed by lateral force microscopy (LFM) mode using micro-centilever. Hydrogen and carbon concentrations of a-C:H films were studied by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometer (RBS) and the structure of these films from FT-IR are also discussed. In order to a-C:H film properties are determined by the relative amounts of sp¹, sp² and sp³ bonding between the carbon atoms.

U3.8

SULFONATED POLYSTYRENE IONOMERS NEUTRALIZED WITH MIXTURES OF VARIOUS CATIONS STUDIED BY DYNAMIC MECHANICAL AND SMALL-ANGLE X-RAY SCATTERING TECHNIQUES. Ho Seung Jeon and Joon-Seop Kim, Chosun Univ, Dept of Polymer Science & Engineering, Gwangju, KOREA.

The effects of the addition of mixed cations, i.e. Na⁺/Cs⁺, Ba²⁺/Cs⁺, and Ba²⁺/Zn²⁺, to the acid form sulfonated styrene copolymers on their dynamic mechanical properties and morphology were investigated. It was found that the matrix glass transition temperatures did not change with the ratio of the one cation to the other. As expected, however, the ratio of one cation to the other in the mixed cations affected cluster glass transition temperatures significantly. It was also found that the activation energies for the glass transitions for the matrix phase remained constant, while those for the cluster phase changed with the ratio of the two cations. In addition, the position of the SAXS peak was found to be affected by the type of cations. From the results obtained above, the decrease in the cluster T_g with increasing the amount of cesium and zinc cations in Na/Cs, Ba/ Cs, and Ba/Zn mixtures, were explained on the basis of the considerations of the size, charge, and type of cations, which alter the degree of clustering as well as ion-hopping mechanism.

U3.9

MECHANICAL PROPERTIES OF P(S-co-ITANa)/P(S-Co-MANa), P(S-co-SSNa)/P(S-co-MANa), AND P(S-co-ITANa)/P(S-co-SSNa) IONOMER HOMOBLENDS. Sung-Hwa Oh and Joon-Seop Kim,

Three different sets of styrene-based ionomer homoblends containing ca. 5 mol% of ionic repeat units, i.e. poly(styrene-co-sodium itaconate) [P(S-co-ITANa)]/poly(styrene-co-sodium methacrylate) [P(S-co-MANa)] ionomer blends, sodium sulfonated polystyrene [P(S-co-SSNa)]/P(S-co-MANa) ionomer blends, and P(S-co-ITANa)/P(S-co-SSNa) ionomer blends, were prepared and their dynamic mechanical properties were investigated. It was observed that with increasing itaconate content in the blend of P(S-co-ITANa)/P(S-co-MANa) ionomers the multiplet of the P(S-co-MANa) ionomer disrupted initially very rapidly, and ionic modulus of the blend increased drastically. In the case of P(S-co-ITANa)/P(S-co-SSNa) ionomer blends, again, the ionic modulus increased significantly with increasing itaconate content. In these two ionomer blend systems, the itaconate, having two ionic groups per ionic repeat unit, influenced the properties of the blends more noticeably than the other two ionic units, containing only one ionic group per ionic repeat unit. In the blend system of P(S-co-SSNa)/P(S-co-MANa), as expected, the cluster loss tangent peak shifted to higher temperature, ionic modulus decreased, but the ionic plateau extended more with increasing the ratio of the P(S-co-SSNa) content. However, it should be mentioned that when the ion contents of the methacrylate and sulfonate ionomers increased to over 6 mol%, at which the cluster phase of the P(S-co-MANa) ionomers is known to become dominant, compared to the matrix phase, the three loss tangent peaks were observed, which implies that methacrylate-rich and sulfonate-rich phases exist together. This might be due to the fact that a copolymerization effect becomes stronger; that is, with increasing ion content the role of ionic units in random copolymer ionomers becomes more important, compared to the role of host non-ionic units. As a concluding remark, the properties of these three ionomer blend systems depend on the degree of clustering, type of ionic groups, and the number of ionic groups per repeat unit.

U3.10

COMPUTATIONALLY DETERMINING THE MORPHOLOGY AND MECHANICAL PROPERTIES OF FILLED DIBLOCK COPOLYMERS. Gavin A. Buxton and Anna C. Balazs, Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.

We combine two 3D computer simulations, one that models the phase segregation of diblock copolymers and the selective ordering of nanoparticle inclusions, and another that enables the micromechanical investigation of the resultant solid composite. The diblock copolymer melt is described using a Cahn-Hilliard methodology, with the nanoparticle motions being described using brownian dynamics. We then take the morphology of the filled diblock copolymer material and investigate the mechanical properties of this nanocomposite. The elastic properties of the highly heterogeneous nanostructural system are elucidated through the direct simulation of the local elastic deformations using a Lattice Spring Model. The macroscopic elastic properties of the material are therefore determined, while novel insights into the important role played by the ordering of these nanofillers are revealed. In particular, the confinement of nanoparticles within a given domain of a bicontinuous diblock copolymer structure is found to cause dramatic clustering effects and the particles percolate to form essentially a rigid backbone throughout the material. This continuous distribution of fillers significantly increases the reinforcement efficiency of the nanoparticles. We can, therefore, relate the composition of the diblock copolymer melt and the thermodynamic interactions between the particles and the different polymer phases to the macroscopic mechanical properties of the resultant filled polymer.

U3.11

STRESS ANALYSIS OF 4-POINT BEND TEST FOR THIN FILM ADHESION. Sassan Roham, Kedar Hardikar, Peter Woytowicz, Novellus Systems Inc., Computational Modeling, San Jose, CA.

Four point bend (4PB) tests are currently used to characterize the adhesive strength of thin films. Of particular interest are low k films whose strength properties are normally less than traditional dielectrics such as glass. A finite element analysis of a 4PB specimen is conducted in order to better understand the results and limitations of such testing. We discuss the classical equation used to convert 4PB test data into fracture energy and show results associated with short crack lengths (for which the classical formulation is not valid). We also present lower bound estimates of adhesion strength for anomalous tests (such as when the film fails in a cohesive rather than an adhesive mode). These bounds are compared against values computed using alternate formulations from the literature and are shown to be in good agreement. Finally, interpretation of 4PB test data is discussed and suggestions for successful testing of such films are made.

U3.12

HIGH STRENGTH AND SUPERPLASTICITY OF NANOSTRUCTURED MATERIALS. Vitaly Shpeizman, Ioffe Physicotechnical Institute of the Russian Academy of Sciences, St. Petersburg, RUSSIA.

The leading role of grain boundaries in the processes of deformation and fracture for nanostructured materials has made possible to reach their extremely high strength characteristics at low temperatures [1] and to observe superplasticity phenomenon at high temperatures [2]. Tests were carried out on a number of materials (Ni, Nb, Cu and Cu:ZrO₂ composite, Al-alloy) obtained by multiple equichannel angular pressing. The temperature range was from liquid-helium temperature up to nanostructure distortion one. Comparison of mechanical characteristics of polycrystals with nano- and large-sized grains at liquid-helium temperature showed that the first had more expressive "serration-effect" which observed in wider temperature and strain-rate ranges. The difference in mechanical behavior under tension and compression for nanocrystals as well as the various impurities influence on yield stresses was detected. The thermal effects at a stress jump observed upon transition of a Nb-sample (or Nb-strip placed closed to the sample) from the superconducting state to the normal state were estimated. At high temperatures the stability of nanostructure in Cu increased by doping of ZrO₂ or HfO₂ particles. The constant-rate tensile deformation and creep of Al-alloy exhibited superplasticity at temperatures of 600-670 K and relative-strain rate of 10⁻²-10⁻³ s⁻¹. The relative axial deformation at fracture was about 2000%. It was shown that, upon tension with a constant rate, a steady stage appeared: if true stress and strain are taken into consideration, the stress changed with deformation in accordance with well-known formula $\epsilon \sim \sigma^n \exp(-U/kT)$ with constant coefficients. From this it follows that, upon deformation of nanocrystals under superplasticity conditions, an equilibrium structure is formed, which remains unaltered until the sample breaks down. References. 1. V.V. Shpeizman, V.I. Nikolaev, B.I. Smirnov, A.B. Lebedev, V.I. Kopylov. Physics of the Solid State. 42, 6, 2015-2020 (2000). 2. M.M. Myshlyayev, V.V. Shpeizman, M.M. Kamalov. Physics of the Solid States. 43, 11, 2099-2104 (2001).

U3.13

BEHAVIOR OF ORDERED MESOPOROUS SILICA UNDER COMPRESSIVE STRESS. Francesco Di Renzo, Anne Galarneau, Helene Cambon, Francois Fajula, ENSCM-CNRS, Labo Materiaux Catalytiques, Montpellier, FRANCE.

Which is the lowest size scale at which classical mechanical models for cellular materials can be applied? The narrow distributions of pore size and wall thickness of micelle-templated silicas at the nanometer scale provide ideal benchmarks for the evaluation of mechanical models. Stress/strain relationships under uniaxial compression have been determined for ordered mesoporous silicas with different structures (MCM-41, MCM-48, SBA-15). A model of sphere bed has been used to correlate the compressive strain with the textural properties of the samples. The effects of mesopore topology, secondary microporosity and secondary mesoporosity have been taken into account.

U3.14

NANOMECHANICAL CHARACTERIZATION OF BONE. Thorsten Staedler, Eve Donnelly^a, Marjolein C.H. van der Meulen^a, and Shefford P. Baker, Department of Materials Science and Engineering, Cornell University, Bard Hall, Ithaca, NY. ^aDepartment of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY.

Bone is a complex natural composite showing a lamellar structure on the micro scale. In this study, scanning nanoindentation was used to access the mechanical properties of single lamellar and inter-lamellar trabecular bone. Only the combination of a careful sample preparation, metrological characterization of the sample surface, and a scanning nanoindenter proved to be able to provide an insight into individual mechanical properties of the lamellar structures. The results of quasi-static as well as the first dynamic nanoindentation tests of bone will be reported and discussed. The dynamic measurements covered a frequency range of 10-220 Hz. By careful surface preparation, we were able to achieve a surface roughness of only 18-20 nm RMS on a lateral scale of about 10 micrometers. Nonetheless, this mandates indentation depths in the range of 100 nm and above in order to minimize the effect of topography on the measurement. This requirement conflicts with the need to keep the probed volume small enough to sample only one component at a time. A simple volume averaging model was developed and used as a tool to determine when individual lamellar bone structures were being probed and to help determine the properties of the lamellar and inter-lamellar bone materials.

U3.15

NANOINDENTATION CHARACTERIZATION OF LASER MODIFIED A319Al ALLOY COMPOSITE SURFACE LAYER.

S. Nayak^a, G.M. Pharr^{a,b}, Laura Riester^b and Narendra B. Dahotre^a;

^aUniversity of Tennessee, Knoxville, TN; ^bOak Ridge National Lab, Oak Ridge, TN.

In this work, A319Al alloy has been modified by laser on the surface. Microstructure and nanoindentation were carried out on these samples. Microstructures indicate extreme refinement in laser surface melted region. Initial cell size of as-received A319Al alloys were $\approx 50 \mu\text{m}$ whereas the laser modified region has cell size of $\approx 2\text{-}3 \mu\text{m}$. Nanoindentation was carried out to evaluate the property of local volumes. Average hardness of the laser treated samples showed an increase (1.25 GPa) over that of as-received A319Al (1.1 GPa). The large standard deviation associated with A319Al (32%) was reduced to 2%. The hardness and elastic modulus values (derived from the continuously measured stiffness) were analyzed to investigate size effect from a "composite" perspective. Also, the unloading load vs. displacement data were curve fitted to power law. The elastic and plastic behavior of the laser modified sample was compared with that of Al and Si to correlate structure and properties of the laser modified composite material.

U3.16

GRAIN BOUNDARY CHARACTERS AND SLIDING OF [0001] SYMMETRIC TILT BOUNDARIES IN ALUMINA.

Katsuyuki Matsunaga, The Univ of Tokyo, Engineering Research Institute, Tokyo, JAPAN; Hitoshi Nishimura, The Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN; Hiroyuki Muto, Toyohashi Univ of Technology, Dept of Materials Science, Toyohashi, Aichi, JAPAN; Takahisa Yamamoto, The Univ. of Tokyo, Dept of Advanced Materials Science, Tokyo, JAPAN; Yuichi Ikuhara, The Univ of Tokyo, Engineering Research Institute, Tokyo, JAPAN.

Alumina bicrystals with [0001] symmetric tilt grain boundaries were fabricated by diffusion bonding at 1500°C in air, and their atomic structures were studied using high resolution electron microscopy (HRTEM) and static lattice calculations. In order to examine behavior of grain boundary sliding, compressive creep tests were performed at 1450°C using the bicrystals. HRTEM observations showed that several grain boundaries studied here have asymmetric atomic arrangements with respect to grain boundary planes. The creep curves were found to exhibit different profiles depending on grain boundary characters, which indicates that grain boundary structures are important for grain boundary sliding.

U3.17

DEVELOPMENT OF A NANOSTRUCTURED FERRITIC ALLOY (NFA). Matthew J. Alinger, G. Robert Odette, University of California, Materials Department, Santa Barbara, CA.

Iron powders containing $\sim 14\%$ Cr and smaller amounts of W and Ti can be mechanically alloyed (MA), consolidated and heat treated to produce very high densities of Y2O3 particles and/or coherent solute clusters enriched in Y, O and Ti along with nanoscale grains. These alloys manifest very high strength (static and creep) and corrosion-oxidation resistance up to temperatures well in excess of 700C. As-processed room temperature Vickers hardness of the powders ranges up to ~ 1000 dph. The nano-structures are remarkably stable, with room temperature Vickers hardness values up to ~ 475 dph after heat treatment or consolidation by HIP processing at temperatures of 1150C. The recrystallization temperatures are about 1300C. Other salient microstructural characteristics of these alloys include dislocation substructures, residual porosity following consolidation, as well as additional porosity that develops during high temperature heat treatments, and non-equiaxed/textured grain structures produced by high temperature extrusion. The evolutions of both the micro- and nano-structures through the various stages of mechanical alloying, consolidation and heat-treatment are characterized by a combination of techniques including XRD, SANS, TEM, atom probe, microhardness and several other complementary methods. The effects of the alloy composition MA milling parameters and consolidation path on these evolutions are examined. Tensile and fracture toughness properties of selected alloys are also presented. These observations are used to guide models of the underlying thermo-kinetic processes that mediate the, micro- and nano-structure formation and evolution and stability as well as their corresponding effects on key mechanical properties.

SESSION U4: TESTING NANOSCALE MATERIALS
Chairs: William W. Gerberich and Jeffrey N. Florando
Wednesday Morning, April 23, 2003
Metropolitan I (Argent)

8:30 AM *U4.1

MICROSAMPLE TENSILE TESTING AND MODELING OF MECHANICAL BEHAVIOR IN NANOCRYSTALLINE METALS.

