
C
S
P The DOE Center of Excellence for the
Synthesis and Processing
of Advanced Materials



BASIC ENERGY SCIENCES
DIVISION OF MATERIALS SCIENCES

SAND--96-1136

Research Briefs

January 1996

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

29

MASTER

TABLE OF CONTENTS

PREFACE	4
THE CENTER'S MEMBER LABORATORIES	6
CENTER PROJECTS AND THEIR COORDINATORS	7
EXECUTIVE SUMMARY	8

Research Briefs

CONVENTIONAL AND SUPERPLASTIC METAL FORMING.....	14
New Scaling Relationships Have Been Discovered for the Dislocation Cell Structures in Deformed Metals	14
Ultrasonic Monitoring of Rolling and Recrystallization Textures in Aluminum	16
Formability of Al-Mg Alloys in the Solute Drag Regime	18
MATERIALS JOINING	20
Characterization of High-Speed Al-Cu Electron Beam Welds.....	20
Models Predicting Weld Solidification Behavior and Microstructure Are Being Developed and Verified	22
Joining of SiC-Based Ceramics for Elevated Temperature Applications.....	24
Low-Temperature Joining of Ceramics and Ceramic Matrix Composites	26
NANOSCALE MATERIALS FOR ENERGY APPLICATIONS.....	28
Synthesis and Properties of Semiconductor Nanocrystals.....	28
Applications of Semiconductor Nanocrystals.....	30
Early Stages of Sintering in Nanoparticle Systems	32

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.



MICROSTRUCTURAL ENGINEERING WITH POLYMERS	34
Polyphosphazene Membranes for Separation and Speciation	34
Polymer-Based Materials With Controlled Porosity	36
Synthesis and Characterization of a New Family of Anion Complexing Agents.....	38
TAILORED MICROSTRUCTURES IN HARD MAGNETS.....	40
A Metallurgical Approach Toward Alloying in Rare Earth Permanent Magnet	40
Importance of Grain Boundary Composition and Structure to Magnetic Reversal Processes in Advanced Permanent Magnets.....	42
Alloy Design of $\text{Nd}_2\text{Fe}_{14}\text{B}$	44
PROCESSING FOR SURFACE HARDNESS.....	46
Low-Stress, Ultra-Hard, Low-Wear Carbon Films.....	46
Synthesis of Hard Boron Suboxide Thin Films Using Electron Cyclotron Microwave Plasmas	48
Accurate Measurement of Film Stress Using Micromachined Cantilever Beams: Application to Cubic Boron Nitride.....	50
MECHANICALLY RELIABLE SURFACE OXIDES FOR HIGH-TEMPERATURE CORROSION RESISTANCE	52
Oxidation Performance of Plasma-Synthesized Alumina Coatings	52
Impurity Segregation To Alumina-FeAlCr Alloy Interfaces.....	54
Strain Development In Thin, Thermally Grown Alumina Layers	56

PREFACE

This publication, *Research Briefs*, is designed to inform present and potential customers and partners of the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials about significant advances resulting from Center-coordinated research. The format for *Research Briefs* is an easy-to-read, not highly technical, concise presentation of the accomplishments. Each *Brief* provides a statement of the motivation for the research followed by a description of the accomplishment and its significance.

The Center is a distributed center for promoting coordinated, cooperative research partnerships related to the synthesis and processing of advanced materials. It was established by the Department of Energy's Division of Materials Sciences, Office of Basic Energy Sciences and the DOE Laboratories in recognition of the enabling role of materials synthesis and processing to numerous materials fabrication- and manufacturing-intensive technologies. The participants include investigators from 12 DOE national laboratories, universities and the private sector. The Center has a technology perspective provided by a Technology Steering Group.

The overall objective of the Center is,

To enhance the science and engineering of materials synthesis and processing in order to meet the programmatic needs of the Department of Energy and to facilitate the technological exploitation of materials.

Synthesis and processing (S&P) are those essential elements of Materials Science and Engineering (MS&E) that deal with (1) the assembly of atoms or molecules to form materials, (2) the manipulation and control of the structure at all levels from the atomic to the macroscopic scale, and (3) the development of processes to produce materials for specific applications. Clearly, S&P represent a large area of MS&E that spans the range from fundamental research to technology. The goal of basic research in this area ranges from the creation of new materials and the improvement of the properties of known materials, to the understanding of such phenomena as diffusion, crystal growth, sintering, phase transitions, etc., in relation to S&P. On the applied side, the goal of S&P is to translate scientific results into useful materials by developing processes capable of producing high quality cost-effective products.

The technical emphasis of the Center has been on a number of focused multilaboratory projects which draw on the complementary strengths of the member institutions in their ongoing research programs. These projects were selected on the basis of the following criteria:

- scientific excellence
- clear relationship to energy technologies
- involvement of several laboratories
- strong existing or potential partnerships with DOE Technologies-funded programs
- strong existing or potential in-kind partnerships with industry

Each Project is coordinated by a knowledgeable representative from one of the participating laboratories. The Projects and their Coordinators are listed in the accompanying table. The first seven Projects were initiated in the fall of 1994, whereas the last one on High Efficiency Photovoltaics was recently developed for start in 1996. In this first issue of *Research Briefs* we have selected a few accomplishments from each of the seven initial Center Projects. An Executive Summary provides highlights of these accomplishments organized by Project. Readers are encouraged to contact any of the Coordinators for information about the Center and its accomplishments.

George A. Samara
January 1996

THE CENTER'S MEMBER LABORATORIES

The member laboratories of the Center are:

- Ames Laboratory (Ames)
- Argonne National Laboratory (ANL)
- Brookhaven National Laboratory (BNL)
- Idaho National Engineering Laboratory (INEL)
- University of Illinois Frederick Seitz Materials Research Laboratory (UI/MRL)
- Lawrence Berkeley National Laboratory (LBNL)
- Lawrence Livermore National Laboratory (LLNL)
- Los Alamos National Laboratory (LANL)
- National Renewable Energy Laboratory (NREL)
- Oak Ridge National Laboratory (ORNL)
- Pacific Northwest National Laboratory (PNNL)
- Sandia National Laboratories (SNL)

CENTER PROJECTS AND THEIR COORDINATORS

PROJECT	COORDINATOR(S)
Conventional and Superplastic Metal Forming	W. (<u>Bill</u>) G. Wolfer (SNL/CA) Phone: (510) 294-2307 FAX: (510) 294-3231 E-mail: wgwolf@sandia.gov
Materials Joining	R. <u>Bruce</u> Thompson (Ames) Phone: (515) 294-9649 FAX: (515) 294-4456 E-mail: thompsonrb@ameslab.gov
Nanoscale Materials for Energy Applications	<u>Daniel</u> S. Chemla/ <u>Mark</u> Alper (LBNL) Phone: (510) 486-6581 FAX: (510) 486-4995 E-mail: dschemla@lbl.gov & dalper@lbl.gov
Microstructural Engineering with Polymers	Gregory (<u>Greg</u>) J. Exarhos (PNNL) Phone: (509) 375-2440 FAX: (509) 375-2186 E-mail: gj_exarhos@pnl.gov
Tailored Microstructures in Hard Magnets	<u>Bob</u> Dunlap (ANL) Phone: (708) 252-4925 FAX: (708) 252-4798 E-mail: bddunlap@anl.gov
Processing for Surface Hardness	James (<u>Jim</u>) B. Roberto (ORNL) Phone: (423) 576-0227 FAX: (423) 574-4143 E-mail: jlr@ornl.gov
Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance	<u>Linda</u> L. Horton (ORNL) Phone: (423) 574-5081 FAX: (423) 574-7659 E-mail: hortonll@ma160.ms.ornl.gov
High Efficiency Photovoltaics	<u>Satyen</u> Deb (NREL) Phone: (303) 384-6405 FAX: (303) 384-6481 E-mail: satyen_deb@nrel.gov
Overall Center Coordinator	<u>George</u> A. Samara (SNL/NM) Phone: (505) 844-6653 FAX: (505) 844-4045 E-mail: gasamar@sandia.gov

EXECUTIVE SUMMARY

The *Research Briefs* presented in this publication are intended to inform the Center's present and potential customers and partners about significant advances resulting from Center-coordinated research. Selected accomplishments from each of the Center's initial seven focused projects are presented. This Executive Summary states the overall objective of each project followed by highlights of the accomplishments presented later in more detail.

Conventional and Superplastic Metal Forming

Objective

To concentrate on those aspects of deformation mechanisms which improve formability in conventional metal forming and which contribute to superplasticity in fine-grained light weight materials.

Highlights

- Although the complexity of microstructures resulting from metal forming processes had appeared to defy any quantitative interpretation, Center researchers have recently discovered scaling relationships indicating that universal laws govern the evolution of the dislocation structure and resulting grain refinement during large strain plastic deformation. This discovery has the potential of improving the formability of metals and the properties of resulting products. (pp. 14-15)
- An ultrasonic technique sensitive to differences in bulk rolling and recrystallization textures of Al has been developed. Key advantages of this technique over other approaches (e.g., X-ray measurements) are that it provides a volume (not near surface) average of the texture and is compatible with the manufacturing environment. Texture influences the formability and properties of sheet metal. (pp. 16-17)
- Results on Al-Mg alloys show that enhanced ductility through viscous solute drag of dislocations in the warm forming regime may provide an economical way for improving the formability of these light weight alloys. (pp. 18-19)

Materials Joining

Objective

To improve the reliability of the processes used to join materials into more complex structures serving a variety of energy-related functions.

Highlights

- Studies of the microstructure of Al-Cu alloys at low and high electron-beam welding speeds revealed fine equiaxed grains at low speeds and large columnar grains at high speeds, contrary to common microstructural development in alloys. This indicates that grain growth and not nucleation is the controlling solidification mechanism in high-speed welding. (pp. 20-21)
- Models are being developed to predict weld solidification behavior in order to select weld processes and parameters for optimizing weld microstructure and performance. Model results on Al-Cu welds compare favorably with experimental measurements. (pp. 22-23)
- Two different techniques for joining silicon carbide (SiC)-to-SiC suitable for high temperature applications have been developed. SiC-based ceramics and composites offer the potential for significant efficiency improvements in power generation and energy conversion. Both techniques can be adapted for in-field component fabrication and repair. (pp. 24-27)

Nanoscale Materials For Energy Applications

Objective

To significantly enhance the technological exploitation of novel nanoscale materials in energy and other commercial applications by developing synthesis and processing approaches that allow control of size, surface passivation and the interconnection and assembly of nanoparticles.

Highlights

- A wide variety of high quality nanocrystalline semiconductors in a range of sizes have been successfully grown by colloidal, inverse micelle and ion implantation techniques, and theoretical approaches have been developed to understand their electronic/optical properties. These achievements represent important advances towards the ultimate utilization of these exciting materials. (pp. 28-29)

- A prototype light emitting diode (LED) has been successfully fabricated by sandwiching nanocrystalline CdSe layers between semiconductor polymer contacts. The color of the emitted light can be controlled (red-to-blue) by changing the size of the nanocrystals. (pp. 30-31)
- A synthesis and characterization facility has been developed which is capable of producing nanoparticles from various materials by magnetron sputtering, transporting these particles under ultra-high vacuum to a high resolution transmission electron microscope, and studying (in-situ) their sintering and interactions with substrates and surrounding media. The work is complemented by molecular dynamics simulation of the early stages of the sintering process. (pp. 32-33)

Microstructural Engineering with Polymers

Objective

To develop new multiphase materials that retain the processability of organic polymers but share the properties normally associated with inorganic materials.

Highlights

- Two new routes for the synthesis of inorganic and molecularly mixed inorganic-organic polyphosphazene membranes and porous films have been developed. These polymers and polymer blends, which offer significant advantages over other separation systems with respect to durability in harsh ambient environments, have many potential applications in the fuels industry and environmental cleanup. (pp. 34-35)
- Advanced routes have been developed for the synthesis and processing of bulk and thin film low-density ceramics and polymer-based materials having continuous and controlled porosity at the nanometer scale. These materials (aerogels) have exceptional insulating, acoustic and optical properties. (pp. 36-37)
- A new family of stable anion complexing agents based on either cyclic, linear or branched amines containing electron withdrawing side groups has been developed. In addition to complexing anions in electrolyte batteries, these compounds increase the transport number of Li^+ ions, a key to improving the performance of Li batteries. (pp. 38-39)

Tailored Microstructures in Hard Magnets

Objective	<i>To improve hard magnets by understanding, in terms of the microstructures achieved, the magnetic and mechanical properties of materials produced by a number of synthesis and processing approaches.</i>
Highlights	<ul style="list-style-type: none">• The addition of transition metal carbides, especially TiC, has been shown to produce enhanced nucleation, and hence finer grain size and improved magnetic properties of the commercially important Nd₂Fe₁₄B-based permanent magnets. (pp. 40-41)• High resolution electron microscopy and nanoscale chemical analysis have led to the discovery of a previously unknown amorphous, iron-rich grain boundary phase in mechanically-processed rare-earth iron boron (RE₂Fe₁₄B) magnets. This result explains why the coercivity of these alloys is below its theoretical limit and suggests metallurgical modifications to improve it. (pp. 42-43)• Motivated by the need to improve the poor fracture resistance of Nd₂Fe₁₄B magnets, a 3-point bend test was implemented and shown to be capable of quantitatively distinguishing the fracture toughness among samples prepared by different manufacturers and processing methods. This accomplishment is a first step towards developing correlation between fracture toughness and microstructure. (pp. 44-45)

Processing for Surface Hardness

Objective	<i>To use the integrated capabilities of the participating laboratories to address critical issues which limit synthesis and processing for improved surface hardness.</i>
Highlights	<ul style="list-style-type: none">• Alternating hard and soft multilayer carbon thin film structures have been successfully grown by cathodic arc deposition. The hardness of these structures was found to be the weighted average of the constituent layers, whereas the observed growth-produced compressive stress in the structures was ~50% lower (leading to better adhesion to the substrate) than the weighted average of the stresses in the constituent layers. The average wear rate of the multilayer films was 10 - 1000X less than that for other hard coatings. (pp. 46-47)

- An electron cyclotron resonance (ECR) plasma reactor has been used to successfully produce amorphous thin films of boron suboxide whose hardness (30 GPa) is comparable to, and hardness/modulus ratio significantly greater than that of sapphire. (pp. 48-49)
- A micromachined silicon cantilever beam technique has been developed to accurately measure growth and processing stress in thin films. The technique was used to show that film stress increased dramatically with increasing cubic boron nitride (cBN) in ion-assisted BN deposition, but the stress is not responsible for the increased cBN content, contrary to earlier belief. (pp. 50-51)

Mechanically Reliable Surface Oxides For High-Temperature Corrosion Resistance

Objective

To generate the knowledge required to establish a scientific basis for the design and synthesis of improved (slow growing, adherent, sound) protective oxide coatings and scales on high temperature materials without compromising the requisite bulk material properties.

Highlights

- It has been demonstrated that plasma-deposited, submicron thick alumina coatings can provide excellent high temperature oxidation protection to Fe-Al-Cr alloys. Adhesion of the alumina to the alloy is further enhanced by the presence of Zr in the alloy. Plasma synthesis has the potential of depositing dense, strongly adhering coatings at relatively low cost. (pp. 52-53)
- Auger electron spectroscopy has revealed elevated levels of sulfur at the oxide-metal interface in thermally-grown alumina on a Fe-28Al-5Cr (at.%) alloy. The presence of sulfur at this interface correlated with poor scale adhesion. For an alloy with 0.1 at.% Zr added, no sulfur was observed at the interface and there is good scale adhesion -- results that suggest modification of the interface as a means for developing reliable surface oxides. (pp. 54-55)
- The shift of the "ruby line" fluorescence has been used to provide a quantitative method of determining the compressive strain in thermally-grown alumina coatings on Fe-Al-Cr alloys. Lack of this information has often been a barrier to understanding and modeling how oxide coatings and scales accommodate thermally-generated stresses and thus to assessing the mechanical reliability of surface oxides. (pp. 56-57)

RESEARCH BRIEFS

New Scaling Relationships Have Been Discovered for the Dislocation Cell Structures in Deformed Metals

D. A. Hughes, *Sandia National Laboratories, Livermore, California*

D. C. Chrzan, *Lawrence Berkeley National Laboratory*

Q. Liu and N. Hansen, *Riso National Laboratory, Roskilde, Denmark*

Motivation -- Large strain deformations take place in many metal forming processes such as sheet forming, forging, extrusion, and sheet rolling. In all these cases, the plastic deformation creates a subdivision of the initial grains into smaller crystallites separated by dislocation walls. This refinement of the original grain structure by cold working is of course an ancient technique for imparting superior mechanical properties to the finished product. Modern applications of this technique include the angular equal-channel die pressing for producing superplastic alloys to obtain submicron grain sizes. In spite of the fact that dislocation cell formation and grain refinement have been observed and studied extensively, the complexity of the deformed microstructure appeared to defy any quantitative interpretation in terms of universal models. The discovery of the scaling relationships described below indicate that universal laws do exist which control the evolution of the dislocation structure as a function of the plastic deformation.

Accomplishment -- Samples of pure aluminum with an initial grain size of 300 μm were cold rolled ranging from 5% to 50% reduction. Convergent beam Kikuchi analysis was performed on TEM specimens made from the deformed samples and the misorientation angles across dislocation boundaries were determined. Two different types of dislocation boundaries were identified. Long, continuous dislocation

boundaries which have been called geometrically necessary boundaries (GNBs), and smaller scale cell boundaries termed incidental dislocation boundaries (IDBs). The average misorientation angles, Q , for IDBs increases linearly with the square root of the strain while that for the GNBs increases by a higher power according to the results shown in Figure 1. The frequency distributions of misorientation angles, $P(q, Q)$, were also measured for each type and at four different strain levels, namely 0.06, 0.1, 0.4, and 0.8. Although each distribution is very different, it was discovered that they can all be scaled according to $P(q, Q) = \text{const.} (q/Q)^{a-1} \exp(-a q/Q)$ where a was found to be 3. The scaled distribution functions are shown in Fig. 2.

Significance -- The distributions of misorientation angles for different plastic strains can all be characterized by a universal function with one characteristic parameter, the average misorientation angle. The latter in turn is related to the plastic strain. The existence of the scaling relationship and the universal distribution function for the misorientations indicates that the deformation structure and its evolution are governed by relatively simple laws for the collective properties of dislocation microstructures produced by plastic deformation of polycrystalline metals with medium to high stacking fault energies.

Contact: Darcy A. Hughes, Sandia National Laboratories/California
Phone: (510) 294-2686 Fax: (510) 294-3410 E-mail: darcy_hughes@sandia.gov

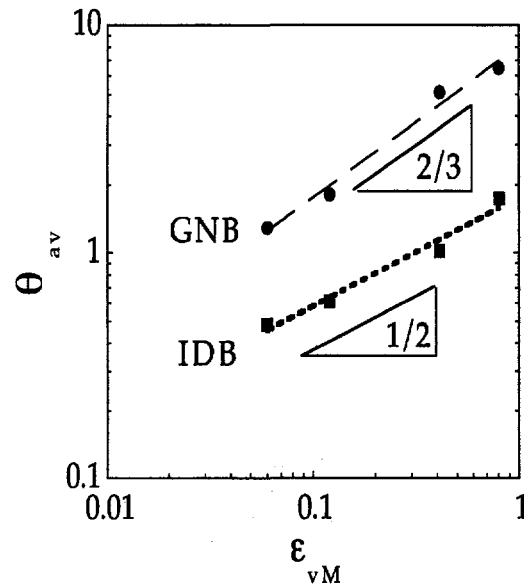


Figure 1. Average misorientation as a function of the deformation (von Mises) strain.

