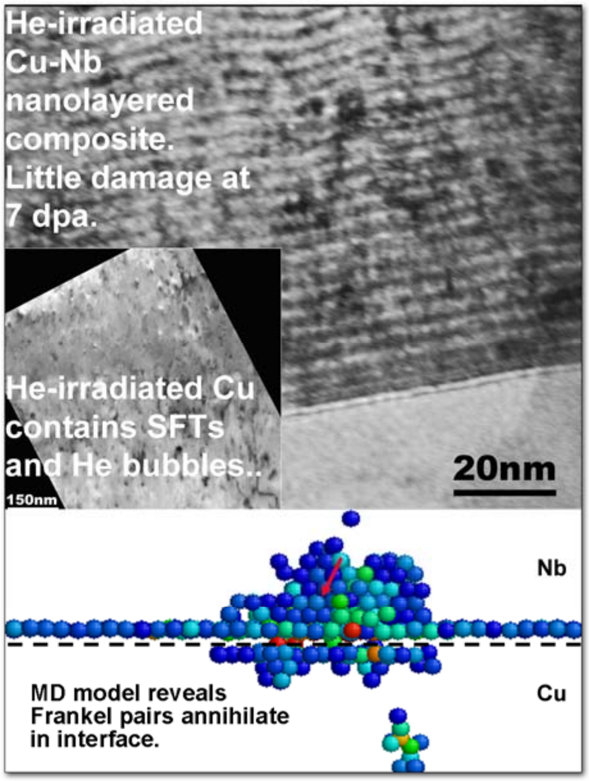
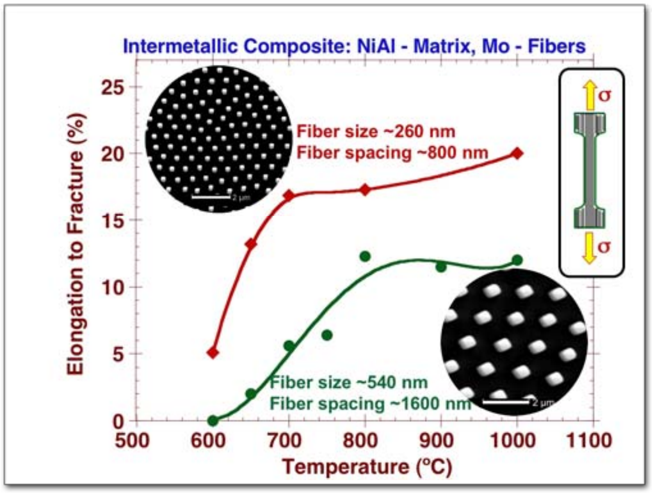
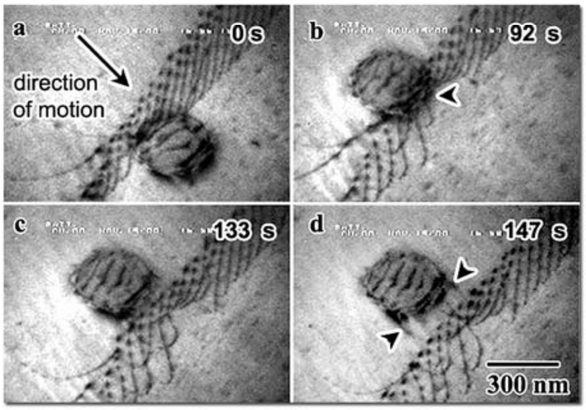
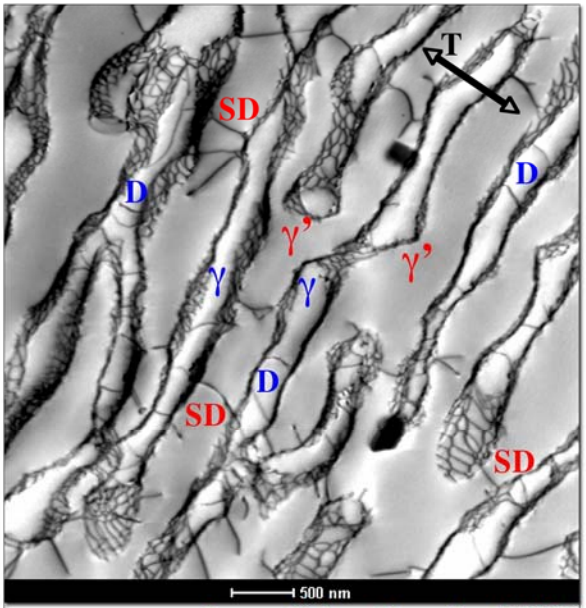
Mechanical Behavior Contractors Meeting - 2006

March 15-17, 2006 – Sheraton Gunter Hotel, San Antonio, TX









Superdislocations in γ' (SD)
Dislocations in γ (D)

Office of Basic Energy Sciences

Division of Materials Sciences and Engineering

Office of Science

U.S. DEPARTMENT OF ENERGY

Cover

Top left:	No He bubbles or mixing is evident in a Cu-Nb nanolayered composite implanted with He atoms to 7% creating about 7 dpa. Inset shows a high density of defects and He bubbles in a Cu sample subject to identical irradiation conditions. An MD model reveals that many Frankel pairs created in a cascade recombine in the interfaces in the Cu-Nb composite. **Courtesy:** *Richard Hoagland (Los Alamos National Laboratory)*
Top right:	Effect of length-scale on the elongation to fracture of directionally solidified NiAl reinforced with continuous Mo fibers. **Courtesy:** *H. Bei and E. P. George (Oak Ridge National Laboratory)*
Bottom left:	Interaction of an array of edge dislocations with an Al_3Sc particle at 673K. Note the change in interface contrast as the dislocations interact with and leave the particle. **Courtesy:** *Ian Robertson (University of Illinois*)
Bottom right:	Bright-field image of dislocation structures in a single crystal superalloy crept to 6% strain, corresponding to the early stages of tertiary creep. **Courtesy:** *Mike Mills (Ohio State University)*

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2006 DOE/BES Mechanical Behavior Contractors Meeting

Foreword

This volume highlights the scientific content of the Mechanical Behavior Program Contractors Meeting sponsored by the Division of Materials Sciences and Engineering (DMS&E) in the Office of Basic Energy Sciences (BES) of the U. S. Department of Energy (DOE). This meeting, held on March 15-17, 2006, in San Antonio, Texas, is the third in a series of research theme-based Contractors Meetings in DMS&E.

The Mechanical Behavior program features basic research with an emphasis on the atomic level understanding of the relationship between mechanical behavior and defects in order to develop predictive models of materials behavior for the design of materials having superior mechanical behavior. The purpose of the Contractors Meeting is to bring together researchers funded by BES in this research area, to facilitate the exchange of new results and research highlights, to foster new ideas and collaborations among the participants, and to identify needs of the research community. The meeting will also help DMS&E in assessing the state of the program, identifying programmatic needs, and charting potential future directions. The meeting agenda reflects the major research themes currently supported by the program.

We thank all of the invited speakers and meeting attendees for their active participation in sharing their ideas and research results. The dedicated efforts of the meeting chairs, C. T. Liu of the University of Tennessee and Michael Baskes of the Los Alamos National Laboratory, in organizing and coordinating the meeting are gratefully appreciated. Special thanks especially go to Sherry D. Samples CPS of the Oak Ridge National Laboratory for taking charge of the logistical aspects of the meeting.

Yok Chen and Don Parkin
Division of Materials Sciences and Engineering
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

U. S. Department of Energy
Office of Basic Energy Sciences
Mechanical Behavior Contractors Meeting

March 15-17, 2006
C. T. Liu (UT) and Mike Baskes (LANL), Meeting Chairs

Wednesday, March 15, 2006

3:00 – 6:00 p.m.	Registration
5:00 – 6:00 p.m.	Reception (soft drinks and cash bar)
6:00 – 7:00 p.m.	**** Welcoming Dinner ****
7:15 p.m.	*Introductory Remarks* – Yok Chen and Don Parkin Department of Energy (DOE) Organizers
7:30 p.m.	*DOE Perspective* - Harriet Kung Director, Division of Materials Sciences and Engineering
Session I	**Visionary Session** Chairs: Yok Chen and Don Parkin, Department of Energy
8:00 – 8:40 p.m.	Ladislas Kubin (CNRS-ONERA) *The Future of Plasticity: a Multiscale Viewpoint*
8:40 – 9:20 p.m.	Herbert Gleiter (Forschungszentrum Karlsruhe, Germany) *Are There Ways to Produce Materials Beyond the Limitations of Today?*

THURSDAY, MARCH 16

7:30 – 8:30 a.m.	**** Breakfast will be provided ****
Session II	**Mechanical Failure** Chair: Mike Baskes, Los Alamos National Laboratory
8:30 – 9:00 a.m.	Ben C. Larson (Invited Speaker), Oak Ridge National Laboratory *High-Resolution 3D X-Ray Microscopy for Investigating Mechanical Behavior*
9:00 – 9:30 a.m.	James S. Langer, University of California, Santa Barbara *Theories of Strongly Nonequilibrium Phenomena, Especially Deformation and Failure in Noncrystalline Solids*
9:30 – 10:00 a.m.	Michael J. Mills, Ohio State University *Mechanisms of High Temperature/Low Stress Creep of Ni-Based Superalloy Single Crystals*
10:00 – 10:15 a.m.	**** Break ****
10:15 – 10:45 a.m.	Michael E. Kassner, University of Southern California *Long Range Internal Stresses and Mechanisms of Cyclic and Monotonic Deformation*
10:45 – 11:15 a.m.	Charles J. McMahon, Jr., University of Pennsylvania *The Use of High-Strength Steels to Contain Hydrogen*
11:15 – 11:45 a.m.	Michael K. Miller, Oak Ridge National Laboratory *Stable Nanoclusters and Mechanical Behavior of Metallic Materials*
11:45 – 12:15 p.m.	**Interactions and Discussions**
12:15 – 1:15 p.m.	**** Lunch ****

Session III Plastic Deformation

<u>Chair</u>: C. T. Liu, University of Tennessee

1:15 – 1:45 p.m.	Xun-Li Wang (Invited Speaker), Oak Ridge National Laboratory *In-situ study of mechanical behavior by neutron scattering*
1:45 – 2:15 p.m.	Vaclav Vitek, University of Pennsylvania *Atomistic Studies of Deformation and Fracture in Materials with Mixed Metallic and Covalent Bonding: Transition Metals and Their Compounds*
2:15 – 2:45 p.m.	Easo P. George, Oak Ridge National Laboratory *Mechanical Behavior of B.C.C-Derivative Intermetallics and Bulk Metallic Glasses*
2:45 – 3:00 p.m.	**** Break ****
3:00 – 3:30 pm.	Robert O. Ritchie, Lawrence Berkeley National Laboratory *Mechanical Properties of Materials Across Varying Length Scales*
3:30 – 4:00 p.m.	Mingdong Cai, Washington State University *Electron Emission as a Probe of Plastic Deformation in Single Crystal Metals*
4:00 – 4:30 p.m.	S. Bulent Biner, Ames Laboratory *Modeling and simulation of inhomogeneous deformation behavior of metallic glasses and their composites*
4:30 – 5:00 p.m.	**Interactions and Discussions**

Session IV: Poster Session (Heavy hors d’oeuvres and cash bar)

6:30 – 8:30 p.m.	Marek A. Przystupa, University of California, Los Angeles *Harper-Dorn Creep of fcc, bcc and hcp Metals and Alloys*
	Amit Misra, Los Alamos National Laboratory Stability of Nanolayered Materials Subjected to Large Plastic Strains, Cyclic Loading and Radiation

Posters continued

Joe A. Horton, Oak Ridge National Laboratory
Synthesizing intermetallic composites with well-controlled microstructures and understanding their small-scale mechanical behavior

Shefford P. Baker, Cornell University
Influence of Interfacial Chemistry on the Thermomechanical Behavior of Thin Film Metallizations

Yu Qiao, University of Akron
Size Effect in Cleavage Cracking in Polycrystalline Thin Films

Pedro Ponte Castaneda, University of Pennsylvania
Multiscale modeling of nanostructured triblock copolymers

Perry H. Leo, University of Minnesota
Microstructural Evolution and Interfacial Motion in Systems with Diffusion Barriers

Mingdong Cai, Washington State University
Study of the Martensitic Transformation in Shape Memory Alloy Using Photoelectron Emission Microscopy

Chun-Hway Hsueh, Oak Ridge National Laboratory
Effects of Dopant Segregation on Lattice-Diffusional Creep of Nanocrystalline Ceramics

Antoni P. Tomsia, Lawrence Berkeley National Laboratory
Interfaces at High Temperature: From Basic Studies to Materials Fabrication

David L. Olmsted, Sandia National Laboratories
Computing the Mobility of Grain Boundaries

Rodney McCabe, Los Alamos National Laboratory
Semi-Automated EBSD-based Twin Analysis and Coupled EBSD/TEM Analysis of Zirconium Deformation Mechanisms

Gwenaelle Proust, Los Alamos National Laboratory
Characterizing the Hardening Response of Zirconium

Posters Continued

Jerry A. Floro, Sandia National Laboratories
Using Elastic Strain to Self Assemble (Potentially) Functional Nanostructures

John P. Sullivan, Sandia National Laboratories
Dissipation and Collective Phenomena in Coupled Mechanical Systems

Jason T. Roland, University of California, Irvine
Synthesis and Single Molecule Studies of Titin-Mimicking Modular Polymers

FRIDAY, MARCH 17

7:30 – 8:30 a.m.	**** Breakfast will be provided ****
Session V	**Microstructural Effects on Mechanical Behavior** Chair, C. T. Liu, University of Tennessee
8:30 – 9:00 a.m.	Ian M. Robertson (Invited Speaker), University of Illinois *Correlating dislocation behavior with macroscopic mechanical properties directly in the TEM through use of a novel tensile test device*
9:00 – 9:30 a.m.	Carlos N. Tome, Los Alamos National Laboratory *A multi-scale study of the role of microstructure in the deformation behavior of hexagonal materials*
9:30 – 10:00 a.m.	William C. Johnson, University of Virginia *Microstructural Evolution and Interfacial Motion in Systems with Diffusion Barriers*
10:00 – 10:15 a.m.	**** Break ****
10:15 – 10:45 a.m.	N. J. Tao, Arizona State University *Probing Electromechanical Properties of Single Molecules*
10:45 – 11:15 a.m.	Karl A. Gschneidner, Jr., Ames Laboratory *A new paradigm: Ductile intermetallics! The rare earth RM B2 CsC1-type intermetallics*

11:15 – 11:45 a.m.	Paul F. Becher, Oak Ridge National Laboratory *Microstructural Design of Advanced Ceramics*
11:45 – 12:15 p.m.	**Interactions and Discussions**
12:15 – 1:15 p.m.	**** Lunch ****

SESSION VI Size Effects on Mechanical Behavior

<u>Chair</u>: Mike Baskes, Los Alamos National Laboratory

1:15 – 1:45 p.m.	J. Charles Barbour (Invited Speaker), Sandia National Laboratories *Nanomechanics Opportunities at the Nanoscale Science Research Centers*
1:45 – 2:15 p.m.	William D. Nix, Stanford University *Length-Scale Effects in Plasticity*
2:15 – 2:45 p.m.	Julia R. Weertman, Northwestern University *Microstructural Stability and Mechanical Behavior in Nanocrystalline Metals*
2:45 – 3:00 p.m.	**** Break ****
3:00 – 3:30 p.m.	Richard G. Hoagland, Los Alamos National Laboratory *Deformation Physics of Ultra-fine Scale Materials*
3:30 – 4:00 p.m.	Zhibin Guan, University of California, Irvine *Nano-Structured Biomimetic Polymeric and Hybrid Materials for Advanced Mechanical Properties*
4:00 – 4:30 p.m.	Jerry A. Floro, Sandia National Laboratories *Mechanics of Small Length Scales*
4:30 – 5:00 p.m.	**Interactions and Discussions**
6:00 p.m.	**Dinner**
	Summary Yok Chen and Don Parkin, DOE

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SESSION I:

VISIONARY SESSION

Chairs: Yok Chen and Don Parkin (DOE)

The Future of Plasticity: a Multiscale Viewpoint

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Expectations and Objectives

This text is not a presumptuous attempt at predicting the future. It is simply based on possible extrapolations of present evolutions to the short and mean terms. It presents a probably incomplete and not totally objective discussion of long-standing problems that may be approached and hopefully solved in the next years. There will always be a demand for improving existing materials or devising new ones that satisfy a number of criteria in terms of various types of properties and concerns. However, the present shift of interest from structural materials to functional, nanostructured and biological materials looks irreversible. We can anticipate that the continuous increase in computing power will result in larger scale simulations yielding access to more accurate results or more complex problems. As presently witnessed, it may also induce a decrease in experimental and modeling efforts. Keeping a balance between these approaches is more than ever a necessity within the present viewpoint.

The topics discussed in this abstract are restricted to dislocation-mediated plasticity in crystalline matter. Irrespective of the specific material investigated, the deformation conditions and the characteristic dimensions considered, from nanosized objects to plastic flow in the earth mantle, the bases of dislocation theory remain the same and only their point of application differs. For this reason, the present abstract is based on a multiscale perspective. It also assumes that efforts devoted to the improvement of fundamental understanding will not be discontinued.

Establishing a physical theory of plasticity was from the very beginning, and still is, a long-term objective for dislocation theory. Many doubt that this goal will ever be reached [1] and they may be right. Indeed, the intricate multidimensional puzzle to be assembled involves too many pieces with very different sizes and fairly complex shapes A more realistic objective consists in making all possible efforts to remove all the existing phenomenology from upper scales of modeling and reduce as much as possible parameter fitting procedures. This will occur by extending bottom-up analyses, redeeming present weaknesses at all scales and finding better solutions for performing scale transitions. A number of challenges exist, which may be approached by continuous progress based on the presently established concepts.

Conceptual breakthroughs cannot be anticipated. New theoretical perspectives may arise from statistical physics or non-linear dynamics and breakthroughs may emerge from novel numerical and experimental approaches. Regarding experimental aspects, one may hope that some preliminary attempts will materialize. This concerns, for instance, high resolution transmission electron microscopy observations of the core structure of screw dislocations [2,3], or of kinks and kink pairs [4], the development of local X-ray diffraction analyses toward the *in situ* observation of inter- and intragranular deformation in the bulk [5], or analyses of local signals generated by dislocation motion [6].

Atomic Scale and Transition to Mesoscopic Scale

At present, the transition between atomic and mesoscopic scales is not a major issue. Information passing can be achieved in different manners, for instance by incorporating activation energies into Boltzmann probabilities, by feeding microelastic models with atomistic output or via kinetic Monte Carlo simulations. The direct coupling of atomic simulations with mesoscopic or continuum simulations has already been attempted, albeit with mixed results. It is still of interest for several problems mentioned below, and also for developing a connection between local states of stress during plastic flow and damage studies, including fracture processes.

In terms of simulation methods, we may expect a development of *ab initio* computations and of physically motivated potentials, partially fitted to the output of *ab initio* studies, at the expense of semi-empirical and empirical potentials. One may also hope that more attention will be paid to the development of static methods for determining activation energy pathways and the stress dependence of activation energies. The applications discussed below reflect the expectations of communities working at the upper scales.

Whereas the elastic theory of dislocations is in quite good shape, dislocation theory is far from complete because of our imperfect knowledge of dislocation cores and of their behavior under stress. Completing our understanding of all major dislocation core processes should be a major concern at atomistic scale. Such studies are often less spectacular than "mass" investigations, but they have a broader and more substantial impact on modeling in the long run. Completing dislocation theory means, for instance, solving such pending questions as the stress dependence of activation energies - for kink-pair mechanisms in materials with high Peierls stress, - for the cross-slip mechanism in various crystallographic structures, and - extending similar studies to compounds, non-metallic oxides and ceramics up to minerals of interest to geophysicists.

Owing to the present difficulties in incorporating chemical effects at the upper scales a substantial effort could be devoted to atomic-scale investigations on this problem. This implies, for a start, examining the static and dynamic interactions of dislocations with point defects, solute atoms [7], clusters and short-range order.

Another major issue, which constitutes a bottleneck to modeling at upper scales, is dislocation nucleation at free surfaces, grain boundaries, crack tips, under a nanoindentor etc. The question of homogeneous nucleation is now practically solved, but heterogeneous nucleation at local imperfections, in dislocation-free crystals or in nanometric volumes of materials and under high stresses, still constitutes a tough challenge. It is related to a group of emerging phenomena occurring in small volumes under high stresses, like crossed effects between stress or dislocation flux and other physical properties and different types of interactions between dislocations and interfaces.

A third domain of investigation involves obtaining a more complete understanding of complex coupled processes that require mass simulations. This huge field includes, of course, radiation damage, shock loading, the deformation of nanograins and nanobeams, but also dry friction, wear, machining, etc. Tools need, however, to be developed in order to go beyond spectacular illustrations and extract quantitative information on the underlying mechanisms.

Issues at the Mesoscale

Atomistic input will govern to some extent the pace of progress through the classes of materials that can be the object of reliable investigations. There are nevertheless important questions to solve, which can, in broad terms, be classified into two categories involving different levels of modeling. The first category deals with single crystal and consists in going beyond the yield stress and elementary interactions of dislocations with themselves or other defects. The main issue is concerned here with collective dislocation behavior and strain hardening. The second category involves treating more complex materials and processes, in which the heterogeneity of stress fields requires making a connection between physical analyses and continuum methods for solving a boundary value problem. In both cases, the objective of formulating models with improved predictive value will imply a close connection between modeling and simulation. To avoid a long enumeration of dislocation and plasticity processes [8], which would practically cover all chapters of plasticity, only a few specific topics are highlighted. Most of them can, in practice, be approached at different levels of sophistication.

Modeling the single crystal constitutes one of the earliest and most long-standing objectives of dislocation theory. It will be still be necessary to complete this task if one wishes to achieve meaningful progress in more complex situations. At this scale, the legacy of physical metallurgy consists in a wealth of careful experiments and observations in controlled conditions, of which some could hardly be reproduced nowadays. Due to the present emphasis on modeling and simulations, there is a tendency to omit comparison to experiment and ignore experimental facts that were well known, but not necessarily understood, years ago. In terms of modeling, early studies aimed at unraveling the most significant mechanisms and back-of-envelope calculations were deemed sufficient for this purpose. More sophisticated models based on elasticity theory, some of them dealing with atomic-scale processes, were also developed. Several strata of models were accumulated, some qualitative and others quantitative, which need to be trimmed or sometimes simply discarded, checked and cast into a formal three-dimensional frame suitable for a connection with the continuous framework.

As far as the elementary elastic interactions of dislocations with other defects is concerned, the picture is almost complete or under completion. By lack of motivation, the modeling of some basic mechanisms has remained stagnant for years, but the situation may change because of the present emphasis on nanostructured materials. In this domain, the problems of heterogeneous dislocation generation and of the dislocation – grain boundary interaction were already mentioned. Another question that may or may not emerge, is that of dislocation climb and power law creep. For obvious reasons of time scale compatibility this is not a simple problem to treat at the mesoscale. It is relevant of numerical simulations going beyond the simple dimensionality considerations and 2D vision that characterize the present status of this question. In the domain of structural materials, investigating the plastic properties of alloys, strain localizations, and multi-defect processes constitutes another obvious area of interest.

In spite of many attempts, dislocation patterning phenomena are still not understood. The so-called principle of similitude, that relates stress to the inverse of pattern wavelength is not convincingly modeled and the similitude constant cannot be predicted. It is now clear that the adequate way for approaching self-organization processes consists in elaborating evolutionary laws for dislocation densities in space and time. This fundamental problem also has a practical importance, as reflected by the old controversy about how and in which conditions microstructure governs strain hardening. In continuum mechanical terms, the same question is translated in terms of a distinction between isotropic hardening, which does not requires a full description of the dislocation microstructure, and kinematic hardening that does, because internal stress patterns matter during a change in strain path. Going from monotonic deformation to simple changes in strain path, like Bauschinger tests and cyclic deformation, should then provide a valuable approach for setting some bases. The objective could be here to put an end to the following paradox. There are several dislocation-based constitutive formulations for the polycrystal, of which some are quite efficient although they require adjusting a number of parameters[9]. None of them is, however, amenable to a consistent description of single crystal properties.

The Hall-Petch behavior in polycrystals is another poorly known type of collective behavior and the same paradox applies to it. There are currently many discussions on the modifications of Hall-Petch behavior in materials with fine and ultra-fine grain sizes. However, the conventional Hall-Petch law is the subject of contradictory models originating from different periods of dislocation history. One has *inter alia* 2D models of dislocation pile-ups, models based on the accommodation of lattice rotations by geometrically necessary dislocations and models based on the limitation of dislocation mean free-paths by grain boundaries. Strengthening the bases is all the more important as size effects in small dimensions, for example in thin metallic layers, are related to either line tension effects, Hall-Petch effects, or a blend of both.

Going to more complex processes, another white spot in our current understanding resides in the absence of any theory for the superposition of mechanisms. Semi-empirical rules like stress additivity and Wegard's law (rule of mixtures) are still frequently used to derive the flow stress of engineering alloys hardened by solute atoms and various types of precipitates. It may well be that non linear composition rules are more frequent than usually thought.

Finally, it is a matter of imagination combined with a good bibliography to find areas in the field of dislocation-based plasticity that deserve being serious reexamined.

Modeling and Connection to the Continuum

At present, three types of approaches, which are at various stages of development, seem able to establish a connection between dislocation theory and the mechanical response. They will not be elaborated independently of each other and will need input from atomic scale to guide modeling or determine unknown parameters. To investigate the topics listed above, it will be a matter of appreciation to decide which method is the most suited one. Comparison with experiment will also be vital, all the more as the early literature contains many very careful tests and observations that are now falling into oblivion.

*Continuum Theory of Dislocations***.** The first set of methods, which is presently in its infancy[10], consists in revisiting the continuum theory of dislocations. The long term aims look very ambitious and may require substantial conceptual efforts. In substance, the classical static theory developed by Kröner and followers is to be extended in the form of a full theory of plastic flow, able to treat microstructures and the mechanical response, in three dimensions and with all boundary conditions at the defect scale and in the continuum. For this purpose, kinetic evolutionary laws for the dislocation densities, in time and 3D space, have to be developed from statistical mechanics considerations. All relevant elementary dislocation mechanisms must then be introduced. To avoid dealing with too small time and length scales, statistical coarse graining procedures also have to be developed. The boundary value problem has to be implemented but adequate boundary conditions applying to dislocations and dislocation fluxes must also be cared of. If this program can be realized, even partial results will be of great interest.

Constitutive Formulations. It is possible to develop many types of dislocation-based constitutive formulations for strain hardening or patterning without resorting to the heavy framework of continuum dislocation theory. Then, provided that the variables are dislocation densities in slip planes, these constitutive laws can be inserted into crystal or polycrystal plasticity codes, which care of lattice rotations and boundary conditions. For polycrystal studies, the meshing of individual grains presents the enormous advantage of removing the usual assumptions on the uniformity of intergranular deformation. This method also allows a more accurate prediction of slip systems and textures. It is useful for academic purposes but, thanks to the presently available computing power, it starts percolating into industrial laboratories dealing with structural materials. This evolution is certainly bound to significantly expand in the coming years.

Numerical Tools. 2D dislocation dynamics (DD) simulations exist in many variants. They present the advantage of being simple and the disadvantage of often being too simple. Developing 3D DD simulations is a quite demanding task, which requires enormous investments in terms of time and effort. For this reason, making such simulations accessible to potential users in the form of shareware codes may become the main driving force for progress. The limitation to small strains will somehow be extended but there is perhaps no real point in going beyond of a few percent to address the present challenges, provided that it is obtained in a truly representative volume. Contributing to modeling efforts should, indeed, add a new dimension to the present investigations. In a more or less distant future, the question of going to large strains will be posed. One may then have to devise new types of simulations, dealing for instance with dislocation groups rather than individual dislocations [11].

DD simulations of single crystals do not involve solving a boundary problem in the sense of continuum mechanics, although they involve periodic boundary conditions on dislocation fluxes. They can be developed for a number of individual mechanisms and for collective dislocation behavior, especially for guiding theoretical work on dislocation patterning and strain hardening. Provided that sufficient atomistic input exists, they can be extended to other structures than face-centered or body-centered cubic, including non-cubic structures.

There are two types of mesoscale simulations of dislocations that incorporate a solution to boundary value problems. The phase field method basically works in the reciprocal scale. With respect to all other simulations, it presents the enormous advantage of being able to treat the coupled evolution of concentration fields and elastic fields. Considering its present early stage of development, a few years will be needed before this method fully realizes its potential in the domain of plasticity. DD simulations can also be coupled in real space with traditional continuum simulations, typically Finite Element or equivalent methods. These hybrid codes materialize the "great unification" of defect theory and continuum mechanics. They are yielding access to a wide open field that stretches from nanometric components to damage and fracture. Altough the limitations are the same as in conventional DD simulations, one may have great expectations on the developments to come.

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Are there Ways to Produce Materials beyond the Limitations of Today?

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Since the discovery of metals, about 7000 years ago, new materials are produced by means of modifying their microstructure. The microstructure was modified by changing one or both of the following two parameters.

(i) The concentration, and/or the spacial distribution (e.g. solid solutions, precipitates etc.) and/or the chemical character of the alloy elements added.

(ii) The character of lattice defects introduced (e.g. dislocations, grain boundaries etc.) and/or the concentration and/or the spacial distribution (e.g. a uniform or non-uniform distribution) of the defects incorporated into the materials.

This approach has the following two limitations. (i)In general, alloying of elements/compounds with different types of chemical bonds is not possible, e.g. Au cannot be alloyed with NaCl. (ii) By incorporating lattice defects into a crystal, the crystal structure can (in general) not be changed, e.g. Cu retains an fcc lattice structure with and without dislocations.

Clearly, the way to new types of materials would be open if one or both limitations mentioned above could be removed.

In this talk it will be discussed how one can modify the atomic structure of solids by incorporating lattice defects and how one may be able to alloy compounds with different types of chemical bonds e.g. how one may alloy ionic and metallic materials.

SESSION II:

MECHANICAL FAILURE

Chair: Mike Baskes (LANL)

High-Resolution 3D X-Ray Microscopy for Investigating Mechanical Behavior*

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Although x-ray microscopy dates to the 1940's, revolutionary advances in x-ray microscopy are now in progress. The availability of high-brilliance synchrotron x-ray sources, recent developments in high-precision x-ray focusing optics, and the development of new x-ray diffraction and contrast imaging techniques has stimulated entirely new x-ray microscopy capabilities, including submicron 3D spatial resolution. Of course, electron microscopy techniques provide structure and spectroscopy tools with better spatial resolution for samples up to a few tenths micron thickness and electron backscattering diffraction (EBSD) microscopy provides detailed surface structure and microstructure information with submicron resolution. However, the inherently non-destructive, penetrating nature of x-ray microscopy and its complementarity with electron techniques are the important aspects for mechanical behavior investigations addressing critical mesoscopic length scales of tens-of-nanometers to hundreds-of-microns. X-ray microscopy provides the capability of 3D sub-micron spatially-resolved measurement [1] of local crystal structure, phase, orientation, and both elastic and plastic strain tensors in single crystals, polycrystals, composites, functionally-graded, and deformed materials on length scales ranging from nanometer length scales to hundreds of microns and beyond.

Virtually all technological and biological materials owe their desirable physical properties to inhomogeneous electronic and mechanical structures on length scales ranging from atomic sizes to nanometers, microns, and millimeters. Thus, non-destructive investigative probes with a range of penetration distances and varying spatial resolutions are essential in order to realize a full understanding of the microstructure, properties, and the evolution of materials. Examples of three-dimensional, hard x-ray (> 5 keV) microscopy imaging of chemical and density fluctuations will be presented [2]. 3D measurements of thermal grain-growth in polycrystals and nano-indentation induced deformation in ductile and brittle materials will be used to illustrate the direct, quantitative link that is now possible between the microstructure and evolution in real materials and increasingly powerful computer simulations and multi-scale modeling. Ongoing developments and direct correlations between x-ray and electron microscopy of deformed metal microstructures will be discussed as well. As time permits, prospects for x-ray beams of a few nanometers diameter will be considered, along with the potential for sub-nanometer 3D spatially-resolved structural measurements using coherent beams and direct Fourier transformation.

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THEORIES OF STRONGLY NONEQUILIBRIUM PHENOMENA, ESPECIALLY DEFORMATION AND FAILURE IN NONCRYSTALLINE SOLIDS

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Program Scope: The principal goal of this program has been to bridge the gap between atomistic theories of solid dynamics and engineering practice. To do this, we need phenomenologies that are based firmly on fundamental principles of physics and realistic molecular-scale models, and yet are simple enough to be applied to a broad range of materials in a wide variety of nonequilibrium circumstances. They ought to be as useful as, and not enormously more complicated than, the Navier Stokes equation for fluid dynamics or the equations of Hookean elasticity, which describe wide ranges of phenomena with just a small number of constitutive parameters. I see no reason why a similarly useful phenomenology should not be feasible in nonequilibrium solid mechanics, especially for amorphous materials which are liquid-like in all but a few essential respects.

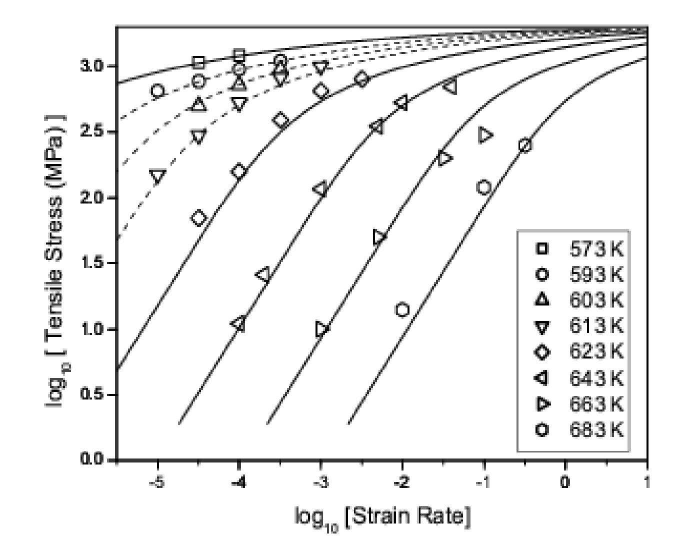
In developing a theory of deformation and failure of amorphous solids, my coworkers and I have followed Turnbull and Cohen, Spaepen, Argon, and others by assuming that the materials of interest are basically deformable elastic solids, and by focusing attention on the places in these solids – “flow defects” or “shear transformation zones” (STZ’s) – where irreversible rearrangements of the constituent molecules can take place. Our first priority was to provide a firm physical and thermodynamic basis for theories of this kind and to compare their predictions with recently emerging experimental data. The next stage of the project has been to develop continuum theories that can be used to solve problems involving large plastic deformations, shear banding instabilities, and ultimately fracture and other failure modes.

When dealing with deformable amorphous materials, it is essential to take into account the strongly temperature dependent, “super-Arrhenius” rate factors that characterize their behaviors near the glass transition. Until recently, we have been satisfied simply to insert phenomenological relaxation rates (derived from measured Newtonian viscosities) at the places in our equations where they are needed. Despite over fifty years of investigation and much heated controversy, there is still no agreed-upon, fundamental understanding of these rates. (I am among those who are highly skeptical of certain recent theoretical approaches.) The success of our STZ theory has suggested some new approaches to the puzzles of glass dynamics; and some of the ideas emerging in that effort have provided new insight regarding the STZ theory.

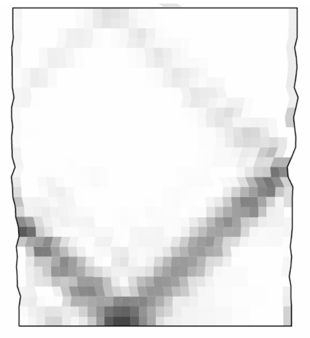
Recent Progress and Future Directions: The STZ project was given a large boost by the publication in 2003 by Lu et al. (the group of W. Johnson at Caltech) of a remarkably extensive set of measurements of the mechanical properties of a bulk, multicomponent metallic glass ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$). In particular, their data for applied stress as a function of plastic strain rate extend over such a large range of strain rates and temperatures that they indicate clearly a transition between linear Newtonian viscosity at low rates and high temperatures and apparent nonlinear "superplasticity" at higher rates and lower temperatures. This was precisely the kind of experimental information that we needed for a critical test of our version of STZ theory. Before we could make this test, however, we had to extend our theory to include the thermal effects that had so far been omitted. At stresses below a yield stress, our low-temperature theory says that the steady-state strain rate vanishes, *i.e.* that the material deforms a finite amount and then becomes jammed. On the other hand, at temperatures above the glass transition, thermally assisted STZ rearrangements must enable nonzero strain rates at arbitrarily small driving forces. We have examined two, somewhat different versions of STZ theory that include thermally assisted creep below the yield stress. Here I shall mention just one of those versions – the effective-temperature theory.

The concept of effective temperatures in the nonequilibrium theory of noncrystalline materials has emerged vigorously in the physics literature but has not, so far as I know, appeared before now in engineering solid mechanics. The basic idea is that a nonequilibrium system such as a deforming solid, even when it is deforming very slowly, may be qualitatively different thermodynamically from a system in thermal and mechanical equilibrium. Specifically, during irreversible plastic deformation, the slow, configurational degrees of freedom associated with molecular rearrangements may fall out of thermal equilibrium with the fast, vibrational degrees of freedom that couple strongly to a thermal reservoir. The statistical properties of both of these kinds of degrees of freedom may be described by "temperatures" in that they both maximize their respective entropies; thus the two temperatures may be different from one another under nonequilibrium conditions. The effective temperature is somewhat similar to the free volume introduced by Spaepen and others, and can be used in one of the same ways, i.e. in a Boltzmann-like factor to determine the density of flow defects or STZ's. The important difference is that the effective temperature is a measure of the configurational disorder in the system. Like ordinary temperature, it is a thermodynamically well defined intensive quantity, and does not necessarily carry any implication of volume changes.

In my latest paper on this topic [4], I incorporated the effective temperature into the STZ theory in two ways. First, I argued that the nonequilibrium steady-state value of the STZ density should be proportional to a Boltzmann factor in which the bath temperature is replaced by the effective temperature. Then I used detailed balance to introduce this Boltzmann factor as the ratio of the STZ annihilation and creation terms. Second, in order to write an equation of motion for the effective temperature, I assumed that its heat source is the rate of energy dissipation associated with plastic deformation. I also assumed a cooling mechanism that drives the effective temperature toward the bath temperature in the absence of external forcing. With this coupling between the effective temperature and the bath temperature, the theory becomes capable of predicting calorimetric behavior, *e.g.* the results of DSC measurements, as well as the response of the material to mechanical tractions. To illustrate the success of this version of the STZ theory, I show a log-log plot of stress versus strain rate showing data points from Lu *et al.* and theoretical curves for eight different temperatures. There are only two adjustable parameters, an overall time scale and the strength of the coupling between the effective temperature and the bath temperature. The agreement seems quite satisfactory.



It is not difficult to write down a fully tensorial, continuum version of the STZ theory, but implementing this in the solution of free-boundary problems is a major numerical challenge. We have published a simple analysis of a necking instability [1]; and Eastgate has written a more extensive report on those efforts [6]. At present, I am looking for numerical specialists who might like to work with me to extend these calculations to situations involving shear banding and fracture. To illustrate what I have in mind, I show one of Eastgate's as-yet unpublished STZ simulations of shear banding under uniaxial tensile stress. The stress is applied to the smooth horizontal surfaces; the vertical sides are initially rough free boundaries.



My most active – and speculative – direction of investigation at the moment is the search for a fundamental theory of super-Arrhenius rate factors. I started by trying to understand how the spontaneous, thermally activated creation of STZ's might be slowed anomalously near the glass transition, as it must be in order to produce the observed (apparent) divergence of the Newtonian viscosity. The idea that seems promising is that, at low enough temperatures, the creation mechanism requires the collective excitation of chains of molecular displacements. Such chains have been seen in molecular-dynamics simulations of glass forming liquids by Glotzer and coworkers. A key ingredient of the theory appears to be the configurational disorder that is intrinsic to glassy materials. When disorder is included in the calculation of the activation free energy for excitation chains, the theoretical relaxation time – and thus the STZ-related viscosity – exhibits a Vogel-Fulcher divergence at a nonzero temperature T_0, in good agreement with experiment. The next challenge for this theory is to understand the apparent relations between dynamics and thermodynamics of glasses – the vanishing configurational entropy at the Kauzmann temperature T_K, the equality between T_0 and T_K, and the relationship between the jump in the specific heat at T_K and the dynamic fragility at the glass temperature. These relationships emerge in the excitation-chain theory via a dynamic length scale – the minimum size of the excitation region – that diverges at T_0 and suggests a mechanism by which ergodicity is gradually broken during the glass transition. Needless to say, this is a work in progress.

Recent DOE-Supported Publications:

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Mechanisms of High Temperature/Low Stress Creep of Ni-Based Superalloy Single Crystals

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Program Scope

Cast nickel-based superalloys are used for blades in land-based, energy conversion and powerplant applications, as well as in aircraft gas turbines operating at temperatures up to 1100°C, where creep is one of the life-limiting factors. Creep of superalloy single crystals has been extensively studied over the last several decades. Surprisingly, only recently has work focused specifically on the dislocation mechanisms that govern high temperature and low stress creep[1-3]. Nevertheless, the perpetual goal of better engine efficiency demands that the creep mechanisms operative in this regime be fully understood in order to develop alloys and microstructures with improved high temperature capability. At present, the micro-mechanisms controlling creep before and after rafting[4] (the microstructure evolution typical of high temperature creep) has occurred have yet to be identified and modeled, particularly for [001] oriented single crystals. This crystal orientation is most interesting technologically since it exhibits the highest creep strength.

