

SYMPOSIUM Q

Q: Mechanical Properties of Nanostructured Materials and Nanocomposites

December 1 - 5, 2003

Chairs

R. Krishnamoorti

Dept. of Chemical Engineering
University of Houston
4800 Calhoun
Houston, TX 77204-4004
713-743-4312

E. Lavernia

College of Engineering
University of California-Davis
Davis, CA 95616
530-752-0554

I. Ovid'ko

Inst of Problems of Mechanical Engr. RAS
Bolshoj 61, Vas. Ostrov
St. Petersburg, 199178 RUSSIA
7-812-321-4764

C. S. Pande

Naval Research Laboratory
Code 6325
Washington, DC 20375
202-767-2744

G. Skandan

Nanopowder Enterprises, Inc.
Ste. 102/103
201 Circle Dr.
Piscataway, NJ 08854-3908
732-868-1906

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* Invited paper

8:30 AM *Q1.1

Mechanical Response of Nanostructured Materials: Critical Experiments and Models. Subra Suresh, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

This presentation will provide a summary of our recent work on deformation, damage evolution and failure in a variety of nanostructured metals and alloys prepared through different processing methods. Particular attention will be made to probe the effects of composition and processing route on the evolution of defects, damage and cracking. In-situ and ex-situ electron microscopy observations will be combined with detailed computational simulations to extract quantitative insights into the conditions governing the occurrence of different deformation mechanisms. Results of critical experiments dealing with the effects of grain size on the rate sensitivity of deformation, fracture toughness, fatigue crack growth and total fatigue life will be examined by comparing nanostructured metals with ultra-fine-crystalline and microcrystalline metals and alloys. Some overall strategies for optimizing strength, ductility and failure will also be highlighted on the basis of these critical experiments.

9:00 AM Q1.2

Direct Observations of the Transmission of Strain between Grains in Ultrafine-Grained Material. Andrew Minor², Erica Lilleodden^{1,2}, Eric Stach² and John William Morris^{1,2}; ¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California; ²materials science division, Lawrence Berkeley National Laboratory, Berkeley, California.

We have used a unique in situ nanoindentation stage in a transmission electron microscope to image and study the transmission of plastic deformation between grains in material of ultrafine grain size. Three mechanisms are observed: (1) the boundary moves as a whole, changing the volume of the original grain (normal displacement) or its shape (tangential displacement or sliding); (2) individual dislocations or groups of dislocation cross the boundary; (3) showers of dislocations emanate from the boundary into the adjacent grains. The mechanism that is dominant in a particular case depends on the material, the shape and state of the boundary and the local nature of the applied load. We shall document the mechanisms of strain transmission with real-time movies taken during in situ nanoindentation and discuss the metallurgical and microstructural criteria that appear to govern the choice of mechanism. The behavior of aluminum alloys and structural steels with various compositions and microstructures will be described.

9:15 AM Q1.3

Studies of Deformation and Fracture Behaviors in Electrodeposited Nanocrystalline Nickel-Iron Alloys. Hongqi Li and Fereshteh Ebrahimi; Materials Science and Engineering, University of Florida, Gainesville, Florida.

In this study, the deformation and fracture behaviors of electrodeposited nanocrystalline Ni-6%Fe and Ni-15%Fe alloys were investigated. The analysis of chemical composition was carried out using a microprobe. The line-broadening method was employed to calculate the average crystallite size from the XRD results. The grain size distribution was evaluated using the TEM technique. The tensile test of the dog-bone shaped specimens having a gauge length of 7 to 10mm was conducted within the strain-rate range of $5 \times 10^{-3} \text{ s}^{-1}$ to $5 \times 10^{-6} \text{ s}^{-1}$ at room temperature. Fracture surface and the necking geometry of the samples were examined using SEM. The nanocrystalline Ni-Fe deposits were produced under similar deposition parameters. However, increasing the iron content from 6% to 15% resulted in a decrease in the average grain size from approximately 55nm to approximately 11nm. The tensile strength of the Ni-6%Fe alloy was in the range of 950 to 1050 MPa. These samples fractured in a knife-edge behavior with a slanted fracture surface. Within and near the necked regions, the deformation bands were observed on the surface of the samples. Decreasing the strain rate resulted in a longer necked region with a higher density of deformation bands. These observations were consistent with the larger tensile elongations obtained at the lower strain-rates. The Ni-15% Fe samples, which had an average crystallite size of 11nm, showed noticeable plastic elongations as well as very high strengths (2.0 to 2.2 GPa). These samples failed in a rather brittle manner. In spite of the absence of apparent necking, high magnification SEM studies showed that fracture occurred by the formation of shallow microvoids. However, further investigation revealed the presence of deformation bands within a narrow region close to the fracture surface. In this

presentation the effects of grain size, grain size distribution and strain-rate on the deformation and fracture of nanocrystalline Ni-Fe alloys will be discussed. Keywords: Nanocrystalline, Ni-Fe alloys, Tensile test, Fracture, Strain rate.

9:30 AM Q1.4

Deformation of Electrodeposited Nanocrystalline Ni and Ni-based Alloys. Sharvan Kumar¹, Subra Suresh² and Joe A Horton³; ¹Division of Engineering, Brown University, Providence, Rhode Island; ²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Electrodeposited nanocrystalline Ni with grain sizes ranging from 25 nm to 1000 nm, and Ni-W and Ni-Fe alloys with average grain sizes of the order of 20 nm and 10 nm respectively have all been deformed in-situ in the TEM and their deformation response and fracture characteristics have been recorded. The as-deposited microstructures include a large number of growth twins and their possible role in affecting subsequent deformation will be discussed. Plastic deformation, mediated by slip, is noted at a global level in the large-grained material but diminishes to a local level in the finer-grained material and eventually to brittle failure in the 10-20 nm grain size range. Deformation twinning is observed in limited circumstances and its importance in influencing overall deformation prior to fracture is examined. Depending on grain size and hydrogen content, fracture path varies from transgranular dimpled rupture to brittle intergranular failure.

9:45 AM Q1.5

Grain Size Effects on the Fatigue and Fracture Behavior of Nanocrystalline Metals. Timothy Hanlon, Lubos Prchlik and Subra Suresh; Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The fatigue crack initiation and growth behavior of metals and alloys is known to be influenced significantly by grain size. Based on experimental results obtained from microcrystalline (mc) metals, with grain size typically larger than $1 \mu\text{m}$, it is widely recognized that an increase in grain size generally results in a reduction in the fatigue endurance limit. However, a coarser grain structure can also result in an increased fatigue threshold stress intensity factor range, as well as a decrease in the rate of fatigue crack propagation. The applicability and relevance of these trends, extracted from a wealth of experimental data obtained primarily on microcrystalline metals and alloys, to ultra-fine-crystalline (ufc) metals (grain size between 100 nm and $1 \mu\text{m}$) and nanocrystalline (nc) metals (grain size less than 100 nm) is relatively unknown. In particular, the fatigue response of nanocrystalline metals and alloys has remained largely unexplored. In this work, the fatigue and fracture behavior of electrodeposited, fully dense, nc pure Ni was studied. The fatigue response of nc Ni was also compared with that of ufc and mc Ni wherever appropriate. It was found that grain refinement to the nanocrystalline regime generally leads to an increase in resistance to failure under stress-controlled fatigue whereas a deleterious effect was seen on the resistance to fatigue crack growth. Similar experiments were performed on additional ufc material systems, produced using alternate processing techniques such as cryomilling or equal channel angular pressing, to explore the generality of the above trends.

10:30 AM *Q1.6

Microstructures and Mechanical Properties of Bulk Nanocrystalline Al-Mg Alloys For High Strength and Enhanced Toughness. Zonghoon Lee¹, David Witkin², Enrique Lavernia³ and Steven Nutt¹; ¹Department of Materials Science, University of Southern California, Los Angeles, California; ²Department of Chemical Engineering and Materials Science, University of California at Irvine, Irvine, California; ³Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California.

Two different types of bulk nanocrystalline Al-Mg alloys were investigated and compared. Firstly, we report microhardness measurements and anisotropic microstructures in an Al-7.5%Mg alloy produced by high pressure torsion (HPT) consolidation of pre-alloyed cryomilled powders. Consolidation of powders by HPT produced elongated nanocrystalline grains of $\sim 30 \text{ nm}$ width along the torsion direction and microhardness values over 3.5 GPa. The large increase in microhardness that derives from the nanocrystalline grains created by cryomilling will undoubtedly translate to higher yield and ultimate strengths. However, this may be accompanied by a marked loss in ductility, and will probably require some sacrifice in strength to achieve levels of toughness that are acceptable for practical applications. Secondly, multi-scaled (bimodal structured) Al-7.5%Mg alloys were prepared by blending of cryomilled nanocrystalline powder and unmilled coarse-grained Al-7.5%Mg powder, resulting in

extrusions with high strength, enhanced ductility and toughness. Al-7.5%Mg powders were cryomilled and combined with unmilled Al-7.5%Mg, then consolidated by hot isostatic pressing and extruded to produce bulk materials. The deliberate addition of unmilled powder produces a multi-scale microstructure by design. The matrix is nanostructured, containing grains 100-300 nm, while the elongated bands are coarse-grained aligned along the extrusion direction. Unlike other reports, the increased ductility and toughness arise from the addition of a coarser-grained fraction. This process demonstrates a new approach to designing and producing bulk nanocrystalline metals that exhibit a combination of high strength and enhanced ductility and toughness. Designing multi-scale structures with specific nano-scale phases, dimensions and morphologies enables us to optimize select combinations of properties.

11:00 AM Q1.7

Mechanical properties of a cryomilled nanostructured Al-Mg alloy. Bing Q. Han¹, Farghalli A. Mohamed², Clifford Bampton³ and Enrique J. Lavernia¹; ¹Univ. of California, Davis, Davis, California; ²Univ. of California, Irvine, Irvine, California; ³Rocketdyne Division, Boeing, Canoga Park, California.

A nanostructured Al-Mg alloy with grain sizes of approximately 100 nm was manufactured by a cryomilling process, which includes cryomilling, consolidation of cryomilled aluminum powders and extrusion. The tensile behavior at room and elevated temperatures as well as microstructural characteristics were investigated in the present study. Inspection of experimental results reveals that the cryomilled nanostructured Al-Mg alloy has a very stable microstructure and exceptional mechanical properties. The correlation among cryomilling processing, microstructural characteristics and mechanical properties was discussed.

11:15 AM Q1.8

Fatigue Crack Growth and Fracture Toughness in Bimodal Al 5083 Bulk Nanocrystalline Materials. Peter S. Pao, Harry N. Jones and Chia R. Feng; Code 6325, Naval Research Laboratory, Washington, District of Columbia.

The fatigue crack growth rates and fracture toughness of bulk nanocrystalline Al 5083 having a bimodal grain size distribution were investigated. The nanocrystalline particulates were prepared by mechanically ball milling spray atomized Al 5083 powders in liquid nitrogen. This nanocrystalline powder was blended with 50% spray atomized large grained Al 5083 powders. The blended powder was then degassed, consolidated by hot isostatic pressing, and extruded into rods. The bimodal Al 5083 thus produced consists of nanocrystalline grains and elongated coarse grain bands. While the yield strength of the bimodal Al 5083 is about 30% lower, its tensile ductility is almost double that of the all nanocrystalline Al 5083. In addition, the fracture toughness of the bimodal material is about 80% higher than that of the all nanocrystalline counterpart. Fatigue crack growth rates of bimodal Al 5083 are significantly lower than those of all nanocrystalline Al 5083. The higher fatigue crack growth rates in the all nanocrystalline Al 5083 may be attributed to the much smoother fracture surface morphology and lower roughness induced crack closure. The fracture toughness and fatigue crack growth response of the bimodal Al 5083 and the all nanocrystalline Al 5083 will be discussed in terms of the differences in underlying microstructure, texture, sharpness, and deformation mechanisms.

11:30 AM Q1.9

Processing and mechanical properties of nano-structured vanadium. Qiuming Wei¹, Tong Jiao¹, Kalia T Ramesh¹ and En Ma²; ¹Mechanical Engineering, The Johns Hopkins University, Baltimore, Maryland; ²Materials Science and Eng, The Johns Hopkins University, Baltimore, Maryland.

Our knowledge of the mechanical behavior of nano-structured materials is extremely limited at the present time. Much less has been known about the mechanical properties and the various factors that influence these properties in the case of nano-structured metals with bcc (body centered cubic) structures. Our previous work showed that consolidated nano-structured bcc iron deforms via shear banding under both quasi-static and dynamic loading (Q. Wei, D. Jia, E. Ma and K. T. Ramesh, Appl. Phys. Lett. 81, 1240-1242 (2002)). In this work, we have processed nano-structured vanadium, a bcc metal with a moderate melting temperature (2183 K) by high-energy ball milling followed by two-step consolidation. The temperature of the final hot-consolidation was monitored so that grain growth was restricted. We have characterized the microstructure of the consolidated, fully dense material using X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that the grain size of the consolidated V is around 100 nm. Mechanical properties of the nano-structured V were studied under both quasi-static loading and dynamic loading (Kolsky bar). To observe the deformation and failure

process, the side faces of the samples were polished to mirror finish, and a high-speed camera with the capability of capturing 100 million frames per second was used to record a movie of the specimen under dynamic loading. It was found that nano-structured V fails with cracks along the loading axis under quasi-static loading. Under dynamic loading, it fails in a very similar manner to that of metallic glasses, i.e., via shear banding.

11:45 AM Q1.10

Rate-Dependence and Cycle-Dependence of the Mechanical Response of Nanocrystalline Metals. Ruth Schwaiger, Benedikt Moser and Subra Suresh; Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Understanding the rate-dependence of deformation is vital to developing a comprehensive framework for the quantitative modeling of deformation and failure of nanocrystalline metals and alloys. In particular, two issues of fundamental and practical interest arise in the context of rate-dependence of nanocrystalline materials. 1. What is the effect of loading rate on the deformation response of nanocrystalline metals (with grain size typically less than 100 nm) and how does such response differ from that of conventional microcrystalline materials (with grain size typically larger than 1000 nm) and ultra-fine-crystalline metals (grain size in the range 100-1000 nm)? 2. When nanocrystalline metals and alloys are subjected to cyclic loads, what are the contributions to overall deformation and damage evolution from time-dependent and cycle-dependent mechanistic processes? We studied the influence of grain size on the rate dependence of deformation through a systematic series of critical experiments on two model systems, electrodeposited fully-dense ultra-fine crystalline (ufc) and nanocrystalline (nc) Ni with average grain sizes of 320 nm and 40 nm, respectively. Rate-dependence of deformation and damage evolution was studied by two independent experimental methods, namely depth-sensing indentation and tensile testing. Using nanoindentation the tested volume of material is scaleable with respect to the microstructure enabling us to obtain a better understanding of the relation between structure and properties. Nanocrystalline Ni was found to exhibit a positive strain-rate sensitivity in flow stress, an effect that was not found in ufc Ni. Fractography on tensile specimens revealed considerable local plastic deformation. A clear difference in fracture surface topography between high and low strain rate testing indicates a transition in deformation mechanism depending on the applied strain rate. Cyclic indentation was employed to explore the time-dependence and cycle-dependence of nanocrystalline metals subjected to repeated loading. The results of such experiments of cyclically indented nanocrystalline metals are also compared with those obtained from conventional fatigue tests.

SESSION Q2: Nanocomposites I
Chair: Chandra Pande
Monday Afternoon, December 1, 2003
Room 311 (Hynes)

1:30 PM *Q2.1

Improved Fracture Toughness and Superplasticity in Advanced Nanocrystalline Ceramic Composites. Joshua D. Kuntz, Guo-Dong Zhan and Amiya K. Mukherjee; Chemical Engineering & Materials Science, University of California, Davis, California.

Nanocrystalline materials have demonstrated very interesting changes in physical, chemical and mechanical properties at severely diminished length scales. This article focuses on the topic of nanocrystalline ceramic composites specifically designed for applications requiring improved fracture toughness and also improved superplastic properties. The difficulty in producing fully consolidated ceramic composites that retain a nanocrystalline structure is the main hurdle for thorough investigations in this area. This obstacle has been overcome in the current investigation through the use of a fast, comparably lower temperature, sintering technique e.g., Spark Plasma Sintering. Alumina based nanocomposites incorporating carbon nanotubes and additionally incorporating nanocrystalline niobium have yielded fracture toughness values that have exceeded that for pure nanocrystalline alumina by more than 300%. In another alumina-based three-phase nanocomposite, refinement of grain size produced a structural state where superplasticity can be realized at a temperature 350 K lower than what was reported previously. Details of microstructure and mechanistic interpretation will be presented to explain the experimental observations. This research is supported by grants from the U.S. Army Research Office (G-DAAD19-00-1-0185) with Dr. William Mullins as the Program Manager and from the U.S. Office of Naval Research (N00014-00-0186) with Dr. Lawrence Kabacoff as the Program Manager.

2:00 PM Q2.2

Mechanical Properties of Superhard Nanocomposites with a High Thermal Stability. Ali S. Argon² and Stan Veprek¹;

¹Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching/Munich, Germany; ²Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Massachusetts.

Superhard nanocomposites, nc-MnN/a-XxYy(M: transition metal that forms a stable, hard nitride (X: Si, B) with hardness of 40-100 Gpa are prepared by plasma CVD or PVD under a sufficiently high nitrogen activity and deposition temperature that allow the formation of a stable nanostructure by self-organization upon strong thermodynamically driven phase segregation. Few nanometer small MnN nanocrystals are "glued" together by a monolayer of thin non-metallic boron or silicon nitride. The correctness of the high value of the hardness was verified by calculating the hardness from the size of the remaining plastic indentation using a calibrated SEM. These nanocomposites display an extraordinary combination of a high hardness, high elastic recovery (up to 94%), high resistance against fracture by crack formation and tensile strength (measured by indentation at a scale of several microns) of 5 to 40 GPa which is approaching the ideal strength of flaw-free strong materials. These properties can be understood in terms of conventional fracture physics scaled down to a nanometer level of the small nanocrystals where crystal plasticity is absent and crack initiation requires a very high threshold stress. The interfacial monolayer of Si₃N₄ or BN with strong bonding to the nanocrystallites and high structural flexibility avoids grain boundary sliding. With increasing thickness of this interface the hardness decreases, possibly due to an increase of a liquid-like component. Upon indentation, these materials operate in a regime of strongly non-linear elasticity where the local inhomogeneous pressure enhancement of the elastic constants and, thus the plastic resistance have to be accounted for. Because the presently available FEM codes do not consider such dependencies they do not allow the required exact modeling for a deeper understanding of the form of plastic deformation of these materials. We shall discuss the possible mechanisms of strength and plastic flow semi-quantitatively.

2:15 PM Q2.3

Nanotube-Diamond Composites. Dieter M. Gruen¹ and Jeffrey W. Elam²; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Energy Systems Division, Argonne National Laboratory, Argonne, Illinois.

The synthesis both of nanotubes and of diamond films by chemical vapor deposition methods are by now well established techniques. The simultaneous synthesis of the "strongest" (nanotubes) and the "hardest" (diamond) substance to produce a composite material with potentially desirable properties had to our knowledge not previously been described. Theoretical calculations on diamond clusters [Ree et al, *Physica B*, **265**, 233 (1999)], on nanotubes [Park et al, *Phys. Rev. B*, **65**, 121405 (2002)] and on the growth of diamond by the carbon dimer molecule [Sternberg et al, *Phys. Rev. B*, **63**, 165414 (2001)] have elucidated the close energetic relationship between these two forms of carbon. Calculations extrapolated to cluster sizes between $\sim 10^3 - 10^4$ atoms, indicate that the heats of formation of nanotubes and diamond differ by only 1-2K cal/Mol. By adjusting conditions, it might then be possible to deposit nanotubes and diamond simultaneously for example by achieving kinetic control over the respective reaction rates. Essentially, one needs to achieve control over the growth rates of nanotubes and diamond independently to adjust the ratio of these two forms of carbon in the composite. It is well known that nanotube synthesis requires a transition metal catalyst such as Fe, Ni or Co. It occurred to one of us (DMG) that the concept of "distributed" catalysis might serve to control the overall rate of nanotube synthesis. A number of ways of achieving this came to mind all of them requiring in essence a non-uniform distribution of catalyst particles on the surface of a substrate. To demonstrate the viability of the concept, an experiment will be described in which the deposition conditions were typical of those used for the synthesis of ultrananocrystalline diamond (UNCD) films [Gruen, *Ann. Rev. Mat. Sci.*, **29**, 211, (1999)]. This involves chemical vapor deposition from a microwave plasma consisting of 1% CH₄ in 99% Ar. The substrate was SiC containing 0.4% Fe. Examination of the deposits showed continuous UNCD films with many nanotube (NT) inclusions. The NT/UNCD ratio increased with increasing temperature in the range 600 - 700°C. Representative SEM images will be shown and discussed. We believe that simultaneous NT and UNCD deposition has been achieved resulting in the creation of a composite material. The mechanical, electrical, and optical properties of the films need to be elucidated. *Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

2:30 PM Q2.4

Three Dimensional Atom Probe Microscopy of Ag-Cu

Nanocomposites Synthesized by Elevated Temperature High-Energy Ball Milling. Pascal M Bellon¹, Fang Wu¹, Dieter Isheim² and David N Seidman²; ¹Materials Science and Engineering, University of Illinois, Urbana, Illinois; ²Materials Science and Engineering, Northwestern University, Evanston, Illinois.

We present an atom probe (AP) study of nanostructured Ag-Cu powder material obtained by variable temperature ball-milling. This characterization is supplemented by using a wide variety of transmission electron microscopy techniques, and hardness of the various nanocomposites is measured by nanoindentation. This research demonstrates that by tuning the competition between thermally activated decomposition and forced mechanical mixing, it is possible to adjust the scale of nanocomposites, from about 2 to 30 nm in the Ag-Cu system. The three dimensional atom probe provides also unique information that challenges our current knowledge on the processes leading to forced atomic mixing in materials under intense plastic deformation Ag₅₀Cu₅₀ powders were ball milled in a SPEX 8000 shaker mill at temperatures ranging from ambient to 230°C, in a controlled argon atmosphere. Sharp tips suitable for atom probe field ion microscopy were prepared following the method we developed and tested on cryomilled powders [1]. Three dimensional reconstructions of atom distribution were obtained using an energy-compensated position-sensitive atom probe. Real-space analysis of the data was carried out using an in-house software, ADAM, which allows the construction of compositional histograms and of iso-concentration surfaces. Reciprocal-space analysis, performed by Fourier transforms of the atom maps, was used to determine quantitatively the scale of decomposition. This scale increased with the milling temperature, from about 2 nm at 120°C, to 8 nm at 180°C. Milling at 230°C leads to the dynamical recrystallization of the powders, resulting in much larger decomposition scale, typically 30 nm. The nano-hardness of these powders is found to increase with the milling temperature, from 5.3 GPa at 120°C to 5.9 GPa at 230°C. [1] Fang Wu, P. Bellon, T. Lusby, A. Melmed, *Acta Mater.*, **49**, 453 (2001).

2:45 PM Q2.5

Instrumented Indentation Technique of Laser Induced Fe-Oxide/Al Reaction Composite of Nanoscale. S Nayak¹,

Narendra B Dahotre^{1,2} and Laura Reister²; ¹University of Tennessee, Knoxville, Tennessee; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The surface layer of A319Al alloy is modified by selectively remelting by laser energy. Under similar laser parameter, A319Al alloy is surface modified by incorporating iron oxide. Iron oxide reacts readily with Al to form a reaction-composite. The iron oxide reacts with aluminum to form aluminum oxide and Al-aluminides. Also, a bulk composite was produced. Instrumented indentation technique is employed to measure mechanical properties of the laser-melted layer as well as reference bulk oxide/metallic composite. Berkovich tip was used to indent the material for 200nm, 500nm and 1000nm depths. The hardness, H and elastic modulus, E were found to be 1.22 GPa and 78.2 GPa respectively for 1000 nm indenter depths with minimal variance. The same for substrate possessed significant scattering. Also, the H and E stiffness increased with decreasing depth of indentation. Closer examinations suggested that when the heterogeneity in the material is in the scale of indentation depth, significant scattering takes place and the hard phase Si influence the average properties. Nanoindentation stiffness vs. depth data also revealed properties of individual phase in the multi-constituents composite material. The four point bend test results of the materials (coating/bulk) agrees with the indentation results.

3:30 PM *Q2.6

Bulk Composite Components Fabrication with Retained Nanostructure. Suresh C. Kuiry¹, Petya M. Georgieva¹, Keith E. Rea¹, Arvind Agarwal², Tim Mckechnie³, Scott O'Dell³ and Sudipta Seal¹; ¹AMPAC/MMAE, University of Central Florida, Orlando, Florida; ²Mechanical and Materials Engineering, Florida International University, Miami, Florida; ³Plasma Process Inc., Huntsville, Alabama.

Nanostructured materials exhibit enhanced mechanical, magnetic, electrical and optical properties. In order to realize the benefit of such novel properties, it is extremely important to consolidate nanostructured materials into bulk component maintaining the nanophase. The presence of nanophase in a composite matrix plays an important role towards enhancement of mechanical properties. However, the loss of nanoscale structure due to excessive grain growth during consolidation using the conventional techniques, remains a major problem. The present study summarizes the extensive research efforts towards successful development of bulk components with retained nanostructure in several systems with various combinations, such as metal/metal (Al-Si, W-Re), metal/ceramic (W/HfC, Ni/Al₂O₃, Al/Al₂O₃), and ceramic/ceramic (nano-Al₂O₃/micro-

Al₂O₃). Detailed results on the use of plasma forming technique to prepare bulk components with retained nanostructure in the aforementioned combinations are reported. The paper highlights the present status and future challenges for producing bulk nanostructured components.

4:00 PM Q2.7

The Temperature Dependent Damping Behaviors of VO₂ and ZnO Nanocomposites for Structural Material Applications. Ramazan Asmatulu, Rick O. Claus, Jeff B. Mecham and Dan Inman; FEORC, Virginia Tech, Blacksburg, Virginia.

Damping properties of materials are of great interest in applications of vibrating units for NASA, aircraft, and other transportation vehicle companies. It is known that at high vibration frequencies, crack propagation or other mechanical failures can occur and cause gross failure of the structure. Recently, our research has focused on the development of composites with nano-crystalline ferroelastic components to develop a new class of materials having temperature dependent damping properties, which can make the materials potentially ideal for airplane wings and other vehicles to damping performance. In the present studies, near nanoscale fine particles including VO₂, ZnO and SiO₂ were incorporated into polymer adhesives, and the obtained nanocomposites were applied as thin films between aluminum test coupons. A number of mechanical damping tests were conducted on the thin adhesively bound layers of the sandwiched Al substrates at frequency ranges of 0 - 2 kHz and over a broad temperature range. The mechanical vibration test results showed that VO₂ and ZnO gave significantly higher negative-stiffness (or damping) at approximately 68 C and 24 C; however, SiO₂ did not show the similar damping properties, which is the lack of the ferroelasticity of the later material. For example, approximately 15% and 12% damping values were achieved at first and second resonance frequencies, respectively, which can potentially prevent mechanical stresses on the materials when VO₂ was present. This significant improvement on the damping of the nanocomposite material may be attributed to the fact that the transformation of the ferroelastic materials occurs from monoclinic to tetragonal at those particular temperatures. It was also observed the etching of substrate surfaces improved adhesion and contributed consistent results to vibration testing reproducibility. As a result, it can be concluded that nanocomposite films containing ferroelastic materials can be an important method to achieve large damping responses over a broad temperature range.

4:15 PM *Q2.8

Structural stability of nano-clusters. Jeff T. De Hosson, Tomas Vystavel, George Palasantzas and Siete Koch; Applied Physics, University of Groningen, Groningen, Netherlands.

The growth of thin films by direct deposition of nanoclusters has attracted considerable interest, both from a fundamental and a technological point of view. The advantage of the method based on the gas aggregation technique is that well-adhered metallic films can be produced on a wide variety of substrates. In this paper transmission electron microscopy is employed for investigating the structural stability of nano-sized clusters (Cu, Fe, Nb, Co) as deposited and after in-situ annealing treatments under high vacuum conditions. Growth front aspects of the nanocluster films are investigated by atomic force microscopy. The rms roughness amplitude evolves with deposition time as a power law, leading also to a power law increase of the local surface slope. The scaling exponents point at a complex non-linear roughening mechanism. Annealing of Fe clusters, which are in contact, leads to their fusion and formation of larger clusters preserving their crystallographic structure. The truncated rhombic dodecahedron was found as the most probable shape of the Fe clusters, which differs from former theoretical predictions based on calculations of stable structural forms. Coalescence of Nb clusters does not occur even at the highest temperatures (8000C), which is attributed to the presence of facets and the occurrence of oxidation during heat treatment. It is observed that Co nano clusters directly in contact with the substrate are immobile, whereas clusters on top of other Co clusters can move during high temperature annealing to further coalesce. During coalescence of clusters of similar size (diameter ~40-60 nm), the clusters rearrange themselves in an arc shape area where a finite size neck is formed leading thereafter to full coalescence.

