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Chemistry & Materials Science Progress Report

Weapons-Supporting Research
and
Laboratory Directed Research & Development

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Foreword

The research reported here in summary form was conducted during the first half of FY93 under the auspices of Weapons-Supporting Research (WSR) and Laboratory Directed Research and Development (LDRD).

WSR is the principal source of discretionary funds to support fundamental research in the Chemistry and Materials Science (C&MS) Department. WSR provides the scientific and technological base required in the longer term for the success of the Weapons Program. This year, the major changes in our WSR program were to convert the plutonium thrust to a uranium thrust, to separate the theory components of each of our WSR programs, and to recombine these efforts into a new theory thrust. In this way, the theory group can develop more effectively the strategies and capabilities needed to address the overall WSR program needs as requirements and individual projects change.

Administratively, work funded by WSR is organized into three categories:

- Block-funded programs ("thrust areas"), each of which typically involves several senior scientists in a coordinated, focused approach to a scientific or technological problem.
- Research groups consisting of two or three scientists.
- A few smaller projects led by individual investigators.

LDRD-funded work, which broadens the exploratory research base of C&MS, consists of several categories of discretionary research activities. Of these, Exploratory Research in the Directorates (ERD) and Director's Initiatives are included in this report. The former incorporates Exploratory Research in the Departments (Departmental), Exploratory Research in the Institutes, and Exploratory Research in the Programs (formerly SR).

The results reported here are for work in progress; as such, they may be preliminary, fragmentary, or incomplete. Before quoting or otherwise referring to any report herein, readers should consult one of its authors to obtain current information.

J. Wadsworth

Weapons-Supporting Research

Thrust Areas

Growth, Structure, and Reactivity of Surfaces and Thin Films

L. L. Chase, *Thrust Area Leader*

Overview

The objectives of this new thrust area are to investigate the growth, structure, and chemical activity of surfaces and thin films, emphasizing actinide elements and their alloys. These properties are important for Defense Program technologies because they are relevant to environmental stability, containment, compatibility, fire safety, and methods of willful destruction of nuclear weapons. There are two synergistic themes to this research: (1) interaction of surfaces and thin films with the environment and (2) growth, structure, and electronic properties of thin films and modified surface layers.

Previously the topic of a WSR group effort, the investigation of electronic structure and surface reactivity of thin films of uranium on various substrates continues. Uranium overlayers were deposited on palladium, and their mode of growth, their electronic structure, the reactivity of uranium with gases such as O₂ and CO, the bulk diffusion of uranium, and compounds of uranium produced by adsorption of gases were investigated. Our main objectives are to evaluate the usefulness of thin layers in studying (1) the stability of actinide-containment metal interfaces subject to heat and corrosive gases and (2) the possible use of actinides as reaction centers for catalysis.

In order to complement these investigations of surface reactions in ambient conditions, a molecular beam reactive scattering chamber (which is nearing completion) will be used to obtain kinetic information regarding thin-film formation and surface reactions.

Nucleation, growth, and structure of uranium deposited on the basal plane of highly oriented pyrolytic graphite (HOPG) were investigated. Cluster nucleation and "ripening" behavior occur at <800 K, and a change in structure to an apparent β phase of uranium occurs at >900 K. This demonstrates that single-crystal films of β -uranium can be formed on HOPG. This may prove to be a useful substrate for studying the reactivity and corrosion of uranium films because difficulties in interpretation caused by diffusion of reactants into the bulk are avoided with thin-film substrates.

A new surface-physics facility was completed that incorporates *in situ* sample preparation, electron diffraction, and atomic-resolution imaging with scanning tunneling microscopy. A study of defect creation on the (100) surface of silicon by low-energy xenon irradiation was initiated, with the goal of investigating the role of interlayer hopping on surface and multilayer annealing.

One of the most important challenges for thin-film technology is the development of ultrasmall microelectronic devices. It is important to understand how electrons propagate through such small structures. Novel experiments involving the boron core-level photoelectron emission from delta-doped silicon:(111):boron are in progress to investigate this behavior.

Atomistic Approach to the Interaction of Surfaces with the Environment

C. A. Colmenares and T. H. Gouder

We continued our study of the electronic structure and surface reactivity of thin layers of uranium on various substrates. We investigated uranium overlayers on palladium at very low coverages (below monolayer range), as opposed to our previous concentration on multilayer systems. We characterized the mode of growth, the electronic structure, the uranium reactivity with gas molecules (CO and O₂), and the bulk diffusion of uranium and uranium compounds formed by gas adsorption. We had two main objectives: (1) to investigate the usefulness of thin layers in stabilizing actinide-containment metal interfaces under heat and corrosion, with a possible application to the long-term storage of nuclear waste, and (2) to study the interaction of dispersed uranium surface atoms with low-reactivity gas molecules (CO), with possible application to the use of actinides as promoters and local reaction centers in catalysis. We also resumed the study of the uranium-carbon system.

Introduction

The interaction of "surfaces" with the "environment" may be studied by measuring the effect of adatoms (clusters to films) on the atomic and electronic structures of surfaces and on their reactivity and how, in turn, a surface may change the properties of the adatoms themselves. Actinide elements are particularly interesting as adatoms or substrates because they have 5f electrons at the Fermi-level that may be delocalized (as with uranium) and thus be available for reaction or may be close to localization (as with plutonium) and not be readily accessible. Further, these 5f electrons may be easily probed by XPS, UPS, and synchrotron radiation, and thus electronic changes induced by substrates or adatoms may be measured conveniently.