In this program, we have embarked on an extensive plan of experimental investigation designed to elucidate these creep mechanisms. The focus of our initial studies has been TEM studies of creep-deformed Rene N5 – a compositionally complex, third generation alloy. This alloy and closely-related variants are of great interest to GE Aircraft and Pratt&Whitney for recent engine designs. We have begun our studies with this alloy since we wish to establish baseline behavior in terms of deformation mechanisms in this technologically most relevant alloy system. In spite of exhaustive mechanical testing of this alloy, little or no substructure analysis is available regarding the deformation mechanisms of this alloy in the open literature. We are presently concentrating on determining the detailed dislocation processes and microstructure evolution occurring during creep. This information is also providing crucial experimental framework for the development of a realistic phase-field model of microstructure evolution (rafting) and deformation in these alloys, in collaboration with Professor Yunzhi Wang co-workers in the Center for the Accelerated Maturation of Materials (CAMM) at OSU.

Recent Progress

A series of creep single crystal N5 tensile creep specimens are being analyzed in terms of phase evolution and dislocation substructure variation as a function of creep strain. These [001] oriented samples have been kindly provided by G.E. Aircraft Engines in support of this program, and have offered us a systematic view of the processes associated with creep at several important stages of total life. Several additional aspects of this work are unique relative to previous literature. We have focused on examination of longitudinal (instead of transverse) specimen sections in order to more readily characterize phase morphology and dislocation structures. Deformation substructures have been examined using bright field STEM imaging of dislocations. Although not a new technique[5-6] it has not been widely utilized for deformation substructure analysis. However, we have found it to be particularly useful for examining dislocation structures in fine-grained polycrystalline materials, and for obtaining large fields of view for assaying deformation mechanisms and dislocation density measurements over relatively large specimen regions. Since this technique produces images while sampling a range of diffraction angles, dislocations produce contrast even when specimens are bent and have varying thickness – effects which generally obscure dislocations when using conventional diffraction contrast imaging.

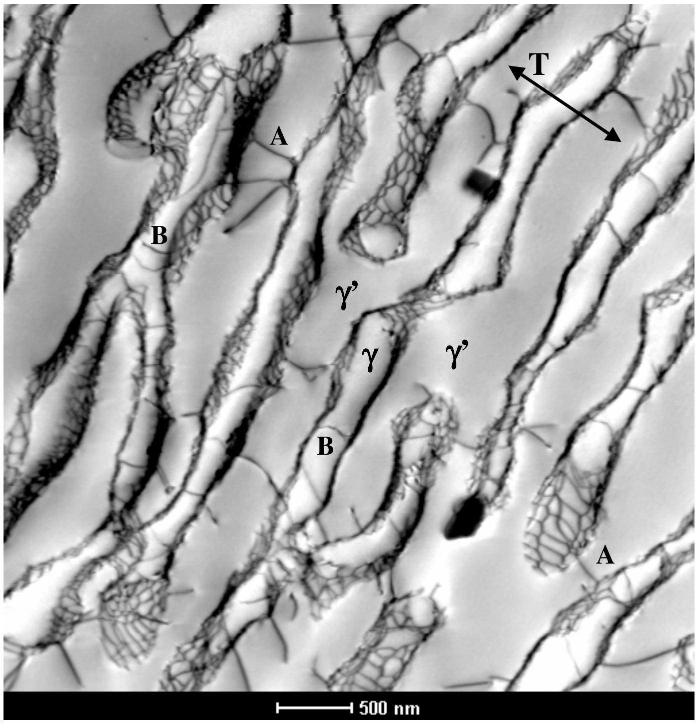

Figure 1: Bright field STEM image of longitudinal section after 6% creep strain at 982°C and 193 MPa. "T" indicates the orientation of the tensile axis. Channeling dislocations in both γ' and γ are indicated at "A" and "B", respectively.

Shown in Figures 1 is a bright-field STEM image of a representative specimen region crept to 6% plastic strain. This condition corresponds to the early stages of tertiary creep. The rafting process is observed to be complete after only 1% strain. As a consequence, the f.c.c γ phase and $L1_2$ γ' phase form an irregular, alternating multilayer structure. The layers are aligned perpendicular to the applied tensile axis, as expected based on previous studies of negative lattice misfit alloys[7]. Each layer is relatively continuous after the small creep strain. A phase field model that reproduces these remarkable morphological changes is being developed in conjunction with this program, and initial results of this model are described below. At the larger strain level shown in Figure 1, the γ phase is no longer continuous, but instead γ layers now exhibit frequent lateral terminations. The apparent discontinuity in the γ phase has been described as a "topological inversion"[8] when compared with the initial, uncrept structure in which the γ phase is the matrix, and the γ' phase is in the form of cuboidal, precipitates.

Extensive dislocation activity is apparent in the γ' phase in all samples examined, as exemplified in Figure 1. Dislocations can be observed traversing the γ' phase in numerous locations. These dislocations are clearly connected to the interfacial networks at the γ/γ' interfaces on either side of the γ' phase (as at "A"). These dislocations are predominantly a[100] and a[010] type, with a smaller number of a[001] and a<110> type dislocations. The presence of the a[100] and a[010] dislocations is remarkable since there is no resolved glide or climb force operating on them due to the applied stress. It might be argued that these dislocations are remnant from the initial coalescence of the γ' cuboids during rafting. With the aide of the excellent statistics that is possible using the bright-field STEM imaging mode, we have found that the density of these dislocations is distinctly increasing with strain level, which is the first definitive proof that these dislocations are indeed active during creep deformation. These observations support a qualitative model for creep of rafted structures which assumes that the channeling of the a<100> dislocations through the γ' phase is the rate-limiting process. Note that there also exist dislocations traversing the γ phase as well (as at "B"). In our model, motion of these matrix dislocations actually produce work due to the applied stress, unlike the channeling a[100] and a[010] dislocations in the γ' phase. The critical role of the latter, however, is to eliminate interface dislocation content, thereby reducing the local backstress such that matrix dislocation activity can proceed. These observations also provide important insight into the origin of the gradually increasing creep rate typically observed during low stress, high temperature creep of blade alloys. As the γ phase becomes discontinuous, then the dislocations in the γ' are no longer constrained to channel laterally, but may also traverse to neighboring γ' layers, thereby dramatically increasing the effect that each individual γ' dislocation can have on the recovery of the interfacial networks in many layers.

Aided by these detailed observations, a phase field dislocation[9]-microstructure[10] model is being developed to simulate the rafting process. In this model, dislocation motion in γ channels is driven by the local stress. The local stress acting on the matrix dislocations includes contributions from lattice misfit, the external load, and other dislocations. Simultaneously, the diffusion-mediated evolution of microstructure is determined by both chemical driving forces and elastic interactions with dislocations, as well as the effect of lattice misfit. Through this integrated approach, rafting of the γ' phase has been predicted under various conditions of misfit sign and loading type, and the results agree with our experiments and other analyses. It has also been found that modulus mismatch is not a necessary condition for rafting, as has been assumed previously in the elasticity-based models for rafting[11-12].

Future Plans

We will complete our study of the N5 single crystal specimens deformed at 982°C. We also plan to analyze specimens that have been deformed to less than 1% strain in order to obtain additional insight into the mechanisms active during rafting.

In the coming year, we will also initiate a parallel study of a Ni-Al-Mo alloy as a model system for which thermodynamic, kinetic, elastic contant and lattice mismatch data are presently known. The single crystals will be grown in the facilities of Professor Tresa Pollock of the University of Michigan. The composition of the model alloy has been identified, and the crystal growth will be carried out soon. For instance, an alloy of composition Ni - 6%Al -15.1%Mo (in wt. %) yields a lattice misfit (at 985 °C) of –0.45%[13]. The stress and temperature conditions for which rafting occurs have also been established[13]. This simplified alloy system will enable a more direct connection to the phase field modeling described above. In particular, the kinetics for rafting will be measured using SEM characterization, and used to directly validate the phase field model for rafting. TEM analysis will also be required to confirm that the creep processes that we have identified in the N5 alloy are also operative in the model Ni-Al-Mo alloy. If this is the case, then we will work to incorporate these mechanisms into the phase field model, and in particular the importance of a<100> dislocations as a recovery mechanism during creep. The predictions of this refined phase field model in terms of creep rate will then be compared directly with creep experiments.

We are also planning an exciting set of *in situ* TEM heating experiments. TEM foils will be extracted from pre-crept samples, and annealed in the microscope, and the dynamic recovery processes observed directly. We will prepare transverse foils, having their [001] foil normal parallel to the tensile axis. With this orientation, thin foil effects on the relaxation process will be minimized. The γ/γ' interfaces, and the interfacial networks will be lying *within* the foil, and will not be intersecting the foil surfaces with high frequency. Ideally, we will strive to make observations such that a single γ' raft (and the upper and lower γ/γ' interfaces) are fully contained within the TEM foil. Considering that the γ' laths are typically between 0.2 and 0.5μm in thickness, this scenario should be achievable using our the bright-field STEM imaging mode, or using the Gatan Energy Filter (GIF) to eliminate inelastically scattered electrons. These *in situ* observations will provide us with an understanding of the dynamic proceses that we must consider in the phase field model. For instance, of primary interest is how the interfacial network responds in the wake of a channeling a<100> dislocation in the γ'.

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Long Range Internal Stresses and Mechanisms of Cyclic and Monotonic Deformation

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Program Scope

Internal stresses are widely suggested to exist in the vicinity of dislocation heterogeneities in deformed microstructures. The heterogeneities include edge dislocation dipole bundles (veins) and the edge dipole walls of persistent slip bands (Pubs) in cyclically deformed materials and cell and subgrain walls in monotonically deformed materials. Evidence for such long-range internal stresses (LRIS) includes stress-dip tests, dislocation pinning of loaded materials, *in-situ* deformation experiments, and x-ray line broadening. Other experiments, including recent dipole separation observations and convergent beam electron diffraction experiments, are less supportive of LRIS. The interpretation of asymmetric x-ray peak line-broadening in cyclically deformed metals in terms of back stresses (or LRIS) has been investigated analytically through computer simulation of x-ray line profiles. In addition, synchrotron x-ray microbeam diffraction experiments have been used to make direct measurements of lattice strain within cell interiors in compression and tension deformed (100) Cu single crystals. An assessment of LRIS is important in understanding plasticity in general, and cyclic deformation in particular where strain reversals are experienced after relatively small strain amplitudes.

Recent Progress

a. X-Ray Line Broadening Analysis

It has been argued that a heterogeneous microstructure is associated with long range internal stresses (LRIS), often in a convenient and simple two-phase composite model. While this model is straightforward, the evidence to support LRIS has been indirect. In particular, the analysis of Bragg profile line-broadening and asymmetry[1] has been used as supporting evidence of the existence of LRIS. Proponents argue that the asymmetric line profiles can be decomposed into two symmetric peaks – a large peak associated with cell interiors and a smaller peak corresponding to the smaller volume of material associated with the long-range internal stress of the dislocation cell walls. Typically, values of the LRIS are suggested to be a factor of 2-3 larger than the applied stress.

Computer simulation of x-ray line profiles was undertaken by the authors[2] in order to determine what crystalline defect arrangements may lead to asymmetry. The technique calculates atomic positions based on elastic theory, then uses a kinematic scattering approximation in which reciprocal space intensities are calculated using the squared Fourier transform (structure factor) of the real-space atomic arrangement. X-ray diffraction line profiles are thus calculated for the specific crystal lattice and atomic defects that are modeled. In our most recent effort, diffraction from screw dislocation dipoles was simulated to test the analytical asymmetry predictions of Gaal.[3] These simulations successfully replicated the behavior predicted by Gaal, as the x-ray line profile calculated for the polarized dipole ensemble was found to be asymmetric, and had a peak offset relative to the randomly polarized dipole ensemble. In these simulations, the “crystal” was circular, with a diameter of 200a, where “a” is the lattice parameter with an underlying square atomic grid; the dipole spacing was 10a.

The locations of the 191 dipoles in each simulation were determined randomly for each of 5000 iterations, and the scaled dislocation density (with a zero net Burgers vector) was the same as that used by Gaal. Although no direct calculations of LRIS were made from this dislocation arrangement, the random positioning of the dipoles within a constrained volume suggests that stress fluctuations occur only on length scales comparable to the mean dipole spacing. That is, only short-range internal stresses (SRIS) exist. It should be mentioned, however, that this simulated microstructure may not realistically reflect observed microstructures; the dislocation density of dipoles necessary to provide the pronounced asymmetry observed in, for example, monotonically deformed Cu appears to be an order of magnitude too low. It should also be mentioned that Mughrabi and coworkers[1] imply that the heterogeneous stress-state leads to interface dislocations that tend to form dipoles across the "phases" or heterogeneities.

b. Synchrotron X-Ray Microdiffraction Experiments

Again, evidence to support the existence of LRIS has, most recently, largely been based upon the composite model argument following Mughrabi in conjunction with (asymmetric) x-ray diffraction line profile analysis.[4-8] Careful experimental methods have been used to achieve the angular resolution and statistical precision in the wings that is necessary to accurately measure the asymmetry, which is correlated to LRIS in the Mughrabi model[8] Synchrotron sources are especially well suited, in general, to perform this type of experiment due to the high degree of collimation of the x-ray beam and the relatively large amount of signal available when measuring diffraction line profiles using a large sample to detector distance. Coupled with studies of dislocation substructure, this type of diffraction experiment has been used to support the LRIS argument.

Borbely and Blum coupled asymmetry measurements with a direct or *in-situ* "internal stress" (strain) measurement technique.[5] The XRD line profiles provided the expected asymmetry under stress at elevated temperature. However, the *unloaded* specimen retained a majority of the asymmetry despite elevated temperature exposure. To the extent that the asymmetry under load is reflective of LRIS, the unloaded specimens appear to "lock in" these stresses. However, if LRIS relaxes during unloading from high temperatures, then the asymmetry would probably be due to other sources than LRIS. Further investigation is needed to clarify these results. In order to assess the connection between LRIS and the asymmetric XRD results, it would be ideal to measure the internal stress as a function of position in the heterogeneous substructure, *in-situ*, and simultaneously measure the x-ray line asymmetry while the bulk specimen is under stress.

Very recently, Larson et al. have developed a microbeam x-ray technique that allows measurement lattice parameters (i.e., strain) in small volumes within the bulk specimen.[9] This is an important new development. The spot size of this new technique (0.5 μm diameter) is small enough to allow probing within dislocation cells interior in a bulk specimen.[9,10] Local data acquisition is possible on the length scale that is necessary to answer our present questions regarding LRIS. The 3D x-ray microscopy technique is also known as differential-aperture x-ray microscopy, or DAXM. In typical diffraction experiments of this type, the diffracted Laue patterns from various grains or differently strained volumes would overlap on the CCD detector, thus convoluting the diffraction pattern. However, the DAXM method *deconvolutes* these overlapping profiles using knife-edge type profiling; by step-scanning a 50 μm diameter platinum wire through the diffracted beams (in front of the CCD detector), the location of the scattering volume along the incident x-ray beam is determined by triangulation with knowledge of the CCD pixel locations and the instantaneous stepped location of the front side of the circular cross-section wire. Computer analysis of the diffraction profiles with the triangulation data for each Pt step position allows the calculation of depth-dependent Laue diffraction patterns with sub-micron spatial resolution. This final resolution of approximately $0.5 \times 0.5 \times 1.0\ \mu m^3$ is only possible with the less than half-micron beam diameter, submicron steps of the Pt profiler, and fine CCD grid and triangulation of the collated CCD patterns.[9]. Generation of such high resolution microbeams has been made possible by the work of Ice[10] using elliptically figured, crossed Kirkpatrick-Baez focusing mirrors and undulator x-rays at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL).[10]

We deformed [100] oriented copper single crystals in compression and tension (10-40%) to fixed strains that led to dislocation cell structures with 1/3 – 2/3 μm mesh sizes which are often large enough for the ~0.5 μm synchrotron beam to probe material inside of cells without including the cell walls. Cu with this history has been confirmed to exhibit the expected asymmetry by others.[8] Thus, we had the ideal situation where x-ray line asymmetry is observed to increase from one sample to the next, and we can also measure the local changes in internal stress across the microstructure within those same samples. We used the above discussed 3D x-ray microscopy technique to compare the x-ray line profiles and their measured asymmetry with direct cell interior lattice parameter measurements on a sub-micron length scale.

Thus, in a similar manner to the method used by Straub et al.[11] and the earlier work of one of the authors[12] where CBED was used to probe specific locations within the cell interiors, we were able to use the synchrotron beam to probe across cells of our bulk deformed Cu samples. The length scale of the microstructure was assessed by TEM from the NCEM at LBNL.

X-ray microbeams were used to measure the lattice parameter within dislocation cells in compression and tension-deformed Cu and in undeformed Cu. The elastic strain in cell interiors in compression deformed Cu (compared to undeformed Cu) was found to be positive have a range of values. For tension deformed Cu, the cell interior lattice parameters corresponded to negative strains, again with a range of values. This is direct evidence of a LRIS. The peak asymmetry also reverses. The values of the LRIS in the cells measured correspond to 0.15-0.28 the applied stress. From Mughrabi et al. we can estimate for [100] deformed Cu the volume fractions of cell wall (f_w) versus cell interiors (f_c) for our cases. For Cu compressed to -0.277 and tensile deformed to 0.306 strains, $f_c \cong 0.67$, $f_w \cong 0.33$. This implies from the composite model, $\Delta\tau_w = -2\Delta\tau_c$. The important finding is that the spatially resolved measurements of cell interior strain in Cu confirm that x-ray peak asymmetries reflect LRIS, but the magnitudes of the measured strains suggest the stresses are relatively small. Although the stains are consistent with the more recent work of Mughrabi, some of which is not yet published, they are significantly lower than that predicted by the general community.

Future Plans

The cell interior results appear fully valid, but some additional tests on Cu cell interiors are warranted. The next set of experiments should also include attempts to measure the strains in cell walls, which requires some experimental refinements. This should be followed by measurements for characteristic asymmetry, and the verification of Poisson strains. The previous work emphasized monotonically deformed Cu single crystals, but other systems that do not show or only show relatively weak x-ray peak asymmetry, such as Al, and cyclically deformed Cu to presaturation are important to investigate, as well, in order to form a fundamental understanding of LRIS. Ideally, these tests should be performed under load, but this is an experimental challenge since the duration of the test may currently exceed the stability of the specimen location.

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The Use of High-Strength Steels to Contain Hydrogen

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Past research on hydrogen-induced cracking in high-strength steels has tended to focus on either one of two types of behavior: brittle intergranular cracking, especially as influenced by segregated impurities, or cracking due to enhanced dislocation mobility in the presence of hydrogen. However, there is ample evidence that both kinds of behavior can exist in a given steel, depending on the values of three controlling variables: the impurity content, the yield strength, and the hydrogen fugacity. What we are actually dealing with is a type of ductile-brittle transition from a plasticity-related, displacement-controlled cracking to a classical brittle intergranular decohesion, both induced by the presence of hydrogen.

The work that supports this has been carried out on two types of steel. One was a high-toughness, moderately high-strength 5%NiCrMoV steel with 0.13%C (based on HY130), and the other was a less-tough 1.8%NiCrMo steel with 0.4%C (based on 4340). The impurity content in the grain boundaries was varied by controlling the composition of the steel or by aging treatments to allow impurity segregation. The strength was varied by changing the tempering temperature. The hydrogen fugacity was changed by the external hydrogen pressure. The results support the contention that, for a given steel and impurity level, there must exist a transition diagram in strength / fugacity space that shows the boundary between “ductile” and brittle behavior, and that by changing the impurity level this boundary can be moved.

The significance of this is that there exists a domain of safe use of a steel of controlled purity in hydrogen that can extend to strength levels much higher than is popularly believed. For example, the 5%Ni steel of sufficient purity cracks by plastic shear at stress intensities above about 90MPavm at a yield stress level of 1050MPa. This is high enough to be considered tough-enough behavior to qualify the steel for containing hydrogen.

What remains to be done is to determine the boundaries of the safe domains for such steels as a function of their levels of purity. That is, the transition diagrams remain to be determined. That is one of the main thrusts of our current research.

Stable Nanoclusters and Mechanical Behavior of Metallic Materials

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Program Scope

Nanoclusters (2-4 nm in diameter) were observed recently in a ferritic alloy (12YWT, Fe-12Cr-3.0W-0.4Ti-0.24Y_2O_3, wt%) prepared by mechanical alloying. These nanoclusters are enriched with Ti, Y, and O atoms, as revealed by atom probe analyses.[1,2] The clusters appear to be stable during long-term creep tests at 650-900°C, and responsible for reducing the creep rate by six orders of magnitude.[3] In view of these important results, we developed the BES program on stable nanoclusters in metallic matrices in September, 2004. The goal of this program is to attain a fundamental mechanistic understanding of the formation mechanism, thermal stability, and hardening mechanism of stable nanoclusters in metallic matrices. Nanophase materials are known to be metastable in nature; consequently, these materials in bulk forms are usable only at relatively low temperatures because of coarsening processes that occur rapidly at elevated temperatures. The stable nanoclusters that are the focus of the current research are an exception to this norm. The study of the scientific mechanisms associated with these stable nanoclusters will possibly lead to identification of novel material states that are capable of extending the useful temperature range of nanophase materials from ambient to elevated temperatures. Initial study will focus on Fe-based alloys, with the intention to extend our study to include other metallic systems containing potentially stable nanoclusters. This research is composed of two major tasks: (1) theoretical and experimental studies of the formation mechanism and thermal stability of stable nanclusters in metallic systems using atom-scale characterization tools, and (2) experimental and modeling studies of hardening mechanisms of stable nanoclusters at ambient and elevated temperatures.

Recent Progress

Our experimental effort was initially focused on determining the thermal stability of nanoclusters formed in 12YWT alloy. In this study, alloy samples were heated to temperatures above 1000°C in an inert atmosphere, followed by direct water quenching. Quenched samples were then characterized by local electrode atom probe (LEAP) analyses. As indicated in **Fig. 1**, nanoclusters enriched with Ti, Y and O solute atoms in 12YWT are stable at temperatures at least to 1380°C. The nanocluster formation in 12YWT was also characterized as a function of temperature by small angle neutron scattering (SANS) at the Hahn-Meitner-Institute Berlin. The in situ SANS study reveals a bimodal distribution of 2 nm nanoclusters and 12 nm nanoparticles at elevated temperatures. Preliminary analyses indicate that 2-nm nanoclusters are stable at temperatures to 1400°C. Thus, both studies have demonstrated that the nanoclusters are thermally stable at 0.91 T_m(1400°C) of the alloy!

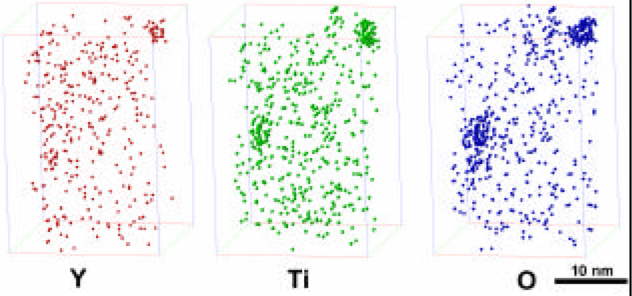

Figure 1. Atom maps of extruded SM4 after annealing for 1 h at 1380°C and water quench. Two Ti-, Y- and O- enriched nanoclusters are evident.

The mechanical properties of 14YWT with stable nanoclusters have been studied by compressive creep tests and dislocation analysis using weak beam techniques. Dislocation dipole structures were observed in the samples annealed at 1100°C for an extended time. Since a dipole is in essence two dislocations of opposing sign, there is a strong driving force for the opposing arms to move together and annihilate. Thus, the frictional force resisting annihilation of the dipole can be estimated based on the model for an elastically isotropic material.[4] Using the height of the dipole as 50 nm, we derive a strong shear stress of 460 MPa against the dislocation motion. The alloy samples show fine grain sizes (submicron) with elongated grain structures. Nevertheless, the alloy exhibited excellent creep resistance (creep rate = $3.2\text{x}10^{-9}\text{s}^{-1}$) when tested both longitudinally and transversely at 800°C and 250 MPa. All these results can be rationalized by pinned grain boundaries and dislocations which are decorated with nanoclusters, as revealed by LEAP.

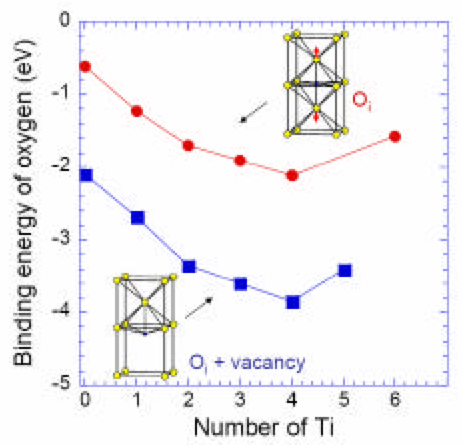

Figure 2. Binding energy of oxygen in the form of oxygen-vacancy pair (O_i-vacancy) and interstitial oxygen (O_i) as a function of the number of its neighboring Ti atoms. The presence of Ti and vacancy has a drastic effect in increasing the binding energy of oxygen in Fe.

The solubility of oxygen in defect-free Fe is known to be very low in the equilibrium condition. Our first-principles calculations found that the markedly low solubility of O in Fe is attributed to the relatively weak bonding for O in Fe. On the other hand, we predict a very strong bonding between oxygen and vacancies in Fe. It follows that, in order to enhance the solubility of O in Fe, it is necessary to create a high concentration of vacancies as the *pre-existing* defects. In fact, by considering the energetics of the reaction Fe:O → (Fe+vacancies) + FeO, we demonstrated that the oxygen solubility in bcc-Fe can be as high as the concentration of pre-existing vacancies.

In **Fig. 2** we show the binding energies of oxygen in the form of interstitial oxygen (O_i) and O_i-vacancy pair in the Fe lattice with their neighboring Fe atoms progressively replaced by Ti atoms. Two significant results were found: (1) for both cases, the presence of Ti increases the binding energies of oxygen in Fe, and the oxygen binding energy increases (i.e., more negative) as the number of its neighboring Ti atoms increases; and (2) the presence of vacancy drastically increases the binding energy of oxygen in the O_i-vacancy pair from that of oxygen in the defect-free lattice (i.e., O_i), particularly in the presence of Ti. Our results suggest that vacancies play an indispensable role in enhancing the oxygen binding energy in the presence of Ti and bring the binding energy of oxygen closer to the formation energy of TiO_2, and thus a stabilization of coherent nanoclusters in the Fe lattice becomes feasible.

Future Plans

Stability of Nanoclusers in Fe-Based Alloys. Theoretical modeling, atomic-scale characterization, and physical-metallurgy analysis reveals the importance of Ti, O, Y and vacancy concentrations on the stability of nanoclusters in ferritic alloys. Series of Fe-based alloys will thus be prepared for studying the individual and collective roles of these elements in nanocluster stability. The stability of nanoclusters formed in these alloys will be studied systematically as a function of aging time and temperature. Nanoclusters and precipitates formed in these alloys containing different combinations of Ti, O and Y (Zr) will be studied by atom-scale tools, including HRTEM, STEM and SANS. Defect structures in these alloys will be controlled by quenching from temperatures close to their melting point, followed by different cold or warm work conditions. In order to understand their thermal stability, alloy specimens will be aged at different times and temperatures. The kinetic results so obtained will be used to analyze the cluster stability and growth mechanism.

First-principles calculations indicate that vacancies play a vital role in the formation and stability of nanoclusters containing oxygen. Thus, the vacancy concentration in these alloys as well as 12YWT alloys will be determined. The measurements will be carried out with the collaboration of Prof. Gary Collins at Washington State University and Dr. Jun Xu at ORNL. The combination of both positron lifetime spectroscopy and two-detector coincidence experiments of Doppler broadening can identify not only the type of defects but also elements surrounding defects in nanoparticles.[5,6] This information is vitally important for us to develop an atomic model to construct nanoclusters.

Study of Stability and Coarsening of Nanoclusters by Atom Probe Tomography. The extent and amplitude of the solute segregation of the different elements in the solute-enriched regions, i.e., the Cottrell atmospheres, in the vicinity of the cores of the dislocations will be investigated with LEAP in pre-stressed specimens. In addition, the spacing and size of the nanoclusters along the dislocations will be characterized. The oxygen concentration in the matrix will also be investigated with LEAP. Additional alloys containing a combination of Y_2O_3+ FeO powders will be characterized with LEAP. These alloys are designed to increase the oxygen content of the matrix without increasing the yttrium level. Some porosity has been observed after annealing at elevated temperatures. The nature of this porosity will be investigated to establish if it is due to the oxygen coming out of solution (along with some carbon contamination) as CO or CO_2 or due to the argon atmosphere used during milling that is not outgased, or possibly due to the dissolution of the nanoclusters. Also, clusters formed in power-metallurgy materials doped externally with oxygen will be studied by LEAP.

Study of Cluster Formation and Stability from First-Principles Calculations. Results of our calculations have shown that as point defects (vacancies, solute atoms and interstitial oxygen atoms), each of these defects individually has a high energy, indicating little solubility in the Fe lattice. However, clusters of these, near a vacancy, could have very low energy, and therefore could have a high solubility. Thus, the stability of the clusters is connected to the fact that individual high energy point defects form a low energy bound state. The complexity of the cluster formation poses great challenges to the theoretical investigation. These challenges include the need to predict the solubility limits of O (limited by the formation of various complex oxide structures), determining the “windows” of O/Ti and O/Y atomic ratios for cluster formation, and understanding the individual as well as the collective roles of Y, Ti, and O in the formation and stability of clusters. Furthermore, the theoretical modeling has to include various structural variables, such as vacancies, lattice strains, and chemical profiles of clusters. Understanding the stability of clusters also inevitably involves the study of diffusion processes of O-vacancy pairs at high temperatures. Nevertheless, the focus of the theoretical investigation is not on the simulation of cluster sizes and distributions or on the diffused interfacial structures and chemistry. The key role of the theory is to understand the relationship among energetics, electronic structure, defects, and local bonding geometry of O with Ti and Y. The theory will help explain why the unique combination of Y, Ti, and O is required for cluster formation. In essence, the theory will define the conditions under which the oxygen atoms are soluble in the Fe matrix in the presence of dissolved Ti and/or Y atoms without forming any of the many stable oxide compounds (such as TiO_2, Y_2O_3, and $Y_2Ti_2O_7$).

Study of the Hardening Behavior at Ambient and Elevated Temperatures

(i) Strengthening at Ambient Temperatures. In-situ deformation experiments will be carried out in a TEM at room temperature to gain information on the nature of the dislocation-nanocluster interaction. At first sight, such experiments may seem unrealistic. Assuming a typical TEM foil thickness of 100 nm, the nanoclusters with sizes and spacings of 4 and 10 nm, respectively, will overlap and give rise to a mottled contrast at best. However, a moving dislocation interacts primarily with those nanoclusters that are within 4 nm of its glide plane. Since weak beam dislocation images at 300 kV are as narrow as 1 nm, it may be possible to determine the angle of the bowing of the dislocations at the nanoclusters. The bowing angle is a measure of the obstacle strength and can be compared to the predictions of the various models.

(ii) Creep Mechanisms at High Temperature. TEM-based characterization of crept microstructures will be of great importance for the development of physically-based models for creep. With respect to studies, the magnetic effects in these ferritic alloys are a concern. However, experience to date with microscopy of these samples indicates that magnetic effects are not severely limiting with these materials. Deformation substructures will be examined using bright field STEM imaging of dislocations. Analysis of overall dislocation curvatures can be used to quantitatively measure the frictional forces (either due to solute strengthening or nanoscale clusters) acting on dislocations at creep temperatures. Ordinarily, it is desirable to observe creep substructures after cooling samples while still under creep load in order to preserve the configuration existing under stress. However, for purposes of measuring the frictional forces acting on dislocations, it is advantageous to perform the TEM studies on samples that have been *unloaded and held at temperature* to allow any high temperature anelastic processes to take place. In this case, the remaining dislocation curvatures will enable us to determine directly the frictional forces present at creep temperatures since these must balance the line tension forces.

A natural complement to these studies will be to perform *in-situ* TEM heating experiments on samples that have been cooled under load. Re-heating samples to elevated temperatures will enable us to dynamically observe dislocation motion driven by local line tension. Direct interaction with nanoparticles may be observable as transient cusps that may form on the dislocation lines during unbowing. Among the advantages of this approach for the present study are the following: (a) high quality imaging conditions should be achievable using the Gatan double-tilt heating holder at OSU; (b) thin-foil and surface effects can be minimized since even curved dislocations lying in the foil will be acted upon by line tension. Conventional weak beam and bright field/dark field STEM imaging will be employed.

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SESSION III:

PLASTIC DEFORMATION

Chair: C. T. Liu (Univ. of Tennessee)

In-situ study of mechanical behavior by neutron scattering

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Structure-property relationship is the fundamental building block of materials science. Dramatically different properties are realized when atoms are packed differently at the local atomic scale. At a larger length scale, the microstructure also influences the properties of a material.

Neutrons advance our understanding of materials through the determination of their structures at various length scales. In addition to their well-known uses in characterizing the structure at the atomic scale, neutrons are also effective for probing structural features at the meso-scale, which include grain-orientation-dependent strains, preferred crystallographic orientation, crystallographic defects and the subgrain structure, phase segregation, and grain size distribution. For materials going through a phase transformation, the eventual microstructure is often determined by the kinetics. Thus, knowledge of the phase transformation kinetics is an important piece of the puzzle for complete understanding of the microstructure which by and large governs the mechanical behavior.

Since the 1980s, neutron diffraction has been used to study the mechanical behavior of materials. Much of the work in the early days was strongly oriented towards mechanical engineering, involving the determination of the residual stress distribution in components and the use of these data in design and life prediction. Opportunities for fundamental research began to emerge when it became evident that some of the experimental data could not be understood within the framework of the continuum theory and simple thermal-mechanical simulations. In particular, in-situ measurements of the grain-orientation-dependent or intergranular strains under uni-axial loading have been extensively used to provide insights of the deformation mechanisms in polycrystalline materials.

We have recently used neutron diffraction to investigate deformation by cyclic loading. Full grain-orientation-dependence measurements established that large intergranular stresses develop during cyclic loading, due to a combination of elastic and plastic anisotropy. Analysis of the peak widths indicate that for stainless steel subjected to a high-cycle fatigue test, the dislocations are mainly of edge rather than screw type. A stroboscopic method was used to determine the evolution of the intergranular stresses throughout a loading cycle during fatigue life. For some alloys, cyclic loading also leads to phase transformation. For ULTIMET, a Co-based alloy, in-situ neutron diffraction measurements reveal that the fcc→hcp phase transformation is accompanied by an incubation period and increases progressively with increasing numbers of fatigue cycles.

Deformation in nanostructured materials is another topic of interest lately. Molecular dynamics simulations suggest that when the grain size is reduced to ~10 nm, the deformation mechanism is dominated by grain-boundary activities. Through the measurement of inter- and intra-granular strains, we are able to observe the grain-orientation-dependent load partition during uni-axial loading. Using these experimental data, we show that the plastic deformation in nanostructured nickel is mainly limited to the grain-boundary zone.

Nanostructured materials are known to exhibit unusual properties. Unusually low creep rate is found for oxide-dispersion-strengthened steel, a Cr-based steel alloyed with a minor amount of W, Ti and Y. Microscopy and atom probe tomography studies suggest that the presence of Y-Ti-O nanoclusters is responsible for the excellent thermal stability. Small angle neutron scattering measurements show that the nanoclusters have a bi-modal size distribution, with centroids around 2 and 12 nm, respectively. Furthermore, in-situ measurements demonstrated that these nanoclusters are stable up to 1400 °C, ~90% of the melting temperature.

With the commissioning of the Spallation Neutron Source (SNS), there will be new scientific opportunities in the study of mechanical behaviors by neutron scattering. Indeed, a dedicated instrument is already under construction at the SNS to serve the needs of the community. The instrument is named VULCAN, after the Roman God of Fire and Metalworking. The design goals for VULCAN include the following:

- rapid volumetric (3-dimensional) mapping with a sampling volume of ~mm^3 and a measurement time of minutes
- very high spatial resolution (0.1 mm) in one direction
- ~20 well defined reflections for in-situ loading studies
- ability to study kinetic behaviors in sub seconds
- simultaneous characterization capabilities, including dilatometry, weight, and microstructure

Special sample environments, such as load-frame and furnaces, will be provided as an integrated part of the instrument. With the unprecedented flux provided by the SNS and improved instrumentation, it will be possible to conduct in-situ, time-resolved measurements under real thermal-mechanical deformation conditions. A state-of-the-art, event-based data acquisition system will greatly facilitate the analysis of time-resolved data. Simultaneous measurements of diffraction and small angle scattering data will prove to be particularly useful for investigating the kinetics of complex phase transformations where the structure is evolving at multiple length scales. New scientific opportunities with VUCLAN will be discussed.

This research was sponsored by the U.S. Department of Energy, Division of Materials Sciences and Engineering, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory managed by UT-Battelle.

Atomistic Studies of Deformation and Fracture in Materials with Mixed Metallic and Covalent Bonding: Transition Metals and Their Compounds

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Scope of the Program

The goal of this research program is generation of knowledge that is needed for the fundamental, atomic level understanding of the deformation and fracture mechanisms in transition metals, specifically Ir, Mo, W, Nb, Ta and bcc iron, as well as in compounds based on these metals, such as $MoSi_2$, Mo_5Si_3, Mo_5SiB_2, Ir_3Nb, Ir_3Zr. The motivation for investigation of these materials is two-fold. First, they are befitting as high-temperature materials, some of which, for example Ir and its alloys and molybdenum silicides, have exceptional corrosion resistance. Hence, they are of notable interest to the Department of Energy in the context of improving the thermal efficiency of energy conversion systems and advanced engines. Secondly, these materials are representative of a broad class of technologically important metallic materials in which the bonding is mixed metallic and covalent and thus atomic interactions depend on both separation of atoms and bond angles. This presents a formidable scientific challenge for atomic level studies of defects, such as dislocations and interfaces that govern mechanical and other physical properties of materials. In order to tackle this problem we have adopted the bond order potentials (BOPs) that have a sound physical basis in quantum mechanical analysis of cohesion and are eminently suitable for materials with mixed metallic and covalent bonding[1-4]. Using these potentials we study dislocations core structures and the dislocation glide under the effect of applied stresses, investigate structure and properties of grain boundaries and using these results develop models for plastic deformation and fracture. Such models are essential for advancement of fundamental understanding of the mechanical behavior of materials that play a crucial role in applications ranging from power generation systems to nanoscale structures, in particular if they are to withstand high temperatures and corrosive environments.

Recent results

The BOPs are a real-space semi-empirical description of interactions between the atoms that is based on the tight-binding approximation and for metals studied in this program further rooted in the d-band model. They have now been developed for several transition bcc metals, in particular molybdenum and tungsten, the fcc transition metal iridium and $MoSi_2$[5-8]. This development encompasses not only construction of the potentials but also thorough testing that involves extensive *ab initio*, density functional theory (DFT) based calculations. These tests include in the first place calculations of the energies of alternative crystal structures and comparison with analogous calculations performed using the DFT based *ab initio* methods. Next the transferability of the BOPs to atomic configurations that deviate significantly from ideal crystal structures is studied by computing the energies along tetragonal, trigonal and hexagonal transformation paths, defined in Ref. 9. For the same reason, the phonon spectra are evaluated for several symmetrical crystallographic directions and compared with available experiments. Using these potentials we have studied dislocation core structure and dislocation glide in molybdenum and iridium[5, 8, 10-14].

In the case of molybdenum (and recently also tungsten) we modeled the core structure and glide of the 1/2[111] screw dislocation. The calculated structure of the core agrees excellently with that found in the recent *ab initio* calculations[15]. The observed glide behavior not only agrees with available *ab initio* data but is in agreement with many experimental observations and explains the primary reason for the breakdown of the Schmid law in bcc metals. An important aspect, not appreciated until recently, is the effect of stresses perpendicular to the slip direction that induce very significant tension/compression asymmetries and may even bring about dislocation glide on slip systems with low Schmid factors in preference to systems with high Schmid factors[12]. These calculations demonstrate that it is the combined effect of the so-called twinning-antitwinning asymmetry and shearing perpendicular to the Burgers vector that explains and describes exhaustively the non-Schmid effects. In order to characterize properly the plastic behavior on the scales ranging from nano to macro in the framework of continuum mechanics the corresponding yield criteria must include these effects and the results of atomistic studies lead to formulation of such physically based yield criteria[11, 12, 16].