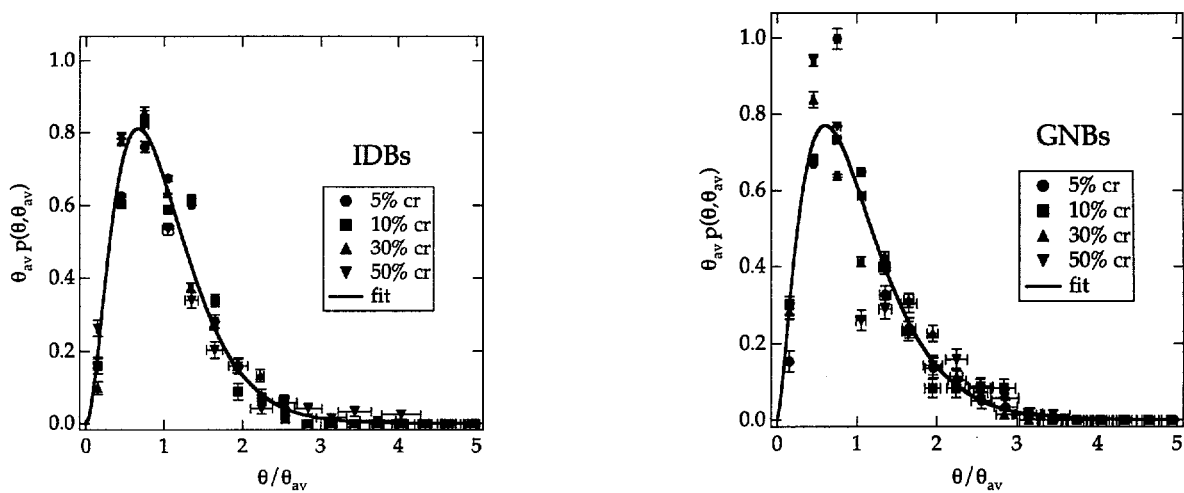


Figure 2. The scaled distributions of misorientation angles are shown to coincide for different levels of deformation. (cr = cold reduction)

Ultrasonic Monitoring of Rolling and Recrystallization Textures in Aluminum

R. B. Thompson, *Ames Laboratory*

R. Bolingbroke, *Alcan International*

Motivation -- The texture (preferred grain orientation) of aluminum alloys plays an important role in determining the ability of sheet to be formed into complex parts such as beverage cans or automotive components. For example, the processes of rolling and recrystallization produce textures which have dissimilar influences on formability, and processing is designed to balance their influences such that optimum forming characteristics are realized. Quality control tools are desired which can be used to ensure that this has been properly accomplished.

Accomplishment -- An ultrasonic technique has been developed which is sensitive to the differences in rolling and recrystallization textures. The technique involves measuring the anisotropy of the velocity of guided modes propagating in the plane of the sheet. In particular, the velocities of longitudinal Lamb modes are measured for waves propagating at 0, 45, and 90 with respect to the rolling direction. As shown in the top accompanying figure, the angular variation is dramatically different for rolling and recrystallization textures, with the former having a minimum velocity near 45 and the latter having a maximum. It is also possible to extract from this information certain parameters which play a prominent role in the quantitative analysis of texture and forming properties. For example, the parameter C_4^{13} ,

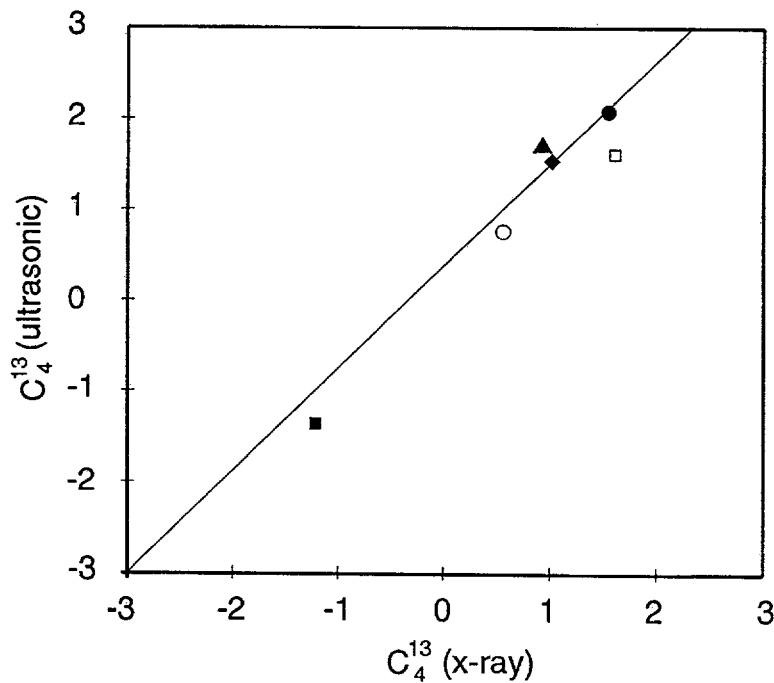
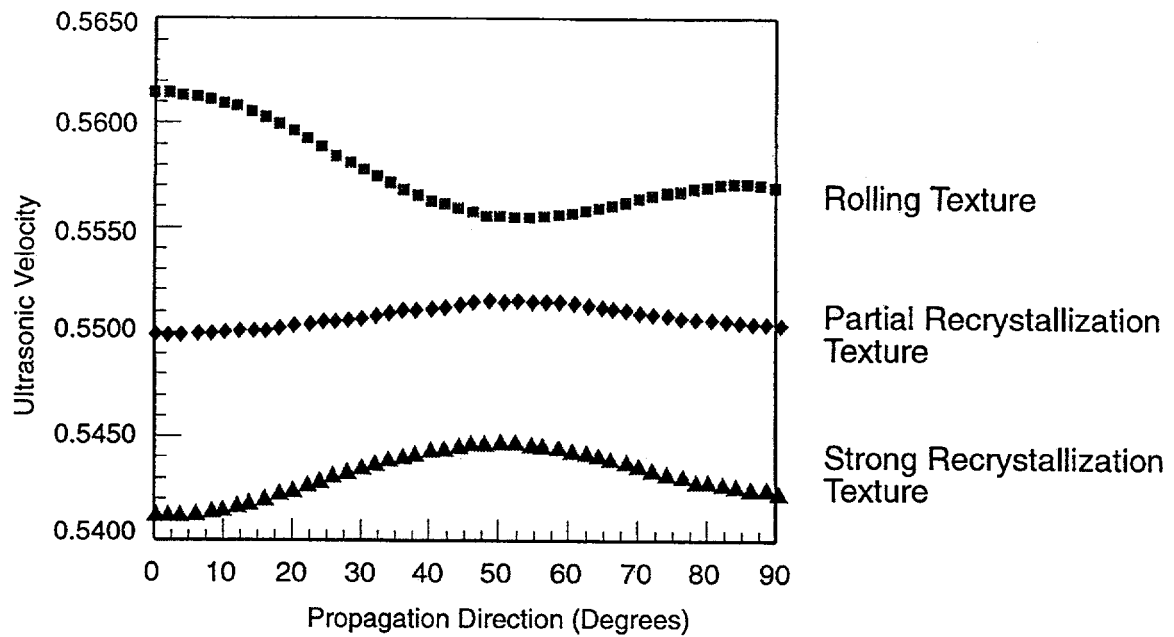
which is closely related to the degree of recrystallization of a sheet, is proportional to the quantity $[v(0) + v(90) - v(45)]$, where v is the measured velocity. The lower accompanying figure presents a validation of the ability of ultrasound to sense this parameter by plotting the values of C_4^{13} inferred from ultrasonics against the values inferred from x-rays for a set of six samples. An important aspect of the technique is that the waves are excited and detected by electromagnetic-acoustic transducers (EMAT's), which require no physical couplant.

Significance -- The control of texture is an important part of the strategy for processing sheet metal. Attractive features of the ultrasonic technique include the facts that a volume average is sensed and that there are no radiation hazards, both in contrast to x-ray measurements. The former is significant since it is the volume average of the texture that controls the forming characteristics of the sheet, not just the texture of a very near surface skin as sensed by x-rays. The fact that the measurements can be made with couplant-free EMAT's, as opposed to the traditional fluid-coupled, piezoelectric probes, greatly increases the opportunity for making measurements in the manufacturing environment, including the possibility of on-line measurements.

Contact:

R. Bruce Thompson, Ames Laboratory

Phone: (515) 294-9649 Fax: (514) 294-4456 E-mail: thompsonrb@ameslab.gov



Ultrasonic velocity measurements can be used to monitor the degree of recrystallization in an aluminum sheet. The upper figure shows the change in the velocity, as a function of angle in the plane of the sheet, as a rolling texture evolves into a strong recrystallization texture. The lower figure compares numerical values of the texture coefficient C_4^{13} , inferred from such velocity measurements, to values determined by x-ray diffraction. This coefficient provides a measure of the degree of recrystallization.

Formability of Al-Mg Alloys in the Solute Drag Regime

G. A. Henshall and D. R. Lesuer, *Lawrence Livermore National Laboratory*

Motivation -- Our objective is to examine "extended ductility" of Al-Mg alloys in the warm forming regime (roughly 200-400°C). In this regime, solute drag of dislocations leads to strain-rate sensitivities near 0.3 and, therefore, large tensile ductilities. Evaluation of alloy chemistry, metallurgical variables, and processing conditions controlling ductility and warm formability of these alloys will be used to better understand the deformation and failure mechanisms in solution-hardened Al-Mg alloys, and to define the critical processing variables required to provide optimal formability.

Accomplishments -- Experiments were performed using two binary alloys: Al-2.8 wt.% Mg and Al-5.5 wt.% Mg. Within this range, the Mg concentration only slightly affects strength and has no significant effect on the failure strain (e_f), which reached values as high as 325%. The tensile ductility was found to correlate strongly with the strain-rate sensitivity (m) and failure occurred by necking to a point. The value of m was controlled by the diffusion-compensated strain rate during testing. Tests performed under widely different temperatures and strain rates resulted in a similar e_f if the diffusion-compensated strain rates were similar. This finding suggests that e_f is controlled by the viscous drag of solute atmospheres by moving dislocations during grain matrix flow.

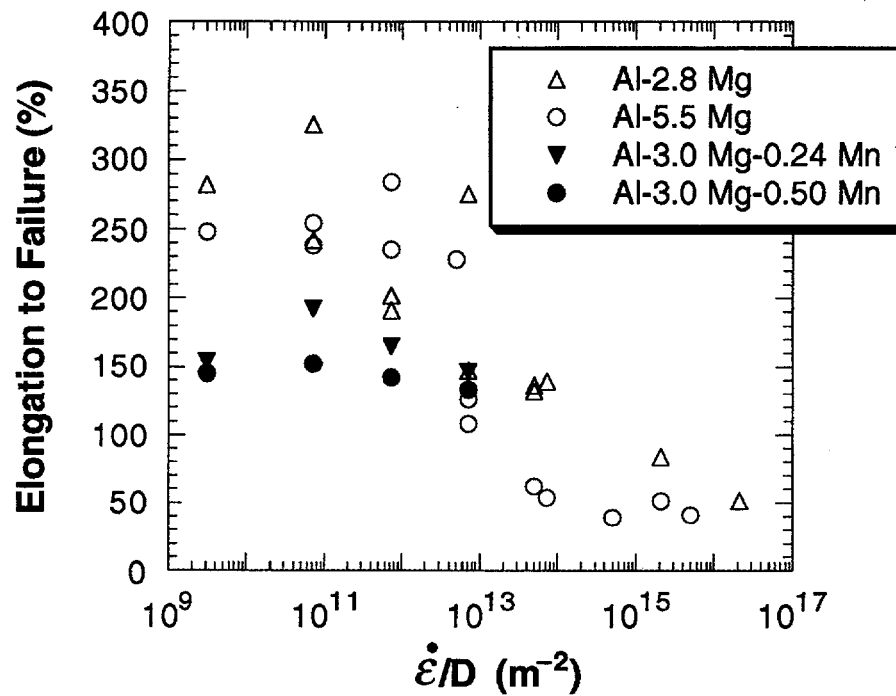
A numerical model of neck growth properly predicts e_f in these binary alloys, indicating

that tensile ductility is controlled by the value of m when failure occurs by necking. Since there is little strain hardening in the regime where ductilities are large, the strain-hardening rate does not need to be included in the analysis.

Further experiments using an extremely coarse grained Al-2.8 wt.% Mg alloy showed that enhanced ductility is not significantly degraded by an increase in grain size. This finding further supports the hypothesis that solute drag of dislocations during grain matrix flow, not grain-boundary sliding, accounts for the large tensile elongations observed in these materials. Finally, experiments were performed using high purity Al-3Mg-0.25Mn and Al-3Mg-0.5Mn alloys. The compositions and processing histories of these alloys were determined following consultation with J. Vetrano at PNL. As shown in the figure, Mn decreases the strain-rate sensitivity of Al-Mg during solute-drag deformation, resulting in lower elongations of 150% to 200%. Mn has a secondary effect of causing ductile fracture before necking to a point when added to Al-Mg in a concentration of 0.5 wt.%.

Significance -- These results indicate that enhanced ductility through solute drag may provide an economical way to improve the formability of Al-Mg alloys.

Contact: G. A. Henshall, Lawrence Livermore National Laboratory
Phone: (510) 423-4417 Fax: (510) 423-7040 E-mail: henshall1@llnl.gov



The tensile elongation to failure as a function of diffusion-compensated strain rate for two binary Al-Mg alloys and two ternary Al-Mg-Mn alloys. Ductilities are largest in the solute drag regime (diffusion-compensated strain rates below $7 \times 10^{12} \text{ m}^{-2}$). In this regime, the ductility decreases as Mn concentration increases.

Characterization of High-Speed Al-Cu Electron Beam Welds

S. A. David and J. M. Vitek, *Oak Ridge National Laboratory*

R. Trivedi and M. Kramer, *Ames Laboratory*

Motivation -- The reliability and performance of welds strongly depends on processing conditions, microstructure, and properties. In addition, the presence of gradients, which are intrinsic to the welding process, can often lead to the formation of defects and variations in properties, and they may be the cause of poor performance and lack of reliability. The motivation for this Project is to address the problem of gradients in weldments and to assess the extent of the gradients as well as the potential influence they may have on weld performance. The specific objective of the Oak Ridge National Laboratory task is to investigate the microstructural evolution and gradients in weldments as a function of welding process and process parameters. Grain structure formation, solidification substructure development, and non-equilibrium phase formation are issues of interest. Analysis is carried out in conjunction with theoretical support from Ames.

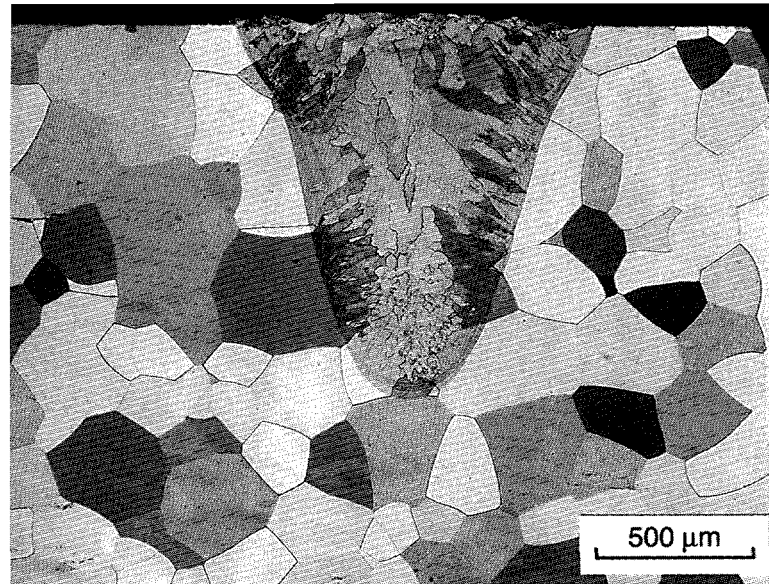
Accomplishment -- The investigation of the aluminum-copper system was initiated. Two different alloys were identified for testing, Al-1%Cu and Al-4%Cu. In order to coordinate activities with Ames Laboratory, the alloys were the same as those being studied at Ames, and were in fact supplied by Ames. Electron-beam welds were made on these two alloys at welding speeds ranging from 30 to 1000 in/min. These extreme conditions were investigated in order to assess the tendency of these alloys to form

metastable phases during rapid solidification conditions typical of electron beam and laser welding. Fine, equiaxed microstructures were found at low welding speeds while large columnar grains were found at high welding speeds. These results are contrary to typical solidification observations in which finer microstructures are prevalent at the higher cooling rates associated with high-speed welding. An example of the typical weld microstructures is given in the figure. In addition, at very high welding speeds, banding patterns indicative of convective flow patterns in the weld pool were observed.

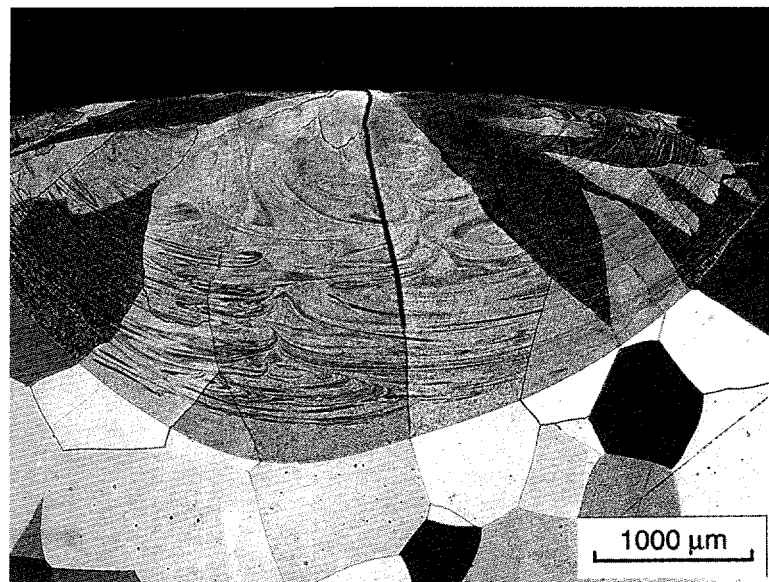
Significance -- The observation of coarser grains at higher welding (solidification) speeds is contrary to common microstructural development in that finer grains are normally found at higher solidification rates. The results indicate that there may be competition between nucleation and growth such that at the higher welding speeds, growth is the controlling solidification mechanism and only limited nucleation takes place. Further analysis of these results is being carried out. The observation of flow patterns in the rapidly solidified material may be useful in that it may provide a means of experimentally studying flow behavior in weldments. Such information would be very useful in testing theoretical computational models that predict flow behavior in welds.