The Uranium-Palladium System

At very low dosages, uranium deposits on the top surface of palladium. It neither agglomerates in clusters nor diffuses into the substrate. All uranium atoms are located in a similar chemical environment, and the 5f electrons seem to be localized. In this dispersed phase, the uranium atoms lose their initially high chemical reactivity, as shown by CO exposure studies. Below a critical concentration of about 0.5 monolayer (ML), heating of the sample leads to the desorption of

previously chemisorbed CO, whereas above this concentration, CO dissociates. At low uranium coverage, CO dissociation thus becomes an activated process.

This passivation of surface uranium atoms is attributed to the solid-state interaction between uranium and the substrate and provides the necessary condition for investigating actinides as catalytically active substances. On the other hand, O₂ adsorption always leads to the oxidation of surface uranium, at all coverages, which shows that uranium still retains part of its reactivity.

We developed a new technique for investigating chemical reactions and bulk diffusion of uranium overlayers. The technique is time-resolved, thus allowing us to study several consecutive or parallel diffusion processes when they differ in activation energy. This will be very useful for investigating heterogeneous systems such as overlayers of metals and reaction products on substrates.

We first applied the technique to the U-Pd system. Bulk diffusion and dissolution of uranium metal were shown to proceed in several steps. First, reactive interdiffusion results in the formation of UPd₃ below 200°C and stops once all surface uranium has reacted. The driving force for this reaction is provided by the heat of formation of the intermetallic. A more detailed study actually allows the identification of two low-temperature reactions with very similar activation energies, which we tentatively

attribute to the reaction of overlayer and island uranium with palladium. Further studies are planned to confirm this.

Above 600°C, the intermetallic decomposes and uranium diffuses into the bulk. We also studied the diffusion of uranium overlayers that we exposed to O₂. Oxygen adsorption results in the oxidation of all surface uranium to UO₂, and the diffusion study shows neither alloy formation nor decomposition reactions but only one diffusion process at high temperature, which coincides with the oxide decomposition.

The Uranium-Carbon System

We also resumed our study of uranium overlayers on graphite. This substrate was chosen because it shows extremely low interaction with overlayers and therefore should allow investigation of the electronic structure of small clusters and overlayers of uranium without influence of the substrate.

Again we concentrated on coverages below 1 ML. We found clear indication for 5f localization by XPS, and the uranium 4f emissions showed an intense satellite at 6 eV and an increase in binding energy. At all coverages, uranium shows a high reactivity. Adsorption of 10 Langmuirs (L) of O₂ results in the complete oxidation of all surface uranium for coverages around 1 ML.

Our results do not agree with those from a previous STM study of uranium overlayers on graphite,¹ in which it was claimed that uranium stays metallic under atmospheric pressure for 10 minutes (equivalent to 10¹¹ L of O₂). When oxidation finally occurs, the authors refer to it as "tip enhanced" surface oxidation of uranium. There must be another explanation for their observation, but because of the lack of spectroscopic data with which to identify the composition of the surface, it is difficult to speculate on this behavior.

Reference

1. R. J. Tench, W. J. Siekhaus, and M. Balooch, "Atomic Study of Nucleation, Epitaxy, and Film Growth," *Chemistry and Materials Science Research Report*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-20622-91-1 (1991), p. 50.

Publication

T. Gouder and C. A. Colmenares, "A Surface Spectroscopy Study of Thin Layers of U on Polycrystalline Palladium," submitted to *Surf. Sci.*

Presentations

1. T. Gouder and C. A. Colmenares, "Study of Thin Layers of Actinides. Present Status and Future Use of Synchrotron Radiation," ALS Workshop: Synchrotron Radiation in Transactinium Research, Lawrence Berkeley Laboratory, Oct. 1992.
2. J. G. Tobin, G. D. Waddill, T. Gouder, and C. A. Colmenares, "The Search for X-Ray Absorption Circular Dichroism in Actinide Materials: Preliminary Experiments Using UFe₂ and US," ALS Workshop: Synchrotron Radiation in Transactinium Research, Lawrence Berkeley Laboratory, Oct. 1992.
3. T. Gouder, C. A. Colmenares, J. Tobin, and G. D. Waddill, "Synchrotron Radiation Study of the Surface Reactions of Polycrystalline U and UFe₂ with O₂, CO and H₂S," SSRL 19th Annual Users' Meeting, Stanford, CA, Oct. 1992.

Seminar

T. Gouder and C. Colmenares, "Study of Near Surface and Bulk Diffusion of Uranium in Palladium by Auger Spectroscopy," Seminar hosted by Prof. D. Olander, Nuclear Engineering Department, University of California, Berkeley, CA, Feb. 1993.

Molecular Beam-Surface Reactions

A. V. Hamza, M. Moalem,* M. Balooch, and W. J. Siekhaus

We have completed the initial phase of construction of molecular beam-reactive scattering apparatus.

Technical Activity

The system consists of three differentially pumped vacuum chambers (see Fig. 1). The source chamber, which houses the reactant gas source and the modulation assembly, is pumped

to $<2 \times 10^{-7}$ Torr by a 5000 l/s diffusion pump. A collimating orifice 1 mm in diameter separates the source and target chambers. The target chamber is pumped to $<6 \times 10^{-10}$ Torr by a cryopump.

Figure 1. Top view, schematic of the modulated molecular beam apparatus.