In the case of iridium atomistic simulations of the screw dislocation performed using the constructed BOP find a planar core structure that corresponds to dissociation into Shockley partials but also a metastable, non-planar core. Owing to the strong angular character of interatomic bonding in iridium, arising from the partially filled valence *d*-band, the non-planar configuration for the screw dislocation core is unique to iridium and does not exist in other fcc metals. Investigation of transformations between the two core configurations suggests that these transformations represent the basis for a mechanism for cross-slip that neither requires thermal activation nor full constriction of the partials in the primary plane. The associated high rate of cross-slip leads to the creation of high densities of Frank-Read sources and subsequently to a dislocation density that increases exponentially with plastic strain and thus to extremely strong work hardening[8, 14]. This dislocation mechanism naturally explains why extremely pure single crystals and polycrystals of iridium undergo cleavage and/or brittle intergranular fracture at temperatures up to 500°C after extensive plastic deformation, which is in contrast with all other fcc metals[17-19].

Future studies

Studies of the deformation behavior of bcc transition metals will concentrate in two directions. First we shall extend our calculation to include bcc iron. This extension represents a major new step since the interatomic potentials must now include the magnetic effects since the bcc structure of iron is stabilized due to magnetism[20]. Developments of such potentials have recently been advanced by Dudarev and Nguyen-Manh of Culham Laboratory, U.K., with whom we have developed an extensive collaboration[21, 22]. The second development involves inclusion of temperature and strain rate into the models of the motion of screw dislocations. This development will utilize the atomistic results but will be based on the mesoscopic dislocation theory of the formation of kink pairs as a mechanism for overcoming the Peierls barriers.

For Ir we shall investigate the structure and properties of grain boundaries in order to elucidate the observed intergranular brittleness of this metal in pure state. In this study we compare grain boundary structures and the intergranular cohesion in iridium and copper. The reason is to elucidate the influence of different type of bonding that is practically purely metallic in copper but mixed metallic and covalent in iridium.

Finally, we shall develop potentials and investigate dislocations in iridium based compounds Ir_3Nb, Ir_3Zr and expand the BOP developed for $MoSi_2$ towards Mo_5Si_3, Mo_5SiB_2. In the former case the *ab initio* calculations of generalized stacking faults that will reveal the positions and energies of stacking-fault-like planar defects are currently in progress. These results will be used in further analyses of dislocation dissociations and related structures of dislocation cores and establishment of relationship with mesoscale and macroscale plasticity.

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Mechanical Behavior of B.C.C.-Derivative Intermetallics and Bulk Metallic Glasses

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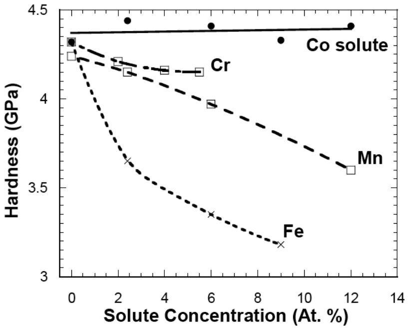
Program Scope

The objective of this program is to develop improved understanding of ordered intermetallics and advanced metallic alloys, with emphasis on the fundamental variables that control phase stability, microstructure, and mechanical behavior. Ordered intermetallics have attractive mechanical and physical properties at elevated temperatures, but poor ductility at low temperatures. In this program, innovative processing techniques and state-of-the-art analytical tools are used for microstructural control and characterization. Atomistic calculations of defect energetics and behavior are employed to provide fundamental understanding of the physical mechanisms that give rise to specific mechanical properties. Phase stability, point defects, and magnetic properties are correlated with site occupation, atomic bonding, and electronic structure. Strengthening and toughening mechanisms are investigated in multiphase intermetallic composites having well-defined constituent shapes and sizes over multiple length scales. Efforts are also devoted to the study of the mechanical behavior of multi-component metallic and intermetallic alloys that form the base for many bulk metallic glasses in both single-phase and composite forms. The understanding gained as a result of this program is expected to contribute to the development of broad scientific principles for the design of next-generation advanced materials for use in extreme conditions in a variety of energy-related applications.

Recent Progress

Because of space limitations it will not be possible to describe fully our recent research progress; rather only selected highlights are provided below. A partial list of publications resulting from this work is provided at the end of this abstract.

The effects of transition-element additions in Ni-40Al were investigated by experimental studies and theoretical calculations. Cobalt atoms on the Ni sublattice do not affect the lattice parameter or hardening behavior of Ni-40Al. However, Fe, Mn, and Cr, which occupy mainly the Al sites, produce an unusual softening (Fig. 1) and lattice expansion. First-principles calculations predicted that these solute atoms with large unfilled *d*-band electrons develop large magnetic moments and effectively expand the lattice when occupying the Al sites.[1] The theoretical predictions were verified by electron energy loss spectroscopy (EELS) and magnetic susceptibility measurements and the observed softening was quantitatively explained by taking into account the replacement of Ni anti-site defects (potent hardeners) with weaker Fe, Mn, and Cr defects. This study has identified a new metallurgical parameter, magnetic coupling between solute and host atoms, that needs to be included in solid solution hardening theories, in addition to the classical atomic size and modulus misfit parameters.



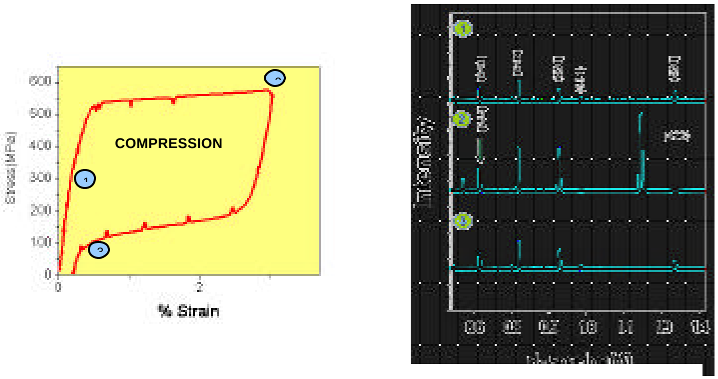


Fig. 1 (left): effects of various solutes on the hardness of Ni-40Al. **Fig. 2** (center and right): neutron diffraction spectra obtained at different points (1,2,3) on the stress-strain curve of Fe$_3$Al

We showed[2] for the first time that ~10% tensile strain is recoverable in single crystals of Fe$_3$Al at room temperature (giant pseudoelasticity or superelasticity), which is double the highest previously reported strain recovery.[3] In situ neutron diffraction showed that the intensities of several diffraction peaks reversibly increased/decreased during loading/unloading (Fig. 2). These changes are indicative of a stress-induced phase transformation, which may be the result of pseudo-twinning or coordinated APB motion that produce long-period superstructures. In the limited range of $2q$ that we could sample so far, none of the new peaks that appeared during the pseudoelastic deformation were disallowed peaks for the $D0_3$ crystal structure. Additional neutron diffraction and TEM experiments are planned to shed light on the operative physical mechanisms.

We showed with nanoindentation[4] that plasticity initiates in BMGs at shear stresses of ~$G/10$ (G is the shear modulus), confirming that plastic deformation can occur only at stresses approaching the theoretical strength of an ideal solid. Almost as soon as plasticity is initiated, though, BMGs become unstable and deform by highly localized shear.[5] The source of this shear localization is widely thought to be strain softening. We have recently obtained unambiguous evidence of strain softening in a Zr-based BMG that was compressed to strains as high as 80%. We also developed a new conceptual approach to evaluate the strength of metallic glass systems from a free-volume point of view.[6] Using the physical analogy between plastic deformation and the glass transition, we have found that the strength of amorphous structures depends on both the localized shear mechanism and the atomic cohesive energy. Interestingly, we find that the strength (s_f) at ambient temperature (T_0) can be predicted by a characteristic parameter $?T_g/V = (T_g - T_0)/V$ according to the following equation: $s_f = 1.1s_y = 55\ ?T_g/V = 55\ ?T_g\ ?_0/M$, where s_y is the yield strength, T_g the glass transition temperature, T_0 the ambient temperature, V the molar volume, M the molar mass, and $?_0$ the density at T_0. As shown in Fig. 3, the predicted strength was unambiguously validated using experimental data for a number of metallic glass systems. The unified equation derived here is able to explain the relatively low strengths reported recently for Ca-based and Ce-based BMGs, which overturns the conventional wisdom that BMGs are much superior in strength to conventional crystalline metals. This observation provides strong evidence for the notion that the mechanical energy density for plastic deformation is similar to the thermal energy density for the glass transition in BMGs, demonstrating the intrinsic similarity between these two physical processes in amorphous structures.

Future Plans

“*Unusual” mechanical behavior of B2 and* $D0_3$*-structured intermetallics*—Although NiAl has many attractive features, its brittleness at low temperatures needs to be overcome before it finds engineering application as a structural material. Poor cleavage strength is widely viewed as the main reason for its poor ductility and brittle fracture. We have shown that magnetic coupling affects solid-solution strengthening in NiAl alloys. The next step therefore, is to determine its effect on atomic bonding and fracture strength. We propose to conduct a systematic study of NiAl alloys, in which different levels of transition elements, including Fe, Mn and Cr, are added to control atomic bonding. The mechanical properties, in particular, tensile ductility and fracture mode, will be determined and correlated with electronic structure effects predicted from first-principles calculations. Two other *B*2 systems will also be investigated: FeCo, because it is brittle despite having many of the “textbook” requirements for good ductility (including 5 independent slip systems, low ordering temperature, and low yield strength),[7] and the rare-earth transition-metal *B*2 compounds, because they are surprisingly ductile despite lacking 5 independent slip systems.[8] In both these cases, our preliminary results suggest that stress-induced phase transformations may play a role in the observed mechanical behavior. Therefore, we plan to perform in situ neutron diffraction experiments to correlate with first-principles predictions of phase stability in these systems. Phase stability is also the key to understanding giant pseudoelasticity in Fe_3Al. Therefore, we plan to perform additional experiments on the HIPPO beam line at LANL, as well as TEM experiments on pre-strained specimens to unravel the underlying physical mechanisms.

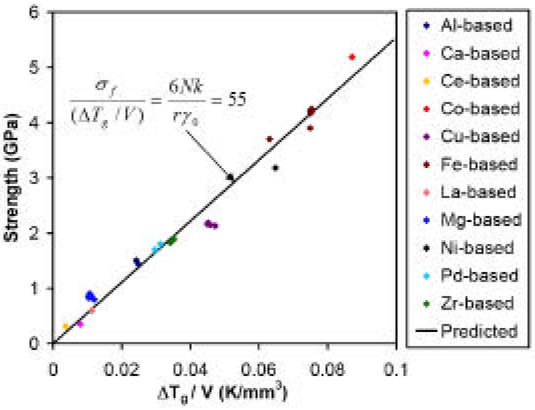


Fig. 3 Dependence of the fracture strengths of BMGs on glass-transition temperature and molar volume.

Mechanical behavior of BMGs—Our recent work has shown that by carefully controlling the specimen aspect ratio and strain rate, it is possible to plastically deform a BMG to strains as high as 80%. This is much higher than anything that has been previously reported and opens up a whole new field of research. We plan to correlate the observed strain softening with shear band density in order to identify a microstructural model for the observed behavior. By investigating changes in physical and mechanical properties as a function of plastic strain and subsequent annealing treatments, we plan to better understand the physical mechanisms responsible for strain softening and other unusual aspects of the mechanical behavior of BMGs. Recently, a number of investigators have observed a correlation between the strength of BMGs and their elastic properties, such as ν (Poisson’s ratio), E (Young’s modulus), and G (shear modulus). However, there is scant theoretical justification for these relationships. In addition, a large scatter of data was observed when the strength of BMGs is plotted against a simple parameter based on elastic modulus. For viscous materials without defect structures, the deformation behavior is expected to be controlled by elastic and thermodynamic properties. We intend to derive a general correlation among elastic moduli, thermodynamic properties, and material parameters of BMGs. As part of this effort, we will use molecular dynamics simulations of deformation as a function of strain rate, aspect ratio and ν, to examine how they affect material behavior.

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Partial list of DOE Sponsored Publications in 2003-2005 (out of ca. 100 total)

1. *Directional Solidification and Microstructures of Cr-Cr$_3$Si Near-Eutectic Alloys*, H. Bei, E. P. George, E. A. Kenik, and G. M. Pharr, *Acta Mater*., **2003**, 51, 6241.
2. *Electronic Stability of Magnetic Fe/Co Superlattices with Monatomic Layer Alternation*, G. A. Farnan, C. L. Fu, Z. Gai, M. Krcmar, A. P. Baddorf, Z. Zhang, and J. Shen, *Phys. Rev. Lett.* **91**, 226106 (2003).
3. *First-principles study of point-defect structures in C15 ZrCo$_2$ and B2 ZrCo*, M. Krcmar and C. L. Fu, *Phys. Rev. B*, **2003**, 68, 134110.
4. *Ab Initio Calculation of Bulk and Defect Properties of Ductile Rare-Earth Intermetallic Compounds*, J. R. Morris, Y. Y. Ye, Y. B. Lee, B. N. Harmon, K. A. Gschneidner, Jr., and A. M. Russell, *Acta Mater.*, **2004**, 52, 4849.
5. *Microstructures and Mechanical Properties of Directionally Solidified NiAl-Mo Eutectic Alloys*, H. Bei and E. P. George, *Acta Mater*., **2005**, 53, 69.
6. *Influence of Indenter Tip Geometry on Elastic Deformation During Nanoindentation*, H. Bei, E. P. George, J. L. Hay, and G. M. Pharr, *Phys. Rev. Lett*., **2005**, 95, 045501.
7. *Dynamic Evolution of Nanoscale Shear Bands in a Bulk-Metallic Glass*, B. Yang, M. L. Morrison, P. K. Liaw, R. A. Buchanan, G. Y. Wang, C. T. Liu, and M. Denda, *Appl. Phys. Lett*., **2005**, 86, 141904.

Mechanical Properties of Materials Across Varying Length Scales

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Program Scope

The structure of materials invariably defines their mechanical behavior. However, in most materials, specific mechanical properties are controlled by structure at widely differing length scales. Examples of this are the dimensions that affect deformation versus fracture. Deformation may be influenced by characteristic dimensions in the realm of nano- to micrometers, such as a Burgers vector or precipitate spacing, whereas the fracture properties generally involve mechanistic phenomena that occur over much larger size-scales. Nowhere is this more apparent than with biological materials. Human bone and nacre, for example, are sophisticated composites whose unique combination of mechanical properties derive from an architectural design that spans nanoscale to macroscopic dimensions, with precisely and carefully engineered interfaces. The fracture resistance of such materials originates from toughening mechanisms at each of these dimensions. Few structural engineering materials have such a hierarchy of structure, yet the message from biology here is clear – there is a need in the design of new materials to develop mechanisms at a multiple of length scales in order to create new hybrid materials with unique mechanical properties.

Our research is focused on probing the mechanisms of deformation, fracture, creep and fatigue at such multiple dimensions in a wide range of structural materials, from ceramics to metals, from silicon to glass, from composites to mineralized tissue. To date, we have shown how atomic-scale manipulation at grain boundaries in ceramics can radically change their macroscopic toughness properties, how tough ceramic/metal and ceramic/polymer layered composites can be made by tailoring the degree of constraint and nature of the interfaces, how micron-scale thin films of silicon are prone to premature failure by fatigue whereas bulk Si is immune, and how understanding the toughening of bone and nacre can facilitate the development of new ceramic/polymer/metal composites with unprecedented properties.

Here we present several of these examples, comprising the role of nanoscale interfacial films in controlling the macroscopic mechanical properties of ceramics, the unique fatigue behavior of silicon at micron-scale dimensions, and a lesson from Nature on bone and nacre for the design of superior structural composites for nonbiological needs.

Recent Progress

Nanoscale structure and bulk properties of ceramics (Ziegler *et al*., *Science,* 2004)***:*** Bulk ceramics such as Si_3N_4 display high strength, negligible creep, good oxidation resistance and good thermal shock properties; however, their structural application is severely limited by low toughness. In our work, we have examined the role of rare-earth atoms (which are added as sintering aides) in modifying the chemistry of grain boundaries in Si_3N_4 to change the crack path from transgranular or intergranular; transgranular fracture invariably results in low toughness, whereas in microstructures with elongated grains interspersed with a nanoscale boundary phase, intergranular fracture can lead to much higher fracture resistance due to the development of grain bridges. It is known that the strength and toughness are markedly affected by the boundary phase chemistry, although an understanding of how this nanoscale phase governs the macroscopic mechanical properties has been limited because its amorphous morphology and small dimension make analysis difficult. STEM and associated EELS, however, permit probing of the local atomic structure and bonding characteristics with a resolution of ~0.1 nm. We have demonstrated that the macroscopic toughness of a rare-earth doped Si_3N_4 specifically relies on the atomic structure, local chemistry and bonding at the interfaces. Specifically, we have examined the immediate interface between matrix grains and the amorphous intergranular film, extracting unique structural and atomic bonding information. In particular, we related the structure of the interface to the atomic size and electronic structure of the rare-earth elements within the intergranular film. Our objective was to identify the bonding sites for a large selection of rare-earth additives, namely La_2O_3, Sm_2O_3, Er_2O_3, Yb_2O_3 and Lu_2O_3. The STEM images in Fig. 1 depict an interface between the intergranular phase and a Si_3N_4 matrix grain for the five sintering types. Whereas La atoms show no specific or periodic connection, the bonding of Sm, Er, Yb and Lu atoms along the Si_3N_4 prismatic plane is periodic and occurs at very specific atomic sites (A and B). These observations demonstrate that the interfacial bonding of these elements is controlled by atomic size, and that this has a direct bearing on the macroscopic fracture toughness, which increases with ionic radius. The small atoms attach in pairs at specific and periodic sites (position A), whereas with increasing atom size the pair-separation increases such that larger atoms, must adapt a new single-atom, periodic bonding configuration (position B). With a further increase in atom size, i.e., La, the attachment to the interface forfeits all periodicity and site-specific atomic bonding. This result has broad implications for the understanding of the mechanical properties of ceramics, and for associated computational modeling of the precise role and atomic structure of the thin intergranular phase.

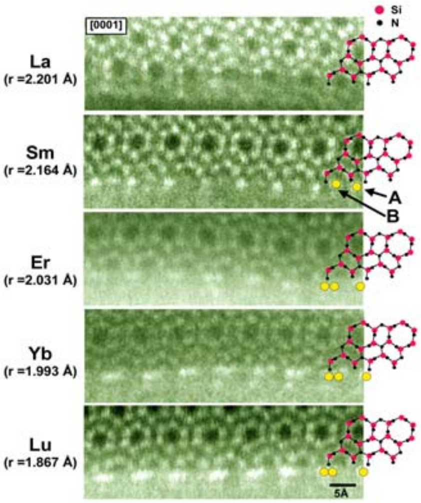

Fig. 1. *STEM images of doped Si_3N_4, showing how the matrix structure ends at the interface with the intergranular phase, i.e, with open hexagonal rings. Two distinct atom positions, A, B, are identified at the interface.*

Fatigue of silicon in small (micron-scale) volumes (Alsem *et al*., *APL*, 2005)***:*** A second example where scale has a profound effect on mechanical behavior is the fatigue susceptibility of thin micron-scale films of polysilicon; such structural films are widely used in MEMS for such applications as sensors, actuators and nano/micro-scale power generators. Since the surface-to-volume ratio of these films is very large, traditional models for failure of bulk materials may not be applicable. Specifically, bulk silicon is totally immune to cyclic fatigue failure; however, silicon at micron dimensions is highly susceptible and displays "metal-like" stress/life (*S/N*) behavior in ambient air, with an apparent fatigue limit at $\sim 10^9$ cycles on the order of half the single-cycle strength. Using a combination of micron-scale mechanical fatigue testing and high-voltage transmission electron microscopy, we have proposed that micron-scale silicon fatigue is associated with stress-induced surface oxide thickening and moisture-assisted subcritical cracking in the amorphous SiO_2 oxide layer (*reaction-layer fatigue*). An example of such stable oxide cracks, each only ~50 nm in size, is shown in the TEM micrograph in Fig. 2. No such failures were observed *in vacuo* or with films coated with an alkene-based self-assembled monolayer of 1-octadecene, which suppresses oxide formation. Using the changes in the resonant frequency to monitor *in situ* the growth of such cracks, we demonstrated that the critical crack size for the entire Si structure to fail was less than the oxide film thickness. This implies that the entire fatigue process of crack initiation, growth and final failure occurs *within the oxide layer*. Since in bulk silicon, the critical crack size would be far larger than the oxide film thickness, there is no mechanism for a time/cycled delayed fracture to occur; consequently, bulk silicon is not susceptible to cyclic fatigue failure. The proposed reaction-layer fatigue mechanism is important as it provides a means for the delayed failure of micron-scale materials that are ostensibly immune to stress-corrosion cracking and fatigue in their bulk form.

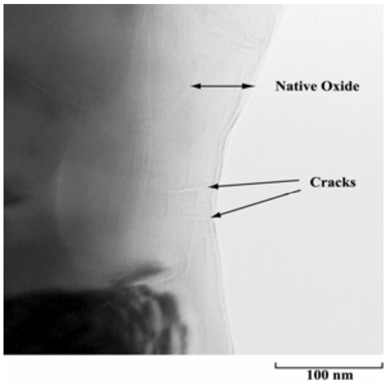

Fig. 2: *High-voltage TEM image showing stable, ~50 nm, cracks, in the amorphous surface* SiO_2 *layer formed during cyclic loading. Image intentionally defocused to facilitate the observation of the cracks.*

Whereas microscale silicon MEMS machines may be prone to fatigue, it is likely that some of the more recent designs for nanoscale machines may be far more fatigue resistant. Recently in collaboration with Alex Zettl, we have developed a nano-powered nanomotor. Power is derived from a single nanocrystal ram sandwiched between two carbon nanotube lever arms by using an electrical current to "pump" indium metal from an atom reservoir between the two arms. Power densities range from 0.02 to 8 GW/m^3.

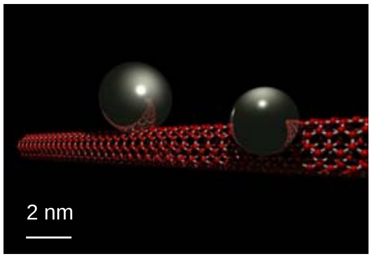

Fig. 3: *Animation of the mass transport of indium metal along a carbon nanotube, driven by changes in electrical current.*

Bio-inspired synthesis of ceramic/polymer composites (Deville *et al.*, *Science*, 2006)***:*** Bone is a ceramic (apatite)/polymer (collagen) composite with a hierarchical structure comprising characteristic structural features from molecular to near-macroscopic dimensions. We have studied the origins of the toughness of bone, and the biological material nacre, to gain insight into new ways to design high-toughness materials. We find that toughness is developed primarily by crack bridging at multiple dimensions, e.g., from individual collagen fibrils at sub-micron dimensions to "uncracked-ligaments" at sub-millimeter dimensions; however, it is structure at the larger length scales that dictates the fracture properties.

Armed with such biological insight, we have used novel processing routes to generate layered composites with structures resembling bone and nacre at several length scales (Fig. 4). Properties are achieved through control of layer thickness, selection of components, and manipulation of roughness and adhesion at the organic-inorganic interface. The approach is to make layered, porous ceramic scaffolds via directional freezing of concentrated ceramic suspensions; growing ice is used as the ceramic particles concentrate in spaces between the ice crystals. The ice is then sublimated leaving a ceramic scaffold whose microstructure is a negative replica of the ice. In this way, we have achieved layered microstructures with layer thicknesses varying from one to hundreds of microns. These composites display highly specific properties, in particular high toughness combined with low stiffness, from a variety of mechanisms involving deflection at interfaces and resultant crack bridging.

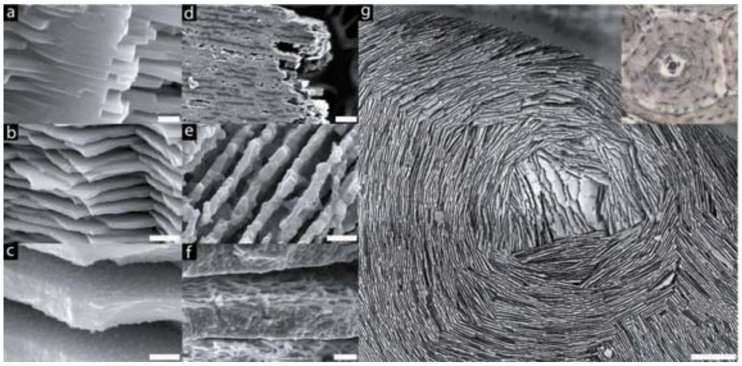

Fig. 4: *Comparison of natural and processed synthetic materials. Typical scanning electron micrographs of abalone shell (a)-(c) and of the synthetic materials (alumina-epoxy composite and porous alumina) (d)-(f). Many of the natural features of nacre are clearly mimicked here, such as the fracture surface morphology (a-d), the thickness of the layers (b-e) the surface roughness of the layers (c-f). Control of the mesostructure in alumina (g) by patterning the surface of the cold fingers on which the ice crystals grow. Mesostructure similar to osteonal bone can be obtained (human cortical bone in insert□) Scale bars: (a) 1 µm, (b) 2 µm, (c) 0.5 µm, (d) 100 µm, (e) 5 µm, (f) 10 µm, (g) 500 µm.*

Concluding Remarks and Future Plans

We believe that the inspiration of Nature in the identification and promotion of strength and toughening mechanisms at multiple (nanoscale to near-macroscopic) dimensions provides a key to the synthesis of new high-toughness hybrid materials with unique and unprecedented combinations of properties. In particular, by manipulating the character and evolution of the interfaces in such materials, i.e., *interfaces by design*, we believe that we can control and tailor mechanical properties for a wide spectrum of structural applications.

DOE Sponsored Publications (2003-2006) (archival journals only, partial listing from 80 total)

1. *Atomic-Resolution Transmission Electron Microscopy of a Y_2O_3-Containing Silicon Nitride Ceramic*. A. Ziegler, C. Kisielowski, M. Hoffmann, R. O. Ritchie, *Journal of the American Ceramic Society*, **2003**, 86, 1777-1785.
2. *Mechanistic Fracture Criteria for the Failure of Human Cortical Bone*. R. K. Nalla, J. H. Kinney, R. O. Ritchie, *Nature Materials*, **2003**, 2, 164-168.
3. *Carbon Nanotubes as Nanoscale Mass Conveyors*. B. C. Regan, S. Aloni, R. O. Ritchie, U. Dahmen, A. Zettl, *Nature*, **2004**, 428, 924-927.
4. *Interface Structure and Atomic Bonding Characteristics in Silicon Nitride Ceramics.* A. Ziegler, J. C. Idrobo, M. K. Cinibulk, C. Kisielowski, N. D. Browning, R. O. Ritchie, *Science*, 306, **2004**, 306, 1768-1770.
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9. *Nanocrystal-Powered Nanomotor.* B. C. Regan, S. Aloni, K. Jensen, R. O. Ritchie, A. Zettl, *Nano Letters*, **2005**, 5, 1730-1733.
10. *Incomplete Similarity and Fatigue-Crack Growth*. R. O. Ritchie, *International Journal of Fracture*, **2005**, 132, 197-203.
11. *Freezing as a Path to Build Complex Composites*. S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia. *Science*, Jan. **2006**, 311.

Electron Emission as a Probe of Plastic Deformation in Single Crystal Metals

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Program Scope

We are exploiting the phenomenon of photoelectron emission as a probe of deformation processes in metals, principally single crystal and polycrystalline aluminum. Dislocations intersecting the surface produce patches of low work function metal which emit electrons when illuminated with the appropriate ultraviolet radiation. We have chosen 248-nm excimer laser radiation and the mercury lamp as the major light sources to monitor the real-time formation of slip bands on single-crystal aluminum. In collaboration with NIST, we have constructed and tested a UHV-compatible tensile stage for straining single crystal aluminum under controlled conditions. We have also prepared single crystal aluminum tensile specimens. In recent work, we have established significant correlations between the rate of photoelectron emission and dislocation dynamics predicted by percolation theory.

Recent Progress

A. Oxide effect on the photoemission.

To optimize the signal to noise ratio, it would be convenient to be able to distinguish electrons emitted from bare patches of aluminum exposed by dislocation motion from those which pass through the native oxide of undeformed material. Some distinction appears to be possible on the basis of the time required for electrons to reach our detector. We observe two time-of-flight peaks in the photostimulated electron (PSE) signal. Typical PSE signals before and after deformation is shown in figure 1. The intensity of the slower (lower kinetic energy) electrons actually grows in the initial stages of oxidation, consistent with energy loss due to inelastic scattering in the oxide. Further, it is not strongly affected by deformation. The intensity of the faster peak decreases with oxide thickness, and is strongly affected by deformation. Substracting the intensity of the slow peak from the total electron signal significantly improves the correlation between photoelectron intensities and strain events. This work helped establish the optimum oxidation treatment for subsequent photoelectron measurements during deformation.

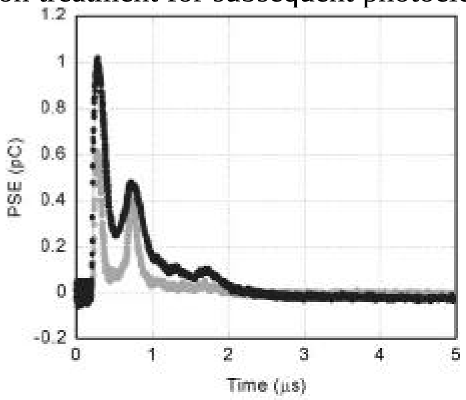


Figure 1. Photostimulated electron (PSE) signals versus time due to single laser pulses before (gray dots) and after (black dots) deformation of aluminum oxidized three hours at 200 °C. The measured oxide thickness is 3.6 nm.

B. Onset of strain localization.

In the initial stages of tensile testing, polycrystalline material deforms rather homogeneously. At some point, deformation localizes along a band of grains. Further deformation is to a large degree confined to a band which then moves along the gauge section. Although this localization process has been the subject of extensive modeling efforts, quantitative real-time measurements of strain localization are desired to constrain the models. We take advantage of the fact that the fraction of dislocations intersecting the various surfaces of the gauge length is changed by strain localization. This changes the rate of photoemission growth. The photoemission data also show curvature after the onset of strain localization, consistent with strain hardening.

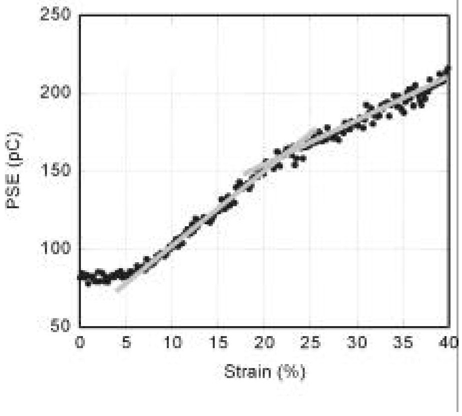


Figure 2. Integrated PSE signals associated with fast electrons (first time-of-flight peak) versus strain during tensile testing of a polycrystalline 1200 aluminum. The change in slope near 22% strain corresponds to the onset of strain localization.

C. Slip and texture development in cube-textured aluminum.

We have estimated the photoelectron energy distribution during a tensile deformation of cube-textured aluminum with a retarding energy analyzer. The work function of the (100), (110) and (111) surfaces of aluminum are 4.41, 4.01 and 4.24 eV, respectively. Thus changes in the energy distribution allow for a semiquantitative determination of changes in (111) surface area (due to slip) relative to changes in the area of (110) surfaces, which can be attributed to grain rotation. By comparing changes in the electron energy distributions with electron backscattered diffraction measurements on the same surfaces, we confirmed that the observed changes in photoelecton energy distributions in cube-textured aluminum were consistent with the observed degree of slip on (111) planes versus grain rotation on (110) planes.

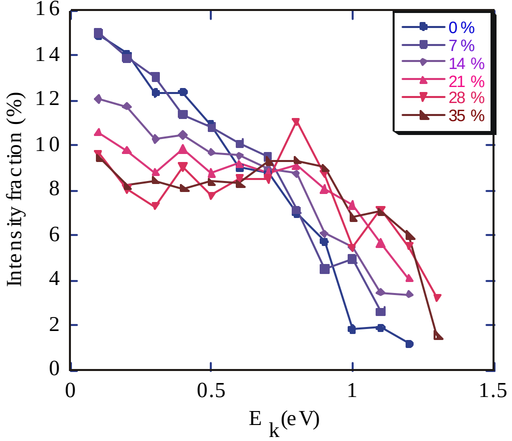


Figure 3. Intensity fraction of electrons associated with the faster electrons (first time-of-flight peak) versus kinetic energy for several sample strains during tensile deformation.

D. Photoemission measurement of single-crystals.

Theoretical work by Robb and Levine suggests that the emergence of dislocation structures during the deformation of pre-strained single crystal FCC metals displays stochastic properties similar to earthquakes [1,2]. We have detected step-like increases in photoelectron intensity associated with step-like discontinuities in stress consistent with discrete deformation events in prestrained, single crystal aluminum specimens with various orientations at different strain rate. Photoemission signals from as-cut, single crystal aluminum increased much more smoothly, consistent with the lack of dislocation cell structure in these samples during the initial stages of deformation. Figures 4 and 5 show the detected increase of PSE with strain of a pre-strained $(1\bar{1}0)[112]$ single crystal using an excimer laser and a filtered Hg lamp as light sources, respectively. The discontinuities in PSE signals for both cases strongly support the heterogeneous nucleation and growth of slip bands during deformation.

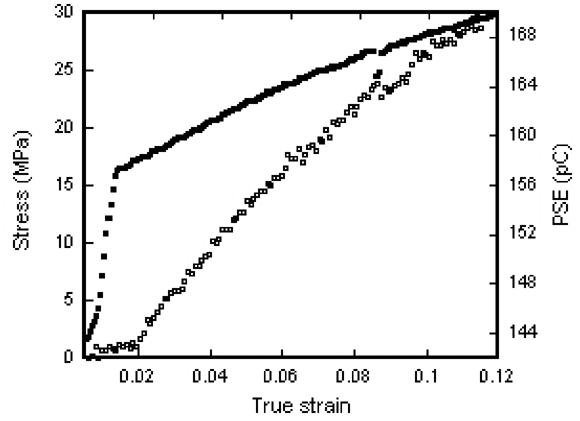
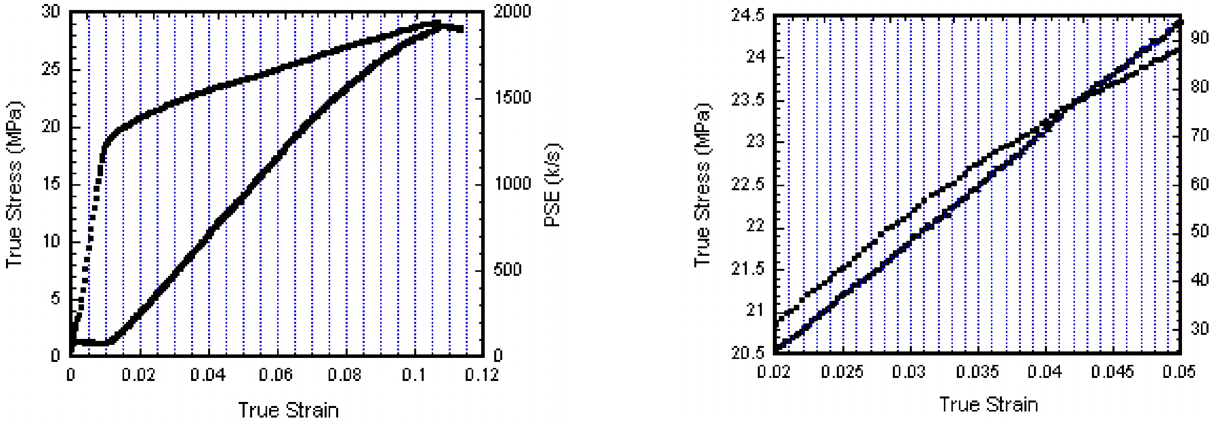


Figure 4. PSE and stress vs. strain of a pre-strained single crystal with an orientation of $(1\bar{1}0)[112]$ during a deformation at a crosshead speed of 5.0 µm/s. PSE obtained using pulses of an excimer laser with a wavelength of 248 nm.



a b

Figure 5. PSE and stress vs. strain using a filtered Hg lamp as light source.

Work in progress.

Percolation theory predicts significant spatial, as well as temporal heterogeneity. Recently, an *in situ* AFM study of the kinetics of the slip band formation in single crystal aluminum reveals two modes: constant band width and constant slip density [3]. Although AFM offers sub-nanometer vertical resolution and sub-micrometer lateral resolution, image acquisition consumes fairly long amounts of time, which complicates its application in higher strain rate deformation. Significantly, scanning laser confocal microscopy (SLCM) allows us to perform imaging slip band development in real time at higher strain rates. We expect this work will provide information over larger areas (roughly 500 µm × 500 µm) than AFM (typical maximum 50 µm × 50 µm). A SLCM compatible tensile stage is under construction.

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2. M. Cai, S. C. Langford, L. E. Levine and J. T. Dickinson, **"Observation" of dislocation motion in single crystal and polycrystalline aluminum during uniaxial deformation using photoemission technique**, Mater. Sci. Engin. A **2005**, 400-401, 476-480.
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6. H. Cao, D. Ma, K. Hsieh, L. Dong, W.G. Stratton, P.M. Voyles, Y. Pan, M. Cai, J.T. Dickinson and Y.A. Chang, **Computational thermodynamics to identify Zr-Ti-Ni-Cu-Al alloys with high glass forming ability**, (submitted to Acta Mater.)
7. M. Cai, L. E. Levine and J. T. Dickinson, **Photoemission of Al Alloys during Tensile Deformation**, (in preparation for submission to J. Appl. Phys.).
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Modeling and simulation of inhomogeneous deformation behavior of metallic glasses and their composites

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Program Scope

The deformation behavior of metallic glasses, MGs, is usually classified as inhomogeneous or homogenous deformation. Inhomogeneous deformation occurs at temperatures well below the glass transition temperature. The formation of localized shear bands and very limited plastic strain to failure are the typical characteristics of this deformation behavior. In contrast, homogenous deformation takes place near the glass transition temperature and exhibits almost super-plastic behavior without the localization of deformation. The current consensus for explaining the inhomogeneous deformation of MGs is the cooperative behavior of small clusters of randomly close-packed atoms, so-called shear transformation zones (STZs). These STZs create a localization of displacements in surrounding regions that triggers the evolution of highly localized shear bands during the deformation. Therefore, while the fundamental mechanism for irreversible deformation of crystalline solids is the dislocations, in BMGs it is the instabilities associated with STZs. Early theoretical developments of STZs in amorphous systems are given in Spaepan [2] and Argon [3,4] and more refined treatment of STZs are found in studies of Falk and Langer [5,6].

Currently, various composite microstructures have been pursued, with the notion that if somehow, these localized shear bands are diffused or arrested within the microstructure; higher ductility levels can be achieved for the MGs. The choice of the reinforcement for this purpose is usually a metallic crystalline solid with better ductility than the constituent metallic glass matrix. Reinforcements ranging from those with relatively low yield strength and elastic modulus such as Cu and Ni, to others of high strength and high stiffness such as Mo, Nb, Ta and W are being considered. Also, various crystalline ductile intermetallic phases have been in-situ produced within the MG matrix as the reinforcement, either during the solidification process from the melt or post heat treatments near their glass transition temperature.

We are investigating these deformation modes ranging from molecular dynamics, MD, simulations to quasicontinuum and continuum scales. The ultimate objective is the development of constitutive models that predict not only the load response, but also the microstructural evolution during deformation (e.g., inhomogeneous and homogeneous) of metallic glasses at the continuum level. These models are needed to study and understand more complex deformation modes such as fatigue, creep-fatigue and fracture.

Recent Progress

A novel indentation technique coupled with high-speed photography has been developed that enables in-situ observation of the shear bands evolution during inhomogeneous deformation of metallic glasses under a cylindrical indenter. These experiments provide information not only on the spatial distribution but also on the time evolution of the shear bands under the indenter during the course of deformation. These data are essential to our constitutive modeling of metallic glasses at the continuum scale. We will able to compare our simulation results not only for the load response, but also the evolution of the microstructure.

The nature of the plastic yield criterion for metallic glasses is another point of controversy, with some studies reporting yield behavior of metallic glasses is in line with that crystalline materials and von Mises constitutive model is adequate, while others are suggesting strong fundamental differences. In particular, it is unclear whether a pressure-dependent yield criterion such as the Mohr-Coulomb type, usually used to describe the behavior of granular material, is more appropriate. To elucidate this behavior, a series of molecular dynamics simulations under uniaxial tension, compression and biaxial loading on a two-dimensional model binary amorphous system were performed. The yield surface on the biaxial stress field was thoroughly described and clearly illustrated a strong pressure dependency of the yield surface for our model system. Moreover, the constant value determined for the Mohr-Coulomb constitutive model from our simulations predicts a shear band angle of 40.28^0, which is in agreement with experimental values typically reported to be in the range of $39.5\text{-}43.7^0$ for MGs.

Yield behavior of bulk metallic glasses containing voids was elucidated by using unit-cell analyses and the relevant material parameters; and the results were compared with the available constitutive models. These analyses clearly show that caution needs to be taken in transferring the constitutive models associated with void growth and ductile damage in usual metallic materials to bulk metallic glasses, largely because of different deformation modes in bulk metallic glasses resulting from the pressure dependency of yield surface and intrinsic softening behavior. With the constitutive model calibrated from the unit-cell analysis, the influence of a wide range of parameters: mechanical properties, volume faction and morphology of ductile reinforcements, on the ductility of metallic glass composites were explored. The results indicate that, even though the ductile reinforcements may alter the evolution and morphology of the shear bands, the overall failure behavior is still controlled by the metallic glass matrix, leading to very little or no improvement in the composite ductility in comparison to the ductility of metallic glass matrix. The results were substantiated with the in-situ observations made during the deformation of metallic glass composites containing up to 40% volume fraction ductile reinforcements.