Contact: R. Bruce Thompson, Ames Laboratory
Phone: (515) 294-9649 Fax: (514) 294-4456 E-mail: thompsonrb@ameslab.gov

a)



b)



Weld microstructures in electron-beam welded Al-4%Cu alloy. (a) 150 °/min weld showing fine grain structure in weld and (b) 500 °/min weld showing coarse grain structure and banding pattern indicating convective flow in the weld pool.

Models Predicting Weld Solidification Behavior and Microstructure Are Being Developed and Verified*

J. A. Brooks, N. Y. C. Yang, M. Li, Sandia National Laboratories, Livermore
A. W. Thompson, Lawrence Berkeley National Laboratory

Motivation -- During weld solidification, alloying elements partition between the solid and liquid, oftentimes leaving large compositional differences within different regions of the solidified dendritic structure. The non-uniform composition can result in weld properties being considerably inferior to those of the finely-tailored base material. It is desirable to be able to model the solidification process so one can select weld processes and parameters to optimize weld microstructure and performance.

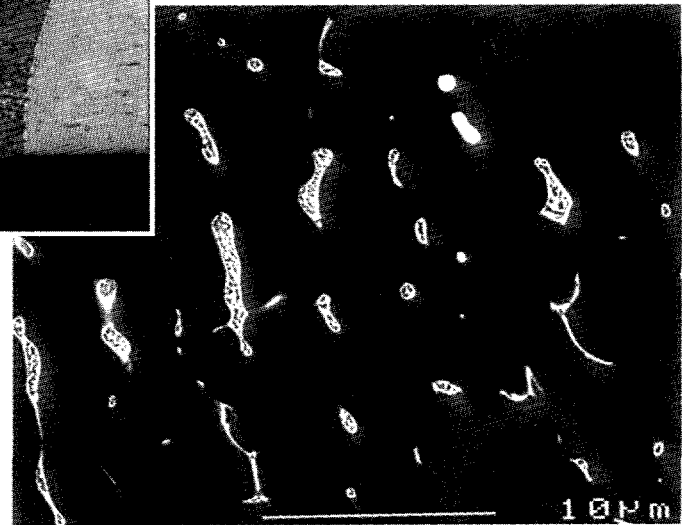
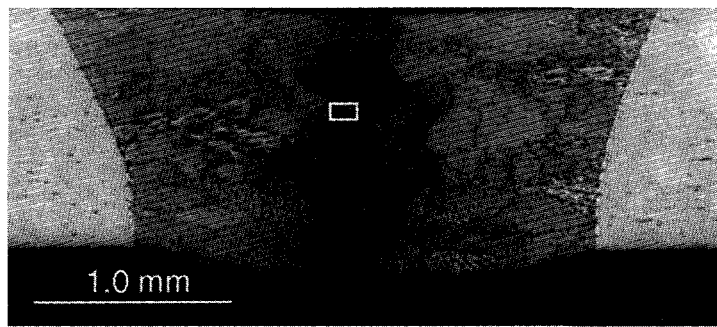
Accomplishments --We have modeled the solidification behavior of Al-Cu welds for a range of alloy compositions. The models incorporate a finite element (FEM) thermal analysis which predicts the solidification velocity and cooling rates occurring along different regions of the weld pool interface. These are the two primary solidification parameters which control the weld structure. The output from the thermal analysis is incorporated into a solidification model to

predict solidification temperature range, volume fraction of solid and liquid during different stages of solidification, and the composition and volume fraction of different phases of the final weld structure. As the figure shows, results of the analysis compare favorably with experimental measurements especially at low Cu concentrations.

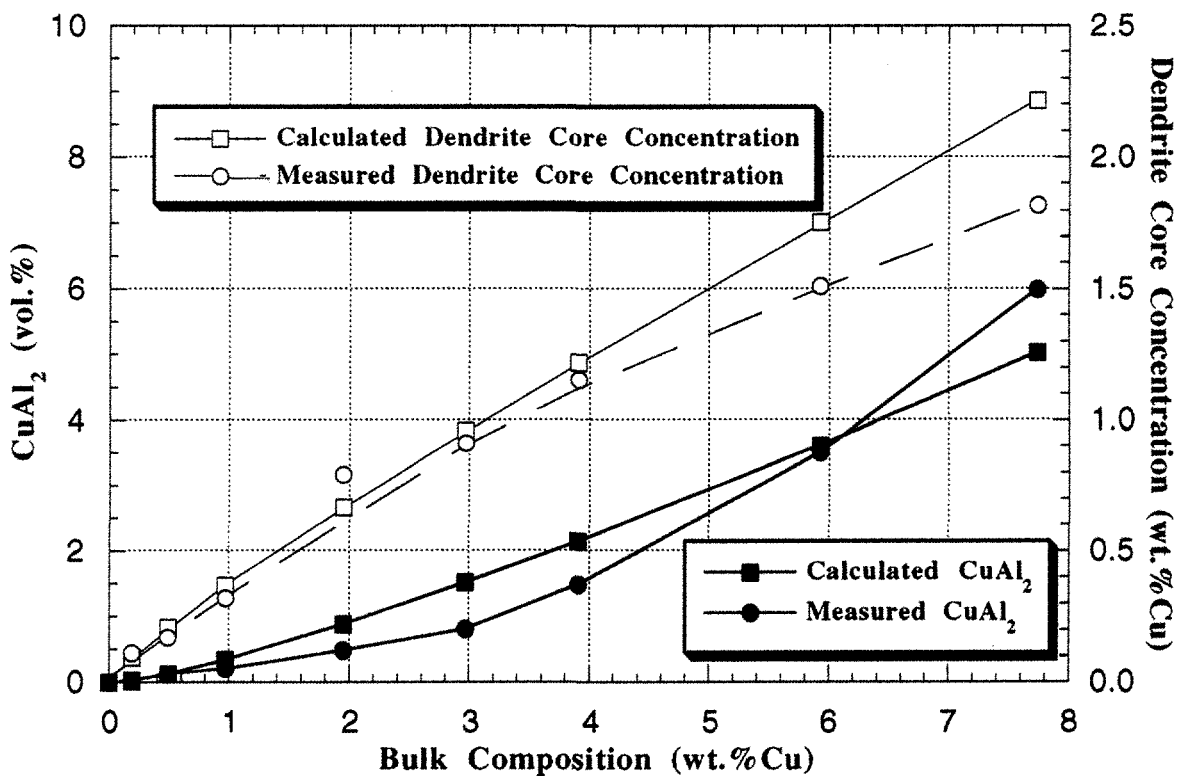
Significance -- The weld solidification models are being incorporated into larger FEM thermomechanical codes to predict solidification cracking behavior. These codes provide the welding engineer with a powerful tool which can be used to develop a weld process in which these often catastrophic defects can be eliminated. Results from these codes are also being used in conjunction with fracture studies to better understand the mechanical behavior of welded structures. The ability to predict solidification behavior and weld structure so that one can optimize the weld process can result in tremendous improvements to weld performance and production costs.

Contact: John Brooks, Sandia National Laboratories, Livermore, California
Phone: (510) 294-2051 Fax: (510) 294-3410 E-mail: jabrook@sandia.gov

*Research sponsored by the Division of Materials Sciences and by Defense Programs, U.S. Department of Energy.



Weld in Al-Cu alloy showing weld macrostructure, and, at higher magnification, the weld microstructure containing secondary solidification product CuAl_2 at interdendritic boundaries.



Measured and calculated dendrite core concentration and volume fraction of eutectic solidification constituent θ (CuAl_2) in Al-Cu welds made at 1.3 cm/sec.

Joining of SiC-Based Ceramics for Elevated Temperature Applications^{*}

B. H. Rabin, *Idaho National Engineering Laboratory*

J. K. Weddell, *DuPont Lanxide Composites, Inc.*

N. Q. Minh, *AlliedSignal, Inc.*

Motivation -- SiC-based ceramics and composites offer the potential for significant efficiency improvements in power generation and energy conversion systems. Practical and reliable ceramic-to-ceramic and ceramic-to-metal joining techniques are required to fully realize the advantages of these materials in industrial applications. In addition, numerical modeling capabilities are needed to support joining development efforts and to assist in joint behavior prediction and evaluation.

Successful joining methods will permit the fabrication of large and complex shaped parts, and will allow integration of ceramic components into existing structures. The goal of this task is to develop joining techniques applicable to SiC ceramics and fiber-reinforced SiC matrix composites, with emphasis on producing ceramic-to-ceramic joints for use in elevated temperature structural applications.

Accomplishment -- Research conducted at the Idaho National Engineering Laboratory (INEL) has led to the development of a technique which permits the fabrication of SiC-to-SiC joints suitable for elevated temperature applications. In this process, which employs methods similar to those used to manufacture commercial reaction bonded silicon carbide, liquid silicon capillary infiltration of SiC+C tape cast precursors is carried out at ~1450°C. Joints having room temperature strengths exceeding 250 MPa are obtained, and joint strengths are maintained at temperatures up to ~1200°C. Joining can be accomplished without the need for high pressure equipment, therefore the

technique can be modified to allow in-field component fabrication and repair. The accompanying figure shows several examples of pressureless sintered SiC parts that have been joined, along with a micrograph of a polished joint cross section. The joint material consists primarily of SiC and Si, so there is little property mismatch and therefore low residual stress in the joints. Technology transfer activities are in progress to move the joining method from the laboratory scale to industrial practice.

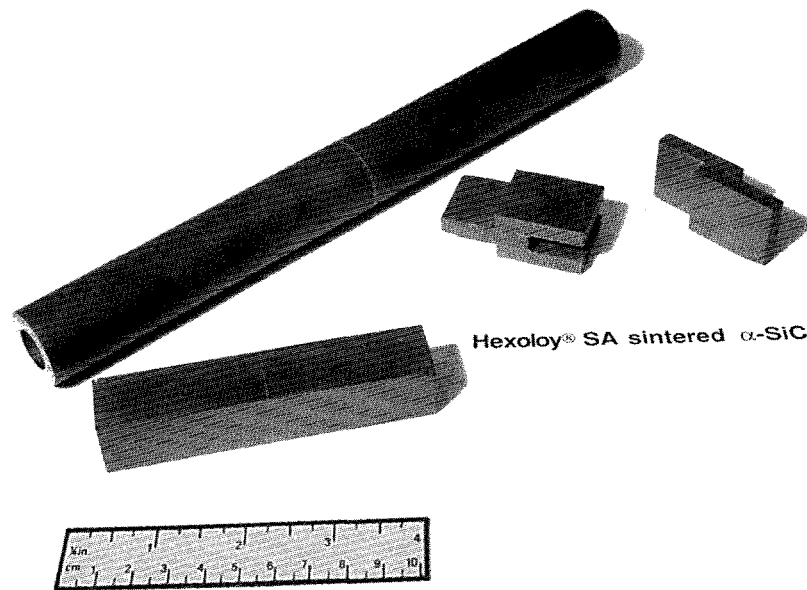
The INEL research has also developed extensive modeling capabilities for predicting residual stresses and thermomechanical behavior of dissimilar material joints and graded materials, an important tool for further development of useful ceramic-to-metal joining methods.

Significance -- The ability to fabricate SiC-to-SiC joints having excellent elevated temperature properties will allow the industrial utilization of SiC in numerous applications where higher operating temperatures result in improved energy efficiency. For example, collaboration with AlliedSignal is focused on the development and construction of an industrial scale high pressure SiC heat exchanger using commercially available pressureless sintered SiC. Work with DuPont Lanxide Composites is examining the applicability of the joining method to fiber-reinforced SiC composites which offer the possibility for improved reliability in applications such as gas turbine components, radiant burner tubes, petrochemical processing systems and heat exchangers.

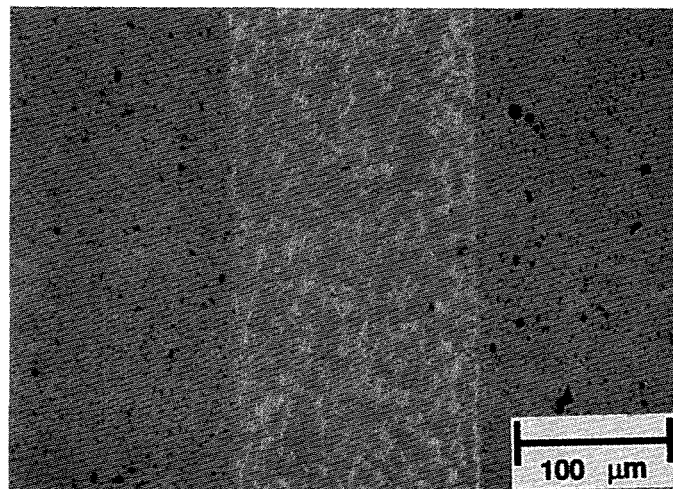
Contact: B. H. Rabin, Idaho National Engineering Laboratory

Phone: (208) 526-0058 Fax: (208) 526-0690 E-mail: bhr@inel.gov

^{*}Partially supported by the Continuous Fiber Ceramic Composites Program, Office of Industrial Technologies, Office of Energy Efficiency and Renewable Energy.



Examples of joined SiC parts.



Optical micrograph showing the microstructure of the ceramic-to-ceramic joint.

*Low Temperature Joining of Ceramics and Ceramic Matrix Composites**

I. E. Anderson, S. I-Maghsoodi, Ö. Ünal, M. Nosrati and T. J. Barton, Ames Laboratory

B. C. Mutsuddy and A. Szveda, Dow Corning Corporation

W. E. Bustamante, Amercom, Inc.

Motivation -- U. S. industry that is involved in high temperature processing operations, e.g., metal heat treating, petroleum refining, glass processing, and power generation, has a critical need for ceramic and ceramic fiber/ceramic matrix composite (CFCC) materials, especially SiC ceramics. The processing environment of these operations is typically characterized by severe oxidation, corrosion, and erosion problems that result in a short life for most common materials. SiC ceramics and SiC-based CFCC materials should extend greatly the lifetime of such components. One critical roadblock to implementation of a material substitution is that, in both manufacturing and field installation environments, there is a need to produce bigger and more complex shapes by joining simpler and smaller ceramic bodies. Unfortunately, a practical SiC ceramic joining technology is currently nonexistent.

Accomplishment -- This Project has developed a novel approach for the joining of SiC ceramics and CFCC components using "glue" which is converted to a strong joint during simple thermal processing. Initial studies were focused on SiC/SiC joining using preceramic polymers and metal alloy powders developed in the Ames Laboratory. The joining materials were prepared by uniformly mixing liquid silicon-acetylene polymers and fine spherical alloy powders (both prepared at Ames Lab) into a viscous paste-like material. The SiC surfaces were cleaned and the joining paste was applied manually. Immediately after joining, the glued assemblies were pressed together by hand in air

at room temperature, sandwiching the glue mixture so that the joining materials conformed to imperfections in the adhered surfaces giving the green assemblies some strength. Finally, the assemblies were fired in an inert atmosphere by heating without pressure at 10°C per minute to 1200°C, holding for 2 hours at 1200°C, and cooling to room temperature. Initial studies of the microstructure revealed good adhesion with uniform loading. Initial ambient temperature strength measurements on SiC CFCC/CFCC butt joints revealed a bend strength of 50 to 70MPa. Qualitative testing of the effect of prolonged exposure (100 hours) to air at high temperature (1100°C) indicated that SiC CFCC/CFCC joints retained structural integrity for mechanical handling at ambient temperature. More extensive testing in-house and at our industrial partners is in progress.

Significance -- An exciting aspect of this joining technique is the ease of field use. When glued green assemblies were fired in air with a propane flame, high quality joints were obtained. The most important benefit of this technique is the application of heat only to the joint area. In fact, we have repaired several broken SiC elements of a resistance heated tube furnace by this method in less than 15 minutes. An example of this joining technique is shown in the following illustration. The repaired elements were used in the furnace for 3 months up to 1200°C without any problems. Recently, the propane flame firing approach has been demonstrated on CFCC material as well.

Contact: Iver E. Anderson, Ames Laboratory

Phone: (515) 294-8252 Fax: (515) 294-8727 E-mail: andersoni@ameslab.gov

*Partially supported by the Continuous Fiber Ceramic Composites Program, Office of Industrial Technologies, Office of Energy Efficiency and Renewable Energy.



Joining of SiC resistance heating elements with Ames Lab glue using a propane torch flame (flame temperature of about 1200°C). The SiC element took less than 15 minutes to repair and has lasted for more than 3 months of furnace service.

Synthesis and Properties of Semiconductor Nanocrystals

M. J. Heben, O. I. Miéié*, A. J. Nozik* and A. Zunger, National Renewable Energy Laboratory
C. W. White, J. D. Budai, J. G. Zhu and S. P. Withrow, Oak Ridge National Laboratory
J. P. Wilcoxon, D. E. Bliss, P. P. Newcomer and G. A. Samara Sandia National Laboratories/NM

Motivation--Semiconductor nanocrystals or quantum dots (QDs) show very profound changes in their fundamental physicochemical properties when their size becomes comparable to the deBroglie wavelength of their charge carriers. This size quantization effect produces unique carrier dynamics and has potentially important applications in novel solar photon conversion, optoelectronics and photocatalysis. In a coordinated effort, Center participants are emphasizing different material systems and approaches to produce and understand these QDs. (See also the following report).

Accomplishment -- Colloidal dispersions of the III-V compounds GaP, InP and GaInP₂ from 1.4 to 4.0 nm in diameter were synthesized and studied at NREL. TEM lattice fringe images and x-ray diffraction showed excellent crystalline quality. The optical absorption spectra were strongly blue shifted with decreasing particle diameter, and for the first time the InP QDs showed strong excitonic features at room temperature. The emission spectra of GaP and InP QDs showed strong PL intensity and band edge emission. The dependence of InP QD band gap on QD size was found to be much weaker than predicted by the effective mass approximation. New pseudopotential methods were developed that can treat 1000 atom nanostructures and thus transcend effective-mass based k-p methods. Optical properties of silicon QDs, wires, and films were calculated; and an indirect-to-direct transition in GaAs QDs as a function of their radii was predicted.

At SNL the emphasis is on metal sulfides as potential photocatalysts. High quality

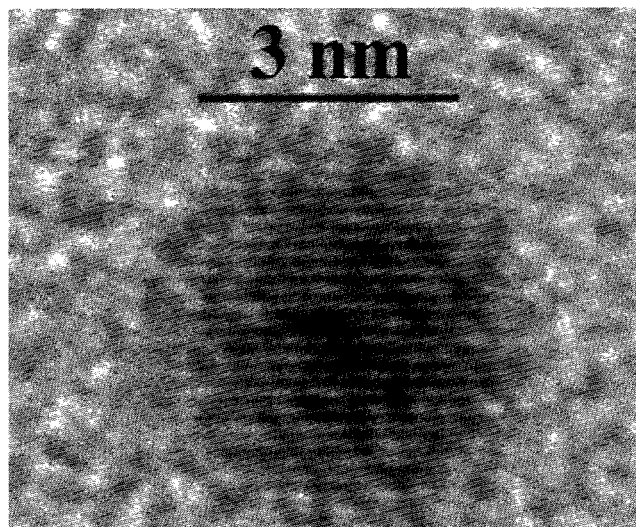
QDs of PbS, FeS₂, and MoS₂ were grown in inverse micelles and their structural and optical properties studied. Their bandgaps, which are typically in the infrared in the bulk, can be shifted to the near ultraviolet by reducing size. Results on metal capping the QDs show that surface related states of one material can be excited through states of a different interior material. This effect has important ramifications for photocatalysts since the functions of energy absorption and energy transfer can be separated. Materials for the interior of the QD can be chosen to be efficient absorbers of light energy, while materials on the surface can be chosen to be efficient at transferring energy to reactants.