* Postdoctoral Research Associate, University of California, Berkeley

Samples are placed on a button heater, and the surface temperature is monitored by an infrared pyrometer. The molecular beam is incident on the sample at 45° to the surface normal. The detector samples reflected or desorbed molecules at the specular reflection angle, -45° . An extra-nuclear quadrupole mass spectrometer (detection up to 1400 amu) is housed in the detector chamber, which is pumped by an ion pump to a pressure $<5 \times 10^{-10}$ Torr, and views the entire sample area. Lock-in amplification techniques are used to obtain the magnitude and phase of the first Fourier component of the scattered signal. The amplitude of the scattered signal is a measure of the strength of the reaction, and the phase lag is a measure of the residence time of the molecule on the target, after correction for transit to and from the sample.

Construction is being accomplished in four phases:

1. Testing by scattering C_{60} from a convenient target. This phase is completed.
2. Constructing and installing the *supersonic* gas source.
3. Adding Auger electron spectroscopy (AES) optics and an in-line-of-sight mass spectrometer. (Both of these items are shown in Fig. 1 but are not yet acquired. In any surface experiment, a minimum requirement is to characterize the surface composition. AES is particularly useful in this respect. The in-line mass spectrometer will allow necessary characterization of the incident beam.)
4. Installing a bellows assembly (shown in Fig. 1 but not yet acquired) to vary the distance of the detector from the sample to characterize the energy of the scattered molecules and a rotating detector to measure angular distributions of the scattered molecules.

Publication

M. Moalem, M. Balooch, A. V. Hamza, W. J. Siekhaus, and D. R. Olander, "Surface Mobility of C_{60} on SiO_2 ," *J. Chem. Phys.* (in press).

Scanning Tunneling Microscopy of Nucleation and Growth of the β Phase of Uranium on Graphite

R. J. Tench, M. Balooch, and W. J. Siekhaus

We have studied the nucleation and growth of uranium on the basal plane of highly oriented pyrolytic graphite deposited by laser ablation (excimer with 308-nm wavelength, 20-ns duration, and 4×10^8 W/cm² power density) by scanning tunneling microscopy (STM) under ultrahigh-vacuum conditions.

Results

Laser-ablated uranium formed clusters of varying size on the graphite surface. By means of Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), the uranium deposit was found to be contamination-free and showed that no carbide had formed with the graphite. Surface diffusion of uranium was observed for coverages of less than a monolayer as a result of annealing the substrate above 800 K, as evidenced by the decreased number density and the increased size of the clusters of samples.

Novel formation of ordered uranium thin films was observed for coverages greater than two monolayers after annealing above 900 K. The structure of these films (see Fig. 1) displayed uniform step heights of about 5.5 Å, with some samples showing as many as three steps in the uranium deposit. This value of 5.5 Å is very close to the c_0 lattice constant (5.656 Å) of the β phase of uranium crystals.

STM images showed faceted edges to the platelets with included angles of 120°, which again indicates existence of the β phase of uranium.

In addition, it was possible to achieve very close to atomic resolution on the top of this platelet (see Fig. 1). The image shows an open hexagonal structure, with hexagon diameters of approximately 5 Å. This agrees very well with the 5-Å-diameter hexagons for either the B or C layers of the β phase of uranium.

Figure 1. Surface structure of uranium film on graphite. Image is 80 Å square.

Presentation

R. J. Tench, W. J. Siekhaus, and M. Balooch, "Nucleation and Growth of Uranium and Nickel on Graphite Studied by Scanning Tunneling Microscopy," 182nd Meeting of the Electrochemical Society, Oct. 1992.

Surface-Physics Research

P. Bedrossian

A new surface-physics facility that incorporates in situ sample preparation, electron diffraction, and atomic-resolution imaging with scanning tunneling microscopy (STM) was commissioned in October, 1992. A study of defect creation on Si(100) by low-energy (≈ 200 -eV) xenon irradiation was initiated, with the goal of identifying a transition temperature for the onset of multi-layer annealing via interlayer hopping of individual silicon atoms.

Technical Activities

We previously found that ion irradiation in the low-energy regime results in damage that is confined predominantly to the outermost atomic layer of the substrate and that surface evolution under such sputtering is dominated by the interaction of individual surface vacancies created by the sputtering process. In order to distinguish, to the extent possible in *post mortem* STM analysis, the effects of defect creation and defect annealing, singular Si(100) surfaces (misorientation $< 1/25^\circ$) were used. Processes mediated by the creation and interaction of surface vacancies could therefore be distinguished from step-mediated processes. Whereas atomic steps might be expected to play a significant role in the annealing of ion-induced defects, a low step density would minimize the proportion of defects actually created at steps.

Adatom generation under higher-energy sputtering [5-keV argon on Cu(100)] has been predicted from molecular-dynamics simulations.¹ Simulations have also predicted adatom generation by lower-energy ions (< 20 -eV argon) through individual atomic displacements on both reconstructed Ge(100) and Si(100).² At sufficiently high substrate temperatures, adatoms generated during ion bombardment could either incorporate at step edges or hop between levels, annihilating a mobile vacancy or filling a vacancy island. At sufficiently low substrate temperatures, mobile adatoms that no longer possess sufficient kinetic energy either to overcome potential barriers to interlayer hopping or to reach step edges are left to nucleate adatom islands. Experimental verification of adatom creation during low-energy irradiation of silicon and an understanding of the kinetics of those

mobile adatoms are crucial to developing models of ion-beam enhancement of epitaxial growth.