K.J. Hemker, En Ma, and J.F. Molinari, Johns Hopkins University, Depts. of Mechanical Engineering and Materials Science and Engineering, Baltimore, MD.

The reliability of next-generation MEMS, NEMS, magnetic and ultra-hard films, and micro/nano devices, in general, will be closely tied to their mechanical performance. To be truly predictive, a fundamental description of the mechanical behavior of nano-scale structures must be based on a solid understanding of operative deformation mechanisms, but many of the plasticity models that were developed to describe conventional materials are known to break down at or near the nano-scale. The overriding intellectual challenge of the work described in this talk is to develop a science based methodology for measuring, describing and modeling deformation and fracture processes at or near nanometer length scales. Recent efforts at developing microsample tensile testing techniques, which afford us the opportunity to characterize small-scale and highly scale-specific properties, will be described. Results of on-going efforts to characterize the tensile strength of nanocrystalline microsamples will be presented, and transient microsample experiments designed to uncover and characterize the dominant deformation mechanisms will be outlined. Preliminary results of finite element (FE) calculations, containing physical models that are based on experimental findings and incorporating cohesive elements with atomistic descriptions of grain boundaries in nanocrystalline materials, will be presented and used to model the collective macroscopic response of a compilation of nanocrystalline grains. The support of National Science Foundation (Grant No. DMR0210215) is gratefully acknowledged.

9:00 AM U4.2

MECHANICAL TESTING OF MICRON-SIZE SAMPLES IN UNIAXIAL COMPRESSION. M.D. Uchic, D.M. Dimiduk, Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH; J.N. Florando, Lawrence Livermore National Laboratory, Livermore, CA; W.D. Nix, Stanford University, Department of Materials Science and Engineering, Stanford, CA.

In this study we present a general methodology to conduct a uniaxial compression experiment on micron-size samples—i.e., specimen having a diameter on the order of a few microns—where these samples have been fabricated from a bulk quantity of material (which has been made by an arbitrary process). By shrinking the size scale of the conventional uniaxial compression test, we now have a method to explore specimen size effects at micron-length scales for bulk materials. This method also has the potential to allow for the characterization of the single-crystal constitutive response from a single grain/microconstituent of a polycrystalline/polyconstituent material. Specifically, we demonstrate how to use a Focused Ion Beam (FIB) to machine micron-size mechanical test specimens into the surface of a material, where the test structures can range in size from sub-micron to tens of microns in diameter. The mechanical properties of these samples can be measured in uniaxial compression using a nanoindenter fitted with a flat-ended tip. We present data from small sample experiments conducted on a single-crystal elemental metal (Ni), as well as single-crystal intermetallic alloy (Ni₃Al), and we compare these data with tests conducted on conventional-sized samples.

9:15 AM U4.3

COPPER THIN FILM MECHANICAL CHARACTERIZATION BY TENSILE AND INDENTATION TESTING. David Read and Roy Geiss, National Institute of Standards and Technology, Boulder, CO; Richard Emery, Components Research, Intel Corporation, Chandler, AZ; Guanghai Xu and Tracey Scherban, Technology Development Quality and Reliability, Intel Corporation, Hillsboro, OR.

The mechanical properties of sputtered and electroplated copper films were investigated by microtensile testing of free-standing films and nanoindentation of supported films. Microtensile specimens with gauge lengths of 190 micrometers and widths of 7 to 20 micrometers were fabricated using a lithographic process. Some samples were annealed before being tested. Tensile elongation to failure ranged from close to zero to a maximum value of about 0.08. Despite this relatively limited tensile ductility, scanning electron microscope (SEM) observations of the fracture surfaces indicate locally ductile behavior in both sputtered and electroplated films. The yield strength and tensile strength of the sputtered film are nearly twice that of the electroplated film, due largely to grain size differences. The elastic modulus obtained from microtensile measurements is about half that derived from nanoindentation. Low tensile moduli in thin films have been previously reported, with possible explanations including film anelasticity and crack opening and closing at grain boundaries.

9:30 AM U4.4

STUDIES ON THE ELASTIC BEHAVIOR OF NANOPARTICLE CHAIN AGGREGATES USING A NOVEL NANOSTRUCTURE MANIPULATION DEVICE. Yong J. Suh, Rajdip Bandyopadhyaya, and Sheldon K. Friedlander, Dept of Chemical Engineering, University of California at Los Angeles, CA.

Nanoscale studies were conducted on the dynamic behavior of individual nanoparticle chain aggregates (NCA) and their networks. For this purpose, a novel device was fabricated to apply tension to NCA under controlled conditions. The device is composed of a specimen support and a cartridge. The specimen support is a deformable alloy disc with a narrow slit across which the NCA are deposited; the cartridge is used to connect the specimen support to a specimen elongation support holder. The aggregates were stretched using the specimen holder to widen or narrow the slit gap at speeds from 0.5 to 300 nm/s and the motion was observed with a transmission electron microscope. Most of the studies were made with carbon NCA (primary particle size 11 to 16 nm) generated by laser ablation of a graphite target. The aggregates were deposited on the specimen support (disc) to form bridges across the slit. When tension was applied, the NCA remained attached to the slit edges. The chains stretched because kinks on the scale of a few particle diameters were straightened by rotation and/or grain boundary sliding at particle-particle interfaces. After the chain became taut, increasing tension produced little additional extension. Eventually, the chain broke and the elastically strained portions along the NCA recovered. This led to fast contraction of the two broken ends. In one of the cases studied in detail, a small primary particle in the chain doubled in length before the chain broke at this site. This probably occurred because of the high tensile stress in the small particle. In a separate set of experiments, a network of carbon NCA was produced by increased deposition around the slit of a specimen support. Chains in the network broke successively as the network stretched. Some of the chains broke midway and not at the junctures with each other. They rapidly contracted in a way similar to that of the individual aggregates. Applications to the behavior of nanocomposite materials composed of blends of NCA and molecular polymers (e.g., rubber) are discussed.

10:15 AM U4.5

AN IN-SITU TEM NANOINDENTER SYSTEM FOR DEFORMATION STUDIES OF SUB-MICRON WIRES. M.S. Bobji and J.B. Pethica, Univ of Oxford, Dept of Materials, Oxford, UNITED KINGDOM; B.J. Inkson, Univ of Sheffield, Dept. of Engineering Materials, Sheffield, UNITED KINGDOM.

To quantify the mechanical properties of sub-micron wires, an in-situ nanoindenter system is being developed for a Transmission Electron Microscope. This miniature displacement controlled nanoindenter will fit inside a side entry specimen holder. The displacements are generated by means of a tube piezo and the force is measured using a fibre optic interferometer. The force-sensing element is a specially designed spring made out of Cu-Be alloy. For coarse positioning, a 3-axis inertial positioner has been developed. This positioner has a range of 5mm with a 300 nm resolution. The system is being used to investigate the deformation of Cu, Al and Ti nano wires under W contacts. The electron transparent specimen is made using Focused Ion Beam microscope and the tungsten tip is polished electrochemically.

10:30 AM U4.6

MEASURING AND OBSERVING THE INDENTATION BEHAVIOR OF SILICON THROUGH IN SITU NANOINDENTATION IN A TEM. A.M. Minor and E.T. Lilleodden, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA; E.A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; M. Jin and J.W. Morris, Jr., Dept of Materials Science and Engineering, University of California, Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

We present real-time observations of nanoindentation into silicon, which show extensive dislocation-based plasticity at room temperature. Upon unloading, the plastically deformed volume leads to a residual stress that can induce non-crystallographic fracture. These results can be explained in part by the unique wedge geometry of the samples used. The silicon wedge samples were fabricated through bulk micromachining into wedges that are terminated by a plateau of either 20 or 150 nm. When compared to conventional indentation into a half-space, the wedge geometry yields a different stress state underneath the indenter. A method for extracting quantitative load vs. displacement data from the voltage-controlled in situ nanoindentation experiments will be discussed. FEM analysis of the wedge sample geometry and conventional nanoindentation techniques are also used in support of the in situ nanoindentation experiments. Combining all of these techniques, the deformation

mechanisms in silicon will be discussed in terms of the competition between dislocation nucleation and phase transformation during the initial stages of indentation.

10:45 AM U4.7

SURFACE MECHANICAL PROPERTY DETERMINATION OF SOFT MATERIALS THROUGH AN AFM NANOINDENTATION EXPERIMENT. Olivier Noel, Maurice Brogly, Gilles Castelein and Jacques Schultz, Université de Haute Alsace et Institut de la Chimie des Surfaces et Interfaces (ICSI), Mulhouse, FRANCE.

Atomic Force Microscopy (AFM) gives the opportunity to perform nanoindentation experiments. This technique has been used to probe model cross-linked polydimethylsiloxane networks (PDMS) in order to extract their surface mechanical properties. Macroscopic Young modulus have been determined and lies over two decades. In order to obtain quantitative measurements with the AFM, systematic studies have to be performed (preferentially based on model systems) so that this technique can be calibrated. Especially the radius of the tip has been determined by performing a nanoindentation experiment on a model soft material. A discussion about the difficulties to find out mechanical properties of soft materials is proposed. In particular, Young moduli of each sample have been calculated by using different contact mechanics theories (Hertz and JKR theories) and a power law expression. A comparison with the macroscopic moduli has showed that the contribution of the adhesion cannot be neglected at the nanoscopic scale. Consequently, the influence of the indentation depth and of the contact time between the probe and the sample, has been studied. From then on, the contact mechanics relationships (which depend on the geometry of the tip) have to be redefined. In parallel, micro indentation experiments (Vicker's tip) were also performed and compared with the others results. At the end, we hope to propose you a finite element simulation (using Castem software) of an AFM nanoindentation experiment (at present, still under elaboration) that includes the adhesive and viscoelastic behaviours of the material, as well as the effect of an loading-unloading cycle of the tip.

11:00 AM U4.8

ANALYSES OF THE ELASTIC MODULUS OF A THIN POLYMER FILM. Soline Roche, Sandrine Bec, Jean-Luc Loubet, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes, FRANCE.

This paper discusses the interaction between mechanical properties of a thin layer and its substrate. The underlined questions are: how the substrate's mechanical properties affect those of the film; how the layer's thickness affects its mechanical properties. Nanoindentation tests are performed on polymer films of different layer thicknesses laid on a silica substrate. The mechanical response corresponds to those of the substrate and the film taken as a single whole. Our aim is to understand the elastic behaviour of the film inside this structure. Modelisations are used to estimate the elastic modulus of the film apart of the global value measured. A comparison of the different literature's models is presented. For layers which are thin and "compliant" applied on "hard" substrates, an increase of the film elastic modulus along indentation is observed. We attribute this increase to an "anvil effect", to the dependency of bulk elastic modulus with the hydrostatic pressure which occurs during the compression of the film. The relevant experimental parameters governing the phenomenon are pointed out: the ratio between the film thickness and the contact radius, the ratio between the substrate hardness and the film modulus, the experimental temperature in front of the glass transition temperature. In conclusion, some rules are proposed to understand specific behaviour of nanometric layer.

11:15 AM U4.9

INCREASING INITIAL YIELD STRESS AT SMALL LENGTH SCALES. I. Spary^a, A.J. Bushby^a, N.M. Jennett^b, and G.M. Pharr^{c,d}; ^aCentre for Materials Research, Queen Mary, University of London, UNITED KINGDOM; ^bMaterials Centre, National Physical Laboratory, Teddington, UNITED KINGDOM; ^cOak Ridge National Laboratory, Oak Ridge, TN; ^dMaterials Science and Engineering Department, University of Tennessee, TN.

Plasticity size effects are well known in a wide variety of situations where either the material microstructure or a strain gradient exist at small length scales. Several theories have been developed to describe changes in the work hardening behaviour under these conditions but none that predict a change in the initial yield stress. Careful studies by Chaudhri et al and Pharr et al have unambiguously demonstrated plasticity size effects in ductile metals. In those experiments indentation stress-strain curves were generated using spherical indenters with radii ranging from a few micrometres to several hundred micrometres and these were compared to data from conventional uniaxial tests. Large radius indenters produced a single indentation stress-strain curve independent of indenter radius with a power law hardening coefficient equivalent to that in the compression

tests. However, for smaller indenters the indentation stress-strain curves appeared at progressively higher pressures for smaller radius indenters. In this paper we model those experiments using finite element analysis methods. By inputting the uniaxial stress-strain data to the model (effectively, using von Mises criterion) the indentation stress-strain curves for the macro size indenters are reproduced. However, the model shows no length scale dependence for any size of indenter. We show that by off-setting the compression stress-strain curve by increasing the initial yield stress and inputting this data to the model, the indentation behaviour of the smaller radius indenters can be modelled. The increase in yield stress with decreasing indenter radius is demonstrated for Cu, W and Ir and is shown to be consistent with the initiation of yielding over a finite volume.

11:30 AM U4.10

ON THE RELATION BETWEEN THE INDENTER SIZE AND THE GRAIN SIZE: RESULTS FROM ATOMISTIC SIMULATIONS.

A. Hasnaoui, D. Feichtinger, P. M. Derlet, H. Van Swygenhoven, Paul Scherrer Institut, Villigen-PSI, SWITZERLAND.

Atomistic studies of nanoindentations have been performed on nanocrystalline samples with different mean grain sizes (6 and 12nm) and single crystal samples, in order to study the influence of the microstructure on the mechanism responsible for dislocation nucleation during displacement controlled indentation. A hard-sphere indenter applied to a thin film geometry with an infinitely hard substrate is used and the simulations are done using molecular dynamics and conjugate gradient techniques. The size effect due to the relation between indenter size and grain size is discussed: for the same indentation depth, differences in the force-displacement curve are found when the indentation is contained within one grain or when at smaller grain sizes, the indentation covers different grains. Careful examination of the activity under the indenter show that (1) the GB act as a sink for dislocations emitted under the indenter (2) collective motion of grains pointing towards the presence of GB sliding (Phys. Rev. B, 2003).

11:45 AM U4.11

ON THE DECOUPLING OF CHEMICAL AND MECHANICAL SURFACE CONTRIBUTIONS IN A FORCE-DISTANCE CURVE MEASURED BY AFM ON MODEL POLYMERS. Maurice Brogly, Olivier Noel, Gilles Castelein, Jacques Schultz.