At ORNL, Si and Ge QDs embedded in SiO₂ and Al₂O₃ were synthesized by ion implantation followed by annealing. These cubic QDs are randomly oriented in amorphous SiO₂, but are three-dimensionally aligned in the crystalline α -Al₂O₃ matrix. Strong visible photoluminescence near 1.7 eV is observed in SiO₂ samples containing Si nanocrystals. By implanting combinations of different ions, alloy and compound QDs (SiGe, GaAs, CdSe) have been successfully synthesized. SiGe and GaAs possess the expected diamond and zincblende structures, respectively, but CdSe can be formed in either a hexagonal or zincblende structure.

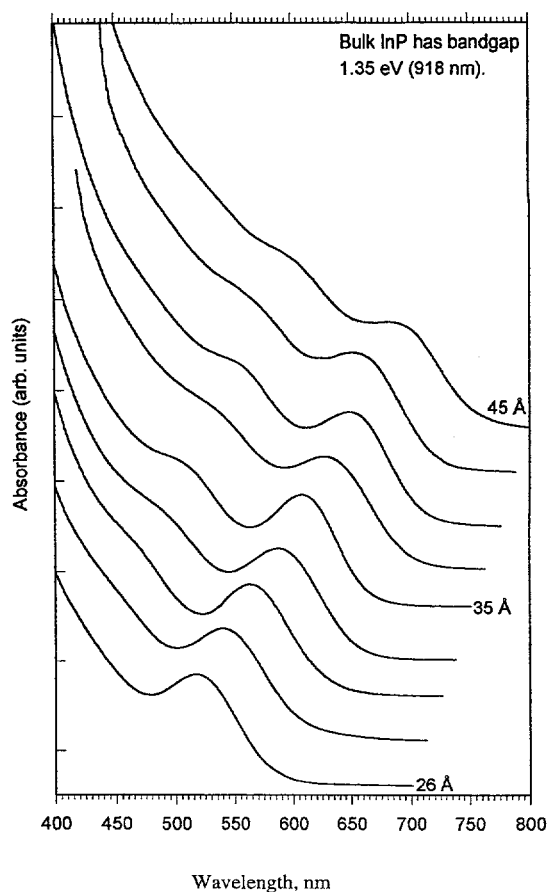
Significance --Our successful synthesis of a wide variety of high quality QDs and development of novel theoretical approaches represent important advances towards the ultimate understanding and utilization of these exciting materials.

Contact: Mark Alper, Lawrence Berkeley National Laboratory
Phone: (510) 486-6581 Fax: (510) 486-4995 E-mail: mdalper@lbl.gov

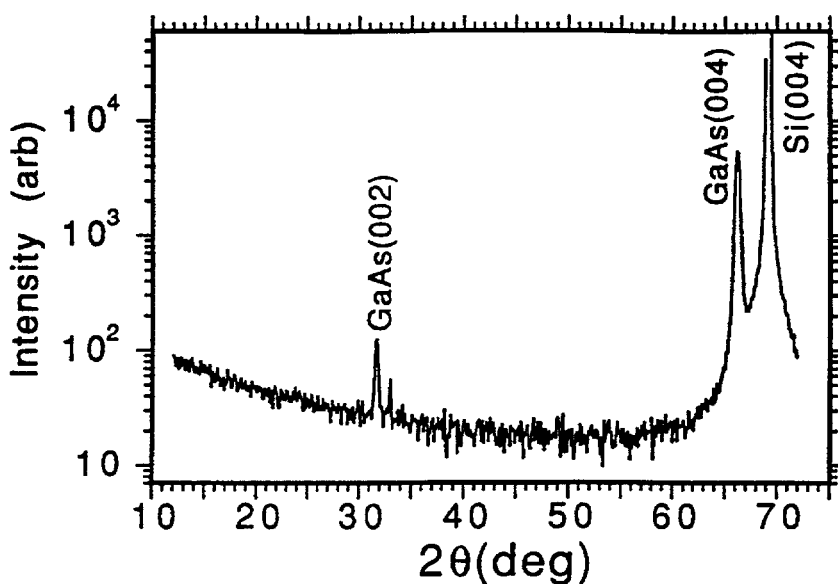
* Supported by BES/Division of Chemical Sciences.



A high resolution transmission electron micrograph of a 3 nanometer (.0000003 centimeter) diameter lead sulfide cluster on a carbon film. The image shows excellent lattice fringes (parallel lines) revealing the high crystalline quality of the nanocluster.



Absorption spectra of InP quantum dots as a function of particle diameter ranging from 45 to 26 Å showing a large and increasing blue shift with decreasing size and structure in the spectra due to size quantization effects.



X-ray diffraction θ -2 θ scans showing the presence of GaAs nanocrystals in silicon produced by ion implantation.

Applications of Semiconductor Nanocrystals

Paul Alivisatos, *Lawrence Berkeley National Laboratory*

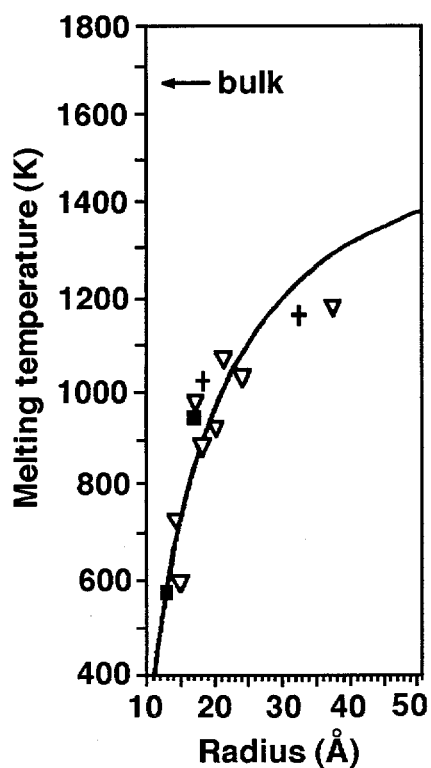
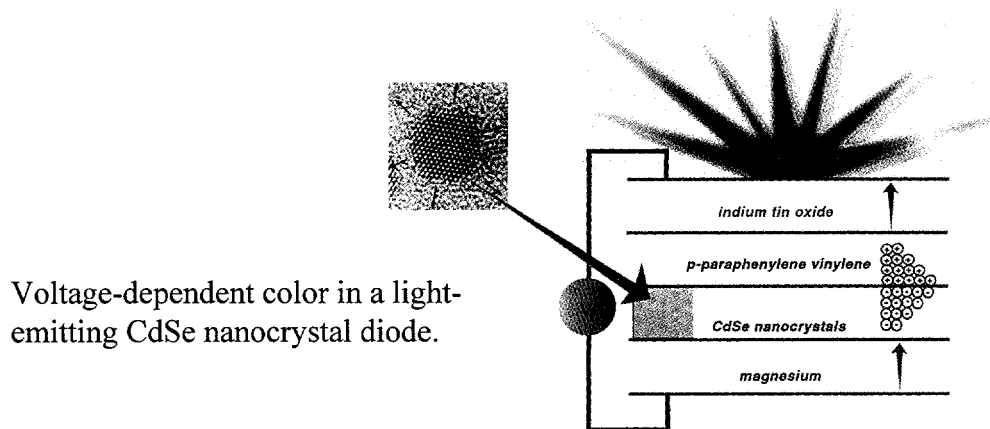
Motivation -- Researchers at LBNL have pioneered inexpensive, solution-phase, colloidal chemistry techniques that can prepare II-VI semiconductor nanocrystals with high crystallinity and narrow size distribution. The electronic properties of these nanocrystals (e.g., the band gap) are a sensitive function of the size of the crystals. As one component of this research effort, LBNL researchers are collaborating with other personnel in the Center for Excellence to investigate ways in which such nanocrystals may be applied to the development of new, low-cost electro-optic and photovoltaic devices.

Accomplishment -- Semiconductor nanocrystals can be deposited readily as monolayers or in multilayer structures, allowing their incorporation into electronic devices. Center researchers have fabricated prototype light emitting diodes (LEDs) by sandwiching nanocrystalline CdSe layers between semiconductor polymer contacts (see figure). The researchers demonstrated that the light emitted by the device could be controlled by changing the size of the nanocrystals - smaller crystals emitted blue light, larger ones red. It is possible that by using multilayers of nanocrystalline materials with different sizes, LEDs with a variable color output may be fabricated. This is not possible in LEDs

fabricated from bulk semiconducting materials. Because of their large surface to volume ratio, nanocrystals melt at substantially lower temperatures than the corresponding bulk solid. It is possible that thin semiconductor films can be formed by depositing nanocrystals via wet chemistry techniques, followed by a heating step that fuses the crystals together. The lower melting point of the nanocrystals will allow deposition of semiconductor layers on heat-sensitive substrates (e.g. glass), due to the lower processing temperatures required. In addition, the cost of such a fabrication technology is potentially very low compared to current chemical vapor deposition methods because expensive vacuum processing steps are not required. As a first step in demonstrating the viability of this technology, a reduction in melting point of over 1000°C was demonstrated in CdTe nanocrystals (see figure). A collaboration has been established with NREL to investigate the feasibility of this technique for fabricating large-area photovoltaics at low cost.

Significance -- The Center researchers have demonstrated that device fabrication using semiconducting nanocrystals may represent a low-cost and versatile alternative to traditional, vacuum-based semiconductor processing. Both light emitting and photovoltaic devices can be fabricated with wet-chemistry techniques.

Contact: A. Paul Alivisatos, Lawrence Berkeley National Laboratory
Phone: (510) 643-7371 Fax: (510) 642-6911 E-mail: alivis@garnet.berkeley.edu



A dramatic decrease in the melting point of nanocrystals is observed as their size decreases. The melting point of 15 Å CdTe nanocrystals is more than 1000°C less than the value for bulk materials.

Early Stages of Sintering in Nanoparticle Systems

D. Olynick, M. Ghaly, H. Zhu, J.M. Gibson, and R.S. Averback, *University of Illinois/Urbana*

MOTIVATION -- The incorporation of nanoparticles in the synthesis of new materials for catalysis, magnetics, electro-optics, and coatings has been undergoing enormous advances. In several of these applications, the interactions of the nanoparticles with themselves (for sintering), with substrates (for catalysis), and with a surrounding matrix (for magnetics and electro-optics) significantly influences the properties of the material. For continued rapid progress in this field, an understanding of the different nanoparticle interactions is essential.

ACCOMPLISHMENT -- The difficulty of experimentally investigating nanoparticle interactions lies in the need to synthesize, process, and characterize these materials, all without ever exposing them to contaminating influences. Over the past two years we have developed, with support of the Center, a system in which nanoparticles of nearly any materials type, can be synthesized and transported through a UHV line to a high resolution, UHV electron microscope (UHV-HRTEM). We further showed, that owing to the ultra small size of the nanoparticles, molecular dynamics (MD) is a practical means to investigate their interactions, and that the combination of TEM and MD is particularly illuminating. Figure a schematically illustrates the nanoparticle characterization facility (NCF). Magnetron sputtering vaporizes materials from any target in a high pressure background of inert or reactive gases to form nanoparticles. The particles are then transported to the UHV-HRTEM for

observation. *In situ* thermal treatment or gas exposure is also possible. Figure b, e.g., shows the effect of oxygen exposure on the sintering and morphology of Cu nanoparticles. Notice that the clean nanoparticles are sintered, even at ambient temperature. The MD simulations, illustrated in Figure c, show that sintering occurs by plastic deformation of the particles, owing to their large surface stresses. A surprising feature is that even at room temperature the particles rotate to form a low energy (twin) boundary.

SIGNIFICANCE -- The development of the NCF now makes it possible to investigate a wide range of problems involving nanoparticle systems. Most promising is the capability for *in situ* studies of nanoparticle interactions with substrates and the effects of gas-dosing on nanoparticle structure, in the context of catalysis. The versatility of the NCF makes studies of various nanoparticle systems possible. Our first investigations of sintering illustrate that the huge stresses developed at the nanoparticle contacts lead to sintering and other structural changes in the particles. This leads to a wealth of opportunities for building nanoparticle-substrate heterostructures, where the structure is tuned for specific applications.

The NCF facility is expected to soon become a focus for collaborations in the Center especially with the work on magnetic nanoparticles and catalysis.

CONTACT: Robert Averback, University of Illinois/Urbana
Phone: (217) 333-4302 Fax: (217) 244-2278 E-mail: Averback@uiuc.edu

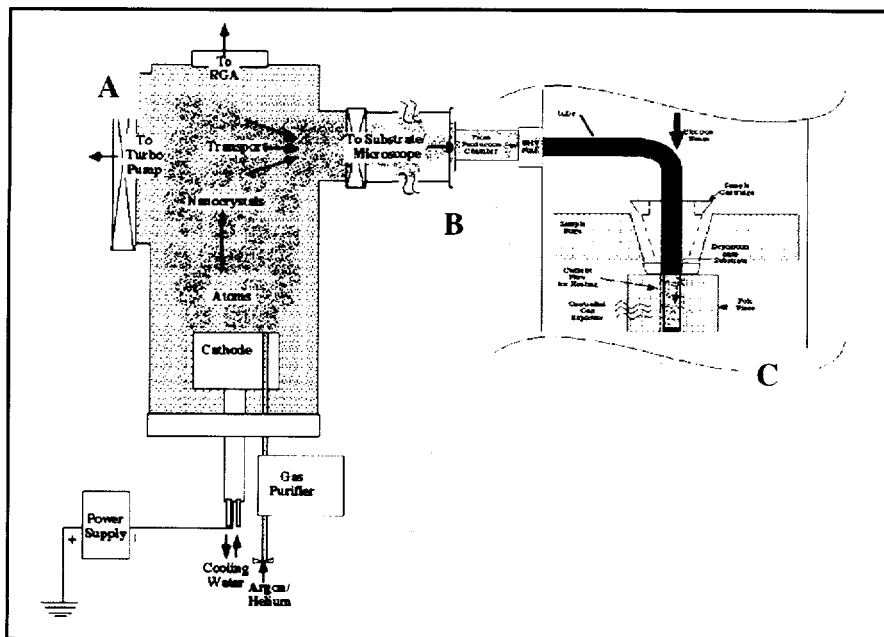


Figure a: Experimental Apparatus A) Production chamber. B) Transport Assembly. C) UHV-HRTEM chamber.

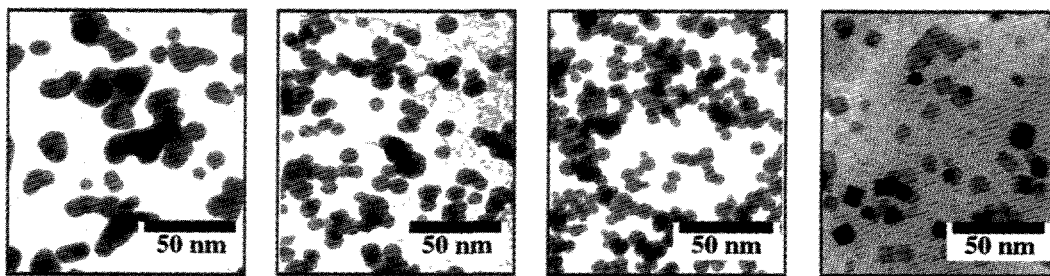


Figure b: Oxygen effects on copper nano-particle morphology - oxygen exposure partial pressure increases from 0 to 1×10^{-3} torr from left to right.

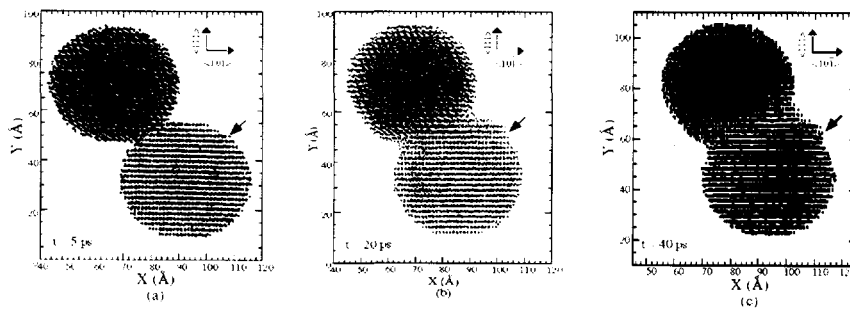


Figure c: Molecular dynamics simulation of two copper particles sintering at time = 5, 20, and 40 ps.

Polyphosphazene Membranes for Separation and Speciation

E.S. Peterson, *Idaho National Engineering Laboratory*

W.D. Samuels and M. A. Josowicz, *Pacific Northwest National Laboratory*

Motivation -- Phosphazene polymers and polymer blends offer enhanced radiation, thermal and chemical stability over conventional organic polymer systems rendering them useful for the development of molecularly specific sensors or for applications as separation membranes in hostile environments. Such materials can be custom tailored to a specific purpose while maintaining both chemical and physical stability in harsh environments. In addition, these polymer systems have been found to exhibit unrivaled versatility in three key separation areas: pervaporation, vapor transport, and nanofiltration. New routes to the preparation of these materials in the form of layers or thin films which support enhanced diffusion have recently been developed.

Accomplishment -- Inorganic polymer membranes and molecularly mixed inorganic-organic porous polymer films were prepared by means of a thermal ring-opening polymerization route or a recently patented anodic electropolymerization process. Molecular blends of polyphosphazene separation membranes, $-[N=PRR']_x$, have been prepared, where the substituent groups R and R' represent both hydrophilic and hydrophobic moieties. The hydrophobic groups impart good film forming characteristics to the blend, while the hydrophilic groups enhance water diffusion through the film thereby improving separation efficiency. Figure 1 illustrates a solvent-swelling mechanism whereby an increase in

flow through the membrane is achieved. An alternate method for enhancing flow requires development of a homogeneous pore structure in the membrane. This has been achieved recently using anodic electropolymerization to assemble a molecularly mixed quinone-phosphazene film at an electrode surface as current is passed through a solution containing one of several quinone type aromatics and a cyclic phosphazene trimer. By varying precursor concentrations, electrode potential, and current, a porous microstructure can be engineered into the film as shown in Figure 2. Both synthetic routes produce membranes which exhibit high diffusivity.

Significance -- Phosphazene polymers and polymer blends offer significant advantages over other separation systems with respect to durability in harsh ambient environments. For example, fuel gases such as methane can be separated readily from acid gases (CO_2 , H_2S , SO_2) at high temperatures with little measurable degradation to the membrane or separation efficiency over time. Possible applications in the fuels industry as well as in activities requiring clean-up of combustion emissions are evident. In addition, such membranes are effective at removing chlorinated hydrocarbons from both air and water waste streams. Appropriately tailored inorganic polymer membrane materials also may find applications as exchange media for clean-up of coolant water in electric power generating plants.