Future Plans

We will continue to study the deformation behavior of metallic glasses within a homogenous deformation regime. Moreover, to the best of our knowledge, the effects of multiaxial stress-states have not been evaluated for this deformation mode. From our previous MD simulations, it is clear that the evolution of the free volume controls the deformation at this regime; however, the role of stress triaxiality on the evolution of free volume remains unclear. We will extend our MD simulations from unixial loading to multiaxial loading in this deformation regime.

The mechanical properties of metallic glasses are widely known to depend on processing history details; however, the reasons for this are not well understood. We will elucidate this behavior by utilizing MD simulations together with a quasi-continuum simulation approach that we are currently developing. For this purpose, amorphous systems will be created by equilibrating the binary system at several different liquid temperatures and then quenching at different rates. The main objectives of these studies are to investigate how frozen-in correlations affect deformation behavior and how they can be quantified before and during the deformation.

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- **"**Ductility of metallic glasses and their composites with ductile reinforcements: A numerical study" S.B. Biner, *Acta Materialia* (in press).
- **"**Experimental observations of cylindrical indentation of a metallic glass" A. Antoniou, S.B. Biner and A.F. Bastawros. *MRS proceedings* (in press).
- **"**Creep deformation behavior of a model metallic glass: A molecular dynamics simulation" S.B. Biner, *International Conference on Micromechanics and Microstructure Evolution: Modeling, Simulation and Experiments,* Madrid, Sept. 2005
- "Deformation behavior of a Zirconuim based metallic glass during cylindrical indentation: In-situ observations" A. Antoniou, A.F. Bastawros, C.C.H. Lo and S.B. Biner, *Materials Science and Engineering A*, **394**, 96, (2005).
- **"**Absence of crystallization during cylindrical indentation of a Zr-based metallic glass" M.J. Kramer, D.J. Sordelet, A.F. Bastarows, X. Tan, and S.B. Biner, *Journal of Noncrystalline Solids*, **351**, 2159, (2005).
- **"**Fundamental mechanisms of deformation in simulations of metallic glass nanoindentation" S.B. Biner, Proceedings of *"3th International conference on Computational modeling and Simulation of Materials"* Eds. P. Vincenzini et.al., p709, 2004.

SESSION IV:

POSTER SESSION

Harper-Dorn Creep of fcc, bcc and hcp Metals and Alloys

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Program Scope

Harper-Dorn (H-D) creep is observed in metals and geological materials exposed to very low stresses at temperatures close to the melting point. It is one of several types of creep processes wherein the steady-state strain rate is proportional to the applied stress, Nabarro-Herring creep and Coble creep being two other important processes. H-D creep can be somewhat insidious because the creep rates are much larger than those expected for Nabarro-Herring or Coble creep. Since the working conditions of structural components of power plants and propulsion systems, as well as olivine rocks forming the earth's mantle all involve very low stresses, an understanding of the factors controlling H-D creep is critical in preventing failures associated with those higher-than-expected creep rates. The primary goal of this investigation is to obtain missing microstructural information on the evolution of the dislocation structures during Harper-Dorn creep and static annealing of materials with the fcc, bcc and hcp structures; in our view these evolutionary processes are intimately related. Such information is currently incomplete for fcc materials and is unavailable for materials with bcc and hcp structures and is critically needed for validations of all existing and future H-D creep models. The second goal is to test the predictive capabilities of the dislocation network model of H-D creep. In the current stage of the program the data on static annealing are generated and used to predict the H-D creep curves and dislocation link-length distributions in the various materials tested. These predictions will be compared with the creep curves and link-length distributions obtained experimentally. The materials selected for this study are fcc Al and Pb, a bcc Mg-11 wt% Li alloys and a hcp Mg – 0.68 wt% Zr alloy. Both alloys are solid solutions. These materials have been chosen because of their relatively low melting temperatures. This significantly simplifies creep testing and cooling after testing to preserve the high temperature dislocation structures. The final outcome of the program will be (1) a detailed database on the microstructural changes taking place during H-D creep in fcc, bcc and hcp metals and (2) a critical test of the dislocation network theory for predicting H-D creep curves in metals and alloys.

Recent Progress

The emphasis of our recent efforts has been on quantitative characterization of the evolution of the dislocation networks during annealing of pure aluminum samples, representing materials with the fcc crystal structure. For this purpose the samples were pre-deformed by creep at 913 and 619 K and then annealed. The higher deformation temperature was selected to generate starting dislocation networks similar to those forming during Harper-Dorn creep and the lower, to obtain higher dislocation densities suitable for reliable estimates of the parameters of the network growth law. The annealing temperatures for the samples pre-deformed at 913 K were 913, 863 and 817 K and for those deformed at 619 K they were 913, 733 and 619 K. The particular temperatures were selected to obtain data points equally spaced on the 1/T scale, which is convenient for further analysis. After annealing, the samples were electropolished and used for measurements of the dislocation densities and dislocation link-length distributions using etch-pit methods [1].

For samples annealed after loading at 913 K there is a tendency to form low-angle grain boundaries at short annealing times. With further annealing those boundaries dissolve, the dislocation structure becomes uniform and the dislocation density decreases and eventually reaches a plateau value. The plateau density appears to be the same for all three annealing temperatures and equal to 323 ± 60.4 mm^{-2}. This is the "frustration density", i.e. the density at which the availability of links with Burgers vectors suitable for the annihilation reactions has been exhausted. Figure 1 shows a comparison of the initial and annealed dislocation link-length distributions, obtained from etch pit data, with the link-length distribution for aluminum obtained under steady-state creep conditions in our earlier studies of H-D creep [2]. The data from all the distributions collapse onto a single curve, which is in accord with our theoretically predicted time-invariant scaling behavior [3]. This result is the first ever convincing proof that the evolution of the dislocation network during static annealing is the same as that during H-D creep.

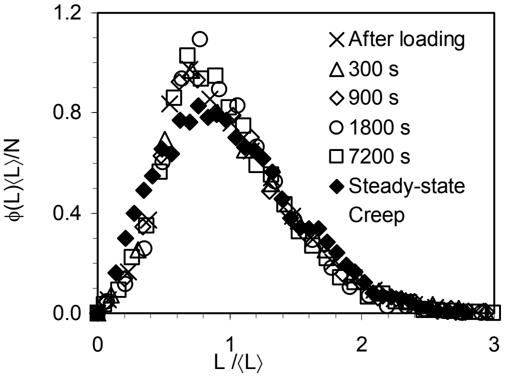

Figure 1. Experimental results showing the normalized dislocation link length distributions, *$\phi(L)$*, for pure aluminum samples annealed at 913 K. ⟨L⟩ is average link length and N number of links per unit volume.

For the sample pre-deformed at 619 K at various stresses and then annealed at 913, 733 and 619 K the frustration density is independent of the initial dislocation density but the frustration level does depend on the annealing temperature and varies from 3500 mm^{-2} to 1000 mm^{-2} for annealing temperatures of 619 K and 913 K, respectively. For all testing conditions the obtained link length distributions are also time invariant and have shapes similar to those shown in Figure 1. This result suggests that dislocation networks formed during creep deformation at 913 K and 619 K are similar and that they exhibit similar annealing kinetics.

Parallel work focused on annealing studies of a Mg-0.5 wt.% Zr alloy; these represent materials with the hcp structure. These studies resulted in the development of (1) the annealing procedure to obtain grains on the order of 1 mm which are required for our studies and (2) the dislocation etch-pitting technique. It is important to point out that developing those procedures is a very time consuming and tedious trial-and-error process. Our etch pitting method was adopted from the work of Sokolskii [4] and Sasaki and Marukawa [5]. For this purpose the samples were first mechanically polished, then chemically polished by immersing in a 10% solution of nitric acid and finally etched in a solution of 30 g of ammonium nitride in 50 cm^3 of water. The optimum etching time was determined to be 2 minutes. We are currently refining the etch-pitting methodology, incorporating an intermediate electropolishing step, which should result in the improvement of etch-pit clarity.

Future Plans

Our plans for the immediate future include (1) analysis of the annealing data generated for the pure aluminum samples, (2) continuation of the annealing studies of our model hcp and bcc alloys and (3) refinement of our dislocation-network characterization methodology. Data on the change of the dislocation density and link length distributions with annealing time and temperatures will be used to find the rate constant, k, in the link-length growth law, $g(L,t)$, which has the following form [3]:

$$g(L,t) = \frac{dL}{dt} = \frac{k}{L^*(t)} \frac{u-1}{u^m} \tag{1}$$

where k and m are stress-independent material constants and $u = L/L^*(t)$ is a normalized link length. $L^*(t)$ is a characteristic length serving as a natural scaling factor; links larger than $L^*(t)$ grow while those smaller than $L^*(t)$ shrink. From the coarsening theory it also follows that the average value of $\langle u \rangle = \langle L \rangle / L^*$ is a material constant [6] and that, after assuming that the average link length, $\langle L \rangle$, is related to the dislocation density, ρ, through the relationship $\langle L \rangle = \beta \rho^{-1/2}$, the change of ρ with time is governed by the relation:

$$\frac{1}{\rho} - \frac{1}{\rho_o} = \left(\frac{\langle u \rangle}{\beta} \right)^2 \frac{2m^m}{(m+1)^{m+1}} k \cdot t = \kappa \cdot t \tag{2}$$

where ρ_o is an initial dislocation density. Eq. (2) is valid both for H-D creep and for initial stages of static annealing, hence initial slope of the plot of $1/\rho$ vs t for the latter is equal to κ. The value of k can be subsequently found by estimating $\langle u \rangle$, m and β from the experimental link length distributions [3]. The final step in the analysis will be prediction of the H-D creep rate, which, according to the network theory [3], is equal to:

$$\dot{\varepsilon} = \frac{C \langle u \rangle b^2 k}{8\Gamma} \rho \sigma \tag{3}$$

where b is the Burgers vector, Γ is the dislocation line tension, σ is the applied stress and C is a material constant that can be readily obtained from the experimental link-length distribution. All quantities in eq. (3), with the exception of ρ and σ, are then material constants that can be obtained from the static annealing data. Consequently, eq. (3) can be used to predict H-D creep rates and, after integrating, creep curves based on the information obtained from static annealing without the need for time consuming creep testing.

We also plan to refine our link-length measuring procedure. Our current method of obtaining link-length distributions from etch pits is a modification of the method proposed by Oden et al. [1,7]. We are exploring the possibility of using Voronoi diagrams [8] for estimating local dislocation densities and subsequently local link lengths. In this method the dislocation pit structure is divided into Voronoi polygonal cells with each polygon encompassing the area that is closer to a given pit than to any other pit. The cells then divide the area in a unique and unambiguous way and the reciprocals of the cell areas represent the local dislocation densities. The preliminary results indicate that our current method gives a larger number of links in the small size range compared to that obtained from Voronoi diagrams. This is similar to what was observed by Egneberg and Lagneborg [9] and suggests that our current method may overestimate the number of small links. Since that particular part of the distribution is used in the estimation of the link annihilation rates in our H-D creep model, we need to determine the source of the discrepancies.

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Stability of Nanolayered Materials Subjected to Large Plastic Strains, Cyclic Loading and Radiation

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We used room temperature rolling to explore the deformation behavior of nanolayered materials to large plastic strains. For an initial layer thickness of about 75 nm, Cu-Nb nanolayered composites exhibited remarkable plastic flow stability even after 150% elongation in the rolling direction. The nanolayers exhibited uniform reduction in layer thickness, with no damage accumulation in the form of dislocation cell structures. Furthermore, the Kurdjumov-Sachs orientation relationship was retained after rolling. However, for initial layer thickness of a micrometer or higher, dislocation cell structures formed within the individual Cu and Nb layers and the initial Kurdjumov-Sachs orientation relationship was lost after rolling. The suppression of damage accumulation in nanolayered materials after plastic deformation was the basis to explore the fatigue resistance of these materials. We observed extraordinary resistance to accumulation of fatigue damage, compared to monolithic materials.

Synthesizing intermetallic composites with well-controlled microstructures and understanding their small-scale mechanical behavior

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Program scope

Materials with well-controlled microstructures and sub-micron length scales have the potential for unique combinations of mechanical properties, e.g., metals with nanometer grain sizes exhibit ultra-high yield and fracture strengths, good wear resistance, and enhanced superplastic formability at low temperatures.[1,2] To model and predict how mechanical properties change with length scale in composite materials, knowledge of the properties of the individual phases as well as how they interact with each other is required. Although these mechanical properties can sometimes be deduced from measurements on bulk specimens, it is not always possible due to difficulties in producing bulk materials with compositions and structures similar to those formed in-situ in the composite. In such cases, mechanical measurements using localized probing techniques like nanoindentation are employed.[3] Nanoindentation is often performed with a Berkovich indenter which has the shape of a three-sided pyramid with triangular faces. Real Berkovich indenters are not perfectly sharp but blunt to various degrees. Therefore, knowledge of the indenter geometry is critical to the understanding mechanical properties obtained by nanoindentation.

The objective of this program is to understand the effects of small length scales on a number of deformation phenomena associated with multiphase microstructures and to yield valuable input for prediction and modeling efforts. Specific tasks include: (1) synthesizing composites with self-similar patterned microstructures over a range of length scales, (2) obtaining single crystal mechanical properties of the constituent phases using a combination of nanoindentation and electron backscattered diffraction techniques, (3) measuring the tensile properties of the overall composite as a function of temperature/strain rate, (4) analyzing and modeling the deformation mechanisms and effects of length scales.

Recent progress

Well-aligned and self-similar patterned microstructures have been produced by directional solidification of eutectic alloys in an optic floating zone furnace. The systems that have been investigated include NiAl-Mo, Cr-Cr_3Si, V-V_3Si, and FeCo-VC. Their microstructures represent two kinds of important composite geometries, lamellar and fibrous. Figures 1 and 2 show examples of the fibrous microstructure of a NiAl-Mo eutectic alloy and the lamellar microstructure of a Cr-Cr_3Si alloy. Under carefully controlled solidification conditions, lamellar spacing and fiber size can be varied without changing the morphology of the microstructures, e.g., the diameter of Mo fibers in NiAl-

Mo can be changed from 250 nm to 1 µm, and the lamellar spacing of Cr-Cr_3Si changed from 1 to 5 µm.[4,5]

Figure 3 shows how nanoindentation is used to measure the mechanical properties of the individual phases in a Cr-Cr_3Si lamellar composite. As shown in Fig. 3 (a), several of the indents were located entirely within one of the two phases. Therefore, modulus and hardness of the individual phases can be determined. By combining these results with electron backscatter diffraction data, it is possible to determine the elastic constants of a single phase in a multiphase composite provided that enough independent directions can be probed.[6]

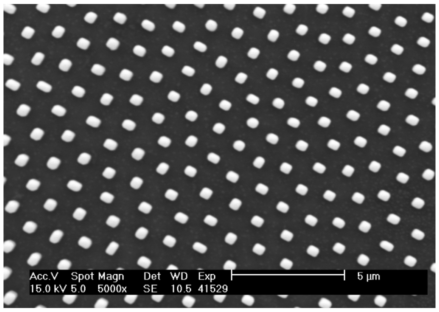


Fig. 1 SEM micrograph showing a transverse section through the well-aligned rod-like microstructure of a NiAl-Mo eutectic alloy.

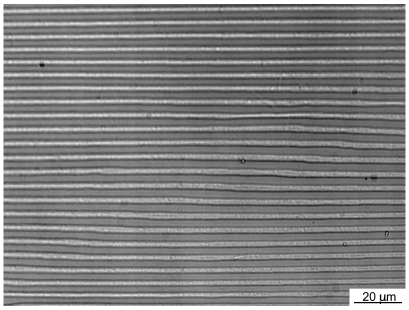


Fig. 2 Optical micrograph showing a longitudinal section through the well-aligned lamellar microstructure of a Cr-Cr_3Si eutectic alloy.

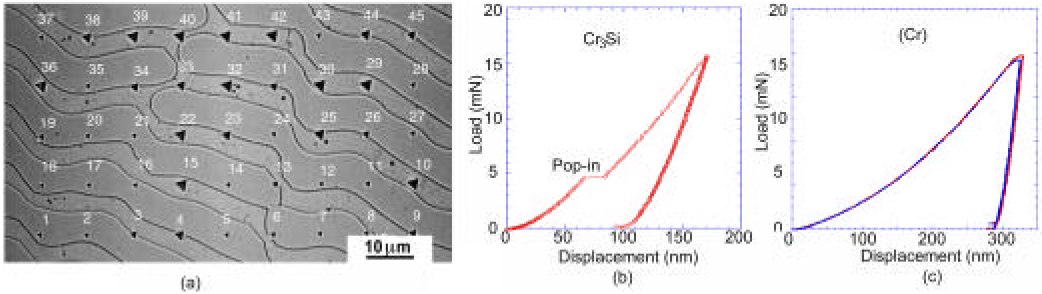
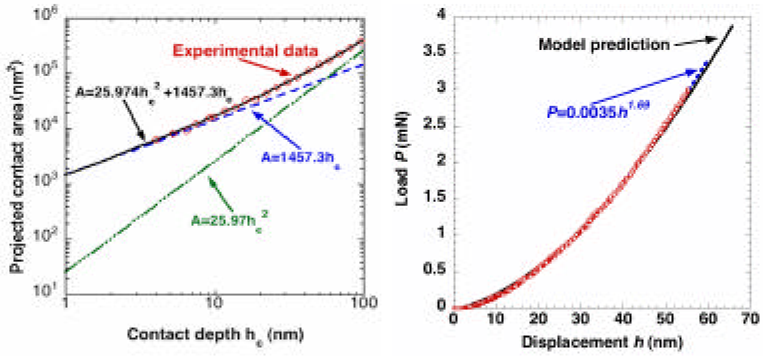


Fig. 3 **(a)** Optical micrograph showing the locations of the indents in a fully lamellar structure **(b)** Typical load-displacement curve obtained in the Cr_3Si phase, showing pop-in behavior during loading; **(c)** Typical load-displacement curve of the Cr-phase.

Although nanoindentation is a useful technique for measuring the mechanical properties of small volumes of materials, the tip geometry of the indenter must be precisely determined, especially at the very shallow indentation depths needed to probe fine scale microstructures. Also, many interesting phenomena happen at small depths, e.g., a pop-in event is observed in the Cr_3Si phase at a depth of ~75 nm [Fig. 3 (b)]. To date, most investigators have made the simplifying assumption that the indenter tip is spherical. In reality, indenter tips are much more complex. We developed a new method to describe the tip shape using the experimentally determined area function of the indenter at small depths (0-100 nm). [7] It is found that, as shown in Fig. 4 (a), a simple two-parameter relation ($A = a_1 h_c^2 + a_2 h_c$) can accurately describe the geometry of the indenter tip. The form of this relation has a simple physical interpretation, with the first term representing a conical or pyramidal indenter (a_1 = 24.56 for a perfect Berkovich indenter), and the second term describing a spherical indenter at very small depths h_c. Our analysis accurately predicts the elastic load-displacement curve [Fig. 4 (b)], and allows the theoretical strength of a material to be determined from pop-in data. Application of our new method to single crystal Cr_3Si shows that the predicted theoretical strengths are within 12% of the ideal strength $G/2\pi$, where G is the shear modulus.[7]



(a) (b)

Fig. 4 **(a)** Measured area function for the Berkovich indenter at depths up to 100 nm (circles) compared to the area function used in our calculations. **(b)** Experimental measurements (circles) of the elastic load-displacement behavior for a (110) Cr_3Si below its first pop-in. Shown for comparison are the model predicted behavior (solid line), and a power law fit of the data (dashed line)

Future plans

We plan to expand both the growth conditions and compositional space investigated in order to synthesize specimens with a wider range of microstructural length scales as well as different kinds of composites, e.g., ductile matrix with brittle second phases, brittle matrix with ductile second phases, and brittle matrix with brittle second phases. Microstructural stability and mechanical properties will be investigated as a function of externally applied temperature and stress fields and internal variables such as second phase size/spacing and interface chemistry. The mechanisms of stress/strain transfer across phase boundaries in the composites will be investigated by in-situ neutron diffraction and transmission electron microscopy studies. The goal is to determine the characteristic length scales at which qualitatively different mechanical behavior is observed and the underlying physical phenomena operating in the different regimes.

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Influence of Interfacial Chemistry on the Thermomechanical Behavior of Thin Film Metallizations

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Program Scope

The development of reliable nanofabricated devices is expected to have a tremendous impact on the nation's energy future by providing both extremely high functional densities and access to phenomena that are not otherwise available. In this program, relationships among microstructure, interface chemistry, and mechanical behavior of thin metal films on oxide or nitride layers are elucidated. This combination of materials is found in an extremely broad range of nanofabricated devices. Due to differential thermal expansion, metallizations in such devices support extremely high stresses, which can lead to device failure. However, the mechanical behavior of these metallizations can deviate sharply from that which would be expected based on bulk scaling laws. These deviations are not well understood. Many of the non-bulk-like behaviors of thin metallizations can be attributed to mechanisms that depend on conditions at the interfaces between the film and adjacent layers. In this program, we produce model sets of samples with precisely controlled interface chemistry, characterize and model the structure and chemistry of those interfaces in detail, and examine the relationships among the interface structure and chemistry, microstructure and mechanical properties of the metal films.

Recent Progress

In the past two years we have achieved significant results in several areas:

1. Interface chemistry, adhesion, and mechanical behavior of Cu thin films on SiO_2 and SiN_X. Small changes in oxygen content at Cu/SiO_2 and Cu/SiN_x interfaces have dramatic effects on the thermomechanical behavior of thin Cu films [1]. In particular, "anomalous" behaviors—negative yielding, inelastic deformation at very low stresses, and others—are correlated with a certain range of oxygen content [2]. To determine if these effects arise from changes in interfacial adhesion, we prepared Cu films with varying oxygen concentrations on aluminoborosilicate glass (Corning Eagle^{2000TM}, used for flat panel displays) and on Cu/SiN_x barrier layers on Si substrates. A new test was developed to measure adhesion at Cu film/ceramic substrate interfaces [3,4]. It is similar to "superlayer" adhesion tests in that a highly stressed driver layer, Cr in this case, is deposited on top of the target layer in order to provide driving force for delamination. Innovations in our method include simple means of patterning blanket films into strips, use of amorphous carbon layers to provide reliable crack initiation, use of graded driver films to obtain a range of driving forces in a single experiment, and automated digital data acquisition. For Cu films deposited with moderate oxygen content on glass substrates, additional oxygen significantly increases adhesion. A model based on subcritical delamination rate theory predicts the density of strong Cu-O-Si bonds across the interface from the delamination rates and agrees very well with densities estimated from the oxygen uptake during deposition [4]. For Cu/SiN$_x$ interfaces prepared with much lower interfacial oxygen content, addition of oxygen *lowers* adhesion, in agreement with predictions based on Gibbs' adsorption theory [5]. Calculations based on EELS results confirm these observations.

2. Effect of oxygen on microstructure and stress relaxation of different texture components in thin Cu films. Previous work on Cu films revealed that grains with (111) orientations had high stresses and strain hardening rates, while (100) oriented grains had low stresses and hardening rates [7]. These results suggested a possible mechanism for the large anelastic effects observed [2] in oxygen containing films. If stresses are different in these orientations, accommodations must occur near (111)/(100) grain boundaries to maintain stress field continuity. If interface sliding is allowed, material near the grain boundary can slide locally towards the high-stress grain, lowering the stress in that grain and increasing the stress in the low-stress grain. If this is a temperature-dependent process, strain energy could be stored in one part of a temperature cycle and become available to drive anelastic recovery in another. Negative yielding could arise when, for example, one part of the film relaxes towards zero from tension, while other parts relax towards zero from compression. It would be possible for the average stress in the film to rise, although the stresses in both components were decreasing. We determined stresses in the (111) and (100) components in thin Cu films during thermal cycles using x-ray strain measurements at the Cornell High Energy Synchrotron Source (CHESS). Both orientations show the same anomalous behavior and relaxation results, proving that (111)/(100) grain interactions are *not* the source of the anomalous behavior [8]. In microstructures studies using focused ion beam (FIB) and electron beam backscattered diffraction (EBSD) methods, the grain size of oxygen containing films was less than that of oxygen-free films. In ongoing work, we are determining the grain size distributions of the different texture components separately.

3. A new diffractometer system for thermomechanical studies of thin films and patterned structures using synchrotron radiation. We developed a new system (diffractometer, sample stage [9], and detectors) for conducting thermomechanical studies at CHESS. This equipment has several advantages for this type of work. First, the diffractometer is based on the 6-circle κ-geometry, allowing access to any scattering vector above the sample plane, and eliminating the limitations in the scattering vectors that can be used in more typical ω geometry and 4-circle setups. Second, the sample stage can operate in UHV or inert atmospheres from room temperature to 1000°C and incorporates active compensation for displacements caused by thermal expansion. Third, line and area detectors are incorporated to accelerate data collection. Fourth, the G-line charter allows significant flexibility in allocating beam time so that a variety of experiments are possible. DOE researchers interested in conducting experiments using this equipment should contact the PI.

4. Plastic deformation and elastic stress redistribution in (011) Aluminum single crystal and bicrystal thin films. An interesting model system for understanding how stresses are accommodated in thin layers is (011) oriented bicrystal aluminum films. The two grain orientations in these films both have [011] parallel to the film normal but are rotated 90° with respect to each other in the plane of the film. Al is nearly isotropic elastically, but the (011) orientation has two differently oriented sets of slip systems leading to plastic anisotropy. Planes in one set are inclined to the film plane and in the other are perpendicular to the film plane. Only the inclined planes develop a nonzero resolved shear stress due an imposed thermal strain. Thus, plastic deformation relaxes the strain only in the (100) in-plane direction, and the stress state becomes rapidly anisotropic. We generated a model for plastic deformation based on the critical strain for dislocation motion on the different planes and found that it agreed well with substrate curvature stress measurements along the [100] and $[01\bar{1}]$ directions in (011) oriented single crystal Al films reported by Traub and Volkert [10]. We used x-ray diffraction to determine the stresses in the same directions in 500 nm thick Al bicrystal films. In sharp contrast to the single crystal results, there is little difference in the stress levels in the two in-plane directions [11,12]. We developed a simple elastic/plastic model for stress redistribution at grain boundaries which shows that an isostress state can be reached if strain is transferred across boundaries such that grains deform elastically along $[01\bar{1}]$ but plastically along [100] [12].

5. Thermomechanical behavior of Ta thin films: effect of oxygen on the β–α phase transformation and discovery of a new microstructure. Tantalum thin films can be deposited in the equilibrium bcc α phase or in a metastable tetragonal β phase. We deposited Ta thin films in both phases on oxidized Si substrates and measured their thermomechanical behaviors during thermal cycling *in-situ* using substrate curvature stress measurements. Stress-temperature data for oxygen-free films deposited in the β phase contain large tensile stress jumps which X-ray measurements show to correspond with the β–α phase transformation [13, 14]. To our knowledge, this is the first report of the thermomechanical behavior in a oxygen-free Ta films. We are presently engaged in studies which show that the thermomechanical behavior depends strongly on whether oxygen is incorporated into the film during deposition, following deposition, or during thermal cycling. The big news here, however, is the discovery of a *new microstructure*, to our knowledge never before seen in a metallic material. While films deposited in the α phase have the textured columnar grain structure common to metal films, films produced via the phase transformation have the microstructure shown in Figure 1 [15]. These data were generated by EBSD. The color at each pixel represents the out of plane orientation with red = (100), green = (101), and blue = (111). Black lines indicate boundaries with total misorientation between pixels > 8˚, and grey lines indicate boundaries with misorientations from 4 to 8˚. Neither the high- nor the low-angle boundaries form a closed structure. This is because the out of plane orientation rotates smoothly with position in the plane of the film. For example, the orientation along the red line in Fig. 3 changes at a constant rate of about 4˚/µm. While continuously rotating crystal orientations have been found in metal single crystals deformed in uniaxial tension, and in liquid crystals, we can find no evidence of reports of microstructures with extended constant orientation gradients in either bulk or film form. We are developing a model for the rotations based on periodic arrays of dislocations.

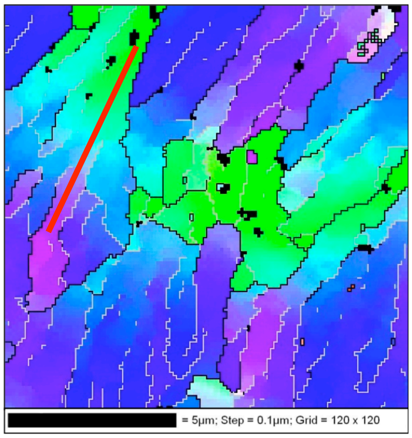

Figure 3. Microstucture of a phase transformed a-Ta film.

Future Plans

We will focus on two broad areas. First, since we have added the ability to make quantitative adhesion measurements to our existing capabilities to produce films with excellent control of structure and composition, to make high resolution thermomechanical stress measurements, and to examine interface bonding in detail via EELS, we will combine these methods to study the mechanisms that determine stress levels and related phenomena such as electromigration and stress voiding. Second, with the completion of our new diffractometer system, we will pursue a detailed study of stress distributions in thin film metallizations, and their relation to microstructure. This will involve detailed modeling of the shapes of x-ray peaks obtained from different orientations and continuum and mechanistic modeling in addition to an extensive experimental effort. Two new projects are expected to be spun off into separately funded efforts. First, our new adhesion test will be developed into a high-throughput test method in which arrays of test strips mapping of a wide range of interface conditions are tested simultaneously. Second, we will conduct an experimental and modeling program to understand the nature of the β–α phase transition in Ta films and the unusual microstructure shown in Fig. 1 in order to determine what other systems might show this behavior, and the properties and possible uses of the new microstructure.

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“Quantitative measurements of subcritical debonding of Cu films from glass substrates” M. Pang and S.P. Baker *Journal of Materials Research* **20** 2420 (2005)

“Effect of oxygen on adhesion between Cu thin films and SiN_x barrier layers” S.P. Baker, M. Backhaus-Ricoult, M. Pang, R. Knepper, *in preparation* (2006)

“Thermomechanical behavior of (011) oriented single crystal and bicrystal Al films” D.E. Nowak, E. Stach, O. Thomas, S.P. Baker, *in preparation* (2006)

“Effect of oxygen on the thermomechanical behavior of tantalum thin films during the β–α phase transformation” R. Knepper, B. Stevens, and Shefford P. Baker, *in preparation* (2006)

“Microstructure of oxygen-free phase transformed α-Ta films” Knepper, R. K. Jackson, R.S. Fertig III, and S.P. Baker, *in preparation* (2006)

Size Effect in Cleavage Cracking in Polycrystalline Thin Films

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Program Scope

The reliability of polycrystalline thin films is essential to assuring safe performance of micro/nano-electromechanical systems. Usually, they are of through-thickness grain structures and are brittle at working temperatures, and therefore their fracture properties are dominated by the resistances offered by grain boundaries to cleavage cracking [1,2]. As a cleavage crack front propagates across a high-angle grain boundary, it would first penetrate across a number of break-through points [3], and the persistent grain boundary areas would then be separated through shear fracture or ligament bending [4,5]. It is, therefore, envisioned that as the film thickness is smaller than the characteristic distance between the break-through points, which is often in the range of 0.5-5 microns, the crack front transmission can be significantly confined by the film surfaces, leading to an either beneficial or detrimental size effect. That is, the fracture toughness of the polycrystalline thin film is not a material constant; rather, it highly depends on the film thickness. Since this important phenomenon has not received the necessary attention, we propose to carry out a systematic study on fracture resistances of bicrystal silicon films. The film thickness will range from 1 to 1000 microns, and the crystallographic orientations across the grain boundaries will be controlled precisely so that the size effect and the geometrical factors can be analyzed separately. The study will starts with thick films. Once the crack front transmission process is relatively well understood, it will be extended to thin films. This project will shed light on crack-boundary interactions in confining microenvironments, which has both great scientific interest and immense technological importance to the development of fine-structured devices.

Recent Progress

The testing samples of thicknesses in the range of 100 μm to 1 mm have been successfully prepared, as shown in Fig.1(a), for which we have developed lab techniques of combined polycrystal characterization and thermal modification as well as bicrystal harvesting and thinning to overcome the following hurdles: (1) the sample must contain and only contain two large grains with the crystallographic orientations being significantly different, i.e. the grain boundary must be high-angle; (2) the grain boundary must be clean and oxide free; (3) the samples thickness should be controllable in a broad range so as to investigate the size effect; and (4) most importantly, a pre-crack must be produced with the crack tip arrested by the grain boundary so that the fracture resistance of the grain boundary can be measured.

Preliminary fracture experiment on these silicon bicrystal samples is being carried out. The results are quite encouraging. As shown in Fig.1(b), it is clear that the fracture surface shifts form the cleavage plane of grain “A” to that of grain “B” across the grain boundary. Different from what we observed in iron-silicon bicrystals [6], the front transmission in a silicon sample does not demand shear deformation or fracture of the grain boundary itself; rather, separation of a secondary cleavage plane in grain "A" takes place, by which the crack can "channel" through the boundary affected zone. Detailed fractography study is in progress to understand the details of this phenomenon.

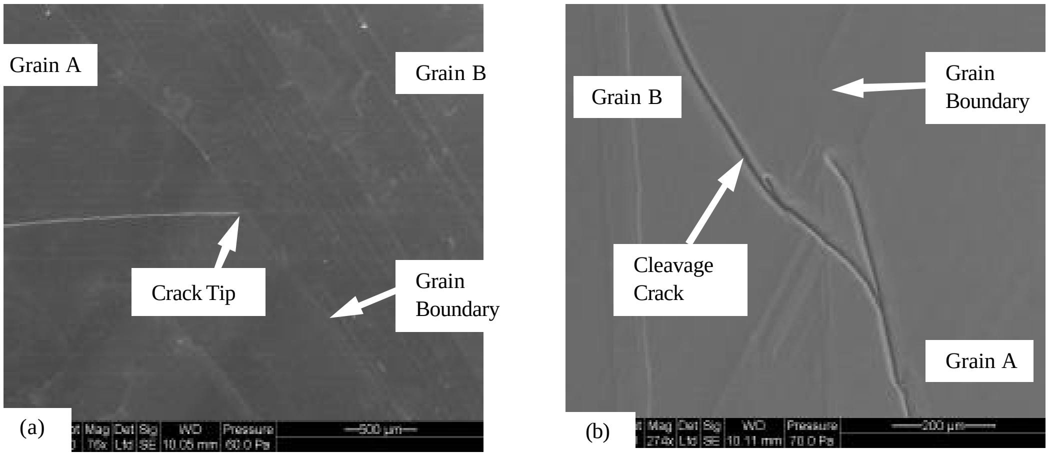

Fig.1 SEM microscopy of (a) a cleavage crack tip arrested by the high-angle grain boundary of a boron doped silicon bicrystal and (b) a cleavage crack across the high-angle grain boundary of a boron doped silicon bicrystal.

Based on the analysis of energy balance of cleavage front propagation in heterogeneous environments, the upper limit and the lower limit of the size dependence of grain boundary toughness have been predicted. The upper limit is reached when the persistent grain boundary areas are sufficiently tough such that the final separation of crack flanks occurs after the crack trapping effect is fully overcome (see Fig.2). Under this condition, there is a transition range of film thickness around 1-2 times of the width of break-through windows in which the size effect is pronounced. In the transition range, as the film thickness increases, the grain boundary toughness becomes larger. Below or above this range, the grain boundary toughness is somewhat size independent. The lower limit is obtained as the persistent grain boundary areas fail during the crack front transmission process. In this case, the film thickness effect is pronounced for cracks shorter than 500 times of the film thickness.

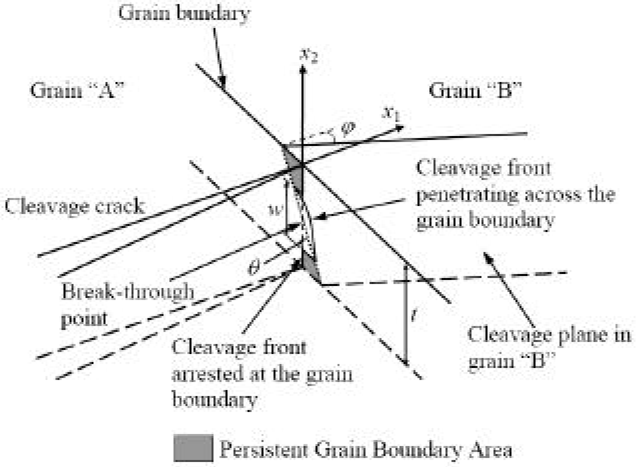

Fig.2 A schematic diagram of the cleavage front transmission across a high-angle grain boundary.

Future Plans

We plan to continue the experimental study on silicon thin films of various thicknesses. For relatively thick films of thicknesses larger than 100 μm, the sample preparation techniques have been well established and the investigation will be focused on the dependence of grain boundary toughness on crystallographic misorientations. The precracked bicrystal samples will be fractured under nearly pure mode-I loadings. Due to the large number of available cleavage planes in silicon and the large T-stress, the misorientation angles should be smaller than 20°. The development of break-through points and the behaviors of persistent grain boundary areas will be observed directly on the fracture surfaces, which will provide an important basis for determining the thickness of silicon thin film samples.

Silicon thin film samples will be fabricated from the thick film samples via chemical-mechanical polishing and enhanced etching. The sample thickness will be controlled from less than 1 μm to 100 μm. The grain boundary toughness will be measured under both mode I and mode II loading. The former is relatively simple and suitable for theoretical analysis; the latter is more close to the working conditions of micro/nano-electromechanical system components. Since the final thickness is quite small, a protection frame will be produced surrounding the sample during the polishing and etching processes, and be broken off just before the fracture test. All the residual stresses in the thin film caused by the deposition, polishing, and etching will be released when the protection frame is broken. If necessary, high-temperature annealing will be performed to further lower the level of residual stresses. Based on the experimental data, as well as the SEM and TEM analyses, the factors governing the boundary toughness can be discussed quantitatively. If possible, an environmental chamber will be designed to perform the microscale fracture experiment at temperatures in the range of 20-600°C, which will shed light on the influences of the dislocation behavior and the grain boundary shearing. A number of promising experiments will be analyzed in detail to relate the plastic deformation to their slip ingredients by a variety of available methods such as etch pitting, polarized optical microscope observation, and electron back scatter diffraction. Note that the influence of free surfaces (or film thickness) and adjacent grains (or grain size) can be quite different, which can be examined by testing free-standing and rigid-substrate-supported samples of similar grain structures.

The measured boundary toughness can be used in a variety of methods to estimate the global cracking resistance of fine-grained materials. Here, different modes of possible crack advance must be considered, ranging between monolithic quasi-straight crack fronts to intricately percolating cleavage cracking processes through grains as conceived by McClintock [2]. To establish the dominant form of crack advance, fracture experiments in textured and non-textured polysilicon samples with various grain sizes will be performed, followed by examining the cleavage river markings through the field of fractured fine grains. The simplest method to assess the global fracture resistance could be a variant of crack trapping models that will amount to a crack-front-line-average of the individual energy release rate of neighboring grains as in the model of Rose [7], which has been found to be reasonably accurate when compared with the more elaborate crack trapping model of Bower and Ortiz [8], as was verified by Mower and Argon [9]. If the advance of the macrocrack is found to be more tortuously percolating through grains as noted by Becham and Pellox [10] and considered by McClintock [2], a more detailed numerical simulation will be necessary. The actual result is likely to be in between the monolithic and the fully tortuous cases, where the former is likely to result in a position independent cracking resistance while the latter may have the elements of a rising resistance, i.e. R-curve, form. The important size effect on the global fracture resistance can then be discussed by incorporating the model of the resistance of individual grain boundaries into this framework. In order to gain a deeper insight into the crack front transmission behaviors, especially for thin films of thicknesses less than 1 μm, a molecular dynamics enhanced finite element analysis will be conducted to visually demonstrate the effectiveness of the important factors, such as film thickness, crystallographic misorientations, as well as grain boundary structures.