4:45 PM Q2.9

Toughening Mechanisms in Nanotube Reinforced Ceramic Composites. Zhenhai Xia¹, Brian W. Sheldon¹, Laura Riester², William A. Curtin¹, Hao Li¹, Jianyu Liang¹, Baohe Chang¹ and Jimmy Xu¹; ¹Division of Engineering, Brown University, Providence, Rhode Island; ²High Temperature Materials Lab, Oak Ridge National Lab, Oak Ridge, Tennessee.

Ceramic composite coatings were fabricated by growing multi-walled carbon nanotubes into a porous alumina. This template consists of

cylindrical, parallel pores in a highly ordered, hexagonal array. The resulting unidirectional nanotube reinforced composites are exceptionally well suited for investigations of mechanical properties. Nanoindentation demonstrates that these materials exhibit the same principle toughening mechanisms that are known to operate in more conventional ceramic composites, notably crack deflection, crack bridging, and nanotube pullout. Evidence of nanotube necking and buckling suggests that additional mechanisms may also contribute to the composite toughness. A detailed finite element model was developed to describe the deformation of the composite during nanoindentation. Applying this computational method to the data gives values for the axial Young's modulus of 200-570 GPa, depending on the nanotube geometry and quality. Several methods of altering the basic composite material were also investigated, including crystallization of the alumina matrix, annealing the carbon nanotubes, and converting the carbon nanotubes to silicon carbide.

SESSION Q3: Nanostructured Bulk Materials II

Chair: Thomas Tsakalakos

Tuesday Morning, December 2, 2003

Room 311 (Hynes)

8:30 AM *Q3.1

Testing Techniques for Mechanical Characterization of Nanostructured Materials. Carl C. Koch², r o scattergood², k l murty², r k guduru², g trichy² and k v rajulapati²; ¹Materials Science and Engineering, NCSU, Raleigh, North Carolina; ²Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ³Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Testing techniques for nanostructured materials will be described and discussed. In those cases where sufficient bulk material can be processed, as for example by electrodeposition, then the usual ASTM standard mechanical testing methods can be used. However, for many experimental nanostructured materials made by, for example, inert gas condensation, ball milling and powder compaction, high pressure torsion, or vapor deposition methods, the geometry and/or size of the available specimens requires non-standard test methods. This talk will describe the variety of mechanical testing methods that can be applied to small sample sizes. The measurement of elastic properties will be briefly reviewed. For nanostructured materials in the form of thin films, the primary mechanical testing probe is nanoindentation. Hardness has also been used for the majority of mechanical tests on nanostructured materials, especially in the earlier work in this field. In order to probe the mechanical behavior of nanostructured materials in more depth several non-standard methods which reveal plastic deformation properties include the miniaturized disk bend test (MDBT), the automated ball-indentation (ABI) test, and the shear punch test. Results from the authors' laboratory using these methods on both conventional grain size and nanostructured materials will be given. Reduced size tensile or compressive test samples have been used by a number of laboratories. Comparisons among the various test methods in terms of the mechanical properties of selected nanostructured metals will be presented. The authors' research is funded by the U.S. National Science Foundation under grant number DMR-0201474.

9:00 AM Q3.2

Recovery and Recrystallization Behavior of a Nanocrystalline Al-Mg Alloy Prepared by Cryogenic Ball Milling. Fei Zhou^{1,2}, Xiaozhou Liao³, Yuntian Zhu³ and Enrique Lavernia¹; ¹Chemical Engineering and Materials Science, University of California, Davis, Davis, California; ²Chemical Engineering and Materials Science, University of California, Irvine, Irvine, California; ³Division of Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico.

The recovery and recrystallization of a cryogenically ball milled Al-7.6 at% Mg alloy with a grain size of ~25 nm were studied using differential scanning calorimetry, x-ray diffraction and transmission electron microscopy. Recovery occurs during annealing from 100 to 230°C resulting in strain relaxation and grain coarsening, and recrystallization proceeds at higher temperatures up to about 370°C with further grain growth. The stored enthalpy release during recovery was estimated to be ~450 J/mol, which is considerably higher than that in Al processed by other known cold-working methods. The origin of the measured enthalpy was discussed in detail. Only a fraction of the measured enthalpy was found to arise from the enthalpy releases due to grain coarsening and the reduction of high dislocation density. Both recovery and recrystallization give rise to non-uniform, bimodal grain size distributions, which may result from heterogeneous nanostructures in the as-milled state. The detailed microscopic observations strongly support that grain coalescence is a feasible mechanism for grain coarsening during the recovery.

9:15 AM Q3.3

The Microstrain Generation in Cryomilled Nickel by Impurity Nitrogen Atoms, Kyung H Chung and Enrique J

Lavernia; Chemical Engineering and Materials Science, UC Davis, Davis, California.

The residual microstrains in cryomilled Ni, processed under various cryomilling conditions were examined by XRD and analyzed through the single line approximation (SLA) method. The average residual microstrains are determined to be in the range of $2 \times 10^{-3} \sim 6 \times 10^{-3}$. The measured microstrain is proposed to evolve from the presence of N and O as impurity atoms in the Ni lattice. N and O are introduced from the environment and then their solubility in Ni is enriched via the generation of defects that occurs during cryomilling. The stable site for N and O atoms in Ni is the octahedral site, and the size of N and O atoms exceed those of the octahedral site of Ni by 48 % and 16 %, respectively. Accordingly, a lattice strain field is expected around interstitial N atoms that are located at octahedral sites. By comparing the crystal structure around octahedral site, the stable site for impurity N atoms, in the Ni lattice with that of Ni₃N structure, the lattice strains are estimated to be in the range of 5 ~ 15 %. The result show that the (200) plane has strains that are two times higher than those in other planes, and this is argued to be the reason for the measured anisotropy of residual strain in Ni after cryomilling.

9:30 AM Q3.4

Relationships Between Nanostructures and High-Temperature Creep Properties of Al-Sc, Al-Sc-Mg, and Al-Sc-Zr Alloys. Emmanuelle A Marquis, Fuller B Fuller, David N Seidman and David C Dunand; Materials Science & Engineering, Northwestern University, Evanston, Illinois.

The room temperature strength and high temperature creep properties of Al-Sc, Al-Sc-Mg, and Al-Sc-Zr alloys in the temperature range 573 to 673 K, in parallel with the temporal evolution of their nanostructures, employing Vickers microhardness, and optical, scanning electron, transmission electron, high resolution electron, and 3D atom-probe microscopies. The nanostructures all consist of nanoscale coherent Al₃Sc (L12) precipitates, in equilibrium with a-Al (FCC); the volume fraction of Al₃Sc is <0.75 %. At high-temperatures all alloys exhibit a threshold stress for creep, which increases with increasing coherent Al₃Sc precipitate radius; the state of coherency is determined by transmission electron and high-resolution electron microscopies, thereby demonstrating that the interfaces are free of misfit dislocations for a mean radius, $\langle r \rangle$, <15 nm. The threshold stress for creep, normalized by the Orowan stress for dislocation looping, versus $\langle r \rangle$ data all lie on a single curve. An existing model (Marquis and Dunand, Scripta Materialia, 2002) for this curve, based on a climb-controlled bypass mechanism, is in semi-quantitative agreement with the $\langle r \rangle$ dependence of the threshold stress for all alloys. This climb model includes the elastic interactions of a dislocation with the stress field of a coherent Al₃Sc precipitate. Alternatively a general climb model without elastic interactions predicts that the threshold stress is independent of $\langle r \rangle$ and is therefore invalid. For semicoherent precipitates, with radii >15 nm, the threshold stress for creep remains high, most likely due to interfacial misfit dislocations. At room temperature the strength of the Al-Sc alloys is determined by shearing of the Al₃Sc precipitates for a $\langle r \rangle$ < 2 nm and by the Orowan dislocation looping mechanism for $\langle r \rangle$ > 2 nm. While for the Al-Sc-Mg alloy at room temperature the strength is controlled by solid-solution strengthening and shearing mechanisms for $\langle r \rangle$ < 2 nm and an Orowan dislocation looping mechanism for $\langle r \rangle$ > 2 nm. This research is supported by the Department of Energy, Basic Sciences Division.

9:45 AM Q3.5

Mechanical and Physical Properties of Bulk Ag-Cu Nanostructured Alloys Prepared by Slow Melt Quenching. Ricardo B. Schwarz, Tongde Shen and Manuel L. Lovato; MST-8, MS G755, Los Alamos National Laboratory, Los Alamos, New Mexico.

Nanocrystalline metals and alloys are expected to possess unique mechanical properties, such as a combination of high strength and ductility. However, industry has not yet taken advantage of these properties because high-quality nanocrystalline materials are difficult to prepare in bulk form. Bulk nanocrystalline materials have been prepared by electrodeposition but, with the exception of copper, these materials are brittle, most likely because of grain-boundary contaminants. Bulk nanocrystalline materials prepared by powder consolidation usually contain inter-granular voids, trapped gases, and other impurities that significantly degrade their mechanical properties. We have used a flux-melting and water-quenching method to prepare fully-dense 5-mm diameter Ag-Cu rods having crystal sizes of 50 nm. The mechanical (hardness, strength, ductility, strain hardening exponent, and strain-rate sensitivity) and physical (elastic moduli, thermal conductivity, electrical resistivity, and heat capacity)

properties have been investigated. The nanocrystalline Ag-Cu rods have a strength of 550 MPa in both tension and compression. In contrast, in most nanostructured materials prepared by powder consolidation the strength in tension is only 1/2 that in compression. Our Ag-Cu rods have an elongation to failure of ~ 10%, which greatly exceeds that of pure nanocrystalline Ag or Cu, both having similar crystal size to our alloy. In both tension and compression, the Ag-Cu alloy work hardens with a strain-hardening exponent of approximately 0.1, which is higher than that (~ 0) found in sub-micron-crystal-size nanocrystalline Cu prepared by severe deformation, but lower than that (0.22) found in electrodeposited nanocrystalline Cu. The electrical conductivity of our Ag-Cu rods is approximately 80% that of oxygen-free polycrystalline Cu.

10:30 AM *Q3.6

Meso-to-Nano-scopic Polycrystal/Composite Strengthening. Ronald W. Armstrong¹, Hans Conrad² and Frank R.N. Nabarro³;

¹Munitions Directorate, AFRL/MNME, Eglin Air Force Base, Florida; ²Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina; ³School of Physics, University of the Witwatersrand, Johannesburg, 2050, South Africa.

A great challenge associated with quantitative specification of the structural strength properties of nanometrically-scaled polycrystals and/or composite materials relates to connection of their measured or predicted mechanical behaviors with those microstructural, and larger, scale material deformation properties seemingly well-established during the past century [1]. The main issue is whether there is only a scale change to be applied to the same dislocation generation/interaction mechanisms operating within the grain volumes and grain boundary regions of the larger scaled materials. Here, the deduced indication, from graphically-displayed experimental results compiled on a Hall-Petch-(H-P)-type friction stress and dislocation stress intensity, k , basis, is that the mechanical property transition should be relatively smooth, even across boundaries between modeled differences in dislocation behaviors [2]. This is not to say, however, that the predicted connection of dislocation mechanisms will not be upset, possibly, by failure to achieve the demanding quantitiveness predictably needed for the finer-scaled materials of: (1) full structural characterization; (2) reliable mechanical testing; and, (3) detailed model computations. At nanoscale dimensions, the very significant influence on strength values of the different mechanism-based material parameters in the various constitutive equation descriptions shines-through and provides opportunity of clarifying conditions for any transition in grain boundary strengthening or weakening behaviors [3]. ----- 1. R.W. Armstrong, Plasticity: Grain Size Effects, Encyclopedia of Materials: Science and Technology (Elsevier Science Publishers, Oxford, UK, 2001) pp. 7103-7114. 2. H. Conrad, Grain Size Dependence of the Flow Stress of Metals from Millimeters to Nanometers, submitted for The Minerals, Metals and Materials Society (TMS) Armstrong Symposium, 2003, to be published in Metall. and Mater. Trans A. 3. F.R.N. Nabarro, Grain Size, Stress and Creep in Polycrystalline Solids, Soviet Physics - Solid State Physics, 42, 1417-1419 (2000).

11:00 AM Q3.7

Deformation and Failure Modes in Nanocrystalline Solids. Ilya Ovid'ko, Institute of Problems of Mechanical Engineering RAS, St. Petersburg, Russian Federation.

This presentation gives a brief overview of theoretical models of plastic deformation and failure processes in nanocrystalline (nano-grained) materials. Special attention is paid to theoretical models which describe the physical mechanisms - lattice dislocation slip, grain boundary sliding, grain boundary diffusional creep, triple junction diffusional creep, rotational deformation - of plastic flow in nanocrystalline materials with emphasis on competition and interaction between these deformation mechanisms (modes) and explanation of the key experimentally detected facts. Theoretical representations on failure processes in nanocrystalline materials are discussed which take into account the specific structural and behavioral features of these materials under mechanical load.

11:15 AM Q3.8

Phase Mixture Models for Metallic Materials with Submicrometer Scale Grain Size. Yuri Estrin, Hyoung Seop Kim and Mark B. Bush; Materials Engineering and Technology, Clausthal University of Technology, Clausthal-Zellerfeld, Germany.

Deformation behavior of ultrafine grained metallic materials will be discussed. A model that accounts for the salient features of strain hardening and ductility of face centered cubic metals will be presented. It is based on the notion that grain boundaries can be considered as a separate phase whose plastic flow is governed by a diffusion mechanism. A second phase, viz. the grain interiors, are considered to deform by a combination of dislocation glide and mass

transfer by diffusion. Experiments on Cu confirm the results of modelling with regard to strain hardening, as well as a trend to loss of room temperature ductility with decreasing grain size [1]. A second model to be presented was designed to describe microstructure refinement under severe plastic deformation. It is also based on the concept of a phase mixture, the phases this time being the dislocation cell walls and the cell interiors. Simulations of the evolution of the cell size and texture, and of the concomitant strength variation under equal channel angular pressing of Cu and Al are in good accord with experiment, which confirms the predictive capability of the model. References [1]. Y. Estrin, H.S. Kim and M.B. Bush, in: Encyclopedia of Nanoscience and Nanotechnology, H.S. Nalwa, Ed., American Scientific Publishers, 2003. [2]. S.C. Baik, H.J. Hellmig, Y. Estrin and H.S. Kim, Z. Metallkunde 94, 754-760 (2003). [3]. S.C. Baik, Y. Estrin, H.S. Kim and R.J. Hellmig, Mater. Sci. Eng. A351, 86-97 (2003).

11:30 AM Q3.9

Dislocation Confinement and Ultimate Strength in Nanoscale Polycrystals. Qizhen Li¹, Peter Hazzledine², Michael Mills¹ and Peter M. Anderson¹; ¹materials science and engineering, the Ohio State University, Columbus, Ohio; ²Wright-Patterson AFB, Dayton, Ohio.

In nanostructured polycrystals, hardness and strength are greatly enhanced compared to their microstructured counterparts. As grain size is decreased, Hall-Petch behavior is observed initially, and a plateau or softening of hardness and strength is exhibited frequently when grain size goes to nanoscale regime. We propose a dislocation-based model to explain this phenomenon. Dislocation nucleation and propagation is studied in a 2D hexagonal grain array, in which the dislocations can nucleate on grain boundaries or at triple junctions. During deformation, the resolved shear stress will activate selected sites with favorable dislocation content. At larger grain size, dislocations are predicted to nucleate and propagate on a confined grain-by-grain level. At smaller grain size, dislocation cannot be confined to an individual grain as they expand. Here, material strength shows a plateau that is independent of grain size.

11:45 AM Q3.10

Computation of Mechanical Properties of Nanostructured Materials. Petya Georgieva^{1,2,3}, Sudipta Seal^{1,2,3} and Suresh Kuiry^{1,2,3}; ¹AMPAC and MMAE, University of Central Florida, Orlando, Florida; ²AMPAC and MMAE, University of Central Florida, Orlando, Florida; ³AMPAC and MMAE, University of Central Florida, Orlando, Florida.

Nanostructured materials exhibit enhanced mechanical, magnetic, electrical and optical properties. The grain size and the presence of metallic nanoparticles as a second phase in a ceramic matrix play important roles in enhancing the mechanical properties and fracture toughness of any nanocomposite system. The aim of the present study was to investigate the mechanical properties of the Ni/alumina nanocomposite system. Preliminary computation considering the roles of grain boundary diffusion, triple junctions, and dislocation pile-up in the nanometer domain grain size was carried out, which help pinpointing the applicability of Hall-Petch and inverse Hall-Petch relations for evaluating the mechanical properties of metal-ceramic nanocomposite. The outcome of the investigation is expected to be a valuable tool in designing bulk nanocomposite components comprising of metallic nanoparticles in ceramic matrix.

SESSION Q4: Nanocomposites II
Chairs: Ramanan Krishnamoorti and Ganesh Skandan
Tuesday Afternoon, December 2, 2003
Room 311 (Hynes)

1:30 PM *Q4.1

Mechanical Properties of Nanocomposites. Thomas Tsakalakos¹, Richard Lehman¹, Thomas Nosker¹, Jim Idol¹, Richard Renfree¹, Ken Van Ness², Steve Wolbach¹ and Jennifer Lynch¹; ¹Cer. & Mat. Engineering, Rutgers University, Piscataway, New Jersey; ²Engineering Physics, Washington and Lee University, Lexington, Virginia.

In immiscible polymer blend materials (IMPB) we observed melt domains in the nanoscale range with very large aspect ratios capable of being generated by manipulating shear rate, temperature and viscosity during melt processing and by selecting the polymer pair to conform to the requisite viscosity/volume fraction relationship. Properties of IMPB have recently shown remarkable enhancements. Nanotechnology of dispersion of nanoparticles in IMPB has also been found to be critical component in fabricating nanocomposites of extraordinary structural and functional performance. Among the various methods that are currently used are functionalization techniques such as coating of nanoparticles with proper material in

order to maximize homogeneity of dispersed nanoparticles in the polymer matrix. Al₂O₃/TiO₂ and other ceramic nanoparticle PMMA/PC nanocomposites will be discussed. The mechanical properties of a nanocomposite consisting of 5wt% ceramic (87:13wt% Al₂O₃:TiO₂) in polymethylmethacrylate (PMMA) were investigated. In this paper, the adhesion and dispersion of functionalized nanoparticles were examined. The dispersion of the ceramic in the PMMA matrix proved to be more effective than that of adhesion. By proper dispersion, translucent non-porous nanocomposites with increased toughness, strength, hardness, and scratch resistance were fabricated with high reproducibility. Other systems will be reviewed with emphasis on mechanical and magnetic properties. We gratefully acknowledge the support of AMIPP.

2:00 PM Q4.2

An Explicit 3D Chain and Node Mesoscale Network Model for Silica-filled Polydimethylsiloxane. David Edward Hanson, Theoretical Division, Los Alamos National Lab, Los Alamos, New Mexico.

We present a numerical mesoscale model that describes the stress/strain properties of a mesoscale volume element of silica-filled polydimethylsiloxane (PDMS) under tensile or compressive strain. An explicit 3D network, composed of randomly dispersed nodes (filler particles), multiply connected by a large number of chains (PDMS polymers), is strained by an affine transformation. The resulting macroscopic stress is computed by summing the chain tensile forces over free surfaces of the volume element. The non-entropic forces used in the model are computed from atomistic simulations of individual chains for two cases: chains undergoing extension from a nutured initial state, or a chain interacting with a hydroxylated silica surface. The forces are computed from changes in the internal energy as a function of the end position of the chain. The distribution of chain lengths of the interparticle connecting segments and free ends are assumed to be Gaussian. The model is validated by comparison of the predicted stress/strain behavior to experimental data.

2:15 PM Q4.3

Static Uniaxial Compression of Polyisoprene-Montmorillonite Nanocomposites Monitored by ¹H Spin-Lattice Relaxation Time Constants. G. Michelle Poliskie¹, R E Cohen² and K K Gleason²; ¹Material Science and Engineering, MIT, Cambridge, Massachusetts; ²Chemical Engineering, MIT, Cambridge, Massachusetts.

Increases in the surface area of Cloisite[®] clay in cis 1,4-polyisoprene nanocomposites were monitored during uniaxial compression. Uniaxial compression was performed using a novel compression device, which allowed for acquisition of either magic angle spinning or static spectra. Interaction of the Fe⁺³ in the clay with the polymer decreases the polymer's ¹H spin-lattice relaxation time constant (T₁). An increase in the surface area of the clay platelets has been observed by a decrease in the polymer's T₁ with successive amounts of strain. Furthermore, the observation of these changes with ¹H NMR is limited by the dispersion of the clay. The clay clumped together to form large micron clusters when using both unmodified Cloisite[®], Na⁺, and Cloisite[®] modified with a polar surfactant, methyl, tallow, bis-2-hydroxyethyl quaternary ammonium. For the nanocomposite containing Na⁺ exchanged clay the polymer's ¹H T₁ decreases by .5 s at 40% strain. Likewise when using the methyl, tallow, bis-2-hydroxyethyl quaternary ammonium exchanged clay, the polymer's ¹H T₁ decreased by .4 s at 40% strain. This corresponds to a 20% and 14% increase in the clay's surface area, respectively. Nonpolar surfactants, such as dimethyl, dehydrogenated tallow quaternary ammonium and dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium, allowed for dispersion on a nanoscale and showed no strain induced change in surface area. When the polymer matrix was crosslinked no change in surface area could be observed regardless of the surfactant employed.

2:30 PM Q4.4

Mechanical properties and filler distribution as a function of filler content in fumed silica filled PDMS samples. Marilyn Emily Hawley¹, Debra A. Wroblewski¹, E. Bruce Orler¹, Robert Houlton J. Houlton¹, Kiran E. Chitanvis¹, Geoffrey W. Brown¹ and David E. Hanson²; ¹Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Theoretical, Los Alamos National Laboratory, Los Alamos, New Mexico.

Using both atomic force microscopy (AFM) phase imaging and tensile stress-strain measurements, we studied a series of model fumed silica filled polydimethylsiloxane (PDMS) samples that varied in filler content from zero to 50 parts per hundred (phr) to determine the relationship between filler content and stress-strain properties. A

speedmixer was used to disperse the filler. Samples were compression molded. Samples with zero, 20, 35, and 50 phr filler were examined by AFM phase imaging to determine filler size and distribution. 35phr was found to give the best mechanical properties. A small tensile stage designed to fit in the AFM stage, was used to measure mechanical properties. Samples were not pulled to break in order to study Mullins and aging effects. In the latter case, four dog-bone shaped specimens, cut from the same sample containing 35phr filler, were pulled the same day. One each was then pulled at one-week intervals up to 4 weeks then compared to initial results to determine the degree to which these samples recovered their initial stress-strain behavior as a function of time. One of the sample was pulled again after 26 weeks. In addition, a similar sample was tested before and after heat treatment to determine if heating accelerated recovery of the stress-strain behavior. A clear Mullins effect was seen and mechanical properties were optimum at 35 phr. Within experimental error, no change was seen in mechanical behavior as a function of time or heat-treatment. Finally, a permanent set of about 3 to 6 percent was observed for the 35phr samples.

2:45 PM Q4.5

Viscoelastic properties of Alumina/PMMA nanocomposites - relaxation spectra. Amitabh Bansal¹, B. J. Ash², L. S. Schadler¹ and L. C. Brinson³, ¹Department of Materials Science and Engineering & Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; ²Sandia National Laboratories, Albuquerque, New Mexico; ³Department of Mechanical Engineering, Northwestern University, Evanston, Illinois.

Polymethylmethacrylate (PMMA) nanocomposites were prepared by free radical polymerization of methylmethacrylate in the presence of alumina nanoparticles. At an optimum filler content, the resulting composites display a room temperature brittle-to-ductile transition showing increases in the strain-to-failure of more than 1000%. Concurrently, the glass transition temperature (T_g) drops from 119 °C for the neat PMMA to 95 °C at low filler concentrations. The changes in the thermal behavior are thought to be due to a highly mobile fraction of PMMA which has been confirmed by ²H NMR. Developing a further understanding of these novel behaviors, we measured the viscoelastic properties of the nanocomposites using dynamic mechanical analysis (DMA). Relaxation spectra calculations using a Prony series approximation of the Maxwell model are consistent with the drop in T_g . The relaxation spectra for nanocomposites with altered T_g : (a) shift by five orders of magnitude for two filler sizes - 17nm and 39nm indicating similar increases in mobility of polymer chains and (b) shift without change in shape indicating an unbiased increase in mobility for all segments. Follow-on investigations into the effects of particle size, using monodisperse particles, and particle/polymer interface conditions on this behavior are ongoing.

3:30 PM Q4.6

Rubber Toughened Epoxy Nanocomposites: Mechanical Properties. Balakrishnan Subramanian and Dharmaraj Raghavan; Chemistry, Howard University, Washington, DC, District of Columbia.

The technology to toughen a highly crosslinked epoxy resin without undue sacrifice in the desirable mechanical properties of resin by the addition of elastomeric particles is well known. In this regard, the use of preformed rubber particle in epoxy resin has been shown to have distinct benefits in controlling the morphology of rubber dispersants and the overall toughness of rubber dispersed epoxy resin. On the other hand, the loading of nanoclay platelets in epoxy resin lead to improvement in stiffness and often does not dramatically influence the toughness of nanocomposite. It would be highly desirable if the improvement in the toughness of rubber dispersed epoxy matrix can be translated to improvement in the overall mechanical properties of nanoclay filled rubber dispersed nanocomposite. Our objective is to investigate the role of rubber dispersed epoxy resin as matrix material in the formulation of toughened nanocomposite. The octadecyl ammonium ion exchanged clay and preformed rubber dispersed in epoxy along with epoxy resin was allowed to swell with a small amount of swelling agent, tetrahydrofuran (THF). The mixture was subjected to sonication using sonic dismembrator and was placed in vacuum oven at 60 °C for 5h to remove remnants of THF. The morphology of clay platelets and mechanical properties of cured nanocomposite sample was examined using XRD and TEM, and tensile testing apparatus, respectively. Rubber toughened epoxy nanocomposites showed synergistic effect of rubber toughening and stiffness improvement due to clay addition, on the overall tensile properties compared to that of pristine epoxy resin. Acknowledgment : This project is funded by AFOSR

3:45 PM Q4.7

An Intermediate TCE Nanocomposite Coating for Thermal Barrier Coatings. Otto J Gregory¹, Markus A Downey¹, Steven P

Wnuk² and Vincent Wnuk²; ¹Chemical Engineering, University of Rhode Island, Kingston, Rhode Island; ²HITEC Products, Inc., Ayer, Massachusetts.

Thermal barrier coatings (TBC/s) are widely used to protect metallic components in gas turbine engines from the high temperature combustion gases. Failure at the substrate-bond coat interface in TBC/s by decohesion can occur due to large thermal stresses induced by a mismatch in the thermal expansion coefficients (TCE) between the metallic bond coat and ceramic top coat. Recent research indicates that peaks and valleys associated with the rough surfaces of thermally sprayed bond coats can act as stress concentrators and initiation sites for microcracks. A viable solution is the addition of an intermediate TCE coating comprised of NiCoCrAlY and alumina. This intermediate TCE coating would have three advantages: first, the coating would have thermal expansion properties somewhere between those of NiCoCrAlY and alumina; second, the coating would improve adhesion by effectively infilling the valleys of the thermal-sprayed bond coat and third the coating would form an effective seed layer for the thermal sprayed ceramic overcoat. However, for such a coating to be successful, the particle size of the intermediate coat has to be smaller than the peak to valley distance at the bond coat top coat interface, which is typically 3-10 μm . Physical vapor deposition processes such as sputtering, would satisfy this criteria due to the nanoscale particles attainable with non-equilibrium, low temperature processes. Therefore, to screen a large number of different sputtering compositions that would satisfy the criteria, a combinatorial chemistry approach was taken whereby nanocomposite coatings were prepared by co-sputtering from two different targets. Inconel 718 substrates were sprayed with NiCoCrAlY bond coats and masked to form well-defined combinatorial libraries. The substrates were then placed between a NiCoCrAlY target and an alumina target and the composition of each combinatorial library was dependent on the position relative to each target. A ceramic top coat was then thermally sprayed over each combinatorial library and thermally fatigued in a computer-controlled burner rig. The fatigue life of each of the combinatorial libraries was measured in terms of cycles to failure, with each surviving between 7 and 99 cycles. The composition of the combinatorial library with the longest fatigue life was determined by SEM equipped with EDS. An optimal composition of 60 wt% alumina and 40 wt% NiCoCrAlY was established for this library. A sputtering target of this composition was fabricated by thermal spraying a mechanical mixture of metallic and ceramic powders onto a stainless steel backing plate and an intermediate TCE coating was sputtered onto thermally sprayed NiCoCrAlY. The bond coated Inconel 718 substrates complete with intermediate TCE coating were sprayed with alumina and thermally fatigued. The fatigue life of TBC/s prepared in this manner was more than tripled in burner rig tests.

4:00 PM Q4.8

Characterization of Strain-Tolerant Ceramic/SAM Bilayer Coatings. Quan Yang¹, Tolulope O. Salami², Kaustubh Chitre¹,

Hungcheng Lu¹, Scott R. J. Oliver² and Junghyun Cho¹; ¹Mechanical Engineering, State University of New York, Binghamton, New York; ²Chemistry, State University of New York, Binghamton, New York.