Contact: Greg Exarhos, Pacific Northwest National Laboratory
Phone: (509) 375-2440 Fax: (509) 375-2186 E-mail: gj_exarhos@pnl.gov

Physical Description of Dynamic Membrane Mechanism

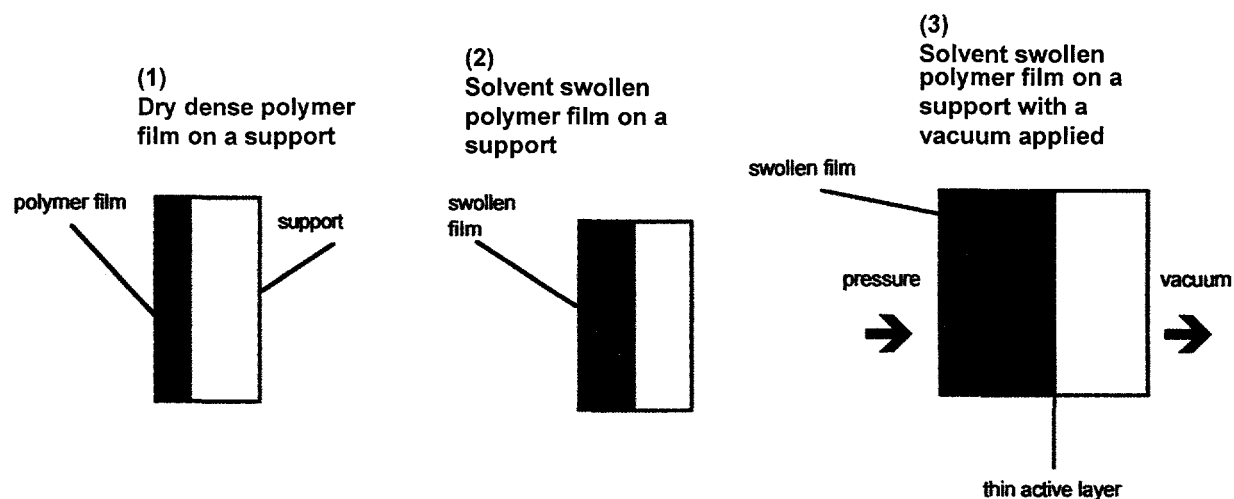


Figure 1. Vacuum filtration enhances fluid transport through the membrane

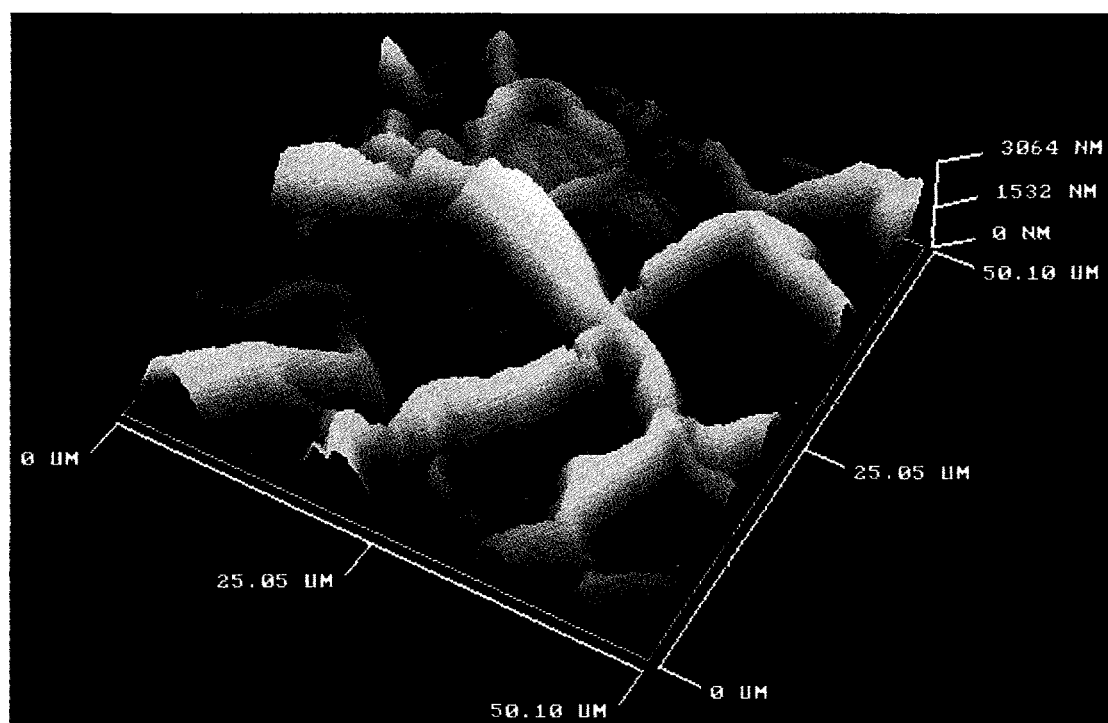


Figure 2. Atomic Force Microscope image showing the porous microstructure of a molecular polymer blend (quinone + hexachlorophosphazene trimer) formed by the anodic electropolymerization process.

Polymer-Based Materials With Controlled Porosity

R.W. Pekala, *Lawrence Livermore National Laboratory*

A. J. Hurd, *Sandia National Laboratories*

W.D. Samuels, *Pacific Northwest National Laboratory*

Motivation -- Advanced processing routes for the synthesis of low density ceramic and polymer based materials having continuous and controlled porosity at the nanometer level have stimulated industrial interest as a result of the atypical thermal, acoustic, optical, and electrical properties which these tailored materials exhibit. From a thermal conductivity standpoint, the presence of a homogeneous distribution of nano-pores in a support matrix, which can be derived through a super-critical fluid processing route, affords a significant decrease in heat flow, rendering such materials superior for insulation applications. To improve the mechanical properties of these otherwise fragile monoliths for building applications, polymer blend and polymer-reinforced ceramic composites have been developed.

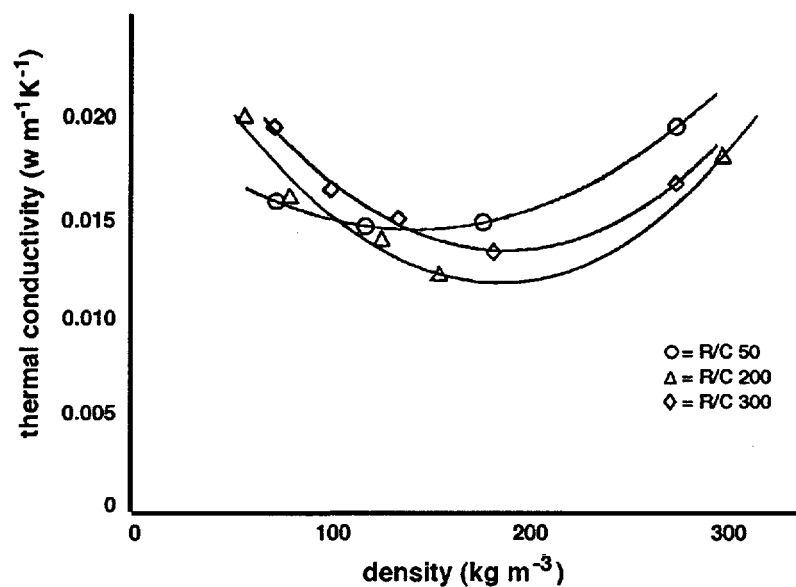
Accomplishment -- Different compositions of resorcinol-formaldehyde (R/F) polymer gels have been prepared by a polycondensation route using selected additions of a polymerization catalyst (C). The R/C ratio was found to alter the surface area, pore size, and attendant mechanical properties of the derived aerogel materials. Competing effects of particle interconnectivity and pore size on measured thermal conductivity are illustrated in the top figure. A broad minimum is observed since the matrix conductivity increases monotonically with density while the gaseous and radiative contributions to the conductivity decrease with density. Similar results are observed in porous materials prepared by means of supercritical fluid processing of silica aerogels in which the

precursor alkoxide containing solutions also contain fluorinated phosphazene polymers. The added polymer coats the porous matrix imparting enhanced mechanical stability. In the dried material, egress of water through the porous matrix is hampered as a result of the hydrophobicity of the polymer coating.

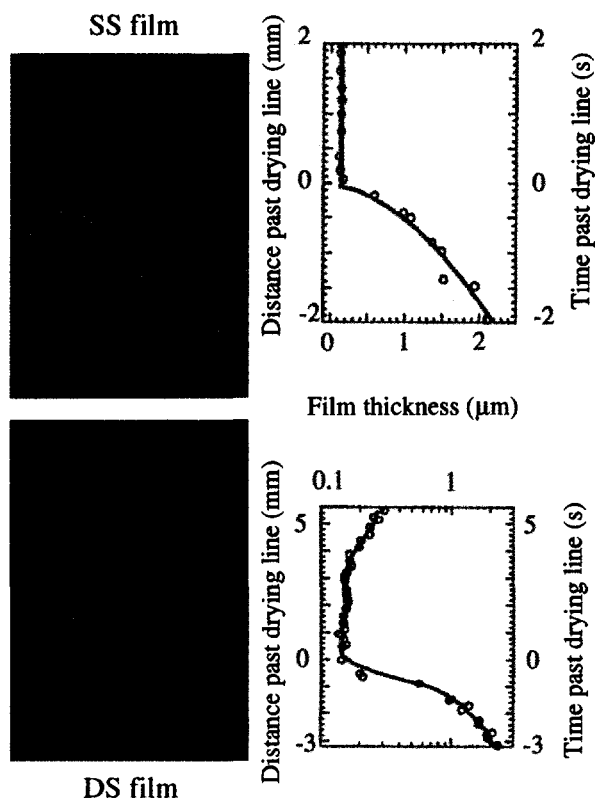
Once thought impossible to produce, aerogel films became a reality via an ambient-pressure aerogel process developed by Center researchers that does not require autoclave conditions (see Fig.). The measurement of aerogel film thermal properties is proving very difficult though the structure of the films appears to mimic bulk.

Significance -- Some 40% of the total energy used in the United States can be apportioned to the building industry. Heat loss from or heat egress into a dwelling is mitigated by thermal insulation which is integrated into the walls, roofs, and windows. In addition appliances, pipes, and both heating and cooling systems require insulation in order to curb energy usage. Improvement to existing thermal insulation material can result in a marked increase in energy efficiency and associated reduction in total energy cost. Materials having controlled pore nanostructures have been shown to significantly reduce thermal conductivity and are candidates for next generation insulation materials. Continuing activities in this Project are focused on the development of advanced processing methods to implement batch processing of these materials.

Contact: Greg Exarhos, Pacific Northwest National Laboratory
Phone: (509) 375-2440 Fax: (509) 375-2186 E-mail: gj_exarhos@pnl.gov



Variation in thermal conductivity as a function of density for nanoporous resorcinol-formaldehyde polymers prepared using several resorcinol/catalyst ratios.



Ellipsometric images of a zone near the drying line during processing of an aerogel film. The standard sol (SS) displays normal drying while the derivatized sol (DS) that makes aerogel films exhibits "springback" in which the thickness rebounds during drying.

Synthesis and Characterization of a New Family of Anion Complexing Agents

H. S. Lee, X. Q. Yang and J. McBreen, *Brookhaven National Laboratory*

Motivation -- Improved battery performance in lithium based systems can be realized if an electrolyte can be developed which increases both the extent of ion dissociation and the Li^+ transport number. What is needed are anion complexing agents that are stable in the battery environment. Although many cation-selective crown ethers and cryptands are known, only a few host compounds bind anions selectively. The field of anion receptors is a very active field of research with most of the work aimed at molecular recognition to mimic how ion-binding proteins control ion transport in biological membranes. Present anion receptors are based either on positively charged sites, hydrogen bonding, or Lewis acid metal centers. None of these are suitable for use in batteries or electrochemical sensors.

Accomplishment -- A new family of stable anion complexing agents has been synthesized. These are either cyclic, linear or branched aza compounds in which the H on the N is replaced by an electron withdrawing group such as CF_3SO_2 , CF_3CO , CN or SO_2CN . They function with anions in much the same way as crown ethers act with cations. This has been confirmed in extensive x-ray absorption (XAS) studies in LiBr, LiCl at the respective Br and Cl K edges and in LiI at the I L_1 edge. These agents greatly increase the conductivity of non-aqueous

electrolytes. For instance, the conductivity of 0.1 M LiBr in tetrahydrofuran (THF) is increased by two orders of magnitude on the addition of 0.1 M of a cyclic aza compound.

Significance -- The key to improving battery performance is to increase both ion dissociation and the Li^+ transport number in the electrolyte. In the past cation complexing agents such as crown ethers and cryptands have been used as additives in polymer electrolytes. The new aza compounds are preferable since they complex anions and will increase the transport number for Li^+ ions. Unlike most known anion complexing agents, which are based on hydrogen bonding, these complexing agents are stable in the presence of lithium. Hence they can be considered for use in lithium batteries. The XAS results indicate that the ability of the linear aza compounds to complex anions depends on the anion size and the chain length of the aza compound. Thus it may be possible to tailor complexes for specific anions. This could have application in molecular recognition in the biomedical field and in sensors. Also it may be possible to devise polymer electrolytes based on anion complexation. These would have very high transference numbers for the cation.

Contact: James McBreen, Brookhaven National Laboratory
Phone: (516) 282-4513 Fax: (516) 282-4071 E-mail: mcbreen@bnlcl1.bnl.gov

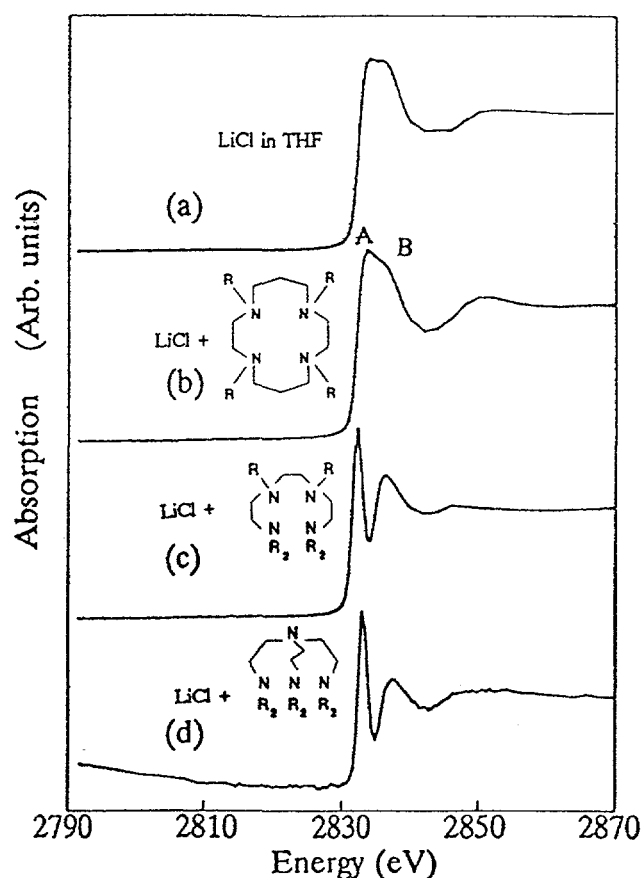


Figure showing near edge x-ray absorption (NEXAFS) at the Cl K edge for LiCl solutions in THF; (a) 0.2 M LiCl and in the same solution with additions of cyclic (b), linear (c) and branched (d) aza complexing agents ($R = CF_3SO_2^-$), aza structures are shown in the figure. The absorption edge at 2830 eV is due to x-rays having sufficient energy to excite Cl 1s core electrons. The features between 2830 and 2840 eV are due to transitions of the 1s electrons into empty 3p states. In a symmetrical environment ((a) and (b)) the 3p states are degenerate and there is a single peak. When Cl is complexed with the linear or branched aza compounds ((c) and (d)) the degeneracy is lifted and the peaks are split.

A Metallurgical Approach Toward Alloying in Rare Earth Permanent Magnet Systems

**R. W. McCallum, M. J. Kramer, K. W. Dennis, *Ames Laboratory*
D. J. Branagan, *Idaho Engineering National Laboratory***

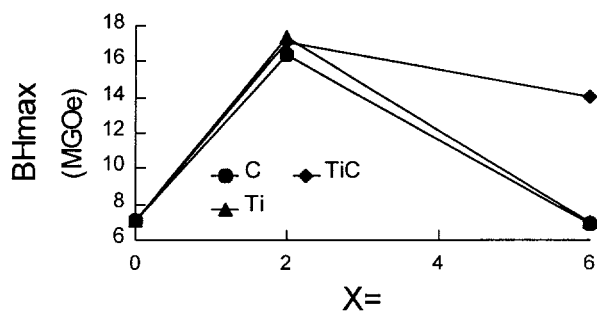
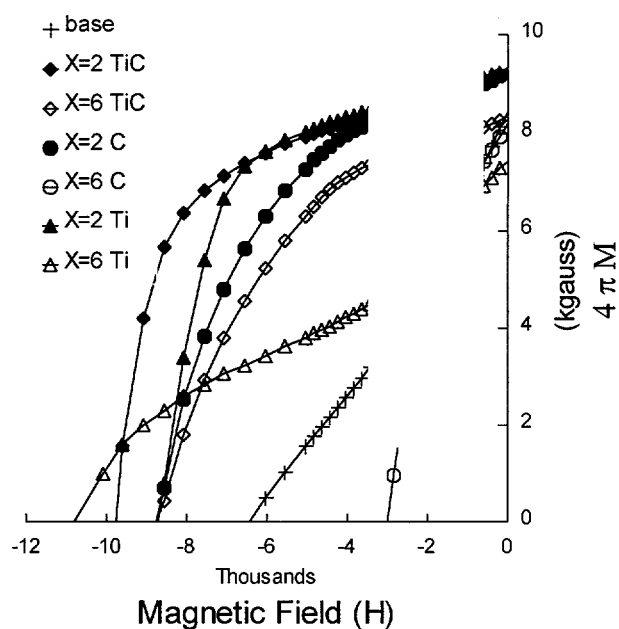
Motivation -- Bulk magnetic materials comprise a large economically important class of materials. For a ferromagnetic material, the response of the bulk magnetization to an external field is governed by the creation and motion of domain walls which separate the material into regions with different directions of magnetization. If the domain walls are hard to nucleate or are strongly pinned to defects or grain boundaries in the material, large magnetic fields are required to change the net magnetization and the material is considered magnetically hard. The dependence of domain wall formation and motion on extrinsic variables means that microstructure plays a crucial role in determining the bulk magnetic properties of these materials. The microstructure of a material may be controlled through the use of metallurgical additions. We have studied the role of a number of additions in the commercially important $\text{Nd}_2\text{Fe}_{14}\text{B}$ based permanent magnets.