Figure 1 is an STM image of Si(100) that resolves the individual silicon dimer rows of the 2×1 reconstruction of that surface. Irradiation by 200-eV xenon at 488°C (Fig. 2a) and 436°C (Fig. 2b) at a fluence corresponding to removal of one third of a monolayer (ML) results in the formation of monolayer-deep vacancy islands. Diminished mobility of surface vacancies created by sputtering at the lower temperature results in a higher density of smaller vacancy islands. That the depressions are exactly one atomic layer deep is verified by Fig. 2c, a detail of Fig. 2b in which the silicon dimer rows inside the depressions are perpendicular to those of the outermost layer. A qualitative change in surface morphology occurs below 370°C. The appearance of adatom islands in Fig. 3, acquired following 200-eV xenon sputtering of Si(100) at 362°C, offers the first direct experimental verification of adatom creation during ion irradiation of a semiconductor surface. Inhibition of interlayer hopping of silicon adatoms below 370°C leads to the nucleation of adatom islands during sputtering. This, in turn, sets a lower bound on the temperature range in which 200-eV xenon sputtering of Si(100) results in two-layer removal.

Further work will examine

- The effect of incident ion energy and mass on the creation rates for specific defects.
- The identification of a displacement threshold for surface atoms by sputtering.
- The kinetics of silicon adatoms created by sputtering on surfaces roughened by sputtering.
- The interaction of defects created by low-energy ion irradiation with adsorbate atoms such as germanium.

Figure 1. A 700-Å STM image of atomically clean Si(100), showing individual silicon dimer rows and two single atomic steps. The gray scale is keyed to vertical displacement of the STM tip.

Figure 2a. A 4200-Å STM image of singular Si(100) following removal of $\approx 1/3$ ML by 200-eV Xe ions at 488°C. Depressions are 1 ML deep.

Figure 2b. A 4200-Å STM image of singular Si(100) following removal of $\approx 1/3$ ML by 200-eV xenon ions at 436°C.

Figure 2c. A 700-Å detail of Fig. 2b, showing individual silicon dimer rows.

Figure 3. A 2000-Å STM image of singular Si(100) following removal of $\approx 1/3$ ML by 200-eV xenon ions at 362°C, showing both monolayer-deep adatom islands and monolayer-high vacancy islands.

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Publication

P. Bedrossian and E. Kaxiras, "Symmetry and Stability of Solitary Dimer Rows on Si(100)," *Phys. Rev. Lett.* 70, 2589 (1993).

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1. P. Bedrossian, "Low-Energy Ion Irradiation of Silicon Surfaces," Physics Department Colloquium, Arizona State University, Tempe, AZ, Feb. 1993.
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Quantum Electron Transport through Ultrathin Films

L. J. Terminello and E. Tamura

One of the most important challenges for thin-film technology will be the fabrication of ultra-small microelectronic devices. In the limit of complete miniaturization, device materials will be no more than a small ensemble of carefully assembled atoms. In this limit, the need will be great to understand how electrons propagate through such small structures.

Introduction

Low-energy ("hot")-electron scattering through atoms can be studied as a component of understanding the classical or semiclassical models of electron transport in materials. The importance of this research will be realized when quantum-effect devices (device material of only a few atoms) become viable.

Most research in electron transport deals with the macroscopic view of inelastic processes governing electron propagation in the solid state. Most measurements are interpreted theoretically using Monte Carlo simulation methods. Such calculations treat the electron-electron and electron-phonon components of the inelastic processes, but ignore the electron-core-potential interaction. Very few experiments have attempted to measure electron-atom scattering cross sections at low kinetic energies, yet this component of electron propagation will be critical to understanding and predicting the behavior of future quantum-effect devices.

Experiment

The initial experiments that we designed to address this question have measured the electron angular distribution pattern of the boron 1s photoemission at 29 and 176 eV. This measurement was made using synchrotron radiation-based photoemission and took advantage of the unique geometry of the delta-doping compound of Si(111):boron. The unique surface geometry of this system places a single boron atom two layers

down from the silicon surface adatom. Therefore, by photoexciting the boron 1s core electron, the kinetic energy of which is selected with tunable and monochromatic synchrotron radiation, one can measure the electron propagation through the silicon adatom uniquely. This measurement was made efficiently using a multiple-angle electron energy analyzer. From the electron angular distribution pattern measured in our initial experiment, the scattering cross section for a single silicon atom can be extracted.

Our initial assessment of the experimental results shows that qualitative differences exist between the low- and high-kinetic-energy data that require a better understanding of the origin of these intensity differences, particularly at low energy. To accomplish this, we have begun a multiple-scattering, local-density-approximation simulation of these results. First, we will isolate the contribution of the single silicon forward-scattering atom to the total electron angular-distribution pattern. Second, we will identify the origin of the off-normal fine structure present in the low-kinetic-energy measurement.

With these simulations, we will be able to better identify the contribution of single-atom, low-kinetic-energy, electron propagation in solids. Only with this combination of experiment and theory can this valuable information be obtained. Further experimentation will measure the boron 1s photoelectron angular distribution patterns for kinetic energies below 25 eV. These will be compared to the higher kinetic-energy patterns measured at 29 and 176 eV and calculations at isoenergetic kinetic energies.

Uranium Research

L. R. Newkirk, *Thrust Area Leader*

Overview

Basic research into the metallurgical properties of uranium alloys represents a redirection of our actinide research activities. Lawrence Livermore National Laboratory was recently named Lead Laboratory for Uranium Fabrication in the Nuclear Weapons Complex Reconfiguration Program, a role that carries with it the need to support basic research in uranium metallurgy. This new responsibility, combined with practical limitations on the productivity of basic plutonium research, led us to realize that our limited resources for basic research in actinide metallurgy would have maximum scientific and programmatic impact if redirected toward uranium alloys.