Ceramic coatings can provide an ideal protection for MEMS structures while imposing a great challenge in processing a prime, reliant coating due to their inherent brittleness and defects formed during processing. In an attempt to compensate for the weakness of the ceramic coating, we have developed a low-temperature solution precursor process of creating strain-tolerant, protective bilayer coatings. The bilayer consists of an integrated ceramic-organic hybrid material. The top ceramic coating (e.g., ZrO₂, YSZ, Al₂O₃) offers an inert, protective layer. At the same time, the underlying nanometer scale organic coating, fabricated by the self-assembly, provides compliance for the overlying hard coating upon mechanical and thermal stresses. In addition, these organic self-assembled monolayers (SAMs) act as a 'template' by forming a proper surface functionality for the subsequent growth of hard ceramic coatings. Molecular level understanding of the microstructure and micromechanics involved in the synthesis and processing of the coating is systematically studied by a variety of characterization techniques, such as XRD, AFM, electron microscopes and nanoindentation. This work is also complemented by numerical simulation to have a clearer understanding of the stress development in the ceramic coating and its interfacial properties. The combined analyses are used to better understand certain experimental observations, and also to guide a development of the micromechanics model for the strain-tolerant bilayer coating system.

4:15 PM Q4.9

Mechanical Properties of Nano-Composites by Simulation. Suchira Sen¹, Pawel Koblinski² and Sanat Kumar¹; ¹Chemical Engg., Rensselaer Polytechnic Institute, Troy, New York; ²Materials Science and Engg., Rensselaer Polytechnic Institute, Troy, New York.

Mechanical properties of nano-composite polymer melts are studied using equilibrium Molecular Dynamics simulations. We simulate melts beyond their entanglement threshold, and the nano-particles were idealized as spheres interacting through the Lennard Jones potential. The polymer-particle interaction studied was purely attractive. Several systems with attraction varying from weakly attractive to strongly attractive systems are studied to gain insight on how this interaction affects the mechanical properties. The zero-shear rate viscosity show significant increases over the neat system and it increases with increasing attraction between the polymer-particles. The relaxation modulus computation from the viscosity also exhibits increasing mechanical reinforcement of the composites. We offer some explanation of the observations as the effect of various factors acting in tandem, e.g. reduced mobility of all entities, and increased packing of polymers around particles causing local glassy states, and the formation of polymer bridges.

4:30 PM Q4.10

Effect of nm-Thin inorganic Layered Fillers on the Crystallization of Polymers. Evangelos Manias, Materials Science & Engineering, Penn State University, University Park, Pennsylvania.

The crystallization behavior of polymers in nanocomposites with inorganic fillers (montmorillonite layered silicate, MMT) will be presented. Three different polymers will be comparatively discussed [poly(vinyl alcohol) (PVA), syndiotactic-polystyrene (sPS), and poly(ethylene oxide) (PEO)] representing three types of filler/matrix interactions: strong specific interactions (PVA/MMT), weak/negligible interactions (sPS/o-MMT), and "unfavorable" (PEO/MMT). In the case of PVA/MMT, crystallization of PVA is strongly promoted by MMT, also stabilizing a new crystal form not found in bulk PVA. For sPS/o-MMT, crystallization is only moderately affected, exhibiting traces of simple heterogeneous nucleation and mostly bulk-like crystal structures, with very small traces on non-bulk crystals. For PEO, crystallization is impeded near the MMT surfaces, due to coordination of the surface cations to the PEO. In all cases smaller spherulite sizes develop when filler is added, independent of the size of the bulk polymer spherulites, whereas the crystallization temperature changes reflect the strength of the polymer/surface interactions.

4:45 PM Q4.11

Friction and Wear Characteristics of Inorganic Particle Filled Polymer Nanocomposites. Praveen Bhimaraj¹, Richard W.

Siegel¹, Linda S. Schadler¹, Kevin Freudenberg², Jason Action², Gregory W. Sawyer² and Greg Toney³; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Mechanical and Aerospace Engineering, University of Florida, Gainesville, New York; ³Albany International Research Corporation, Mansfield, Massachusetts.

The tribological properties of composites of poly(ethylene) terephthalate filled with inorganic nanofillers will be presented. Results show that the addition of nanofillers increases the wear resistance by as much as 45%. Simultaneously, the friction coefficient decreases by 24%. The improvement in friction and wear characteristics is attributed to a change in polymer matrix properties as well as an enhancement in the self-lubrication character of the composite. Wear tests on iso-crystalline samples coupled with study of the test counterfaces reveal the importance of the transfer film. In addition, the role of filler size (ranging from 17nm to 12 microns) will be highlighted. The effect of a compatibilized interface between filler and matrix will also be reported.

SESSION Q5: Poster Session
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

Q5.1

Abstract Withdrawn

Q5.2

Size-induced Tetragonal to Monoclinic Phase Transition in Zirconia Nanocrystals. Gianguido Baldinozzi¹, David Simeone^{2,1}, Dominique Gosset², Michael Duthel² and Jan Kusinski^{3,1}; ¹SPMS, CNRS-Ecole Centrale Paris, Chatenay-Malabry, France; ²SRMA, CEA Saclay, Gif-sur-Yvette, France; ³Academy of Mining and Metallurgy, AGH, Krakow, Poland.

High resolution neutron powder diffraction experiments at several temperatures allow to monitor the uniaxial strain and the phase transition as a function of the size of zirconia nanoparticles. The tetragonal structure observed in the nanocrystals is identical to the

one usually observed in micrometric zirconia crystals above 1400 K. The phase transition occurs above a threshold crystal size. These results are discussed within the Landau formalism and they can be understood as a mechanism of size-dependent phase transition where the primary order parameter is altered by the nanoparticle size.

Q5.3

Superplastic Flow Localization in Nano- and Fine-grained Materials. Sergey Bobylev, Mikhail Gutkin, Ilya Ovid'ko and Nikolai Skiba; Institute of Problems of Mechanical Engineering RAS, St. Petersburg, Russian Federation.

A theoretical model is suggested which describes the experimentally detected phenomenon of superplastic flow localization in nanocrystalline materials. In the framework of the model, the deformation localization is related to such deformation-induced structural transformations as decay of low-angle boundaries and migration of triple junctions of grain boundaries. With representations of the model, dependences of the yield stress on parameters characterizing the ensembles of grain boundaries, their triple junctions and plastic strain degree are revealed. The results of the model account for experimental data from mechanically loaded nanocrystalline materials, reported in the literature.

Q5.4

In-situ Profile Analysis at the Swiss Light Source: A New Non-destructive Technique to Study Deformation Processes. Zeljka Budrovic, Helena Van Swygenhoven and Peter M Derlet; Paul Scherrer Institute, PSI-Villigen, Switzerland.

A new way to follow the microstructural evolution during deformation has been developed at the Swiss Light Source. The high intensity and the use of a microstrip detector covering a diffraction angle of 40 degrees with an angular resolution of 0.0037 degrees allow to study in-situ the X-ray diffraction profile during straining. A miniaturized tensile machine in which dogbones with several gauge dimensions can be deformed, is mounted on the goniometer of the beamline. The broadening and position of the peaks is followed dynamically, providing information on limitations in the spatial extent of the coherent scattering volumes (in our case the grain size), inhomogeneous strain (coming from dislocations, GB dislocations, triple junctions etc), twinning and faulting. It is shown that information on the peak broadening during loading, unloading and relaxation of the samples provide invaluable information on the deformation processes acting in bulk samples.

Q5.5

Microstrain effect on tensile properties of nanocrystalline Cu. Lei Lu, S.X. Li and K. Lu; Shenyang national laboratory for materials science, Institute of Metal Research, CAS, Shenyang, China.

The nanocrystalline (nc) Cu samples with different levels of microstrain but the same grain size were obtained by cold rolling an electrodeposited nc Cu specimen. Tensile tests show that with an increment of microstrain from 0.03% to 0.14%, the yield strength of the nc Cu sample increases from 94 MPa to 425 MPa, but the ductility decreases from 30% to 1.3%. The effect of microstrain on tensile properties in nc Cu sample might be attributed to the change in the densities of dislocation at the grain boundary or the grain boundary energies. This investigation demonstrates that the mechanical properties of nc materials are determined not only by the grain size but also the microstructure of the grain boundaries.

Q5.6

Mechanical Properties of a Graphite Oxide Plane. Philippe Peyla, Andrei Ince and Alain Pasturel; LPM2C, Universite Joseph Fourier, Grenoble, France.

The deformation of a graphite atomic plane in presence of oxygen atoms (i.e. a graphite oxide plane) is studied with ab initio calculations and continuum theory of elasticity. We calculate the mechanical response (rigidity in flexion and in extension) of a graphite atomic plane. We show that the presence of oxygen impurities induces a nano-corrugation of the carbon atomic plane that enhances drastically the flexion rigidity modulus while in-plane rigidity modulus remains unaffected. These results could have some important implications on elaboration of carbon based fibers, or on carbon nanotubes in presence of oxygen. First results about elastic interaction of oxygen atoms on a graphite surface have been published in Phys. Rev. B66, (Brief Report), 172101 (2002).

Q5.7

Synthesis of Zr-Ti-X alloy by mechanical alloying. Nuria Llorca, Patrick Olier, Benjamin Villeroy and Gerard Allan; DECS/SE2M/LSMH, CEA, Gif sur Yvette, France.

Mechanical alloying was used in the investigation of Zr-Ti alloys in order to establish solid solubility at room temperature. The ultra-fine and amorphous microstructure is studied. Different compositions and different process conditions were used to understand the alloying mechanism. Characterisation of the alloys is useful for knowing the crystal sites and thus optimise post-treatments.

Q5.8

Response Of PNZT To Sharp And Blunt Indentation.

Thomas Frank Juliano^{1,2}, Thomas Buchheit², Chad Watson³ and Yury Gogotsi¹; ¹Materials Science and Engineering Department, Drexel University, Philadelphia, Pennsylvania; ²Microsystems, Materials, Tribology and Technology Department - Organization 1851, Sandia National Labs, Albuquerque, New Mexico; ³Ceramic Materials Department - Organization 1843, Sandia National Labs, Albuquerque, New Mexico.

Instrumented indentation experiments on niobium-modified lead zirconate titanate (PNZT) 95/5 reveal events in both the loading and unloading segments of the load-displacement curves, depending on whether a sharp or blunt indenter tip is used. These events may be due to hysteresis, domain reorientation and/or pressure-induced phase transformations. Currently, the origin of such events is not well understood. To understand these events, PNZT with an average grain size of approximately 10 μm was probed with a Berkovich indenter tip, and 20 μm and 300 μm diameter spherical indenter tips. Indentation depth, maximum load and loading/unloading strain rate were varied to observe the response of PNZT to various contact pressures and loading conditions. Raman micro-spectroscopy, scanning electron microscopy, and electron backscatter diffraction were utilized to help correlate events in the load-displacement curve to their origins. The effect of lead oxide content on the indentation response of PNZT 95/5 ceramics are also examined. Results demonstrate the usefulness of the unique combination of characterization techniques, and also in understanding structural changes that occur in PZT at high pressures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States DOE under Contract DE-ACO4-94-AL85000.

Q5.9

Simulation of Formation and Mechanical Properties of Metallic Bilayer Films.

Yoshiaki Kogure and Masao Doyama; Materials, Teikyo University of Science & Technology, Uenohara, Yamanashi, Japan.

Formation of metallic thin films and mechanical properties of Cu thin films, Ni/Cu and Ag/Cu bilayer films have been investigated by means of molecular dynamics computer simulation. An embedded atom method potential functions developed by the present authors was reasonably applied for the simulation, where the surface effects played essential role. Ni or Ag atoms are deposited on [100] or [111] surfaces of Cu substrates. Several conditions for the growth rate and the substrate temperature are tried and the morphology of surfaces and interfaces of bilayers, Ni/Cu and Ag/Cu, are investigated through the cross sectional view and top view of the films. The vibrational states of atoms are determined from the power spectra of vibration of atoms in free oscillating films and elastic constants of the films are evaluated. The external stresses are also applied to make plastic deformation, when the dislocations and the defect clusters are introduced in films and interfaces. One of the purposes of present simulation is to investigate the fundamental natures of the nanoindentation, which characterize the mechanical properties of thin films.

Q5.10

Auto-Organized Nanostructures; Aging Phenomena in (Ti,Al)N and (Ti,Zr)N Thin Film Systems.

A. Horling¹, J. Sjolen², T. Larsson², L. Karlsson², M. Oden³ and L. Hultman¹; ¹Department of Physics, Linköping University, Thin Film Physics Division, SE-581 83 Linköping, Sweden; ²Seco Tools AB, Research & Development, SE-737 82 Fagersta, Sweden; ³The Sirius Laboratory, Lulea University of Technology, Division of Engineering Materials, SE-971 87 Lulea, Sweden.

Aging phenomena in thin films including spinodal decomposition resulting in mechanical hardening is introduced as a field of study in nano science and technology of materials. Films synthesized by physical vapor deposition (PVD) techniques are particularly interesting since both surface- and in-depth decomposition can take place in metastable alloys quenched deep into the miscibility gap. To assess the phase transformations *ab initio* studies of compounds in different crystal structures were performed. It is concluded that both the Ti-Al-N and Ti-Zr-N systems are apt to decompose spinodally due to a negative 2nd derivative of the Gibbs free energy. Thus, the systems initially gain energy by decomposing into TiN and AlN-/ZrN-rich components of cubic structure for which there is little volume mismatch. The cathodic arc deposition process operating at

kinetically limited conditions and with ion bombardment-induced recoil mixing of surface atoms was utilized for the synthesis. NaCl-structure $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ($0 \leq x \leq 0.67$) and $\text{Ti}_{1-z}\text{Zr}_z\text{N}$ ($0 \leq z \leq 0.89$) alloys with compositions deep in the miscibility gap were deposited onto cemented carbide substrates. Phase composition was studied using X-ray diffraction (XRD) and cross-sectional transmission electron microscopy (XTEM). Films subjected to isothermal annealing in Ar atmosphere at 700-1100 $^\circ\text{C}$ exhibited a broadening of the (200) peak in both nitride systems as the result of compositional modulations in form of nm-thick lamellas. For the Ti-Al-N case, the intermediate cubic domains transform into their stable phases TiN and wurtzite-structure AlN by a nucleation and growth process during further thermal treatment. A slight hardness increase from 35 GPa (as-deposited) to 37 GPa (900 $^\circ\text{C}$ for 2 h) was observed for the (Ti,Al)N films in the corresponding temperature range. This is effective hardening considering that TiN films exhibit a softening from approximately 34 GPa (as-deposited) to 29 GPa (annealed at 700 $^\circ\text{C}$ for 2 h) due to lattice defect recovery and recrystallization during the corresponding post-deposition annealing. The findings show that supersaturated transition metal nitride ternary systems become auto-organized with nm-sized domains during annealing. This enables a self-adaptation process for such coating materials to obtain a retained – or even increased – hardness in, e.g., applications involving frictional heating during wear. The presented methodology – with DFT calculations, materials synthesis and structural analysis – also has relevance for studies of Group-III nitride wide band-gap semiconductor systems.

Q5.11

Mechanical Effects In Meso-Porous Silicon Nanostructures.

Charles Populaire¹, Boudjema Remaki¹, Vladimir Lysenko¹, Daniel Barbier¹, Hans Artmann² and Thorsten Pannek²; ¹Laboratoire de Physique de la Matière, INSA de Lyon, Villeurbanne, France; ²FV/FLD, Robert Bosch GmbH, Stuttgart, Germany.

Stress effects induced by oxidation and capping of porous nanostructures are studied using topographic measurements and finite element simulations. An original analysis of the strain at the free surface of porous silicon pattern embedded in bulk Si regions allows to determinate the Young's modulus of the porous layers. Moreover, the columnar morphology of the Si nanocrystallites network is shown from the characteristic shape of the strained porous layer profile to clearly induce a mechanical anisotropy. Moderately oxidized, 70% in porosity, porous silicon patterns were investigated. Correlation of our measurements with X-ray data reported in literature brings to the fore the macroscopic strain being close to the silicon lattice relative increase revealing an elastic deformation regime. Compared with bulk silicon, the porous silicon Young's modulus is unexpected low and strongly anisotropic. An effective Young's modulus around 1 GPa is found with an anisotropy factor of about 3 which remains constant with the oxidation rate. Large influence of capping layers deposition on mechanical strain of porous silicon tubs corroborates these unexpected low and anisotropic Young's modulus values. A phenomenological model for such a mechanical behavior taking into account porosity and percolation strength factor of the randomly arranged as-prepared and partially oxidized porous Si nanostructures is proposed.

Q5.12

Abstract Withdrawn

Q5.13

Predicting the Self-Assembled Morphology and Mechanical Properties of Mixtures of Diblocks and Rod-like Nanoparticles.

Gavin A. Buxton, Zhenyu Zhou and Anna C Balazs; Dept. Chemical Engineering, Univ. Pittsburgh, Pittsburgh, Pennsylvania.

We couple a morphological study of a mixture of diblock copolymers and rod-like, solid nanoparticles with a micromechanical simulation to determine how the spatial distribution and aspect ratio of the particles affects the mechanical behavior of the composite. The morphological studies are conducted through the SCF/DFT technique, which couples the self-consistent field theory (SCFT) for the diblocks and a density functional theory (DFT) for parallelepiped particles. Through the SCF/DFT calculations, we obtain the equilibrium morphology of the diblock/particle mixtures. We find that the distribution of particles within the polymers is dependent not only on the relative interaction energies between the particles and the different blocks, but also on the aspect ratio of the rod-like solids. 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 bonds. A stress is applied to the LSM lattice, and we calculate the local stress and strain fields and overall elastic response

of the material. We find that high aspect ratio rods can dramatically increase the Young's modulus of the material. By integrating the morphological and mechanical models, we can isolate how modifications in physical characteristics of the particles and diblocks affect both the structure of the mixture and the macroscopic behavior of the composite. Thus, we can establish how choices made in the components affect the ultimate performance of the material

Q5.14

Abstract Withdrawn

Q5.15

Grain-boundary sliding and separation in nanocrystalline materials: a continuum model. Lallit Anand¹, Yujie Wei² and Subra Suresh³; ¹Mechanical Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Materials Science and Engineering, MIT, Cambridge, Massachusetts.

To model the effects of grain boundaries in polycrystalline materials we have coupled a standard crystal plasticity model for the grain interiors with a new elastic-plastic grain-boundary interface model which accounts for both reversible elastic, as well as irreversible inelastic sliding-separation deformations at the grain boundaries prior to failure. We have used this new computational capability to study the deformation and fracture response of nanocrystalline nickel in simple tension. The results from the simulations capture the experimentally observed stress-strain curves, and the dominant fracture mechanisms in this material. The macroscopically observed nonlinearity in the stress-strain response is mainly due to the inelastic response of the grain boundaries. Plastic deformation in the interior of the grains prior to the formation of grain-boundary cracks was rarely observed. The stress concentrations at the tips of the distributed grain boundary cracks, and at grain-boundary triple junctions cause a limited amount of plastic deformation in the high strength grain interiors. The competition of grain boundary deformation with that in the grain interiors determines the observed macroscopic stress-strain response, and the overall ductility. In nanocrystalline nickel, the high yield strength of the grain interiors and relatively weaker grain-boundary interfaces account for the low ductility of this material in tension.

Q5.16

Impact of light on nanoindentations in dislocation-free ZnO nanobelt. Minhua Zhao¹, ZhongLin Wang² and Scott X Mao¹; ¹Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The photoplastic effect (PPE) denotes the impact of light on the flow stress or hardness of a material. The positive PPE exists if materials become stronger under illumination, while the negative PPE represents light-induced softening. Dislocation charging is generally accepted as the cause of the PPE. Although the PPE has been reported in a broad variety of non-metallic materials including (0001) ZnO, all of them are bulk materials and not dislocation-free. The preexisting dislocations may complicate the analysis of the dislocation nucleation and movement. Hence it is critical to study the PPE in initially dislocation-free material. In this study, impact of light on nanoindentations in dislocation-free ZnO nanobelt (Zheng Wei Pan, Zu Rong Dai, Zhong Lin Wang, Science, Vol. 291, 2001:1947) was investigated. A positive PPE was found in ZnO nanobelt, which was compared with that of (0001)ZnO bulk. The probable explanation of the discrepancy between nanobelt and bulk was discussed.

Q5.17

Abstract Withdrawn

Q5.18

Deposition of TiN/NbN superlattice hard coatings by ionised magnetron sputter deposition. Yi Long, R.J. Stearn, Z.H. Barber, S.J. Lloyd and W.J. Clegg; Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

TiN/NbN superlattice coatings have been deposited epitaxially on MgO (001) substrates by ionised magnetron sputter deposition. A radio frequency (r.f.) coil within the deposition chamber was used to generate an inductively coupled plasma between the substrate and the targets, promoting energetic bombardment of the growing films with ions of both background gas atoms and depositing species. In this work the substrate bias was maintained at -100 V and the effect of varying the ion flux onto the sample was studied by changing the r.f. powers to the coil. The results showed that the hardness of a TiN single layer increased from 9 GPa to 21 GPa and the surface roughness decreased from 8.0 nm to about 1.6 nm compared with simple DC magnetron sputtering. For NbN, the r.f. effect on hardness and surface quality was less pronounced but the deposition rate

increased four-fold. Multilayers with varying wavelengths from 2.2 nm to 21 nm were deposited using the optimum condition of r.f. power found above and showed a hardness of 28 GPa compared with that of 21 GPa for a TiN single layer and 16 GPa for a NbN layer grown under the same conditions. A comparison of the structure and deformation patterns following nanoindentation has been carried out using transmission electron microscopy. The multilayer films were also characterized by high angle X-ray diffraction and low angle X-ray reflection, including simulations, to determine the composition and strain modulation correlated with the changes in hardness.

Q5.19

Dislocation Confinement and Ultimate Strength in Nanoscale Metallic Multilayers. Qizhen Li and Peter M. Anderson; materials science and engineering, the Ohio State University, Columbus, Ohio.

In nanostructured metallic multilayers, hardness and strength are greatly enhanced compared to their microstructured counterparts. As layer thickness is decreased, three different regions are frequently observed: the first region shows Hall-Petch behavior; the second region shows an even greater dependence on layer thickness; and the third region exhibits a plateau or softening of hardness and strength. The second and third regions are studied using our discrete dislocation simulation method. This method includes the effects of stress due to lattice mismatch, misfit dislocation substructure, and applied stress on multilayer strength. To do so, we study the propagation of existing threading and interfacial dislocations as the applied stress is increased to the macroyield point. Our results show that in region 2, dislocation propagation is confined to individual layers initially. This "confined layer slip" builds up interfacial content and redistributes stress so that ultimately, the structure can no longer confine slip. The associated macroyield stress in this region depends strongly on layer thickness. In region 3, layers are so thin that confined layer slip is not possible and the macroyield stress reaches a plateau that is independent of layer thickness. The value of this plateau is shown to scale with mismatch in lattice parameter.

Q5.20

Modeling the Contact Stiffness Between a 2D Voronoi Honeycomb and a Flat Rigid Surface. Richard Dean Widdle¹, Thomas N Farris², Anil K Bajaj¹ and Patricia Davies¹; ¹School of Mechanical Engineering, Purdue University, West Lafayette, Indiana; ²School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana.

Open-cell foam can be thought of as a network of interconnected struts. To study the contact stiffness behavior, one can imagine the foam boundary to be characterized by struts that are free at one end, while the base-end is connected to the interior of the foam. In previous studies, the base-end was assumed to be built into a rigid surface, i.e., the surface struts were constrained to have zero displacement where they would connect to the foam interior. Using this assumption, contact stiffness properties have been derived for foam and researchers have used these models to study the effects of variations in strut length and orientation angle. In this study the assumption that the surface elements are built in is relaxed by modeling the elastic behavior of the foam interior. The foam interior is modeled as a network of struts within a finite element formulation. The two-dimensional foam, or honeycomb, finite element models are constructed by using Voronoi tessellations, thus providing realistic irregularity. The contact is modeled by using one of two conditions: zero friction or very high friction to prevent slip. Numerous finite element models are generated to study the contact stiffness as a function of the relative density and degree of regularity of the foam. It is found that including the foam interior and its associated behavior in the model results in a significant reduction in the predicted contact stiffness.

Q5.21

Mechanical behavior of nanocrystalline aluminum alloys. Tim Wilson¹, Hahn Choo^{1,2} and Peter K. Liaw¹; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Bulk nanocrystalline aluminum alloys were fabricated by consolidating amorphous aluminum alloy powders synthesized by mechanically alloying (MA) of Al-Y-Fe-Ni elemental powder blends. The mechanical behavior of the nanocrystalline aluminum alloys consolidated at various temperatures was characterized using tensile testing and compared to the mechanical properties of the MA amorphous powders measured by an indentation technique. This study also examines the feasibility of producing nanocomposites with a bimodal grain-size distribution by consolidating the MA powders with elemental crystalline aluminum powders with a varying particle size. The tensile strength and ductility of the nanocomposites will be correlated to the grain-size distribution in the composite.

Q5.22

High Ductile Silicon Dioxide Aerogel Thin Films at Ambient Pressure. Brian P. Mosher and Taofang Zeng; Mechanical & Aerospace Engr., North Carolina State University, Raleigh, North Carolina.

Silica aerogels, mostly made of mesopores, are sol-gels that are supercritically dried to form an incredibly lightweight, thermally unconducting, yet brittle material. Aerogel thin films have found applications as low-k materials and thermal insulation materials for MEMS. Remarkable steps have been taken to control the properties of aerogels at the nanometer level such as controlling the surface area, density, pore volume, and pore size distribution via different sol-gel and supercritical drying processes. Still, aerogels remain brittle and delicate. Increasing the mechanical strength and the flexibility or the ductility, while retaining the low conductivity of a material, is a challenging and intriguing topic. This study proposes a new method to improve the mechanical strength and the ductility of thin film aerogels dried at ambient pressure. We nanoengineer the aerogel thin films through the addition of a specific inorganic/organic conglomerate to the sol-gel process, and temperature-controlled processing. The backbone of silica aerogel thin films is fine-tuned and reinforced. Mechanical tests and measurement of thermal conductivity find that the modulus of elasticity is lowered; the mechanical strength is improved; while the thermal conductivity of the aerogel thin film is not greatly affected.

Q5.23

Grain size dependence of the compressibility of nanocrystalline nickel. Shi-Jin Zhao, Karsten Albe and Horst Hahn; Institute of Materials Science, TU Darmstadt, Darmstadt, Germany.

The grain size dependence of the bulk modulus of nanocrystalline nickel (nc-Ni) is investigated by means of molecular dynamics simulations. For different samples with average grain radii ranging from 1 to 20 Å the bulk modulus is obtained from the Birch-Murnaghan equation of state at 0 K and room temperature. We observe an increasing compressibility with decreasing grain size due to the increasing number of grain boundary atoms. This observation can be fully described with a two phase model which depends on the average grain size and the bulk modulus of both, the ideal crystal and the grain boundary phase. We prove that the elastic behavior of the grain boundary phase is different from that of the bulk structure and amorphous bulk phase.

Q5.24

Length Scale Effects in Fatigue of Cu Thin Films. Reiner Moenig^{1,2}, Guangping Zhang² and Cynthia A. Volkert¹; ¹Forschungszentrum Karlsruhe, Karlsruhe, Germany; ²Max Planck Institute for Metals Research, Stuttgart, Germany.

Nanocrystalline metals have much higher yield stresses than their coarse-grained counterparts. It is hoped that this high strength will translate into improved fatigue reliability, at least under high cycle loading conditions. However, during fatigue testing the microstructure of many nanocrystalline metals is not stable and typically evolves by grain growth and shear band formation. In contrast, annealed metal films have a stable microstructure with a grain size that is on the order of the film thickness. This offers the possibility to study the fatigue behaviour of fine-grained metals with a stable microstructure as a function of film thickness and grain size. The development of severe surface damage and failure as a result of thermal-mechanical fatigue has been studied in Cu films with thicknesses down to 100 nm. It is observed that the fatigue-induced surface damage and the dislocation structures depend strongly on film thickness and grain size. In particular, periodic surface extrusions which form in bulk fatigued samples due to repetitive dislocation glide, do not form in films with thicknesses below roughly 200 nm. Instead, the damage forms as grain boundary grooves and sunken grains and appears to be controlled by surface and grain boundary diffusion rather than by dislocation mechanisms. In fact, plan-view TEM studies show that the characteristic dislocation structures which are responsible for extrusion formation in bulk metals, cease to form below a crystal dimension (either film thickness or grain size) of roughly 3 µm. Details of the damage evolution, cycles to failure, and a comparison with bulk nanocrystalline metals will be presented.

Q5.25

Plastic Deformation and the Role of Fault Formation in the Equation of State of Micron Size Intermetallic Alloys Under Non-Hydrostatic Pressure. John K Vassiliou¹, Jens W Otto², G Frommeyer³, P Pinto¹ and J J Davis¹; ¹Physics, Villanova University, Villanova, Pennsylvania; ²Joint Research Center for the European Commission, Brussels, Belgium; ³MPI Eisenforschung, Dusseldorf, Germany.