Accomplishments -- Starting with stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$, the role of transition metal carbide additions in both the direct solidification of the hard magnetic phase from the melt and the crystallization of the hard phase from an amorphous precursor has been studied. Compound additions of group IVA, VA, and

VIA transition metals along with carbon were added to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ system. Transition metal carbide (TMC) formation was found for the group IVA and VA transition metals. All the TMC precipitates observed formed with a one to one stoichiometry. The most promising addition was found to be TiC which influenced the microstructure in a number of ways. First, the solidification rates necessary to obtain an amorphous precursor were drastically reduced. In addition, the crystallization temperature of the glass was increased, resulting in a finer, more uniform microstructure with correspondingly enhanced magnetic properties. Finally the TiC precipitates which formed during crystallization served to pin the grain boundaries during high temperature annealing so that good magnetic properties are maintained over a higher processing temperature range.

Significance -- The ability to produce materials with good permanent magnetic properties at low solidification rates opens up a variety of possible processing routes for producing powders for bonded magnets. Not only may such processes as gas atomization be used to produce powders, but the process parameters are relaxed so that high temperatures can be used to form more compact and durable parts with an optimum microstructure.

Contact: R. William McCallum, Ames Laboratory
Phone: (515) 294-4736 FAX: (515) 294-4291 E-mail: mccallum@ameslab.gov



Demagnetization curves and maximum energy product for $(\text{Nd}_{2/17}\text{Fe}_{14/17}\text{B}_{1/17})_{100-2x} + \text{Ti}_x\text{C}_x$, $(\text{Nd}_{2/17}\text{Fe}_{14/17}\text{B}_{1/17})_{100-x} + \text{Ti}_x$, and $(\text{Nd}_{2/17}\text{Fe}_{14/17}\text{B}_{1/17})_{100-x} + \text{C}_x$. The alloys were melt spun at 40m/sec to obtain an amorphous precursor and then annealed at 650°C for 1 hour to crystallize the material. For small concentrations, all additives produced enhanced nucleation, and hence finer grain size and better magnetic properties. For higher concentrations, the individual addition of Ti or C resulted in a loss of the hard magnetic phase while the TiC addition maintains the phase.

Importance of Grain Boundary Composition and Structure to Magnetic Reversal Processes in Advanced Permanent Magnets

L. H. Lewis, Yimei Zhu and D. O. Welch, Brookhaven National Laboratory

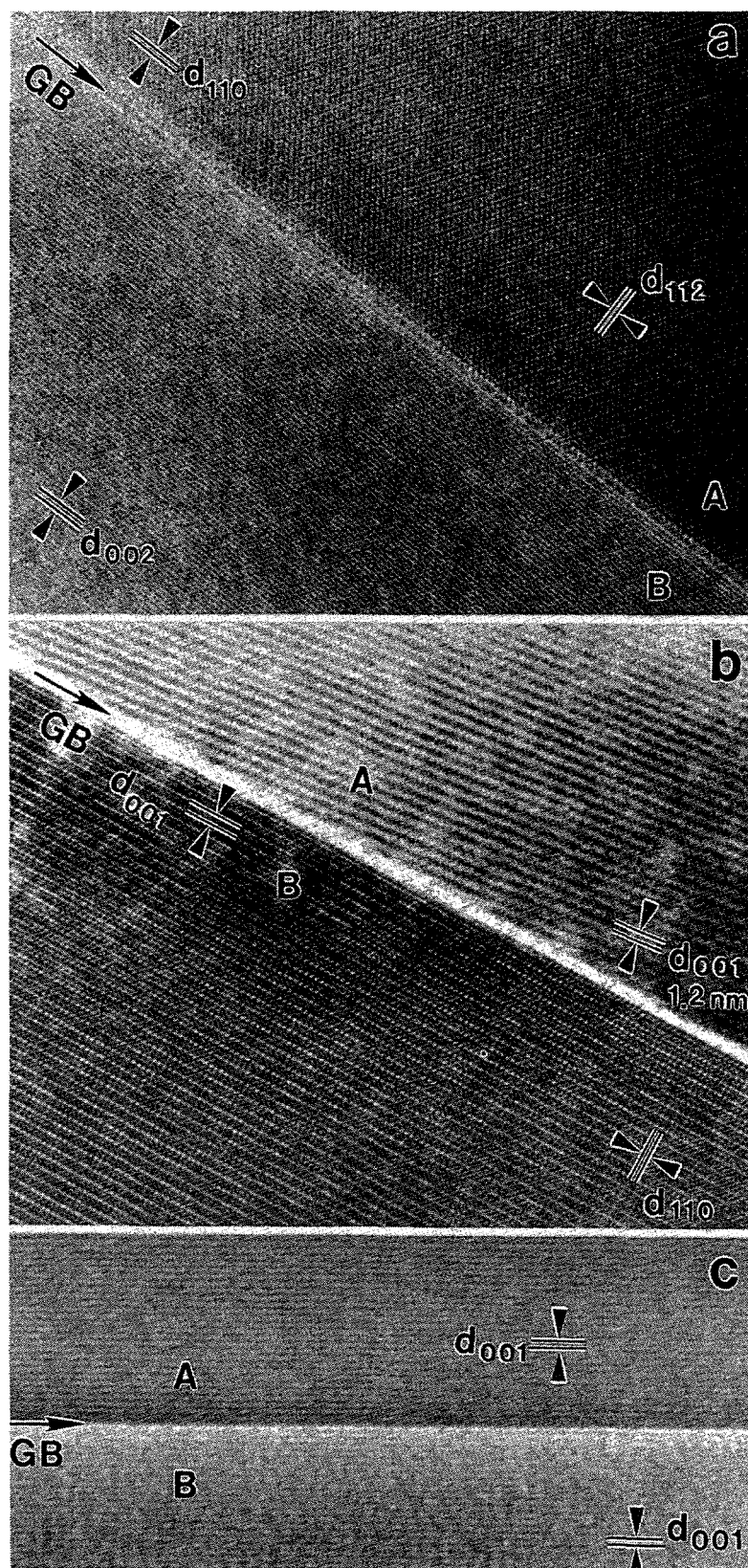
Motivation -- While magnets based on the rare-earth (RE)/transition metal compounds with the composition $\text{RE}_2\text{Fe}_{14}\text{B}$ ($\approx \text{RE}_{12}\text{Fe}_{82}\text{B}_6$) offer excellent room-temperature properties, at elevated temperatures they are plagued by a low resistance to demagnetization (coercivity), among other difficulties. For bonded magnets made from $\text{RE}_2\text{Fe}_{14}\text{B}$ this means that operating conditions are restricted to temperatures in the range 140°C - 180°C , which limits their use in many motor applications. To improve the magnetic properties at elevated temperatures it is necessary to obtain a detailed understanding of the interactions, both exchange and magnetostatic, that result from the magnet's microstructure, which controls the coercivity and its temperature dependence, and to use such understanding to engineer improved magnets.

Accomplishment -- High-resolution electron microscopy and nanoscale chemical analysis demonstrated that the nature of the intergranular phases depends on the character of the boundary between the grains and detected the presence of a previously unknown amorphous, iron-rich grain boundary phase in two thermomechanically-processed rare-earth magnets with bulk compositions $\text{Nd}_{13.75}\text{Fe}_{80.25}\text{B}_6$ and $\text{Pr}_{13.75}\text{Fe}_{80.25}\text{B}_6$. The intergranular phase occurs primarily on grain boundaries parallel to the tetragonal $\text{RE}_2\text{Fe}_{14}\text{B}$ phase c-axis and has an

average width of 8 - 12 Å in the Nd-based magnet and 15 - 20 Å in the Pr-based magnet. The microstructural and nanocompositional evidence, combined with initial magnetization curves and the character of coercivity development at elevated temperatures suggest that the dominant reversal mechanism in these magnets is nucleation of reversed domains in the iron-rich intergranular region which likely possesses reduced anisotropy. The presence of this inter-granular phase is also likely to promote exchange coupling between adjacent grains, which can reduce the coercivity below that for uncoupled grains.

Significance -- This research helps to clarify some of the reasons that the coercivity of polycrystalline $\text{RE}_2\text{Fe}_{14}\text{B}$ permanent magnets is reduced below its theoretical limit and why it is sensitive to temperature. The conclusions reached suggest methods to improve the temperature coefficient of coercivity in die-upset $\text{RE}_2\text{Fe}_{14}\text{B}$ magnets. An ideal microstructure for a nucleation-type magnet consists of grains of a magnetically hard phase that are isolated from interacting via exchange interactions with one another. Therefore, segregation of non-magnetic atoms to the grain-boundary phase via metallurgical manipulation would produce higher-coercivity magnets.

Contact: Laura H. Lewis, Brookhaven National Laboratory
Phone: (516) 344-2861 Fax: (516) 344-4071 E-mail: lhlewis@bnl.gov



High-resolution images of large-angle grain boundaries in (a) $\text{Nd}_{13.75}\text{Fe}_{80.25}\text{B}_6$ and (b), (c) $\text{Pr}_{13.75}\text{Fe}_{80.25}\text{B}_6$. An amorphized intergranular phase is visible in (a) and (b) but not in (c). The boundary planes are as follows: (a) $(110)_A // (001)_B$; (b) $(109)_A // (001)_B$; (c) $(001)_A // (001)_B$. GB indicates the position of the grain boundaries. d_{112} , d_{110} , d_{001} , and d_{002} indicate the spacings of the corresponding lattice planes.

Alloy Design of Nd₂Fe₁₄B Permanent Magnets

J. A. Horton and D. S. Easton, Oak Ridge National Laboratory

J. W. Herchenroeder, Magnequench International, Inc.

Motivation -- Permanent magnet motors using Nd₂Fe₁₄B magnets are generally lighter and more energy efficient than the motors they replace. New applications include appliance motors, automotive accessory motors such as an on-demand electric power steering pump and electric vehicle wheel motors. Poor fracture resistance is a major concern for industrial production, handling, and use. The demanding electric vehicle wheel motor application requires an improvement in the fracture stress before commercial production is feasible. The hard magnetic phase, Nd₂Fe₁₄B, has a large unit cell, low symmetry, and no deformation modes. In order to improve the toughness, techniques derived from toughening of ceramics and from alleviating the brittleness of other intermetallic alloys are being applied to the Nd₂Fe₁₄B magnets.

Accomplishment -- Measurements of the fracture toughnesses of commercial magnets ranged from 2.5 to 5.5 MPa√m (see table). The measurements are sensitive enough to distinguish between manufacturer and processing method. A chevron notch, 3-point bend test that is used to test ceramics and other brittle intermetallics was utilized. Because of the large deliberate notch, this test minimizes the effect of flaws and surface cracks and yields a toughness value

representative of the innate properties of the material. In addition, fewer tests are needed to result in reproducible values as compared to a strength test in which surface flaws and cracks are present. Toughness itself is essentially a measure of the absorbed energy during crack propagation. For the tests reported here, with the specimen geometry used, and with toughnesses greater than 3 MPa√m, controlled crack propagation occurred. For the specimens with the lower values, catastrophic failure occurred and a different method was used to calculate the toughness. (For comparison purposes, alumina has a toughness of 3 to 4 MPa√m.)

Significance -- Demonstrating that a quantitative measurement can yield reproducible results and can distinguish between manufacturers, and between the two main processing methods is an important first step to improve the mechanical properties of the Nd₂Fe₁₄B magnets. Through this Center's activities a common site will be used to make these measurements for magnets produced by other laboratories using different methods of synthesizing and producing magnets. A correlation of toughness with microstructure should lead to improvements of mechanical properties without degrading the magnetic properties.

Contact:

Joe Horton, Oak Ridge National Laboratory

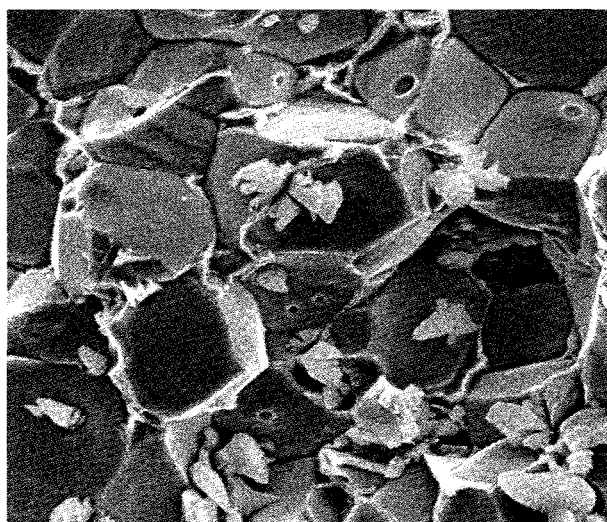
Phone: (423)574-5575 Fax: (423)574-7659 E-mail: htn@ornl.gov

Fracture Toughness, K_{IC} , of Commercial $Nd_2Fe_{14}B$ Permanent Magnets*

Process	Manufacturer	Grade or energy product	K_{IC} , MPa \sqrt{m}	# of tests
Spin Cast & Hot Pressed	Magnequench MQ2	E1	$2.5 \pm 0.2^\dagger$	8
Spin Cast & Die Upset	Magnequench MQ3	E1	$2.7 \pm 0.5^\dagger$	6
Spin Cast & Die Upset	Magnequench MQ3**	H	4.4 ± 0.3	8
Crushed & Sintered	ShinEtsu	45	3.9 ± 0.2	7
Crushed & Sintered	Sumitomo	40	4.4 ± 0.2	6
Crushed & Sintered	Vacuumschmelze	42	5.5 ± 0.2	8

*All specimens, 40 mm span.

**Die upset by Daido Steel Co.

 † Calculated by peak load method, others calculated by area method for controlled crack growth.10 μm

Intergranular fracture surface in a crushed and sintered $Nd_2Fe_{14}B$ magnet showing the behavior of the second phase particles.

A chevron notch, 3-point bend test is able to distinguish the fracture toughness level between manufacturer and production method for $Nd_2Fe_{14}B$ permanent magnets. Baseline property measurements correlated with microstructure and the ability to reliably track small changes in the toughness is essential to improving the mechanical properties of the $Nd_2Fe_{14}B$ magnets. In demanding applications such as electric vehicle wheel motors, an improvement in the mechanical properties is needed before commercial production is feasible.

Low-Stress, Ultra-Hard, Low-Wear Carbon Films

J. W. Ager III, S. Anders, A. Anders, I. G. Brown, *Lawrence Berkeley National Laboratory*
K. Walter and M. Nastassi, *Los Alamos National Laboratory*

Motivation -- Researchers at LBNL and elsewhere have discovered that thin, ultrahard films of carbon can be synthesized by depositing carbon ions from the gas phase under conditions in which the ion energy is controlled precisely. Film with a hardness of up to 60% of that of diamond (the hardest known material) and 85% diamond-like sp^3 bonding can be made at an optimal ion energy of 100 - 200 eV. However, substantial residual stresses in excess of 10 GPa appear to be an intrinsic part of the growth process. These large compressive growth stresses adversely affect the adhesion of the films such that they often fail by delamination in wear tests. Furthermore, the intrinsic film stress limits the thickness to which the ultrahard film can be grown; above a critical thickness that is only 50 nm for the hardest films, the stress causes the film to delaminate from the substrate.

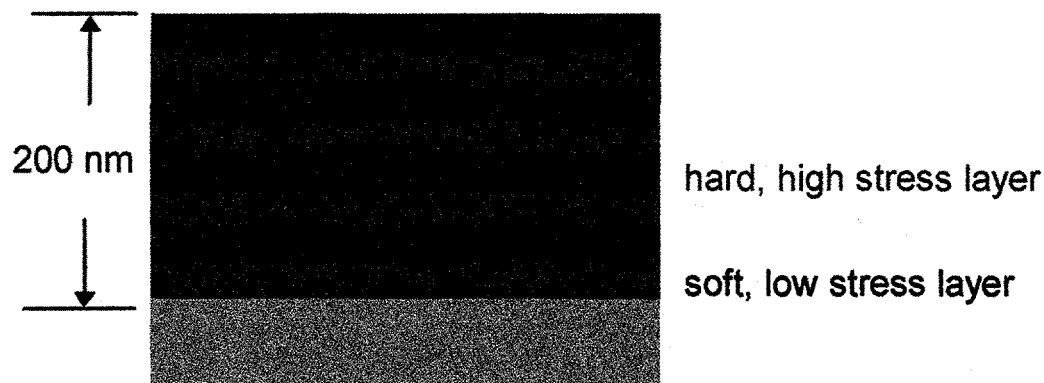
Accomplishment -- LBNL researchers have developed a method to *independently* control hardness and stress in ultrahard amorphous carbon films.

Aided by modeling provided by researchers at Los Alamos National Laboratory, the LBNL researchers designed *multilayer structures* and grew them by cathodic arc deposition. The structures consist of an initial thin layer of low stress material grown with a 2000 V substrate bias which mixes carbon ions into the substrate for enhanced adhesion, followed by alternating harder (high stress) and softer (low stress) layers

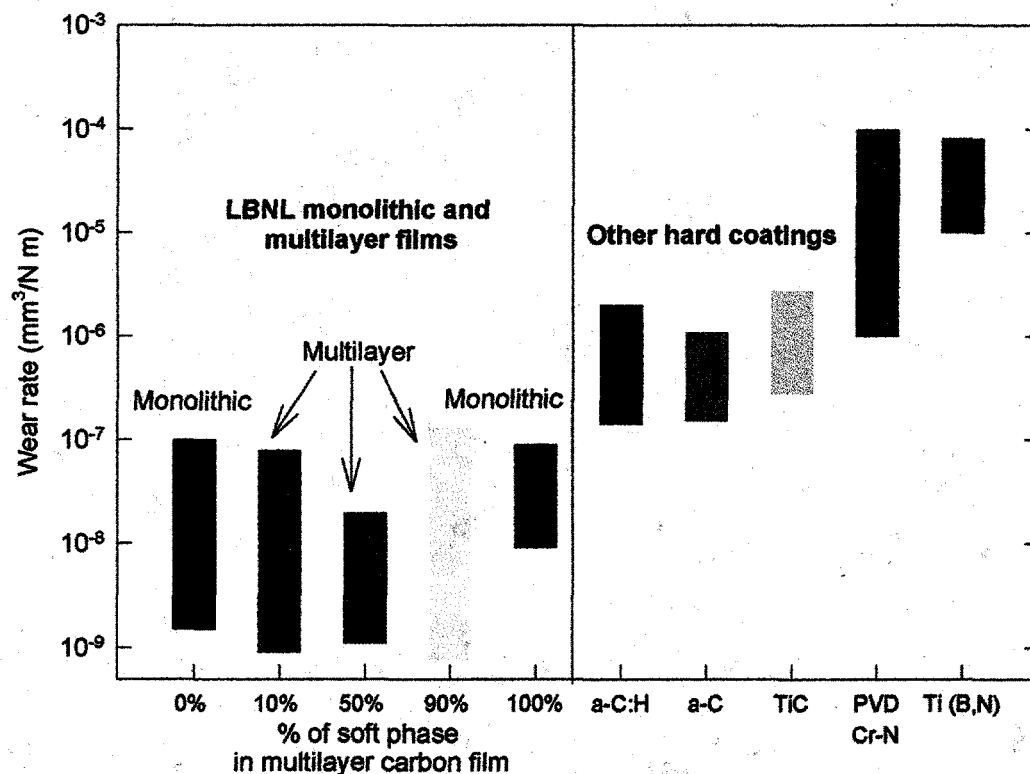
(see figure). The relative thicknesses of the hard and soft layers can be controlled and optimized for best performance. It was found that the hardness of the multilayer structures is the weighted average of the constituent layers (i.e. alternating layers of the same thickness of a hard and a soft film would give a hardness halfway between the layer hardnesses). However, the observed stress was found to be approximately 50% *lower* than the weighted average of the stresses. Films with lower stress are expected to have superior adhesion. The wear rates of the multilayer films have been measured by Center researchers at LANL and are exceedingly low (see figure). The average wear rate of the multilayer films was 10-1000x less than that of other hard coatings. The multilayer film that consists of equal layers of hard and soft material had an average wear rate that was 5-10x less than that of the monolithic hard and soft films.