Uranium and uranium-alloy components play an important role in nuclear weapon design and fabrication. An understanding of the basic metallurgical behavior of these materials is a necessary and important underpinning for developing and ensuring their performance within the fabrication constraints that will be associated with the modern reconfigured weapons complex. These constraints will combine the environmental concern associated with processing radioactive materials with the need to guarantee specific aspects of performance in a weapon environment. As a result of over 40 years of research on uranium and uranium alloys, both within the weapons complex and elsewhere, a great deal of basic information is already available; however, the metallurgical complexity of these materials has left many scientifically interesting and important questions to be addressed.

Although not as complex as plutonium, pure uranium is a metallurgically complicated material. It exists in three solid phases: a high-temperature, bcc phase (γ); an intermediate, highly complex, tetragonal phase (β); and a low-temperature, orthorhombic phase (α). These phases have dramatically different mechanical properties, and the phase transformation from β to α can be complex. As alloying elements (particularly refractory metals) are added to uranium, the metastable phase behavior becomes increasingly complicated. Upon quenching from the γ (bcc) region, various new phases are observed. These phases (α' , α'' , γ^0 , and γ^s) are various distortions of the basic α phase, (α' and α''), and the γ phase, (γ^0 and γ^s), some of which form through very complex martensitic transformations. These various phases have different and sometimes seemingly anomalous mechanical properties. In addition, the corrosion sensitivity of the alloy will be highly dependent on the alloying element, its concentration, and possibly the resulting phase structure.

The research program consists of two distinct areas of effort. The larger and more ambitious of these focuses on the mechanical properties and phase transformations

associated with a narrow but extremely important compositional region in the uranium/niobium system. By virtue of its stainless properties, this is a very important alloy system, and improving our basic understanding of its constitutive relationships will ultimately assist our development of alternate fabrication technologies such as spin-forming. The second and smaller area of research will focus on characterizing the phase relationships in several uranium/refractory metal alloy systems. This will provide insight in evaluating potentially interesting binary uranium systems for either corrosion resistance or other valuable metallurgical properties.

Mechanical and Microstructural Properties of U-6Nb

G. Gallegos, P. Johnson, and A. Schwartz

Because of its unique properties, U-6Nb has important weapons applications and, because of its unusual mechanical behavior, is also of scientific interest. At low strains, for example, a "double-knee effect" is observed in the stress/strain relationship typical of a shape-memory alloy. The deformation mechanism at low strains has been attributed to twinning and intertwinning (neither of which has been proven). This deformation mechanism eventually becomes exhausted when the variants are aligned with respect to the imposed strain or become immobilized by collisions with grain boundaries. At this point, it is assumed that normal plasticity by dislocation motion begins, and subsequent straining can permanently alter the structure such that the recoverable strain during reversion is reduced. The second yield point, corresponding to the onset of dislocation motion, is rather soft—or gradual—in this alloy. This may indicate that a continuously increasing fraction of fully detwinned grains contributes to work hardening in what appears to be the detwinning regime. These mechanisms may operate differently in the orthorhombic or monoclinic U-Nb phases (α' and α'') than in the tetragonal phase (γ^0).

Approach

U-6Nb typically is used in an aged condition after quenching from the high-temperature γ phase. Although evidence of dislocations and subgrains has been observed, this is believed to be the result of the quenching operation. This project focuses on enhancing our understanding of the deformation behavior of U-6Nb in the α'' and γ^0 phases. Specifically, we expect to better understand the effect of shear stresses on both the low-strain (double-knee area) and high-strain deformation. High-strain deformation is of interest for formability studies, but data are limited to studies in tension. The approach for this project is to conduct torsion tests in the appropriate regimes and to combine these with microstructural characterization by transmission electron microscopy (TEM).

We expect that the behavior during this deformation mode, if accomplished by the motion of twin boundaries, should depend on the initial variant size and orientations and the amount of strain that can be accommodated per unit motion of the twin boundaries. Complete reversion to the initial microstructure is possible, in principle, by heating into the higher-temperature γ phase field, followed by cooling to retransform to the initial microstructure, thereby recovering the strain.

Progress

Most of the effort on this project has been to optimize the torsion specimen geometry for obtaining the desired data. Torsion testing was chosen to allow the work-hardening behavior to be studied to high strain levels, beyond the 30- to

50-percent limit caused by geometric softening in a tensile test.

To obtain a sensitive measurement of the double-yield behavior, it is necessary to maintain the strain profile as uniformly as possible across the cross section of the torsion specimen. This requires a hollow specimen configuration.

Thin-walled torsion testing requires a very short specimen length to avoid buckling, which raises questions as to the influence of end and surface effects. For this investigation, therefore, we have decided to test thick-walled, hollow, torsion bars.

An exact solution for the stress at the outer fiber of such a specimen exists in the form of a modified Field-Backofen equation. We have tried four different geometries of torsion specimens and grips in order to optimize the geometry to meet the requirements. The most recent specimen geometry appears to meet our criteria, although buckling continues to present a problem. This specimen design will be refined, and testing on U-6Nb should begin shortly. The data acquisition program for these tests has been completed.

We have obtained a U-6Nb plate to be used for these studies. The plate has been characterized by chemical analysis, and x-ray-diffraction studies are under way to determine the texture of the plate. The first set of tests will be performed on a U-6Nb (U-14 at.% Nb) alloy sample that was

processed to obtain predominantly α'' , with a small fraction of γ^0 .