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Multiscale modeling of nanostructured triblock copolymers

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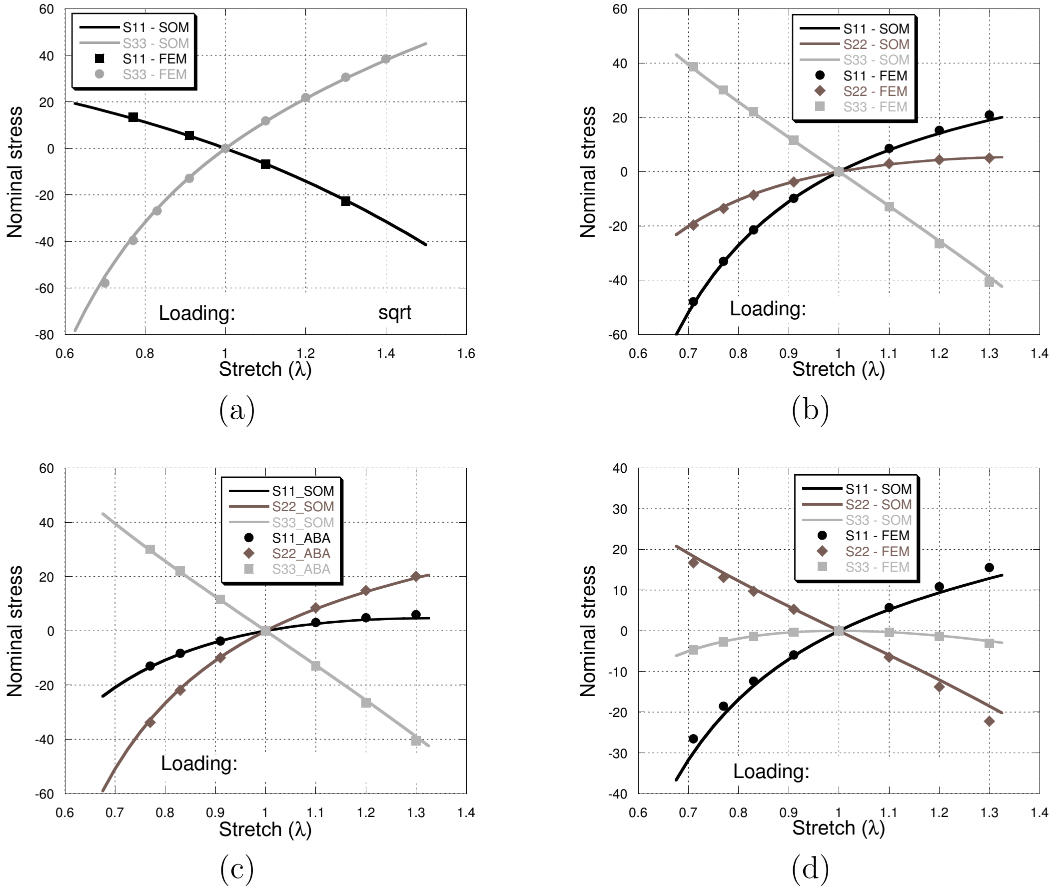
1 Program Scope

This program makes use of newly developed homogenization techniques to carry out a *multiscale* analysis of "oriented" and "unoriented" ABA triblock copolymers systems [1]. The main objective is to characterize the effect of the material structure at the domain (nanoscale level) and grain (microscale level) levels on the large-deformation mechanical properties (macroscale level) of these multiphase systems. Thus, the main scientific questions that we propose to answer are: (*a*) Of the four known domain structures that are possible in these systems (spheres, cylinders, double-gyroids and lamellae), which one provides the most effective reinforcement effect for small and large deformations? (*b*) How does the answer to this question depend on the "texture" of the macroscopic (polycrystalline) sample? (*c*) What are the implications of deformation-induced "microstructural evolution" (i.e., changes in the shape, size and orientation of the reinforcing domains, as well as changes in the texture, and grain shape and orientation) on the overall stability of the sample to finite deformations? This is a very important question as the development of instabilities is known to severely affect the overall response of these systems. (*d*) What are the effects of domain and grain boundaries on the macroscopic response of the samples?

We will *validate* our models against direct numerical simulations, especially for oriented samples with periodic nanostructures. This will be accomplished through comparisons with direct simulations available from the group headed by Pierre Suquet at the CNRS/LMA in Marseilles. We also propose to *validate* our models against experimental data available from the literature. In particular, we will make use of comprehensive experimental work of Thomas' group at MIT both for "oriented" and "unoriented" samples.

2 Recent Progress

The homogenization framework has been improved in order to be able to handle the strong nonlinearities associated with incompressible behavior (elastomeric phase). This work has been published in Ref. [2]. The framework was extended to be able to handle periodic microstructures, and has been validated through comparisons with full numerical simulations being carried out by J.-C. Michel at the CNRS/LMA in Marseilles. These comparisons include not only the macroscopic stress-stretch relations for these materials, but also for the possible development of "macroscopic" instabilities, which is a much more sensitive test of the capabilities of the method. A publication is in preparation and nearing completion [3].



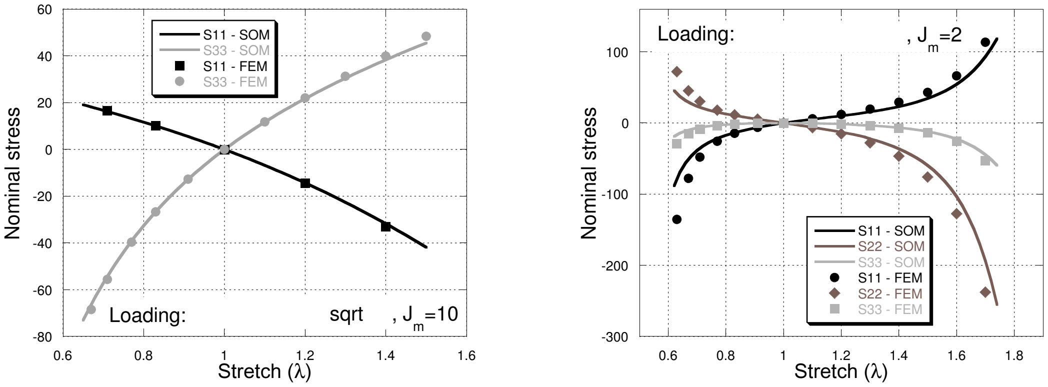
(a) (b)

(c) (d)

Figure 1: Nominal stress versus applied stretch in thermoplastic elastomers with a neo-Hookean matrix phase and a cylindrical microstructure: Comparison of homogenization (SOM) predictions with FEM results. (a) Axisymmetric loading along the fiber direction. (b) Transverse loading along one symmetry direction. (c) Transverse loading along the other symmetry direction. (d) Simple shear in the transverse direction.

The method was implemented for the layered microstructures, where exact analytical solutions are possible, at least up to the point of "macroscopic" instabilities. A Gent-type model was chosen for the soft, elastomeric matrix phase and a J-2 deformation theory model was selected for the hard, glassy, fiber phase. We have tried to compare with published work by the group of Thomas at MIT, as well as recent work by the group of Jean-Yves Cavaillé of the INSA de Lyon (France). It was found that the theoretical predictions were extremely sensitive to imperfections in the materials, which are always present in the experimental results. For this reason, a comparison between the "perfect" layered microstructures and the "imperfect" experimental results is not appropriate. A publication for the perfect geometries is in preparation [4]

The method has also been implemented for the cylindrical microstructures, and a publication is in preparation for the monodomain samples [5]. The predictions of the second-order homogenization method (SOM) have been compared with FEM simulations.



(a) (b)

Figure 2: Nominal stress versus applied stretch in thermoplastic elastomers with a Gent matrix phase and a cylindrical microstructure: Comparison of homogenization (SOM) predictions with FEM results. (a) Axisymmetric loading along the fiber direction with lock-up parameter $J_m = 10$. (b) Simple shear in the transverse direction with lock-up parameter $J_m = 2$.

Figures 1 and 2 show these comparisons for various loading conditions and constitutive models for the elastomeric matrix phase. It is seen that the agreement is quite good, which justifies the use of the SOM predictions. In addition to the computational efficiency of the SOM estimates, it was found that the SOM predictions were much more stable (from a computational point of view) than the FEM predictions, which failed to converge at relatively small deformations. These microstructures were also found to be highly susceptible to imperfections, due to the possible development of instabilities in the finite strain domain.

3 Future Plans

We will implement the method for "polydomain" samples with layered microstructures and investigate the effect of texture in these samples. In particular, we will test our hypothesis that the experimental observations for the "monodomain" samples may be modeled with polydomain samples with strong, but imperfect textures. This is already being done for the lamellar crystals and will be done also for the cylindrical crystals. Predictions will also be generated for the "unoriented" samples, and comparisons will be attempted with experimental results from the literature. Both the macroscopic behavior and the microstructure (texture) evolution will be tracked by the model and compared with available experimental data. The results and comparisons with experiments for the monodomain and polydomain samples with cylindrical microstructures will be completed. The homogenization model will be implemented for the BCC microstructures, both in monodomain and polydomain forms, and results will be generated and compared with experimental work available from the literature.

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Lopez-Pamies, O. and Ponte Castañeda, P. (2006). Homogenization estimates and macroscopic instabilities for thermoplastic elastomers with layered microstructures. *In preparation.*

Brun, M. and Ponte Castañeda, P. (2006). Homogenization estimates and macroscopic instabilities for thermoplastic elastomers with cylindrical microstructures. *In preparation.*

Microstructural Evolution and Interfacial Motion in Systems with Diffusion Barriers

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Program Scope

Material systems used in microelectronics and micromachines, functionally graded coatings, lead-free solders, and structural composites share the characteristic that multiple material phases are in close spatial proximity. These material systems operate under a range of temperatures and temperature gradients, are subject to non-uniform and non-hydrostatic stress fields, and are sometimes subjected to high electrical current densities; such systems are rarely in thermodynamic equilibrium. Consequently, interdiffusion between materials and the nucleation and growth of new phases at interphase interfaces can occur, thereby altering physical and mechanical properties and resulting in a potential reduction of both the reliability and operational lifetime of the system.

The objective of this research is to elucidate the influence of compositional, elastic, and electric fields on diffusional phase transformations in systems removed from equilibrium and under driven conditions (such as large imposed electric current densities) in the presence of diffusion barriers. In order to do so, numerical tools to simulate interdiffusion and phase transformations in stressed, multilayered structures with multiple atomic constituents and material phases are being developed and implemented using Cahn-Hilliard equations, phase field models, and multi-grid numerical solution techniques. The models include position and phase-dependent mobilities, elastic constants, and electrical resistivities and have been informed by recent experimental work on Sn-Ni-Ag lead-free solders. Numerical simulations have focused on two-phase and three-phase thin-film systems in the presence of electrical fields or in the presence of a diffusion barrier. Simulation tools and theoretical analyses are used to identify the critical parameters that govern interdiffusion and the location and sequence of new phase formation in these systems.

Efforts to understand phase transformations under driven conditions have led to a parallel theoretical investigation of amorphization of metallic alloys during ball milling. The primary objective is to identify the connection between the thermodynamic characteristics of the material, the defect structure and relaxation and recovery properties, and the input power on the temporal evolution of metastable and amorphous phase formation, particularly cyclical amorphization. An experimental effort examining the interplay between two possible crystalline phases and an amorphous phase has been initiated.

Recent Progress

Cahn-Hilliard and phase field modeling without electric current: Cahn-Hilliard type equations to model one-dimensional evolution of microstructure in bulk alloys with elasticity[1,2] have been extended to two- and three-dimensional systems.[3,4] A new analytical method has been developed for solving the elastic fields arising from compositional self-strain in a solid film on a compliant substrate. The solution is based on formulating the equations of elasticity in the film and substrate in terms of either the Airy stress function in 2D or displacement potentials in 3D.[4,5] The analytic solution shows the explicit connections among system parameters and has the potential to significantly reduce computational cost as compared to methods based on finite differences[6] or micro-elasticity.[6,7]

Simulation results using the analytic solution show the role of compositional strains and elasticity on spinodal decomposition and coarsening.[4] Results in two- and three-dimensions confirm earlier one-dimensional results that elastic effects can favor nonequilibrium phases, significantly alter kinetic paths, and generate unexpected sequences of phase formation. Results show that elasticity generally speeds up the phase transformation process as long as the elastically preferred state is accessible by diffusion. There is a strong effect of elasticity on evolution patterns owing to the effective bending of the film generated by epitaxial misfit between the film and substrate. This bending gives rise to mass flux in the thickness direction, which in general favors phases forming parallel to the film-substrate interface. Interfacial (gradient) energy, on the other hand, favors columnar structures, especially for thin films, and so the stability of different film configurations depends on the relative strengths of elasticity and gradient energy. For example, multilayer structures are less stable than bilayer or columnar structures. Also, when the bending of the film is small, as in free-standing films with no substrate, elasticity has negligible effect on phase geometry and so only columnar structures are observed.

Phase Transformations in the Presence of Electric Currents: Code to simulate phase transformations at solder joints and metallization contacts using Cahn-Hilliard and phase-field models has been developed and tested. Composition, phase, elastic, and electric fields are solved simultaneously using the appropriate governing equations as a function of time. The four coupled partial differential equations are solved using a multi-grid technique developed in collaboration with mathematicians J. Lowengrub and S.M. Wise at UC-Irvine. The constitutive laws for diffusion depend on the electric current through electromigration[9] as well as on the local composition, electric, and stress fields. The dependence of the electrical conductivity and elastic constants on the local composition and phase, and the coupling between the electrochemical potential and the compositional and misfit strains are included.

Simple theoretical analysis and experimental observations in Sn/Ag and Sn/Ni systems[9] suggest different temporal exponents for the thickening rate of a growing intermediate phase in the presence of electric current than the usual linear or square-root of time kinetic laws. Simulations in 2D to investigate the validity of these predictions are underway.

The one-dimensional results are also being used as the base state in a full linear morphological stability analysis of the growth of a planar interface in the presence of an electric current. Preliminary results suggest that interfacial instability depends strongly on the electrical conductivities of the phases and may diminish as the intermediate phase grows.

Cahn-Hilliard gradient energy coefficient: Expressions for the Cahn-Hilliard gradient energy coefficient k for binary and ternary face-center-cubic crystals were derived by consideration of pair-wise, three-body, and four-body nearest-neighbor interactions. The resulting equations are expressed in terms of the interaction energies of clusters of atoms, and are related to bulk thermodynamic data available in CALPHAD databases. The three- and four-body interactions introduce composition dependence in k and provide a means for estimating k in some of the experimental systems used in the simulations. Values of k calculated for the Al-Zn system are in good correlation with those deduced from experiment. The composition dependence of k was also shown to affect microstructure during simulations.

Amorphization during Ball Milling: A system of thermodynamic balance equations to describe the time evolution of a two-phase, crystal-amorphous element of material undergoing ball milling has been derived. The thermodynamic state of the microstructure is assumed to depend on the phase fraction, the deformation state of each phase, and the temperature. The constitutive laws for the state of deformation account for energy storage due to defect creation and for recovery processes that decrease the stored energy of the system. Three steady-state solutions were found for a variety of assumed constitutive laws; a state of crystalline phase only, a state of amorphous phase only, and a two-phase system consisting of a mixture of crystalline and amorphous phases.

A linear stability analysis was performed for each steady-state solution has been analyzed and the results displayed on bifurcation diagrams where the steady-state phase fraction was plotted as a function of the input power. For certain combinations of materials parameters and rate constants, the two-phase, steady-state system exhibited oscillatory behavior in which the phase fraction of the amorphous phase oscillates about the steady-state value (asymptotically stable spiral point). This thermodynamic approach can be extended to more complex driven systems.

Future Plans

Short-term plans focus on exploiting the code that we have developed during the past couple of years to investigate intermediate phase growth in high electric current densities both in the presence and absence of diffusion barriers. These simulations are informed by experiments in the Sn-Ni-Ag ternary system and are intended to explore basic aspects of the phase transformation. Efforts will include determining the functional dependence of the thickening rate of a growing intermediate phase on the magnitude of the induced electric current, identifying how the quantitative aspects of the phase thickening rate change when the direction of the applied electric field is changed, and clarifying the interplay between compositional strain, electric field and electric resistivity on the morphological stability of the growing interface, which experiment suggests also depends on the direction of current flow. Intermediate-term efforts will focus on identifying the influence of a diffusion barrier on these characteristics of the phase transformation in systems with high electric current densities. In addition, the thermodynamic analysis of amorphization and phase transformations during ball milling is being extended to three-phase systems with compositional demixing. The theoretical work is being coupled with thermodynamic data bases in an effort to predict phase evolution during ball milling in ternary alloys. This later work is being performed in collaboration with G.J. Shiflet and J.K. Lee.

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Study of the Martensitic Transformation in Shape Memory Alloy Using Photoelectron Emission Microscopy

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Program Scope

The thermally-induced martensitic transformation in polycrystalline shape memory alloys (SMA) can be probed using photostimulated electron emission (PSE), ultra-violet photoelectron spectroscopy (UPS), and photoelectron emission microscopy (PEEM). Solid-state phase transformations in crystalline materials alter the lattice electronic structure and typically produce a corresponding change in the surface work function. *In-situ* photoemission measurements can provide quantitative, spatially resolved information on surface fraction of austenite and martensite phases as the transformation proceeds. In this project, we employ PEEM to probe both surface electronic structure and microstructural changes in real time. Photoelectron emission microscopy shows promise to improve our understanding of martensitic transformations in shape memory alloys.

Recent Progress

A. CuZnAl alloy.

Typical PEEM images acquired before and after the thermal martensitic transformation in a CuZnAl shape memory alloy are shown in Fig. 1. The phase transformation appears at 48 °C during heating and at 42 °C upon cooling. The transformation is marked by a sharp change in photoelectron intensity, which is reflected in the darker image of (b), the austenite phase. The difference in the photoelectron intensity before and after the transformation is attributed to a change in work function of about 0.2 eV. This work function change was measured by UPS. In addition, the transformation is accompanied by significant displacement and re-orientation of surface features, as well as surface roughening. The rougher surface of the austenite phases is presumably responsible for the poor contrast associated with pre-existing surface scratches in (b). Photoemission electron microscopy provides real-time information on microstructural changes and phase-dependent electronic properties.

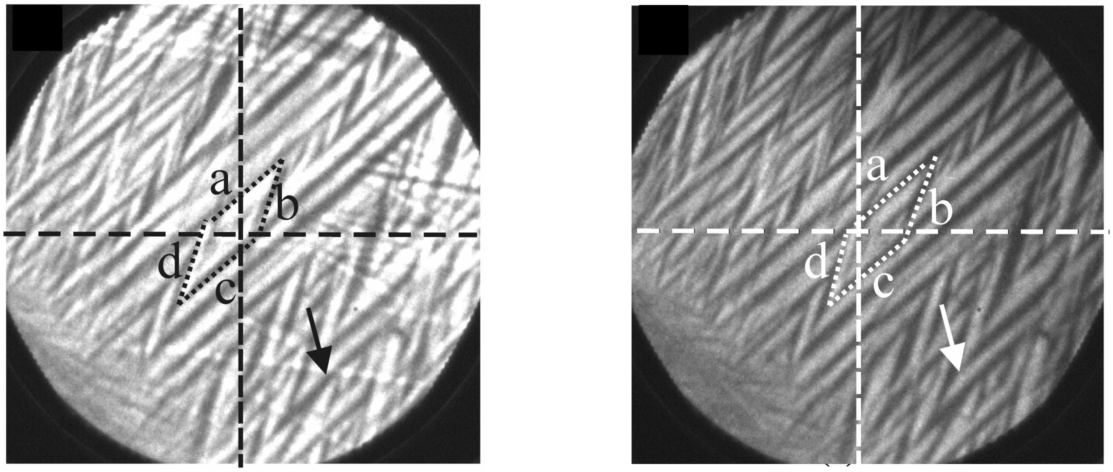
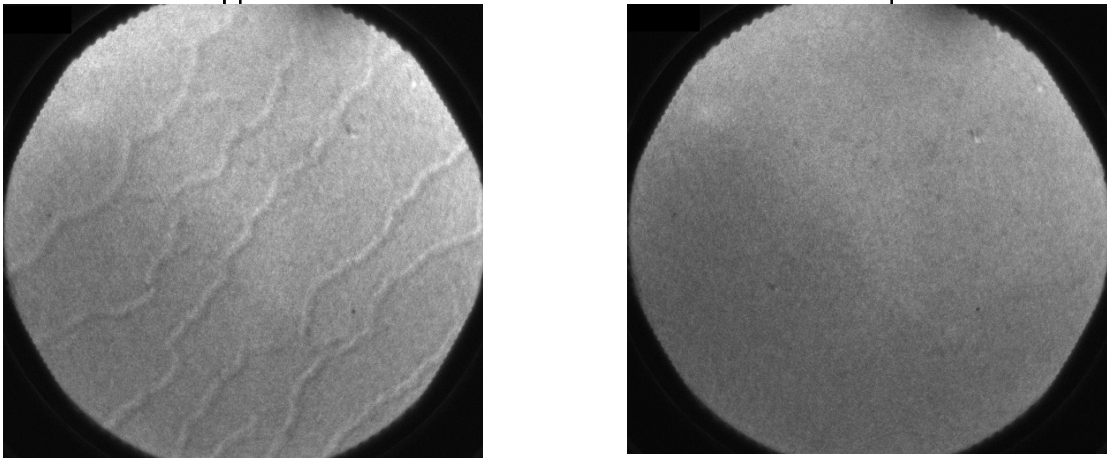


Fig. 1. PEEM images of a CuZnAl alloy showing (a) the low temperature martensite phase and (b) the high temperature austenite phase in the same area as (a). The position of a polishing scratch, visible on the martensite surface but not on the austenite surface, is marked by the arrow. The diamond marks a set of four, self-accommodated variants that are displaced by the transformation. The field of view in each image is 150 µm.

B. NiTiCu thin film.

The work function change accompanying the martensitic transformation of a polycrystalline NiTiCu thin film was observed to be 0.18 eV—similar to that of the CuZnAl alloy above. *In situ* photoelectron emission microscopy studies again revealed distinctive microstructural and intensity changes at the transition temperatures. The image intensity change results from the surface work function change associated with the phase transformation. The disappearance of trenches on the surface at the high temperature is also due to the phase transition. *In situ* AFM was employed to examine the evolution of the trenches with temperature; typical trench cross-sections above and below the transition temperatures are shown in Fig. 3. Both PEEM and AFM confirm that the disappearance of surface trenches is associated with the phase transformation.



a. 25 °C　　　　b. 100 °C

Fig. 2. PEEM image of NiTiCu thin film at two different temperatures (field of view is 150 µm).

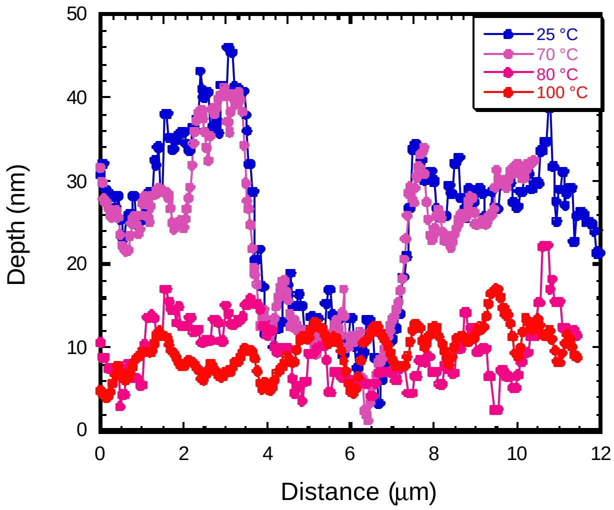


Fig. 3. Cross section of trench profiles measured by an AFM

Work in progress.

Martensitic transformations in shape memory alloys can be induced both thermally and by applied stress. We expect similar surface microstructure changes accompany stress-induced phase transformations. We plan *in situ* PSE measurements with our vacuum compatible tensile stage to track the initiation and progress of the phase transformation with applied strain/stress.

DOE Sponsored Publications in 2004-2006

1. M. Cai, S. C. Langford, J. T. Dickinson, Q. He, W. M. Huang, T. C. Droubay and D. R. Baer, **Study of martensitic transformation in a Cu-Zn-Al shape memory alloy using photoemission**, Proceedings of International Conference on Mechanical Engineering and Mechanics, Nanjing, China, **2005**, 1123-1127.
2. Gang Xiong, Alan G. Joly, Wayne P. Hess, M. Cai and J. T. Dickinson, **Introduction to Photoelectron Emission Microscopy: Principles and Applications**, Journal of the Chinese Electron Microscopy Society, **2006** (in press).
3. Gang Xiong, M. Cai, Alan G. Joly, Wayne P. Hess, Kenneth M. Beck, and J. T. Dickinson, **In-situ photoemission electron microscopy study of thermally-induced martensitic transformation in CuZnAl shape memory alloy**, (to appear in Appl. Phys. Lett.).
4. M. Cai, S. C. Langford, J. T. Dickinson, M. J. Wu, W. M. Huang, G. Xiong, T. C. Droubay and W.P. Hess, **Study of martensitic transformation in a NiTiCu thin film shape memory alloy using photoelectron emission microscopy**, (In preparation for submission to J. Appl. Phys.).

Effects of Dopant Segregation on Lattice-Diffusional Creep of Nanocrystalline Ceramics

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Program Scope

Superplasticity of nanocrystalline ceramics has been the subject of intensive research in the last decade, and the deformation mechanism involves grain-boundary sliding accommodated by lattice diffusion. However, in order to suppress the grain growth and to maintain the small grain size, dopants that segregate to grain boundaries are added. Also, it has been found that the deformation rate of nanocrystalline ceramics under loading is much smaller than that predicted by the lattice-diffusional creep model, i.e., Nabarro-Herring model. This is mainly because of dopant-segregation and formation of a space-charge layer, which induce a local electric field in the grain-boundary region. This local electric field inhibits the diffusion of charge carriers that control diffusional creep. The existing analytical model on the effects of segregation-induced local electric field on lattice-diffusional creep of nanocrystalline ceramics was derived under the assumption that the grain size is much greater than the width of the space-charge layer. This assumption can become inappropriate for nanocrystalline materials. Here, we re-analyzed the model without that assumption. Using yttria tetragonal zirconia (YTZP) as an example, we found significant differences between earlier results and our results when the grain size is less than 50 nm.

Recent Progress

The space charge theory was first postulated by Frenkel.[1] Because of the different formation energies of point defects in ionic crystals, the lattice discontinuities (e.g., surfaces, grain boundaries, and dislocation cores) carry an electric charge due to excess ions of one sign, and this charge is compensated by a space-charge layer of the opposite sign adjacent to these lattice discontinuities. An electrostatic potential difference between the lattice discontinuities and the bulk exists in the presence of the space-charge layer (Fig. 1(a)). The effects of dopant segregation on deformation of nanocrystalline ceramics were analyzed by Gómez-García *et al.* recently by considering a spherical grain.[2] For YTZP, the grain boundary carries a positive charge resulting from segregation of Y^{3+} which is compensated by a negative space-charge layer of ionic defects of Y^{3+} substituting for Zr^{4+}, and the charge carrier controlling diffusion, Zr^{4+}, is depleted in the space-charge layer.[3,4]

In the absence of electrostatic potential, the constitutive equation for creep by grain boundary sliding accommodated by lattice diffusion is[5,6]

$$\dot{\varepsilon} = A\frac{Gb}{kT}\left(\frac{\sigma}{G}\right)^n\left(\frac{d}{b}\right)^p D, \tag{1}$$

where $\dot{\varepsilon}$ is the creep rate, A is an empirical constant, G is the shear modulus, σ is the uniaxial applied stress, b is the Burgers vector, d is the grain size, and D is the lattice diffusion coefficient of the charge carrier. The stress exponent $n = 2$, and the grain size exponent $p = -2$. In the presence of electrostatic potential, the creep equation becomes[2]

$$\square = \square A \frac{Gb}{kT}\left(\frac{\square}{G}\right)^{2}\left(\frac{d}{b}\right)^{\square 2} D, \qquad (2)$$

where □ is a modification factor accounting for the segregation effects and is a function of Zr^{4+} concentration distribution, the electrostatic potential, the grain radius R (= $d/2$), the width of the space-charge layer l, and the temperature. In this case, the grain size exponent is described by

$$p = \left(\frac{\partial \ln \square}{\partial \ln d}\right)_{\square,T} . \qquad (3)$$

However, in order to obtain closed-form solutions, two simplifications were made by Gómez-García *et al.*: (i) $R >> l$, and (ii) the distribution of electrostatic potential within the layer, $V(r)$, was ignored and a mean value, $<V>$, was used (Fig. 1(a)).

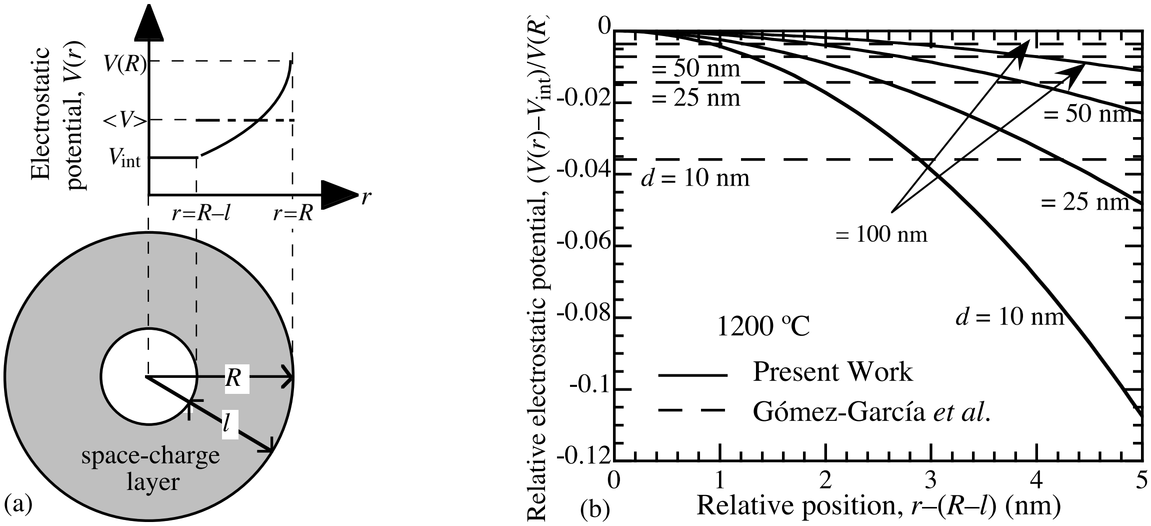

Fig. 1. (a) Schematic showing a spherical grain with a space-charge layer. The electrostatic potential distribution $V(r)$ and its mean value within the space-charge layer $<V>$ are also shown. (b) The relative electrostatic potential within the space-charge layer as a function of the relative position, $r–(R–l)$, at different grain sizes showing the comparison between earlier and our results.

For nanocrystalline materials, the requirement that $R >> l$ (2 to 10 nm) would be violated, and neglect of the distribution of $V(r)$ within the space-charge layer in modeling becomes inappropriate. To make the solutions applicable to nanocrystalline ceramics, we removed Gómez-García *et al.*'s two assumptions and resolved the problem.[7] The materials properties used in calculations are: $l = 5$ nm, $V(R) = –1.5$ V, and unless noted otherwise $T = 1200$ ºC.[2] The relative electrostatic potential $(V(r) – V_{int})/V(R)$ within the layer is shown in Fig. 1(b) as a function of the relative position, $r–(R–l)$, at different grain sizes. Gómez-García *et al.*'s simplified result, $(<V> – V_{int})/V(R)$, is also included for comparison. At $r = R–l$, $(V(r) – V_{int})/V(R) = 0$ and it decreases as r increases. Also, at the same relative position, the difference between $V(r)$ and V_{int} increases as the grain size decreases.

In the presence of space charge, the creep rate is modified by multiplying a factor, □. The earlier and the present solutions for □ as functions of grain size are shown in Fig. 2(a) at different temperatures. The difference between these two solutions for □ increases with the decrease in the grain size. Also, while the earlier solution shows that □ is insensitive to the grain size only when the grain size is sufficiently large, our solution shows that □ is insensitive to the grain size when the grain size is either sufficiently large or extremely small (e.g., R approaches l). The grain size exponents, p, as functions of the grain size are shown in Fig. 2(b). The earlier solution shows that p is –2 when the grain size is sufficiently large and increases with decreasing grain size; however, our solution shows that p increases to a maximum and then decrease rapidly back to –2 at $R = l$. Some experimental data for YTZP are also included in Fig. 2(b) for comparison. While the data agree with predictions in general, the difference between earlier and our predictions is significant when the grain size is less than 50 nm. Creep measurements for grain sizes < 50 nm is required to validate our predictions.

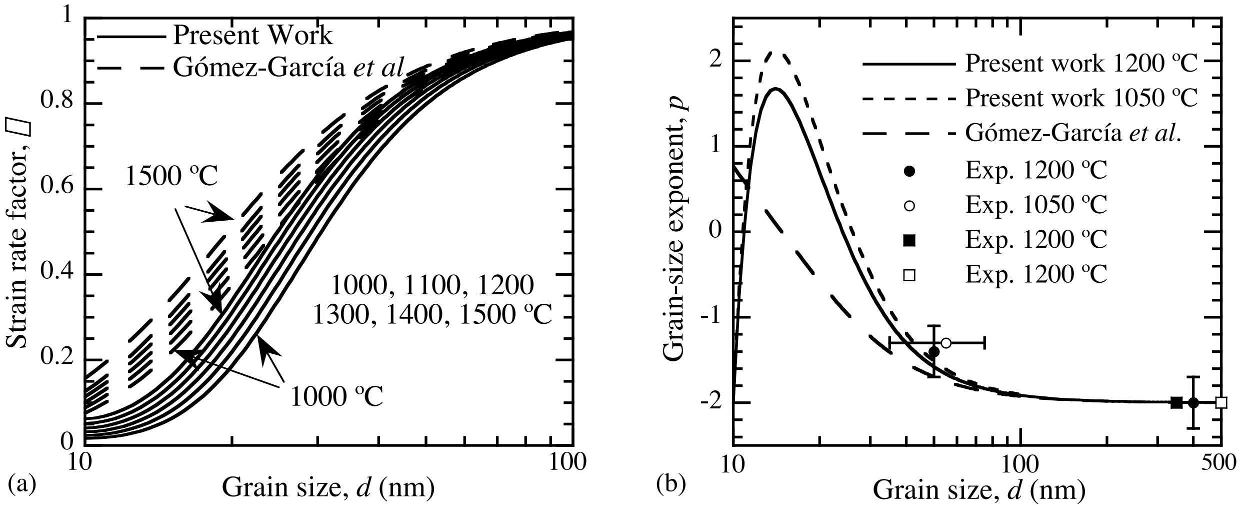

Fig. 2. (a) The creep rate modification factor, □, as a function of grain size at temperatures, 1000, 1100, 1200, 1300, 1400, and 1500 ºC showing the comparison between earlier and our results. (b) The grain size exponent, p, as a function of grain size.

Future Plans

Conventional uniaxial creep tests are generally performed to characterize the superplastic behavior of nanocrystalline ceramics. However, nanocrystalline ceramics are often limited to a few millimeters in dimensions because of processing difficulties. Also, many uniaxial creep tests are required to collect a complete creep data set. Hence, it is imperative to establish an alternative test for use with small specimens and being able to perform multiple tests on a single specimen. The impression creep test, in which a flat-ended cylindrical indenter is loaded on the flat surface of a material, is a most attractive alternative as the indenter diameter can be scaled to test the desired sample size and/or the area of interest.[8] Also, its steady-state displacement rate has the same stress exponent and temperature dependences as the conventional uniaxial creep test.[8] In order to correlate the impression creep data to the uniaxial creep data, the finite element analysis (FEA) has been performed to establish a semi-empirical correlation for materials obeying power-law creep.[9] However, we found that using the existing semi-empirical correlation, the predicted uniaxial creep rate from the measured impression displacement rate is about 2.6 times of its theoretical value for viscous materials (i.e., stress exponent $n = 1$). This discrepancy could result from the fact that the existing semi-empirical correlation was based on FEA for $n \geq 2$. Here, we plan to obtain an accurate correlation by (i) deriving the closed-form solution for a special case of viscoelastic materials (i.e., $n = 1$) subjected to impression creep tests and (ii) simulating impression creep tests for materials obeying power-law creep with $n \geq 1$. While the result obtained from analytical modeling serves as a checkpoint for FEA, the results obtained from the FEA will be used to obtain the accurate correlation. Completion of this work would enable researchers to accurately characterize superplasticity of nanocrystalline ceramics using impression creep tests.

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Interfaces at High Temperature: From Basic Studies to Materials Fabrication

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Scope of the work

Interfacial adhesion and atomic kinetics at high temperatures play a determining role in many modern technologies, from brazing and soldering to composites and thin films. Experiments involving high-temperature liquids are frequently the only available probe to measure the fundamental physical parameters (work of adhesion, interfacial diffusivity, etc.) that control the mechanical behavior of these interfaces and their formation and evolution. In this work, a comprehensive approach that combines analysis of macroscopic and microscopic phenomena, such as liquid spreading or capillary driven mass transport with interfacial characterization down to the atomic level, is used to study interfacial bonding and dynamics. The results are used in the fabrication of novel composites with unprecedented mechanical responses, achieved through a hierarchical material structure from the nano to the meso levels similar to those found in natural materials such as nacre or bone.

Recent Progress

Basic studies of spreading and characterization of interfaces (Saiz & Tomsia, *Nature Materials*, 2004, Lopez-Esteban *et al.*, *Langmuir*, 2005). The forces driving high-temperature spreading and the mechanisms controlling its kinetics are poorly understood. The unsolved challenge is to link macroscopic properties, such as the dynamic contact angle or the speed of the liquid front, to phenomena occurring at the microscopic and even atomic level in the vicinity of the triple solid-liquid-vapor junction. We have developed a unique experimental set-up that allows the manipulation of small liquid drops at high temperature under controlled atmospheres. Processes such as spreading, capillary rise etc can be recorded using high speed photography and examined using computerized image analysis.

In our approach, the spreading process is divided into its constituent steps (fluid flow, adsorption of reactive element, nucleation of the reaction product, and ridging). The structure and composition of the triple junction at each stage is analyzed to identify which step drives spreading and which process controls kinetics. In the non-reactive case spreading is controlled by local energy dissipation at the triple junction (the friction of the triple line). It can be described using a molecular-kinetic model in which atoms from the liquid displace those from the gas at adsorption sites on the solid surface (Fig. 1). The calculated distances between adsorption sites are of the order of interatomic spacings. The spreading activation energies vary between ~300 kJ/mol for silicate glasses (suggesting that the main contribution comes from the liquid/liquid interactions) and ~100 kJ/mol for liquid metals (implying that here the main contribution comes from the solid/liquid interaction). Experiments with metal-metal systems with increased solubility therefore representing a reactive system (e.g. lead-free solders) show similar kinetics. This means that similar mechanisms control the movement of the liquid front in the case of reactive systems, where the driving forces are defined in terms of “non-equilibrium interfacial energies” associated with the unreacted interfaces.

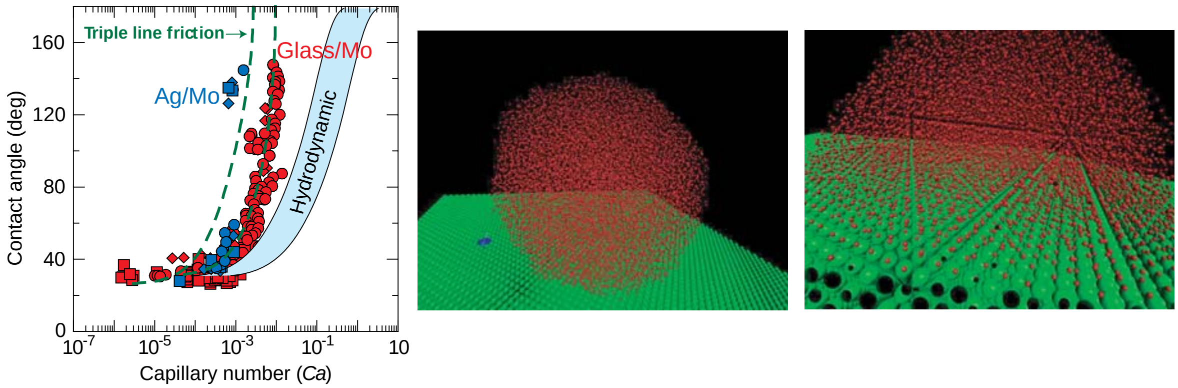

Figure 1. *Plots of capillary number vs. dynamic contact angle for non-reactive high temperature systems (left) ($Ca = \eta v/\gamma_{lv}$, η is the liquid viscosity, γ_{lv} its surface tension and v is the velocity of the liquid front). Despite the fact that the spreading of a small metal drop occurs in milliseconds and molten oxides typically spread in minutes (as expected from the difference in viscosity) the normalized velocities for the liquid metal and the molten oxide are very similar. Spreading is much slower than expected from hydrodynamic models (blue area) that assume that viscous impedance is the main source of dissipation during spreading. The data can be analyzed using a molecular kinetic model where the velocity of the liquid front is controlled by the triple line friction. Physical parameters obtained from the experiments and from molecular dynamics simulations of the spreading of nano-sized metallic drops (right) are in good agreement.*

The spreading analysis was combined with interfacial characterization down to the atomic level. Our initial experiments in model metal/ceramic systems revealed how the interfacial transport rates and anisotropy depend on oxygen adsorption. More recently experiments with lead-free solders on ceramics have shown how adsorption of “active” elements (such as Ti) at the metal/ceramic interface can accelerate atomic transport at the interfaces and enhance spreading and adhesion without the formation of new interfacial phases, which was previously assumed.

Biomimetic Composites (Deville *et al*., *Science*, 2006). The unique properties of natural layered materials such as nacre are achieved through a fine control of the layer thickness, selection of the right components, and manipulation of roughness and adhesion at the organic-inorganic interface. We have developed a novel process to build densly layered composites whose microstructure resemble that of nacre at several length scales.