The Atomic Force Microscope (AFM) is a promising device for the investigation of materials surface properties at the nanoscale. Precise analysis of adhesive and mechanical properties, and in particular, of model surface polymer can be achieved with a nanometer probe. The purpose of this study is to dissociate the different contributions (adhesive and mechanical) included in an AFM force-distance curve in order to establish relationships between viscoelastic properties of the bulk, of the surface and the adhesive forces. Indeed we are interested in the measurements of local attractive or adhesive forces in AFM contact mode, of controlled chemical and mechanical model substrates. Considering that the main technical uncertainties have been listed and minimized, surface force measurements are performed on chemically modified silicon substrates (grafted with hydroxyl, amine, methyl and ester functional groups). The results show that the contribution of the surface chemistry (in particular its hydrophilic features) is dominating in the measurement of the adhesion force. In order to investigate the effects of mechanical or viscoelastic contributions, we achieved force measurements on model polymer networks, whose surfaces are chemically controlled with the same functional groups as before (silicon substrates). Young modulus have been determined and lies over two decades. The results show that the viscoelastic contribution is dominating in the adhesion force measurement. At the end, we propose an original relationship (derived from the Gent and Schultz law), which express the local adhesion force to the dissipation energy in the contact and the surface properties of the material (thermodynamic work of adhesion).

SESSION U5: NANOSTRUCTURED MATERIALS IN 1, 2 AND 3 DIMENSIONS

Chairs: Kathryn J. Wahl and Christopher L. Muhlstein
Wednesday Afternoon, April 23, 2003
Metropolitan I (Argent)

1:30 PM *U5.1

THERMOMECHANICAL BEHAVIOR OF DIFFERENT TEXTURE COMPONENTS IN THIN FCC METAL FILMS. Shefford P. Baker, Cornell University, Department of Materials Science and Engineering, Bard Hall, Ithaca, NY.

Thin metal films are used in a wide variety of nanofabricated devices and are often found to support very large stresses due to differential thermal expansion between the films and the substrates to which they are attached. These stresses are often studied by deducing the average

stress in a film from the curvature that it induces in the substrate. Using x-ray diffraction measurements, we have measured the thermomechanical behavior of (111) and (100) oriented grains separately in polycrystalline Cu and Ag thin films. These orientations are found to behave very differently from one another, and from the average behavior determined from substrate curvature measurements; although the average behavior can sometimes be described as a volume average of the individual texture components. The stress levels in (111) orientations can be several times those in (100) orientations, a significantly larger difference than predicted by the orientation factor. The (100) orientations, by contrast, show relatively little strain hardening and stress levels that are insensitive to the film thickness. Large Bauschinger-like early yielding effects were found in both (111) and (100) orientations. Understanding these behaviors is critical as film reliability is determined by peak stresses, not averaged stresses. Mechanisms based on dislocation motion and interactions, and on sliding at the film/substrate interface are developed to explain the observed phenomena.

2:00 PM U5.2

NANOINDENTATION OF POROUS LOW-k POLYMER FILMS.

Manuel Luis B. Palacio, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; Guanghai Xu, Tracey Scherban, Intel Corporation, Hillsboro, OR; Brad Sun, Intel Corporation, Santa Clara, CA; William W. Gerberich, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The indentation response of thin porous polymer films on silicon substrates is presented. Films of 10, 20 and 35% nominal porosity were examined using a Berkovich tip and compared with the nonporous variant. The elastic modulus was found to decrease by as much as 40% when porosity is introduced. A change in slope in the load-displacement curve was observed after reaching a certain load, indicating that partial pore closure is achieved once the depth is beyond half of the film's thickness. The temperature dependence of the modulus was also examined, and was found to exhibit Arrhenius-type dependence. A modeling approach, originally developed for a linear elastic case, is extended to account for pore deformation. Its predictions closely approximate experimental moduli from indentation.

2:15 PM U5.3

ELASTIC PROPERTIES OF LITHOGRAPHICALLY PREPARED NANOSTRUCTURES.

Ryan Hartschuh, Alexander Kisliuk, Alexie P. Sokolov, Dept of Polymer Science, Univ Akron, Akron, OH; Arpan P. Mahorowala, IBM, TJ Watson Research Center, Yorktown Heights, NY; Wen-li Wu, and Christopher L. Soles, NIST Polymers Div, Gaithersburg, MD.

In the semiconductor industry, it is critical to understand if nanostructuring changes the physical properties of a material appreciably from their bulk values. For example, deep UV lithography is used to print the latent image of a structure into a thin photoresist film. An aqueous solvent then dissolves the exposed region of the film, leaving a nanostructured polymer behind. Later this nanostructure is transferred into the silicon through a reactive ion etch. While the nanostructured polymer is temporary and sacrificial, its mechanical properties are of paramount importance to the quality of the final structure. There are capillary forces from the aqueous developer that can deform or collapse neighboring structures if the dimensions are small enough. To avoid this buckling or collapse, chip designers need materials properties such as the elastic modulus and it crucial if reduced dimensions affect the modulus of the nanostructured polymer. In this work we use Brillouin scattering to quantify the acoustic modes in polymer thin films and nanostructured parallel lines. In the films we see the traditional surface (Rayleigh) and longitudinal guided modes, and these can be used to estimate the bulk and the shear modulus of the polymer film. In the nanostructured parallel lines, we observe an additional mode that appears to be a breathing mode of the line. We study this breathing mode as a function of line thickness in both the lithographically prepared polymeric structures as well as corresponding structures once they transferred into the silicon oxide substrate via a reactive ion etch. The possibility of using these modes to extract reliable mechanical properties is discussed in detail.

2:30 PM U5.4

NANO-INDENTATION OF POLYMER FILMS TO ESTABLISH CONNECTIONS BETWEEN NANOSCALE STRUCTURE AND MECHANICAL PROPERTIES. Matthew R. Begley and Kyle C.

Maner, University of Virginia; Marcel. Utz, University of Connecticut.

We report a thorough nano-indentation study of glassy polymer thin films, both homogeneous and micro-phase separated at the 50nm scale. Growing evidence suggests that the thermomechanical properties of polymer materials depend on the experimental length scale at small dimensions. For instance, the elastic modulus of thin

polymer films has been shown to depend on film thickness. Recent results from our group have indicated an intimate link between the density of molecular entanglements ρ_e and the spatial extension of plastic relaxation events in glassy polymers. Thus, marked changes in the plastic properties must be expected as the experimental length scale approaches the mean distance between entanglements. Our study therefore focuses on the PS-PPO compatible blend system, in which ρ_e can be controlled by composition. Thin films of different composition with thickness on the order of 1000 nm were created via spin-casting, and tested via nanoindentation in a variety of rate-dependent tests. In addition, a new approach involving indentation of axisymmetric freestanding membranes has been developed, using a combination of spin-coating and preferential etching of micro-capillary arrays. The additional tests are designed to identify substrate effects on both material properties and test interpretation. These tests and accompanying numerical models will be discussed in the context of: (i) clearly identifying scale-dependence of mechanical properties from direct nanomechanical characterization, and (ii) identifying nanoscale characteristics underpinning plastic deformation in polymers. In extension of the above work, results will also be presented on polystyrene-hydrogenated polyisoprene diblock copolymers, which are phase separated on a length scale of about 50nm, and on a novel class of block copolymers based on metal-ion chelate block linkages.

2:45 PM U5.5

EFFECT OF TEMPLATING BYPRODUCTS ON ADHESION OF NANOPOROUS THIN FILMS. Dan A. Maidenberg, Stanford Univ, Dept of Materials Science and Engineering, Stanford, CA; Willi Volksen and Robert D. Miller, IBM-Almaden Research Center, San Jose, CA; Reinhold H. Dauskardt, Stanford Univ, Dept of Materials Science and Engineering, Stanford, CA.

From biological scaffolds to dielectric layers in microelectronics, nano-templated organic-inorganic hybrid materials are being developed to provide a versatile class of highly porous materials with tunable properties. Through selection of porogen molecules, controlled nanometer-sized pores may be produced at selected volume fraction. However, while materials may be designed for electrical, optical, or even biological properties, the incorporation of porosity may significantly affect the mechanical properties of the materials, especially as they relate to fracture toughness and adhesion to adjacent materials. Generally, the fracture toughness of brittle glasses is known to degrade in the presence of porosity, and such behavior has also been found for thin porous films. In the present study, we demonstrate that with appropriate selection of MSSQ precursors and porogen molecules, highly porous films may be created that exhibit remarkable adhesive and fracture resistance properties. Treatments of the porous layer involving exposure to UV/ozone was found to increase the adhesive properties of films containing 50% porosity by an order of magnitude, from 2 J/m² to over 20 J/m². Such unique effects on mechanical behavior are described in terms of molecular byproducts of the pore creating process itself, specifically porogen residuals that provide molecular bridging mechanisms to markedly effect fracture resistance. Detailed characterization results together with modeling of the toughened mechanisms are discussed.

3:30 PM U5.6

GREEN NANOCOMPOSITES - PATHWAY TO THE FUTURE FOR BIOBASED POLYMERS. A.K. Mohanty, L.T. Drzal and M. Misra, Composite Materials and Structures Center, Department of Chemical Engineering and Materials Science, Michigan State Univ, E. Lansing, MI.

Environmentally benign materials (EBM) are the wave of the future to save our world from growing pollution threat. Biopolymers are now moving into the mainstream and the polymers that are biodegradable or based on renewable "feedstock" may soon be competing with the commodity plastics. Performance limitations and high cost have put these biopolymers in to niche market. Renewable resource-based green plastics including cellulose esters (plastics made from wood cellulose), polylactides or PLA (corn-derived plastic) and polyhydroxyalkanoates (bacterial biopolyesters) have attracted recent attentions as potential replacements of existing fully petroleum-derived non-biodegradable polymers both on cost and performance basis with added advantages of bio-based origin and eco-friendliness. To find new and emerging applications of biopolymers through innovative technology is a formidable task for scientists. The nano-reinforcements pose strong future for biopolymers in finding new green nanocomposite materials for various applications in green automotive parts, electronic cases and green packaging. Green nanocomposites are fabricated from bioplastics and organically modified clays through melt-processing route. Effects of process engineering on performance of nanocomposites are analyzed. We found that extrusion followed by injection molding rather than extrusion followed by compression molding exhibited better performance of the resulting bioplastic-clay green nanocomposites. Through TEM studies, the differences in

nanocomposite performances of such two processing approaches are explained. Extent of intercalation and or exfoliation of nanoclay in polymer matrix are responsible for improved performance of the nanocomposites. True nanocomposites exhibit improved strength/stiffness without sacrifice of toughness besides showing much reduced gas permeability (improved barrier properties), lower coefficient of thermal expansion (CTE), improved heat deflection temperature and reduced water absorption. This presentation will give an overview on the current status and future prospective of biodegradable polymer - clay based green nanocomposites and would highlight the importance of nanotechnology in improving the performance of the emerging green plastics. Acknowledgements: This research is supported by NSF-NER 2002 Award No. BES-0210681.

3:45 PM U5.7

HIGH STRAIN-TO-BREAK VALUES OBSERVED IN PERIODIC SILICA/POLYMER COMPOSITE MATERIALS. Bradley L. Kirsch, Sarah H. Tolbert, University of California, Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA; Xu Chen, Jun Tian, Vijay Gupta, University of California, Los Angeles, Dept of Mechanical & Aerospace Engineering, Los Angeles, CA.

Disordered inorganic/organic composites are lightweight materials that potentially hold promise for a variety of applications, but generally have poor mechanical stability. However, it is possible to produce well-ordered inorganic/organic composites that exhibit long-range periodicity using self-assembly techniques. Recent results demonstrate that these periodic composites exhibit superior compressive properties compared to disordered systems. In this work we explore how ordering inorganic/organic materials affects the tensile properties of honeycomb-structured (SBA-15) silica/polymer composite films. We show that the absolute value of the tensile strain to break is larger than that of bulk silica. We also show significant differences in the strain-to-break values between the axes parallel and perpendicular to the cylindrical organic domains. These results are strong indications that the mesoscale hexagonal architecture produces the superior mechanical properties. The ratio of the strain to break in the parallel direction to the strain to break in the perpendicular direction is approximately constant with variable film thickness, while the magnitude of the strain to break in both directions is proportional to the film thickness. This demonstrates that the phenomenon is not simply a thin film effect, but rather a property that is inherent to the well-ordered mesostructure. We have also modeled this system using finite element analysis, and the results are in good agreement with the experiments. This work demonstrates the utility of tailoring mechanical composites on different length scales to produce desirable mechanical properties in nanoscale materials.

4:00 PM U5.8

SYNTHESIS AND PROCESSING OF SINGLE-WALL CARBON NANOTUBES/CERAMIC NANOCOMPOSITES WITH NOVEL PROPERTIES. Guo-Dong Zhan, Joshua D. Kuntz, and Amiya K. Mukherjee, Department of Chemical Engineering and Materials Science, University of California - Davis.

The extraordinary mechanical, thermal and electrical properties of single-wall carbon nanotubes (SWCN) have prompted intense research into a wide range of applications in materials, electronics, chemical processing, and energy management. There have been many predictions of the reinforcing effects of carbon nanotubes in various composite matrices but large improvements in properties have not yet been convincingly demonstrated. For instance, only a 24% increase in toughness has been best obtained in alumina based systems. In the present study, we have successfully realized this possibility in reinforcing nanocrystalline ceramic nanocomposites for the first time. Fully dense SWCN/alumina nanocomposites with nanocrystalline alumina matrix have been fabricated at sintering temperatures as low as 1423 K by novel spark-plasma-sintering. A great improvement in fracture toughness has been achieved in these nanocomposites. Microstructural investigation including HRTEM showed that the effective bonding of ropes with the matrix plays a central role in the reinforcing effect. This investigation was supported by a grant (#G-DAAD 19-00-1-0185) from US Army Research Office with Dr. William Mullins as the Program Manager.

4:15 PM U5.9

PARAMETRIC RESONANCE BEHAVIOR AND MECHANICAL PROPERTY STUDIES OF NANOWIRES IN FREE-SPACE. Min-Feng Yu, Univ. of Illinois at Urbana-Champaign, Dept. of Mechanical and Industrial Engineering.

The extremely small dimensions of nanostructures imply unique mechanical/electronic properties for their potential applications, which, however, also impose great challenges for many experimental studies. We developed a nanomanipulation device for use inside a scanning electron microscope, which is capable of nanometer resolution motion, and free-space manipulation and characterization

of nanostructures. We report the realization of parametric resonances of individual nanowires using an oscillating electric field. Resonances at drive frequencies near $2f_0/n$, where f_0 is the nanowires fundamental resonance, for n from 1 to 4, were observed and analyzed. (High order parametric mechanical resonance for n up to 4 was only recently observed in microscale MEMS resonators.) Regions of instability were mapped, and hysteresis in the parametric resonance response was observed. A theory that includes a forcing term proportional to the amplitude of the resonance was used for the analysis, which agrees well with the experiment. The resonances were found to originate from the amplitude dependent electric force acting on the nanowire and can be described by the Mathieu equation, which has known regions of instability in parameter space. We will also report the studies of other mechanical property (modulus, tensile and shear strength, and deformability) of various nanostructures (nanotube, nanowire and nanoribbon) using the free-space manipulation and characterization technique, and advanced microscopy. See references: Min-Feng Yu, et al. Phys. Rev. B, 66, 073406(2002); Min-Feng Yu, et al. Phys. Rev. B 64, 241403R (2001); Min-Feng Yu, et al. Phys. Rev. Lett. 85, 1456(2000); Min-Feng Yu, et al. J. Phys. Chem. B. 104, 8764(2000); Min-Feng Yu, et al. Phys. Rev. Lett. 84, 5552(2000); Min-Feng Yu, et al. Science 287, 637(2000).