Characterization of microstructural changes is off to a solid start. Beginning with the rolled U-6Nb plate material, 3-mm-diameter rods were extracted along the three principal directions: along the rolling direction in plane, perpendicular to the rolling direction in plane, and transverse. The materials-handling procedures were developed to obtain the 3-mm-diameter disks required for TEM.

After a number of failed electropolishing attempts using different solutions, a suitable electrolyte has been discovered that produces reasonable amounts of electron-transparent material. Further adjustments in the electropolishing parameters—including voltage, current, temperature, and electrolyte composition—should lead to even better thin foils.

Preliminary TEM has revealed a two-phase microstructure. The matrix phase, which constitutes about 99% of the thin area, has a medium density of twins but few visible dislocations. The second phase appears to be an ordered intermetallic compound. Phase identification and detailed microstructural characterization are beginning at this time and will provide the basis for further study into the deformation mechanisms active in this alloy.

Phase Diagrams of Uranium/Refractory Metals

F. Y. L. Génin

The goal of this study is to review selected binary phase diagrams of uranium/refractory-metal alloys in order to identify systems with potentially interesting metallurgical or corrosion-resistant properties. The refractory metals of interest here are Cr, Hf, Mo, Nb, Ta, Ti, V, W, and Zr. The study will first concentrate on Nb, V, W, and Mo.

Progress

Initially, the phase diagrams were examined for violations of general thermodynamic rules, such as the consistency of the initial slopes of the solidus and liquidus in relation to the Van't Hoff equation:

$$\left(\frac{dX}{dT}\right)_{\text{solidus}} - \left(\frac{dX}{dT}\right)_{\text{liquidus}} = \frac{\Delta H_{\text{fusion}}}{RT_m^2} \quad (1)$$

The results of this evaluation for the uranium refractory-metal systems are given in Table 1.

Table 1. Results of phase-diagram examination for adherence to thermodynamic rules.

System	Solidus slope ^a	Liquidus slope ^a	Difference (absolute value)	$\frac{\Delta H_{\text{fusion}}}{RT_m}$
Mo-U	-10,290	-1120	1260	2460
Ta-U	-99,000	-3960	4125	2465
V-U	-20,130	-1070	1130	1750
W-U	$-\infty$	-3480	3480	3200

^a Slopes $\frac{dX}{dT}$ in °C/100 at. %.

For molybdenum, the value of ΔH_{fusion} as determined from the phase diagram is high by a factor of 2, and the molybdenum-rich solidus should connect with the uranium-rich solidus, which indicates that the curvature of the molybdenum solidus is incorrect. The opposite is true for tantalum; i.e., ΔH_{fusion} is too low. For vanadium, the liquidus curve seems too steep. This observation is supported by the fact that the liquidi from each side of the phase diagram should join. For tungsten, the difference of slopes is consistent with the prediction.

The thermodynamic parameters for the liquid and solid solutions have been computed for the U-Nb and U-Ta systems.

Liquid Alloys

Pure uranium and refractory metal were taken to be the standard states in the present calculation. The chemical enthalpy of formation, $\Delta_f H_{\text{chem}}$, for the liquid alloys was calculated using the model proposed by Niessen et al. The calculated values of $\Delta_f H_{\text{chem}}$ were fitted to the following expression, where x is the mole fraction of refractory metal:

$$\Delta_f H_{\text{chem}} (\text{J/mol}) = x(1-x)(\Theta_1 + \Theta_2 x) . \quad (2)$$

To calculate the Gibbs free energies of the liquid alloys, an ideal entropy of mixing behavior was assumed. The parameters Θ_1 and Θ_2 are given in Table 2.

Solid Alloys

The chemical enthalpy of formation for the bcc phase was assumed to be the same as that of the liquid phase. Miedema has pointed out that an elastic contribution to the heat of formation for the solid alloys must be added to the chemical contribution. The elastic contribution, $\Delta_f H_{\text{elas}}$, was calculated by using the method outlined by Miedema. The total enthalpy of formation was fitted to the following expression:

$$\Delta_f H_{\text{solid}} (\text{J/mol}) = \Delta_f H_{\text{chem}} + \Delta_f H_{\text{elas}} = x(1-x)(\Theta_3 + \Theta_4 x + \Theta_5 x^2) . \quad (3)$$

The parameters Θ_3 , Θ_4 , and Θ_5 are given in Table 2. Using these parameters, we computed the solidi and liquidi, which did fit well with experimental results. On the other hand, experimentally determined thermodynamic parameters do not fit the model. Experiments have therefore been planned for the U-Nb and U-V systems to validate existing experimental data.

Table 2. Thermodynamic parameters for liquid and solid solution.

System	Θ_1 ^a	Θ_2 ^a	Θ_3 ^a	Θ_4 ^a	Θ_5 ^a
U-Nb	14,927	1874.8	27,407	-272.0	-1731.8
U-Ta	12,318	1547	25,302	1314	-7874.2

^a J/mol.

Fundamentals of the Physics and Processing of Metals

W. H. Gourdin, *Thrust Area Leader*

Overview

In the first half of FY93, the Metals Research Program has continued to shift its focus to the properties and processing of ordered intermetallic materials. This change is part of a long-range plan to gradually shift the emphasis of the program and make it more directed. The project on the stability of metallic superlattices led by Marcel Sluiter was terminated early in the year, but Alan Jankowski fabricated a limited number of Ti_2/Cr_2 multilayers to verify the relative stability of (111) and (110) layer orientations. Using grazing-incidence x-ray diffraction, he demonstrated that multilayers with (111) orientation decay more slowly than those with (110) orientation, in qualitative agreement with the calculations of Sluiter and Turchi.