Significance -- To date, only very simple multilayer structures have been explored. It is possible that more sophisticated structures will produce even lower stress films, while retaining the film hardness and low wear rate. Notably, multilayer structures are no more costly to produce in a cathodic arc deposition chamber than are single layer films. Applications for the multilayer carbon films includes coating for computer hard disk and read-write heads, tooling, and wear components in automobiles.

Contact: Joel W. Ager III, Lawrence Berkeley National Laboratory
Phone: (510) 486-6715 Fax: (510) 486-4114 E-mail: ager@lbl.gov



Wear rates of Protective films



Alternating layers of softer and harder amorphous carbon films are deposited using a cathodic arc process to make multilayer films. The multilayer film has 50% less stress than expected from the monolithic hard and soft films; this leads directly to increased adhesion in the multilayer films. The wear rates of the multilayer films were measured under a variety of conditions and compared to other hard films. The average wear rates of the multilayer films are exceedingly low -- e.g., more than 100x lower than titanium carbide. The optimal multilayer film has equal layers of hard and soft material - its average wear rate is 5-10x lower than of the monolithic hard and soft films.

Synthesis of Hard Boron Suboxide Thin Films Using Electron Cyclotron Microwave Plasmas

S. M. Gorbatkin, R. L. Rhoades, C. Doughty, K. B. Alexander, T. Y. Tsui, and W. C. Oliver

Oak Ridge National Laboratory

D. L. Medlin, *Sandia National Laboratories, Livermore*

A. Jankowski, *Lawrence Livermore National Laboratory*

Motivation -- Boron suboxides (B/O atom ratios > 1) are an interesting class of hard materials that, similar to the cases of diamond and cubic-BN, have been synthesized in various forms for over 25 years using high temperatures and pressures. They are hard and resistant to thermal and chemical degradation, and some phases have been found to scratch the (111) diamond face and easily wear down a diamond tip. Furthermore, boron oxide also exists in a form known to have excellent lubrication properties, and thus it may be possible to synthesize a thin film materials system which is comprised of only two elements and provides both a hard underlying coating with a lubricating overlayer. Despite such encouraging results, little research has been directed towards boron suboxide thin films.

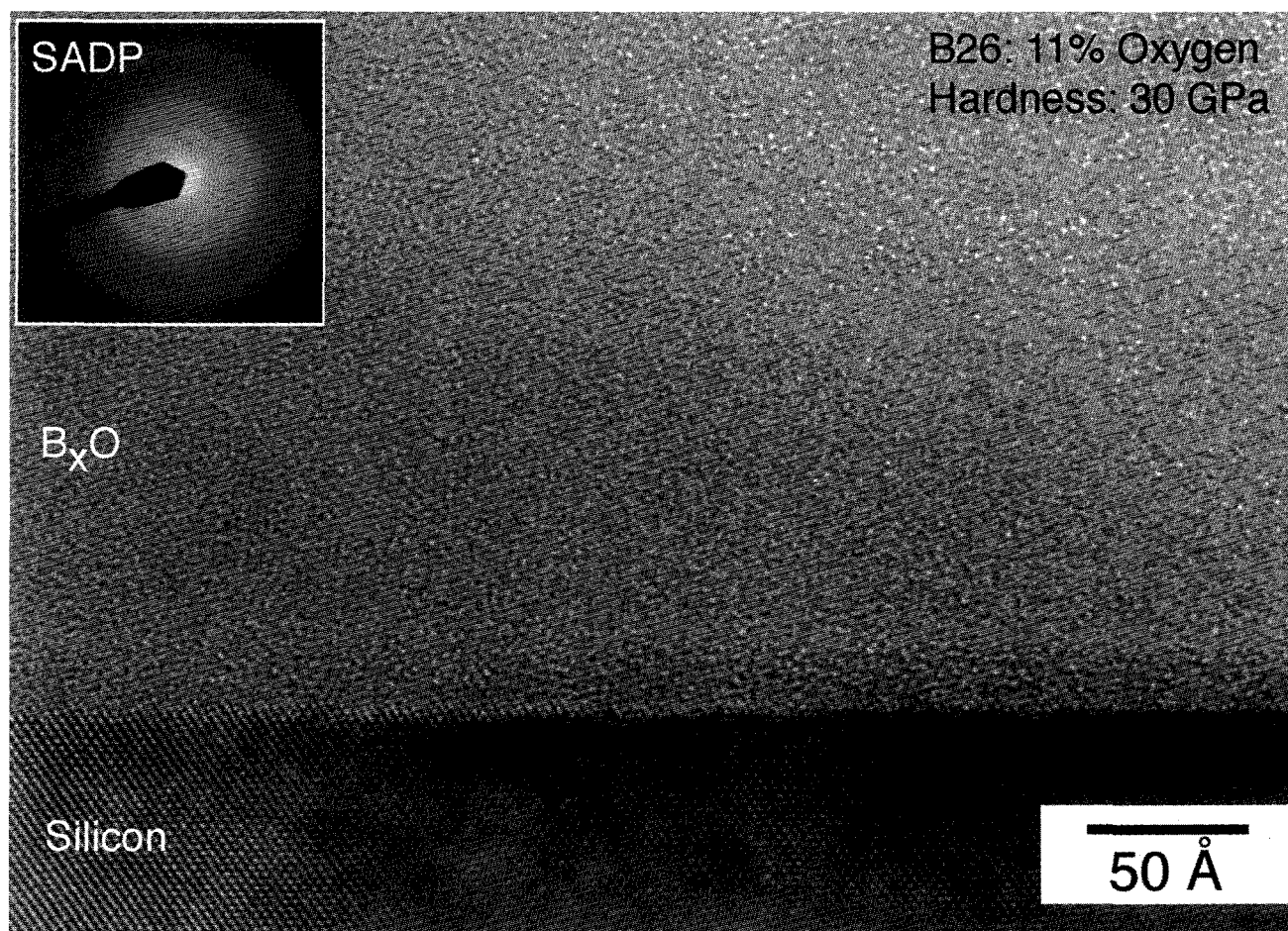
Accomplishment -- Unique thin films of boron suboxide have been fabricated which have friction coefficients of 0.13, hardnesses of 30 GPa, near that of sapphire, and significantly higher hardness/modulus ratios of 0.10 compared to 0.068 for sapphire. The hardness/modulus ratio indicates how much strain the material can accommodate elastically, and a high value is desirable for protective materials. The technique used to fabricate the thin films at Oak Ridge National Laboratory couples either an effusion cell or sputter target, which serves as a source of pure boron, to an argon/oxygen

plasma formed using electron cyclotron resonance. Typical ion energies are less than 50 eV, with approximately 100 eV incident on the growing film surface per deposited atom.

Transmission electron microscopy (TEM) studies at Sandia National Laboratories reveal an amorphous structure for the hard films, with the nucleation of nanometer size crystalline regions present in softer films with higher oxygen levels. Comparisons using TEM to sputtered pure boron films prepared at Lawrence Livermore National Laboratory, combined with electron energy loss spectroscopy, reveal similar local structural environments for the boron atoms in all films.

Significance -- Any application requiring resistance to friction and wear is a potential end use of these films, including power generation, machining, magnetic data storage, and optics. The development of amorphous, boron suboxide thin films represents the discovery of an alternative to amorphous hard carbon, already widely used in the microelectronics industry for hard disk coatings. Development of a detailed understanding of the formation mechanisms of hard, amorphous boron suboxide hard coating may also provide some clues on how to obtain even harder phases, comparable to those which scratched diamond.

Contact: Steven M. Gorbatkin, Oak Ridge National Laboratory
Phone: (423) 576-6502 Fax: (423) 576-8135 E-mail: GSS@ornl.gov



The figure shows a high resolution transmission electron microscopy (HRTEM) image of a boron suboxide hard coating near the interface with a silicon substrate. The inset shows a selected area electron diffraction pattern obtained from the film. The results show that the film is amorphous and devoid of long range structural order. Our current electron microscopy efforts are focused on applying diffraction and spectroscopic methods to determine the short-range order in these amorphous films with the goal of determining the influence of oxygen on the film structure and properties.

Accurate Measurement of Film Stress Using Micromachined Cantilever Beams: Application to Cubic Boron Nitride

P. B. Mirkarimi, D. L. Medlin, and K. F. McCarty, Sandia National Laboratories, Livermore
G. F. Cardinale, Sandia National Laboratories, Livermore & University of California, Davis, CA
J. C. Barbour, Sandia National Laboratories, Albuquerque, NM

Motivation -- Thin-film materials are broadly used in technology. Residual stress is commonly found in films and usually leads to deleterious effects such as substrate curvature or film delamination. On the other hand, stress can be used to alter the film properties. For example, it has been suggested that the high-temperature, high-pressure phase cubic boron nitride (cBN) is formed in film growth through the large compressive stress generated in ion-assisted processes. The typical approach to measuring film stress relies on substrate curvature determination, which has poor spatial resolution and poor sensitivity. The motivation of this work was two-fold: 1) to develop a method to accurately measure film stress with high spatial resolution and high sensitivity and 2) to assess the role of compressive stress in cBN film formation.

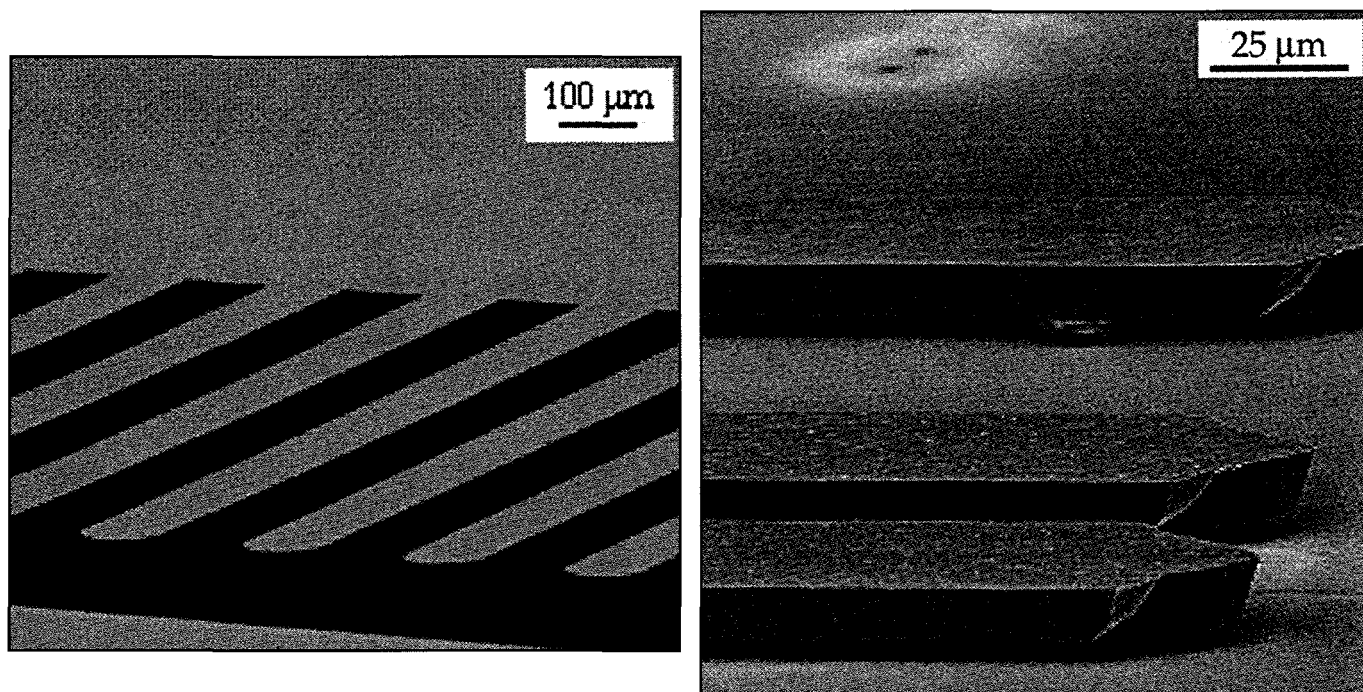
Accomplishment -- We developed a process for micromachining silicon cantilever beams using photolithography and a two-step etch technique. Process optimization gave clean, uniform beams of single-crystal silicon. Boron nitride films were deposited on the beams using ion-assisted pulsed laser deposition. In collaboration with Sandia/New Mexico, the film composition was determined using Rutherford Backscattering Spectrometry and Elastic Recoil Detection. The phase composition of the films was varied from entirely sp^2 -bonded BN (i.e., graphite like) to nearly entirely sp^3 -bonded BN (i.e., diamond

like). Film stress deduced from the bending of the beams, was found to increase dramatically with increasing cBN content. Using a quantitative model, we showed that the film stress increases simply because the elastic modulus of cBN is substantially larger than that of graphitic BN. That is, straining (soft) graphite-like BN produces much less stress than the equivalent strain in (hard) cBN.

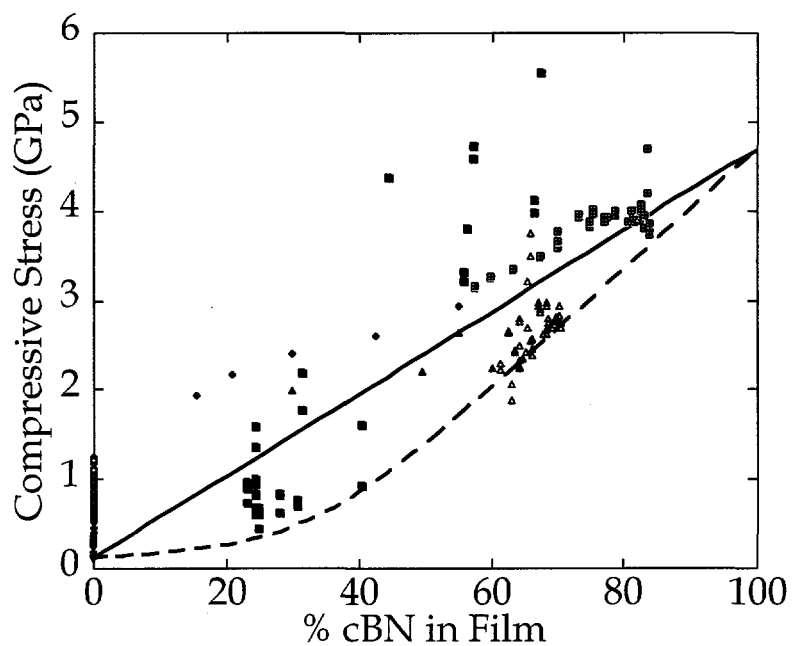
Significance -- Micromachined beams offer significant advantages over traditional wafer bending techniques. Being about 10 microns thick and about 0.1 mm^2 in area, micromachined beams have greater sensitivity and reduce errors from film-thickness non-uniformities. In collaborative efforts, the micromachined beams will be used to quantify film stress in aluminum/aluminum oxide films being produced at Sandia/New Mexico and boron suboxide films being produced at Oak Ridge National Laboratories.

The increase in stress with cBN content has been proposed as proof that cBN is formed under metastable conditions through the high compressive stress generated in an ion-assisted process. Our analysis shows that this reasoning is invalid. While stress may be involved in cBN formation, this conclusion cannot be reached from the stress measurements.

Contact: Kevin F. McCarty, Sandia National Laboratories, Livermore
Phone: (510) 294-2067 Fax: (510) 294-3231 E-mail: mccarty@ca.sandia.gov



Scanning electron micrographs showing the cantilever beams micromachined from a silicon wafer.



Increase of compressive film stress with cBN content. Dashed and solid lines are model results assuming that the film's mechanical properties vary with phase content of the film according to either a rule-of-mixtures or effective medium approximation, respectively.

Oxidation Performance of Plasma-Synthesized Alumina Coatings*

I. G. Brown, P. Y. Hou, *Lawrence Berkeley National Laboratory*

P. F. Tortorelli, K. B. Alexander, *Oak Ridge National Laboratory*

Motivation - Minimizing the deleterious effects of elevated-temperature oxidizing environments is a key aspect of the development of high-temperature materials. The resistance to such reactions is best afforded by the formation of stable surface oxides that are slow growing, sound, and adherent to the substrate and/or by the deposition of coatings that contain or develop oxides with similar characteristics. This latter approach can be used as an alternative to reliance on a protective surface oxide grown during exposure of the substrate material to a high-temperature oxidizing environment. The use of plasma synthesis to deposit thin alumina coatings on selected alloys is being examined as a method of tailoring the characteristics of surface oxides to establish exceptional high-temperature corrosion resistance. This technique was chosen because it has the potential to deposit dense films with strong adhesion to the substrate.