4:30 PM U5.10

NANOMECHANICAL IMAGING OF MULTI-WALLED CARBON NANOTUBES. Lata Muthuswami, School of NanoSciences, University at Albany, Albany, NY; P.M. Ajayan, Dept of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY; Robert Geer, School of NanoSciences, University at Albany, Albany, NY.

Carbon nanotubes represent a singular example of a molecular system offering emergent functionalities derived from its nanoscale size. It has been aggressively researched for uses in nanocomposites owing to its outstanding mechanical properties and in nanoelectronics for both its metallic and semiconducting character. To date, experimental investigations of the mechanical properties of individual nanotubes have treated the entire tube as a classical uniform beam or cylindrical shell and derived elastic information (modulus, Poissons ratio, etc.) based on those assumptions. To investigate intra-tube variations of mechanical response the nanomechanical mapping of individual multi-walled carbon nanotubes (MWNTs) has been undertaken. Ultrasonic force microscopy has been used to measure the relative axial and radial variations of contact stiffness of individual MWNTs synthesized using chemical vapor deposition (CVD) and arc-discharge (A-D) techniques. For CVD-based MWNTs the contact stiffness of the tube was seen to vary strongly across volume defects (axial variation of the tube radius) and is assumed to result from the high crystalline defect density associated with such radial variations. These observations support recent experimental data of effective Youngs modulus inferred from nanotube vibration amplitudes. Discrete mechanical defects have also been imaged in A-D MWNTs for which the radius is constant as a function of axial position. Local continuum elastic models are used to quantify the contact stiffness over small (10 nm x 10 nm) regions of the tube.

4:45 PM U5.11

SILYLATION OF LOW-STRUCTURED COLLOIDAL SILICA NANOPARTICLES FOR REINFORCEMENT IN SILICONE ELASTOMERS. Timothy C. Chao, Dow Corning Corporation, New Ventures R&D, Midland, MI; Debora F. Bergstrom, Dendritic Nanotechnologies Limited, Mount Pleasant, MI.

Aqueous suspensions of colloidal silicas are readily silylated with chlorosilanes in the presence of acid and isopropyl alcohol without aggregation of the silica particle. By using a mixture of chlorosilanes, spherical nanoparticles with controlled functionality can be made and transferred to an organic phase to provide stable, water free suspensions. The hydrophobic colloidal silica particles readily disperse into silicone polymers. In order to provide mechanical reinforcement comparable to traditional fumed silicas, a high filler loading of 60 wt % mono-dispersed 20nm colloidal silicas need to be used. Recently the unique low-structured pearl necklace-shaped colloidal silicas become commercially available. These nanoparticles are successfully silylated and they maintain the original structures as evidenced by transmission electron microscopy (TEM). They are compounded into silicone polymers at 25 - 30 wt % and they provide excellent viscosities and mechanical properties, especially the tear strengths. In this presentation, the silylation, characterization and mechanical properties of colloidal silica nanoparticles in silicone elastomers will be covered.

SESSION U6: POSTER SESSION
Chairs: Kathryn J. Wahl and Harriet H. Kung
Wednesday Evening, April 23, 2003
8:00 PM
Golden Gate (Marriott)

U6.1

ANALYSIS OF DISLOCATION NUCLEATION UNDER A NANOINDENTER. Chuanli Zhang, Guanshui Xu, Department of Mechanical Engineering, University of California, Riverside, CA.

We present an analysis of dislocation nucleation under a nanoindenter based on the Peierls-Nabarro dislocation model. By incorporating atomic information into the variational boundary integral method, we have determined the embryonic dislocation profiles and their associated activation energy required to activate the dislocations from their stable to unstable saddle point configurations. We have also obtained the indentation force and displacement relation for a case that involves nucleation of multiple discrete dislocations under the indenter. The results have direct correlation with the recently observed discrete plastic deformation in nanoindentation experiments.

U6.2

DEFORMATION PROCESSES DURING NANOINDENTATION OF Ti_3SiC_2 . A. Murugaiah, M.W. Barsoum, S. Kalidindi and T. Zhen, Department of Materials Engineering, Drexel University, Philadelphia, PA.

This paper discusses the deformation processes during the nano indentation of Ti_3SiC_2 , a thermodynamically stable nano-laminate. In this presentation we report on the load/depth-of-indentation response of Ti_3SiC_2 surfaces loaded with a 13.5 μm spherical tipped diamond indenter up to loads of 500 mN. Combining scanning electron microscopy and orientation imaging, two surfaces were identified; one in which the basal planes were parallel to, and the other normal to the surface. Not surprising for such a plastically anisotropic material, the response was anisotropic and comprised of two regimes. At the higher loads (200-500 mN) damage was initiated and resulted in delaminations when loaded parallel to, and smaller microcracks when loaded normal to the basal planes. At lower loads (5 mN - 200 mN), the response was unique to Ti_3SiC_2 and resulted in almost fully reversible closed hysteresis loops. Subsequent repeated (up to 5) loadings on the identical location not only resulted in fully reversible, reproducible hysteresis loops, but resulted in the hardening of the indented volume. Despite the fact that the Hertzian stresses at the tip of the indenter were of the order of 15 GPa and the repeat nature of the loadings, almost no trace of the indentations were found. This response is believed to be due to the formation of microscopic incipient and regular kink bands. In that respect it is not unreasonable to think of Ti_3SiC_2 as behaving as a dislocation-based elastomer in the sense that it can be loaded repeatedly without damage and dissipate significant amounts of energy during each cycle.

U6.3

DEFORMATION OF SMALL VOLUMES OF MATERIAL STUDIED USING STRAINED LAYER SUPERLATTICE STRUCTURES. K.M.Y. P'ng, A.J. Bushby and D.J. Dunstan, Centre for Materials Research, Queen Mary, University of London, UNITED KINGDOM.

Mechanical studies of semiconductor superlattices have shown that the onset of plastic deformation under an inhomogeneous stress is a process that takes place simultaneously across a finite volume of the order of a micron across. The deformation behaviour of materials under contact loading is of prime technological importance, and a criterion for yielding is important as a design tool. As technology moves increasingly to smaller scales in thin film coatings, nanostructured materials and micro-electro-mechanical systems, existing yield criteria fail rather badly. The ability to incorporate known internal stresses, and to vary the stress and thickness of individual layers in a semiconductor superlattice, is a very powerful tool, opening up new possibilities for investigations that cannot be achieved by varying external stresses on a specimen that is sensibly homogeneous. In this way, from the initial yield stress of single-crystal strained-layer superlattices under indentation, we demonstrate a new criterion, of which the key feature is that it is to be averaged over a finite volume. By careful design of the superlattice stress, in individual layers and in bands forming low yield stress material within the structure, the size and position of the initial yield volume can be determined and the yield criteria deduced.

U6.4

NANOINDENTATION TESTING TO OBSERVE SLIP TRANSFER ACROSS GRAIN BOUNDARIES. K.A. Nibur, D.F. Bahr, and D.P. Field, Washington State University, Mechanical and Materials Engineering, Pullman, WA.

Nanocrystalline materials are increasingly coming into the focus of cutting edge metallurgy. With it comes the importance of understanding and predicting how dislocations are able to transfer across grain boundaries. Current empirical techniques for observing slip across boundaries relies heavily on the use of TEM which is effective, but also technically challenging and time consuming. Recent advances in indentation testing coupled with orientation imaging

microscopy allow slip across grain boundaries to be easily observed and measured. Because of the relative ease of this procedure, numerous boundaries of different misorientation can be tested in a reasonable time span. Atomic force microscopy reveals slip steps on the surface around an indentation. These steps can be used to determine the active slip system. When slip crosses a boundary, the steps visible in each grain identify all active slip systems that intersect the free surface. The extent of slip transfer can be compared with different strain fields as well as variations in the angle between intersecting slip planes within the boundary. A series of nanoindentations along grain boundaries of various misorientation angles in large grained materials is presented to demonstrate this technique. Comparisons are made with indentations in fine grained materials to understand nanoindentation results from nanocrystalline solids.

U6.5
INTERFACIAL STUDIES IN CLAY POLYMER NANO-COMPOSITES. H.A. Goldberg, C.A. Feeney, M. Farrell, D.P. Karim, InMat LLC; G. Collins, Z. Ophir, and M. Jaffe, Biomedical Engineering, NJIT.

Clay polymer nanocomposites have been shown to provide large improvements in both the barrier properties and modulus over unfilled polymers. On the other hand, in most cases, the strain to failure is significantly reduced. In order to control the flexibility of these materials it is important to also control the degree of dispersion and the interactions between the nanodispersed clay and the polymer. InMat's elastomeric barrier coatings provide an example of a nanocomposite system in which the filler dispersion can be controlled, and the large reduction in gas permeability provides evidence for good dispersion. Typically, a mineral filler in an elastomeric matrix would lead to a large reduction in flexibility. However, InMat has shown that control over the clay polymer interface can reduce this loss in flexibility. More direct evidence for particle dispersion has proved hard to acquire. For example, electron microscopy is difficult due to the elastomeric matrix. In this paper, we will discuss the use of thermally stimulated current measurements (TSC) as a tool that is sensitive to the clay-polymer interface. We will discuss its utility in determining the mobility of polar species at the interface. We will compare these results with DSC, thermal expansion, and mechanical measurements in order to determine the utility of this technique for understanding clay polymer nanocomposites. Particular attention will be paid to the choice of matrix and exfoliated clay and their role in determining the composite properties.

U6.6
DUAL TRIBOLOGICAL BEHAVIOR OF A NANOLAYERED CERAMIC: Ti_3SiC_2 . Alexandra Souchet, Julien Fontaine, Michel Belin, Thierry Le Mogne, Jean-Luc Loubet, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes, Ecully, FRANCE; Michel W. Barsoum, Drexel University, Department of Materials Engineering, Philadelphia, PA.

The MAX phases are new, thermodynamically stable, nanolayered ternary carbides and nitrides. These materials can have a big potential in tribological applications due to their structure, as graphite or molybdenum disulfide. For example, the friction coefficients of the basal planes of Ti_3SiC_2 have been shown to exhibit very low friction coefficients. The aim of this study is to better understand the tribological behavior of polycrystalline Ti_3SiC_2 against stainless steel. Experiments have been conducted on a ball-on-flat tribometer ($\sim 25^\circ C$ and $\sim 30\%$ relative humidity) that simultaneously measures friction coefficients and electrical contact resistance. Different ball diameters and normal loads were used that resulted in contact pressures between 0.35 and 1.25 GPa. Two different tribological behaviors were observed, both with relatively low friction coefficients for ceramics. The first behavior, referred to as type I, is characterized by a friction coefficient around 0.15. Wear of Ti_3SiC_2 plane is low and a transfer film containing titanium and carbon is formed on the ball. The other behavior, type II, is characterized by a friction coefficient that starts at around 0.15 and then increases to about 0.4. At the end of the experiment, the ball is worn, and compacted wear debris containing iron can be found on the plane. The two behaviors seem to be independent of contact pressure, but are rather sensitive to normal applied load. The transition between these two regimes will be discussed, in light of electrical contact measurements during sliding.

U6.7
MECHANICAL PROPERTIES OF NANOSTRUCTURED AND PREFERENTIALLY ORIENTED HYDROXYAPATITE COATINGS GROWN BY PULSED LASER DEPOSITION. Hyunbin Kim, Shane A. Catledge, Yogesh K. Vohra, and Renato P. Camata, University of Alabama at Birmingham, Dept. of Physics, Birmingham, AL; William R. Lacey, University of Alabama at Birmingham, Dept. of Prosthodontics and Biomaterials, Birmingham, AL.

Hydroxyapatite (HA) $[Ca_{10}(PO_4)_6(OH)_2]$ among calcium phosphates is commonly coated onto orthopedic and dental metallic implants to speed up bone formation around devices, allowing earlier stabilization in a patient. Studies in the past decade have indicated that pulsed laser deposition (PLD) may be the most suitable means of placing thin HA coatings on these implants because of its demonstrated control over stoichiometry, crystallinity, and nanostructure. These characteristics determine the mechanical properties of the films that must be optimized to improve the performance of load-bearing implants and other devices that undergo bone insertion. In this work we have used PLD to produce nanostructured and preferentially oriented HA coatings and evaluated their mechanical properties. Pure, highly crystalline HA coatings on Ti-6Al-4V substrates were obtained using a KrF excimer laser (248nm) with energy density of $4\sim 8J/cm^2$ and deposition temperature in the range of $500^\circ C\sim 700^\circ C$. Scanning electron and atomic force microscopies reveal that our careful manipulation of energy density and substrate temperature has led to films made up of HA grains in the nanometer scale. Broadening of x-ray diffraction peaks as a function of deposition temperature suggests that it may be possible to control the film nanostructure to a great extent. X-ray diffraction also show that as the laser energy density is increased in the $4\sim 8J/cm^2$ range, the coatings become preferentially oriented along the c-axis perpendicular to the substrate. Nanoindentation measurements show improved hardness and Young's modulus in oriented films that can be attributed to the crystallites alignment in the anisotropic hexagonal HA structure caused by the highly energetic plume during deposition. Preferential orientation, nanostructure, and phase make-up all significantly influence on the mechanical properties. We will discuss how each of these factors affects hardness and Young's modulus of the HA films. (Funded by NIH: NIDCR 1R01 DE013952-02 A1, NSF: DMR-0116098).

U6.8
MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NANOLAYERED TiN/Cu THIN FILMS. Yau Yau Tse, Abadias Gregory, Anny Michel, Christophe Tromas, Michel Jaouen, Laboratoire de Metallurgie Physique, Université de Poitiers, Futuroscope-Chasseneuil, FRANCE.