Our efforts to understand the role of boron and other solutes in Ni_3Al have made good progress. As stated in previous reports, our goal is to understand details of the role of solutes such as boron in promoting enhanced ductility in the hope that the knowledge we gain can be applied to other, more technologically important systems. Our theoretical studies have shown a sharp contrast between the changes induced by a ductility enhancer such as boron and an embrittling agent such as hydrogen. Difference plots of electron density show that boron promotes a more uniform distribution of charge throughout the Ni_3Al lattice. This distribution is of the same general character as we found previously in pure Ni_3Al , which suggests that the presence of boron may improve cohesion when the matrix structure is modified as it is near a grain boundary. Conversely, hydrogen tends to deplete the charge in the interstitial regions and to modify the Ni-Al bonding. This disruption of the bond structure suggests reduced cohesion. Experimental work has concentrated on preparing for mechanical tests of bicrystal specimens, both natural and artificial, and at the end of March, equipment and software were in place to determine the crystallographic orientation and mechanical properties of the specimens. We also established a collaboration with the University of California at Irvine to study grain-boundary sliding in bicrystal specimens, which we will provide.

If intermetallic materials are ever to have a significant impact on the gas-turbine industry, methods must be developed to join them both to themselves and to other superalloys. Straightforward application of traditional methods, however, is frequently unsatisfactory because of the high melting points of these materials and the fact that they are brittle. Mike Strum's study of stoichiometric interlayer bonding of intermetallics, a new project this year, is exploring one possible novel approach to joining NiAl , an alloy of particular interest for engine applications.

Solute Segregation Behavior in Ni₃Al-Based Ordered Alloys

W. H. Gourdin, P. E. Johnson, N. Kioussis,* and A. Gonis

The objective of this project is to provide a fundamental understanding of the effects of ternary solutes on intergranular cohesion and ductility in L1₂ ordered intermetallic alloys.

Summary

Attention has focused recently on the electronic structure of highly ordered intermetallic compounds containing transition metal elements and, in particular, on understanding the relationship between the electronic structure, macroscopic fracture behavior, and solute content. The exceptional high-temperature strengths exhibited by many of these materials are thought to originate in the nature and extent of local electronic-charge transfer, which is also responsible for the stability of these compounds.

The role of boron in polycrystalline Ni₃Al has become a paradigm for solute effects in which the appropriate selection of an interstitial dopant can completely suppress brittle behavior.

The ability of low dopant levels to segregate to grain boundaries and dominate the fracture mode undoubtedly depends on the local defect structure itself, as well as the specific modification of the electronic structure provided by the presence of the dopant. However, recent results in the literature indicate that boron may also mitigate the effects of hydrogen introduced into the lattice from the ambient atmosphere.

We are addressing these issues theoretically with a series of first-principles calculations on bulk Ni₃Al, with and without boron, and experimentally through a set of tests that allow simultaneous measurements of the chemistry, structure, and plastic behavior of individual grain boundaries.

Progress

On a miniature load frame, we are measuring the mechanical behavior of bicrystals cut from a large-grained boule. These experiments will explore the effects of crystal and boundary

orientation on the local strain accommodation and cohesive strength—with and without boron—of single, well-defined grain boundaries.

Tests with straight bar specimens late last year and early this year made it plain that a simple friction grip arrangement would not be satisfactory for these tests. Even specimens heat-treated to minimize boron segregation showed a surprising amount of ductility, and the stresses during deformation became large enough to produce significant slipping, thereby compromising measurements of strain. We redesigned the grips to accommodate miniature shoulder (“dog-bone”) specimens with a 1- × 1- × 3-mm gauge length and had several specimens fabricated. We also acquired, calibrated, and installed a miniature clip-on strain gauge to allow us to directly measure the strains in the vicinity of the grain boundary. Such measurements are important because we want to distinguish between the effects of boron on the boundary’s cohesive strength and the local accommodation of strain near the boundary. At the end of the first half of FY93, we were ready to begin testing with the modified specimens and apparatus.

To be most informative, the orientation of the two halves of each bicrystal must be well known. To accomplish the necessary measurements using electron backscattering patterns (EBSP), we acquired and learned to operate a computer, data-acquisition hardware, and necessary software. This equipment will be used in conjunction with a scanning electron microscope equipped with an EBSP camera at the University of California, Santa Barbara.

The ductility of the straight bar specimens, even when treated to minimize the amount of boron present (according to conventional wisdom found in the literature), is puzzling. To investigate, we hydrogen-charged a specimen and fractured it immediately in an inert environment (argon). Auger measurements showed little if any boron at the boundary, although accurate abso-

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lute measurements are difficult to obtain. Nevertheless, this observation is consistent with our notion that some boundaries may be intrinsically strong, regardless of the presence of boron.

Professor J. Earthman, U.C. Irvine, will study the effect of boron on the sliding of planar grain boundaries in bicrystals fabricated on our just-completed diffusion-bonding machine. His measurements will complement our tensile experiments on the same boundaries. Initial plans are to study a $\Sigma 3$ $\{110\}$ twin, a $\Sigma 5$ $\{210\}$ boundary (already on hand) and a "random" boundary of the same orientation as a natural bicrystal cut from the large-grained boule.