The elastic and plastic deformation of micron size anisotropic polycrystals of Ni₃Al and Cu₃Au intermetallic alloy has been studied under non-hydrostatic conditions by energy-dispersive X-ray diffraction (EDX) in a diamond-anvil cell. Compression was achieved by confining the samples in a viscous fluid or directly between the diamond anvils. Deviatoric forces are introduced in the samples as a result of the increasing viscosity with pressure and the eventual glassification of the pressurizing medium or by the contact forces of the diamond anvils. Line shifts and line profiles were used to analyze elastic and plastic strains. Plastic deformation is due to the onset of non-hydrostatic stresses and the introduction of stacking faults and dislocations. A volume incompressibility due to plastic deformation and the saturation of the stacking fault probability is followed by an elastic compression of a fully plastically deformed state. The compression of this state is isotropic and independent of the presence and type of the pressurizing medium. From the measured strains at different crystallographic orientations the uniaxial stress and the stacking fault probability as a function of the confining pressure are derived and their role in the equation of state is examined. Using finite elasticity, the equation of state is derived in the presence of stacking faults and uniaxial stresses.

Q5.26

Mechanical properties of nanostructured AlN-TiN multilayered thin films. Cindy Waters, Dhanaanay Kumar, Sergey Yarmolenko and Jagannathan Sankar; North Carolina A&T State University, Greensboro, North Carolina.

In this paper, studies will be presented on the synthesis and characterization of AlN-TiN multilayered structures with enhanced mechanical properties (viz. their hardness and fracture toughness). The multilayered structures were generated using a pulsed laser deposition (PLD) technique. The thickness of each component was systematically varied to understand its role in the overall mechanical properties of the AlN-TiN multilayered thin film structures. The hardness and fracture toughness of these film composites were determined using nanoindentation at various indentation loads. In order to measure the indentation depth and crack length with precision, an atomic force microscope (AFM) in conjunction with Image Pro Software was utilized. Subsequently, to understand the role of the microstructure on the mechanical properties of the multilayered structures, highly sophisticated structural characterization techniques such as scanning transmission electron microscopy with atomic number (Z) contrast (STEM-Z) and electron energy loss spectroscopy (EELS) with atomic resolution were used. These techniques have provided important results regarding the microstructure before and after the nanoindentation fracture events.

Q5.27

Modeling of Deformation Behavior in Nanoscales. Masato Hiratani and Vasily V Bulatov; CMS/MSTD, Lawrence Livermore National Laboratory, Livermore, California.

Plastic behavior confined within the nano-scale structures such as thin-film composite, nano-wires, or nanocrystals are known to behave much differently from those in bulk materials. Prediction and control of dislocation motion as strain carriers during production process are crucial to functionals of the microcomponents. In this study, discrete dislocation dynamics (DD) is used to investigate the deformation behavior in metallic nano-wires and nano-grains with ingrown dislocations and sources. DD simulations are run for fcc metals with high stacking fault energy (Al and Pd) and bcc metals (Mo and Fe) with either rigid boundaries or dislocation textured grain boundaries. Results indicate size dependence of the yield stress and deviation from Hall-Petch relation in nano-scales due to the suppression of dislocation motion and multiplication by microstructures. Evolution of stress distribution associated with localized/ piled-up dislocations is also monitored to predict the nucleation sites of microcracks. In addition, dislocation based cracks are implemented as local stress concentrators once their nucleation criterion is met, which result in complex dislocation configurations by dislocation screening near crack tips and boundary effects. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48, and the support of the DOE (Grant No. DE-FG03-01ER54629).

Q5.28

Structural organization in a Glass Sponge from the nano to the macro scale. Vikram Sundar¹, Maggie Cocca¹, Andrew D Yablon² and Joanna Aizenberg¹; ¹Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; ²OFS, Murray Hill, New Jersey.

Nature has through the course of evolution developed optical systems that are unparalleled in modern technology. In particular, sophisticated skeletal designs that in addition to providing the mechanical support may function as high-performance optical devices,

were discovered. Here we report on the exceptional optical and structural properties of hexactinellid glass sponge Euplectella. First, their spicules are shown to have a characteristic layered substructure, and a non-uniform refractive index profile with a high index core and low index cladding. Such a layered structure provides a natural crack-arresting mechanism in these fibers and increases their fracture toughness. Next, chemical and structural analysis indicates a hierarchical assembly of the surrounding cage from these spicules. Results from mechanical and structural characterization are presented and indicate the existence of the reinforced composite on the macroscale that has been constructed in a truly bottom-up fashion.

Q5.29

Abstract Withdrawn

Q5.30

Multilayered Carbon Films For Wear Resistance.

Peter C.T. Ha¹, David R McKenzie¹, Derry E Doyle³, Jaromir Audy³, Michael V Swain² and Dougal G McCulloch⁴; ¹Applied and Plasma Physics, University of Sydney, Sydney, New South Wales, Australia; ²Biomaterials Science Research Unit, University of Sydney, Sydney, New South Wales, Australia; ³School of Engineering and Science, Swinburne University of Technology, Melbourne, Victoria, Australia; ⁴Department of Applied Physics, RMIT, Melbourne, Victoria, Australia.

Carbon is a promising material for tribological applications. In this paper, we examine the effect on the wear performance when the carbon film is deposited as a multilayer. Multilayer films have been reported to have increased hardness, increased elastic modulus and increased fracture toughness when compared to single component films [1]. We created carbon multilayer structures by periodic variation of the bias voltage in a DC filtered cathodic arc, fitted with a 2-20 kV pulsed bias power supply. The indentation hardness of the films was measured using a nanoindenter. Dark field and bright field transmission electron microscopy was used to examine the nanocomposite structures. We show that the elastic modulus and fracture toughness depend on the period of the structure. Performance tests on drills showed that promising increases in lifetime are possible.

Q5.31

Modeling of Deformation in Bimodal Nanocrystalline Gold Using an Atomistic-Based Continuum Approach. D. H. Warner, F. Sansoz and J. F. Molinari; Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

Nanocrystalline metals are found to exhibit improved elongation to failure compared to amorphous metallic alloys, while maintaining relatively high yield strength. The ductility of nanocrystalline metals however is still significantly lower than that observed in coarse-grained microstructures. Recent work has shown that this trade off can be avoided by processing bimodal microstructures, which incorporate distributions of micrometer-sized grains inside a nanocrystalline matrix. These novel microstructures display elevated yield strength while maintaining ductility comparable to that of their microcrystalline counterparts. The increase in ductility is believed to result from plastic deformation within the larger grains, however the details of the local stress states emanating from these highly non-homogeneous microstructures is not fully understood. Additionally, the application of these new microstructures to technologically pertinent applications, such as thin nanocrystalline films, has yet to be explored. The current study presents a model to characterize the effects of bimodal grain size distribution on the mechanical properties of thin nanocrystalline films. In this model, a 2D continuum analysis of approximately 400 grains is performed using finite element method. Particular attention is paid to capture the polycrystalline structure details and to incorporate cohesive and sliding strengths at grain boundaries, so that relevant information at the atomic-scale is taken into account, while maintaining a very low computational cost. Crystal lattice statics simulations of different grain boundary structures are used to obtain the atomistic information supplied into the cohesive interfaces. These atomistically-informed continuum calculations are carried out to determine the stress-strain response of free-standing gold thin films exhibiting a texture such that the {111} crystallographic planes are aligned with the plane of the film. This approach is shown to provide strong insights for interpreting the interactions between grain size distribution, local stress levels and underlying deformation mechanisms.

Q5.32

The early stages of stress development during epitaxial growth of Ag/Cu multilayers. Stephane Labat, Franck Bocquet and Olivier Thomas; TECSEN, Université d'Aix-Marseille III, Marseille, France.

The early stages of stress development during epitaxial growth of metal layers with a large misfit in lattice parameters still need in-depth understanding. In this particular study we have focused on Ag-Cu system, which is immiscible and exhibit a large 14% misfit in lattice parameters. Ag/Cu multilayers have been grown by ultrahigh-vacuum evaporation on Si (111) maintained at -30°C, 30°C or 100°C. The thickness of the individual layers is about 100 Å. All the films present the same (111) orientation with a well defined in-plane orientation: $\langle 110 \rangle$ Cu or Ag // $\langle 110 \rangle$ Si. The stress was monitored during growth with a home-made laser curvature measurement device. The stress vs thickness behaviour is highly asymmetric when comparing Ag/Cu and Cu/Ag. Indeed Ag grown on Cu does not develop any measurable stress at any thickness or temperature, whereas Cu grows on Ag under tensile temperature and thickness-dependent stress. The temperature dependence of this stress relaxation cannot be interpreted with a standard relaxation model including dislocation motion. A possible way to understand the stress temperature dependence is to consider the evolution of microstructure during growth

SESSION Q6: Nanostructured Films and Coatings

Chairs: Bing Han and Asiru Vasudevan

Wednesday Morning, December 3, 2003

Room 311 (Hynes)

8:30 AM *Q6.1

Polymer based-single walled nanotube nanocomposite thin films. Peter F Green, Chemical Engineering, The University of Texas at Austin, Austin, Texas.

The properties of polymer films in the thickness range of nanometers to tens of nanometers often differ substantially from the intrinsic bulk behavior, due largely to the increasing influence of entropic effects (confinement and chain segment organization) and to interfacial interactions. Polymer thin films play an important role in many technologies, ranging from lubricating layers and membranes to components in a range of microelectronic devices and sensors. Thin film composites of polymers with single walled carbon nanotubes (SWNTs) offer particularly interesting opportunities because of unusual properties (such as exceptionally high moduli and unusual electrical conductivity characteristics) that the nanotubes possess. We are interested in the influence of single walled carbon nanotubes on the glass transition temperature and on other relaxation processes in polymer thin films. The glass transition temperature of polystyrene based nanocomposite films (containing ~1% SWNT), thinner than $h=45$ nm, decreased with decreasing film thickness, h . This phenomenon also occurs in thin PS films, however the magnitude of the depression in PS is appreciably larger (~10 degrees at $h=20$ nm). For thicker films the difference between the T_g of PS and of the nanocomposite is much smaller, ~3 degrees. In addition to the glass transition other properties such as the viscosity undergo substantial changes. In the bulk the viscosity of PS-SWNT is a factor of 3 larger and increases with decreasing h . These observations will be discussed during this presentation.

9:00 AM Q6.2

Fracture Toughness vs. Plastic Deformation in Nanoparticle Filled Silica Thin Films. Etienne Barthel¹, Michaela Klotz¹, Sophie Besson^{1,2} and Thierry Gacoin²; ¹Surface du Verre et Interfaces, CNRS/Saint-Gobain, Aubervilliers, France; ²Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, Palaiseau, France.

We have investigated the mechanical properties of a series of 300 nm thick nanostructured silica films deposited on glass. These films, which are obtained by a templated sol-gel process exhibit ordered porosity in the nm range. They are used as a matrix in which monodisperse semi-conductor nanoparticles are grown, for optical coatings applications. However, it has been observed in scratch tests that the filled films have a propensity for delamination. This fact motivated our mechanical investigations. Since an equivalent bulk material cannot be synthesized, we resorted to nanoindentation to characterize the mechanical response of these films. Young's modulus and intrinsic film hardness were determined by nanoindentation to 30 nm: introduction of the particles leads to an increase of both Young's modulus and hardness by a factor of two. Gas adsorption measurements allowed the pore fraction and the density of the walls to be determined. From this knowledge, it appears that the intrinsic Young's modulus of the layer is well accounted for by an effective medium model of the Voigt-Reuss-Hill type. The intrinsic modulus of the walls thus determined is consistent with literature data at the same density. A tentative interpretation for the increase in the plastic response of this type of materials will be given. It is less straightforward, however, as it is expected that densification plays a crucial role in the plastic deformation processes. Finally, a simple mechanical criterion balancing crack propagation and plastic

deformation show that a parallel increase in Young's modulus and hardness favors stress relaxation through delamination rather than plastic yield, in agreement with the scratch test observations.

9:15 AM Q6.3

Nanoindentation : hardness and phase transition in a thin film of silicon. Hebbache Mohamed, Physics, university Paris 7, Paris, France.

Silicon is widely used in bulk and thin films in many industrial applications. Its mechanical properties are investigated on increasingly tiny scales. Nanoindentation is a technique which allows the measurement of hardness by pressing into a flat surface of the material a shaped indenter. The analysis of the load-displacement curve allows the determination of a number of useful engineering properties, such as fracture toughness and elastic moduli. A high non-hydrostatic pressure, i.e., a shear component and a compressive hydrostatic component is generated beneath the indenter. Small regions of silicon undergo structural transformations like in a diamond anvil cell. For instance, a semiconductor-metal phase transition takes place for a load of 12 mN. The corresponding penetration depth is about 90 nm. The non-reversibility of this transformation, due to plasticity, hinders the appearance of new applications like detectors of ultra-low forces or impacts. Nanoindentation experiments show that the hardness increases with the penetration depth and reaches a maximum at the phase transition point. From the theoretical point of view, nanoindentation is a contact problem which has been partially solved. Much of the theoretical works are restricted to isotropic solids. Little attention has been paid to anisotropy, anharmonicity and structural transformations which occur beneath the indenter. These issues have been studied recently [1-2] in the framework of a 3D contact theory [3] and elastic theory of phase transitions [4].
References : 1. Nanoindentation of silicon and structural transformations : 3D contact theory M. Hebbache and M. Zemzemi, Phys. Rev. B 67, 233302 (2003). 2. Nanoindentation : depth dependence of hardness in silicon M. Hebbache and M. Zemzemi, Phys. Rev. B (2003), to appear. 3. J. R. Willis, J. Mech. Phys. Solids 14, 163 (1966). 4. R. A. Cowley, Phys. Rev. B 13, 4877 (1976).

9:30 AM Q6.4

Nanostressors and the Nanomechanical Response of a Thin Silicon Film on Insulator. MingHunag Huang¹, Feng Liu¹, P. P. Rugheimer², D. E. Savage² and M. G. Lagally²; ¹Materials Science and Engineering, University of Utah, Salt Lake City, Utah; ²Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

Pseudomorphic three-dimensional nanoscale Ge islands grown on thin silicon-on-insulator substrates can induce significant local bending of the silicon template layer. This behavior is distinctive different from that observed for Ge growth on thick Si substrates. We employ molecular dynamics simulations and analytical models to confirm the local bending of the Si template and to show that its magnitude approaches the maximum value for a freestanding membrane. MD simulations demonstrate that the existence of a transition from extended to local bending with decreasing island density and substrate thickness. Our analytical models demonstrate that the large magnitude of local bending indicates that the Si template acts like a freestanding layer during the growth of Ge islands and the bending of the Si layer is assisted by substantial viscous flow of SiO₂ underneath the Si layer. The reduced viscosity required for this flow is made possible by the very high local shear stress and the strong dependence of viscosity on shear stress. This work is supported by DOE.

9:45 AM Q6.5

Formation of Misfit Dislocations in Nano-Scale Ni-Cu Bilayer Films. David Mitlin¹, Amit Misra¹, Velimir Radmilovic², David J. Embury², Michael Nastasi¹, Richard Hoagland¹, John P. Hirth¹ and Terence E. Mitchell¹; ¹MST-8, Los Alamos National Laboratory, Los Alamos, New Mexico; ²National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ³Materials Science, McMaster University, Hamilton, Ontario, Canada.

This study investigates the mechanism of interface dislocation formation in a 5.0 nm Ni film epitaxially deposited on 100 nm of (001) Cu. Threading dislocations that pre-exist in the Cu substrate extend into the coherent Ni overlayer during growth and propagate in the [110] and [-110] directions along the interface. These dislocations are perfect glide dislocations with mixed character and lying on the {111} Ni planes, and were by far the most numerous in the microstructure. A few Lomer edge dislocations lying on the (001) Ni-Cu interface were also detected. Closely spaced adjacent pairs of perfect dislocations were commonly observed at the interface. This dislocation configuration, along with several others that were observed, is explained in terms of the ability of favorably oriented dislocations to cross-slip.

10:30 AM *Q6.6

Hyperkinetic Spray of Nanostructure Aluminum Alloys. Leonardo Ajdelsztajn¹, George E Kim³, Bertrand Jodoin² and Julie M Schoenung¹; ¹Chemical Eng. & Materials Science, University of California at Davis, Davis, California; ²Mechanical Eng. Dept., University of Ottawa, Ottawa, Ontario, Canada; ³Perpetual Technologies, Montreal, Quebec, Canada.

Aluminum 5083 powder was mechanically milled under liquid nitrogen and subsequently sprayed using hyperkinetic spray technique. The resulting nanocrystalline coatings were evaluated using XRD, SEM, TEM, micro- and nanoindentation. The coatings show negligible porosity and excellent interface with the substrate material. Hyperkinetic spray technique has demonstrated a great potential to spray nanocrystalline materials (low temperature and low oxidation), not only from the standpoint of coating fabrication, but also as a potential for near net-shape fabrication of bulk nanocrystalline materials. The use of hyperkinetic spray as a new method to produce bulk nanocrystalline materials was successfully demonstrated in this work.

11:00 AM Q6.7

Work Hardening and Fracture In Room Temperature Rolled Nanoscale Copper-Niobium Multilayers. Amit Misra, Richard G. Hoagland, Duncan L. Hammon, Xinghang Zhang, J. David Embury and John P. Hirth; Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

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. These nanoscale materials also exhibit extraordinary mechanical stability during room temperature rolling, undergoing uniform reduction in layer thickness to high levels of plastic strain without the formation of the classical dislocation cell structures. In this presentation, the mechanisms of work hardening, in the absence of the dislocation cell structures, will be discussed. Limited deformability is observed at layer thickness less than around five nanometers, although the fracture is by shear. The dislocation mechanisms of deformation in nanolayered composites and their implication on mechanical stability versus shear localization are discussed. This research is funded by DOE, Office of Science, Office of Basic Energy Sciences.

11:15 AM Q6.8

Strengthening Induced by Nanoscale Twinning in Cu/330 Stainless Steel Multilayers and Single Layer 330 Stainless Steel Thin Films. Xinghang Zhang, Amit Misra, Haiyan Wang, Mike Nastasi, John D Embury, Terry E Mitchell, Richard G Hoagland and John P Hirth; Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Metallic multilayered composites synthesized by sputter deposition exhibit very high strengths as the bilayer period approaches a few nanometers. In the present investigation on Cu/austenitic 330 stainless steel multilayers and single layer 330 stainless steel films, we have found a high density of growth twins and stacking faults. The stainless steel layers, in particular, exhibit twinning and faults on the scale of 3-4 nm resulting in hardness that is about an order of magnitude higher than bulk 330 stainless steel. A model is developed that accounts for the formation of nanoscale twins during sputter deposition in terms of the twin boundary or stacking fault energy and deposition rate. Molecular dynamics simulations show that at nanometer length scales where plasticity is controlled by the motion of single rather than pile-ups of dislocations, twin boundaries are very strong obstacles to slip. These observations provide a new perspective to producing ultra-high strength metals by utilizing growth twins with nanometer-scale spacing. This research is funded by DOE, Office of Science, Office of Basic Energy Sciences.

11:30 AM Q6.9

Plastic Deformation and Wear Mechanisms of Sputtered Nano-Columnar TiN Coatings. Ma Kung-Jeng¹, Chao Choung-Lii³ and Chien Hsi-Hsin²; ¹Mechanical Engineering, Chung-Hua University, Hsin Chu, Taiwan; ²Mechanical Engineering, Chung-Hua University, Hsin Chu, Taiwan; ³Mechanical Engineering, Tam-Kang University, Tamsui, Taipei, Taiwan.

Even though high strengths have been obtained in most ceramic coatings, it has also been shown that some ceramic coatings undergo extensive plastic deformation during indentation and scratch tests. It is essential to understand the mechanisms behind this fascinating mechanical behaviour. A typical microstructure of a magnetron sputtered TiN coating with a fully dense nano-columnar structure. Obvious plastic flow has been observed in fine columnar or nanocrystalline TiN coatings when sliding against 200 um tip radius

diamond. This provides an alternative mechanism to release stored elastic strain energy, rather than by premature cracking or microbuckling to dissipate strain energy. The wear of coating materials is believed to include the mechanisms of plastic flow and surface fatigue. The friction coefficient is about 0.1 from initial sliding, and then gradually decreases to a stable value (0.045~0.07, dependent on the load) in the reciprocating multipass wear test. It is suggested that the adhesion component of friction can be neglected due to the weak interfacial adhesion bonds between diamond and TiN. The ploughing and plastic deformation component of friction may become important in these cases. However, normally the energy losses through inelastic deformation of the sliding solids is appreciably less than the dissipation through the interfacial reaction. It is the reason why a low coefficient of friction can be obtained. The deformation loss may be more important in relation to the wear or surface fatigue than they are in relation to friction.

11:45 AM Q6.10

Elastic Modulus of Nanocrystalline Niobium Thin Films.

Rajarshi Banerjee¹, Evan Sperling¹, Gregory B Thompson¹, Sangita Bose², Pushan Ayyub² and Hamish L Fraser¹; ¹Materials Science and Engineering, The Ohio State University, Columbus, Ohio; ²Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, Maharashtra, India.

Nanocrystalline thin films of Nb with crystallite sizes varying from 5 nm to 30 nm have been deposited using high pressure magnetron sputtering under UHV conditions. The structure of these films as a function of grain size has been characterized using x-ray diffraction and TEM. With increasing pressure of the sputtering gas, there is a decrease in the average crystallite size in these films. The decrease in crystallite size in turn is accompanied by a lattice expansion in the bcc phase of Nb. There is however no evidence of a change in crystal structure with decreasing crystallite size. Nanoindentation experiments conducted on these films suggest that for crystallite sizes greater than ~ 6 nm, there is a reduction in the modulus of these films with decreasing crystallite size. This decrease in modulus has been successfully modeled using an equation of state for metals based on the lattice expansion of the bcc Nb phase. However, for crystallite sizes less than ~ 6 nm, there is an anomalous increase in the modulus of the thin films despite the substantially expanded lattice of the bcc Nb phase. Interestingly, independent investigations of the transport properties of these nanocrystalline Nb films suggest that at around the same critical crystallite size (~ 6 nm), there is a metal to non-metal transition. These results and their possible implications on the elastic modulus of the Nb films will be discussed in this paper.

SESSION Q7: Nanostructured Bulk Materials III
Chairs: Sudipta Seal and Subra Suresh
Wednesday Afternoon, December 3, 2003
Room 311 (Hynes)

1:30 PM Q7.1

Fracture mechanisms of nanocrystalline Ni. Diana Farkas¹, Helena Van Swygenhoven² and Peter Derlet²; ¹Materials Science, Virginia Tech, Blacksburg, Virginia; ²Paul Scherrer Institut, Villigen, Switzerland.

We present an atomistic study of the mechanisms of crack propagation in nanocrystalline Ni with grain sizes varying from 5 to 12 nm. We observed intergranular fracture propagation that advances through the creation of nano-sized cracks which are nucleated on grain boundaries ahead of the main crack. The intergranular fracture process is accompanied by a significant degree of plastic deformation which mainly occurs through grain boundary mechanisms. Some degree of dislocation activity is also observed with Shockley partial dislocations being emitted from the crack tip and grain boundaries in the vicinity of the tip. These dislocations are then absorbed by a neighboring grain boundary.

1:45 PM Q7.2

Agreement Between Simulations and Experiment on Deformation Mechanism in Nanocrystalline Metals?

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

Molecular dynamics simulations highlight the role of the GBs in the deformation mechanism by means of two processes: the first can be identified as GB sliding triggered by atomic shuffling and stress assisted free volume activity, the second is the process where GBs act as source and sink for partial dislocations promoting GB relaxation and reorganization of the remaining GB dislocation (PRB 66 (2002), ZFM special issue for H. Gleiter 2003). It is shown that the emission of a partial dislocation causes local stress relief in the GB during

deformation resulting in an apparent lower stacking fault energy together with local changes in the GB structure, therefore inhibiting the immediate relief of the trailing partial. The detailed atomic process behind the emission of the dislocation from the grain boundary and the role played by the local stress in the GB are discussed. However, due to the inherent time restrictions of the MD technique, full dislocations or mechanical twinning can not be excluded. Both deformation mechanisms are at the origin of the formation of local shear planes that facilitates plastic deformation and explains dimple structures on the fracture surface (Science 300 (2003) 1550). The proposed mechanisms are interpreted in terms of experimental results obtained on electrodeposited nanocrystalline Ni: the initial apparent hardening followed by a softening and the limited ductility are discussed in the framework of the deformation mechanism suggested by the simulations. The synergies provided by the computer simulations and classical experimental investigations have resulted in the development of a very successful new experimental approach: in-situ diffraction profile analysis at the Swiss Light Source. First results demonstrating the source and sink activity of nanosized GBs are presented.

2:00 PM Q7.3

Crossover From Dislocation Slip to Grain-Boundary Based Deformation in Nanocrystalline fcc Metals by

Molecular-Dynamics Simulation*. Vesselin Yamakov¹, Dieter Wolf¹, Simon Phillpot¹, Amiya Mukherjee² and Herbert Gleiter³; ¹Materials Science Div., Argonne National Lab., Argonne, Illinois; ²Dept. of Chem. Engrg. & Materials Science, University of CA at Davis, Davis, California; ³Institute for Nanotechnology, Karlsruhe Research Center, Karlsruhe, Germany.

We use molecular-dynamics simulations to elucidate the transition with decreasing grain size from dislocation slip to a grain-boundary based deformation mechanism in nanocrystalline fcc metals. Our simulations reveal that this crossover is accompanied by a pronounced transition in the mechanical behavior of the material; namely, at the grain size where the crossover occurs (the "strongest size"), the strain rate under tensile elongation goes through a minimum. This simultaneous transition in both the deformation mechanism and the corresponding mechanical behavior offers an explanation for the experimentally observed crossover in the yield strength of nanocrystalline materials, from Hall-Petch hardening to "inverse Hall-Petch" softening. Building on the fundamental physics of deformation as exposed by our simulations as a function of the stacking-fault energy, we propose a two-dimensional stress-grain size deformation-mechanism map for the mechanical properties of nanocrystalline fcc metals at low temperature. The map captures the transition from dislocation slip to grain-boundary governed deformation and incorporates the effects due to the different stacking-fault energies and elastic properties associated with different materials.

*Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-31-109-Eng-38.

2:15 PM Q7.4

Atomistic Sliding Mechanisms of the S=5 Symmetric Tilt Grain Boundary in BCC Iron. Brian Hyde¹, Diana Farkas¹ and Maria Jose Caturla²; ¹Materials Science, Virginia Tech, Blacksburg, Virginia; ²Fisica Aplicada, Univ. d' Alacant, Alicante, Spain.

Atomistic computer simulations were performed to investigate the mechanisms of grain boundary sliding in BCC Fe using the embedded atom method. For this study we have chosen the S=5 [001] (310) symmetrical tilt boundary under shear deformation. The response of the boundary to shear loading was studied by molecular statics and dynamics. Sliding was determined to be governed by GB dislocation activity with Burgers vectors belonging to the DSC lattice. The sliding process occurred by the creation and motion of grain boundary dislocations, including partial grain boundary dislocations that create a different grain boundary structure as an intermediate step in the sliding process. The sliding of the boundary under shear is accompanied by migration of the boundary parallel to itself. In analogy to the deformation of bulk materials, the deformation of this special boundary occurs by dislocations at shear stress values much lower than the theoretical strength of the boundary. The effects of interstitial impurities and vacancies located at the grain boundary on the sliding behavior was studied in the framework of empirical potentials.

2:30 PM Q7.5

Characterization of Micro and Nano Structured Materials Using Derivative and Power-Law Analysis of Load-Displacement Curves In Nano Indentation.

Thomas Frank Juliano, Vladislav V. Domnich and Yury G. Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Depth-sensing indentation is a powerful technique now regularly employed to test the mechanical properties, such as modulus and hardness, of materials at the micro and nano scale. However, much more information may be extracted from load-displacement curves generated by such tests. In this research, curves for Berkovich indentations on fused silica, fullerene thin film on sapphire, CdTe thin film on silicon, single crystal Si, nanostructured CDC films, and a PMMA/HA particle matrix are examined by derivative analysis and power-law curve fitting. The technique is applied to quantify the location of many different types of characteristic events, including cracking, phase transformation, and accelerated elastic recovery, that occur during material loading and unloading. Oftentimes, the corresponding pressures at which these events occur are of great interest. The strengths and limitations of this approach are discussed.

2:45 PM Q7.6

Nanoscale Grain Refinement and Mechanical Properties of Ordered Intermetallics. Alan Duckham¹, D Z Zhang^{1,3}, Dennis Liang², Robert C Cammarata¹, Robert L Leheny², Chia Ling Chien² and Timothy P Weihs¹; ¹Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland; ²Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland; ³Institute of Metal Research, Chinese Academy of Science, Shenyang, China.