Metal/Nitride composite thin films, either in the form of biphasic nanocomposites or multilayers, have attracted considerable interest for their improved mechanical properties. The present study is focused on the TiN/Cu system, of which a strong mechanical (huge difference in shear modulus) and structural (large misfit of 15%) contrast exists between the two materials, making it a prized system to study the interdependence between the growth mode, resulting microstructure and mechanical behavior. TiN/Cu multilayers were grown by high vacuum dual ion beam sputtering deposition with bilayer period ranging from 3 to 50 nm. Both low-angle and high-angle X-ray diffraction (XRD) experiments have been employed to globally characterize the multilayers structure. High angle XRD spectra revealed a (002) TiN and (002) Cu texture, while pure Cu films on Si (001) exhibited a strong (111) texture. Analysis of the stress/strain state of the TiN/Cu multilayers by the " $\sin^2\chi$ method" showed that TiN layers are under large compressive stress, while the Cu layers are under small tensile stress. The microstructure of the multilayers has been scrutinized using HRTEM. A cube-on-cube epitaxial growth mode of Cu on TiN was identified, the presence of (111) faceted islands as well as several lattice defects have been observed in the Cu layers. The effects of interface and bilayer thickness on hardness were investigated by depth-sensing nanoindentation technique. A small hardness increase with decreasing periodicity of the multilayers is observed. The relationship between the h_c/T ratio and the hardness, where h_c is the contact depth and T the total film thickness, was established. The effects of substrate on film hardness were studied by comparison between films deposited on MgO(001) and Si(001) substrates, respectively. The composite hardness on MgO substrate renders larger hardness values than those on Si substrate by about 20%. The effect of pop-in phenomenon in MgO on the resulting hardness for $h_c/T > 0.2$ will be studied. The relationship between the microstructure and hardness were discussed in terms of mechanical models.

U6.9
POINTWISE SYNCHOTRON STRAIN MAPPING OF RELEASED MEMS MIRROR. Y.N. Picard, S.M. Yalisove, Univ of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI; E.M. Dufresne, R. Clarke, Univ of Michigan, Dept of Physics and MHATT-CAT, Ann Arbor, MI; D.A. Walko, Argonne National Lab, Advanced Photon Source, Argonne, IL; D.J. Dagle, D.P. Adams, Sandia National Labs, Albuquerque, NM.

We have used a micron-sized x-ray beam at the Advanced Photon Source to measure and profile strain across a pre-released, 250 micron diameter, metal coated polysilicon micromirror. A 10keV x-ray beam was focused using two bendable Kirkpatrick-Baez mirrors to a $\sim 4\times 12$ micron spot size and used to measure strain at various points across

the micromirror surface. The 2.25 micron thick polysilicon mirror was coated with a low stress, high reflectivity multilayer film of 395ÅTi/1000ÅAu prior to analysis. D_{hkl} spacings for Au and Si planes were measured to assess in-plane and out-of-plane strain, which were then related to the micromirror curvature.

U6.10

TEXTURE AND NANO HARDNESS OF YSZ ELECTROLYTE THIN FILMS PREPARED BY COMBUSTION CVD AND PULSED LASER DEPOSITION. Zhigang Xu, Sergey Yarmolenko, Jag Sankar, NSF Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC.

Yttria stabilized cubic phase zirconia (YSZ) has been used as electrolyte in solid oxide fuel cells (SOFCs) and oxygen sensors because of its high oxygen-ion conductivity over wide range of temperature and oxygen pressure. Thin film is preferred for the YSZ electrolyte in order to minimize the current path in the fuel cell. Present research is geared towards the improvement of fuel cells efficiencies through understanding various materials issues and their performance against the environmental conditions. In this paper, fundamental understanding of hardness and modulus of the film and knowledge concerning the influences of the substrate/interface and crystal sizes on the overall behavior of the electrolyte thin film will be presented. The YSZ thin films were synthesized with atmospheric combustion chemical vapor deposition (ACVD) with liquid fuel and pulsed laser deposition (PLD) techniques on Si(100) and MgO(100) substrates. The particle sizes were controlled in the range from submicron to several nanometers. To increase the strength and ion conductivity of the YSZ thin films, composite films of YSZ and Al₂O₃ (<10 mol %) were processed. The as-grown films were characterized with x-ray diffraction, scanning electronic microscopy and transmission electronic microscopy to identify their microstructures. The effects of the particle size and the addition of Al₂O₃ on the mechanical properties were characterized by nano-indentation. The relationship between micro-mechanical properties, microstructures, and the processing parameters were optimized for desired mechanical properties.

U6.11

USING FLUCTUATIONS TO LOCATE THE SURFACE ROUGHENING TRANSITION. Daniel Bentz, Kenneth Jackson, University of Arizona, Dept. of Materials Science and Engineering, Tucson, AZ.

We have conducted a kinetic Monte Carlo study of the surface roughening transition of the {100} FCC surface by using fluctuation dissipation theory to determine the kinetic coefficients. The simulations were conducted using a spin 1/2 Ising model treatment of the solid-liquid interface with simulation cells 50 by 50 by 10 lattice units in size. Interfaces were studied at equilibrium with an imposed temperature gradient to supply a restoring force for the interface. Fluctuations in the number of solid atoms in the system about the equilibrium position were examined using time correlations. These characteristic times were used to calculate the kinetic coefficient of the system. We have observed a dramatic change in these characteristic times which locates the surface roughening transition.

U6.12

ATOMISTIC MODELLING OF THE DEFORMATION BEHAVIORS OF NANOMATERIALS. K. Shintani, T. Nakajima, Y. Nakura, and S. Kameoka, Univ of Electro-Comm, Dept of ME & Intelligent Sys, Tokyo, JAPAN.

Nanomaterials such as carbon nanotubes, semiconductor nanowires, metallic nanowires, and nanoclusters have a wide variety of applications in the fields of nanotechnology. Carbon nanotubes are about to emerge in the market as a material for electrodes of field emission displays. They are also promising as materials for probe tips of scanning probe microscopes and for nanomanipulators or nanopincettes. Rapid progress of the growth methods of semiconductor nanowires has realized nanowire junctions and nanowire superlattices which will open the world of nanodevices. Metallic nanowires have drawn much attention of researchers since a linear strand of gold atoms at a nanocontact between a scanning tunneling microscopic probe and a metal surface was observed. These nanowires are probably applicable to wiring in nanocircuits. Both knowledge of the mechanical properties of nanomaterials and understanding of their deformation mechanisms are essential to realization of all of these applications. In the application of carbon nanotubes to nanopincettes which hold nanostructures, for instance, their strength and deformation characteristics should be known beforehand. In this study, some atomistic models for the deformations of nanomaterials are proposed, and molecular-dynamics simulations based on such models are performed for elongation, compression, bending, and torsion of nanomaterials.

U6.13

CORRELATION BETWEEN MECHANICAL AND STRUCTURAL PROPERTIES OF TiC AND TiCN THIN FILMS GROWN BY RF SPUTTERING. Abderahim Mani, Pascal Aubert, Philippe Houdy, Université Evry Val Essonne, Laboratoire d'Etude Milieux Nanométrique (LMN), FRANCE; Hicham Khodja,CEA/DSM Laboratoire Pierre, Gif sur Yvette, FRANCE; Florence Mercier, Université Evry Val Essonne, Laboratoire Analyse et environnement, FRANCE.

Titanium carbide, TiC, and titanium carbonitride, TiCN, thin films present attractive mechanical and tribological properties for engineering applications. The aim of this study is to correlate the mechanical properties of TiC and TiCN thin films with the structural properties and chemical composition analysed by X-Ray Diffraction, Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis. Mechanical properties were studied by nanoindentation and were correlated to intrinsic stress calculated by Stoney formula. Thin films of TiC and TiCN were deposited on < 100 > silicon substrate by RF sputtering from a TiC target using respectively an Ar plasma and an Ar - N₂ plasma. Various sputtering total pressure from 0.35 to 1 Pa and sputtering power from 100W to 300W were used. For TiCN samples various Ar / N₂ ratio were used. Apparently linear correlation between intrinsic stress and hardness were found for TiC films. However the hardness increase when the sputtering pressure decrease. The maximum of the hardness, 28 GPa, was obtained for thin films deposited at 0.35 Pa which present a dense structure and a high intrinsic compressive stress of 4.4 GPa. Thin films TiCN were produced at total pressure equal to 0.35Pa with various N₂ partial pressure ranging from 10% to 7010% of total pressure. A hardness of 20GPa was achieved and related to the chemical composition. Finally first results of TiC/TiCN multilayers will be presented.

U6.14

MECHANICAL PROPERTIES OF NANOSTRUCTURED METAL-CERAMIC THIN FILMS. D. Kumar, N. Sudhir, S. Yarmolenko, and J. Sankar, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Thin films composite materials consisting of metallic nanocrystals embedded in an insulator host have been synthesized using alternating-target pulsed laser deposition of Fe/Ni and Al₂O₃. The evaluation of structural quality of the thin film composites using high resolution transmission electron microscopy and scanning transmission electron microscopy with atomic number contrast has revealed the formation of a biphasic system with thermodynamically driven segregation of Ni and alumina during pulsed laser deposition. The best hardness values of the thin film composites, measured using nanoindentation techniques, was found to 20-30% larger than pure alumina films fabricated under identical conditions. The improvement in values of hardness of Al₂O₃ thin films by embedding metal nanocrystals is related to the evolution of a microstructure which efficiently hinders the manipulation and movement of dislocation and the growth of microcracks, which in turn, is achieved by grain boundary hardening.

U6.15

DETERMINATION OF Ag/Ni INTERFACIAL FREE ENERGIES BY BIAXIAL ZERO CREEP EXPERIMENTS. Bing An, Tong-jun Zhang, Chao Yuan, Kun Cui, Huazhong Univ. of Sci. & Tech., State Key Laboratory of Die and Mould Technology, Wuhan, P.R. CHINA; Wei Zhang, University of Maryland, Gaithersburg, MD.

Biaxial zero creep experiments were performed on Ag/Ni multilayer films on Si (111) substrates. An optical apparatus with parallel multi-beams and CCD detector was used for monitoring the curvature changes during heating process. The equilibrium curvature was measured to determine the interfacial free energy of Ag/Ni interfaces, and thereafter their effects on the structural stability of multilayers were investigated. The residual stresses in the Ag/Ni multilayers were slowly close to zero when heating at temperature from room temperature to 450°C. The equilibrium curvature was reached soon after hitting 450°C, and after a long time at this elevated temperature, it seems that no change occurred. Based on the equilibrium between interfacial residual stress and interfacial free energy, a free energy of Ag/Ni interfaces at an equilibrium temperature of 450°C could be determined.

SESSION U7: FAILURE AND FRACTURE IN NANOMATERIALS

Chairs: Neville R. Moody and Anna C. Balazs
Thursday Morning, April 24, 2003
Metropolitan I (Argent)

8:30 AM *U7.1

THE INFLUENCE OF GRAIN SIZE ON THE FATIGUE BEHAVIOR OF THIN POLYCRYSTALLINE FILMS. Oliver Kraft, Cynthia A. Volkert, Forschungszentrum Karlsruhe, Institut für Materialforschung II, Karlsruhe, GERMANY; Ruth Schwaiger, MIT, Dept of Material Science & Eng, Cambridge, MA; Patrick Wellner, Reiner Mönig, Guangping Zhang, Christoph Eberl, Ralph Spolenak, Eduard Arzt, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Nanocrystalline metallic materials are known to have a very high strength compared to their large grained counterparts. However, very little is known about the fatigue behavior of nanocrystalline materials. It is the aim of this paper to discuss the change fatigue behavior of thin polycrystalline metal films as a function of film thickness and grain size in the range from a few microns to 50 nm. Cu, Ag and Al films on substrates were subjected to cyclic deformation, which was induced either by mechanical, thermo-mechanical or acoustical loading. Resulting frequencies ranged from 0.1 to 10^9 Hz. The fatigue damage morphology was found to depend strongly on film thickness and grain size, and to be quite different compared to bulk materials: Failure of thicker films with grains larger than approximately $0.5 \mu\text{m}$ is associated with the formation of extrusions at the surface and voids near the film/substrate interface in the interior of the grains. Transgranular cracks are generated from these voids at the film substrate/interface rather than from the film surface. However in thinner films with fine grains, damage exhibits as intergranular grooving, voiding and possibly cracking while extrusions are still present at the film surface. Furthermore, transmission electron microscopy investigations show a general trend that the dislocation density in fatigued films decreases with decreasing thickness and grain size. These findings indicate that fatigue in nanostructured metallic materials appears to be controlled by diffusive mechanisms and interface properties rather than by dislocation glide and bulk properties.

9:00 AM U7.2

FATIGUE DEGRADATION OF NANOMETER-SCALE SILICON DIOXIDE REACTION LAYERS ON SILICON STRUCTURAL FILMS. Christopher L. Muhlstein, The Pennsylvania State University, Dept. of Materials Science and Engineering, University Park, PA; Eric A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; Robert O. Ritchie, Materials Sciences Division, Lawrence Berkeley National Laboratory and Dept. of Materials Science and Engineering, University of California, Berkeley, CA.

Although bulk silicon is ostensibly immune to cyclic fatigue and environmentally-assisted cracking, the thin film form of the material exhibits significantly different behavior. Such silicon thin films are used in small-scale structural applications, including microelectromechanical systems (MEMS), and display "metal-like" stress-life (S/N) fatigue behavior in room temperature air environments. Fatigue lives in excess of 10^{11} cycles have been observed at high frequency (≈ 40 kHz), fully-reversed stress amplitudes as low as half the fracture strength using surface micromachined, resonant-loaded, fatigue characterization structures. Recent experiments have clarified the origin of the susceptibility of thin film silicon to fatigue failure. Stress-life fatigue, transmission electron microscopy, infrared microscopy, and numerical models were used to establish that the mechanism of the apparent fatigue failure of thin-film silicon involves sequential oxidation and environmentally-assisted crack growth solely within the nanometer-scale silica layer on the surface of the silicon, via a process that we term "reaction-layer fatigue". Only thin films are susceptible to such a failure mechanism because the critical crack size for catastrophic failure of the entire silicon structure can be exceeded by a crack solely within the surface oxide layer. The growth of the oxide layer and the environmentally-assisted initiation of cracks under cyclic loading conditions are discussed in detail. Furthermore, the importance of interfacial fracture mechanics solutions and the synergism of the oxidation and cracking processes are described. Finally, the successful mitigation of reaction-layer fatigue with monolayer coatings is shown.

9:15 AM U7.3

ADHESION OF POLYMER THIN-FILMS AND PATTERNED LINES: EFFECTS OF 1-D AND 2-D CONSTRAINT FROM NANO- TO MICRON- LENGTH SCALES. Christopher S. Litteken, Reinhold H. Dauskardt, Stanford University, Department of Materials Sciences and Engineering, Stanford, CA.

Emerging nanotechnologies require an understanding of the effects of multi-dimensional elastic constraint on the mechanical and interfacial properties of complex device structures. In the present study, the adhesion of interfaces in thin-film structures containing ductile polymer blanket films and patterned lines is reported. The intent of the study was to demonstrate that both the film thickness (50 nm - 5

μm) and the aspect ratio of patterned lines (2 - 12) have a significant effect on the interfacial fracture energy of interfaces adjacent to the ductile polymer. There is currently limited understanding of the effect of dimensional constraint in the plane of the film on local plasticity and associated interfacial fracture energies. Accordingly, the interfacial adhesion of patterned structures containing arrays of polymer/SiO₂ lines with varying aspect ratios was investigated. Macroscopic adhesion values were determined by measuring the critical strain energy release rate, G_c , for debonding of the patterned interface. The yield properties of the polymer films as a function of film thickness was also investigated. Unlike metal films, the polymer yield strength was found to be largely insensitive to layer thickness, while interfacial fracture energy displayed a marked sensitivity to thickness. In addition, decreasing the aspect ratio of the polymer lines was found to significantly increase interface fracture energy. Behavior is rationalized in terms of the effect of stress state on the local fracture mode and the extent of plastic deformation in the polymer line.