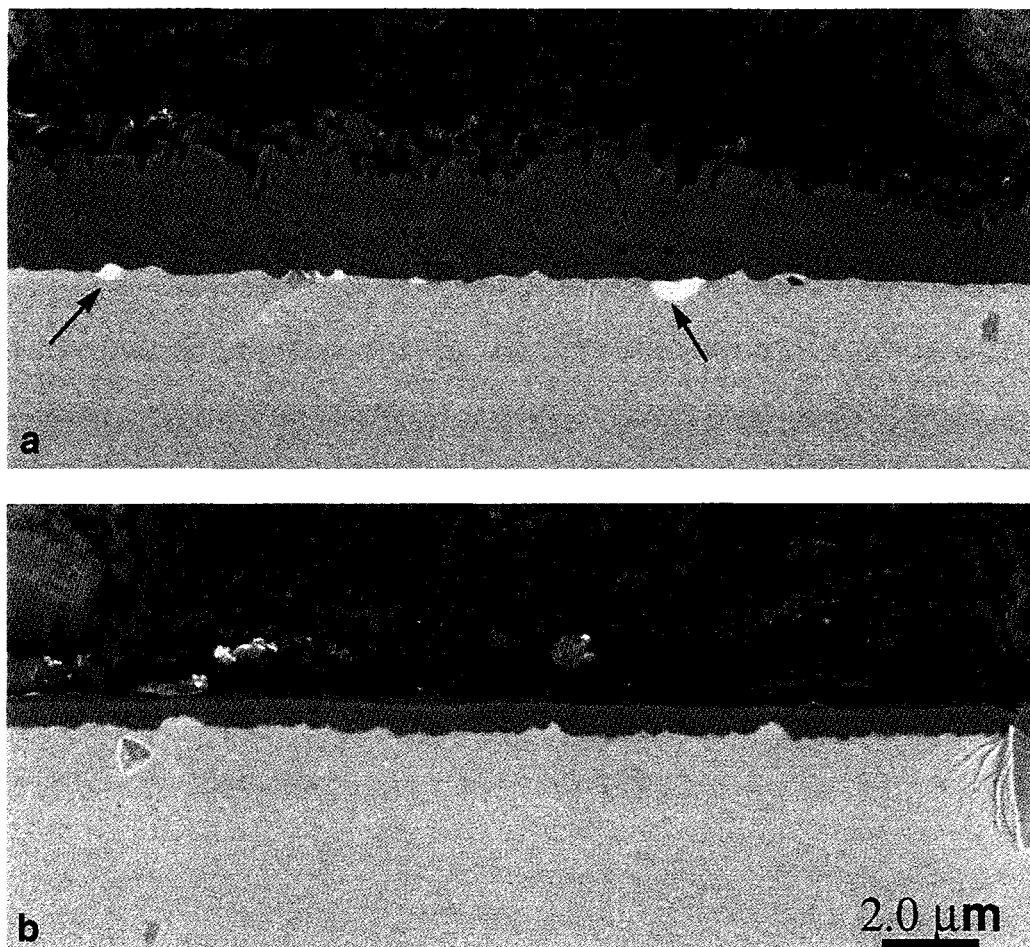
Accomplishment - Plasma synthesis has been used to deposit thin (0.5 - 1 μm) alumina on Fe-Al-Cr(-Zr) alloys. Preliminary experiments have shown that at 1000°C, the overall oxidation rate is lower than that of the matching uncoated alloy. During exposure in the oxidizing environment, oxide was formed between the plasma-synthesized coating and the substrate on which it was deposited, thereby indicating transport of oxygen ions through the original alumina, which was amorphous as deposited but slowly transformed to $\alpha\text{-Al}_2\text{O}_3$. The combined thickness of the thermally formed and deposited surface oxides was less than that of the alumina grown on the exposed, but uncoated Fe-Al-Cr for the same amount of time. It appeared that the presence of

the alumina deposit effectively eliminated the rapid reaction rate associated with the transient oxidation stage that occurs when alumina is grown on an uncoated alloy surface at high temperature. Because the thermally grown alumina forms under the deposit, the adherence of the coating is controlled by the strength of the interface between the alloy and the oxide that develops during exposure to the oxidizing environment. Adhesion at this interface has been shown to be improved when Zr is present in the substrate.

Significance - The demonstration that a plasma-synthesized Al_2O_3 coating can provide high-temperature oxidation protection that is equivalent, or even superior, to that proffered by thermally grown alumina is an important first step in synthesizing improved surface oxides for high-temperature corrosion resistance. Further work is required to establish whether the observed improvement in oxidation resistance is maintained at extended exposure times and to determine how to best control deposition parameters to achieve optimal microstructures and properties. Progress in this latter area is linked to other Project activities aimed at establishing the relationships among composition and properties of the substrate and scale/coating adherence, damage tolerance, and micromechanical properties. In this respect, the finding that coating adherence is controlled by the interfacial bonding between the alloy and thermally grown oxide allows exploitation of the knowledge base that exists for controlling native oxide adhesion by manipulation of substrate composition.

Contact: Peggy Hou, Lawrence Berkeley National Laboratory
Phone: (510) 486-5560 FAX: (510) 486-4995 E-mail: pyhou@lbl.gov

*Research sponsored by Division of Materials Science and Office of Fossil Energy, U. S. Department of Energy, and the Electric Power Research Institute.



Cross-sections of uncoated (a) and coated (b) Fe-28 at.% Al - 5% Cr - 0.1% Zr exposed for 96 h at 1000°C in air. The surface in (b) was first coated with 0.6 μm of alumina deposited by plasma synthesis yet showed a thinner overall oxide layer after exposure; new oxide formed at the interface between the coating and substrate. The bright features indicated by arrows are zirconia-rich particles. The indentations shown are from micromechanical characterization of the surface oxides and substrate.

Impurity Segregation To Alumina-FeAlCr Alloy Interfaces^{*}

P. Y. Hou, R. M. Cannon, *Lawrence Berkeley Laboratory*

K. Natesan, B. W. Veal, *Argonne National Laboratory*

Motivation - The protective surface oxides that provide environmental protection of materials at high temperatures must not only be chemically stable but also adherent to the substrate on which they are grown or deposited. The effective adhesion at the oxide-substrate interface is determined not only by the atomistics of bonding between the principal elements, but also by the interfacial structure, geometric factors, and the nature and extent of defects. The presence of impurities at the interface can influence bonding and defect development as well as reduce the interfacial fracture energy at the lower temperatures where spallation of oxide layers occurs. The chemical characterization of the interface is therefore an important issue in understanding the relationships between oxidation resistance, microstructure, and the mechanical behavior and adhesion of protective surface oxides. These links serve as the foundation of the effort to develop mechanically reliable scales and coatings for high-temperature corrosion resistance. One component of the interfacial characterization effort is the use of Auger electron spectroscopy (AES) to probe the chemistry at oxide-metal interface produced during the high-temperature oxidation of FeAlCr alloys to form surface alumina. The issue of segregation to alumina-alloy interfaces is not only of great current interest for oxidation protection but also for the durability of thermal barrier coatings, which often are designed with an underlying alumina-forming bond coat layer.

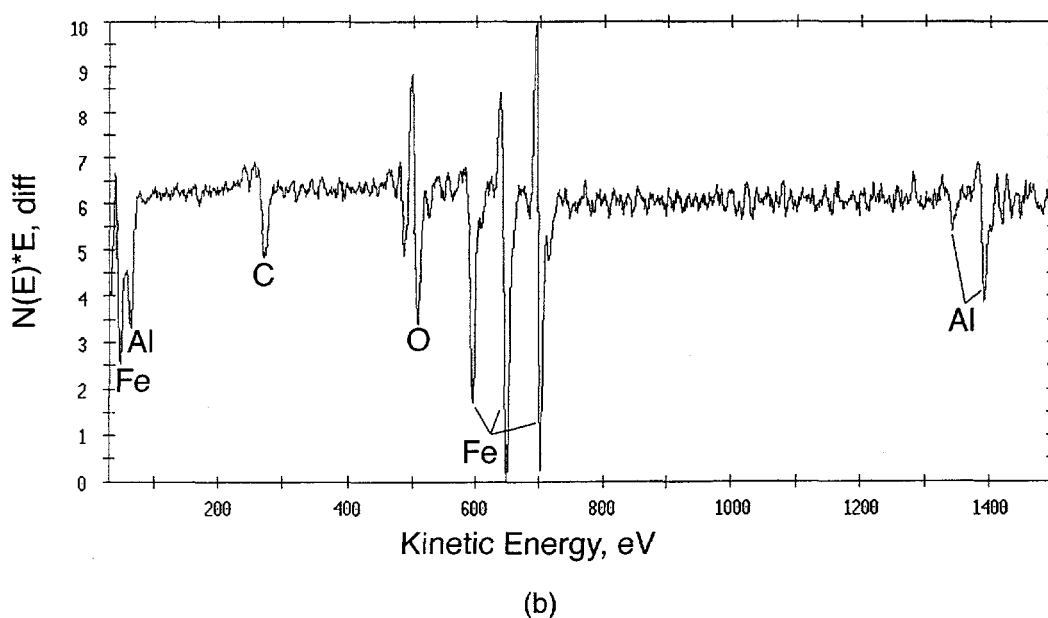
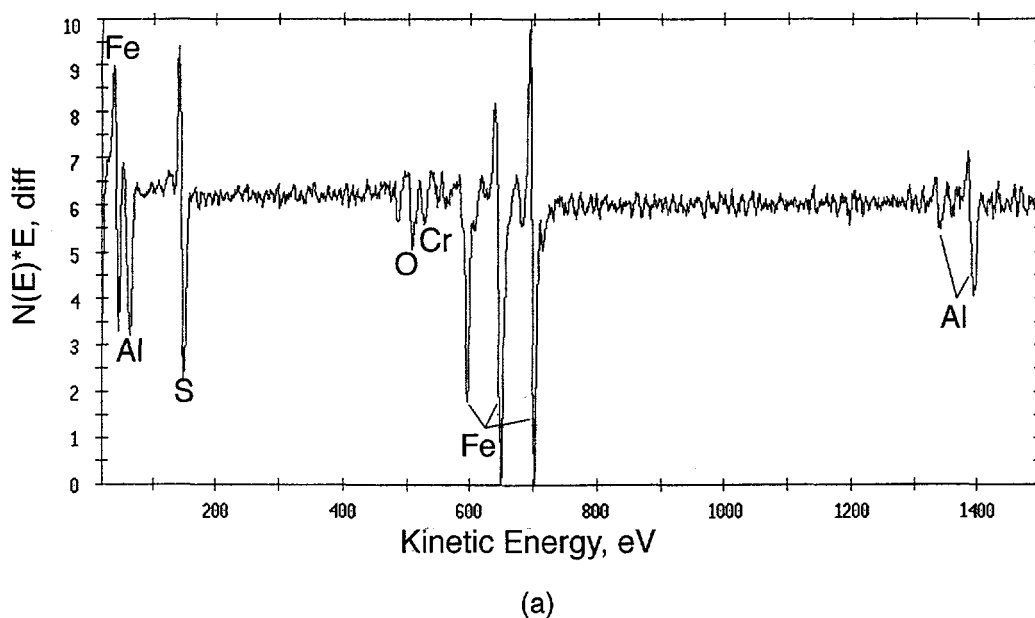
Accomplishment - For Al_2O_3 thermally grown on certain Fe-28Al-5Cr (at.%) alloys, elevated

levels of sulfur were detected at the oxide-metal interface by AES. Such observations were made by in-situ monitoring of a slowly growing scale as well as by ambient-temperature analysis of as-grown oxides. In the latter technique, an oxidized specimen is inserted into a scanning AES system after which the oxide is scratched to expose the oxide-metal interfacial region for analysis. No other impurities were consistently observed at these interfaces, nor was a significant amount of sulfur found in the bulk of the surface oxide. The presence of sulfur at this interface can be correlated with poor scale adhesion: in each case where sulfur was detected, extensive spallation of the thermally grown oxide occurred. On the other hand, the scratch method revealed the absence of sulfur for the case of an alloy (Fe-28Al-5Cr with 0.1Zr) that has been observed to have good adhesion of its thermally grown alumina scale.

Significance - Despite a significant amount of study of Fe-Al-Cr alloys over recent years, the present observations related to sulfur at the oxide-metal interface and the correlation of its presence with scale adhesion were the first such results for this system. These findings are also relevant to other Project work on alumina coatings on FeAlCr alloys: Al_2O_3 forms underneath the deposit during high-temperature oxidation and its ability to bond to the substrate determines whether the coating is adherent. This work is the initial step in defining the role of substrate compositional manipulations (such as the addition of Zr) on impurity segregation and the modification of interface structure in developing reliable surface oxides.

Contact: Peggy Hou, Lawrence Berkeley Laboratory
Phone: (510) 486-5560 FAX: (510) 486-4995 E-mail: pyhou@lbl.gov

^{*}Research sponsored by Division of Materials Science and Office of Fossil Energy, U. S. Department of Energy, and the Electric Power Research Institute.



Auger electron spectra from specimens of Fe - 28 at.% Al - 5% Cr (a) and Fe - 28 at.% Al - 5% Cr - 0.1% Zr (b) that were first oxidized at 1000 and 1200°C, respectively, then scratched to expose the alumina-alloy interfaces for analysis. The alloy with sulfur at the oxide-metal interface showed a tendency for extensive spallation of the thermally grown scale during cooling from the oxidation temperature. The alloy containing Zr did not show sulfur segregation and displayed good scale adhesion during thermal cycling.

Strain Development In Thin, Thermally Grown Alumina Layers*

B. W. Veal, M. Grimsditch, K. Natesan, Argonne National Laboratory

R. L. Williamson, Idaho National Engineering Laboratory

R. M. Cannon, P. Y. Hou, Lawrence Berkeley National Laboratory

Motivation - Protection from environmental corrosion and degradation is required to fully exploit the potential of advanced high-temperature materials designed to improve energy efficiency and minimize environmental impact. The resistance to such reactions is best afforded by the formation or deposition of a stable, slowly growing surface oxide that retains its mechanical integrity in the presence of stresses imposed at high temperature and during thermal transients. A major barrier to understanding and modeling how oxide coatings and scales accommodate such stresses is the lack of accurate and sensitive methods to characterize the strain in these thin (0.5 - 3 μm) surface layers. To this end, fluorescence spectroscopy is being used to measure strains in alumina layers on Fe-Al-Cr alloys. For comparison to the measured values, finite element techniques are being used to calculate strains for Al_2O_3 layers on these substrates based on differences in thermal expansion coefficients.

Accomplishment - Compressive strains in thin thermally grown Al_2O_3 were measured at room temperature by observing the peak shift of the Cr fluorescence line as the growth temperature (and, consequently, scale thickness) was varied. This "ruby line" fluorescence is caused by the excitation of a very small amount of substituted chromium in the alumina. Based on the known piezospectroscopic coefficients and elastic constants for Al_2O_3 , the observed fluorescence shifts are translated into measurements of strain in the scales. The magnitude of the measured strains were in general agreement with the predicted

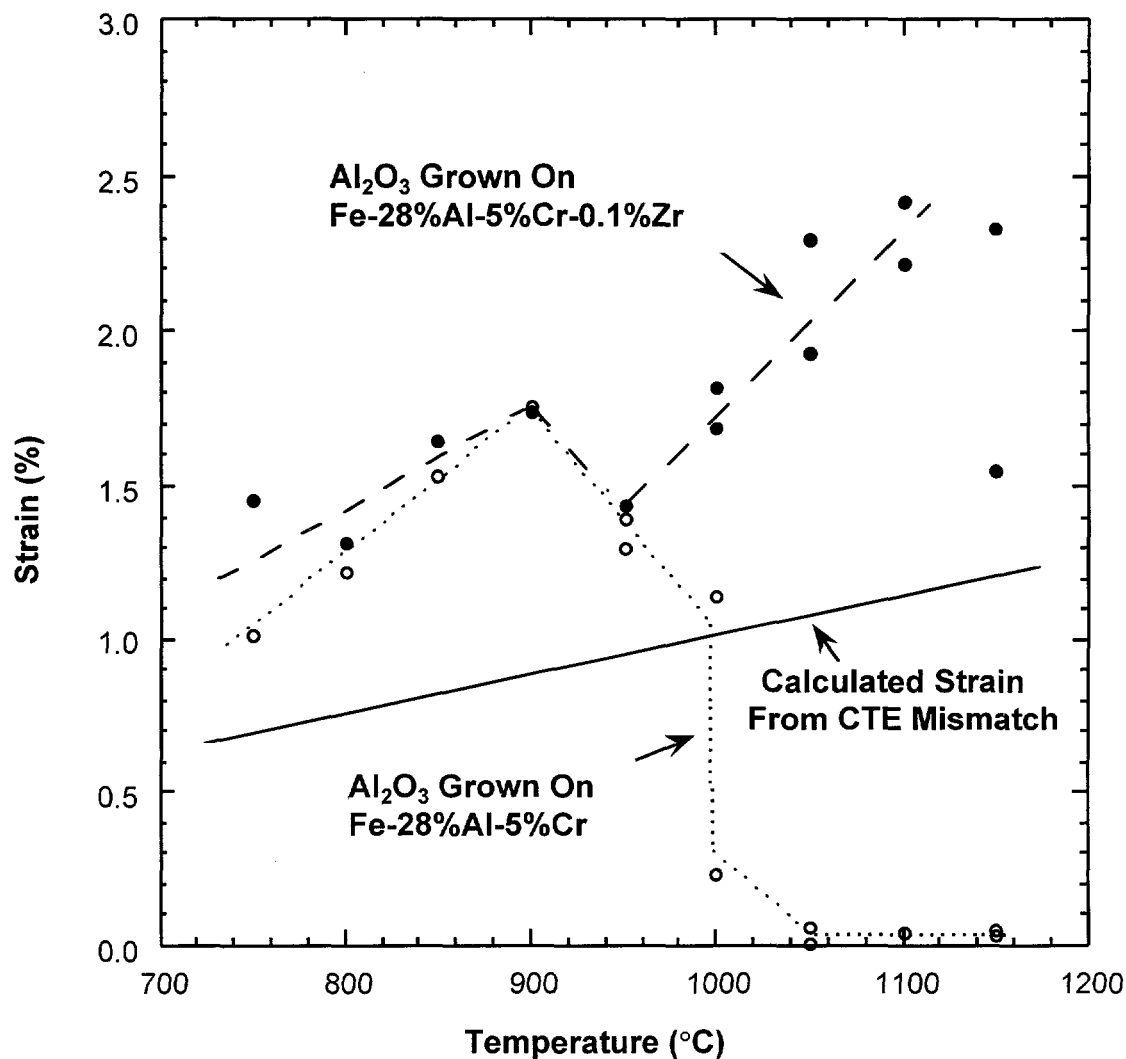
values calculated from the differences in the respective coefficients of thermal expansion (CTEs) of the oxide layer and alloy substrate. The amount of strain (peak shift) increased with increasing reaction temperature until cracking and/or spallation relaxed the stress; at that point, the ruby lines were again located at wavelengths characteristic of an unstrained lattice. The maximum strain measured in this way was found to depend on the composition of the alloy substrate. It was greater for the oxide grown on Fe-28Al-5Cr-0.1Zr (at %) than for the one on Fe-28Al-5Cr. This finding correlates with results from work showing that the presence of Zr substantially improves scale adherence for the Fe-28Al-5Cr system.

Significance - This use of ruby fluorescence is an important development as it forms a key component of determining the overall mechanical reliability of protective surface oxides that offer corrosion resistance at high temperatures. The agreement between measured strains and calculated values based on differences in the CTEs of the alumina and substrate indicate that a major (but possibly not only) contribution to stress generation in these layers comes from thermal cycling; it also validates the use of finite element techniques to model strain development under a variety of geometric and structural conditions. The demonstration that the maximum strains correlate with the onset of observed scale failure indicates that this technique will be valuable in determining whether compositional modification of the substrate or the particular synthesis route can affect strain accommodation.

Contact: Boyd Veal, Argonne National Laboratory

Phone: (708) 252-4957 FAX: (708) 252-4798 E-mail: boyd_veal@qmgate.anl.gov

*Research sponsored by Division of Materials Science and Office of Fossil Energy, U. S. Department of Energy, and the Electric Power Research Institute.



Compressive strain, as measured with the ruby fluorescence technique, in alumina scales thermally grown on Fe-Cr-Al alloys as a function of exposure temperature. Strain in the scales increased with reaction temperature (and scale thickness) until strain relief occurred due to scale cracking and failure. Note that scales on Fe-28 at.% Al-5% Cr-0.1% Zr sustained substantially greater strains than those on Fe-28% Al-5% Cr. The solid line shows the calculated scale compressive strain based on differences in the respective coefficients of thermal expansion for the oxide and for an Fe-Al-Cr alloy when cooled from the oxidation temperature.