We detail a mechanism of grain refinement for ordered intermetallic compounds that leads to fully dense, flaw-free, bulk nanocrystalline structures, and that can result in significant improvements in both strength and ductility. Initial ordered structures can be deformed and disordered by conventional deformation processes. The high driving force for reordering facilitates recrystallization of defect-free ordered nanoscale and ultrafine grains during subsequent annealing at relatively low temperatures. These new structures, which contain many new grain boundaries in an ordered matrix, are highly effective in impeding dislocation motion resulting in appreciable strength increases. Due to the lack of flaws such as porosity and impurities that typically plague more conventional methods of producing nanocrystalline materials, ductility is not compromised, even in tension. The result is a strong, tough bulk material. We will illustrate this type of grain refinement for ordered FeCo intermetallic alloys. A combination of neutron scattering experiments, transmission electron microscopy and differential scanning calorimetry were used to investigate reordering and recrystallization following high amounts of deformation by cold rolling. A series of tensile tests were conducted to investigate strength and ductility over a range of temperatures and we will report tensile strengths over 2 GPa and strength / ductility combinations that rival any known metal or alloy.

3:30 PM Q7.7

Solid-State Amorphization and Defects in Nanocrystalline Al Solid Solution Subjected to Surface Mechanical Attrition Treatment. Xiao-Lei Wu¹, George Ding², Nai-Rong Tao³, Y. S. Hong¹, J Lu⁴ and K Lu³; ¹State Key Lab of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing, 100080, China; ²Department of Computing, Math & Statistics, Grande Prairie Regional College, Alberta, T8V4C4, Alberta, Canada; ³Shenyang National Laboratory for Materials Sciences, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China; ⁴LASMIS, University of Technical of Troyes, Troyes, 10000, France.

Using high resolution electron microscopy the solid state amorphization (SSA) and crystal defects were studied in a nanocrystalline (nc) Al solid solution induced by the surface mechanical attrition treatment (SAMT). It was observed that the dislocation activity dominated during plastic deformation of nc grains with the larger end of the nanometer size regime (around 80-100 nm), by the presence of high density dislocations within the grain interior and near the grain boundary (GB). The dislocation density was measured to be as high as the order of magnitude of $21 \times 10^{16} \text{m}^{-2}$ in the local area near the GB. At higher dislocation density, the dislocation complexes appeared, i.e., the more complicated configurations to reduce the elastic energy resulting from their mutual interactions. Dislocation complexes were probably due to the severe strain and high strain rate during the SAMT. In particular, the localized SSA was observed to initiate along the GB where either high density dislocations or dislocation complexes present. Lattice instability due to elastic distortion within the dislocation core region was suggested to play a significant role in the initiation of the localized SSA at defective sites. The localized SSA should be interpreted in terms of defect-accumulation induced disordering. Meanwhile, the GB of severely deformed nc grains exhibited a continuously varying atomic structure in such a way that the majority of the GB is ordered but revealing corrugated configurations, while along the same GB, localized SSA may occur.

3:45 PM Q7.8

Production and Mechanical Properties of Nanostructured Intermetallics based on TiAl-X and TiAl3-X. Antonio Cabrera¹, Vicente Garibay-Febles², Hector A Calderon¹, Jose Gerardo Cabanas-Moreno¹ and Minoru Umemoto³; ¹Ciencia de Materiales, IPN-Mexico, Mexico DF, DF, Mexico; ²IMP, Mexico, DF, Mexico; ³Toyohashi University of Technology, Toyohashi, Japan.

Production of intermetallic materials in the systems TiAl-X and TiAl3-X (X = Cr, Mn, Fe) has been achieved by means of mechanical milling and sintering techniques. Spark plasma sintering was used since it reduces both time at high temperature and consequently grain growth. The produced materials have grain sizes in the nano and microscale depending on the material and processing variables. Sintered materials in the TiAl-X system are constituted by the gamma and the alpha2 phases while the TiAl3-X alloys are formed only by the cubic L12 phase. The average grains size ranges between 30 and 280 nm. Compression tests have been performed to evaluate their mechanical properties as a function of temperature and grain size. In all cases yield stresses higher than 1 GPa are obtained together with a ductility that depends upon temperature and grain size. No ductility is found for the smallest grains sizes tested (30 nm) at room temperature. Above 673 K, these materials show ductility and additionally they present a quasi superplastic behavior at temperatures higher than 973 K. On the other hand ductility can also be developed in the TiAl3-X alloys by inducing grain growth via annealing. Alloys with grains sizes around 400 nm show high ductility and a large density of microcracks after deformation suggesting that the yield strength becomes lower than the stress to propagate the cracks. In such materials, a considerably high strength is retained up to 873 K. Discussion on the mechanism of deformation in these materials will be given.

4:00 PM Q7.9

In-Situ Synchrotron Study of Phase Transformation Behaviors in Bulk Metallic Glass by Simultaneous Diffraction and Small Angle Scattering. Xun-Li Wang^{1,2}, Jon Almer³, C. T.

Liu², Y. D. Wang¹, J. K. Zhao¹, A. D. Stoica¹, D. R. Haeflner³ and W. H. Wang⁴; ¹Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ⁴Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Phase transformation is a promising way for making nanostructured materials in large quantities. Bulk metallic glass is a case in point. Upon heating into the supercooled liquid region, bulk metallic glass becomes partially crystallized resulting in a microstructure with a high-density ($10^{23} \cdot 10^{24} \text{m}^{-3}$) of nanometer sized crystalline particles embedded in the amorphous matrix. Nano crystallization in bulk metallic glass can be induced under a variety of conditions, including annealing, pressure treatment, and nanoindentation. Just how the crystalline phase nucleates has been a subject of debate. Phase separation is thought to occur prior to crystallization. However, such an argument is difficult to sustain without an experimental demonstration. Indeed, a recent investigation of partially crystallized $\text{Zr}_{57}\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}\text{Ti}_{15}$, combining differential scanning calorimetry, X-ray diffraction, and transmission electron microscopy, suggests just the opposite. Here we report an in-situ synchrotron study, involving simultaneous diffraction and small angle scattering, of the kinetics of phase transformation in $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_{15}$ bulk metallic glass. Our in-situ annealing study was carried out at the 1-ID beamline of the Advanced Photon Source at Argonne National Laboratory, using high-energy (77 keV) x-rays. The experiment provided first demonstration of a phase separation prior to the transformation. Furthermore, there is evidence that nucleation and growth of the crystalline phase occur in separate stages, with different kinetics. Our data support the view that crystalline nucleation is achieved via phase separation through a mechanism of short-range diffusion of small atoms (e.g., Ni) whereas the growth is determined by long-range diffusion. This research was supported by Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

4:15 PM Q7.10

TEM Investigation On Microstructural Characteristics In Nanostructured Al-Mg Alloy. Young Soo Park¹, Kyung H Chung¹, Nack J Kim² and Enrique J Lavernia¹; ¹Chemical eng. & Materials Sci., University of California, Davis, Davis, California; ²Center for Advanced Aerospace Materials, Pohang University of Science & Technology, Pohang, Kyungsang, South Korea.

The microstructural characteristics in nanostructured Al-Mg alloy

fabricated by cryogenic mechanical alloying (cryomilling) were studied using transmission electron microscopy (TEM). Nanocrystalline Al-Mg powders were prepared through cryomilling, and the powders were subsequently degassed, hot isostatically pressed, and extruded. The elongated grains (400~800nm long and 80~200nm width) having stacking faults were newly observed in the bulk nanostructured Al-Mg material after extrusion process. It was also found that nucleation and growth of some nanograins originated at the boundaries of the elongated grains. Equiaxed grains (30nm~100nm) were found along the nanograin boundaries. The grain boundaries of the equiaxed grains showed a strong spreading of thickness extinction contours being a feature of non-equilibrium boundaries. The orientations of the nano grains will be also discussed.

4:30 PM Q7.11

Direct Measurement of the Nanoscale Mechanical Properties of NiTi Shape Memory Alloy. Gordon A. Shaw², Wendy C. Crone¹, A. David Johnson⁴, Donald S. Stone³ and Arthur B. Ellis²; ¹Engineering Physics, Univ. of Wisconsin - Madison, Madison, Wisconsin; ²Department of Chemistry, Univ. of Wisconsin-Madison, Madison, Wisconsin; ³Department of Materials Science, Univ. of Wisconsin-Madison, Madison, Wisconsin; ⁴TiNi Alloy Co., San Leandro, California.

The mechanical behavior of NiTi shape memory alloy (SMA) has been characterized on the scale of 10 nm to several μm for sputter-deposited thin films. In addition to determining hardness and Young's modulus by nanoindentation, atomic force microscopy (AFM) was carried out to quantify shape recovery of the indentations in both austenite and martensite thin films using both Berkovich and cube corner indenters. Johnson's spherical cavity model for a sharp conical indenter was used to predict an upper limit for the indentation recovery ratio observed after heating, which agrees with experimental results for deeper indentations. Indents less than 100 nm deep, however, show markedly increased recovery, with the shallowest indents vanishing almost completely after heating. This is consistent with the depth at which the blunt tip of the Berkovich indenter starts to behave more like a spherical indenter, thereby producing a more uniform stress field and reducing non-recoverable plastic deformation. Nanoscratch experiments on martensite films for applied loads of 10 to 20 microNewtons also show nearly complete shape recovery. In addition, nanosphere lithography was used to fabricate arrays of NiTi nanostructures from the thin films in such a way that the properties of single nanoparticles could be directly probed using nanoindentation AFM.

4:45 PM Q7.12

Creep Behavior of the Directionally Solidified Ceramic Eutectic of $\text{Al}_2\text{O}_3/\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$. Jin Yi¹, Ali S. Argon¹ and Ali Sayir²; ¹Mechanical Engineering, MIT, Cambridge, Massachusetts; ²NASA John Glenn Research Center, Cleveland, Ohio.

The creep resistance of the directionally solidified ceramic eutectic of $\text{Al}_2\text{O}_3/\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$ was studied in the temperature range of 1200-1520°C both experimentally and by mechanistic dislocation models. The topologically continuous majority phase of Al_2O_3 , has a nearly perfect growth texture in the [0001] direction and encapsulates the minority $\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$ phase in a variety of morphologies, mostly in the fibrillar form with a size of around 100-200 nm. This encapsulated minority phase has a close to <112> growth texture, regardless of morphology. The two phases are separated by incoherent, well structured and atomically narrow interfaces. The creep of the eutectic in its growth direction exhibits an initial transient that is attributed to stress relaxation in the coarse $\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$ phase, but otherwise in steady state shows many of the same characteristics of creep in sapphire single crystals with [0001] orientation. The creep strain rate of the eutectic has stress exponents in the range of 4.5-5.0 and a temperature dependence suggesting a rate mechanism governed by oxygen ion diffusion in the Al_2O_3 . Finite element analysis of stress distribution in the two phases and a detailed dislocation model of the creep rate indicate that much of the nano-scale encapsulated $\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$ is too small to deform by creep so that the major contribution to the recorded creep strain is derived from the diffusion-controlled climb of pyramidal edge dislocations in the Al_2O_3 phase. The evidence suggests that the climbing dislocations in Al_2O_3 repeatedly circumvent the $\text{c-ZrO}_2(\text{Y}_2\text{O}_3)$ domains acting as dispersoids resulting in the stress exponents larger than 3. The creep model is in very good agreement with the experiments.

SESSION Q8: Poster Session
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

Q8.1

Lamellar Hexadecyl Aluminum Silsesquioxanes and Isobutyl

Silicates as Synthetic Clays for Nanocomposites.

Thuy Truong Chastek¹, Frederic Lortie², Christopher W. Macosko² and Andreas Stein¹; ¹Chemistry, University of Minnesota, Minneapolis, Minnesota; ²Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Layered silicates and aluminosilicates with covalently attached organic functional groups were investigated as synthetic clays for dispersion and exfoliation in a polymer melt without any added compatibilizers. Clay syntheses were optimized to improve layer stiffness, increase the aspect ratio of clay sheets, and increase the miscibility with desired polymers. Lamellar, mesostructured aluminum silsesquioxanes with hexadecyl groups attached to inorganic layers (C16-LMAIS) were prepared by a sol-gel synthesis in the temperature range from room temperature to 80 deg. C. Powder-XRD patterns confirmed the lamellar phase morphology with d-spacings of 5-6 nm. Electron microscopy showed sheet-like morphology and increased particle sizes at higher synthesis temperatures. The incorporation of organic groups into the inorganic lamellae was confirmed by ²⁹Si-MAS solid-state NMR and IR spectroscopy. The degree of condensation increased with increasing temperature. ²⁷Al-NMR showed the presence of 4-coordinate and 6-coordinate aluminum. TGA indicated 70 % organic content and an increase in thermal stability of the composite with higher synthesis temperatures. The clay thickness was increased with addition of tetraethoxysilanes as confirmed by XRD and TGA. C16-LMAIS was processed with polystyrene by melt blending. Melt rheology was used to determine the modulus of the composite. Lamellar mesostructured silicates with 10 mol % isobutyl groups incorporated into the inorganic layers (iC4-LMS) were prepared at 150 deg. C for 72 h. The lamellar morphology was confirmed by XRD, SEM, and TEM. Isobutyl functional groups were incorporated into the framework as confirmed by IR. iC4-LMS exhibited solvent affinity and network formation with toluene, xylene, styrene, and tetramethyl pentadecane. TEM images showed that lamellar plates re-aggregated after the solvent dried. These materials were investigated for nanocomposite formation by melt blending with non-polar polymers.

Q8.2

A Study on the Microstructure of the Nano Concrete Composite Material. Wei-Ming Hou and Ping-Kun Chang; Civil Engineering, Van-Nung Institute of Technology, Tao-Yuan County, Taiwan.

This study applies three methods: the nuclear magnetic resonance(NMR), the mercury instrument porosimetry (MIP), and the transmission electron microscopy (TEM) to examine the microstructure of the composite material of nano concrete. The test results show that owing to the effect of the nano scale powder, the CH content within the composite material is decreasing, and then the content of C-S-H and C-A-H gel is increasing, filling out the capillary pores. This way, The microstructure of this composite material is transformed in its arrangement, which makes concrete much more well-mixed and more densified, enhancing the compressive and the tensile strength. The permeability is cut down as well. In conclusion, it ends in better durability Key Words: Nano Concrete Composite Material, Microstructure, Nuclear Magnetic Resonance (NMR), Transmission Electron Microscopy (TEM)

Q8.3

Dielectric And Viscoelastic Behavior Of Nylon 6-, Nylon 66-Clay Nanocomposites. Pramoda Kumari Pallathadka¹, Tianxi Liu¹, Shang Shang Tay¹, Phang In Yee¹, Chen Ling¹, Ting Ting Lin¹ and Pisharath Sreekumar²; ¹IMRE, Singapore, Singapore; ²NTU, Singapore, Singapore.

During the past decade much attention has been paid to the development and characterization of nanostructured polymer-clay (layered silicate) composites. The properties of the polymer matrix can be largely improved by a uniform dispersion of layered silicate nanofillers in it. The present study examines the dielectric and the plastic deformation behavior of the nylon 6-clay and nylon 66-clay nanocomposites for a better understanding of their dielectric properties and deformation mechanics. The nanocomposites were prepared by melt compounding and the exfoliation of clay was evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). With increasing clay content (up to 5 wt.% clay), storage modulus increased progressively for both systems by ~0.5 GPa, whereas glass transition temperature remained almost constant for both the nanocomposites. The property improvements were attributed to the nanoscale dispersion of high aspect ratio clay within the polymer matrices. Compared to neat resins, the onset of degradation was nearly 20 degree C higher for nylon 66/clay nanocomposites in both air and N2 environments, whereas it is ~12 degree C higher in N2 environment and there is no change in air with clay loading for nylon 6/clay nanocomposites. The dielectric constant was found to be higher for nylon 66/clay nanosystems compared to

nylon 6/clay nanocomposites; and both nanocomposites exhibited higher dielectric constant than their respective polymer matrices. However, for the sample with lower clay concentration (with 2.5%) the dielectric constant was found to be the highest and it decreases with increasing clay loadings, indicating that fine clay dispersion (exfoliation) plays an important role in the improvement of dielectric property and storage modulus in the nylon 6- or nylon 66-clay nanocomposites.

Q8.4

Mechanical Properties of a Natural Nanocomposite: Ivory. Mary Anne White and Champika Samarasekera; Dalhousie University, Halifax, Nova Scotia, Canada.

Ivory is a composite material composed of inorganic material (hydroxyapatite) in an organic (collagen) matrix. Type I collagen is formed by three protein chains which are wound together to form a triple helical structure. The crosslinking of the collagen molecules gives the structure a high tensile strength and stiffness. Embedded in this are nano-sized hydroxyapatite crystals forming an hcp lattice which provides compressional strength. The tripartite organization of hydroxyapatite and collagen leads to an anisotropic structure for an ivory tusk, usually defined in terms of the radial, circumferential and transverse planes. In this study, the flexural strength and elastic modulus were determined along the transverse and radial planes of ivory.

Q8.5

Functionalization of Carbon Nanotubes with Silicon Carbide Nanolumps. Shuo Chen, Dezhi Wang, Jinyu Lao, Jianyu Huang and Zhifeng Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

Silicon carbide nanolumps on the surface of multiwall carbon nanotubes have been fabricated following the procedure used to synthesize boron carbide nanolumps. The localized solid-state reaction happens between silicon and carbon nanotubes. The structure of carbon nanotubes remains unchanged after the reaction. Through TEM study, it was found that the inner layers of multiwall carbon nanotubes also reacted with silicon to form silicon carbide, which could provide a very strong interface with the matrix of composites. Because of the unique morphology, these modified multiwall carbon nanotubes can be ideal reinforcing fillers for high-performance composites. The fabrication and mechanical properties studies of the composites using such modified carbon nanotubes will also be discussed.

Q8.6

Surface Deformation Behavior of Well Oriented Block Copolymers. Panitarn Wanakamol¹, Yung-Hoon Ha¹, Christian Grippo², Mary Boyce² and Edwin L Thomas¹; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts.

The evolution of the microdomain structure of block copolymers (BCP) during tensile deformation has been extensively studied using a variety of experimental techniques. Most studies employ transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS), which provide detailed information in bulk. In order to better understand surface deformation phenomenon, in situ atomic force microscopy (AFM) is performed on well-oriented BCP. We first produced a near single crystal texture BCP film via the roll casting technique. The deformation behavior of the samples was then monitored over time in real space using an AFM equipped with a special deformation apparatus. To examine the effect of anisotropy, the samples were deformed in different directions relative to the microdomain alignment. We also investigate nanoparticle filled BCPs to understand how the reinforcing particles interact with and modify the deformation field.

Q8.7

Abstract Withdrawn

Q8.8

Mechanical Properties of Poly(L-lactic acid)/Layered Silicate Nanocomposites. Vahik Krikorian^{1,2} and Darrin Pochan^{1,2}; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

In this investigation the mechanical properties of a novel silicate layered nanocomposite based on a biocompatible/biodegradable polymer matrix was studied. Three types of commercially available organophilic clays were employed in order to concurrently study the effect of surfactant compatibility with the polymer matrix on the overall mechanical properties of nanocomposites. Bulk nanocomposites were fabricated via the exfoliation adsorption technique and

nanocomposite fibers were fabricated with electrospinning using Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polyester, as the polymeric matrix. By controlling the extent of organoclay exfoliation one can use this system to directly study the effect of degree of exfoliation on overall mechanical properties. Wide Angle X-ray Scattering (WAXS) data reveals that decreasing the hydrophobicity of the surfactant increases the tendency of the system to exfoliate and randomly distribute the silicate layers throughout the matrix. Transmission electron microscopy (TEM) data shows the ordering of silicate platelets is consistent with the d-spacings obtained from WAXS. Due to the nanometer range dispersion of silicate layers all the nanocomposites retain their optical clarity. Mechanical properties of the fabricated nanocomposites both in the fiber mat form and solution cast films were probed by dynamic mechanical analysis and tensile testing techniques and show significant improvements both in terms of toughness and stiffness when compared to neat PLLA. Higher extent of exfoliation gives rise to higher contact surface area between silicate layers and the matrix and consequently higher stiffness.

Q8.9

Abstract Withdrawn

Q8.10

Abstract Withdrawn

Q8.11

Vibrational Frequency of MgO Nanoparticles in a Polymer Matrix. Prafulla Kumar Jha and Mina K. Talati; Physics dept., The M.S. University of Baroda, Vadodara, Gujarat, India.

The nanoparticles with large surface to volume ratio exhibit anomalous thermal and electrical properties such as the behaviour of specific heat at low temperature, much lower melting temperatures than those of corresponding bulk materials and the enhancement of superconducting transition temperature phenomena are considered to be related directly or indirectly to the modification of phonon spectrum due to the surface and the size effect. Exciton-phonon coupling is a crucial issue in the nanostructure systems and this has motivated much of the previous work on the vibrational modes of the nanostructure systems. MgO nanoparticles are an important material due to their numerous applications. Recently, MgO nanoparticles have been found to be biocidal and useful in destroying bacterium. The MgO nanoparticles are solid biocidal and hence more advantageous in comparison to the normally used gas or liquid biocidal. To the best of our knowledge, the vibrational properties of MgO nanoparticles have not been investigated so far. Hence, it is right time to investigate the vibrational properties of MgO nanoparticles and know its low temperature specific heat behaviour, size dependent melting point etc. In the present work, we report the vibrational frequencies of MgO quantum dots and the effect of coupling between the nanoparticles and surrounding medium. For this purpose, we have used the continuum model by considering the appropriate boundary condition on the surface of the nano crystal [1]. Two types of vibrational modes namely spheroidal mode and torsional mode are obtained, which represent vibrations with dilation and without dilation, respectively. While the spheroidal mode depends on the materials via its sound velocities, the torsional modes do not depend on the material. In the present case for Cl/Ct = 1.367, the phonon frequencies have been calculated for the first time. Our results show the general trends of the phonons behaviour and reveal the important feature of inversely dependence on the size of the particles. We have also calculated the effect of polymer matrix on the breathing mode frequency and found that the frequency of the particular mode decreases. We also observed that the mechanical damping is prominent. [1]. A. Tanaka et al. Phys. Rev. B47, 1237 (1993).

Q8.12

Influences Of Amorphity Nanosize Mo and MoO2 Fillers On Tribological Properties Of Composite Polymeric Materials.

Victor Korunovich Makaryan¹, Razmik Malkhasyan¹, Albert Pogosyan² and Arshak Isadzhanyan²; ¹ATOM SPE, Erevan, Armenia; ²SEUA, Erevan, Armenia.

In the present work the features of creation of composite materials on a polymeric basis with use of nanosize amorphous and crystalline fillers of molybdenum and its oxides are considered. As polymeric matrixes a copolymer of formaldehyde with dioxolan and polyphenylethylen sulfide are chosen. The estimation is given to bonds formed on a macroscopical interface of phases between a polymeric matrix and a grain of filler. Comparative tests of the same composite materials are carried out at replacement of nanosize crystalline fillers Mo and MoO₂ on similar nanosize amorphous materials. It is shown, that improvement of physicomechanical properties of a composite material to the greater degree depends upon surface activity of filler and its ability to be implanted into the structure of a matrix. The

comparative estimation of composite polymeric materials obtained basis of the given two matrixes is made

Q8.13

Mechanical Properties of Chemically Functionalized Clay Vinyl Ester Nanocomposites. Balakrishnan Subramanian and Dharmaraj Raghavan; Chemistry, Howard University, Washington, DC, District of Columbia.

In recent years, the area of nanoclay filled polymer nanocomposites has received considerable attention with the expectation that nanotechnology can lead to lighter and improved performance materials for aerospace and automobile applications. To achieve significant improvement in the properties of polymer nanocomposite, dispersion of clay platelets at the nanometer scale in the polymer matrix is desired. Because of the hydrophilic nature of the clay, often clay must be chemically treated with organic modifier so as to overcome the clay agglomeration and achieve improved clay dispersion. The primary objective of this study is to examine the role of reactive and nonreactive organic modifiers in exfoliation and dispersion of clay platelets in polymer matrix and evaluate the mechanical properties of nanocomposites. The present study represents the first reporting of a long chain reactive surfactant (olefinic functional C19 amine hydrochloride) synthesized from vernonia oil for vinyl ester nanocomposites application. When the clay was ion-exchanged with a combination of reactive and nonreactive (octadecyl amine hydrochloride) surfactant, a partially exfoliated vinyl ester nanocomposite was formulated. When the organoclay and vinyl ester resin were separately soaked in styrene comonomer for 3 h and the mixture was subjected to sonication, a highly exfoliated nanocomposite was formed. The degree of dispersion of the clay platelets in vinyl ester matrix was found to be sensitive to the chemistry associated with clay platelet modification, reactive comonomer and processing conditions. At an organoclay loading of only 3.5wt%, the modulus improved by 20% in partially reactive organoclay system, while the modulus improved by 10% in nonreactive organoclay system compared to that of pristine vinyl ester resin. Through this study, we demonstrate that it is the combination of partially reactive functionalized clay and mixing conditions that promotes layer separation and achieves a greater degree of exfoliation and improvement in the mechanical properties of nanocomposites. Acknowledgment : This project is funded by AFOSR

Q8.14

Mechanical Properties of Nano-Hybrid Films - Influence of Sol-Gel Chemistry. G. Calleja, C. Tartivel, B. A. Latella, D. J. Cassidy, C. J. Barbe and John Bartlett; Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia.

Organic-inorganic nanohybrids obtained by sol-gel processing offer a versatile new approach for fabricating thin films for a wide range of applications, including sensors, waveguides, integrated optics, and corrosion and scratch resistant coatings. A critical issue for technological applications of these coatings is their mechanical behaviour and adhesion to the substrate. By controlling the chemistry of the organic moieties incorporated into the nanohybrids, the mechanical properties of the resulting coatings can be readily modulated to achieve optimum adhesion and hardness required to provide good scratch resistance properties. To investigate the influence of the connectivity of the inorganic network and the chemistry of the organic modifier on the final mechanical properties, coatings were deposited on silicon wafers by spin-coating mixtures of TEOS and 3-glycidioxypropyltrimethoxysilane (GTMS). Processing conditions were chosen to enable the structural evolution of the inorganic and organic networks to be controlled independently. The connectivity of the inorganic and organic networks during processing was investigated by ¹³C- and ²⁹Si-NMR, SAXS, FT-IR and Raman spectroscopy, while the corresponding mechanical properties of the coatings (Young's modulus, hardness and adhesion) were probed via nano-indentation and in-situ tensile testing. The influence of organic chain length and chemical functionality on the structural evolution and mechanical properties of the nanohybrid films was investigated by substituting GTMS with precursors such as methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), phenyltrimethoxysilane (PhTMS), n-octyl-tri-ethoxysilane (OTES) and N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMSPED). The mechanical properties of the coatings were found to be strongly modulated by the size of the organic modifier, with increasing size leading to a corresponding decrease in the Young's modulus. In contrast, only small differences were observed between the mechanical response of films obtained from precursors with similar chain lengths but different chemical functionality. This effect is attributed to nanosegregation of the organic and inorganic domains during the structural evolution of the coatings, which leads to a significant decrease in the long-range connectivity of the network. Increasing the size of the organic substituent promotes nanosegregation. Similarly,

increased ageing of nanohybrid coatings obtained from GTMS (leading to more extensive polycondensation) led to a decrease in both the Young's modulus and hardness and to a corresponding increase in the surface roughness. The relationship between the connectivity of the inorganic network, the volume fraction and size of the organic modifier, and the mechanical response will be discussed.

Q8.15

The Structure and Mechanical Properties of Cu-Nb Nanocomposites. Mikhail Andreevich Tikhonovsky, Natalija F. Andrievskaja and Anatoly I. Pikalov; -, National Science Center "Kharkov Institute of Physics and Technology", Kharkov, -, Ukraine.

The methods of producing nanocomposite wires from two-phase alloys with both ductile phases have been developed. The structure of Cu-Nb nanocomposites and internal stresses in components were studied by transmission electron microscopy and X-ray method. The 0,2-2,3 mm diameter wires with strength 2100-1200 MPa were manufactured. It is found that starting from certain degree of drawing deformation, dependent on the alloy dispersion, the sharp increase in strength takes place. This is accompanied by appearance of certain peculiarities in the structure of material. Firstly, in the nano-scaled niobium fibres, along the wire axis, significant (up to 0,8%) tensile elastic stresses appear. Secondly, the narrow knife-like boundaries along the niobium fibres are observed. The reasons for the structural features observed and the conditions of obtaining the ultimate high strength in the material under consideration are discussed.

Q8.16

Polymer Nanocomposite Prepared by Solid State Extrusion. Cheng-ya Huang¹, Lei Liu¹, Ke-cheng Gong¹ and Hong Li²; ¹College of Materials Science and Engineering, South China University of Technology, Guangzhou, China; ²Guang Dong University of Technology, Guangzhou, China.

Layered silicate has shown some magic reinforcing effect in polymer/layered silicate nanocomposite, especially in polar polymer matrix such as Nylon, however in nonpolar polymer matrix such as PE or PP, the reinforcement of layered silicate seems not play such an important role as polar polymers for the reason of layered silicate's incompatibility with nonpolar polymer matrix. In order to disperse the layered silicate into nonpolar polymer matrix uniformly for the utmost improvement of mechanical properties of conventional polymers like PP or PE, solid state extrusion is used to redisperse those nano-layered silicates such as montmorillonite, mica in PE or PE matrix through the large strains by shear force. The experiment results show that only 2 wt% of mica filled in PE increase the tensile strength of PE more than 4 times and improve the yield strain of PE more than 10 times. WAXS, TEM, DSC have been used to characterize the structure of those polymer/layered silicate nanocomposites.