9:30 AM U7.4

ORIENTATION AND GRAIN SIZE EFFECTS OF THE ADHESION OF THIN DUCTILE FILMS. M.J. Cordill, D.F. Bahr, Washington State University, Pullman, WA.

Adhesion of thin metal films is important to the microelectronics industry. It has been shown that thickness affects the adhesion properties of thin films. As the thickness of a film increases the amount of plastic deformation also increases. This increase in the plastic deformation increases the measured interfacial fracture toughness due to an increase in energy dissipation in the mode II component of loading. When the thickness increases the grain size changes as well. The grain size can be controlled by varying the process conditions used to deposit the film, and post growth processing. In sputtering the pressure or temperature of the substrate can be controlled to produce films with a fine grain structure or with large grains. Electroplating produces a fine grained film and annealing the as deposited film will increase the grain size. This study examines how the grain size will impact the mechanical properties, namely adhesion, of thin ductile films on brittle substrates. The thickness of copper and tin films remained constant while the grain size was changed using controlled process conditions. The grain structure of the films was examined using OIM and AFM. The interfacial fracture toughness of each film was calculated using a tungsten stressed overlayer and mechanics based models. The hardness of the films were correlated to the measured interfacial fracture toughness, and demonstrate that increased hardness correlates to an increased sensitivity to the mode II component of loading.

10:15 AM U7.5

EFFECT OF MOISTURE AND GRADED-LAYER MECHANICAL PROPERTIES ON DEFORMATION AND INTERFACIAL ADHESION. Lorraine C. Wang and Reinhold H. Dauskardt, Stanford University, Department of Materials Science and Engineering, Stanford, CA.

Controlling material properties over nanometer length scales is crucial for current and emerging high-density microelectronic device packages. Miniaturization of devices is increasingly limited by the ability to connect to the device, and the required packaging structures must be fabricated where layer thickness and feature sizes approach micron size scales while achieving the required mechanical, thermal and electrical properties. Second phase additions such as sub-micron sized particles are often added to locally adjust the material properties of constituent layers in the complex package structure. This results in significant variation of mechanical properties over sub-micron length scales. Such manipulation of material structure and its effects on mechanical and interfacial fracture behavior are addressed using experimental and modeling studies. Underfill layers consisting of an epoxy matrix with dispersed silica beads are shown to exhibit variations of elastic and flow properties in excess of three-fold across the layer thickness. Mechanical properties are not only affected by the distribution of second-phase fillers, but also by the adhesion properties of the filler/matrix interface. Interfaces are susceptible to stress corrosion cracking associated with moisture which can lead to progressive debond growth at loads much lower than that required to exceed the critical interface fracture energies. Subcritical debonding is affected by temperature, humidity, and the bond chemistry of the interface. The effects of these variations are considered on the adhesive and subcritical debonding behavior of interfaces between bisphenol F epoxy underfill and either SiO₂ or SiN_x chip passivation. Implications for other constrained complex layered structures are considered.

10:30 AM U7.6

SELF-ASSEMBLED MOLECULAR NANOLAYERS AS INTERFACIAL ADHESION ENHANCERS. G. Ramanath, G. Cui, S. McConaughy, M. Stukowski, P.G. Ganesan, and A. Ellis, Rensselaer Polytechnic Institute, Materials Science & Engineering Department, Troy, NY.

We describe and demonstrate a completely new approach of harnessing nanolayers of self-assembled molecules for enhancing adhesion at thin film interfaces. Recently we showed that <2-nm-thick self-assembled molecular layers (SAMs) are attractive candidates for arresting interfacial diffusion in layered structures. The rationale of using SAMs for enhancing adhesion is based on anchoring the termini of the molecular constituents to the overlayers and underlayers through strong, but highly local, chemical interactions. This unique approach has the potential to obviate interfacial mixing typically necessary for enhancing adhesion by conventional interlayers. These features open up new possibilities for molecular-level tailoring of interfacial properties for future device structures comprised of ultrathin layers and/or molecular assemblies. We illustrate the above concepts by using SAMs of mercapto-trimethoxy-silane (MPTMS) at Cu/SiO₂ interfaces. The thiol group is chosen to effect strong chemical interaction with Cu, while the silane enables the seamlessly anchors the SAM with SiO₂ via covalent Si-O-Si bonds. Four-point bend tests of Cu/MPTMS/SiO₂ show interface debond energy of ~9 J/m², which is 3-times higher than that of Cu/SiO₂ structures. X-ray photoelectron spectroscopy(XPS) measurements of the fracture surfaces show that delamination occurs by cleavage of the C-S bond, leaving the -SH groups on the fractured metal side of the interface. No S was detectable on the SiO₂ fracture surface. These results clearly confirm our vision of using difunctional SAMs as adhesion enhancers. Lower debonding energies obtained from test structures with pyridine- and amine-terminated SAMs indicate that appropriate choice of functional group is critical to enhance adhesion. While multilayer formation during nanolayer assembly is deleterious to adhesion, molecular length of the SAM constituents does not show any observable effect on adhesion. Based on the above, we will present a model to explain the key factors that influence adhesion in SAM-treated Cu/dielectric structures.

10:45 AM U7.7

TRIBOLOGICAL IMPROVEMENTS IN ALUMINUM USING PLASMA SOURCE ION IMPLANTATION SYNTHESIS OF OXIDE NANOPRECIPITATES. Martin Bolduc and Bernard Terreault, INRS-EMT, Université du Québec, Varennes, CANADA.

Improvement of the tribological properties of pure Al and AA7075 (Al-Mg-Zn-Cu-Cr), using oxygen plasma source ion implantation (OPSI), was investigated at process temperatures from 100°C to 460°C. Results from nanoindentation, AFM-nanoscratch and XPS chemical analysis are presented. In pure Al, low temperature treatment (< 200°C) produced an enhancement of the surface hardness up to 6X (to 3 GPa) due to the synthesis of Al₂O₃ nanoprecipitates (~10 nm). The optimisation of the mechanical properties in terms of the oxygen ion dose is discussed. At higher temperature (> 400°C), the improvement is restricted to a thinner, brittle layer, and evidence of fracture appears in the load-displacement nanoindentation curves. In the alloy, low temperature treatment led to a hardness enhancement of up to 3X (to 5 GPa). Although an improvement was also obtained at high temperature, the surface composition and nanostructure was quite different, revealing the presence of MgO nanoprecipitates (~100 nm) to the detriment of Al₂O₃. Preferential Mg oxidation, as a chemical driven force for Mg segregation, induced a complete Al surface depletion. A moderate oxygen content (~30 at.%) combined with lower temperature treatment results in better surface mechanical improvements than extreme oxygen content and higher temperature treatment (which may also adversely affect the bulk properties).

11:00 AM U7.8

MECHANICAL PROPERTIES OF FUNCTIONALLY GRADED NANOSTRUCTURED METALLO-CERAMIC COATINGS ON COBALT CHROME ALLOY. Shane A. Catledge and Yogesh K. Vohra, University of Alabama at Birmingham (UAB), Dept of Physics, Birmingham, AL; Shanna Woodard and R. Venugopalan, University of Alabama at Birmingham (UAB), Dept of Biomedical Engineering, Birmingham, AL.

A functionally graded nanocrystalline metalloceramic coating on cobalt-chrome alloys was investigated with thin film x-ray diffraction (XRD), nanoindentation, and scratch adhesion testing. The gradual transition from metallic to covalent bonding along with a nanocrystalline grain structure provides a unique material system with excellent strength, toughness, and adhesion properties. XRD analysis of the (CrTiN) coating indicates a cubic sodium chloride phase with a = 4.2169±0.0035 Å. Nanoindentation measurements of the coating result in a hardness of 27 GPa and Young's modulus of 320 GPa. The graded metallic/covalent nature of the coating also results in excellent film/substrate adhesion as measured from scratch testing. The gradual transition in bonding from metallic (Cr/CrTi) near the interface to covalent (CrTiN) near the surface provides a combination of exceptionally high toughness and high surface hardness. The high plasticity of 55% for this coating represents a significant increase in toughness over other ceramic coatings having similar hardness.

11:15 AM U7.9

STRUCTURE AND MECHANICAL PROPERTIES OF W/W₂N SUPERLATTICES. L. Maillé, C. Sant, P. Aubert and P. Garnier, Laboratoire d'étude des Milieux Nanométriques, Université Evry Val d'Essonne, Evry, FRANCE.

In this paper, the structure of W, W₂N monolithic tungsten thin films and W/W₂N superlattices has been related to their mechanical properties. Samples have been grown on silicon substrates by reactive RF-sputtering, with a pure tungsten target. W₂N layers are deposited with an atmosphere composed of a mixture Ar+N₂ with two different partial pressure of nitrogen : 10% and 50%. The period thickness of multilayers was decrease from 50 to 2 nm for the two runs. The crystallographic structure and the period thicknesses are determined by a diffractometer (X-ray diffraction, grazing X-ray diffraction and X-ray reflectometry). The stress of the films is obtained by an interferometer and using the Stoney's equation. Hardness and young modulus are measured by a nanoindentation technique combined with an atomic force microscopy. We relate the period thickness and the stress with the hardness of the films. The hardness of the superlattices is increased with decreasing the layer spacing. A hardness value of 19 GPa is reached for a multilayer with a period thickness ~10 nm. This hardness is better than W and W₂N monolayers prepared under the same condition.

11:30 AM U7.10

STUDY OF THE YIELDING BEHAVIOR OF COPPER THIN FILMS ON SILICON SUBSTRATES USING MICROBEAM BENDING. J.N. Florando^a and W.D. Nix, Stanford Univ, Dept of Materials Science and Engineering, Stanford, CA. ^aCurrently at Lawrence Livermore National Laboratory, Livermore, CA.

The yielding behavior of copper thin films with dimensions of 0.5 to 1.7 microns in thickness, and grain sizes in the sub-micron regime, have been investigated using a microbeam bending method. This method uses triangular shaped microbeams, which have the advantage that the entire top surface of the film is subjected to a uniform state of strain, unlike the standard rectangular geometry where bending is concentrated at the support. With this technique, the yielding and strain hardening behavior of Cu thin films on Si substrates has been investigated. The Cu films were sputtered deposited with either a dual or a strong < 111 > texture. For the dual textured film, an analysis of the onset of yielding in the different orientations has been performed using orientation imaging microscopy and a Schmid Factor analysis. Strongly textured < 111 > films were deposited at three different film thicknesses to examine the effect of texture as well as film thickness on the yield properties of the film. The results show the expected result that < 111 > textured films have a higher modulus than the dual textured films. The < 111 > textured films also exhibit a thickness dependence on the yield stress and the work hardening rate, with thinner films having higher yield strengths and higher rates of work hardening. The source of these effects may be explained using current dislocation models from the literature.

11:45 AM U7.11

MECHANICAL BEHAVIOR OF ELASTOMERIC STAMPS DURING MICROCONTACT PRINTING: DIRECT OBSERVATION OF STAMPS AND PATTERNED INK. Kenneth Sharp, Gregory Blackman and Anand Jagota, Central Research, DuPont Co., Wilmington, DE.

Microcontact printing is a straightforward and effective method for generating surface patterns of micron or submicron lateral dimensions. The fidelity of the ultimate pattern is a complex interplay of mechanical behavior of the elastomeric stamp, fluid transfer between surfaces and the ability of the ink to self-assemble on the new surface. We present here experimental observations and modeling of stamp deformation during precise external loads and visualization of inked surfaces by several high contrast analytical methods. Stamp behavior was observed visually in an inverted microscope and load-displacement relationships used to determine onset of failure modes such as roof collapse and buckling of slender relief features as a function of stamp geometry. The load was applied with a glass sphere so as to obviate problems with alignment and to precisely determine contact areas. The work of adhesion between the two contacting surfaces was also determined. A "robotic stamper" fabricated from an AFM can deliver ink under conditions of precise load and registration and can be used to examine dilute patterns from multiple prints following a single inking procedure. Surfaces inked with varying densities or combinations of SAMs can be imaged with excellent contrast by scanning surface potential microscopy (SSPM). The same area of the sample can then be examined using time-of-flight SIMS or scanning Auger nanoprobe with no additional etching or sample preparation. In this way the detailed surface chemistry and purity of the patterned monolayers can be evaluated. The effect of load on ink pattern quality can be quantitatively evaluated.

SESSION U8/W7: JOINT SESSION
MODELS AND EXPERIMENTS IN
NANOSTRUCTURED MATERIALS

Chairs: Helena Van Swygenhoven and Hussein M. Zbib
Thursday Afternoon, April 24, 2003
Metropolitan I (Argent)

1:30 PM U8.1/W7.1

MULTISCALE MODELING OF VOID GROWTH IN DUCTILE METALS. Robert E. Rudd, Eira T. Seppälä, James Belak, Lawrence Livermore National Laboratory, Livermore, CA; Marc C. Fivel, CNRS/INPG, Domaine Universitaire, Grenoble, FRANCE.

Void growth is an important microscopic process in the fracture of ductile metals. Several well-established models are commonly used to describe the development and evolution of void populations through a coarse-grained porosity, but detailed models of void growth with atomic-level specificity have not been available. As the first steps in a hierarchical approach to the modeling of void growth associated with dynamic fracture, we have developed atomistic and mesoscale models [1,2] that describe the evolution of voids under an applied tension. In our simulations this tension arises from expansion at a constant strain rate for comparison with dynamic fracture experiments conducted at LLNL and elsewhere. The hierarchical approach in effect replaces the empirical constitutive relations used in continuum modeling of void growth with classical interatomic force laws, and the elastic and plastic behavior of the metal is derived from the collective response of the atoms. In this talk we compare the evolution of the plastic zone surrounding a growing void for several different ductile metals, including both face-centered-cubic (FCC) and body-centered-cubic (BCC) transition metals. In particular we analyze the character of the dislocation activity, and we contrast the details of this plastic response for several metals. The dislocation characterization and nucleation rules are used to inform a dislocation dynamics simulation in order to extend to longer length scales and slower strain rates. 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] J. Belak, "On the nucleation and growth of voids at high strain-rates," J. Comp.-Aided Mater. Design 5, 193 (1998). [2] R.E. Rudd and J. Belak, "Void Nucleation and Associated Plasticity in Dynamic Fracture of Polycrystalline Copper: An atomistic simulation," Comput. Mater. Sci. 24, 148 (2002).