Homogeneous, layered, porous ceramic scaffolds with controlled layer thickness are built by the directional freezing of concentrated ceramic suspensions. The freezing conditions are designed such that the growing ice has a lamellar microstructure and the ceramic particles concentrate in the space between the ice crystals. Increasing the freezing rate results in finer lamellae without affecting the long range order of the entire structure. Sublimation of the ice yields a scaffold whose architecture is a negative replica of the ice. In this way, we have achieved structures with layer thicknesses that can vary over two decades, from 1 µm (similar to nacre typically ~0.5 □m) to 200 µm. The scaffolds obtained by this process exhibit striking similarities with the meso- and microstructure of the inorganic component of nacre. The layers are parallel to each other and homogeneous throughout the entire sample. Particles trapped in between the ice dendrites lead to a dendritic surface roughness of the walls, just as in nacre. Finally, some dendrites span the channels between the lamellae, mimicking the tiny inorganic bridges linking the inorganic platelets of nacre, which are believed to increase the fracture resistance.

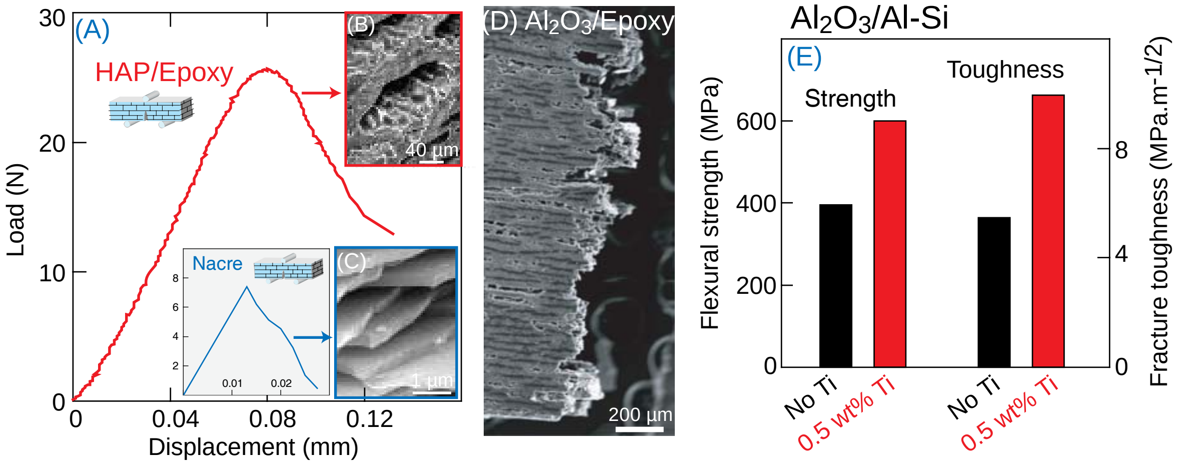

Figure 2. Mechanical response of natural and synthetic composites. *The 3-points bending load-displacement data for hydroxyapatite (HAP)/epoxy composites (A) was qualitatively very similar to that of nacre (C), with a gradually decreasing load after the elastic limit, characteristic of a stable crack propagation and active toughening, for cracks propagating in the direction perpendicular to the inorganic layers. Scanning electron micrographs of the composites (B) and nacre of abalone shell (C) reveal similar features on the fracture surface, with mode I cracks moving away from the notch and deflecting at the lamellae. Extensive crack deflection at the organic/inorganic interface results in tortuous crack paths and contributes to the toughening in both cases (as can be observed for the alumina/epoxy composite in D). The role of the interfacial chemistry, in the bonding between layers and the final mechanical properties of the material, is illustrated in the data shown in (E) for alumina/Al-Si composites (45/55 vol%), the addition of 0.5 wt% titanium to the aluminium alloy significantly increases the strength and toughness of the materials.*

The highly specific properties or nacre (in particular its large toughness) are due to the interaction of its organic and inorganic components. Similar synthetic materials can be prepared by filling the porous ceramic scaffolds with a second organic or metallic phase (Fig. 2). Nature shows that the optimum fracture properties are encountered not only when the organic/inorganic interface is strong, but also when delamination at the organic/inorganic interface occurs before the crack goes across the stiff, brittle layer. It is believed that nature manipulates adhesion in two ways mechanical and chemical. In nacre, this is done by controlling the roughness and the highly specific properties of the polymer adhesive phase. Using the results of our basic studies we can design the composition of the liquid phase to obtain complete infiltration and optimum interfacial adhesion. In this way, our process allows us to control the morphology and the chemistry of the interface. For example, by adding as little as 0.5 wt.% Ti (whose segregation at metal/ceramic interfaces we have observed) to the aluminium eutectic, the strength of Al_2O_3/Al-Si layered composites (60/40 vol.%) can be increased from 400 to 600 MPa and the fracture toughness from 5.5 to 10 MPa□m.

Concluding remarks and future work

Our studies have shown how a wealth of information regarding adhesion and evolution of interfaces can be obtained by combining the analysis of high-temperature capillary driven phenomena with state of the art characterization. In the future, the experimental analysis will be extended to include atmosphere effects and systems with increased reactivity in parallel with theoretical studies and computer simulations. A crucial challenge is to marry atomistic and continuum models in such a way as to improve our understanding of micro-and macroscopic phenomena. One of the goals is to formulate a generalized model for the spreading of high-temperature liquids necessary for the development of new technologies with smaller relevant dimensions that will require accurate flow control. This work is relevant to the mechanics community in two ways: it provides basic information on the adhesion and evolution of interfaces between dissimilar materials and shows that the movement of a liquid front has strong physical parallels with that of a crack tip. Thus lessons learned in one case can be applied to the other.

The aim of our research is to control materials at the atomic and molecular level for tailor-made strong, tough and lightweight composites. Recent successes in the manufacture of novel materials based on natural structures and processes encourage us to pursue this biomimetic route further. The better we understand nature's hierarchical structures and design rules, the more we will be able to emulate and to translate them into nonbiological applications. The mesostructure of natural materials, for example, often determines to a large extent their mechanical response. Our results indicate that the freezing process can be controlled so precisely that mesostructural features and gradients can be built. We strongly believe that this combined approach will open the way for the development of new materials with a tailor-made mechanical responses.

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Computing the Mobility of Grain Boundaries

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Many modern technical materials are designed and manufactured by controlling the evolution of the microstructure. Most of the solid-state microstructure transformations, like recrystallization, grain growth, phase transformation or precipitation, involve the motion of grain boundaries. Grain boundary motion is a product of the driving pressure and the mobility of the grain boundary. The mobility of a solid-state grain or phase boundary is determined by the atomistic mechanisms by which the boundary moves. While uncertainty remains about the exact nature of these mechanisms, it is generally accepted that mobility strongly depends on the crystallographic misorientation between neighboring grains. Current experimental and simulation methods cannot determine the mobility of flat boundaries across the large misorientation phase space. We have developed a new, molecular dynamics method for imposing an artificial driving force on boundaries. This allows us to induce motion in flat boundaries of arbitrary misorientation using considerably smaller systems and shorter times than previously attainable. For different series of boundaries, we find both expected results and unexpected results. Details may be found in K. G. F. Janssens, D. Olmsted, E. A. Holm, S. M. Foiles, S. J. Plimpton and P. M. Derlet, “Computing the Mobility of Grain Boundaries,” Nature Materials, advance online publication, 08 Jan 2006, doi:10.1038/nmat1559.

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Semi-Automated EBSD-based Twin Analysis and Coupled EBSD/TEM Analysis of Zirconium Deformation Mechanisms

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The contribution of twinning to the plastic deformation of hexagonal materials is extremely important. As a consequence, there is a substantial effort in our BES program (focused on hexagonal materials) to characterize twinning from a basic perspective. By working with several materials having different textures, and deforming under different conditions, we have built a robust experimental basis for developing constitutive laws of HCP aggregates. An important component of our project is the microscopic characterization of the microstructure in the deformed material. At temperatures between 76 K and 300 K, up to three twinning and two slip mechanisms can contribute to the deformation of zirconium. A semi-automated EBSD based method is being used to quantitatively analyze the contribution of the three twinning modes as a function of accumulated strain. Measurements made with this method indicate an important contribution from secondary twinning (twins within twins). Bulk texture measurements done by neutron diffraction provide valuable information but fail to identify secondary twins, which are a required piece of information in the development of crystal based constitutive laws. For observing dislocation contributions to deformation, a procedure coupling EBSD and TEM analysis on the same sample is being used. This procedure allows for straightforward determination of orientations favorable for slip (including within deformation twins) and provides information on the type of slip systems active within them.

Characterizing the Hardening Response of Zirconium

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Twinning provides an important contribution to the plastic deformation of hexagonal materials. As a consequence, there is a substantial effort in our BES program (focused on hexagonal materials) to characterize twinning from a basic perspective. In this work, we analyze the role that twin barriers play on the propagation of dislocations in clock-rolled Zr. Our aim is to understand how the interaction between twinning and slip affects the hardening response. Compression samples were deformed at liquid nitrogen temperature (76K) along the through-thickness and the in-plane direction of the plate to create compressive or tensile twins, respectively. The same samples were reloaded at room temperature and large differences in stress-strain response were observed with respect to samples loaded at room temperature from the beginning. Mechanical tests were complemented with texture analysis by neutron diffraction and OIM, and also by polycrystal modeling. We show that twins influence the reload behavior by either reorienting material for easy slip or by providing barriers to slip.

In order to isolate the twin contribution to hardening, a second experiment consisted in annealing the preload samples to recover the dislocations while preserving the twins. In order to guarantee such condition the texture of the preload samples was measured in-situ using neutron diffraction as a function of the temperature. This procedure indicates that above 500 C the texture starts to change as a consequence of twins being annealed. As a consequence, samples pre-loaded at liquid nitrogen were heat treated at 450 C and reloaded at room temperature. Only small differences in the stress-strain response were observed by comparison with non heat treated samples. The latter results points to twins, rather than dislocations, as being responsible for the measured reload response.

Using Elastic Strain to Self Assemble (Potentially) Functional Nanostructures

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Scope:

While research efforts in nanomechanics often focus on the unique elastoplastic responses associated with nanoscale volumes, our work emphasizes the use of very large elastic strains (up to 4%) to actually create nanoscale volumes. Specifically, we use lattice-mismatched heteroepitaxial growth of SiGe on Si substrates to form coherent islands, aka *quantum dots*. Heteroepitaxial quantum dots form as a specific means to relax the misfit strain via the surface-diffusion-mediated 2D-3D transition. Quantum dots are interesting since their bandstructure and electronic properties are size-dependent and therefore tunable; the dot size is determined in principle by the magnitude of the strain, but in practice also depends sensitively on the rate-controlling kinetic processes.

Recent Results:

Our recent work has focused on the self-assembly of complex structures that go beyond simple arrays of individual, randomly-formed quantum dots. We manipulate the growth kinetics to partially retard the collective strain-driven surface roughening instability. In the right kinetic parameter "window", this results in the formation of localized strain-relieving pits (quantum anti-dots) in the otherwise planar SiGe wetting layer, instead of islands. This seemingly small difference turns out to have significant implications for subsequent strain-driven surface morphological evolution. With continued deposition, the pits facet with four-fold symmetry, and material ejected from the pits preferentially nucleates alongside the pit edges. This results in the formation of a symmetric arrangement of four quantum dots in a cloverleaf pattern. Since these dots (which would normally repel one another through the elastic fields in the wetting layer) are elastically bound by the central pit, we refer to the structure as a *quantum dot molecule* (QDM). If, instead of depositing more material, the pits are annealed, we promote a 1D instability that forms long, faceted grooves in the wetting layer, with long, wire-like islands alongside. These structures exhibit the highest shape anisotropy observed in this material system. With additional growth on this structure, we end up simultaneously self-assembling both compact QDMs and highly ramified quantum wires.

The QDM is a candidate structure for the nanologic architecture known as quantum cellular automata. For QDMs to be useful as logic elements, we must reduce their size, be able to position them arbitrarily, and be able to confine carriers within them. We have had some success in reducing QDM size by increasing strain (Ge content of the film), but this needs to be pushed further. QDMs can be positioned precisely into both periodic and aperiodic arrays using pre-patterning of the substrate with a focused ion beam (see the Figure 1). Recent x-ray anomalous scattering results also suggest that there is a significant redistribution of Ge within the QDM, which could confine carriers, but the exact spatial distribution has not been determined yet.

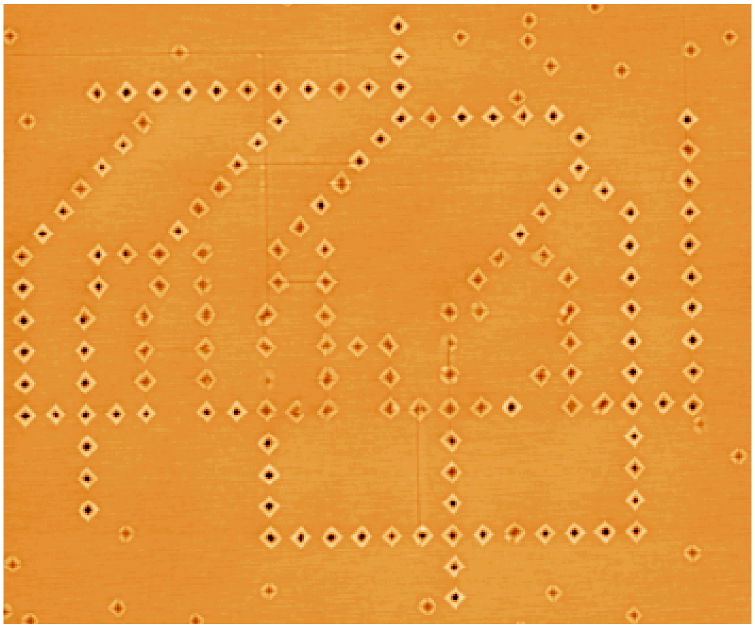

Figure 1: An array of QDMs formed on an FIB pattern representing an adder circuit in the quantum cellular automata architecture. Randomly nucleated QDMS are also observed outside the pattern. This demonstrates an ability to place QDMs in arbitrary, aperiodic patterns.

Future Directions

We will focus on understanding how focused ion bombardment creates preferred nucleation sites for pits, and how this process can be optimized. Understanding the nature and kinetic origins of Ge redistribution within QDMs is also of prime importance, and should provide a great deal of insight into the formation of these novel structures.

Relevant DOE/BES-Sponsored Publications

X-RAY DIFFRACTION MAPPING OF STRAIN FIELDS AND CHEMICAL COMPOSITION OF SIGE:SI (001) QUANTUM DOT MOLECULES, M. S. Leite, J. L. Gray, R. Hull, J. A. Floro, R. Magalhaes-Paniago, and G. Medeiros-Ribeiro, submitted to *Phys. Rev. B* (2005).

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Dissipation and Collective Phenomena in Coupled Mechanical Systems

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Program Scope:

Micro- to nanoscale mechanical oscillators are the keystone to many breakthroughs in nanoscience, such as single electron spin detection using magnetic resonance force microscopy [1] or nanoscale displacement measurement using a nanoscale oscillator coupled to a single electron transistor [2]. It is critical that these micro- and nanoscale oscillators exhibit low internal dissipation in order to provide useful function. Unfortunately, our understanding of internal dissipation in small mechanical structures is limited. The objective of this project is to determine the fundamental mechanisms of energy dissipation in nanoscale structures through experiments on coupled nanoscale oscillators and theoretical calculations of atomic-scale dissipation mechanisms. This research will lead to an understanding of dissipation mechanisms in nanoscale structures and materials having internal structure at the nanometer or less length scale (i.e. nanostructured and amorphous materials).

Our approach combines experiments involving the measurement of dissipation in micro-scale to nanoscale oscillators with theoretical calculations aimed at identifying the atomic mechanisms that lead to dissipation. The experimental approach includes the development and fabrication of sensitive resonator structures displaying flexural and torsional oscillatory modes, measurement of oscillator performance in vacuum as a function of temperature and oscillator geometry, and the creation and measurement of a nanomechanical system consisting of a coupled, two-dimensional oscillator array having a large number of oscillator elements (more than several thousand). The coupled oscillator arrays have an advantage over individual oscillators in that their mechanical resonance modes are easy to detect even at low temperatures, where dissipation due to tunneling states and ballistic phonon transport are important. These arrays are also expected to exhibit interesting collective behavior, due to fluctuations in element dissipation factors and resonant frequencies. To interpret our measurements, a new theoretical approach is being developed to understand the defect-related dissipation mechanisms at the atomic scale. The approach involves molecular dynamics of a small crystal resonator (hundreds to thousands of atoms) that possesses a well-defined atomic defect that has a strain field which couples to the main vibrational mode of the crystal. Mechanical dissipation is observed by following the ring-down in vibration amplitude of the crystal. This study will provide a detailed view of defect-related dissipation processes in nanoscale oscillators.

Recent Progress/Future Directions:

In this newly-established project, the initial research has focused on fundamental studies of mechanical dissipation mechanisms in amorphous and polycrystalline diamond films. Diamond-type materials are attractive for dissipation studies due to the lack of a surface oxide on the resonator surface, the presence of which has been implicated as a dominant dissipation mechanism in silicon-based resonators [3]. Our prior work has shown that mechanical dissipation in amorphous and polycrystalline diamond thin films is controlled by defect-related dissipation mechanisms: the defect couples to the oscillatory strain field, and energy is dissipated as the defect transits between two (or more) energetically degenerate configurations [4, 5]. This dissipation process can be described by a Debye relaxation process with a characteristic defect relaxation time, τ, that is thermally activated. In this work, mechanical resonators were fabricated in amorphous diamond-like carbon films in order to study the temperature dependence of mechanical dissipation under flexural and torsional stress conditions (see Figure 1) [6]. The quality factor of the resonators was observed to decrease continuously from a value of approximately 4×10^3 at room temperature to a value of a few hundred at measurement temperatures exceeding 1000 K. Assuming a Debye-like relaxation for each dissipative defect in this material, the activation energies for these defect relaxation processes may be identified (see Figure 2). We find that the material displays a broad range of defects that gives rise to mechanical relaxation, with an increasing concentration of defects as the activation energy increases from 0.4 eV to over 1.8 eV. There is a slight difference in defect distribution depending on stress state of the resonator (torsion vs. flexure), indicating that the strain field of the defect interacts differently with these two oscillatory strain fields.

Our initial work on polycrystalline diamond resonators (see Figure 3) also shows strong defect-related mechanical dissipation [7]. A peak in the mechanical dissipation at about 673 K was found for doped polycrystalline diamond films, whereas undoped polycrystalline diamond films did not exhibit a peak. This suggests the existence of a boron-related defect in polycrystalline diamond that acts to promote mechanical dissipation. The atomic nature of this defect remains to be identified.

In order to study coupled oscillator physics, a two-dimensional array of coupled oscillators was designed and fabricated. The design consists of a 100 × 100 array of oscillator elements, wherein the oscillator is defined as a node in a grid fabricated from amorphous diamond-like carbon having a tungsten proof mass on top (see Figure 4). The grid lines were patterned to be 500 nm wide using e-beam lithography, while the tungsten (~ 1 μm × 1 μm) was defined using a separate e-beam lithography step. These oscillator arrays exhibit vibrational modes similar to drumhead modes of a stretched membrane. Resonance testing of the arrays revealed a series of resonance peaks, where the lowest frequency peaks were in reasonable agreement with a modal analysis of the simulated array using finite element modeling.

After characterization of the ideal arrays, one of the future areas of research in this project is to create coupled systems where the onset of disorder-induced localization may be observed. Previous studies on 1-D macroscopic coupled oscillator systems have shown that positional disorder is a stronger driver for localization than mass disorder [8]. Our future work in this project is to achieve experimental realization of this disorder-induced localization in two-dimensional oscillator arrays that have been fabricated to contain an intentional defect or defective area. This would represent significant progress in understanding coupled mechanical systems containing disorder.

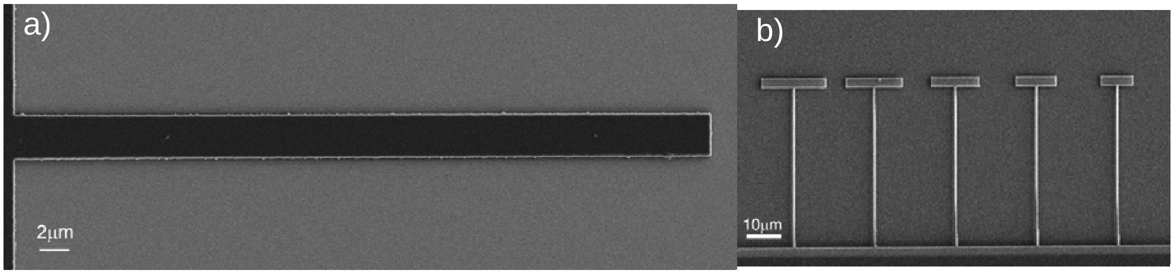

Figure 1. (a) Flexural (cantilever-type) and (b) torsional resonators fabricated out of amorphous diamond-like carbon.

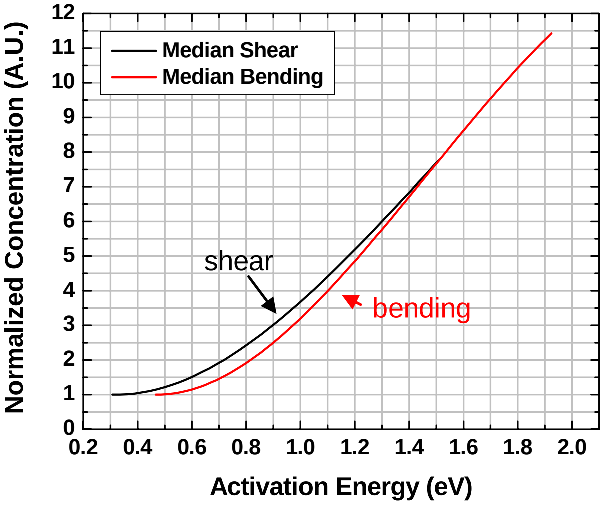

Figure 2. Measured activation energies for mechanically-dissipative defect relaxation processes in amorphous diamond-like carbon.

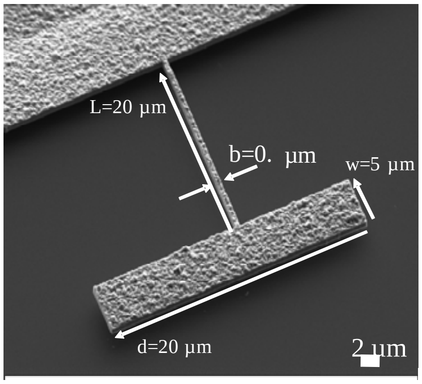

Figure 3. Torsional resonator fabricated out of polycrystalline diamond.

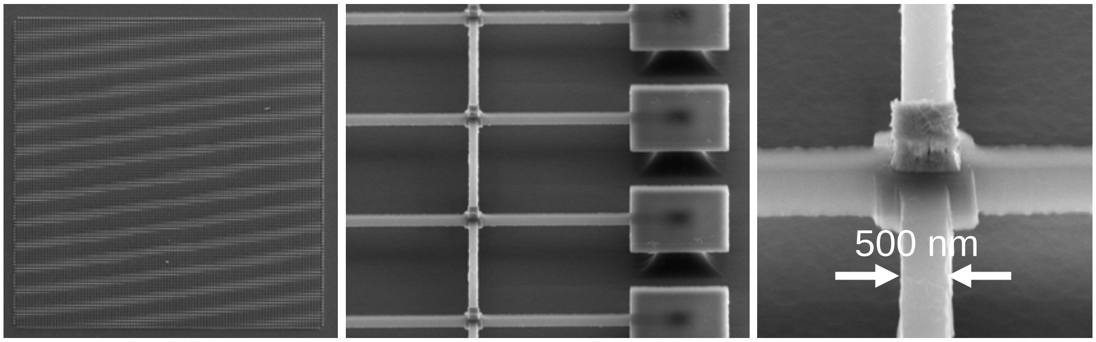

Figure 4. A large coupled oscillator array: (left) the complete 100 × 100 array, (middle) close-up of array edge, and (right) a single element.

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"Temperature dependence of the mechanical properties of tetrahedrally coordinated amorphous carbon thin films," D. A. Czaplewski, J. P. Sullivan, T. A. Friedmann, and J. R. Wendt, Appl. Phys. Lett. **87**, 161915 (2005).

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"High Performance Polycrystalline Diamond Micro and Nano Resonators," N. Sepúlveda, D. M. Aslam, and J. P. Sullivan, submitted to J. MEMS (2006).

Synthesis and Single Molecule Studies of Titin-Mimicking Modular Polymers

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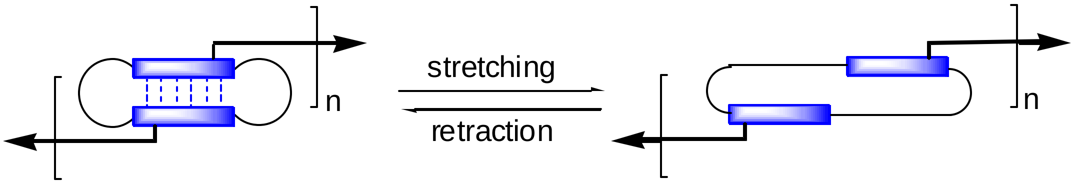

Nature had evolved well-defined supramolecular materials with exceptional properties. The giant muscle protein titin is one of the most studied biopolymers. Recent single molecule nanomechanical studies on titin propose that these exceptional properties arise from a modular elongation mechanism. This unique molecular mechanism allows modular biopolymers to sustain a large force over the extension of the molecule making it both strong and tough, properties that are difficult to combine into a synthetic polymer system. The design of synthetic modular polymers that mimic titin is an ongoing project in our laboratory. We first demonstrated this concept by incorporating UPy units into urethane polymers. We are currently working on peptidomimetic ß-sheet modular polymers in the pursuit of advanced materials.

SESSION V:

MICROSTRUCTURAL EFFECTS ON MECHANICAL BEHAVIOR

Chair: C. T. Liu (Univ. of Tennessee)

Correlating dislocation behavior with macroscopic mechanical properties directly in the TEM through use of a novel tensile test device.

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Studies of dislocation type and distribution following loading has been a standard application of transmission electron microscopy since they were first introduced. Determining how the dislocation microstructure evolves and how to relate it to the macroscopic property requires envisioning the processes and pathways by which the dislocation arrangements evolve and then correlating it with the measured macroscopic property. To gain insight to dislocation reactions and interactions, one possibility is to modify a TEM holder to permit a sample to be deformed while it is being observed. Experiments with such stages have provided considerable insight to dislocations interactions with obstacles and the evolution of microstructure under quasi-static test conditions over a wide temperature range. However, the wedge-shaped sample geometry and the limitation of the stages preclude the direct connection of the microscopic processes with the macroscopic response. Nevertheless, as the following examples demonstrate, new insight to dislocation-defect processes can be made using these conventional stages and samples with complex geometries.

The deformation processes responsible for the dynamic recrystallization during superplastic forming of a material direct from the unrecrystallized state is not well understood. By redeforming interrupted specimens of a superplastic Al-4Mg-0.3Sc alloy at nominally the superplastic forming temperature insight to the processes responsible for the microstructural evolution have been obtained.[1] The series of video-frame images presented in figure 1 show the disintegration of a triple junction due to the accommodation of glissile dislocations released by the dissolution of a sub-grain boundary (not shown) and the accompanying large volume rotation to a common orientation. The glissile dislocations move in grain 1 toward the grain boundary between grains 1 and 2. They are fully accommodated in this boundary with no transmission through it. Correspondingly, there is a considerable increase in the strain energy of the grain boundary, which subsequently results in the breakup of the triple junction as shown in the series of images. The volume rotation is apparent from the change in contrast behind the sliding boundary between grains 2 and 3. This was the first experimental observation of such a process occurring at high temperatures and can account for the randomization of grain orientations that are observed in bulk samples.

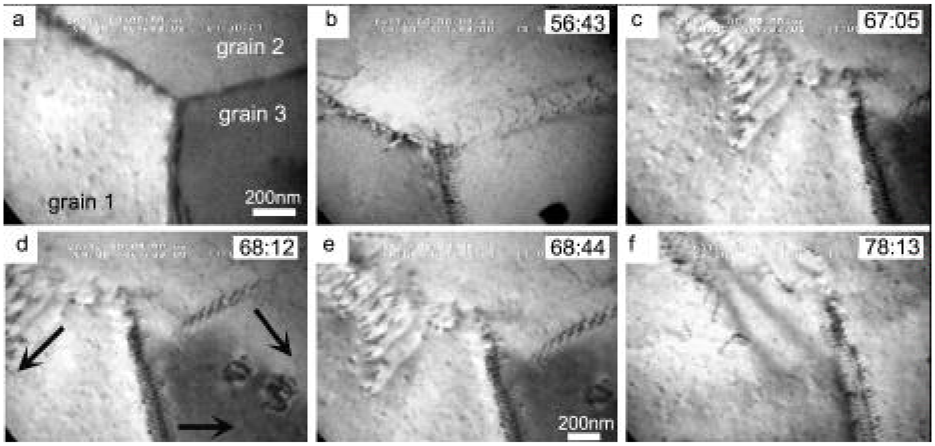

Figure 1. Distintegration of a grain boundary triple junction and the accompanying large-scale volume rotation.[1] The arrows indicate the direction of motion of the subgrain boundaries. Times are in minutes and seconds. Nominal temperature 673K. Time is in minutes and seconds.

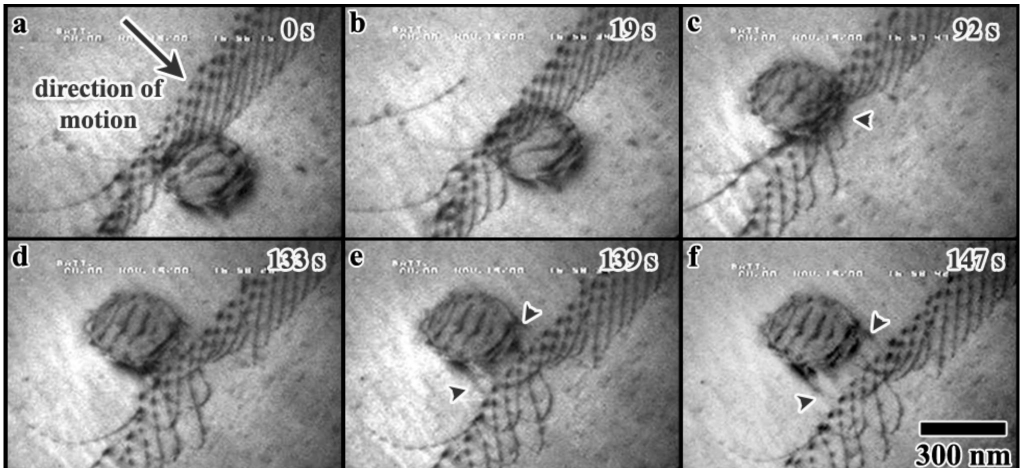

Figure 2. Interaction of an array of edge dislocations with an Al$_3$Sc particle at 673K. Note the change in interface contrast as the dislocations interact with and leave the particle. [2]

The interaction of mobile grain boundaries and isolated dislocations play important roles in several high temperature mechanical properties but models based on basic interactions fail to capture the details of the macroscopic properties. This can be attributed to the simplified interactions used as the basis for the models. An example of the complexity of the interaction is shown in the series of images presented in Figure 2.[2] These were captured from videotape and show the interaction of a glissile low-angle tilt boundary interacting with a large Al$_3$Sc particle at a nominal temperature of 673K. Several of the dislocations interact with the particle and the orientation is such that the interactions of individual dislocations with the precipitate are discernable. Changes in interfacial contrast, compare Figure 2a with Figure 2f, suggest that the dislocations are actively interacting with the interfacial dislocations during the bypass process – this is very different from the normal bypass processes which keep the lattice dislocations isolated from the interfacial dislocations. In Figure 2c, the dislocations interacting with the particle appear pinned, while the rest of the dislocations in the non-interacting segments are still mobile. As the array moves beyond the particle, the interacting dislocations become curved showing that a portion is still in contact with the particle, see Figures 2c-f. This could be because they are either strongly attracted to the precipitate or because their interaction with the interfacial dislocations have temporarily pinned them to the interface. Some of these dislocations break free due to interaction with the sample surface, see Figures 2e and 2f, allowing them to resume their previous configuration in the array. However, in Figure 2f some dislocations are still pinned to the precipitate and they trail behind the rest of the array. This structure of dislocations extending from the grain boundary back to the particle is similar to those observed in post-mortem analysis of bulk deformed material. The altered particle contrast, as a result of the interaction, includes a rotation of the fringes as the dislocations bypass, indicating a change in interfacial strain. The velocity of this dislocation array decreases from 4.6 nm s^{-1} to 4.2 nm s^{-1} during the interaction and subsequently increases to 4.7 nm s^{-1} after it breaks free.

The exposure of materials to irradiation results in a loss of ductility, an increase in strength and can, even in FCC metals, produce what appears as a distinct yield point. Post-mortem examination of the microstructure shows the presence of bands free of irradiation defects. There has been considerable debate about the formation of these bands and the mechanisms by which the interacting dislocations annihilate the irradiation defects. By using a combination of molecular dynamics computer simulations and the *in situ* TEM deformation technique we have been able to gain insight to the defect annihilation mechanisms and the formation of the channels.[3,4] Significant findings related to channel formation include the identification of grain boundaries and sites of stress concentration as sources of the dislocations responsible for creating the channels; the obstacle strength is not constant for a specific defect type but it depends on the geometry of the interaction; the nature of the dislocation determines the efficiency of defect annihilation, with screw dislocations being more effective than edge dislocations; and

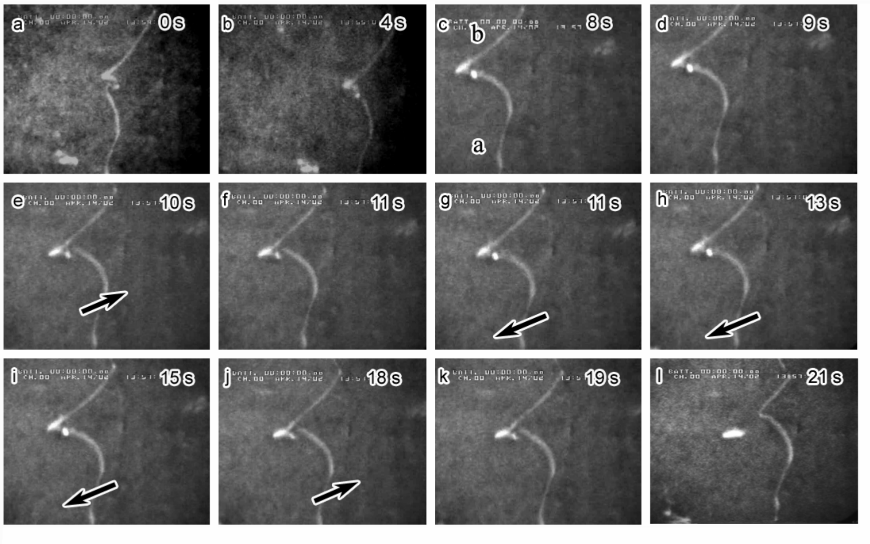

Figure 3. Weak-beam dark-field images showing the interaction of a dislocation with a stacking fault tetrahedron in copper. The arrows indicate the direction of motion of the dislocation, and the letters the dislocation segments on either side of the stacking fault tetrahedron.

a single interaction event is often insufficient to annihilate a defect although it can convert it from one type to another, demonstrating that the defect population evolves with increasing strain. This latter process is seen in the series of images presented in figure 3, which shows a dislocation interacting with a stacking-fault tetrahedron and the conversion of the tetrahedron to a perfect glissile loop. It is interesting to note that the dislocation oscillates back and forth, lacking the inertia to complete the interaction. Using the insights gained from these experiments a continuum model has been developed that captures all of the essential features of the macroscopic stress-strain curve.

The previous interactions were performed using conventional heating straining stages, with no capability to measure the applied load or displacement and therefore correlation with macroscopic properties was not possible. Recently, there have been numerous attempts to fabricate a mechanical test system using microlithographic and MEMS technologies which permit the observation of mechanisms and concurrent measurement of the macroscopic properties. This approach is just emerging and a fully functional device has yet to be used successfully. An example of one such device is shown in Figs. 4a-b.[5,6] Although this device permits observation of the deformation processes and concurrent measurement of the macroscopic response, the device is loaded using a conventional displacement-controlled straining stage. The samples are deposited on a silicon wafer and produced as part of the device, which does introduce new restrictions. The sample has a uniform cross-sectional area, which removes the problem of the wedge-shaped geometry, it can be loaded in true uniaxial tension as the u-springs accommodate off-axis loads; and the sample geometry is amenable to modeling. Figure 4c-f show an application of this device in which the response of a 500 nm Al film was determined and the deformation processes observed. The stress-strain curve shows the same characteristics as curves generated from larger samples; namely an elastic region that is followed by a region of high-work hardening rate and then a region of decreased work-hardening rate. The failure is 30 degrees to the tensile axis and the deformation is confined to the region vicinal to the fracture surface although it does extend several hundreds of nanometers into the gage section. SEM examination of the fracture surface shows a knife-edge, which is consistent with the observed ductility.

Although improvements remain to be made and we need to learn how to conduct experiments with such devices they show what can be done now. It is not hard to imagine that future generations will include load cells capable of applying sufficient load to deform samples under different conditions, resistive heating mechanisms for elevated temperature studies, fatigue and even environmental studies

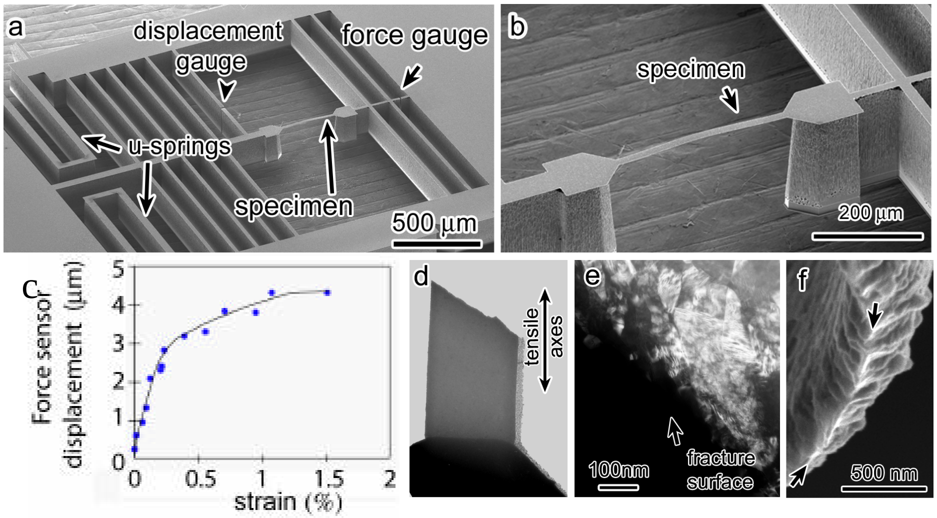

Figure 4. a) SEM image of fabricated device showing critical components, b) high magnification of the tensile sample, c) "stress"-strain curve for 500 nm Al film (force displacement is given instead of stress as the spring constant for converting displacement to stress was not determined. d) shear fracture, e) intense dislocation structure within the shear band, f) SEM image of the knife-edge fracture surface of 500nm thick Al.

etc. This last example shows what will be possible as we become more creative in the technologies employed to create fully functional miniaturized experimental modules for application in a transmission electron microscope.

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A multi-scale study of the role of microstructure in the deformation behavior of hexagonal materials

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MST Division - Los Alamos National Laboratory

Program Scope

The goal of this program is to provide fundamental insight into the mechanical response of hexagonal (HCP) materials, and to understand the role that crystallographic deformation mechanisms play in the mechanical response. Compared to cubic materials, HCP systems are less understood due to the variety of slip and twinning modes that they exhibit, and their complex interactions. Our research incorporates modeling and experimental studies at length scales that range from atomistic to continuum. It draws on a range of Los Alamos characterization and modeling capabilities and expertise, on various University collaborations, and on the unique neutron diffraction capabilities of the BES funded spectrometers SMARTS and HIPPO at the Los Alamos Lujan center. Our deliverables are: material models and constitutive laws for HCP aggregates at the atomistic, intergranular, and polycrystalline scales. The numerical and experimental tools developed, and the knowledge acquired through this program will be of general applicability to low-symmetry materials.

Motivation

Hexagonal metallic aggregates have wide ranging applications in nuclear (Zr), automotive (Mg), aeronautic (Ti) and defense and space (Be) technologies. They exhibit commonalities in their mechanical behavior during plastic deformation, with unique features not found in the 'simpler' cubic materials. The single most distinguishing feature is twinning: it affects anisotropy through inducing dramatic texture changes, and it affect hardening by posing barriers to the propagation of dislocations. Most of the existing constitutive laws pertinent to HCP alloys consist in empirical macroscopic descriptions applicable only to the narrow range of test conditions used in the fitting procedure. *The research associated with this program will bridge the crystallographic and continuum length scales by providing an understanding of the macroscopic response of HCP aggregates in terms of basic microscopic mechanisms.*

The following illustrates the challenge of the task ahead. Cubic aggregates deform by slip on {111} planes along the <110> direction (FCC), or slip on {110} planes along the <111> and <112> directions (BCC). The Critical Stress required to activate those systems can be safely assumed to be the same for all the systems. Hexagonals, on the other hand, may glide on basal, pyramidal or prismatic planes, with <a> type or <c+a> type Burgers vectors. In addition, HCP may exhibit up to two tensile twin modes and up to two compressive twin modes. The threshold stress required to activate each of these slip and twin systems is different from system to system, and from one material to another, and varies drastically with temperature, strain rate and accumulated deformation. Consequently, a comprehensive mechanical characterization that accounts for texture, temperature and rate effects is a daunting challenge and needs to be based on the actual crystallographic mechanisms of each material. For this reason, we specifically study Zr, Mg and Be, although the characterization and modeling techniques are applicable to any system.