Q8.17

Hydrogen-Bonding and Polymer Mediated Assemblies of Nanoparticle towards Biomimetic Membranes. Nancy N Kariuki, Melissa Patterson, Li Han and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

Thin films derived from nanocrystal cores and functionalized linkers serve as attractive candidates for chemical or electrochemical sensing interfaces because of a number of intriguing attributes including a large surface area-to-volume ratio and three-dimensional ligand framework properties. The control of the size, interparticle spatial property, and processability of metal nanoparticles as organic-inorganic composite materials is important for potential sensory applications. This presentation describes the dispersion and assembly of pre-engineered gold and alloy nanoparticles within a polymeric matrix. The goal is to understand the potential membrane properties of the nanomaterials for chemical/biological sensing. The investigation focused on two related aspect of the preparation and characterization. The first dealt with the derivatization of nanoparticle shell with functional groups. The second dealt with the assembly of the functionalized nanoparticles into thin films. Gold and gold-silver alloy nanoparticle, hydrophilic polymers such as poly(2-hydroxyethyl methacrylate), and difunctional alkyl molecular linkers were studied as a model system for thin film assembly of the nanoparticles. Techniques such as NMR, FTIR and UV-Vis and electrochemical methods were used for characterizations. The formation of different morphologies and ordered arrays for the assembly of the nanoparticles was observed. Implications of the findings to the design of nanostructured membranes for chemical/biological sensing or catalytic applications will also be discussed.

Q8.18

Micromechanical Modeling of Polymer/Clay Nanocomposites. Nuo Sheng, Mary C Boyce and David M Parks; mechanical

engineering, MIT, Cambridge, Massachusetts.

Polymer/clay nanocomposites can exhibit markedly enhanced mechanical properties at low weight fractions of clay. Continuum-based composite modeling robustly connects the dependence of enhanced properties to particular features of the second-phase "particles"; especially, the particle volume fraction, aspect ratio, and orientation, and ratios of particle mechanical properties to those of the matrix. However, concepts such as "matrix" and "particle" cannot be directly applied to polymer/clay nanocomposites, due to the hierarchical morphology of intercalated nanoclay and surrounding matrix. We represent the nanoclay by an "effective particle", the volume and mechanical properties of which depend on silica lamina stiffness and the as-processed internal clay structure, the latter characterized by the number of silica sheets per particle and inter-sheet spacing. Various structural/constitutive representations of the resulting "effective particle" can be devised; for each case, macroscopic mechanical properties are then calculated by analytical/numerical micromechanical models based on the "effective particle". Predictions of the macroscopic elastic modulus of polymer/clay nanocomposites, utilizing the "effective particle," are in excellent agreement with experimental data, and quantify the expected benefits of processing towards complete exfoliation of the nanoclay. The adopted methodology offers promise for study of related properties, both mechanical (e.g., thermal expansion) and non-mechanical (e.g., permeability) in polymer/clay nanocomposites.

Q8.19

Mechanical Properties of Boron Doped Diamond Film Prepared by MPCVD. Qi Liang, Shane Catledge and Yogesh K. Vohra; physics, University of Alabama at Birmingham, Birmingham, Alabama.

A chemical vapor deposition hydrogen/methane/nitrogen feedgas mixture with unconventionally high methane (15% CH₄ by volume) normally used to grow ultra-hard and smooth nanostructured diamond films on Ti-6Al-4V alloy substrates was modified to include diborane (10% B₂H₆ in hydrogen) for boron-doping. The flow rates of N₂ and B₂H₆ were varied to investigate their effects on plasma chemistry, film structure, and mechanical properties. It was found that although boron in the plasma can easily be incorporated into diamond films and change the lattice parameter, nitrogen, on the other hand, acts to prevent boron incorporation into the diamond structure. Grazing angle x-ray diffraction shows a strong dependence of diamond lattice parameter with N₂:B₂H₆ flow rate ratio. Also observed is a gradual broadening of the diamond peaks as well as a decrease of diamond peak intensity. It was found that nanostructured boron doped diamond can be obtained at extremely low boron incorporation level. Thermal stability of these films will be evaluated by heating in an oxygen environment above 600°C (the temperature at which non-boron doped nanostructured diamond films begin to break down). Nanoindentation measurements show that the films have high hardness close to that of nanostructured diamond. High film hardness and toughness, combined with good thermal stability and low surface roughness indicate great potential as wear resistant coatings able to withstand high temperature oxidizing environments. We acknowledge support from the Department of Energy (DOE) Grant No. DE-FG03-03NA00067/A000.

Q8.20

A Comparative Wear Assessment of Uncoated and Nanocrystalline and Multilayer Diamond Coated Implants of the Temporomandibular Joint. Malesela J. Papo¹, Shane Catledge¹, Camillo Machado², Somaieh Kashef¹ and Yogesh K. Vohra¹; ¹physics, University of Alabama at Birmingham, Birmingham, Alabama; ²Prosthodontics and Biomaterials, University of Alabama at Birmingham, Birmingham, Alabama.

The service lifetime of medical prostheses can be extended by coating with a highly wear resistant material such as a diamond film. We demonstrated this fact by using microwave plasma chemical vapor deposition (MPCVD) to deposit nanocrystalline and composite diamond thin films on simulated dental implants of the temporomandibular joint (TMJ). The novel composite diamond thin film consisted of a nanocrystalline/microcrystalline/nanocrystalline film configuration that was obtained by varying the composition of N₂ in the feedgas mixture. The thin films were deposited on Ti-6Al-4V substrates that were machined to imitate the condyle and fossa components of the TMJ. Raman and X-ray diffraction (XRD) analysis of both films after deposition indicate a diamond crystalline component, with an average crystallite size of approximately 15 nm. The mechanical properties of these films were evaluated by subjecting them to wear tests in a custom-built mandibular movement simulator (MMS) for 10⁶ loaded cycles, which are equivalent to 8.8 years of typical use. In order to demonstrate the efficacy of these coatings, we included a polished but uncoated condyle/fossa pair as a control. Analysis of the wear surfaces after testing by optical microscopy,

SEM, and Raman spectroscopy showed that damage in both thin films was minimal and did not result in loss of film from the substrate through film delamination and/or cracking. No difference was observed in the wear performance of both films under these testing conditions. However, comparison with an uncoated condyle/fossa pair showed that the thin film coated condyle/fossa pairs had improved wear performance. We acknowledge support from the National Institute of Dental and Craniofacial Research (NIDCR), National Institutes of Health (NIH) under Grant No. 5R01DE013952-03.

Q8.21

Unique Mechanical Properties of Carbon Nanotube Film-Solid State Interfaces. Josh R Gladden¹, Clascidia A Furtado¹, Julian D Maynard¹ and Peter C Eklund^{1,2}; ¹Physics, Pennsylvania State University, University Park, Pennsylvania; ²Materials Science, Pennsylvania State University, University Park, Pennsylvania.

Single wall carbon nanotubes (SWNTs) have unique mechanical properties such as a Young's modulus in the terrapascal range and an extremely high plastic limit. We will describe experiments in which thin (100-1000nm) films of purified carbon nanotube bundles, and also films of individual nanotubes, were deposited on a face of various single crystals polished to have a parallelepiped geometry. The SWNT/substrate system was then mechanically driven through a series of normal modes of vibration while monitoring the resonance line shapes. It was expected that the SWNT mat would introduce added damping to the system and thus lower the quality (Q) factor of the resonances. In fact, it was found that the quality factors increased dramatically for almost all of the modes associated with the five substrates. Also, the effect was found to be strongly dependent on the thickness of the SWNT mat. A model for these surprising observations will be presented.

Q8.22

Diamond-Coated Cemented Carbide Tools: Effect of pre-treatment techniques on film structure and mechanical properties. Vaibhav Vohra, Shane Catledge and Yogesh K. Vohra; physics, University of Alabama at Birmingham, Birmingham, Alabama.

Chemical Vapor Deposition (CVD) using hydrogen, methane, and nitrogen feedgases has proven to be useful in depositing well-adhered nanostructured diamond films on metal substrates. These films have already found a market in the cutting tool industry as coatings on tungsten carbide inserts. The purpose of this investigation is to examine to what degree does thermal and chemical pre-treatments on the tungsten carbide inserts affect their structure and performance. Chemical and thermal pre-treatments have often been used to remove cobalt from the surface, and thereby minimize its catalytic effect of graphite formation. The diamond-coated inserts in our study were characterized using x-ray diffraction, Raman spectroscopy, atomic force microscopy, and Rockwell adhesion testing. Previously, it has been found that the cobalt binder phase (typically 6 wt.%) has caused adhesion difficulties at the substrate-diamond interface because of its propensity for graphite formation during CVD diamond growth, further hindering the performance of the cutting tool. The significance of cobalt in the diamond coating process is an important part of this study. We use an unconventionally high methane concentration in the feedgas in order to saturate the growth surface with carbon and limit migration of cobalt from the bulk. Nitrogen is used in the feedgas in order to provide a tough, single-layer nanocrystalline diamond film structure. A multi-layer (nano-/micro-/nano-crystalline) CVD diamond film is also grown by controlling the flow of nitrogen in order to show its characteristics in comparison with the single layer nanocrystalline diamond film. Preliminary results indicate that our feedgas mixture results in well-adhered nanostructured diamond films for the pre-treated as well as untreated inserts with only very minimal cobalt-induced graphitic formation for the untreated insert. This may lead to diamond-coated inserts that do not require a pre-treatment step in their fabrication. We acknowledge support from the National Science Foundation (NSF), Research Experiences for Undergraduates (REU)-Site award under Grant No. DMR-0243640.

Q8.23

Processing and Mechanical Properties of Baroplastic Materials. Juan Antonio Gonzalez, Metin H Acar, Sang-Woog Ryu and Anne M. Mayes; Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

It has been demonstrated that pressure can be an important thermodynamic parameter for the phase behavior of polymer mixtures. Since microstructure determines the macroscopic behavior of the material, pressure can have an effect on the bulk properties of certain polymer systems. A novel class of materials, termed baroplastics, consists of nanostructured polymer systems that can be processed at reduced temperatures upon the application of pressure. Baroplastics

consist of two components, a low T_g and a high T_g component, that present pressure-induced miscibility, resulting in a mixture able to flow, at temperatures below the T_g of the glassy component, when pressure is applied. Two different classes of baroplastic materials have been developed in our group: block copolymers and core-shell nanoparticles. Both present reduced temperature processing and multiple recyclability. Their nanostructure was characterized by neutron scattering experiments, AFM and TEM. Compression molding of these materials was carried out using simple molds and a standard hydraulic press under different temperatures and pressures. Temperatures as low as room temperature were enough to obtain a well-defined product under the applied pressure. The effects of composition, morphology and processing conditions on the final product are presented and the differences in their mechanical behavior are shown.

Q8.24

Flow-Induced Macroscopic Alignment of Block Copolymer Based Ceramic Hybrid Materials. Anurag Jain¹, Carlos B.W.

Garcia¹, Sol M. Gruner² and Ulrich B. Wiesner¹; ¹Materials Science & Engineering, Cornell University, Ithaca, New York; ²Department of Physics, Cornell University, Ithaca, New York.

Macroscopic alignment of the microstructure of block copolymers under flow fields is a well-established phenomenon. Orientation of the microstructure of block copolymers either parallel or perpendicular to the direction of flow can be achieved by carefully manipulating the flow fields. The directional nature of the physical properties and the single-crystal like microstructure of the resulting materials hold promise for application in diverse fields including fuel cell and separation technology. The performance profiles of the macroscopically aligned single-crystal like monodomains can be considerably enhanced by incorporation of inorganics in the copolymer. Here we present a scheme for the macroscopic alignment of organic-inorganic hybrid materials. The hybrids consist of amphiphilic block copolymers as structure directing agents for ceramic precursors. Varying amounts of the ceramic precursors can be used to obtain different mesoscale structures, such as lamellae and hexagonally packed cylinders. In order to align the microstructure, flow fields must be applied while the microstructure sets. This was done with a custom-built device which subjects solutions of the polymer and ceramic precursor to a steady flow while the solvent evaporates. This flow induces a shearing force, causing macroscopic alignment of the mesoscale structures. Small-angle X-ray scattering (SAXS) was used to quantify the degree of alignment of the hybrids.

Q8.25

Piezo- and Pyro-Resistive Polymer-Nanotube Nanocomposites. Nathan A Pearce², Hilmar Koerner¹ and Richard A Vaia²; ¹Nonmetallic Materials Division, Univ of Dayton Research Institute, Dayton, Ohio; ²Air Force Research Laboratory, AFRL/MLBP, Wright Patterson AFB, Ohio.

Shape-recovery, elastomeric nanocomposites, fabricated via a solution-mediated dispersion of multi-wall carbon nanotubes and polyurethane, exhibit a wide range of piezo- and pyro-electrical properties with numerous industrial, commercial and military applications. In addition to previously demonstrated tensile and survivability enhancements, the percolative morphology of the conductive nanotubes leads to a strong correlation between the polymer morphology (amorphous v. crystalline), nanotube orientation and concentration and the electrical characteristics of the nanocomposite. Small increases in temperature result in decreases in resistivity while low strains contribute to increases in resistivity. It is therefore possible to generate reversible changes in the conductive properties of the elastomer by physical deformation and thermal regulation. In order to tailor the piezo- and pyro-resistive properties of the nanocomposites for a given application, resistivity measurements during tensile deformation and temperature sweeps are compared to crystalline content and nanotube orientation from X-ray diffraction to establish performance-morphology relationships and elucidate the conductivity mechanism in these nanocomposites. The observance of low power resistive heating under DC currents also indicates a potential for an electrically induced shape-memory response with broad implications ranging from self-recovery/healing characteristics and artificial mechano-receptors, to remotely actuated deployment of space structures.

Q8.26

Effect of Coupling Agent on the Dispersion of Polyethylene Terephthalate (PET)/Montmorillonite Nanocomposite Films. Ajit Ranade¹, Nandika Anne D'Souza¹, Bruce Gnade¹, Christopher

Thellen², Danielle Froio², Jeanne Lucciarini² and JoAnn Ratto²; ¹Materials Science & Eng., University of North Texas, Denton, Texas; ²United States Army Soldier Systems Center, Natick, Massachusetts.

Dispersion of organically modified montmorillonite layered silicates (MLS) in a polymer matrix strongly influences the barrier, mechanical and thermal properties of the host matrix. We have observed a non-intercalating & no-exfoliating behavior in amorphous PETG MLS nanocomposites. We observed improvement in barrier properties despite of poor MLS dispersion. Here we investigate the effect of maleic anhydride as a coupling agent on the dispersion behavior in PET nanocomposites and correlate the parameters affecting the dispersion and properties. Nanocomposites of PET with and without the coupling agent were compounded on a twin-screw extruder and films of PET nanocomposites were prepared by flat film extrusion using different screw speeds. X-ray diffraction and transmission electron spectroscopy (TEM) determined the MLS dispersion was improved in some of films. A decrease in oxygen permeation was observed for PET nanocomposite films. Mechanical properties of the nanocomposite films improved compared to the pure PET film. Differential scanning calorimetry (DSC) was used to study the effect of MLS on the crystallinity of PET.

Q8.27

Orientation Effect of Carbon Nanotube under Magnetic Field. Wansoo Huh¹, Sang-Won Lee¹, Jang-Yeop Kim¹, Barry Farmer², Richard Vaia² and Gary Price³; ¹Chemical & Environmental Engineering, Soongsil University, Seoul, South Korea; ²AFRL/MLBP, Air Force Research Laboratory, WPAFB, Ohio; ³Non-Metallic Division, University of Dayton Research Institute, Dayton, Ohio.

For the orientation of carbon nanotube, there are several ways to induce the orientation by applying the forces such as elongational force, shear force, electric field, magnetic field. Depending upon the amount of carbon nanotube, the type of the field, the degree of field power, the polymer characteristics, the viscosity of matrix polymer, the temperature, and the residence time, the orientation effect of carbon nanotube would show different behavior. In this study, the orientation of carbon nanotube in epoxy matrix by applying the magnetic field was studied. The carbon nanotubes of various content from 0.1 wt.% to 10 wt.% were mixed with epoxy and the orientation of carbon nanotube was obtained under the permanent magnet. After inducing the orientation of carbon nanotube, the epoxy matrix was cured by raising the temperature. The degree of orientation of carbon nanotubes was characterized.

Q8.28

Multi-scale simulation of polymer-nanocomposite deformation. Kelly L. Anderson, Sangwook Sihm, Ajit Roy, Richard A. Vaia and Barry L. Farmer; Materials & Manufacturing Directorate, AFRL, Dayton, Ohio.

Various types of nanocomposites are becoming readily available for a plethora of target applications. One Air Force interest is in mechanical reinforcement by epoxy-based composites. However, an understanding of the combined mechanical properties of these composites, as the inclusion dimensions decrease, is lacking. Here, mechanical properties are extracted from atomistic and coarse-grained MD simulations of low-dimensional crystallites immersed in a bath of (pre and post cured) epoxy. These properties are fed into a compatible finite element model for following macroscopic deformation. The load transfer under deformation is examined with all available techniques to explain constitutive behavior and mechanisms of failure in such nanocomposite systems.

Q8.29

Deformation and Fracture Mechanisms of Multi-Walled Carbon Nanotubes. K. J. Ma¹, C. L. Chao² and H. H. Chien¹;

¹Dept of Mechanical Engineering, Chung-Hua University, Hsing Chua, Taiwan; ²Dept of Mechanical Engineering, Tam-Kang University, Taipei, Taiwan.

Carbon nanotubes have demonstrated fascinating mechanical properties. The extremely high stiffness and excellent flexibility during bending and compression has been observed experimentally and studied theoretically. The tensile strength as well as plastic deformation and fracture behaviour of carbon nanotubes, probably more important for material applications, are still lacking experimentally. In this study, we reported simple techniques without contact problems, with which deformation and fracture behaviour of carbon nanotubes under a tensile/torsion forces can be examined. Well aligned multi-walled carbon nanotubes (MWNTs) which were wrapped by the closely contact graphitic carbon layer were synthesized by CVD process. Delicate breaking the amorphous carbon layer by diamond indenter allows the wrapped amorphous carbon layer to crack and separate from the enclosed carbon nanotubes. This provides a tensile stress on the carbon nanotubes and results in plastic extension of carbon nanotubes. High resolution SEM image shows that the necking may occur in different locations simultaneously. Further increasing the tensile force leads to the

nonuniform plastic extension and fracture of carbon nanotubes. Due to shear force and instability involved in the deformation process, twists and necking can be observed on the heavily deformed carbon nanotubes. High resolution TEM image show that bonding breakage prefers to initiate at outmost graphene layer where a higher tension tends to build up. Accordingly, some covalent bonds within the inner graphene layers are possibly to be broken locally and simultaneously. The resulted hole in MWNTs becomes a precursor of fracture. Heavily distorted and merged graphene layers can be observed near the necking/breaking area. It is suggested that vigorous motion of tubes results in collisions and slidings between the graphene layers which leads to the merging of graphene layers.

Q8.30

Effect of nanoscale roughness at organic-inorganic interfaces on mechanical responses in nacre: a model bio nanocomposite. Kalpana S Katti, Dinesh Katti and Shashindra Pradhan; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Nacre the inner layer of mollusk seashells, exhibits unique mechanical properties such as fracture toughness and strength. The hierarchical structure of nacre, consisting of laminated hybrid, organic-mineral platelets, is suggested most often to be the reason for the superior mechanical properties of nacre. Our prior work has addressed the role of several details of nanostructure of the resulting macroscopic response of nacre to loading. A multiscale modeling methodology has been used to incorporate nanoscale phenomena into micro and meso-scale 3D finite element models. The role of nanoscale mineral contacts through organic layers connecting the minerals platelets between layers is quantitatively evaluated. Our simulations indicated a marginal role of the contacts on the elastic and non-linear properties of nacre. In addition, the role of the recently reported nanoscale asperities at the organic-inorganic interfaces is also evaluated. The three-dimensional finite element model was built with asperities incorporated into micro and nano-architecture of nacre. Several simulated tensile and compressive tests were performed on this model by varying yield stress of nacre. This paper presents the results of this simulation, comparing bulk response of nacre in presence and absence of nano-asperities. The complex nature of the hybrid organic-inorganic interfaces in nacre is quantitatively evaluated.

Q8.31

Elastic Properties of Multi-Block Copolymers Investigated Using Self-Consistent Field Theory. Russell B. Thompson and K. O. Rasmussen; Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Multi-block copolymer systems are useful in many areas since they can show improved mechanical properties over corresponding diblock copolymers. It is thought this enhancement results from the bridging between different chemical domains that occurs in multi-block systems. Experimental work has shown that deformations need not be large for the block number to have an affect on elastic properties. We present some preliminary results of a study of chemically symmetric AB multi-block copolymers in the lamellar phase. Specifically, we examine the effect of block number on the elastic properties of the system for small deformations from the equilibrium.

Q8.32

Inhomogeneous Deformation of Polyethylene-Clay Nanocomposites. Sophia Fan, James Lo and Douglas M. Shinozaki; Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, Canada.

The processing history of melt mixed polyethylene-clay nanocomposites is found to affect the dynamic mechanical and uniaxial tensile properties. X-ray diffraction, differential scanning calorimetry, and optical microscopy of intercalated and partially exfoliated systems are used to characterize the inhomogeneity and anisotropy of both the clay and matrix polymer. Evidence for orientation of the both the clay and matrix phases is shown. The composite microstructure and properties depend on the local processing history. The spatial dimensions over which such properties vary are macroscopic, and appear to depend on the local melt strains. Plane strain channel die forming is used to generate oriented clay microstructures. The clay reinforcing phase affects the ductility of the material, largely by influencing the localization of plastic deformation in the pre-yield region. The yield point is related to the critical localization of inelastic processes which include micro-cavitation related to the clay phase. The development of the localization has been measured using a displacement controlled microindenter.

Q8.33

Fatigue and Deformations of Nanostructured vs. Conventional WC-Co Coatings. Ahmed Ibrahim, Mechanical Engineering, Farmingdale State University, Farmingdale, New York.

In this study, the fatigue behavior and deformation of nanostructured and conventional WC-12Co coatings were investigated. The WC-12Co coating deposited onto AISI 4340 steel using the JP-5000 high velocity oxygen fuel (HVOF) system. High cycle rotating cantilever beam fatigue testing was conducted on coated and uncoated 4340 steel specimens. The fracture surfaces of the coated and uncoated specimen were characterized. The mechanisms of deformation in nanostructured and conventional WC-12Co coatings were discussed. The conclusions show that, (i) the coated specimen exhibited significantly high fatigue lives compared to the uncoated specimens, (ii) nanocrystalline WC-Co coating exhibited higher fatigue resistance compared to the conventional WC-Co coating, and (iii) the mechanisms of deformation for nanostructured and conventional WC-12Co coatings are quite different.

Q8.34

Micro Thermal Property of Layered Polymer Thin Films. Wataru Sakai¹, Yoshiji Tatsumi¹, Yukiko Aihara¹, Naoto Tsutsumi¹ and C. K. Chiang²; ¹Polymer Science & Engineering, Kyoto Institute of Technology, Kyoto, Japan; ²Polymers Division, NIST, Gaithersburg, Maryland.

Layered structure of thin polymer film is very important for both device applications and fundamental material sciences. In this paper, simple two-layered structured samples were used for investigation of interfacial interaction between different polymers, A and B. Micro thermal properties of the layered polymer thin films were investigated by micro-tip local thermal analysis. The two-layered films were made by solvent casting and spin-coating method on a detergent glass plate using polystyrene (PSt, A) and cyanide resin (CR-S, B). The thickness of top A layer was changed to less than 100 nm. The local thermal properties of the sample films were studied using μ TA analyzer (TA Instruments) which has a few μ m thermal tip controlled by AFM scheme. The yield curve of μ TA measurement showed two slope-change points of mechanical softening (Ts) due to the glass transition of both polymer layers. We found that the Ts of PSt layer on CR-S layer has the tendency to increase with decreasing the thickness of PSt layer, that is, the thermal mechanical property of the polymer thin layer is extremely affected by neighboring polymer layer. The strong interfacial interaction between PSt and CR-S layers enhanced the rigidity of the main chain of top PSt layer.

Q8.35

Synthesis and Characterization of Doped ZnO Nanowire - Al₂O₃ Membrane Composite. Patrick Griffin, P. J. Resto, D. S. Stone, R. F. Cooper, W. J. Drugan and R. W. Carpick; Mechanics and Materials Program, University of Wisconsin, Madison, Wisconsin.

Zinc oxide nanowire alumina composites can be synthesized in a number of different methods including sol-gel, electrodeposition, and electrophoresis. Here the composites are prepared using an electrodeposition method. Doping the interface with Ti+4 is known to affect the fracture toughness of the interface. In this work we examine the crack deflection at the interface between the alumina matrix and the zinc oxide nanowire using indentation fracture.

Q8.36

Polysulfone/Layered Silicate Nanocomposite. Jong Chan Won, Hyun Suk Kim, Yong-Seok Kim, Mi Hye Yi, Jae Heung Lee and Kil-Yeong Choi; Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon, South Korea.

Polymer/layered silicate nanocomposites have been attracted considerable interest owing to improvements over their pure state or conventional composite in thermal, mechanical, and gas barrier properties by adding a small amount of layered silicates, dispersed on the nanometer scale. Polysulfone has been used plastic plate of display because of clear, rigid, tough thermoplastic with high glass transition temperature. We have prepared polysulfone/compatibilizer/organophilic layered silicate nanocomposite to improve gas barrier property. In this study, the effect of compatibilizer was investigated to improve the dispersity between polysulfone and layered silicate. Compatibilizer which was low molecular weight polysulfone end-capped by long alkyl chain used to improve the dispersity of organo layered silicate in polysulfone resin. In the case of using the compatibilizer, the content of fully exfoliate silicate is more increased than that of composition without compatibilizer. But, the amount of organophilic layered silicate was added above critical amount, layered silicate in composite existed intercalated form. The WVTR of 7wt% layered silicate/compatibilizer/ polysulfone nanocomposite film reduced to one-third as compared to that of pure polysulfone film. Gas permeability is decreased, as the amount of organophilic layered silicate is increased, and it is also increased after critical amount. The structure of polymer nanocomposite was characterized by the TEM

and XRD. The tensile property was measured by UTM. DSC, TGA and DMA experiments revealed the fundamental thermal properties of nanocomposites. This research was supported by a grant M1-02-KR-01-0001-02-K18-01-004-3-0 from Information Display R&D Center, one of the 21st Century Frontier R&D program funded by the MOST, Korea.

Q8.37

An Analytical Model for the Effect of Elastic Modulus Mismatch on Laminate Threshold Strength. Alok Paranjpye and Glenn E. Beltz; Mechanical & Environmental Engineering, University of California, Santa Barbara, California.

A simple model for estimating the stress intensity factor at a crack tip in a two-dimensional bimaterial laminate composite has been developed by Rao et al. This model predicts the stress intensity factor for a crack running perpendicular to the layer structure in the composite, and takes into account the alternating tensile and compressive residual stresses that give the material its damage tolerance properties. A limitation of this model is its assumption of homogenous elastic properties throughout the composite, limiting the accuracy of predictions it can make for real material systems. In separate work, McMeeking and Hbaieb have developed finite element models of the same architecture, which allow for elastic modulus mismatch. In this work, we develop an analytical expression for the stress intensity factor around a crack tip in a laminated composite. To render the problem tractable, the system is assumed to behave as an anisotropic solid when the stress field at the crack tip arises from far field tractions applied at the material boundaries. Comparisons of predictions in different material systems from both the homogenous model as well as the finite element model are presented.

Q8.38

Mechanical Behavior of Electrospun Polyurethane Fiber Mats. Angelo Pedicini and Richard J Farris; Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts.

Electrospinning is a process that utilizes a high electrical potential applied across a polymer solution (or melt) to produce fibers with nanoscale diameters. When a polymer solution is electrospun onto a stationary target, an isotropic mat of fibers is formed. The fibers comprising the mat are typically 50-500 nm in diameter, depending on spinning solution properties. Fiber mats of two commercial thermoplastic polyurethanes, Pellethane 2103-70A and 2103-80AE, were prepared by electrospinning. The stress-strain behavior of the electrospun materials was characterized and compared to the stress-strain behavior of the materials from which they were spun. Although both forms of the materials are mechanically isotropic, fundamental differences in the stress-strain response between the two was observed. The bulk polyurethanes show sigmoidal stress-strain responses, typical of elastomeric materials; the electrospun materials do not. Also, the electrospun materials have significantly lower elongation to failure compared to the bulk. Scanning electron microscopy (SEM) and infrared spectroscopy (FT-IR) were used to characterize the electrospun polyurethanes and to understand the source of the differences in mechanical behavior. IR dichroism indicates molecular orientation in the electrospun fibers and SEM illustrates a strain-induced orientation of the fiber mats; both phenomenon contributing to the fundamental differences in the mechanical behavior of the electrospun materials compared to the bulk. In addition to mechanical characterization, the ability to electrospin fiber mats of various densities allows for modeling tensile properties of the electrospun polyurethanes. The elastic modulus of the electrospun mats is modeled using a relationship developed for cellular solids, in which the modulus and density of a fiber mat are equated through a power-law relationship. The tensile stress of the electrospun mats is modeled using classical composite theory, a rule of mixtures in which the porous volume of the electrospun mats is assumed to have a tensile strength of zero, and the fibers are assumed to have a tensile strength equal to that of the bulk material.