1:45 PM U8.2/W7.2

GRAIN BOUNDARY PROCESSES DURING DEFORMATION OF NANO-SCALE GRAIN BOUNDARY MICROSTRUCTURES: ATOMISTIC SIMULATION STUDIES. Moneesh Upmanyu, Material Science Program, Division of Engineering, Colorado School of Mines, Golden, CO; and B. Radhakrishnan, Computational Materials Science Group, Oak Ridge National Laboratory, Oak Ridge, TN.

We have performed molecular dynamics simulations of deformation of bicrystals in pure Al to study the mechanism of strain accommodation at nano-scale grain boundaries. We first investigate dislocation nucleation as a function of the strain imposed on the bi-crystal. Detailed analyses of the grain boundary structure before and after deformation (in the elastic as well as plastic regimes) are carried out to arrive at the atomistic mechanisms of strain accommodation. The spatio-temporal variation of excess grain boundary quantities such as grain boundary enthalpy, volume, etc., are investigated to determine the dependence of the strain accommodation mechanisms on bi-crystallography. Finally, the effects of such strain accommodation mechanisms on nano-scale plasticity are discussed.

2:00 PM U8.3/W7.3

MOLECULAR DYNAMICS SIMULATIONS OF VOID GROWTH IN DYNAMIC FRACTURE OF FCC AND BCC METALS. Eira T. Seppälä, James Belak, Robert E. Rudd, Lawrence Livermore National Laboratory, Livermore, CA.

Dynamic fracture in ductile metals occurs commonly through the nucleation and growth of voids, with concomitant dislocation formation and propagation. Here we have studied at the atomistic scale the growth of a pre-existing spherical void initially a few nanometers in radius in single-crystal face-centered-cubic (FCC) and body-centered-cubic (BCC) lattices under dilatational strain. Molecular dynamics (MD) simulations using an Embedded-Atom-Model (EAM) potential to model copper and a Finnis-Sinclair potential to model tantalum have been performed at high strain-rates ranging from 10^6 /sec to 10^{10} /sec. We have especially concentrated on the quantitative analysis of the void shape evolution depending on the stress-triaxiality by varying the loading as uniaxial, biaxial, and triaxial expansion. The strain-rate dependence, differences between lattice structures, and the structures of dislocations, which emerge from the void and lead to its growth, have been investigated, too. These atomistic-level studies, which are done at initial system sizes

about $[25 \text{ nm}]^3$ and starting from room temperature, have been compared with continuum calculations and measures such as plastic strain. Also simulations of much larger length-scales, e.g. utilizing a parallel MD code, in order to study several voids are discussed. 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.

2:15 PM U8.4/W7.4

MEASUREMENTS OF SIZE SCALE EFFECTS IN LAYERED STRUCTURES. Ashraf Bastawros, Antonia Antoniou, Iowa State Univ, Dept of Aerospace Engineering and Engineering Mechanics, Ames, IA.

A novel experimental configuration is devised to measure the evolution of the deformation field and the corresponding toughness evolution within soft metallic films constrained by hard layers. The experimental configuration provides pure shear state within the constrained film. The material system utilized comprised ductile layer of Tin based solder, encapsulated within relatively hard copper shoulders. Different Tin-Lead compositions are tested with grain size approaching the film thickness. The in-plan strain distribution within the film layer is measured by a microscopic digital image correlation system. The toughness evolution within such highly gradient deformation field is monitored qualitatively through a 2D surface scan with a nano-indentor. The measurements showed a highly inhomogeneous deformation field within the film with discrete shear bands of concentrated strain. The localized shear bands showed long-range correlations of the order of 3-4 the grain size. A size-dependent macroscopic response on the layer thickness is observed. However, the corresponding film thickness is approximately 100-1000 times larger than those predicted by non-local continuum theories and discrete dislocation.

2:30 PM U8.5/W7.5

TWO BRANCH UNIVERSAL BINDING ENERGY RELATIONSHIP FOR RELAXED SURFACES. Robin L. Hayes, Emily A.A. Jarvis, Emily A. Carter, University of California, Los Angeles, Department of Chemistry and Biochemistry, Los Angeles, CA.

In 1983, Rose, Smith and Ferrante proposed a Universal Binding Energy Relationship (UBER) to describe the bonding between unrelaxed surfaces of many materials. Since then, UBER has been extensively used to represent cohesion between crack surfaces in continuum models. Unfortunately, the traditional UBER model is incapable of capturing the substantial reduction in surface energies often caused by surface relaxation. We ran a series of Density Functional Theory (DFT) calculations where we introduced a crack into a 3D periodic slab and allowed all the ions to relax. The energies of relaxed surfaces can be separated into two regimes: elastic and cracked. In the elastic regime, the introduced crack heals to form a uniformly expanded solid characterized by a chain of harmonic springs if the two surfaces are close enough for the electron density to bridge the gap. In the cracked regime, the traditional UBER functional form captures the correct behavior if the actual interplanar separation between relaxed surfaces is used and the energy is shifted to match the relaxed surface energy. Al and Al_2O_3 display extremely different mechanical behavior which provides a stringent test of the universality of our model. Specifically, (0001) α - Al_2O_3 is a brittle ceramic whose surface ions relax inward by nearly 1 Å, while (111) fcc Al is a ductile metal whose surface ions relax slightly outward by 0.1 Å. Both materials are well described by our 2-branch model. A Taylor expansion of the traditional UBER reveals that both harmonic and anharmonic terms are needed to fit DFT energies that should be purely harmonic. This leads to an artificially high elastic constant which produces errors if the traditional UBER is extrapolated to larger systems. Hysteresis arises from the nearly constant interplanar separation required for crack healing compared to the system size-dependent elastic behavior encountered prior to crack formation.

3:15 PM *U8.6/W7.6

APPLICATION OF A MODIFIED JOGGED-SCREW MODEL FOR CREEP OF TITANIUM ALLOYS AND TITANIUM ALUMINIDES. Subramanian Karthikeyan, Gopal B. Viswanathan and Michael J. Mills, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH.

Stress exponents for creep in the range of five are typically associated with dislocation creep processes, and a strong tendency for subgrain formation. This presentation will demonstrate that there are several important alloy systems that have similar stress dependence, and yet lack this tendency for subgrain formation. Specifically, dislocations in the intermetallic compound γ -TiAl and the hexagonal close packed α -phase of the commercial Ti alloy Ti-6242 tend to be homogeneously distributed with a tendency for alignment along screw orientation. In both alloy systems, the screw dislocations exhibit a large density of pinning points, which detailed transmission electron microscopy

investigation indicate are locations of tall jogs. These observations suggest that the jogged-screw model for creep should be appropriate after suitable modification for the presence of these tall jogs. A modified jogged-screw model has recently been developed as an alternative explanation for creep in these systems. The model parameters are all measurable from TEM experiments, and the model is shown to provide favorable prediction of the observed creep response for both γ -TiAl. This model has also been extended to treat the case of the lamellar microstructures that are common in both γ -TiAl and Ti-6242 alloy systems. A physical explanation for the formation of tall jogs is also described and the potential application of this modified model to other alloy systems is discussed.

3:45 PM U8.7/W7.7

NON-STICK AND SCRATCH RESISTANCE SOL-GEL COATING FOR ALUMINUM. Linda Y.L. Wu and S.K. Chang, Singapore Institute of Manufacturing Technology, SINGAPORE.

PTFE coating has been used for aluminum molds for molding of polystyrene packaging materials. However, this coating does not meet the users' requirements on scratch resistance and durability. Sol-gel technology allows the formation of a ceramic-like material at a lower temperature, which provides higher hardness and better scratch resistance for improved durability. This paper describes a study on the syntheses of a PTFE/SOL-GEL composite material. This coating material combines the desirable non-stick and low friction properties of PTFE filler with the high scratch resistance and durability of a silica-based, ceramic-filled sol-gel material. The influences of colloidal silica, PTFE, aluminum oxide and titanium oxide fillers on the coating's non-stick, friction and scratch properties are investigated. This sol-gel coating is applied to grit-blasted aluminum plates by spraying. The type of solvent used in the coating solution plays an important role in non-stick and friction properties, as well as in layer build-up and crack formation. We have found the optimum combination of fillers and solvent, which gives the maximum crack-free coating thickness. From which, a greatly improved scratch-resistant coating with non-stick and low-friction properties equal to those of PTFE coatings was obtained. The scratch resistance is twice that of the PTFE coating. To further improve the scratch resistance, the grit blasting process was replaced by an electro-chemical surface treatment. This treatment leaves a porous aluminum oxide layer, which allows the sol-gel material to penetrate into its regular micro-pores (130nm), resulting in strong mechanical interlocking. The adhesion between coating and substrate has been improved significantly relative to the normal grit blasting treatment. With this adhesion enhancement, the chipping problem of sol-gel coating was solved and the scratch resistance was increased by 4 times. FE-SEM/EDX, contact angle tester, scratch tester and a pin-on-disc tribometer are used in the evaluation of the coatings properties.

4:00 PM U8.8/W7.8

STRUCTURAL EVOLUTION AND ACOUSTIC PHONON BEHAVIOR IN CRYSTALLINE PtFe LATEX FILMS. Matteo Pierno, Carlo S. Casari, Andrea Li Bassi, Marco G. Beghi, Roberto Piazza, Carlo E. Bottani, INFN - Dipartimento di Ingegneria Nucleare, Politecnico di Milano, ITALY.

The surface and bulk structural evolution of polytetrafluoroethylene crystalline polymer latex films has been studied at a length scale of few hundreds nanometers by atomic force microscopy (AFM) and Brillouin light scattering. Controlling the sintering process we observed a transition from the original particle distribution towards a 'fibrillar' structure characterized by extended crystalline regions embedded in a disordered matrix, which still retains features of the original particulate structure. This transition has led to an observed cross-over from localized acoustic excitations to propagating acoustic phonons related with the mesoscopic elastic properties. The comparison with numerical simulations of the Brillouin scattering cross section shows that fully sintered films do not yet exhibit the dynamical properties of the equivalent compact elastic continuum. This is an evidence of the persisting 'mark' of the original particulate structure after sintering, suggesting that film formation for crystalline polymers may be analogous to sintering of ceramic powders. Brillouin spectroscopy of the latter systems is often difficult due to signal weakness. The formation of films of crystalline polymers can therefore be exploited as a model system to study the elasto-optical properties of granular and disordered media. New phenomenology is thus accessible, which is also relevant for the understanding of the sintering process of ceramic powders.

4:15 PM U8.9/W7.9

GENERALIZED QUASICONTINUA: AN APPROACH TO ATOMISTIC-CONTINUUM MODELING OF COMPLEX OXIDES. Anter El-Azab, Harold Trease, James Rustad, Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, WA.

A formalism of the quasicontinuum method suitable for atomistic-continuum modeling and nanoscale mechanics of oxide crystals with basis is presented. Multiple, interacting quasicontinua, one per sublattice, which overlap in the physical crystal space are used to model complex oxide crystals. The Cauchy-Born hypothesis, which connects atomic coordinates in distorted crystals to the imposed deformation gradient, is assumed to be valid for the individual quasicontinua. Based on a Delaunay triangulation of the crystal and associated interpolation functions, the Cauchy-Born hypothesis is used to derive self-consistent coarse graining of the atomic forces of individual sublattices. Computation of forces and energy, however, takes into account the interaction among atoms on all sublattices. The method thus can be viewed as a numerical implementation of the theory of inner elasticity of crystals with basis. In this presentation, we show predictions of the structure of hematite (Fe_2O_3) crystal with and without imposed crystal distortions and compare with lattice statics method. A shell-type interatomic potential is used which accounts for the polarization of oxygen ions. In this case, the atomic shells associated with every oxygen sublattice are treated as separate sublattices, which amounts to doubling of the oxygen quasicontinua. Applications of the generalized quasicontinuum method developed here to study problems of structure and nanoscale mechanics are also discussed.

4:30 PM U8.10/W7.10

AEROSOL DEPOSITION METHOD (ADM) FOR NANO-CRYSTAL CERAMICS COATING WITHOUT FIRING. Jun Akedo, Maxm Lebedev, Astushi Iwata, Hisato Ogiso, Shizuka Nakano, Inst. of Mechanical Systems Engineering, National Inst. of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

A novel method of ceramics coating based on a particle collision, named as aerosol deposition method (ADM), will be reported. Sub-micron ceramics particles were accelerated by gas flow in the nozzle up to velocity of several hundred m/s and ejected onto the substrate. During impactation and interaction with substrate, these particles formed thick (over $1\mu\text{m}$), dense, hard and transparent ceramics layers with high deposition ratio (2 - 30 $\mu\text{m}/\text{min}$). Depositions were fulfilled at room temperature. No additional procedure for solidifications is required. The results of fabrications, microstructure and mechanical properties of oxide (Al_2O_3 , YSZ, PZT etc), non-oxide materials and some composites will be presented. Hardness of PZT layer was 450 - 500 Hv, which is over that of bulk material. Hardness of Al_2O_3 layer formed at room temperature reaches 2000 Hv, which was measured by nano-indenter system and is comparable with that of bulk material. The adhesion force between the layer and the substrate was over 30 MPa. The microstructures were investigated by XRD and TEM. Every layer has polycrystalline structure with nano-meter order scale. Crystal systems of layers were same as those of starting powders. Reduction of crystallite size from sub-micron order (100 - 500 nm) to nanometer order (5 - 20 nm) was observed during collision of particles.

4:45 PM U8.11/W7.11

SYNTHESIS OF POLYMER/MESOPOROUS SILICA NANOCOMPOSITES WITH ENHANCED MECHANICAL PROPERTIES. Xiangling Ji, Eric Hampsey, Qingyuan Hu, Donghai Wang, Byron McCaughey, Xuan Li, Yunfeng Lu, Department of Chemical Engineering, Tulane University, New Orleans, LA; Weilie Zhou, Advanced Materials Research Institute, University of New Orleans, New Orleans, LA.

Organic/inorganic nanocomposites often show unique properties due to the synergies of both components. Here we report the synthesis and enhanced mechanical properties of poly((3-trimethoxysilyl)propyl methacrylate)-mesoporous silica nanocomposites. The synthesis approach involves infiltration and subsequent polymerization of the monomer (3-trimethoxysilyl)propyl methacrylate within mesoporous silica particles that are prepared using an aerosol-assisted surfactant-assembly process. Compared with poly((3-trimethoxysilyl)propyl methacrylate) polymer, as synthesized nanocomposites show a small decrease in tensile strain but significantly improved tensile strength, modulus, toughness, and thermal stability. Results from scanning electron microscopy (SEM) and other characterizations suggest that entanglement of the molecular chains formed within the mesoporous channels with those in the bulk polymer may attribute to the improved mechanical properties. Since conventional polymer/inorganic composites prepared using dense silica particles as fillers often result in an improved modulus but decreased toughness, this new approach provides a unique route to fabricate nanocomposites with both reinforcement and toughening.