Approach and Recent Progress

In this project we use load path changes in direction and temperature as a paradigm to reveal the role of microstructure in hardening. Such strategy consists in testing the materials along a given direction, at a given temperature and to a certain strain in order to induce a controlled dislocation and twin structure. Subsequently, the material is reloaded along a different direction and/or at a different temperature. The previous work done on FCC provided the team with the kind of synergy and techniques that are the basis of this project. Results of TEM and MD analysis were reported in Refs [1-4]; intragranular models accounting for grain subdivision, deformation banding, dislocation walls, path changes and layered materials were developed and reported in Refs. [5-9]. The ‘strain-path-change’ procedure is particularly revealing when dealing with twinning, because twins induced during the pre-load stage act as barriers to dislocations or to other twins during the reload stage. Take for example the compression curves of rolled Zr shown in Fig. 1 below, corresponding to liquid nitrogen deformation.

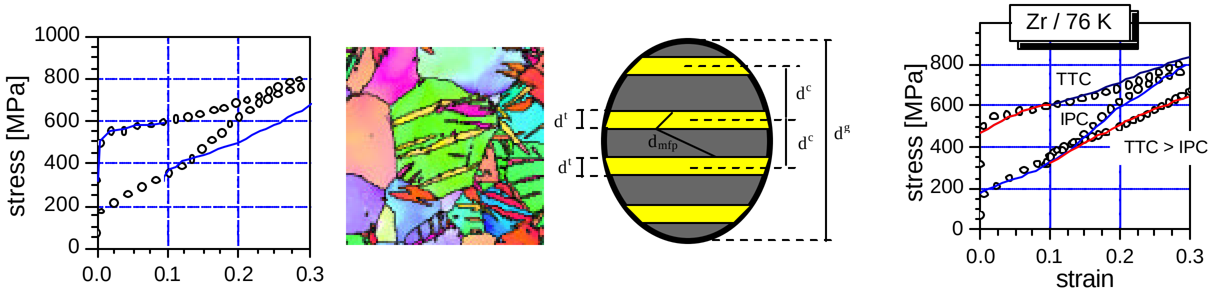

Figure 1: *Right frame:* Quasi-static compression curves of clock rolled Zr at 76 K. Open symbols: monotonic Through Thickness Compression (TTC) and monotonic In-Plane Compression (IPC). Blue solid line: 10% preload TTC followed by 20% reload IPC. *Center frames:* OIM after 10% TTC and schematic of Composite Grain (CG). *Right frame:* stress-strain response predicted using the CG and VPSC.

The anisotropy between Through Thickness Compression (TTC) and In Plane Compression (IPC) is a consequence of the texture. In particular, compressive twins are activated in the former case and tensile twins - together with prism slip - in the latter, with some contribution from pyramidal slip in both cases. The twinned structure after 10% TCC is apparent in the OIM picture. The increasing hardening rate (upward curvature) is characteristic of the increasing twin barriers. Observe that a reload in IPC after 10% TTC (blue curve) encounters the microstructure shown in Fig. 1 (center frame) and gives a very different response than the monotonic loading in IPC.

Since the dislocation-twin interaction plays a dominant role in shaping the response this program is paying particular attention to elucidating such interaction. The questions that we are trying to answer are several: how do twins nucleate and propagate? How do prismatic and pyramidal dislocations interact with twins? Can dislocations dissociate and propagate through the twin interface? Or are they stopped completely by twins? Is slip or twinning active inside twins? What kind of stress relaxation takes place in the matrix and inside the twin when twins are created? Do twins ‘de-twin’ upon load reversal? It is clear that our hardening models require not only a basic understanding of the above mechanisms, but also the implementation of associated numerical models ranging from the micro to the macro scale.

At the microscopic scale we are using a combination of atomistic simulations and experiments to answer these questions. We are developing Modified Embedded Atom Method (MEAM) potentials for use in molecular dynamics simulations to atomistically understand the dislocation-twin interaction and the dissociations occurring at the twin-matrix interfaces. The anisotropy of mechanical response in HCP metals strongly indicates the importance of angular forces in bonding. These forces are accounted in the MEAM model. The EAM model appears to be inadequate to study Zr as shown by the inability of all the current literature models to correctly predict the basal and prism stacking fault energies (200 and 145 mJ/m^2 respectively) [10,11].

On the experimental front, we are addressing these questions by performing in-situ deformation of samples in the TEM. TEM and OIM are used extensively to quantify volume fraction of twins and to correlate twins with grain orientations. A spin-off of this project has been improved automated image recognition software for the scanning microscope, and a technique for identifying regions of interest in samples using OIM and investigating them in detail using TEM. Figure 2 below illustrates this technique.

Since the inception of this project neutron diffraction (performed at the LANL Lujan Center) has been extensively used for characterization of Mg, Zr and Be [12-14]. The penetration power of neutrons allows

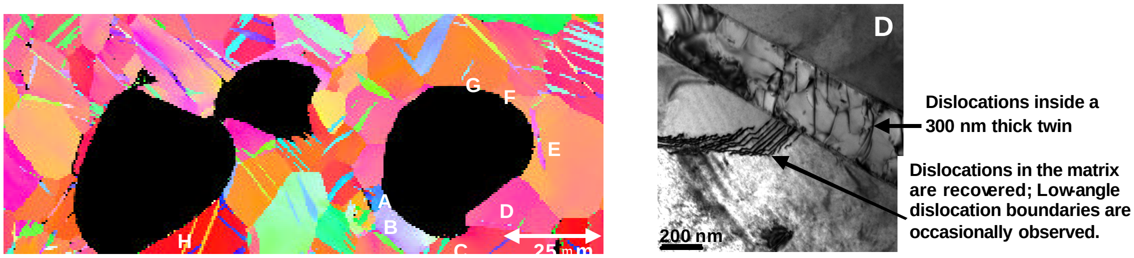

Figure 2: *Left frame:* OIM of rolled Zr deformed 10% in IPC, followed by a 450C anneal for ½ hr. *Right frame:* Bright field TEM image from within grain D containing a twin lamella and residual dislocations.

us to make ex-situ and in-situ measurements of texture and twin fraction evolution under strain and temperature variation in the HIPPO diffractometer. In addition, we use the high resolution SMARTS diffractometer for measuring in-situ evolution of internal strains during loading. The latter technique not only allows us to investigate in fine detail which slip and twin systems are activated and in which sequence, but also provides information about the required threshold stresses, the volume fraction reoriented by twinning, and the associated stress relaxation. These insights help us to develop and validate hardening models for dislocation-dislocation and dislocation-twin interaction.

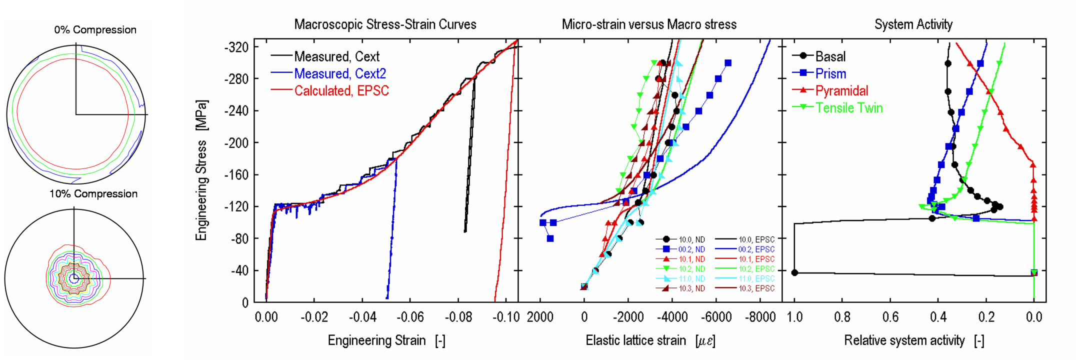

Figure 3: *Left frame:* Initial and final basal pole figures after 10% compression along the axis of extruded Mg bar. Notice dramatic reorientation of basal poles by twinning. *Right frame:* Comparison of experimental and simulated flow curves, internal stresses along the axial direction, and predicted deformation mechanism activities.

The example in Fig. 3 depicts microstrain evolution vs macroscopic stress for several crystallographic orientations, obtained from compressing a previously extruded Mg bar. When measurements are interpreted using the elasto-plastic polycrystal model discussed below, one finds that, in addition to the ubiquitous basal slip and tensile twinning, a certain amount of uncommon (for Mg) prism slip is required at large stresses. In what concerns the stress state in the newly formed twins, the purple points associated with (00.2) planes show that the stress relaxation associated with twinning is so strong as to reverse the sign of the stress inside the affected grains. These results and the polycrystal approach used for interpretation are completely novel.

The insight gained through MD, TEM, OIM and neutron diffraction is used to develop **meso-scale models of the grain.** While traditionally polycrystal models treat the grain as a homogeneous entity, here we treat it as a complex entity with an internal structure (twins, dislocation walls, bands). For the specific case of twining we have developed a Composite Grain model which represents the grain as a stack of twin and matrix layers of evolving thickness (Fig. 1). Compatibility and equilibrium conditions across the twin-matrix interface couple the deformation in each region and affect their slip activity. The separation of the layers defines a mean-free-path d_{mfp} for every slip system. And a directional Hall-Petch effect associated with the barrier that the interface poses to dislocations provides a contribution to hardening from twins. Reorientation by slip and twinning provides the evolution of texture.

Finally, the models at the micro and meso scales are combined into **macro-scale Polycrystal Models** able to simulate plastic or elasto-plastic forming, and to account for texture and hardening evolution. Such models are to be regarded as a higher form of a constitutive law for the specific material. In this project we use a state-of-the-art Visco-Plastic Self-Consistent (VPSC) model [16] and an Elasto-Plastic Self-Consistent model [17] which account for the anisotropy of each grain and the surrounding medium. Since the beginning of this project we have incorporated several improvements to the models quoted above. Figure 1 (right frame) is an example showing that it is possible with this approach to predict the complex stress-strain response and texture evolution associated with strain path changes of Zr tested at 76 K.

The examples presented here are meant to provide a feel for the issues we have set out to solve, the methods used, and their interrelationship. In our presentation we will discuss loading paths that involve changing the temperature and/or the straining direction. We will address the issue of internal strain evolution, hardening and texture development in Zr, Mg and Be and present experimental and theoretical results yielded by our program so far.

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Microstructural Evolution and Interfacial Motion in Systems with Diffusion Barriers

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Material systems used in microelectronics and micromachines, functionally graded coatings, lead-free solders, and structural composites share the characteristic that multiple material phases are in close spatial proximity. These material systems operate under a range of temperatures and temperature gradients, are subject to non-uniform and non-hydrostatic stress fields, and are sometimes subjected to high electrical current densities; such systems are rarely in thermodynamic equilibrium. Consequently, interdiffusion between materials and the nucleation and growth of new phases at interphase interfaces can occur, thereby altering physical and mechanical properties and resulting in a potential reduction of both the reliability and operational lifetime of the system.

The objective of this research is to elucidate the influence of compositional, elastic, and electric fields on diffusional phase transformations in systems removed from equilibrium and under driven conditions (such as large imposed electric current densities) in the presence of diffusion barriers. In order to do so, numerical tools to simulate interdiffusion and phase transformations in stressed, multilayered structures with multiple atomic constituents and material phases are being developed and implemented using Cahn-Hilliard equations, phase field models, and multi-grid numerical solution techniques. The models include position and phase-dependent mobilities, elastic constants, and electrical resistivities and have been informed by recent experimental work on Sn-Ni-Ag lead-free solders. Numerical simulations have focused on two-phase and three-phase thin-film systems in the presence of electrical fields or in the presence of a diffusion barrier. Simulation tools and theoretical analyses are used to identify the critical parameters that govern interdiffusion and the location and sequence of new phase formation in these systems.

Efforts to understand phase transformations under driven conditions have led to a parallel theoretical investigation of amorphization of metallic alloys during ball milling. The primary objective is to identify the connection between the thermodynamic characteristics of the material, the defect structure and relaxation and recovery properties, and the input power on the temporal evolution of metastable and amorphous phase formation, particularly cyclical amorphization. An experimental effort examining the interplay between two possible crystalline phases and an amorphous phase has been initiated.

Recent Progress

Cahn-Hilliard and phase field modeling without electric current: Cahn-Hilliard type equations to model one-dimensional evolution of microstructure in bulk alloys with elasticity[1,2] have been extended to two- and three-dimensional systems.[3,4] A new analytical method has been developed for solving the elastic fields arising from compositional self-strain in a solid film on a compliant substrate. The solution is based on formulating the equations of elasticity in the film and substrate in terms of either the Airy stress function in 2D or displacement potentials in 3D.[4,5] The analytic solution shows the explicit connections among system parameters and has the potential to significantly reduce computational cost as compared to methods based on finite differences[6] or micro-elasticity.[6,7]

Simulation results using the analytic solution show the role of compositional strains and elasticity on spinodal decomposition and coarsening.[4] Results in two- and three-dimensions confirm earlier one-dimensional results that elastic effects can favor nonequilibrium phases, significantly alter kinetic paths, and generate unexpected sequences of phase formation. Results show that elasticity generally speeds up the phase transformation process as long as the elastically preferred state is accessible by diffusion. There is a strong effect of elasticity on evolution patterns owing to the effective bending of the film generated by epitaxial misfit between the film and substrate. This bending gives rise to mass flux in the thickness direction, which in general favors phases forming parallel to the film-substrate interface. Interfacial (gradient) energy, on the other hand, favors columnar structures, especially for thin films, and so the stability of different film configurations depends on the relative strengths of elasticity and gradient energy. For example, multilayer structures are less stable than bilayer or columnar structures. Also, when the bending of the film is small, as in free-standing films with no substrate, elasticity has negligible effect on phase geometry and so only columnar structures are observed.

Phase Transformations in the Presence of Electric Currents: Code to simulate phase transformations at solder joints and metallization contacts using Cahn-Hilliard and phase-field models has been developed and tested. Composition, phase, elastic, and electric fields are solved simultaneously using the appropriate governing equations as a function of time. The four coupled partial differential equations are solved using a multi-grid technique developed in collaboration with mathematicians J. Lowengrub and S.M. Wise at UC-Irvine. The constitutive laws for diffusion depend on the electric current through electromigration[9] as well as on the local composition, electric, and stress fields. The dependence of the electrical conductivity and elastic constants on the local composition and phase, and the coupling between the electrochemical potential and the compositional and misfit strains are included.

Simple theoretical analysis and experimental observations in Sn/Ag and Sn/Ni systems[9] suggest different temporal exponents for the thickening rate of a growing intermediate phase in the presence of electric current than the usual linear or square-root of time kinetic laws. Simulations in 2D to investigate the validity of these predictions are underway.

The one-dimensional results are also being used as the base state in a full linear morphological stability analysis of the growth of a planar interface in the presence of an electric current. Preliminary results suggest that interfacial instability depends strongly on the electrical conductivities of the phases and may diminish as the intermediate phase grows.

Cahn-Hilliard gradient energy coefficient: Expressions for the Cahn-Hilliard gradient energy coefficient *?* for binary and ternary face-center-cubic crystals were derived by consideration of pair-wise, three-body, and four-body nearest-neighbor interactions. The resulting equations are expressed in terms of the interaction energies of clusters of atoms, and are related to bulk thermodynamic data available in CALPHAD databases. The three- and four-body interactions introduce composition dependence in *?* and provide a means for estimating *?* ?in some of the experimental systems used in the simulations. Values of *?* calculated for the Al-Zn system are in good correlation with those deduced from experiment. The composition dependence of *?* was also shown to affect microstructure during simulations.

Amorphization during Ball Milling: A system of thermodynamic balance equations to describe the time evolution of a two-phase, crystal-amorphous element of material undergoing ball milling has been derived. The thermodynamic state of the microstructure is assumed to depend on the phase fraction, the deformation state of each phase, and the temperature. The constitutive laws for the state of deformation account for energy storage due to defect creation and for recovery processes that decrease the stored energy of the system. Three steady-state solutions were found for a variety of assumed constitutive laws; a state of crystalline phase only, a state of amorphous phase only, and a two-phase system consisting of a mixture of crystalline and amorphous phases.

A linear stability analysis was performed for each steady-state solution has been analyzed and the results displayed on bifurcation diagrams where the steady-state phase fraction was plotted as a function of the input power. For certain combinations of materials parameters and rate constants, the two-phase, steady-state system exhibited oscillatory behavior in which the phase fraction of the amorphous phase oscillates about the steady-state value (asymptotically stable spiral point). This thermodynamic approach can be extended to more complex driven systems.

Future Plans

Short-term plans focus on exploiting the code that we have developed during the past couple of years to investigate intermediate phase growth in high electric current densities both in the presence and absence of diffusion barriers. These simulations are informed by experiments in the Sn-Ni-Ag ternary system and are intended to explore basic aspects of the phase transformation. Efforts will include determining the functional dependence of the thickening rate of a growing intermediate phase on the magnitude of the induced electric current, identifying how the quantitative aspects of the phase thickening rate change when the direction of the applied electric field is changed, and clarifying the interplay between compositional strain, electric field and electric resistivity on the morphological stability of the growing interface, which experiment suggests also depends on the direction of current flow. Intermediate-term efforts will focus on identifying the influence of a diffusion barrier on these characteristics of the phase transformation in systems with high electric current densities. In addition, the thermodynamic analysis of amorphization and phase transformations during ball milling is being extended to three-phase systems with compositional demixing. The theoretical work is being coupled with thermodynamic data bases in an effort to predict phase evolution during ball milling in ternary alloys. This later work is being performed in collaboration with G.J. Shiflet and J.K. Lee.

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Probing Electromechanical Properties of Single Molecules

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By wiring a molecule to two electrodes, one can then measure the electromechanical properties of the molecule, and determine how the electromechanical properties are affected by the binding of an analyte species onto the molecule. This is important because it not only offers us with an unprecedented opportunity to understand various phenomena on a single molecule basis, but also is a necessary towards molecular scale devices. The primary goals of this project are to understand how a molecular binding event changes the electrical and mechanical properties of the molecule, and how the mechanical and electrical properties affect each other. The interplay between the electrical and mechanical properties in bulk materials is responsible for piezoelectric, piezoresistive and other important effects. Finding analogous effects in single molecules is exciting. The interplay in molecular systems may also lead to novel phenomena that do not exist in bulk materials. We believe that this study will provide us with new insight into the electromechanical and molecular binding properties of molecules, as well as necessary knowledge and skills toward the ultimate goal of building single molecule sensors and actuators.

Recent Progress

We have focused on molecules with energy levels lying close to the Fermi energy levels of the probing electrodes. The conductivities of these molecules are expected to be sensitive to mechanical forces, molecular binding events and gate electric field. We have studied gate and mechanical force effects on the conductivities of several molecules. Some of the findings are described below.

Gate-controlled electron transport

The building blocks of silicon-based microelectronics are field effect transistors (FET) whose basic function is to switch electrical current between two electrodes on and off with a third electrode (gate). Building a single molecule FET is naturally considered to be a critical step towards the ultimate goal of molecular electronics.(1-3) Experimental demonstration of this FET behavior in single molecules has, however, been a difficult challenge. We have demonstrated a single molecule n-type transistor in which the current through the molecule can be reversibly controlled with a gate electrode over nearly three orders of magnitude at room temperature.

The molecule chosen for this work is perylene tetracarboxylic diimide (PTCDI), a redox molecule with many unique electronic properties. More interestingly, it is one of a few molecules available for use as *n-channel* materials. The high photo and thermal stability of the molecule is an additional feature for molecular electronic applications, particularly at room temperature and single-molecule level. We wired the molecule to two gold electrodes (source and drain) via gold-thiol bonds, and the number of wired molecules is determined by repeatedly forming a large number of molecular junctions.(4) A large gate field is achieved using an electrochemical gate in which the gate voltage is applied between the source and a gate (also called reference electrode) inserted in the electrolyte. Since the gate voltage falls across the double layers at the electrode-electrolyte interfaces, the effective gate-molecule distance is only a few Å, the double layer thickness that is on the order a few solvated ions. This results in a nearly 3 orders of magnitude increase in the source-drain current, in a fashion of a n-type FET. The large current increase is attributed to an electron transport mediated by the lowest empty molecular energy level when it lines up with the Fermi level.

Electromechanical Properties of Single Oligothiophene Molecules

In addition to the gate effect, we have studied the electromechanical properties of single oligothiophene molecules with 3 and 4 thiophene rings (abbreviated as 3T1DT, and 4T1DT, respectively). The longer 4T1DT is more conductive than the shorter 3T1DT. This unusual length dependent conductance was attributed to a smaller HOMO-LUMO gap and a closer position of the HOMO to the Fermi levels of the probing electrodes for 4T1DT. This conclusion is supported by the UV-vis absorption, electrochemical measurements, and also by the dependence of the conductance on the electrochemical gate which shifts the HOMO relative to the Fermi levels. Using the electrochemical gate, we have switched the conductance of the molecules between low and high conductance states via oxidation of the molecules. We have studied the electromechanical properties of Au-oligothiophene-Au junctions. A stretching force causes a large decrease in the conductance, which is attributed to an increase in the HOMO-LUMO gap upon stretching based on the Peierls instability model. Both the 3T1DT and 4T1DT junctions break down when the force is increased to ~ 1.5 nN (a loading rate 40 nm/sec.), corresponding to the breakdown of the Au-Au bond at the contacts.

Future Plan

Effect of molecule-electrode contact

Reproducible measurement of electron transport through a molecule requires a good contact between the molecule and two electrodes. A good contact must be mechanically stable and provide efficient electronic coupling between the molecule and the electrodes, which may be achieved by forming covalent bonds between the molecule and the electrodes. A widely used approach is to choose or synthesize molecules terminated with two thiols which can bind to metals, such as Au, Ag and Pd. Although S-metal bonds may provide neither the most efficient electronic coupling nor the most stable mechanical contact between the molecule and the electrodes, they are straightforward to prepare experimentally. Molecules terminated with pyridine groups are also good candidates to provide reliable molecule-electrode contacts via N-metal bonds. Another candidate linker is isocyanide, which can bind to Pd and Au electrodes. A stretching force on the molecular junction can change the electronic coupling between the molecule and the electrodes via the bond length and angle of the molecule to the electrodes. A stretching force also elongates the metallic bonds near the molecular contacts. Recent theoretical and experimental studies of atomic scale metal wires have shown that a mechanical stretch can induce either an increase or a decrease in the conductance of the metal wires. We will carry out a systematic study of the electromechanical properties of single molecules by varying the chemical bonds at the molecule-electrode contacts and by using different metal electrodes. If the molecule-electrode contacts are indeed responsible for the observed force-induced conductance changes, then the changes should be different for different contacts.

Metal ion binding effect on the mechanical properties

We have observed that the binding of a metal ion onto a peptide can induce a large conformational change in the peptide.(5) We expect that the mechanical properties of the peptide-metal ion complex be very different from the metal ion free peptide. Applying a stretching force on the metal-ion free peptide will stretch the peptide into a linear chain and then followed by breakdown of the molecular junction at the molecule-electrode contact. In contrast, a stretching force on the peptide-metal ion complex must break the metal ion-peptide binding before stretching it into a linear chain. The binding strength of a Cu^{2+} to the peptide is on the order of a few tenths of eV per ion (estimated from the binding constant(6)). So we can easily break these bonds, one by one, and monitor the associated changes in the conductance and force. The force measurement will allow us to extract the binding energy and study the dependence of the binding energy on the type of the metal ion and the sequence of the peptide. Since the binding strength of a metal ion onto peptides is sensitive to the pH of the solution, we will also perform the measurements at different pH. The distance over which a peptide-metal ion complex can be stretched into a linear chain is another important parameter because it will allow us to trace back to the conformational change associated with the formation of the peptide-metal ion complex. By correlating the conformational change with the simultaneously recorded conductance, we will learn how a mechanical force affects the conductance of the peptides. We believe this study will provide us with a better understanding of the molecular recognition properties of peptides.

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A new paradigm: Ductile intermetallics! The rare earth RM B2 CsCl-type intermetallics

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Program Scope

Research is focused on the systematic variations of the non-magnetic-physical and mechanical properties of lanthanide, yttrium, and scandium materials to bring about an increased knowledge and a better fundamental understanding of the electronic, physical, mechanical, and chemical nature of ductile rare earth intermetallic compounds. In particular the aim of the program is to understand the fundamental difference between RM compounds (where R = rare earth and M = a late transition or main group metal), where ductility is easily attained, and other intermetallic compounds, where ductility is seen only under special circumstances.

Recent Progress

In mid-FY2001 we discovered room temperature ductility in ErCu, which has the CsCl-type (B2) crystal structure. This is quite unusual for a stoichiometric intermetallic compound. Tensile tests showed that polycrystalline samples of YCu, DyCu, and YAg: (1) elongate 11%, 16%, and 20%, respectively, at failure; and (2) have K_{IC} fracture toughness values of 12.0, 25.5 and 19.1 $\mathrm{MPa}\sqrt{\mathrm{m}}$, respectively. For comparison, commercial precipitation-hardened Al alloys often have 10 to 15% elongation and K_{IC} values of 20 to 25 $\mathrm{MPa}\sqrt{\mathrm{m}}$. Tensile elongation and fracture toughness values for YCu are lower than those of DyCu and YAg, which may be related to YCu's transformation to the brittle, orthorhombic B27 (FeB-type) structure below room temperature, while DyCu and YAg are monomorphic.

Slip line analysis of YAg and YCu single-crystal tensile test specimens indicated that primary slip occurred on the {110} <010> slip system and secondary slip occurred on {100} <010> with critical resolved shear stresses ranging from 13 to 18 MPa. These two slip systems are insufficient to satisfy the von Mises Criterion for extensive polycrystalline ductility. Electron microscopy **g·b** = 0 out of contrast dislocation analysis shows that the dislocations in both polycrystalline and single-crystal YAg are predominantly <111> type with a lesser amount of the <110> type; this observation appears to be inconsistent with the single-crystal tensile test determination by slip line analysis that only <010> slip occurs in YAg. This apparent inconsistency could be explained by superdislocation slip in which reactions of the type $[\bar{1}11]+[11\bar{1}]\rightarrow[020]$ allow individual <111>-type dislocations to achieve <010> displacements in the crystal. Such superdislocation motion would introduce anti-phase boundaries (APBs) in the crystal, and structures that appear to be APBs have recently been observed during TEM analysis of plastically deformed YZn.

One hypothesis proposed to explain the unusually high ductility of these RM compounds is that their small grain sizes (typically 100 to 500 nm) allow deformation by grain boundary sliding, similar to the behavior of superplastic alloys. To test this hypothesis, polycrystalline YAg and LuCu specimens were tested by strain rate jump tests in which strain rate is abruptly increased from 10^{-4} s^{-1} to 10^{-2} s^{-1} at the moment when 2% elongation is reached during the tensile test. Because their deformation is diffusion-dependent, superplastic materials have high strain rate sensitivity and display a large increase in tensile stress at the strain rate jump. However, jump tests on YAg and LuCu showed no stress increase at the jump, which appears to refute the grain boundary sliding explanation, at least in YAg and LuCu. Other hypotheses proposed to explain the high ductility (e.g., twinning-assisted slip, stress-induced phase- transformation assisted slip, and dislocation reactions) remain to be tested. TEM examination of strained DyCu revealed a non-equilibrium orthorhombic phase, which may provide transformation-toughening at crack tips analogous to that seen in yttria-stabilized zirconia. Tests to confirm or refute that possibility are currently in progress.

Ab initio calculations have been performed on YAg and YCu, and the theoretical values of the lattice constants agree with the experimental values within 0.5%, while the calculated values for the elastic constants (c_{ij}) differ by <3% (except for the C_{12} value for YAg which differs by <7%) compared to the experimental values, which were measured by us. The APB energies and unstable stacking fault energies were calculated for YAg, YCu and NiAl (a brittle B2 phase). The APB energies are high for all three compounds, which makes slip by superdislocation pairs more difficult; however, the values for YAg are significantly lower than those of YCu (and NiAl), which is consistent with the higher ductility of YAg compared to YCu. The unstable stacking fault energies for YAg and YCu, however, are 3 to 4 times smaller than those of NiAl, which may account for the observed ductility in the former two compounds and brittleness in NiAl.

Ab initio calculations have also shown that dislocation line tensions are nearly isotropic in YZn, YAg, and YCu; this finding contrasts sharply with the highly anisotropic line tensions in NiAl and Fe-25%Al intermetallics. This suggests that dislocation cross slip would be easier in the rare earth B2 intermetallics than in the aluminides. Calculations also show that both screw and edge dislocation line tensions in YCu, YAg, and YZn are two to four times lower than in Fe-25%Al and NiAl. This work also indicated that dislocation junction reactions ($[111](1\bar{1}0)$ primary; $[1\bar{1}\bar{1}](110)$ forest) form over much larger angular ranges, have higher energies, and are stronger in Fe-25%Al and NiAl than in YCu, YAg, and YZn.

Future Plans

Our studies will continue to focus on two principal activities: (1) experimental study of polycrystalline and single-crystal rare earth compounds to determine their low temperature heat capacity, elastic constants, electron deformation densities, ductilities from 77 K to 870 K, strain rate sensitivities, Bauschinger effect, slip systems, critical resolved shear stresses, dislocation Burgers vectors, and the presence or absence in deformed metal of APBs, twins, and non-equilibrium phases; and (2) theoretical calculations of the electronic structure and phonon modes of the selected materials used in the experimental portion of this study along with total energy calculations to establish the energy landscape and likely slip plane dynamics. The experimental portion of this work will be done on 11 compositions (YZn, NdAg, GdAg, DyAg, ErAg, YAg, GdCu, DyCu, ErCu, YCu, and LuCu) using tensile testing, TEM (including *in situ* strain stage examination), and XRD. Properties of a smaller number of these compositions will be calculated by *ab initio* methods and compared with the experimental results. If twinning or stress-induced phase transformations are observed, determinations will be made on whether these phenomena are contributing to the high ductility of these materials.

Recent Publications

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Microstructural Design of Advanced Ceramics

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Program Scope

Theory and experiment combine to define (1) the relationships between the properties of ceramics and critical length-scale characteristics and (2) how to tailor these during processing. For example, the effects of sintering additives on the microstructure and interfacial properties are assessed experimentally. The atomic scale segregation of elements and interfacial debonding characteristics are characterized via advanced electron microscopy methods. These are combined with first principles theoretical calculations of the energies and forces associated with chemical bonding to determine the effects of chemical additives in regions of interest (e.g., interfaces) as well as the mechanisms controlling microstructure evolution. The nature of interfacial regions can then be incorporated into classical analyses to understand the effects of nano-scale interfaces on larger scale characteristics of ceramic monoliths and coatings. The combined theoretical and experimental findings provide a quantitative picture of the mechanisms controlling the behavior of ceramic-based systems and an understanding as to how to enhance their properties including fracture and/or deformation resistance.

Recent Progress

Grain growth behavior in silicon nitride (and many other) ceramics is influenced by additives (intentional and unintentional) that promote densification and reside within grain boundaries or intergranular films (IGFs). In silicon nitride ceramics, Si_3N_4 crystallites are typically surrounded by a continuous amorphous silica-rich oxynitride phase that includes the additive species. The silicon nitride family of ceramics often exhibits elongated grain shapes that when controlled can be used to impart significant increases in fracture toughness (Becher et al., 1998). The degree of anisotropic grain growth in Si_3N_4 has been suggested to be due to slow, attachment limited growth in the a-axis direction as opposed to diffusion controlled c-axis growth. Attachment limited growth processes are associated with a dearth of surface steps and current observations reveal that the prismatic surfaces of the grains are indeed atomically smooth (Shibata et al., 2004, Winkelman et al., 2004, Ziegler et al., 2004). This surface morphology, while necessary, is not sufficient to explain why certain rare earth additives are more effective in promoting anisotropic grain growth. Attempts at explaining this based on size of the rare earth ions (or their cationic field strengths) are erroneous and inconsistent with the experimental observations. Instead, the present theoretical studies describe the driving forces that are imposed on competing cations within the chemical gradients that exist within the intergranular films. The differential binding energy (DBE) defines the energy difference for a cation (e.g., La, Gd, Lu) existing in different chemical environments (e.g., in N-rich grain surfaces versus O-bearing regions within the IGF and triple point pockets) and referenced with respect to that of the majority cation Si (Painter et al., 2004; Shibata et al., 2004). First-principles local density calculations then defined the specific adsorption properties of the rare earth adsorbed at the nitride interface.

The DBE results also indicate that because the rare earths have different tendencies to segregate to the grain surfaces in silicon nitride ceramics, they will fill adsorption sites on the prismatic plane surfaces to different degrees. This required knowledge of the adsorption and binding strengths of RE segregants at prismatic grain surfaces, which have been determined by first-principles calculations. The combined results predicted that the filling of adsorption sites on the prismatic plane by the rare earths would be distinctly different (e.g., La > Gd > Lu), which has now been confirmed by atomic resolution scanning transmission electron microscopy

(Shibata et al., 2005). It is this variability in surface decoration and adsorbate binding for this series of rare earths that impacts various phenomena. By dominating the first cation sites on the prismatic grain surfaces at the IGF/crystal interface, the attachment of Si, which is a necessary step for diametrical grain growth, will be effectively impeded. Indeed, the resulting theoretical models are in agreement with measured grain growth aspect ratios for a series of rare earth doped silicon nitride ceramics. They provide a fundamental explanation for observed differences in growth morphologies in terms of the adsorption site occupancies and stabilities of the different rare earths at interfaces of the grains versus that within the amorphous intergranular films (Painter et al., 2004; Becher et al., 2005).

It is recognized that at elevated temperatures there is a flux of atoms to and from these surfaces, and one must consider the surface desorption kinetics that depend upon the energy barrier, $\square$, separating bound and desorbed states (i.e., desorption rate ~ $e^{-\square/kT}$). While explicit quantitative determinations of the barrier height are yet to be determined, due to the current lack of details of the structure within the glass, the DBE model yields an estimate for the relative differences between the adsorbate binding energy at the grain surface relative to that in the glass, and this semi-quantitative indication of the energy barrier trend across the rare earth series is consistent with observations. Future studies of the influence of glass composition on its local structural details combined with the recent advances in theoretical modeling will allow us to treat this much more rigorously.

As noted above, it is recognized that there is a need for more fundamental models of the “structure” and bonding in amorphous oxynitride systems. These can be used to understand how composition alters the characteristics and properties of the amorphous phases and films. Considerable progress has been made in experimental studies on the thermal-mechanical properties of glasses, particularly most recently of the silicon-based oxynitride glasses of interest for the studies of silicon nitride ceramics. For instance, the properties of SiREMe oxynitride glasses are strongly influenced by the RE present and by replacing Al by Mg, as well as oxygen by nitrogen (Ramesh et al., 1997, Becher and Ferber, 2004). However, the community to date has been limited to attempts at correlating rare earth effects based on simple field strength estimations of binding strengths between rare earth ions and the oxygen (or nitrogen) in the glass. Characterization studies are beginning to shed some light upon bonding changes within the bulk glasses related to composition. For instance, initial collaborations involving x-ray photoelectron spectroscopy (Gautier-Soyer, 2005) studies and nuclear magnetic resonance results (Lofai et al., 2004) reveal changes in the oxygen bonding with the rare earths that are well explained by shifts in nitrogen to oxygen preferences of the rare earths predicted by the DBE model. In the SiREMe oxynitride glasses, data indicate that aluminum, unlike magnesium, serves, in part, as a network former (Lofai, 2005), which can strengthen the glass network. This is consistent with the observed properties (Becher et al., 2004). The glass structural characterization will be continued and serve as critical input to a new methodology to model the local structures within the amorphous phases. This study takes advantage of the flexibility of the self-consistent partial wave method to accurately extend the length-scale for investigating complex ceramic systems (Averill and Painter, 1994).

Tailoring the composition of the oxynitride glass comprising the nanometer thick intergranular films within a silicon nitride ceramic has been shown to have a substantial impact on improving other aspects of mechanical behavior. The creep resistance (i.e., the effective viscosity) of many silicon nitride ceramics is dominated by viscous flow in the thin amorphous intergranular films over at least a portion of the creep life. Hence, one needs to assess the influence of the viscosities of the thin amorphous intergranular films as part of the overall (or effective) viscosity of the ceramic. The effective viscosity can be characterized by a “brick wall” model where, for silicon nitride, the grains do not contribute to the deformation (Wilkinson, 1998). Using this model, we find that the creep resistance of silicon nitride ceramics can be increased by at least five orders of magnitude by incorporating the observed increases in the viscosity of the intergranular phase by judicious selection of the rare earth additions plus increases in the nitrogen to oxygen ratios of the SiREMe oxynitride glasses (Becher and Ferber, 2004) plus the reduction of the intergranular film thickness (Wang et al., 1996). These predictions are supported by the observed reductions in creep rates for silicon nitride ceramics containing rare earths of greater atomic number/smaller ionic radius (Cinibulk et al., 1992).

Future Plans

The implications of the importance of atomic and microstructural aspects set the goal of this work: a basic understanding of *how* additives affect critical properties and characteristics, guided by first-principles theory and probed by careful experimentation and high resolution characterization, such that an atomic-level degree of control of the fracture and deformation properties of ceramics is achievable. This proposal concerns research directed to provide a basis for gaining this control. Ceramics are inherently complex mixed-phase materials; amorphous phases are present both as nanometer thick amorphous IGFs and as glassy triple point pockets separating the reinforcing crystalline grains (Clark, 1987). The mechanical and electronic properties of ceramic materials are highly dependent on the chemical bonding within the different phases. The chemical bonding, both across the grain/IGF interface and within the glassy phase, poses a number of challenges to theoretical modeling. The ubiquitous IGFs are often the determining factor in ceramic performance as in silicon nitride ceramics that serves as a model system here. However, only recently have atomic-level effects on their properties and behavior been addressed (Painter et al. 2004). A description of the interfacial (grain boundary) chemistry is essential to understanding ceramic behavior (e.g., interfacial debonding) at the atomistic level. However, it is not complete without also understanding bonding *within* the glassy pockets and IGFs, for it is in these volumes that phenomena (such as intergranular debonding and crack propagation) critical to ceramic structural performance occur. Research on the effects of rare earth additives (RE) on Si_3N_4 grain growth has made it very clear that microchemical interactions at the reinforcing grain interfaces can directly lead to changes in microstructure that dramatically affect ceramic toughening (Sun et al., 1998). The adherence between the grains and IGF directly affects the energy dissipated during debonding of the grain interface in the wake of a propagating crack, and this determines the mechanical properties and fracture toughness of the ceramic. *Understanding and control of the interfacial, intergranular and microstructure characteristics is central to future advanced ceramic development*.

To reach these goals the following issues will be addressed:

1. Theoretical modeling that treats the amorphous region of the IGF together with its link with the interfaces and the crystalline grains, which incorporates data on the effects of composition on local structure in the amorphous phases.
2. The influence of ordering at interfaces and mechanisms that dictate ordering processes,
3. The role of composition of SiRE oxynitride glasses in local structure and the effects on intergranular film characteristics (e.g., London dispersion forces, film thickness, glass properties).
4. The role of adsorption-desorption of additive elements, including rare earths and other elements, on grain growth anisotropy.
5. The relationship between additive effects on Interfacial and intergranular structure and interface debonding and fracture resistance.
6. The role of composition related segregation and intergranular film structure, as well as nano-scale grain size effects, in the deformation and creep behavior of ceramics. The development of theoretical models that address the important length scale characteristics and mechanisms, where the experimental findings and observations serve as input and as means to test and verify the models.

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SESSION VI:

SIZE EFFECTS ON MECHANICAL BEHAVIOR

Chair: Mike Baskes (LANL)

Nanomechanics Opportunities at the Nanoscale Science Research Centers

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Machines of the future will perform work at nanometer length scales through a complex integration of materials that can couple mechanical, chemical, optical and electrical energy between the micro and nano length scales. Structures that transducer chemical energy into microscale mechanical response are already showing promise as highly sensitive chemical and biological detectors. At the same time, the extremely sensitive response of these integrated systems can provide new approaches for studying mechanisms for nanoscale mechanical energy transduction. Achieving this vision will require a better understanding of the mechanical response of materials and structures at the nanometer length scale, where a different set of forces dominate the response of the system in comparison to the macroscale. A tremendous opportunity lies ahead to perform the research necessary in order to reliably predict the behavior of an integrated nanosystem. This talk will examine the opportunities in nanomechanics research that are being pursued at the five BES Nanoscale Science Research Centers and across the world to help bring to reality the vision of integrated nanosystems.

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Length-Scale Effects in Plasticity

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Program Scope

The rapid development of functional materials and devices with nano-scale and micro-scale features has brought about the need to understand and control the mechanical properties of materials at small length scales. Such important mechanical properties as the yield and fracture strength are strongly dependent on microstructure and are very different for materials confined to small volumes compared to their bulk counterparts. The objective of this work is to devise and use nano-scale mechanical testing techniques for studying the mechanical properties of materials and to understand the fundamental defect processes that cause mechanical properties to be length-scale dependent. The work primarily involves the study of strength and plasticity of crystalline materials at small length scales, using nanoindentation techniques. Such studies provide not only basic information about the mechanical properties at small length scales but also insights into the controlling mechanisms of plastic flow. These studies are also expected to provide experimental benchmarks for the multi-scale modeling of mechanical properties of metals. By using nanoindentation and uniaxial compression of micro- and nano-pillars, it is now possible to directly study the strength and plasticity of samples comparable in size to those that can be handled with multi-scale computational methods. This is expected to provide, for the first time, a direct test of the predictions of atomistic and microstructural modeling of deformation. Our work on the fundamental aspects of mechanical properties at small length scales also relates to the growing interest in the mechanical properties of nanostructured materials, as many of our experiments on nano-pillars can serve as models for understanding the plastic flow process in nanocrystalline metals.