Q8.39

Heterogeneous nature of the dynamics close to the glass transition in supported and suspended polymer films. Didier Long and Paul Sotta; Physics, Université de Paris Sud/CNRS, Orsay, France.

Recent experiments have demonstrated that the dynamics in liquids close and below the glass transition temperature is strongly heterogeneous, on the scale of a few nanometers. A model for the glass transition has been proposed recently, which shows that this heterogeneous nature of the dynamics has important consequences regarding the dynamics in thin films. We extend here this model. We show that the dominant relaxation time can be very different in thin films from the one in the bulk, and that this dominant relaxation time depends strongly on the interaction with the substrate, and can be

either much smaller or much larger than the bulk value of τ_α at the same temperature. These results can be interpreted as a shift of the glass transition temperature as compared to the bulk, explaining thereby several features of recent experiments performed in thin films. Our model shows that the shift of glass transition temperature, referred to that of a suspended film, varies like ϵ^{1/γ_2} where ϵ is the adsorption energy per monomer and γ_2 is the critical exponent for the mass of aggregates in the 2D percolation problem. The glass transition temperature appears then to be very sensitive to the interaction with the substrate. We show that the interactions lead to an increase of T_g for ϵ as small as a few $0.01T$ where T is the thermal energy, and that this increase saturates at the value corresponding to strongly interacting films for adsorption energies of order $0.5T$.

Q8.40

Synthesis and Characterization of Thickness-Aligned Carbon Nanotube-Polymer Thin Films. Nachiket R. Raravikar, Linda S. Schadler and Pulickel M. Ajayan; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Aligned nanotube-polymer composite thin films are prepared, where carbon nanotubes are aligned in the thickness direction of the film. This is achieved by infiltration of monomer, Methyl Methacrylate (MMA), into pre-aligned arrays of multi-walled carbon nanotubes and subsequent in situ polymerization to poly-methyl methacrylate (PMMA). For effective infiltration, the infiltrating liquid should wet the capillary walls. Our contact angle measurement and Scanning Electron Microscope (SEM) results indicate that both, MMA and PMMA, wet the nanotube walls well. The nanotubes are well-aligned and well-dispersed in the polymer, as is evident from the SEM images. The films show an increase in microhardness by $\sim 40\%$ over pure PMMA and are also electrically conducting, whereas pure PMMA is an insulator. The thermal stability of PMMA present in these films has improved by $\sim 70^\circ\text{C}$ over pure PMMA. Thus, the technique of polymer infiltration can be regarded as one way to achieve control over some of the main factors, which affect the properties of nanotube-polymer composites, such as, the degree of alignment of nanotubes in composites and the nanotube dispersion in polymer matrix. Also, the infiltration technique is scalable and can be used to infiltrate various types of polymers into the nanotube arrays. Various functional nanotube-polymer architectures are possible based on the films prepared by polymer infiltration into nanotube arrays.

SESSION Q9: Nanoparticles, Nanotubes and Nanoclusters

Chairs: Jeff De Hosson and Ben Wang
Thursday Morning, December 4, 2003
Room 311 (Hynes)

8:30 AM *Q9.1

Nanomechanics of $\sim 1\text{D}$ Materials: Bulk vs Surface In Nanowires, Nanotubes, and Their Assemblies.

Boris I Yakobson, MEMS, Rice University, Houston, Texas.

Nanotubes belong to a broader family of quasi-one-dimensional solids, nanowires – known previously as whiskers. However they possess a unique property of possible complete atomic homogeneity while any bulk-lattice derived $\sim 1\text{D}$ object inevitably invokes at least three levels of heterogeneity: bulk, surfaces-facets, and the edges between them. This generally complicates the physics involved in even primary ground state identification, renders classical Wulff theorem insufficient in small dimensions, and requires careful analysis of the corresponding energy contributions. As a benchmark example of bulk-derived structure we have investigated the ground state of the pristine unpassivated Si wires [1] and show that heterogeneity in surface- and edge-reconstruction plays the key role. In case of nanotubes, heterogeneity can be due to chemical composition as in BN [2]. We have performed comparative analysis of mechanical strength and yield mechanisms in C and BN structures, based on direct computation of the primary defect formation energy, and the activation barriers for this process. Previously discussed Stone-Wales bond-rotation mechanism requires high temperature, while at room temperatures a direct bond-breaking cleavage is more likely to occur within realistic times [3]. SW-process also offers a mechanism for "nanowelding" that is coalescence-merging, investigated recently for C-nanotubes and fullerenes [4]. We will also briefly discuss coupling of mechanical deformations with reversible [5] or irreversible changes in electronic properties. [1] "What is the Ground State Structure of Silicon Nanowires?", Y.Zhao and B.I.Yakobson, Phys. Rev. Lett. (2003, in press). [2] "Thermodynamics of Yield in Boron Nitride Nanotubes", T.Dumitrica, H.F.Bettinger, G.E.Scuseria, and B.I.Yakobson, Phys. Rev. B (2003, in press). [3] T.Dumitrica, T. Belytschko, and B.I.Yakobson, J. Chem. Phys., 118, 21 (2003). [4] Y.Zhao, B.I.Yakobson, and R.E.Smalley, Phys. Rev. Lett. 88, 185501 (2002). [5] A.A.Farajian, B.I.Yakobson, H.Mizuseki, and Y.Kawazoe, Phys. Rev. B 67, 205423 (2003).

9:00 AM Q9.2

Structural and Mechanical Properties of Boron Nanotubes.

Matthew H. Evans^{1,2}, John D. Joannopoulos¹ and Sokrates T. Pantelides^{2,3}; ¹Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ³Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

In this paper we present a theoretical study that unveils novel structural and mechanical properties of boron nanotubes. We show that the lowest energy flat plane boron structure is a triangular lattice with a nearly homogeneous electron density and a threefold degenerate ground state. This degeneracy leads the plane to buckle, resulting in a stable planar phase with an intrinsic directionality not found in carbon graphene planes. When the plane is rolled into a tube, the orientation of the preferred direction strongly affects the resulting properties of the nanotube. We study in detail the two types of achiral tubes, and find dramatic differences in their electronic structure and mechanical properties. Boron nanotubes of any chirality are metallic, and the near absence of interplane interactions suggests that they are unlikely to be multi-walled. Their mechanical properties show a strong chirality dependence that makes it possible to select a tube with the desired elastic response. This ability to fine tune the attributes of boron nanotubes makes them attractive candidates for fabrication and integration in nanomaterials and devices.

9:15 AM Q9.3

Nonlinear Structural Mechanics Based Modeling of Carbon Nanotube Deformation. Antonio Pantano, Mary C. Boyce and David M. Parks; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The deformation behavior of carbon nanotubes (CNTs) has been the subject of numerous experimental, elastic continuum modeling, and molecular dynamics (MD) studies. The small dimensions of CNTs pose challenges for experimental determination of mechanical behavior and properties. Most experimental measurements impose some form of bending on the MWNTs and utilize beam theory to reduce data to an elastic modulus. Beam theory treats the nanotube as a homogeneous solid tube, but does not take into account any specific structural details of nanotubes, such as the nested tube structure of the MWNT and/or the single-atomic-layer nature of each tube wall. It has been observed that MWNTs under bending develop reversible periodic wrinkles on the compressive side of the bend. Inter-wall spacing is preserved during buckling, demonstrating a mechanical effect of the strong normal van der Waals (vdW) interactions present between the walls of MWNTs. The wall-to-wall shear interaction is very compliant and weak compared to the normal vdW stiffness and strength. Electronic and MD simulations of the structure and deformation of CNTs have shown that nanotubes possess an excess internal [strain] energy per carbon atom, relative to an unstrained graphene sheet. This result is in agreement with the prediction of continuum-level elastic shell theory and indicates that carbon nanotubes contain an initial "internal stress". Fitting results from semi-empirical MD studies, tight-binding simulations, local density approximation models, and ab initio energy calculations to elastic shell theory, different investigators determined values of the effective Young's modulus and 'mechanical' wall thickness that enables shell theory to correctly predict the initial deformation of single-wall nanotubes (SWNTs). A nonlinear structural mechanics based approach for modeling the structure and the deformation of single and multi-wall carbon nanotubes (CNTs) is presented. Individual tubes are modeled using shell finite elements, where a specific pairing of elastic properties and mechanical thickness of the tube wall is identified to enable successful modeling with shell theory. The important effects of van der Waals forces are simulated by the construction of special interaction elements. The success of this new CNT modeling approach is verified by comparison with MD simulations and high-resolution images from experiments available in the literature. In particular, the mechanics of wrinkling of multi-wall CNTs during bending and compression are studied, demonstrating the role of the multi-walled shell structure and inter-wall van der Waals interactions in governing buckling and post-buckling behavior.

9:30 AM Q9.4

Buckling Strain of Carbon Nanotubes under Uniaxial Compression. liu yang, NASA Ames Research Center, Moffett Field, California.

A carbon nanotube buckles when compression reaches a certain strain, resulting from the competition between the compression energy built-up with uniform deformation and the bending energy associated with buckling. It is not easy to determine exactly when a nanotube starts to buckle. In this simulation work, we use a genetic algorithm to efficiently determine the critical buckling strain of a carbon nanotube. The results for single-walled tubes show that the inverse of

buckling strain increases linearly with tube diameter. Tubes buckle with un-axisymmetric modes. The number of buckling wave along the circumference increases with tube diameter. These features fit well with continuum mechanics analysis for thin shells. One unique feature for nanotube buckling is that the critical strain depends on tube chirality. The buckling strain of zigzag tubes is higher than that of armchair tubes with same diameter. Buckling for a series of nanotubes with a diameter of 1.4 nanometers show that the buckling strain decreases with the increase of chiral angle. This chirality-sensitive nature of nanotube buckling is related to the fact that compression energy of nanotubes at large strain is sensitive to tube chirality. The critical compression strain for a double-walled nanotube falls between that of the outer and inner shells. The buckling pattern is also a compromise between the two shells. Similar conclusions as for the double-layered tubes hold for other multi-walled nanotubes. The multi-walled tubes do have a larger buckling strain compared to the outermost layer as a single-wall tube, but in a manner different from the thicker shell models. These features are discussed using continuum mechanics with the consideration of the van der Waals interaction between the tubes. The results indicate that the van der Waals interaction plays an important role in the mechanical response of multi-walled nanotubes under compression.

9:45 AM Q9.5

Solid State Property - Bonding Electron Density - Volume Plasmon Energy Relationships: Novel AEM Technique for In Situ Diagnostics of Materials Properties at the Nanoscale. Vladimir P Oleshko and James M. Howe; Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

We show that volume plasmons (i.e., quantized high frequency ($\sim 10^{16}$ Hz) correlated longitudinal electron excitations generated by fast electrons passing through a thin specimen) can be used for probing various material properties at the nanoscale. This is possible because the volume plasmon energy, E_p , is related to the valence electron density, n , which is responsible for the properties, by a resonance angular frequency, ω_p , i.e., $E_p = \hbar/2\pi\omega_p = [(\hbar/2\pi\omega_p)^2 + E_g^2]^{0.5}$, where $\omega_p^f = [ne^2/(\epsilon_0 m)]^{0.5}$ is the free electron plasma frequency, e is the electron charge, ϵ_0 is the permittivity of vacuum, m is the electron mass, and E_g is the bandgap energy. The mechanical properties of single-crystal and polycrystalline metals, nonmetals, and semiconductors can be evaluated from correlation charts of the properties vs. E_p . We found that these relations demonstrate universality and scaling and follow the universal binding energy relation, which originates in the essentially exponential decay of electron density with interparticle separation described by a universal function of the Rydberg type. Variations in the electron density at the boundary of the Wigner-Seitz (WS) cell, n_b , cohesive energy per atomic volume, E_{coh}/V_{wse} , elastic constants, and E_p , exhibit characteristic periodicities with atomic number and parabolic behavior within each transition series, starting from the second period. As a consequence, one can obtain strongly correlated log-log scaling of the power-law type, $P_m = AE_p^B$, where P is the property and A and B are least-squares-fit parameters. The correlation strength decreases with deviations of the WS cell symmetry from spherical that can be quantitatively described within a free-electron approximation. In a field-emission analytical transmission electron microscope, where sub-nanometer electron probes can provide atomic-level spatial resolution with 0.7-1.7 eV energy resolution, such correlations enable in situ evaluation of the intrinsic local solid-state properties without any special set-up and when it is impossible by other means, as illustrated by analyses of nanoprecipitates of the δ' -Al₂Cu and γ -TiH_x phases in alloys.

10:30 AM Q9.6

The Deformation Behaviour of the Raman Radial Breathing Modes of Single-Wall Carbon Nanotubes in Composites. Robert J Young and Marcel Lucas; Manchester Materials Science Centre, University of Manchester and UMIST, Manchester M1 7HS, United Kingdom.

The interest in single-wall carbon nanotubes has increased steadily since their discovery in the early 1990s, due to their exceptional electronic and mechanical properties. Their outstandingly-high Young's modulus (over 1 TPa) and their structure-dependent electronic properties make them ideal candidates for nanoscale sensors. Raman spectroscopy is a technique used widely to study the vibrational modes of carbon nanotubes. It has also proved to be a very powerful and non-destructive method to determine the nanotube structure. The typical Raman spectrum consists of four main features: the G band (near 1600 cm⁻¹), the D band (around 1300 cm⁻¹), the G' band (at about 2600 cm⁻¹) and the low-frequency Radial Breathing Modes (RBMs), which correspond to the collective radial movement of the carbon atoms. The RBM position is inversely proportional to the nanotube diameter and is frequently used to characterize the structure and quality of raw carbon nanotube materials. We will be reporting a Raman spectroscopic study of the

strain-induced intensity variations of the RBMs of single-wall carbon nanotubes (SWNTs) in epoxy/SWNT composites. The RBM intensities have been found to vary significantly over a range of strain between -0.3% and 0.7%. The trend (increase or decrease) as well as the magnitudes of the intensity variation depends on the nanotube diameter and its chirality. Using tight-binding calculations, we have shown that these intensity variations can be explained entirely by resonance theory. The electronic band structure of SWNTs is predicted to vary significantly with uniaxial strain. Electron density of states calculations confirm that the energy separation between the van Hove singularities shifts with strain, becoming closer or further away from the laser excitation energy depending on the nanotube structure. The nanotubes are thus moved closer or further away from resonance, causing the intensity variations. It is demonstrated that through the use of resonance theory, a unique chirality can be assigned to each type of SWNT from knowledge of its RBM position and the effect of strain upon the RBM intensity, thus determining its entire structure.

10:45 AM Q9.7

Raman Investigation of Single Walled Carbon Nanotubes and Fullerene [60] Under High Hydrostatic Pressure.

Maher Sabri Amer¹, Mostafa El-Ashry¹ and John Maguire²;

¹Mechanical & Materials Eng., Wright State University, Dayton, Ohio;

²Polymer Branch, Air Force Research Laboratory, Dayton, Ohio.

Raman spectroscopy is a technique that probes materials on the molecular level by monitoring inherent vibrational modes. The technique has been successfully utilized to investigate material systems on the micro and the meso-scales and more recently has proven its ability to exploring systems on the nano-scale. For example, detailed analysis of the Raman spectrum of a carbon nanotubes provides accurate information regarding the nanotube diameter, chirality, and conductive properties. In this talk, our recent work on Raman investigations of the behavior of single walled carbon nanotubes and Fullerene [60] will be presented. Our experimental results have shown that the blue shift observed in the Raman bands of carbon nano-spheres and nanotubes can be interpreted as the result of surface interactions and that the nano-sphere is neither compressible nor collapsible under hydrostatic pressure up to 10 GPa. The current findings represent a major new thrust for the development of new materials with superior properties and unique applications.

11:00 AM Q9.8

Nanoindentation and Nanoscratch of Vertically Aligned Carbon Nanotubes, PTFE and PMMA Coated Carbon Nanotubes, and ZnO Nanofibers. Hang Jerry Qi¹, Theodoros A.

Akiskalos¹, Ken Teo³, Kenneth Lau², Jiyun Lao⁴, Mary C. Boyce¹, John Robertson³, William I. Milne³, Zhifeng Ren⁴ and Karen K.

Gleason²; ¹Mechanical Engineering, MIT, Cambridge, Massachusetts;

²Chemical Engineering, MIT, Cambridge, Massachusetts;

³Engineering, University of Cambridge, Cambridge, United Kingdom;

⁴Physics, Boston College, Chestnut Hill, Massachusetts.

Recent technology advances enable the growth of vertically aligned nanostructures on a substrate, such as vertically aligned carbon nanotubes by PECVD, and vertically aligned ZnO nanofibers by thermal vapor transportation and condensation. Methods have also been developed to coat the nanostructures with thin layers of polymer. Although extensive research is invested in optimizing processing conditions, comparatively little attention has been given to the mechanical properties of these nanostructures even though the stiffness and mechanical integrity will be important issues in their ultimate success. In this paper, nanoindentation and nanoscratch tests are used to study the mechanical properties and integrity of three types of vertically aligned nanostructures, i.e. vertically aligned carbon nanotubes, PTFE and PMMA coated carbon nanotubes, and ZnO nanofibers. Nanoindentation is conducted by the penetration of a Berkovich indenter into the forests using an atomic force microscopy (AFM), whereas the resistance to nanoindentation, a penetration force vs. penetration depth curve, is measured. Different from indentation on a continuous surface, such as thin film coatings, the resistance to nanoindentation on a vertically aligned nanostructure reveals the successive interactions between the indenter and the tubes as the indenter penetrates into the forest and successively bends each tube encountered during penetration. We hereby are able to deduce the dependence of the resistance to indentation on the key structural features of the nano forest structure (diameter, length and areal density of nanotubes and nanofibers), as well as the bending stiffness and axial modulus of the constituent nanotubes and nanofibers. The effects of coatings on the overall properties of nanotubes are also studied. Finally, the behavior of the nanoforests during scratching is studied where effects of successive tube bending and tube-tube interactions are modeled.

11:15 AM Q9.9

Structural Modification of Nanodiamonds to Onion Like

Carbon. Saikat Talapatra¹, R Ma², Y Y Choi¹, N Chakrapani¹, B Q Wei¹, A Cao¹, R Vajtai¹ and P M Ajayan¹; ¹Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan.

Multi shelled carbon nano structured materials has attracted the interest of many scientist and researchers in the last few decade. Apart from being a good solid lubricant it is one of the possible carriers of 217.5 nm interstellar absorption bumps. Encapsulation of nuclear spins in these structures for possible molecular electronic data storage and quantum computing applications is also proposed recently. Some major restrictions for possible use of these materials are low yield and less control over their size distribution. To some extent these difficulties can be overcome by transforming nano sized diamond particles into carbon onions by thermal annealing. In this study we focused on the structural transformation of nanodiamond powders under different annealing conditions. Various stages of this transformation will be discussed in the light of High Resolution Transmission electron microscopy (TEM), X-Ray diffraction (XRD) and Raman Spectroscopy results.

11:30 AM Q9.10

Modeling of Tethered Nanotube Materials. S. J. V. Frankland¹,

M. N. Herzog², G. M. Odegard¹, T. S. Gates³ and C. C. Fay³;

¹National Institute of Aerospace, Hampton, Virginia; ²National Research Council, Hampton, Virginia; ³NASA Langley Research Center, Hampton, Virginia.

The design of nanostructured materials requires the identification of structure-property relationships which can be facilitated by the usage of multi-scale modeling techniques in conjunction with experimental evidence. In the present work, the effect of functionalization on the mechanical properties of a tethered nanotube material is explored with computational models. Single-walled carbon nanotubes (SWNTs) are covalently linked with 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BABB). Molecular dynamics simulation is used to generate nanotube structures for which the three-dimensional, elastic, constitutive equation is determined. The constitutive properties are determined from molecular dynamics simulation and from molecular mechanics coupled with boundary conditions that have been developed for orthotropic materials. As a first step in the validation of these models, samples of the tethered nanotube material are synthesized using in situ diazonium chemistry, and the resulting material is characterized using thermal analysis (DSC, TGA) and spectroscopy (UV/Vis/NIR, FT-IR, Raman). This paper will present background on the material chemistry, explanations of the analysis methods, predictions of key material properties, and results from relevant experimental test data.

11:45 AM Q9.11

Mechanical Characterization of Polyelectrolyte Multilayer Nanoassemblies. Prem V Pavo¹, Russell E Gorga¹, Dehua Yang³,

Anuj Bellare² and Robert E Cohen¹; ¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Orthopaedic Surgery, Harvard Medical School, Boston, Massachusetts; ³Hysitron, Inc., Minneapolis, Minnesota.

Ultra-thin films, formed by the layer-by-layer deposition of oppositely charged polyelectrolytes, have attracted great interest over the last decade(1); potential areas of application include biomaterials, biosensors, controlled drug delivery, photonic devices, anti-reflection coatings, separation membranes, and materials for reducing friction and wear. The utility of these films is enhanced by their ease of fabrication, robustness, conformal coverage, and excellent adhesion on a wide variety of substrate materials with little or no pretreatment. Their mechanical behavior, however, has not been quantified. Nanoindentation was successfully used to probe the mechanical behavior of these films, assembled using weak polyelectrolytes. Film modulus and hardness, at ambient conditions, were studied as a function of assembly solution pH, film thickness, degree of thermally induced crosslinking, and other processing parameters. We have also studied the mechanical behavior of polyelectrolyte multilayer nanocomposites, produced via the in-situ synthesis of metallic clusters in the film matrix(2). The effect of silver nanoparticle size and volume fraction on the force-displacement curve was investigated. In addition, composites constructed by the layer-by-layer adsorption of multi-wall carbon nanotubes and a cationic polyelectrolyte were characterized to correlate with their observed friction-and-wear behavior. (1) Decher, G.; Schlenoff, J.B. *Multilayer Thin Films*; Wiley-VCH Verlag GmbH & Co. KgaA: Weinheim, 2003. (2) Wang T.C.; Rubner M.F.; Cohen R.E. *Polyelectrolyte Multilayer Nanoreactors for Preparing Silver Nanoparticle Composites: Controlling Metal Concentration and Nanoparticle Size*, Langmuir 2002, 18, 3370-3375.

1:30 PM Q10.1

Theoretical and Experimental Study on Mechanical Properties of Random and Magnetically Aligned Single-Walled Carbon Nanotube Composites. Ben Wang¹, Ravi Shankar¹, Zhi Wang¹, Zhiyong Liang¹, Chuck Zhang¹ and Leslie Kramer²; ¹Industrial Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida; ²Lockheed Martin Missiles and Fire Control - Orlando, Orlando, Florida.

Many researchers consider single-walled carbon nanotubes (SWNTs) as the most promising reinforcement materials for high performance structural composites and multifunctional materials. However, due to poor dispersion, weak interfacial bonding and lack of tube orientation, current nanotube-based nanocomposites fail to realize their anticipated properties. This research investigated the influences of tube dispersion, loading, orientation and interfacial bonding on the mechanical properties of composites. Both random discontinuous and aligned discontinuous reinforcement models of composites were applied to predict the tensile moduli of both individually dispersed SWNT-based and SWNT rope-based composites. By using theoretical estimation of the interfacial shear stress of SWNT/epoxy resin composites, the critical length (l_c) and aspect ratio of SWNTs in the resultant composites were calculated and examined. Additional experiments compared the predictions to actual results. Both random and aligned nanocomposites of purified SWNTs/Epon 862 epoxy resin were fabricated by using nanotube buckypaper/resin infiltration methods developed by the authors. By preforming tube networks before tube/resin impregnation and magnetically aligning the tubes at the National High Magnetic Field Laboratory, the resulting composites showed relatively high tube content (>30wt.%), good dispersion and controlled in-plane tube orientation. The storage moduli of the resultant composites were analyzed with dynamic mechanical analysis (DMA). The storage modulus of the magnetically aligned composites was found to be as high as 40.5GPa. Atomic force microscopy (AFM) and scanning electric microscopy (SEM) were used to examine the nanostructures of the composites. The results show that the formation of SWNT ropes in the composites significantly influenced the mechanical properties. The tube sliding within nanotube ropes was observed in the composites made with aligned nanotubes. The experimental results of the SWNT rope dimensions and properties are in good agreement with theoretical predictions.

1:45 PM Q10.2

Nacre-Inspired Ultrastrong Composites from SWNT and Clay made by Layer-by-layer assembly. Nicholas Alexander Kotov^{3,2}, Arif Mamedov² and Zhiyong Tang³; ¹Chemistry, Oklahoma State University, Stillwater, Oklahoma; ²Nanotechnology, Nomadics Inc, Stillwater, Oklahoma; ³Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Ultrastrong materials present critical important for diverse list of technologies. Two methods of preparation of materials that are both strong and light on the basis of layer-by-layer assembly (LBL) are presented. LBL composites made from single wall carbon nanotubes demonstrated exceptional tensile strength comparable to ultrahard ceramics. Their preparation consists from sequential deposition of slightly oxidized negatively charged nanotubes and positively charged polyelectrolyte which are subsequently chemically cross-linked. The layered composite possess exceptional structural uniformity and strong connectivity of nanotubes with the matrix. Another example of unique mechanical material made by LBL mimics nacre. It is made of layers of clay and polyelectrolyte and reveals essential structural features of nacre. Its strength and toughness originates from multiple ionic crosslinks of the polyelectrolyte molecules and clay surface. Both functional and structural features of nacre are well reproduced in this composite. The molecular mechanisms of deformations are evaluated on the basis of microscopy and stretching curves. Correlations with calculations of stretching experiments are established on the basis of atomic force microscopy images of deformed composites. Methods of optimization of LBL multilayers to obtain record strengths and toughness will be discussed.

2:00 PM Q10.3

Mechanical Properties of Polyaniline/Multiwalled Carbon Nanotube Composite Films. Praveen C. Ramamurthy¹, William R Harrell², Richard V Gregory¹, Bindu Sadandan³ and Apparao M Rao³; ¹Materials Science and Engineering, Clemson University, Clemson, South Carolina; ²Holcombe Department of Electrical & Computer Engineering, Clemson University, Clemson, South Carolina; ³Department of Physics & Astronomy, Clemson University, Clemson, South Carolina.

High molecular weight polyaniline / multiwalled carbon nanotube composite films were fabricated using solution processing. Composite films with various weight percentages of multiwalled carbon nanotubes were fabricated. Physical properties of these composites were analyzed by thermogravimetric analysis, tensile testing, and scanning electron microscopy. These results indicate that the addition of multiwalled nanotubes to polyaniline significantly enhances the mechanical properties of the films. In addition, current in the composite films was measured, and it was observed that the current level in the films increased with increasing multiwalled nanotube content. Furthermore, it was observed that polyaniline containing one weight percent of carbon nanotubes appears to be the most promising composition for applications in organic electronic devices.

2:15 PM Q10.4

Nanotube- and Nanofibre-reinforced Polymer Fibres. Milo Shaffer¹, J Sandler², A Windle², P Werner³, V Altstadt³, F Gojny⁴, K Schulte⁴, M Cadek⁵, W Blau⁵ and M v Es⁶; ¹Dept of Chemistry, Imperial College London, London, United Kingdom; ²Dept. Materials Science, Cambridge University, Cambridge, United Kingdom; ³University of Bayreuth, Bayreuth, Germany; ⁴TUHH, Hamburg, Germany; ⁵Trinity College, Dublin, Ireland; ⁶DSM, Geleen, Netherlands.

There is considerable interest in using nanotubes and nanofibres as reinforcing agents in polymer composites. So far, there has been a significant focus on the fundamental properties of the nanofillers which seem to be very promising. Whilst some encouraging results have been obtained, significant improvements over conventional fillers have proved elusive, for a number of reasons. Therefore, it is particularly interesting to consider the use of nanotubes to reinforce conventional polymer fibres in a manner that is not possible with conventional fillers. We have successfully produced a range of nanocomposite fibres, using different matrices and nanofillers, and found significant improvements in strength and stiffness. Nanotubes were found to be more effective than nanofibres for mechanical reinforcement, although, in all cases, the nanofiller was found to be similarly aligned to the fibre axis. The quality of nanofiller dispersion and orientation was confirmed using electron microscopy and xray diffraction. The influence of nanoparticles on matrix crystallisation dynamics was examined using DSC and detailed X-Ray analysis. The mechanical properties were investigated with a combination of tensile testing and DMTA, and significant increases in modulus and yield strength were observed. Comparisons have been made between moulded and fibrous samples, and between different types of nanotube and nanofibre.