SESSION U9: MODELING DEFORMATION IN
NANOMATERIALS

Chairs: Harriet H. Kung and Matthew R. Begley
Friday Morning, April 25, 2003
Metropolitan I (Argent)

8:30 AM *U9.1

HOW LOCAL SHEAR PLANES CAN CONTRIBUTE TO FRACTURE IN NANOCRYSTALLINE METALS. A. Hasnaoui, H. Van Swygenhoven, P.M. Derlet, Paul Scherrer Institut, Villigen-PSI, SWITZERLAND.

Large-scale molecular dynamics simulations are performed to study the deformation behaviour at 800K of fully 3D nc-fcc Ni. A large sample containing 125 grains with a mean grain size of 6nm was chosen to minimize the effect of imposed periodicity used to simulate bulk properties. During uniaxial tensile deformation collective grain motion occurred and shear planes that extend over a number of grains are formed. The observed underlying mechanisms for their formation falls into three classes: (1) pure GB sliding induced migration of GBs to form a single shear interface consisting of a number of co-linear GBs, (2) coalescence of neighbouring grains that have low angle GBs facilitated by the propagation of partials and subsequent reorientation of both grains (3) continuity of the shear plane by intragranular slip. It will be shown that the local shear planes can explain the dimple-like features observed experimentally in the fracture surface (Phys. Rev. B, 2002).

9:00 AM U9.2

MULTISCALE MODELING OF MECHANICAL RESPONSE OF NANOSTRUCTURES. Vinod K. Tewary and Bo Yang, National Institute of Standards and Technology, Materials Reliability Division, Boulder, CO.

The mechanical response of nanostructures is sensitive to its discrete atomistic structure as well as presence of surfaces and interfaces. The discreteness of the nanostructure is at subnanometer scale and has to be modeled by using lattice theory. The continuum model smears out the discreteness and is applicable at submicrometer scale. On the other hand, measurable parameters like elastic strains are essentially continuum model parameters. Moreover, the nanostructures are usually embedded in a matrix. The interaction between the free surfaces of the matrix and nanostructures is important in determining the mechanical behavior of the system. Hence a theory is needed that can bridge the length scales from subnanometers to submicrometers and model the nanostructures at the atomistic level along with the free surfaces in the matrix. We describe a computationally efficient multiscale Greens function method for modeling the mechanical response of nanostructures. The model accounts for the discrete atomistic structure in the nanostructure and, in the same formalism, treats the free surface of the matrix as a continuum which is justified unless the nanostructure is too close to the surface. Our theory relates the discrete lattice distortion at the atomistic scale in the nanostructure to measurable parameters of the continuum model and bridges the crucial length scales for modeling nanostructures. The method consists of writing the response of the matrix containing a nanostructure in terms of the anisotropic continuum Greens function for the matrix and Kanzaki forces. The Kanzaki forces account for the discrete atomistic nature of the nanostructure and are calculated by using the lattice statics Green's function for a crystallite containing a million atoms. As an example, we apply our method to calculate the strain due to quantum nanostructures of Ge in Si and their interaction with the free Si surface.

9:15 AM U9.3

MULTI-SCALE SIMULATIONS OF INTERFACIAL FRACTURE OF NANOSCALE THIN-FILM STRUCTURES: EFFECT OF LENGTH SCALES AND RESIDUAL STRESSES. Sven Strohband, Stanford University, Dept. of Mechanical Engineering, Stanford, CA; Reinhold Dauskardt, Stanford University, Dept. of Materials Science and Engineering, Stanford, CA.

Plasticity is a significant contributor to the interfacial fracture resistance of multilayer thin-film structures containing ductile layers. In this study we investigate the effect of local residual stresses and length scales on the fracture resistance of thin-film structures. The simulation procedure is multiscale in the sense that the simulation zone encompasses only a small region around the crack tip that includes the multiple layers of interest and the bulk of the sample is modeled using applied boundary conditions on that region. The salient parameters governing a range of contributions to interfacial fracture energy are considered. These include cohesive zone properties and plasticity energy dissipation in adjacent plastic layers. The effects of barrier layer thickness and elastic properties, ductile layer thickness, yield strength, intrinsic fracture energy, and the maximum cohesive stress governing interface separation are reported. Of significant concern for nanoscale structures is the effect of high

residual stresses on debonding with particular attention to the relationship between the stress state in both ductile and elastic layers and the resulting macroscopic debond energy. It is shown that residual thin-film stresses can alter plasticity in the ductile layer and significantly influence the macroscopic fracture energy. It should be noted that the change in fracture resistance is not a result of modification of the debond driving energy, but rather stems from alteration of the yielding process in the ductile layer due to the superposition of the crack tip fields and the local residual layer stress. This superposition significantly alters the onset of yielding which in turn affects the final size and shape of the plastic zone in the ductile layer. Implications for the fracture resistance of nanometer scale device structures is discussed.

9:30 AM U9.4

ATOMISTIC SIMULATION OF FLOW STRESS AND DISLOCATION-INTERFACE INTERACTION IN THIN METAL FILMS. Yu-Lin Shen and Efe S. Ege, Univ of New Mexico, Dept of Mechanical Engineering, Albuquerque, NM.

A significant part of the strength of thin metallic films attached to a stiff substrate is derived from the interface constraint. This is manifested by the high flow stress that can be carried by films on a substrate compared to the case of free-standing films. The substrate effect is typically reasoned from the energy approach involving the formation misfit dislocations at the film/substrate interface. However, there is a general lack of experimental evidence of misfit dislocations in recent electron microscopy examinations of polycrystalline aluminum and copper films. In this study we invoke atomistic modeling to provide a mechanistic rationale for the substrate effect in thin-film strength. Molecular statics simulations were carried out using the pair potential model for copper. The tensile stress-strain response is modeled for the free-standing and substrate-bonded films. It was found that the formation and glide of dislocations readily occur in the stretched free-standing film, inducing slip steps at both surfaces of the film. The existence of an interface with the substrate constrains the dislocation motion in the film and restricts the slip steps to only the free surface. The propensity of film plasticity is dictated by the capability of atoms to slide along the interface. The higher flow stress in the substrate-constrained film, compared to the free-standing film, can be correlated with the atomistic dislocation activities obtained from the simulation.

9:45 AM U9.5

THE EFFECTS OF GRAIN SIZE AND DISLOCATION SOURCE DENSITY ON THE STRENGTHENING BEHAVIOR OF POLYCRYSTALS. S.B. Biner and J.R. Morris, Metal and Ceramic Sciences, Ames Laboratory (USDOE), Iowa State University, Ames, IA.

In this study, the evolution of the flow stress for grain sizes ranging from about 11 to 0.5 μm under shear deformation was examined using two dimensional discrete dislocation dynamics. The grain boundaries were assumed to be both the only sources for nucleation of the dislocations and also the only obstacles to the dislocation motion. The analyses were confined to a single slip system within each grain with varying orientations respect to the slip system of neighboring grains. The simulations were carried out for two sets of system sizes. In the first set of simulations the grain morphology was kept constant and the simulation unit cell size varied from 25x25 to 2.5x2.5 μm . In the second set of simulations the simulation unit cell size was kept at 25x25 μm and the grain size was varied. For the grain size ranges considered, an inverse relationship between the grain size and 0.2% offset flow stress in the form of Hall-Petch relationship $[d]^{-1/2}$ was observed, although there is some uncertainty in the exponent. The evolution of flow stress follows a narrow band when expressed as a function of dislocation density divided by the dislocation source density and hence suggests a scaling with the grain size as seen in an earlier study. This work was performed for the United States Department of Energy by Iowa State University under contract W-7405-Eng-82. This research was supported by the Director of Energy Research, Office of Basic Sciences.

10:30 AM U9.6

PREDICTING THE MORPHOLOGY AND MECHANICAL PROPERTIES OF DIBLOCK /NANOROD COMPOSITES. Zhenyu Shou, Gavin A. Buxton and Anna C. Balazs, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA.

We couple a morphological study of a rod filled diblock copolymer with a micromechanical simulation to determine how the spatial distribution of the rods and the copolymer domains affects the mechanical behavior of the nanocomposite. The morphological studies are conducted through a hybrid approach that couples a self consistent field theory (SCF) for the diblocks with a density function theory (DFT) for the rods. Through these SCF/DFT calculations, we obtain the equilibrium morphology for the self assembled diblock/rod

mixture. The output of the SCF/DFT model serves as the input to the Lattice Spring Model (LSM), which consists of a three dimensional network of springs. In particular, the location of the different phases is mapped onto the LSM lattice and the appropriate force constants are assigned to the LSM sites. A stress is applied to the LSM lattice and we calculate the elastic response of the material. We find that the local stress and strain fields are highly dependent on the properties of the constituents and morphology of the system. By integrating the morphological and mechanical models, we can establish how choices made in the components affect the ultimate performance of the material.

10:45 AM U9.7

RELATIONSHIP BETWEEN THE MOLECULAR STRUCTURE AND THE MACROSCOPIC MECHANICAL BEHAVIOR OF POLYMER BASED NANOCOMPOSITES. Catalin Picu, Murat Ozmusul, Alireza Sarvestani, Dept of Mechanical Engineering, Rensselaer Polytechnic Institute, Troy, NY.

A generic polymer-based nanocomposite in which the polymer matrix is filled with spherical nanoparticles is analyzed. Monte Carlo simulations are performed to determine the polymer chain conformations and dynamics in the vicinity of the curved interface with the filler. The presence of the filler perturbs the polymer generating an "interaction zone" (IZ). The thickness of the IZ depends on the quantity being considered, for example, the IZ is one bond thick if one considers the polymer structure on the bond scale, about 2 gyration radii thick if the polymer structure on the chain scale is discussed, and is significantly thicker if one discusses chain dynamics. When the filler size decreases at constant filler volume fraction, the inter-filler distance decreases such that the whole polymer matrix is perturbed (IZ). Continuum models for the elasticity and viscoelasticity of the composite are derived based on the polymer structure in the IZ determined from atomistic simulations. The continuum models are then used to homogenize the composite on larger scales.

11:00 AM U9.8

THE BEHAVIOR OF NANOPARTICLE CHAIN AGGREGATES UNDER STRAIN - A MOLECULAR DYNAMICS APPROACH. Adamos S. Dalis, Sheldon K. Friedlander, Dept of Chemical Engineering, University of California in Los Angeles, Los Angeles, CA.

Nanoparticle chain aggregates serve as reinforcing fillers that are combined with molecular polymers to produce nano-composite materials, e.g. carbon black in rubber. The reinforcing mechanism due to the incorporation of nanoparticle aggregates is not well understood. Molecular dynamics computer simulations are employed to investigate the behavior of nanoparticle chain aggregates under strain. The interaction potential used is that of Cu obtained with the embedded atom method. Cu was selected as a test material because reliable forms of the interaction potential are available. Single crystal Cu nanoparticles are placed in contact in various configurations including linear and kinked and the structures are initially relaxed with molecular dynamics and/or Monte Carlo steps to establish an initial state. We observe plastic deformation during the sintering process for very small particles (3nm in diameter) at temperatures as low as 300K. The relaxed configurations are then strained to the breaking point at high strain rates (in the order of 1m/s), while the stress components are monitored. We identify mechanisms of strain accommodation such as interface sliding and dislocation gliding on the normal slip system of fcc Cu from the nanoparticle interface to the surface. The nanoparticle array configuration determines the dominant mechanism for plastic deformation.

11:15 AM U9.9

MECHANICS OF COMPRESSIVE STRESS EVOLUTION DURING THIN FILM GROWTH. P.R. Guduru, E. Chason, L.B. Freund, Division of Engineering, Brown University, Providence, RI.

Based on recent in-situ experiments, Chason et al. [1] proposed that the evolution of compressive stress during thin film growth is due to the increase in surface chemical potential in the presence of growth flux and the consequent exchange of adatoms between the free surface and the grain boundaries. Based on this hypothesis, we propose a model for grain boundary stress evolution during thin film growth. The calculations are carried out by solving the periodic wedge problem of Gao et al.[2], modified to account for growth flux. The adatom flux between the grain boundary and the free surface is assumed to be proportional to the difference in chemical potential between the two. These calculations successfully explain a wide range of experimental results, including the development of compressive stress during room temperature growth, effect of growth rate on the kinetics of compressive stress evolution and the continued tensile stress generation during low temperature growth. [1] Chason et al. (2002), Phys. Rev. Lett 88(15). [2] Gao et al. (1999), Acta Mater. 47(10), p.2865.

11:30 AM U9.10

GEOMETRICAL CONTRIBUTION TO YIELD STRENGTH IN SMALL VOLUMES. D.J. Dunstan and A.J. Bushby, Centre for Materials Research, Queen Mary, University of London, UNITED KINGDOM.

Relationships between size, strain gradients and plastic relaxation of stresses have long been proposed and have as long been experimentally ambiguous and theoretically controversial. The 'hardness size effect' has been the archetypal example of plastic deformation in small volumes, in which the resistance to plastic deformation increases as the size of the contact in an indentation test is reduced. In conventional plasticity theory with no length scale, this should not happen. The diverse experimental reports and the many theoretical attempts to explain the phenomenon have resulted in an extensive and often controversial literature. Here we show that the concept of critical thickness, familiar in strained-layer epitaxial growth, can be applied to predict a geometrical yield strength. We generalise the established theory of critical thickness for strained layers to show that there is an increase in the *initial yield stress* for geometrical reasons wherever there is a strain gradient. The theory accounts quantitatively, without free fitting parameters, for experimental data on the torsion of thin wires and the bending of thin beams. The geometrical yield strength arises because plastic relaxation is necessarily a cooperative phenomenon over some length scale.

11:45 AM U9.11

BENDING PROPERTIES OF CARBON NANOTUBES ENCAPSULATING SOLID NANOWIRES. D. Danailov, P. Koblinski and P.M. Ajayan, Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY; S. Nayak, Physics Department, Rensselaer Polytechnic Institute.

Using empirical potentials and atomistic simulations we model three-point bend tests of singlewalled carbon nanotubes encapsulating metal nanowires. The presence of a metal nanowire inside the nanotube greatly suppresses the tube-buckling instability. Increasing tube diameter leads to an increase in the bending strength; however in contrast to hollow tubes, there is no decrease of the maximum deflection before buckling. Analysis of the principal bending vibrational mode shows a lowering of the frequency, associated with increased tube inertia. Remarkably, metal filled tubes exhibit strong damping, whereas unfilled singlewalled and multiwalled tubes show no damping of oscillations. Our studies demonstrate benefits of filling tubes with solids for modifying the bending strength and flexibility suggesting implications for nanotube-based elements in micromechanical devices or nanopores.

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