Recent Progress

In previous work we have shown that the hardness of most crystalline materials increases with decreasing depth of indentation [1]; this is called the indentation size effect (ISE). We and others have assumed that this is caused by geometrically necessary dislocations and strain gradients [2]. Because the first of these experiments involved polished metal surfaces, some questioned whether these effects were caused by polishing artifacts or oxides on the metal surface. We resolved this question by showing that strong indentation size effects are also observed for annealed, coarse-grained gold thin films on silicon substrates [3]. These surfaces were not mechanically polished and were not oxidized. In addition, we took account of indenter tip shape and pile-up effects by using the measured dynamic contact stiffness and the known elastic properties of gold to determine the contact areas in these experiments, thus removing the ambiguities of the earlier experiments.

Because much of our work involves the indentation of thin metal films on substrates, it is necessary to correct for the constraining effects of the substrate, which is usually much harder and stiffer than the film, on these measurements. The aim of these corrections is to determine the true contact pressure during indentation from measurements of the load, indentation depth and stiffness. We have developed a new methodology for calculating the true hardness of thin films on elastically mismatched substrates using an analytical treatment of the elastic indentation of a film/substrate system with a conical indenter given by Yu et al. [4]. The method allows us to determine the contact radius and hardness from the measured contact stiffness and known elastic properties, even for indentation depths approaching the thickness of the film. It shows that the hardness of thin films can be reliably determined from measurements of the contact stiffness provided the elastic properties of the film and substrate are known [5].

We have recently developed techniques for making sub-micron sized pillars of pure gold using both focused ion beam machining and microfabrication methods [6]. We have been testing these pillars in uniaxial compression using the nanoindenter with a flat-ended diamond punch. These geometries are of interest because they allow us to study plasticity in small volumes without the usual effects of strain gradients associated with sub-micron indentation. We find remarkable size effects for plastic deformation, with strengths approaching 1 GPa for pillars as small as 250 nm in diameter, in spite of the absence of strong gradients of strain. Based on the experiments to date, we have proposed that such tiny single crystals are strong because existing dislocations run out of the crystal faster than they multiply. This leads to crystals that are starved of dislocations; when this condition is met, plastic deformation can proceed only if new dislocations are nucleated, a process requiring very high stresses. These findings have led us to a new concept for plasticity in small crystals – strain hardening by dislocation starvation [6].

Future Plans

In all of the experiments described above the quality of the crystalline sample being tested is of great importance. Bulk single crystals have been studied but they must be mechanically polished and that introduces other complicating factors. Deposited thin films are not mechanically polished but they are usually polycrystalline, with grain sizes of the order of the film thickness, with the consequence that grain boundaries can complicate the experiment. For many of these experiments single crystal metal films are needed. We have recently sputter-deposited epitaxial films of gold onto the (001) surface of single crystal MgO substrates using an epitaxial sticking layer of Cr. The resulting (001) oriented epitaxial Au films range in thickness from 1 to 2 microns and are very flat. We are planning to use these new samples for a number of length-scale plasticity experiments.

We propose to examine the indentation size effects in these new samples, using our recently developed technique for correcting for the effects of elastic mismatch on the measured hardness. These new experiments should provide the best and least ambiguous measurements of the ISE to date. We are also planning to use our focused ion beam machining technique to create sub-micron sized pillars in these epitaxial gold films and to study size effects on strength and plasticity in these epitaxial films. Eliminating the grain boundaries and possible polishing artifacts from these samples will allow us to better explore the newly developed concept of hardening by dislocation starvation.

By making pillars in epitaxial gold films on MgO substrates it will be possible to use the x-ray microdiffraction faciltities at the Advanced Light Source in Berkeley to directly observe any lattice curvatures or strain gradients that might be responsible for the high strengths of these tiny gold pillars. The sub-micron sized x-ray beam allows Laue diffraction patterns to be determined for very small crystal volumes [7]. It has not been possible to use this technique to study pillars created in bulk single crystals of gold as it is not possible to distinguish the gold pillar from the gold background on which it rests. For the epitaxial films of gold on MgO it will be possible to create isolated gold pillars resting on a clean MgO surface, thus making it possible to collect Laue patterns from the pillars alone. We expect these measurements to shed new light on the mechanisms of strength of these tiny pillars.

We also plan to use the x-ray microdiffraction faciltities at the Advanced Light Source in Berkeley to measure the expected lattice curvatures and strain gradients in small indentations in copper single crystals. By collecting Laue patterns at various locations around small indentations in Cu it should be possible to directly measure the lattice curvatures created by indentation. The associated geometrically necessary dislocation densities can then be computed from these measurements and the expected hardening effects of these GNDs compared with the observed hardening effects. Here the indentations can be located by placing Pt markers near the indentations using the FIB tool. We expect this experimental approach to provide new information about the defect processes causing the indentation size effect.

Finally, to address the role of grain boundaries and interfaces in plastic deformation at the nano-scale, we are planning to use the pillar compression experiment to study both Al bi-crystals and Al-Sc multilayers with a range of bilayer periods [8-9]. By testing Al bi-crystals at the sub-micron scale we hope to elucidate the role of grain boundaries in the deformation of nanostructured metals. Similarly, by conducing micro-pillar compression experiments on Al-Sc multilayers we expect to directly examine the elastic and plastic properties of these microstructures, supplementing and improving on hardness measurements already made. All of these studies are expected to provide new knowledge on the mechanical properties of materials at the nano-scale and to serve as experimental validation for computational modeling of length-scale plasticity.

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Microstructural Stability and Mechanical Behavior in Nanocrystalline Metals

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Program Scope

There have been long-standing concerns about the stability of the internal structure of nanocrystalline metals. The energy associated with the high density of grain boundaries provides a driving force for grain growth. Even in the absence of external stress, an increase in grain size has been observed over time in samples of high purity nanocrystalline metals held at room temperature [1,2]. Nanocrystalline metals are of interest because of their high strength associated with grain refinement (Hall-Petch effect). Obviously grain growth causes a decrease in strength. In the present grant we are studying grain growth in high purity nanocrystalline metals under various stresses, both monotonic and cyclic, and attempting to determine the mechanisms leading to this growth (e.g., grain rotation, grain boundary migration). The influence of these internal structural changes on mechanical properties is being quantified as a function of time, temperature and stress.

Recent Progress

Samples of high purity nanocrystalline Cu have been synthesized by inert gas condensation and compaction [3]. An important thrust of the project has been to improve the vacuum conditions in the equipment and the operation of the compaction unit. The improvements have led to the production of samples with higher density and purity. Measurements at the LEAP facility at ORNL confirm the purity of the samples. The oxygen content is ~0.1 atomic percent. The density of the samples is ~97-99% of theoretical value. Their grain size distributions are reasonably narrow.

Microhardness measurements were made as a function of indenter dwell time and sample temperature on Cu samples of various grain sizes. Figure 1 (from Ref. [4]) shows the decrease in Vickers hardness as a function of the log of the indenter dwell time for a number of samples with a range of grain sizes. All measurements are at room temperature. For comparison the results for a coarse-grain high purity copper sample are included. It can be seen that the hardness relaxation is linear with the log of indenter dwell time over several orders of magnitude. The rate of relaxation increases with decreasing grain size of the sample. The Hall-Petch strengthening seen at short dwell times decreases as time goes by and the hardness values seem to be converging to a common value at very long dwell times. Figure 2 (from Ref. [4]) shows the hardness relaxation as a function of indenter dwell time at various temperatures for a sample whose initial average grain size was 80 nm. There is a large increase in the hardness as the temperature drops from ambient to that of liquid nitrogen, unexpected for an FCC metal. The coarse-grain sample, included in the figure for comparison, shows no such increase. The relaxation rate is greatest at the lowest temperatures and all the curves tend to converge to a common value at long indenter dwell times.

The pronounced linearity of hardness with log of indenter dwell time suggests that a logarithmic creep mechanism is operative (Ref [5]). However to legitimately apply such a mechanism requires that the microstructure remain constant. TEM measurements of material in the vicinity of the indenter showed that the stresses it produces lead to extensive and rapid grain coarsening. The change in grain-size distribution as a function of indenter dwell time is shown in Fig. 4 (from Ref. [6]) for a sample with an initial grain size of 20 nm. Both the number and volume fraction grain-size distributions show a rapid increase in grain size (doubled in 10 seconds). The influence of temperature is shown in Fig. 5 (from Ref. [6]). Surprisingly, a significant volume of very large grains, ~ 400-700 nm in size, form at liquid nitrogen temperatures. These must contribute to the rapid hardness relaxation observed at the low temperatures. The mechanism of grain growth is not clear. The rapid growth at low temperatures under high stress conditions seems to rule out the operation of a diffusion-based mechanism. Instead coarsening appears to be stress driven. High resolution electron microscopy pictures of samples stressed at room and liquid nitrogen temperatures by Dr. Pratibha Gai (DuPont Research Fellow) show no evidence of subgrain formation, considered part of a grain growth mechanism involving grain rotation and coalescence.

Recent Progress on Other Projects

Fatigue Behavior in Ultra-Fine Grain Copper

High purity Cu samples have been prepared with grain sizes in the low sub-micrometer (UFG) range by cryogenic rolling. Dogbone samples cut from the rolled Cu have been subjected to tension-tension fatigue over a range of maximum stress values to establish an S-N curve (S = maximum stress amplitude; N = number of cycles to failure). In the low cycle fatigue regime the performance of the UFG Cu is appreciably better than that of coarse-grain copper, but the advantage lessens in the high cycle fatigue (HCF) range. Considerable grain growth (and thus softening) is seen in the failed fatigue samples, particularly those tested in the lower stress range. Evenly-spaced parallel surface extrusions were seen on samples fatigued at lower maximum stress amplitudes (~ 200 MPa) and similarly-spaced parallel dislocation lines appear in TEM pictures taken from the same area. There is an indication that the number of low angle grain boundaries has increased, possibly pointing to grain rotation.

Effect of Nanoscale Multilayer Coating on Fatigue Life of Steel

Stoudt, Ricker and Cammarata [7] showed that a nanoscale multilayer Cu/Ni coating on copper fatigue specimens largely suppresses PSB formation during cycling. As a result fatigue life is greatly increased. Under a CINT project in collaboration with Dr. Amit Misra at LANL, we are examining the effect of nanoscale multilayer coatings on the LCF life of a simple low-carbon steel (1020) and an austenitic stainless steel (316). After a number of tries a satisfactory coating procedure has been devised for Cu/Nb coatings. The BCC 1020 steel shows a surface roughening, not PSB formation, during HCF cycling. High resolution SEM measurements have yet to be carried out but it appears that the roughening is less on the coated than on the bare samples. Heat-treated and polished 316 fatigue samples have been sent to LANL for coating.

Future Plans

The stress/strain fields around a microhardness indenter are complex and not independent of time as the indenter sinks into the material. Therefore we are repeating the relaxation experiments on IGC copper in compression. After a value approaching the UTS is attained either the strain or stress is kept constant and the change in the other variable noted. Extensive relaxation has been observed. This work has just begun. A major consideration is the quantification of the grain growth as a function of initial grain size distribution, time, temperature, and initial stress value (is there a threshold stress for grain growth?).

A few more fatigue tests are to be run on the UFG copper and the dislocation lines analyzed for burgers vector and character, with the hope of connecting their activity to the production of the similarly spaced surface extrusions.

Work will continue on the steel samples to examine the effect of the strong multilayer nanoscale coatings on surface roughness that develops during cycling and thus observe how fatigue life is affected.

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* “Time and Temperature Dependent Effects on the Strength of Nanocrystalline Metals”, K. Zhang, J.A. Eastman and J.R. Weertman, in *Advances in Experimental Mechanics*, Carmine Pappalettere, Editor, McGraw-Hill, Milano, Italy (2004) 369.
* The Influence of Time, Temperature and Grain Size on Indentation Creep in High-purity Nanocrystalline and Ultrafine Grain Copper, *Kai Zhang, J.R. Weertman and J.A. Eastman, App. Phy. Lettr. **85** (2004) 5197.*

* *Rapid Stress-Driven Grain Coarsening in Nanocrystalline Cu in Ambient and Cryogenic Temperatures,* Kai Zhang, J.R. Weertman, and J.A. Eastman, App. Phy. Lettr. **87** (2005) 061921.

Nine DOE Sponsored Publications in 2002-2005 from Preceding Grant

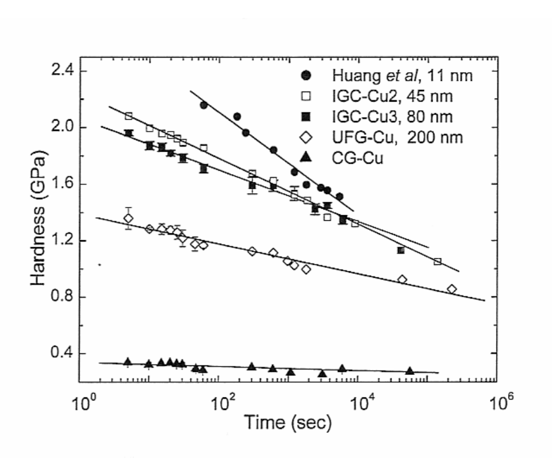

Fig. 1. Hardness of high purity Cu samples as a function of indenter dwell time for various grain sizes.

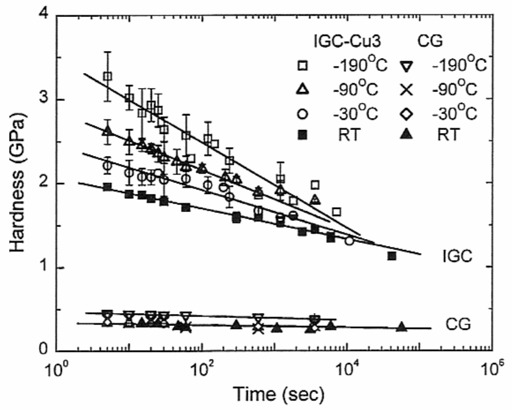

Fig. 2. Hardness of 80 nm and CG samples as function of indenter dwell time for various test temperatures.

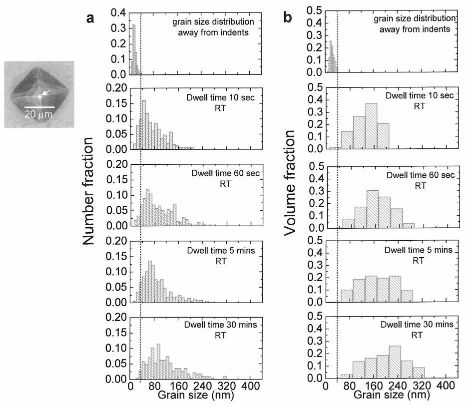

Fig. 3. (a) Number and (b) volume fraction grain-size distributions at various indenter dwell times.

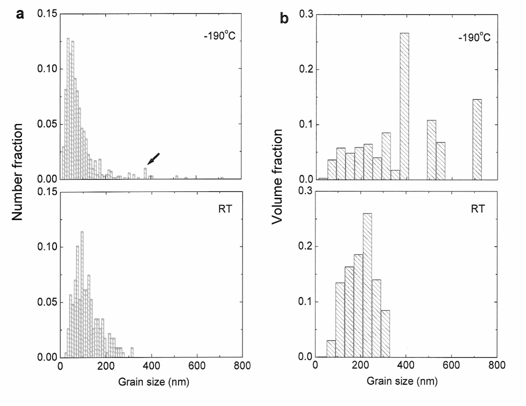

Fig. 4. (a) Number and (b) volume fraction grain-size distributions after 30 min of dwell time for indents made at RT and –190° C.

Deformation Physics of Ultra-fine Scale Materials

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Program scope

The mechanisms that determine strength and failure limits of nano-scale materials lie within new realms of behavior. *The development of the new science of unusual mechanical behavior (e.g., super strong) of nanostructured materials, unexplained by conventional continuum-scale models, is the grand challenge pursued by this program*. In response to this grand challenge, the specific objectives of this program are to understand: (1) the origins of strength in composites made of layers with thicknesses on the order of nanometers, (2) the ultimate strength limit that can be achieved via nanostructuring, (3) role of interfaces in slip transmission and dislocation storage, (4) post-yield behavior, associated with mechanical stability, work hardening, and fracture mechanisms, (5) thermal stability, and (6) stabilization of new or unusual atomic arrangements in nanometer-scale composites. We use a highly synergistic combination of state-of-the-art atomistic modeling and cutting-edge experimental methods that are able to probe the details of the deformation mechanisms in metallic nanolayered composites.

Recent progress

In the last three years, this effort at LANL has produced some significant discoveries and technical accomplishments that will be presented at this meeting as oral and poster presentations.

Oral presentation (R.G. Hoagland), title *"Deformation Mechanisms in Nanolayered Composites"*

The presentation will highlight the following recent accomplishments of this program:

- We developed deformation mechanism maps for nanolayered composites as a function of length scale from micrometer to nanometer. This description involved a dislocation pile-up based Hall-Petch model that applies to composites in the micron to sub-micron range. At smaller thicknesses in the tens of nanometer range strength is determined by a mechanism involving confined layer slip of single dislocations. At still smaller length scales the limiting strength is reached defined by the stress to transmit dislocations across the interface.

- Our atomistic modeling has revealed two categories of interfaces: (i) transparent, and (ii) opaque, so-called because of the nature of the dislocation interactions that determine peak strength. Transparent interfaces occur in iso-structural multilayers (same crystal structure and orientation of both constituents) with slip systems that are contiguous across the interfaces. An example is cube-on-cube Cu-Ni. The interface plays a relatively small role in resisting slip in these materials. Instead these materials derive strength primarily from coherency stress within the layers. On the other hand, opaque interfaces are strongly resistant to slip.

These interfaces occur in systems where the crystals on either side of the interface are misoriented or they do not share the same crystal structure. Such interfaces tend to be weak in shear. *We discovered that an unusually high resistance of these incoherent interfaces to slip transmission originates from dislocation core spreading via shear of the 'weak' interface.*

- A variant of the opaque interface is the twinned interface. Although strong in shear, twinned interfaces also pose a strong barrier to slip because of the change in slip plane and direction at the interface. In certain composites of alternating Cu and austenitic stainless steel layers *we discovered that the steel layer had a preferred orientation of twins normal to the growth direction with an average spacing of only a few nanometers*. Pursuing this observation further, we found that films made entirely of austenitic stainless steel could be produced containing nanometer thick twinned structures. These films possess strengths that are over an order of magnitude greater than bulk austenitic stainless steel, consistent with atomistic model predictions for twinned interfaces.

Poster presentation (A. Misra): "Deformation Behavior of Nanolayered Materials Subjected to Large Plastic Strains and Cyclic Loading"

- We used room temperature rolling to explore the deformation behavior of nanolayered materials to large plastic strains. For an initial layer thickness of about 75 nm, Cu-Nb nanolayered composites exhibited remarkable plastic flow stability even after 150% elongation in the rolling direction. The nanolayers exhibited uniform reduction in layer thickness, with no damage accumulation in the form of dislocation cell structures. Furthermore, the Kurdjumov-Sachs orientation relationship was retained after rolling. However, for initial layer thickness of a micrometer or higher, dislocation cell structures formed within the individual Cu and Nb layers and the initial Kurdjumov-Sachs orientation relationship was lost after rolling. The suppression of damage accumulation in nanolayered materials after plastic deformation was the basis to explore the fatigue resistance of these materials. We observed extraordinary resistance to accumulation of fatigue damage, compared to monolithic materials.

Future Plans

Optimization of interface structure and strength

For composites containing opaque interfaces, we hypothesize that the maximum tensile strength of the composite is related to the shear strength of the interface. Our MD simulations for Cu-Nb revealed that the stress field of glide dislocations can induce shear in an interface. When this occurs dislocations are attracted to the interface. In addition, because of the limited interfacial strength, the in-plane components of the core can spread along the interface, a behavior with several important implications. Firstly, the maximum stresses within dislocation cores diminish as the cores spread thereby reducing the stress available to induce nucleation of slip in the adjacent layer. Secondly, dislocations introduced into interfaces repel continued slip by like-sign dislocations on the same or nearby slip planes, to an extent that depends on core spreading. The repulsion is greater the narrower the core. Such repulsion is tantamount to work hardening, but this contribution to strength diminishes as core spreading increases. These effects are now regarded as having profound importance to determining the achievable strength levels in nanolayered composites with opaque interfaces.

We seek to understand the relation between interfacial shear strength and the strength of the barrier to slip transmission across interfaces. This understanding should enable the design of systems with tailorable mechanical properties. Our approach will involve a combined experimental/theoretical study of several opaque-interface systems such as fcc-W, fcc-Mo, fcc-Ta, and fcc-Nb where "fcc" represents any one of several fcc metals including Cu, Ni, Al, or Ag. These composites should possess the fcc/bcc Kurdjumov-Sachs orientation relationship similar to that observed in Cu-Nb. In addition, in some of these systems intermetallics are energetically favored so that interfacial strength is likely to be large. We will determine the dependence of strength on layer thickness in these materials and characterize their microstructure via TEM. Rolling experiments are planned to explore the post-yield deformation behavior of the composites. Of special interest in these experiments is the lattice rotations, or lack thereof, that provide insight into the nature of the dislocation interactions under conditions where multiple slip systems are active.

Optimization of System Variables

This program has examined, characterized, and modeled nanolayered composites as a function of various system variables, primarily layer thicknesses and interface character/type. It has done so in a way that helps to simplify analysis of the results: the system variable space has been explored in an elementary way by changing only one variable at a time. However, the understanding gleaned from this work points to advantages associated with certain combinations of these variables. For example, Cu-Nb with layer thickness < 5 nm behaves in a brittle manner during rolling, fracturing into small shards during first pass. The reason for this nominally brittle behavior is related to deformation behavior that favors shear instabilities as layer thickness is decreased into the nm range. Interestingly, preliminary experiments show that periodically modulating the layer thicknesses to form thick (e.g. 40 nm) and thin (e.g. 4 nm) layers, a composite is created with nearly the strength of the thinnest layers while possessing sufficient ductility to sustain 25% strain in rolling. The behavior of such *thickness-modulated composites* will be the focus of experiments and analysis in this program with the intent of determining conditions that create both high strength and ductility, at least during rolling.

We also plan to explore *multi-component compositionally-modulated composites* with three or more components to create materials containing both transparent and opaque interfaces. For example, the behavior of a B/C/B/A/C/A system, in which B/A interfaces are transparent (and coherent) while the others are opaque, appears to offer some very intriguing properties because the mechanisms of slip transfer across interfaces vary periodically across the thickness of the composite. We expect that, during rolling, plastic deformation will be distributed equally among the constituents, but the constraints imposed on the slip systems necessary to achieve this are a mystery at this point. Candidate constituents for these studies are Mo (A), W (B), and Cu (C).

Co-deformation of Ductile/Glassy Composites

(collaboration with Prof. Frans Spaepen at Harvard)

Metallic glasses have high yield strengths, since their structure lacks the translational symmetry necessary to involve dislocations with constant Burgers vectors (independent of position) in plastic flow. At low temperatures, plastic deformation occurs in highly localized shear bands, which form as a result of a drop in the local viscosity due to strain-induced disordering. However, as a component in a multilayered metal/glass structure, both the propagation and nucleation of such bands are less likely. Indeed, at micron layer thicknesses, a ductile metallic layer blunts shear bands in the glassy component thereby relaxing the stresses at its leading edge and halting its progress. When the layer thicknesses are reduced into the nanometer range shear bands may not be able to form in the glassy solid. Instead the glassy component may be constrained to deform uniformly. Equally important is the question regarding the mechanism of slip transfer from one metallic layer to another through the intervening glassy layer. In some respects, it appears that the glassy layer would behave as a rather thick version of an opaque interface. We are evaluating the mechanical behavior of a model system, copper / Pd-Si (metallic glass) multilayers, as a function of varying bilayer repeat lengths and the relative thicknesses of the two layers to investigate the strengthening and fracture behavior of nanometer-scale constrained metallic glasses.

Selected recent publications from this program:

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Nanoscale-twirming-induced strengthening in austenitic stainless steel thin films
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Hochbauer, T., Misra, A., Hattar, K., Hoagland, R. G., J. of Appl. Phys., (2005); vol.98, (in press).

Nano-Structured Biomimetic Polymeric and Hybrid Materials for Advanced Mechanical Properties

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Program Scope

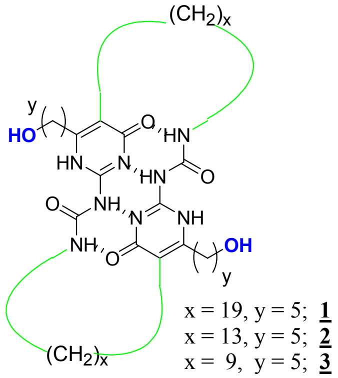
This project draws inspiration from nature to design polymeric and hybrid nanocomposite materials having precise nano-structures for advanced mechanical properties. Specifically, we use modular proteins and biocomposites as the model systems to develop polymers and nanocomposites having defined nano-structures. The remarkable combined strength and toughness of modular protein *titin*, silk and biocomposites derives from their modular structures. Sequential unfolding of the domains provides an elegant molecular mechanism to absorb a large amount of energy while sustaining a large force at the same time.[1-4] Following Nature's strategy, we design and construct synthetic polymers composed of modular structures. The mechanical properties of the created materials will be studied at single-molecule level using atomic force microscopy (AFM), at nanoscopic level by various nanomechanical characterization facilities, and finally at bulk level by standard stress-strain and dynamic mechanical analyses. The molecular parameters of the nano-domains will be varied to systematically investigate the relationship between molecular structures and the single-molecule mechanical properties, which will be correlated with the nanoscopic and macroscopic mechanical properties of the materials. Both the materials designs and the fundamental understanding gained from this multidisciplinary investigation will provide insight and basic information for designing lightweight, strong and tough polymeric and nanocomposite materials to meet many energy related critical technological needs.

Recent Progress

1. UPy-based DCL Modules

In our first generation of modular polymer design, we incorporated ureidopyrimidone (UPy) modules into polymer backbone to induce loop formation.[5-8] Single-molecule force-extension experiments revealed the sequential unfolding of loops. The bulk mechanical properties show that the modular polymer combines high tensile strength, high toughness and elasticity.[5-8] The excellent correlation between the single-molecule and the bulk properties demonstrates our biomimetic concept: the introduction of modular structures held by sacrificial weak bonds into a polymer chain can combine the three most fundamental mechanical properties, i.e., high tensile strength, toughness and elasticity, into one polymer. Whereas the modular concept was demonstrated by the UPy system, the simplicity of the system, however, limits the control over loop domain size or dimerization orientation, making the acquisition and interpretation of single-molecule data difficult and limiting the scope of structure-function studies. To make more well-defined and uniform modular polymers based on UPy quadruple hydrogen-bonding system, we have designed and synthesized three new double-closed loop (DCL) UPy-based sacrificially unfolding modules (**1**-**3**) as shown in Chart 1. We are currently incorporating these new modules into polymers and will investigate their nanomechanical and bulk mechanical properties.

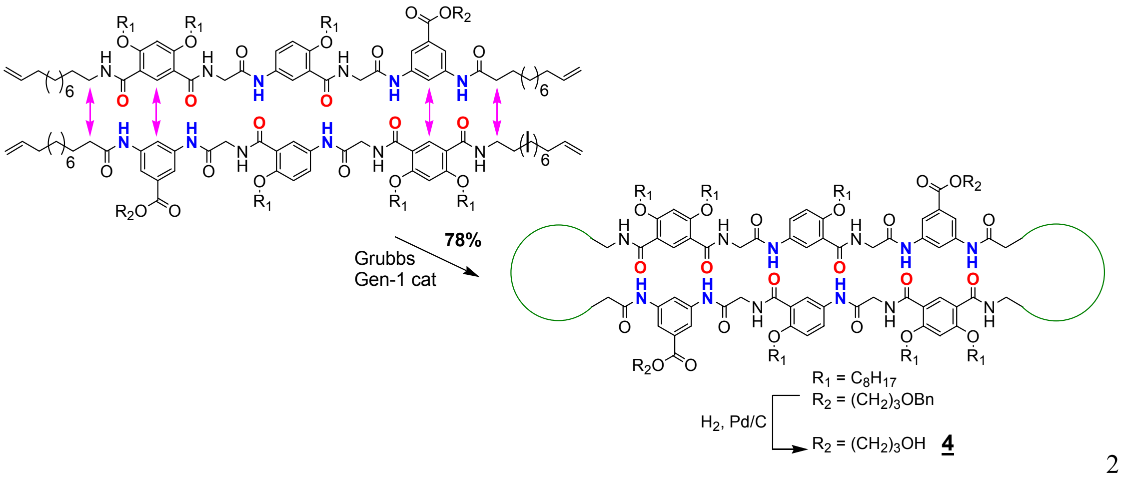
Chart 1. Double-Closed UPy modules



2. Peptidomimetic 6-H Bonds DCL Modules

In our *second generation modular polymer* design, peptide mimicking β-sheet motifs were used to construct modular polymers that have better-defined structures. We have reported previously a quadruple H-bonded β-sheet mimicking double-closed loop (DCL) system. Single molecule force-extension experiments revealed the sequential unfolding of these modules as the polymer is stretched, resulting in more regular sawtooth-patterned curves similar to those seen in titin and and other biopolymers.[9-11] In our systematic structure-property investigation, the binding strength of the DCL modules was adjusted by using different length of hydrogen-bonding motifs. We plan to synthesize a series of modular polymers containing DCL modules with each module having 4, 6, and 8 hydrogen bonds, respectively. During the last half year, we have synthesized the DCL module containing 6 hydrogen bonds (Scheme 1). Its chemical structure has been fully characterized by various NMR techniques and mass spectrometry. We are currently making efforts toward the synthesis of 8 hydrogen bonds DCL module. After finishing the series of module synthesis, we will incorporate them into polymer chains. Their nanomechanical and bulk mechanical properties will be investigated. The correlation of their mechanical properties with their structures will provide fundamental information to the influence of molecular unfolding force on the polymer mechanical properties.

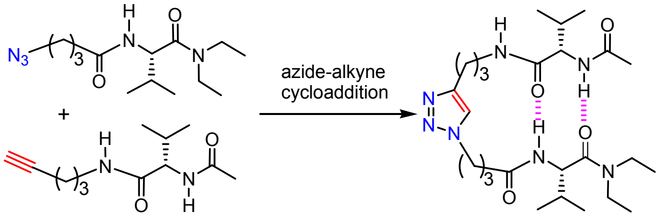
Scheme 1. Synthesis of 6-H β-sheet mimicking DCL module



3. New β-turn strategy for β-sheet containing polymers

In another approach, we aim to construct synthetic polymers having *repetitive folded β-sheet structures* that resemble those observed in natural silks and amyloid fibers. As an important step toward this goal, we first developed an efficient and convergent strategy for constructing a new β-turn mimic.[12] In this approach, we utilized the facile azide-alkyne cycloaddition, commonly referred to as "click chemistry", to construct a new triazole ring based β-turn mimic. Upon mixing two peptides derivatized with terminal azide and alkyne, respectively, the two strands are ligated by formation of triazole ring which induces the formation of β- turn. An important finding from this study is that the tendency of β-turn formation for triazole system is highly dependent upon the linker length and the three-carbon linker was shown to be optimal for stable β-turn formation. Currently we are applying this methodology to the design of polymers with extensive β-sheet structures.

Scheme 2. Click to form β-turns



Future Plan

We will incorporate the UPy DCL modules (1-3) into various polymer backbones. Their nanomechanical properties will be investigated by AFM and mechanical properties will measured by Instron. Both the molecular and bulk properties will be compared to those of the open UPy module-containing polymers. We anticipate seeing better controlled properties from the new UPy DCL modular systems.

For the peptidomimetic modular system, we will continue to synthesize the 8 hydrogen bonds β-sheet mimicking DCL module by following similar strategy used for making the 6 hydrogen bonds DCL module. After completion of synthesis and characterization of series of β-sheet mimicking DCL modules, we will incorporate them into polymers. Again, we will conduct nanomechanical and bulk mechanical property studies to these modular polymers from which structure-property relation will be drawn.

Finally, we will continue exploring the use of "click" chemistry for formation of new β-turn mimics. More importantly, we will apply this efficient methodology to the design of peptidomimetic polymers containing well-folded extensive β-sheet structures, resembling silk and amyloid proteins. Their nanomechanical and bulk mechanical properties will be conducted by following the same protocols we employed for investigating other modular polymers.

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Mechanics of Small Length Scales

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Program Scope:

The burgeoning worldwide interest in nanoscale materials and structures ultimately derives from their strongly size-dependent properties. Size-dependent behavior can provide novel functionalities not obtained with bulk or even microscale materials. Sandia recently combined three existing projects, and one new one, into an overarching project entitled *Mechanics of Small Length Scales*. Broadly, our work investigates (1) the synthesis and elastoplastic properties of nanoscale materials, and (2), the detailed nanoscale behavior underlying larger-scale deformation, material transport, and phase stability.

Mechanics of Small Length Scales encompasses four major thrust areas: Mechanical Properties of Nanostructured Materials, Theory of Microstructures and Ensemble Controlled Deformation, Advanced Growth Techniques and the Science of Epitaxy, and Dissipation and Collective Phenomena in Coupled Mechanical Systems.

Recent Progress/Future Directions:

<u>Mechanical Properties of Nanostructured Materials.</u> The goal of this thrust area is to understand the basic deformation properties of nanostructured materials and the evolution of stress within them.

One current emphasis is targeted toward understanding the thermal stability of pulse laser deposited nanocrystalline nickel films. These films often undergo abnormal grain growth, in which a few grains grow disproportionately with respect to the matrix, as shown in Figure 1a (*in-situ* TEM was done in collaboration with K. Hattar and Prof. I. M. Robertson, Univ. Illinois). Since the resulting bimodal grain structure has unique, often desirable, mechanical properties, it is useful to understand the parameters that control abnormal growth. We anneal the as-deposited Ni films *in situ* in the transmission electron microscope (TEM), and characterize the evolution of the grain matrix. Ni abnormal grains contain a large density of defects, prominently including stacking fault tetrahedra (SFT), as shown in Fig. 1b. SFT are a general feature seen in all our observations of abnormal grain growth, but have not been reported for other nano-metals. SFT are formed when vacancies collect together; finding them in Ni at such low grain growth temperatures (250 to 400°C) is remarkable since they typically require quenching from high temperatures or irradiation to produce lattice displacements (200 kV TEM will <u>not</u> displace atoms in Ni). Moreover, Ni has a high stacking fault energy, so SFT are further unexpected.

SFT indicate the presence a source of vacancies. We believe this source arises from the grain boundaries in the initial nanocrystalline material, which have a density deficit compared to bulk Ni. Grain growth leads to a reduction in the number of boundaries per unit volume of film, which then creates an influx of vacancies into the grains.

Theory of Microstructures and Ensemble Controlled Deformation. The goal of this thrust area is to combine experiment, modeling, and simulation to construct, analyze, and utilize three-dimensional (3D) polycrystalline micro- and nano-structures.

In support of the experimental work on abnormal grain growth described previously, we are extending our successful model for abnormal subgrain growth to include nanocrystalline film structures, including the appropriate geometry, crystallography, and grain boundary properties. The result is a detailed, mesoscale computer model that captures the origin and process of abnormal growth, as shown in Figure 2.

Subsequent computer modeling efforts will focus on quantifying the properties of Ni grain boundaries; in particular, novel molecular dynamics simulations permit the first comprehensive characterization of the boundary mobility. These simulations can also elucidate the interaction between grain boundaries and vacancies that may lead to defect generation. Finally, new polycrystal plasticity models will help characterize the mechanical properties of nanocrystals, with particular attention to the role of the grain size distribution on strength and ductility.

Advanced Growth Techniques and the Science of Epitaxy. This thrust area uses advanced growth techniques and *in situ* diagnostics to develop detailed understanding of the fundamental processes governing thin film growth, epitaxy, and structural evolution.

Our current focus is on the interaction of elastic strain with microstructure and surface morphology, mediated by surface atomic transport. We’ve used lattice mismatch strain during SiGe/Si heteroepitaxy, combined with conditions of limited surface mobility, to self-assemble novel *quantum dot molecules* (QDMs) – symmetrical, bound assemblages of four quantum dots “glued together” by a central pit in the alloy, as shown in Fig. 3. Through extensive growth studies, we have developed a fundamental understanding of QDM nucleation, size-selection, 1D growth instabilities, precision placement, and compositional inhomogeneities. These structures are relevant to the nanologic architecture known as quantum cellular automata.

Extensions of this work will include examining 3D heteroepitaxial quantum dot growth of SiGe alloys on monocrystalline oxide substrates (e.g., STO), where, in addition to strain, interfacial chemistry will play a significant role in determining length scales, elastic interactions, and morphology. We will plan to examine the origins of compressive residual stress and reversible relaxation processes in polycrystalline metal and semiconductor films.

Dissipation and Collective Phenomena in Coupled Mechanical Systems. The goal of this new thrust area is to understand mechanisms of energy dissipation in mechanical systems at length scales down to the nanoscale and to develop understanding of collective phenomena using coupled mechanical systems. The experimental approach of this thrust centers on sensitive experimental techniques to measure and map the mechanical resonance modes and dissipation factors of individual nanoscale oscillators and the creation of unique nanomechanical systems that consist of coupled, two-dimensional oscillator arrays with an extremely high number of oscillator elements. These arrays are also expected to exhibit collective behavior, such as localization and stochastic resonance, due to fluctuations in element positions, dissipation factors, and resonant frequencies.

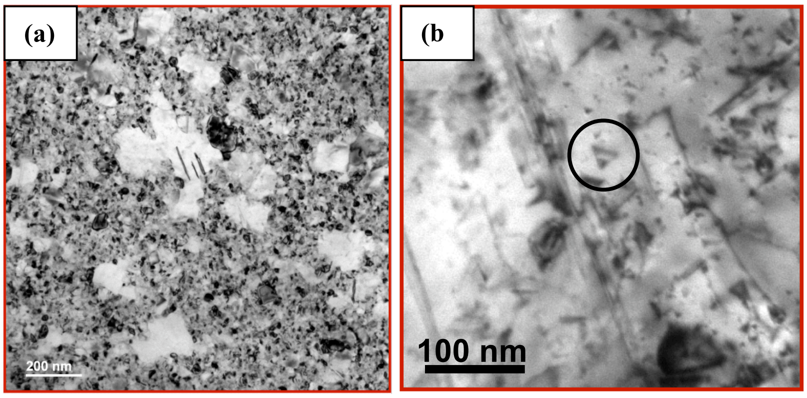
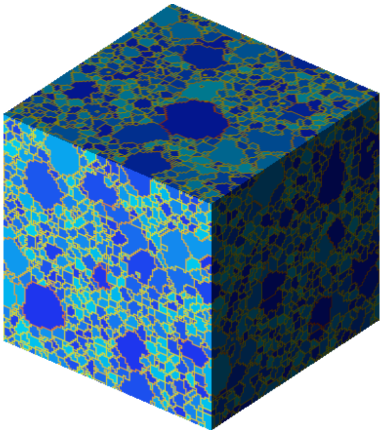


Figure 1. TEM micrographs of abnormal grain growth in nanocrystalline Ni films. (a) Overview of the microstructure after 300^{o}C annealing of the 80 nm thick Ni film in situ in the TEM. (b) Closeup view of a single abnormal grain to show stacking fault tetrahedra (circled).

Figure 2. Computer simulation of abnormal grain growth in tightly textured aluminum polycrystal shows similar abnormal growth characteristics to Ni.



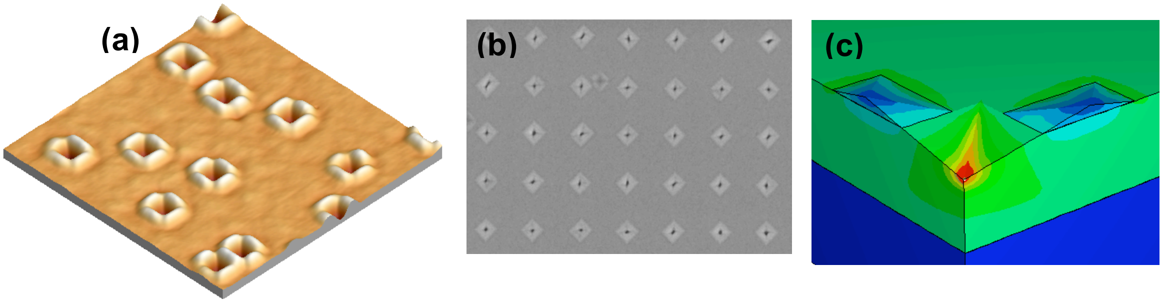


Figure 3: (a) randomly nucleated QDMs on the surface of Si_7Ge_3/Si (001). (b) Periodic QDM array formed by SiGe growth over damage sites created using a focused ion beam. (c) Finite element calculations of strain energy distribution in a QDM.

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