2:30 PM Q10.5

Electrospinning of Carbon Nanotube Reinforced Nanocomposite Fibrils and Yarns. Hoa Le Lam¹, Nick Titchener², Nevin Naguib³, Haihui Ye⁴, Frank Ko⁵ and Yury Gogotsi⁶; ¹Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ²Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ³Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ⁴Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ⁵Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ⁶Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Commercial carbon fibers produced from a polyacrylonitrile (PAN) precursor have reached their performance limit. With an elastic modulus greater than 1 TPa, carbon nanotubes (CNT) are a good candidate for reinforcing the PAN precursor. In this study, single walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT) are used to reinforce PAN and electrostatically assemble into nanofibers through an electrospinning process. Electrospinning allows ultra fine fibers below 100 nm in diameter to be produced. The high aspect ratio and ultra fine diameter of SWNT and MWNT provide extremely high surface area for load transferring. The effectiveness of CNT in load transferring is highly dependent on the degree of dispersion, alignment and interfacial bonding between the CNT and the PAN. Alignment of the CNT can be achieved during electrospinning by the flow of the polymer solution, electrostatic charge and diameter confinement. Dispersion and interfacial bonding between the CNT and PAN is crucial in improving the mechanical properties of the composite nanofibers. Non uniform dispersion of CNT, as well as interfacial bonding between the constituents can cause negative effects in the properties of the nanofibers. This study has demonstrated that composite nanofibers containing SWNT or MWNT can be produced with aligned CNT by an electrospinning process. Preliminary results from Atomic Force Microscopy show significant increase in mechanical properties of the composite nanofibers containing 4 % wt SWNT. Currently, up to 10 wt. % SWNT/PAN nanofibers with diameters in the range of 40 nm to 300 nm have been successfully spun. This may be a promising pathway to produce the next generation of high performance fibers that will help

bridge the dimensiona and properties gap between nanoscopic and macroscopic structures.

2:45 PM Q10.6

Chemical Vapor Surface Modification of Carbon Nanotubes and Its Effect on the Mechanical Properties of Nanocomposites with Poly(Methyl Methacrylate).

Kenneth K.S. Lau, Russell E. Gorga, Robert E. Cohen and Karen K. Gleason; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Pulsed plasma enhanced chemical vapor deposition was utilized to modify the surfaces of carbon nanotubes. The modified and unmodified nanotubes were used in a study of the mechanical and thermal properties of a composite system of carbon nanotubes with poly(methyl methacrylate) (PMMA). By controlling the plasma duty cycle (frequency) and selecting the appropriate precursor chemistry, different coatings that vary in compatibility with the bulk polymer matrix were produced. Low duty cycle MMA plasmas yielded coatings that were similar to bulk PMMA, showing good retention of the ester groups as revealed by Fourier transform infrared spectroscopy. With high duty cycle plasmas, coatings showed a significant loss in ester functionality and a higher degree of crosslinking that deviated from the bulk PMMA structure. Transmission electron microscopy gave coating thicknesses on the order of 5-10 nm. Suspensions of the coated nanotubes (0.001-1 wt %) in PMMA solutions were stable for prolonged periods, showing no flocculation after several weeks, while the uncoated nanotubes settled upon standing after 1 h. Nanotube dispersion in solution-cast films was observed under scanning electron microscopy, showing better dispersion of nanotubes from those modified with more crosslinked coatings. A higher degree of crosslinking is believed to improve coating integrity, enabling it to survive the dissolution step, and imparting the needed surface compatibility with the bulk polymer matrix. Dispersion of the nanotubes in bulk PMMA was also performed by melt processing in a Haake counter-rotating twin screw extruder to produce nanotube-filled composite fibers. Mechanical properties (tensile, impact, and dynamic mechanical) were measured as a function of nanotube loading (1-10 wt %). Tensile toughness of PMMA fibers filled with modified nanotubes was shown to improve by about 50 % compared to fibers with unmodified nanotubes.

3:30 PM Q10.7

Plasma Coating of Carbon Nanotubes for Enhanced Dispersion and Interfacial Bonding in Polymer Composites.

Donglu Shi¹, Jie Lian², Lumin Wang², Mark Schulz¹, David Mast¹ and Wim van Ooij¹; ¹Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; ²Nuclear Engineering, University of Michigan, Ann Arbor, Michigan.

Ultrathin films of polystyrene were deposited on the surfaces of multi-wall carbon nanotubes using a plasma polymerization treatment. These surface-coated nanotubes were incorporated into polystyrene to form a polymer nanocomposite. It was found that the plasma coating greatly enhanced the dispersion of the nanotubes in the polymer matrix. High resolution transmission electron microscopy images revealed an extremely thin film of the polymer layer (~3 nm) at the interface between the nanotube and matrix. Tensile test results showed increased strength in the coated nanotube composite while an adverse effect was found in the uncoated nanotube counterpart. In particular, scanning electron microscopy data showed different fracture behavior between the coated and uncoated composites; the former exhibited shear yielding due to enhanced bonding while the latter fractured in a brittle fashion. The fracture mechanism in the nanotube composite is also discussed.

3:45 PM Q10.8

Intercalated Polymer Nanocomposites Prepared in Supercritical Carbon Dioxide. Manuel Garcia-Leiner and Alan J. Lesser; POLYMER SCIENCE AND ENGINEERING DEPARTMENT, UNIVERSITY OF MASSACHUSETTS AT AMHERST, AMHERST, Massachusetts.

An alternative route to prepare polymer-clay nanocomposites using supercritical carbon dioxide (scCO₂) is described. The presence of clay nanoparticles significantly influences the morphology, foaming process and crystallization of a polymer when processed in scCO₂. Significant increases in cell nucleation and crystallinity are observed even at small clay concentrations, suggesting that both the crystallization and foaming processes are mainly determined by the presence of particles providing available surface for nucleation reducing the overall energy required in these processes. Intercalated structures, where polymer has entered into the clay galleries but has not fully delaminated them into a completely exfoliated structure are successfully produced in the presence of scCO₂ even when favorable interactions between the polymer and the clay are not present. It is suggested that this type of structure provides considerable interactions between silicate layers at

the molecular scale, influencing physical and material parameters, providing property-enhancing characteristics at scales inaccessible for traditional filler materials. The effect of scCO₂ on the polymer intercalation process is analyzed for Poly(trimethyleneterephthalate) (PTT), HDPE and HDPE/(PE-g-PEG) blends both with modified and unmodified clays. By controlling the hydrophilicity of the polymer and clay systems, specific understanding of the effect of scCO₂ on the structure and morphology of the nanocomposites is obtained. WAXS and TEM results show significant increases in the clays d-spacings, suggesting that the plasticization effect of scCO₂ and the deformation during foaming enhance the intercalation process. This behavior is consistent regardless of the nature of the polymer, showing significant amounts of intercalation even in purely hydrophobic polymers.

4:00 PM Q10.9

Mechanical Properties of Polyethylene Containing Defunctionalized Single Wall Carbon Nanotubes.

Meisha Lei Shofner¹, Valery N. Khabashku² and Enrique V. Barrera¹; ¹Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas; ²Department of Chemistry, Rice University, Houston, Texas.

Chemical functionalization of single wall carbon nanotubes (SWNTs) is a method for increasing dispersion and interfacial adhesion in polymer matrix composites. Functionalization addresses these issues by disrupting rope structure and creating a chemical bond between the fiber and the matrix, but changes to the nanotube hexagon structure caused by chemical modifications are expected to have a detrimental effect on the SWNTs' intrinsic mechanical properties. To take advantage of the benefits of functionalization and the desirable properties of unfunctionalized SWNTs, this research studies the effect of removing functional groups from the SWNTs dispersed in a polymer matrix. Removal of the functionalization following processing could produce composites containing well dispersed SWNTs with higher mechanical properties than those containing functionalized SWNTs. Composites containing defunctionalized SWNTs and polyethylene are analyzed to evaluate the effect of functional group removal on the mechanical properties. The mechanical properties are measured using tensile tests and dynamic mechanical analysis. Issues of defects in the SWNT structure, polymer degradation, and changes in the fiber/matrix bonding as a result of functionalization removal are studied using Raman spectroscopy, thermogravimetric analysis, and infrared spectroscopy. An experimental model for composite strengthening through unfunctionalized nanotubes is presented.

4:15 PM Q10.10

Influence of Layered-Silicates on the Phase Separated Morphology of PS - PVME Blends. Koray Yurekli¹, Alamgir Karim², Eric J Amis² and Ramanan Krishnamoorti¹;

¹Chemical Engineering, University of Houston, Houston, Texas; ²Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

The influence of lateral diameter of nanometer thick anisotropic layered silicates on the phase separated morphology of a near critical polystyrene (PS) - poly(vinyl methyl ether) (PVME) blend was examined using atomic force microscopy. Films with comparable amounts of thermodynamically equivalent nanoparticles varying only in lateral disk diameters were examined using a temperature gradient method and showed dramatic differences in late-stage morphology. The blends with small disk diameter (30 nm and 0.5 μm) nanoparticles exhibit a pinning of domain sizes and demonstrate an increase in the number of domains with a higher fraction of near circular structures. On the other hand, for layered - silicates with large disk diameters (10 μm), the nanoparticles do not to affect the morphology of the phase - separated structure and only accelerate the phase separation kinetics. The extent of domain pinning increases with increasing silicate content and results in smaller domains at higher concentrations of silicate.

4:30 PM Q10.11

Raman-Active Nanostructured Materials for use as Novel Stress-Sensitive Polymeric Coatings. Jerome Halary, Paul Cookson, Peter A Lovell, John L Stanford and Robert J Young; Manchester Materials Science Center, UMIST, Manchester, M1 7HS, United Kingdom.

Nanocomposites and nanostructured polymers with unique opto-mechanical properties have been developed as smart coatings for use in a novel, high resolution, non-contact strain-measuring application. Remote Raman spectroscopy is used to monitor optical stress/strain sensitivity of deformed coatings (and deformation micromechanics), and provides local stresses and strains on the micron scale directly from stress/strain-induced Raman band shifts. Two types of polyurethane coatings were developed: (i) microphase-separated copolyurethanes in which the Raman sensitivity

is provided by nanoscale-dispersed diacetylene-containing hard segments produced in situ during polymerisation and (ii) polyurethane nanocomposites comprising a low volume fractions (< 0.1 wt %) of single-wall carbon nanotubes as the Raman-active species. Deformation micromechanics studies on coated substrates provide quantitative correlations between Raman band shifts and stresses and strains applied on the substrate. Polarised Raman spectroscopy enables stresses and strains to be measured in different directions thus allowing principal stresses and strains to be determined. The deformation micromechanics of these nanostructured materials has been investigated by carrying out fatigue experiments (loading/unloading) and also by determining the effect of deformation rate on the materials. Finally, results from stress/strain mapping around defects such as precisely machined holes of different geometries in deformed plates, will be compared with those predicted by conventional stress analysis. Further investigations on the micromechanics behaviour of the Raman-active species have been undertaken. The research is aimed at providing a novel high resolution non-contact technique for the determination of surface stresses and strains in a wide variety of engineering components used in both laboratory and in-the-field (external) applications as well as obtaining a better understanding of the deformation behaviour of nanostructured materials.

SESSION Q11: Nanostructured Bulk Materials and Nanocomposites
Chairs: Peter Green and Boris Yakobson
Friday Morning, December 5, 2003
Room 311 (Hynes)

8:30 AM *Q11.1

On the mechanical stability of nanocrystalline materials by synchrotron probe. Thomas Tsakalakos¹, Igor Zakharchenko¹, Mark Croft⁴, Zhong Zhong², Yuriy Gulak¹, Subra Suresh³ and T. A. Venkatesh³; ¹Cer. & Mat. Engineering, Rutgers University, Piscataway, New Jersey; ²National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York; ³Mat. Sc. & Eng., MIT, Cambridge, Massachusetts; ⁴Physics, Rutgers, Piscataway, New Jersey.

In order to make reliable estimates of nanomaterial component performance it is necessary to have an accurate knowledge of internal stresses field distributions under static or dynamic loads. Synchrotron x-ray scattering techniques for residual strain depth-profiling and tomography-like scatter-intensity profiling of materials are presented. The techniques utilize energy dispersive x-ray scattering, from a fixed micro-volume, with micro-scanning of the specimen being used to profile its interior. The tomography-like profiles exploit scattering-cross-section variations, and can be contrast-enhanced by separately monitoring scattering from different crystal structures. The residual stress profiling of fatigue deformation processes on Ni electrodeposited nanocrystalline bulk specimens showed different internal stress distributions, relaxations and internal fatigue damages suggesting different mechanisms of deformation and damage. The correlation of the internal stresses (stress gradients) with both abrasive and sliding wear properties in Nanostructured and microsize-grain coatings will be also presented. These results could explain the observed enhancement of wear resistance of nanocoatings vs. conventional. A fresh approach to the fatigue crack retardation by overload and other transient effects will be also presented. Overload effects, underload effects and fatigue crack growth resistance with increasing K are all relatable to the internal stresses arising from the dislocations in the plastic zone. Preliminary experiments have shown that the probing sensitivity of the EDXRD method is sufficient to elucidate the origin of this internal stress Kint by mapping the internal stress tensor in and around the plastic zone of a crack in steels and Ni nanocrystalline alloys. Thus, it is demonstrated that, provided an accurate knowledge of the residual stress profiles generated is available and allowance is made for stress redistribution and the multiaxial nature of residual stresses, reliable predictions of damage and performance can be made. We gratefully acknowledge the support of the Office of Naval Research under the Defense University Research Initiative on NanoTechnology (DURINT), which is funded by a subcontract to Rutgers University through the Massachusetts Institute of Technology by the Office of Naval Research under Grant N-00014-01-1-0808. Keywords: Energy dispersive x-ray diffraction, Synchrotron radiation, Residual stress distributions, fatigue, nanocrystalline materials.

9:00 AM Q11.2

Toughening of Nanoporous Glasses Using Porogen Residuals. Dan Maiden¹, Reinhold H. Dauskardt¹, Willi Volksen² and Robert D. Miller²; ¹Materials Science and Engineering, Stanford University, Stanford, California; ²IBM-Almaden Research Center, San Jose, California.

From biological scaffolds to dielectric layers, nano-templated organic-inorganic hybrid glasses are being developed to provide a versatile class of highly porous materials with tunable properties. However, the incorporation of porosity into these low-density brittle glasses is expected to have catastrophic effects on mechanical properties. In this study, we demonstrate remarkable toughening behavior in highly porous Methyilsilsesquioxane (MSSQ) films attributed to molecular bridging by residual porogen molecules. Adhesion data at several selected interfaces is presented as a function of porosity and porogen molecular weight. Interfacial toughening was reported for nanocomposites in which the porogen did not totally volatilize. This resulted in increasing adhesion energy at an MSSQ-SiO₂ interface with increasing porosity. X-ray and infrared spectroscopy clearly show remnants of the porogen molecule at the interface. A molecular bridging model is used to explain increases in the adhesion energy of up to 1000%. Implications of this study pertaining to microelectronics and nanocomposite architecture are discussed.

9:15 AM Q11.3

Strength Variations during Mechanical Alloying Through the Nanostructural Range: Experiments and Atomistic Simulations. Alan C. Lund and Christopher A. Schuh; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

During processes of mechanical alloying the characteristic structural length scales of an alloy, including the phase domain size and the crystallite grain size, decrease gradually to a nanocrystalline or even fully amorphous final state. This method therefore allows a unique avenue to explore the structure-property relationship over several orders of magnitude in length scale. In this work we have considered an ideal equiatomic Ti-Zr system deformed through multiple cold-rolling passes to refine the structural length scales into the nanometer range. The variation of the hardness of the system with decreasing length scale is discussed in terms of traditional Hall-Petch scaling (at the microscale) and its breakdown (at the nanoscale). Large 2-D atomistic simulations have also been performed to capture the final stages of the structural evolution, and to corroborate the experimentally observed trends in hardness.

9:30 AM Q11.4

Synthesis and mechanical characterisation of Fe-based bulk metallic glass composites. Alberto Castellero¹, A L Greer², A R Yavari³ and Akihisa Inoue¹; ¹Institute for Materials Research, Tohoku University, Sendai, Japan; ²Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ³INPG, Grenoble, France.

Mechanical properties (e.g. ductility, toughness and stiffness) in bulk metallic glasses (BMGs) can be successfully improved when particles (e.g. hard ceramics, bcc dendrites and nanocrystals, all showing strong and intimate interfacial bonding with the matrix) are dispersed in the alloy. Methods currently used for the preparation of such composites include mechanically alloying of amorphous powders with the desired volume fraction of crystalline phase, formation of the crystalline phase during the casting of a glass forming melt, partial crystallisation of a metallic glass. The structure and grain size of the particles play a crucial role in interrupting the propagation of shear bands in the amorphous alloy and, consequently, improving the mechanical properties. In this work composites, where particles with different structure (i.e. bcc, fcc and hexagonal) and grain size are dispersed in Fe-based amorphous matrix, were obtained by consolidation of amorphous powders and selected amounts of the crystalline phase, in order to obtain highly dense samples suitable for mechanical testing. Mechanical properties of the composites were compared with those of the corresponding BMG.

9:45 AM Q11.5

Modeling the Dynamic Fracture of Polymer Blends Processed Under Shear. Gavin A. Buxton and Anna C Balazs; Dept. Chemical Engineering, Univ. Pittsburgh, Pittsburgh, Pennsylvania.

We combine a morphological model of the phase-separating dynamics of polymer blends under shear with a simulation of dynamic fracture mechanics to elucidate the effects of domain anisotropy on crack propagation. We use the Cahn-Hilliard (CH) model to evolve a binary phase-separating AB mixture under imposed shear. Highly elongated and anisotropic domain growth ensues, resulting in "strip-like" patterning in the direction of shear. We then take these three-dimensional sheared morphologies and look at the effects of anisotropy on crack growth in the resultant solid material. We employ a dynamic Born lattice spring model (LSM) to simulate crack propagation in the heterogeneous sheared morphologies. The dynamic LSM consists of a three-dimensional network of springs connecting points of mass. We directly map the location of the different phases from the CH lattice onto the LSM lattice and assign local elastic and fracture properties accordingly. The interphase between the A and B

phases is assumed to be weaker than either the pure A or B material. The influence of the orientation of the anisotropic interfacial regions on crack propagation is investigated. We find that the strength and toughness in the plane normal to the shear gradient is reduced, relative to unsheared samples, while the strength and toughness in the plane normal to the shear direction is increased. Through these combined morphological and mechanical studies we have elucidated the complex dependence of dynamic crack propagation on the processing conditions of polymer blends.

10:30 AM Q11.6

Molecular Modeling of the Local Mechanical Properties of Nanoscopic Polymeric Structures. Juan de Pablo¹ and Kenji Yoshimoto¹; ¹University of Wisconsin, Madison, Wisconsin; ²University of Wisconsin, Madison, Wisconsin.

Ultrathin polymer films and nanoscopic polymer structures offer a particularly interesting class of systems in which to study how local phenomena propagate throughout a material, and in which to test the limits of validity of traditional continuum descriptions. Such systems are highly relevant in the technologies being considered for mass-production of next-generation electronic devices. A complete understanding of material properties at nanometer length scales is crucial for development and optimization of such technologies. Recent experimental data suggest that the thermophysical properties of polymeric materials are different in small geometries from those of the bulk. It has been reported, for example, that the glass transition temperature of ultra thin free-standing polymeric films is significantly lower than that of the bulk. This trend, however, appears to be reversed in the presence of strongly attractive substrates. These reported changes have been controversial, and their origin remains elusive. Our own work using local thermal probes indicates that, depending on the nature of polymer-substrate interactions, the glass transition of a thin film can be considerably higher or lower than the bulk value. We use molecular simulations of polymeric molecules to analyze and explain the origin of such behavior. We have developed novel simulation techniques that permit sampling the configuration space of amorphous polymeric glasses, and we have developed formalisms that permit calculation of the local mechanical properties of ultra-small samples. The results of these simulations are used to anticipate the mechanical behavior and eventual collapse of nanoscopic polymeric structures. The insights provided by simulations help explain some of the experimental phenomenology observed in the fabrication of such features. The overall picture that emerges from our experiments and our simulations is that amorphous, glassy polymeric materials exhibit significantly different thermophysical properties in thin-film geometries and nanoscopic structures than in the bulk, thereby offering exciting possibilities for future research and discovery, both at the theoretical and experimental levels. More recently, we have examined the local mechanical properties of polymer nanocomposites. This talk will provide an overview of the simulation methods that have been developed to investigate complex fluids and glassy materials, the experimental evidence that has been gathered regarding size dependence of glass transition phenomena, and our current views on the mechanical properties of glassy, nanoscopic structures and nanocomposites.

10:45 AM Q11.7

Reinforcement of Polymer Melts by Binary Mixtures of Nanofillers. Sanford Sternstein¹, Giorgio Ramorino^{2,1} and Bing Jiang¹; ¹Materials Sci. & Engr., Rensselaer Poly Inst, Troy, New York; ²University of Brescia, Brescia, Italy.

The reinforcement capabilities and associated nonlinear viscoelasticity of polymer melts containing dispersed nanofillers have been reported on previously by this laboratory. A mechanism has been proposed for these phenomena in which the trapping of entanglements at the filler surfaces results in non-Gaussian (Langevin) matrix chain behavior and a substantial increase in matrix component modulus. This increase in matrix modulus is sufficient to explain the very high levels of reinforcement, for example, a 1000 % increase in storage modulus with as little as 12 vol. percent of nanofiller. Various strain history phenomena such as the nonlinearity of storage and loss moduli with increasing strain, or the recovery kinetics of moduli following a large strain perturbation, can all be explained by this model. Furthermore it has been shown that the filler surface treatment has a major effect on the specific shape and dependence of loss factor with strain, as well as the recovery kinetics. In the present paper, the mechanism of reinforcement will be further explored by using binary mixtures of the various fillers. It will be shown that several types of behavior may be observed depending on the particular binary mixture. In some cases the reinforcement follows almost exactly what is predicted from a simple nonlinear mixing rule. In other cases, there are strong deviations from the mixing rule and an "interaction term" needs to be used. The most intriguing case is when the two filler types act synergistically such that the high reinforcement level achieved when a single filler type is used, is also achieved with the binary mixture. In

this case, the nonlinearity observed is additive with the total filler concentration. The concept of a "partial molar storage modulus" will be introduced, and preliminary results presented.

11:00 AM Q11.8

Mechanical Characterization Of Polymeric Nanofibers Using Atomic Force Microscopy. E P S Tan^{1,2} and C T Lim^{1,2}; ¹Division of Bioengineering, National University of Singapore, Singapore, Singapore; ²Department of Mechanical Engineering, National University of Singapore, Singapore, Singapore.

Much interest has been generated recently in the area of tissue engineering to create biological alternatives for implants. Biodegradable polymers in the form of highly porous nanofibrous scaffolds are ideal in accommodating cells and guiding their growth and tissue regeneration in three dimensions. Besides biocompatibility, the structural integrity of the scaffold is important for tissue regeneration to proceed. Therefore mechanical characterization of individual nanofibers is essential in understanding the mechanical properties of nanofibrous scaffolds. However to date, little is done in this area due to difficulty in manipulating ultrafine fibers and measuring the very small force and deformation involved. Thus the atomic force microscope (AFM) is suitable for studying the structural and mechanical properties of single nanofibers. Poly L-lactic acid (PLLA) is one such polymer used for implants in tissue engineering. In this study, the nanofibrous scaffold is fabricated from polymer solution by a procedure involving thermally induced gelation, solvent exchange and freeze drying. A two-dimensional nanofiber network is produced from a dilute polymer solution and deposited on mica substrate for characterization using the AFM. In this study, the surface structure and elastic properties of individual nanofibers are investigated. The phase images of a single nanofiber (50-400nm diameter) obtained using tapping mode AFM reveal a fibrillar morphology with crystalline and non-crystalline regions which is not visible from scanning electron micrographs. The fibrils consist of alternating crystalline and non-crystalline regions. The interfibrillar regions consist of non-crystalline molecules. The Young's modulus is obtained by indenting the nanofiber surface using an AFM tip. The Young's modulus is found to be 1.2 ± 0.4 GPa. The wide range of modulus values obtained is due to the indentation of non-crystalline and crystalline regions within the nanofiber.

11:15 AM Q11.9

Tuning Nanocomposite Properties by Electrical Field Poling of Nanoparticles. Hilmar Koerner¹, Richard A Vaia², John D. Jacobs³ and John D Busbee³; ¹Nonmetallic Materials Division, Univ of Dayton Research Institute, Dayton, Ohio; ²Air Force Research Laboratory, AFRL/MLBP, Wright Patterson AFB, Ohio; ³Air Force Research Laboratory, AFRL/MLMR, Wright Patterson AFB, Ohio.

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. Many references to this technology utilize the moniker 'nano-composites', which invoke parallels to traditional fiber reinforced composite technology and the ability to spatially 'engineer, design and tailor' materials performance for a given application. Traditional composites as well as plastics rely on techniques to take advantage of supramolecular and hierarchical organization to decouple small-strain viscoelastic properties from large strain and fracture properties, simultaneously optimizing strength, toughness and stiffness. The 'nano-composite' field is not unaffected by these concepts, however little consideration have been given to hierarchical structure with respect to large strain and fracture properties. To begin to develop the tools necessary to prescribe morphology, aspects of AC electrokinetics have been investigated to provide non-invasive, spatial and orientational control of organically modified layered silicates. Electric fields smaller than 0.5 V/microns align layered silicate agglomerates and tactoids parallel to the applied field direction in an uncured epoxy matrix. Once the electric field is removed, the samples retain their alignment. The kinetics of the alignment and re-orientation process, examined by in-situ X-ray scattering, is discussed with respect to polarization dependant alignment of mesophases such as liquid crystals and block-copolymers. As predicted, thermal coefficient of expansion, tensile strength and dynamic mechanical response depend on nanoparticle orientation and particle/matrix interface. Dialing-in layered silicate orientation presents new possibilities for investigating mechanical and transport properties at interfaces and provides the initial step to a "true" nano-composite paradigm.

11:30 AM Q11.10

Improvement of Crystallization and Mechanical Properties of PLA by Means of Clay Nanocomposite. Hirotaka Okamoto¹, Mitsuru Nakano¹, Makoto Ouchi¹, Arimitsu Usuki¹ and Yuji

Kageyama²; ¹Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; ²Toyota Motor Corporation, Susono, Shizuoka, Japan.

In view point of environmental conservation, such as reduction of petroleum resource consumption and carbon dioxide emission, wide use of poly(lactic acid) (PLA) is expected as alternative plant-derived material of conventional petrochemical plastics in recent years. PLA is usually used as amorphous material in molded products because of its low rate of crystallization, though it is semi-crystalline polymer. The low Tg of PLA (about 57 deg. C) leads to the low heat distortion temperature (HDT) of PLA products (about 58 deg. C with 0.45MPa load). It is necessary to increase the degree of crystallinity for use of PLA as automotive parts with higher HDT. Some composite materials of PLA with organophilic clay and organic crystal accelerator (OCA) were prepared by melt compounding method in order to improve the rate of crystallization and mechanical properties, especially the HDT. The PLA-clay nanocomposite containing 4.8wt% of organophilic clay showed an exothermic peak corresponding to its crystallization at 2.4 min. in the isothermal measurement of DSC at 100 deg. C from its molten state, although PLA itself did not in the same procedure. The PLA with 1wt% of the OCA also showed an exothermic peak at almost the same position. The peak position shifted to the shorter direction (at 1.9min) and the exothermic heat was larger for the PLA-clay nanocomposite with 1wt% of the OCA. These data indicate that the clay and the OCA accelerate the crystallization of PLA and that their combined use is more effective. It was difficult to produce crystallized specimens by injection molding even if the injected molten PLA was held for 600 sec. at 100 deg. C in the mold. On the contrary, crystallized specimens of the PLA with the clay and/or the OCA were well obtained when the hold time was set at more than 60 sec. The HDT of the specimens that were held for more than 120 sec. in the mold exceeded 120 deg. C. It is about 65 deg. C higher than amorphous PLA. The HDT decreased when the mold temperature was lower than 120 deg. C or hold time was shorter than 90 sec. due to the decrease of crystallinity. Consequently, injection molded products of PLA with higher HDT can be obtained by preparing the PLA-clay nanocomposites with the OCA, which has higher rate of crystallization.

11:45 AM Q11.11

Multiscale model of the mechanical behavior of polymer nanocomposites. Alireza Sarvestani, Murat Ozmusul and Catalin Picu; Rensselaer Polytechnic Institute, Troy, New York.

A molecularly-informed rheological model is proposed to represent the steady state viscoelastic properties of polymers filled with nano-particles. The model is based on the molecular structure of the material obtained from atomistic simulations. It accounts for the creation and annihilation of temporary junctions under the applied macro-deformation. The junctions are due either to topological entanglements or to adsorbed polymer chains on the surface of nano-fillers. The energetics of adsorption/desorption is calibrated based on the atomistic model. The corresponding convection equations representing the time evolution of filler-filler, filler-polymer, and polymer-polymer strands are formulated and solved using initial conditions resulting from Monte Carlo simulations of the equilibrium state. It is shown that the network created by the strands connecting different nano-particles greatly enhances the reinforcement and is responsible for the solid-like behavior of the material at small strains.