Because many boundaries consist of regular arrays of simple polyhedra, we believe that what we learn about the effects of boron in various sites in the Ni_3Al lattice will also apply to its effects at boundaries. Our previous calculations showed that when boron is placed in octahedral interstices, its p states hybridize strongly with surrounding nickel-atom d states. Further, this hybridization is discouraged by the presence of aluminum atoms in the coordinating octahedron.

In the first half of this year, we completed calculations of pure nickel and pure aluminum for comparison with the ordered compound. We also studied the effects of hydrogen, a known embrittling agent, to compare its behavior with our previous results for boron, a ductilizer. To emphasize the possible effects, we used charge-

density-difference plots, which are the difference between the electron-charge-density contours calculated with a solute present and the charge-density contours calculated for the "pure" intermetallic and an isolated solute atom.

Such difference plots for Ni_3Al with boron and hydrogen are shown in Fig. 2, and the difference in the influence of these solutes is striking. Boron contributes charge in the Ni-Ni interstice and generally produces an exaggerated version of the bond structure we observed in the pure compound. This suggests that it may contribute to enhanced cohesion at defects such as grain boundaries. Hydrogen, in contrast, depletes charge in the interstitial regions, which is apparently donated to a more directional Ni-Al bond, suggestive of a more brittle structure. [In the plots, negative values (charge depletion) and positive values (charge enhancement) are shown as dashed and solid lines, respectively.]

Presentation

H. Watanabe, N. Kioussis, R. G. Hemker, A. Gonis, W. H. Gourdin, and P. Johnson, "Effect of Hydrogen and Boron Impurities on the Electronic Structure and Mechanical Properties of Ni, Al, and Ni_3Al ," American Physical Society Meeting, Seattle, WA, Mar. 1993.

Figure 2. Charge transfer on $\{110\}$ by adding B at $1/2 \langle 111 \rangle$ (a) and on $\{110\}$ by adding H_2 at $1/2 \langle 111 \rangle$ (b).

Stability of Artificial Intermetallic Superlattices: An Experimental Study of Ti/X Multilayers

A. F. Jankowski

The objective of this study is to test the theory that specific artificial superlattices are thermodynamically stable or unstable.

Summary

Existence of thermodynamically stable and unstable, body-centered-cubic (bcc) superlattices has been predicted by Sluiter and Turchi.^{1,2} Computations based on chemical disorder have been proposed for hypothetical titanium-based binary systems. Specifically, for multilayer pairs consisting of two monolayers of titanium and two monolayers of X (either chromium or vanadium), energetic stability is predicted for (111), wherein the ordering energy ΔE_{ORD} is less than zero. An experimental study is initiated to synthesize artificial superlattices of Ti_2/X_2 using physical vapor deposition. Grazing-incidence x-ray diffraction is used to monitor the decay of the composition profile for a homogenization series of isothermal anneal treatments. The relative stability of Ti_2/X_2 multilayers with different growth textures is compared with theoretical predictions.

Progress

Synthesis of the superlattice samples, x-ray diffraction characterization, and homogenization processing are complete for the Ti_2/Cr_2 system. A bcc chromium epitaxial layer has induced the growth of the β -titanium phase in the Ti/Cr multilayer. The 0.2- μm -thick films are prepared by the sputter deposition of thermalized neutrals using planar magnetron sources onto room temperature substrates. A powder diffractometer operated in the $\theta/2\theta$ mode using copper $K\alpha$ radiation reveals the texture of the film deposits. Films of $\text{Ti}_{1.84}/\text{Cr}_{2.04}$ (110) and $\text{Ti}_{1.90}/\text{Cr}_{2.07}$ (111) are grown on substrates of amorphous silica and crystalline sapphire, respectively. The composition of the films is determined from matching calibrated quartz-crystal monitor readings with total-thickness profilometer measurements. Measurement of the film concentration is confirmed by using Auger electron spectroscopy coupled with depth profiling.

The relative stability of the Ti_2/Cr_2 superlattice specimens can be compared from a plot of the normalized reflected intensity at grazing incidence as a function of homogenization time (see Fig. 1). The composition profile has clearly decayed more rapidly in the [110] growth direction than in the [111] direction. These results at 200°C are in qualitative agreement with the prediction by Sluiter and Turchi for the behavior of the superlattices at 0 K. A detailed analysis of the crystallographic-dependent interdiffusivities is in progress, along with computation of the system activation energy from additional homogenizations conducted at 400°C

Figure 1. Intensity of the first-order grazing-incidence reflection for the Ti_2/Cr_2 (111) and Ti_2/Cr_2 (110) films is plotted as a function of time at 200°C. The normalized intensity values indicate a more rapid initial decay in the [110] direction than in the [111] growth direction, in qualitative agreement with the Sluiter-Turchi predictions for Ti/Cr.

References

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2. M. Sluiter and P. Turchi, "Phase Stability of Artificial Superlattices: Chemical-Order Effect," *Phys. Rev. B* **46**, 2565 (1992).

Stoichiometric Interlayer Bonding of Intermetallics

M. J. Strum and G. A. Henshall

The objective of this study is to develop an understanding of isothermal thin-film bonding processes and apply such methods to the joining of refractory ordered intermetallics.

Summary

Our present goal is to develop a predictive understanding of the isothermal bonding process in which elemental films placed at the joint interfaces react to form a joint with the same stoichiometry as the parent material. This joining method, conceived by the authors, is a modification of conventional liquid-assisted diffusion-bonding processes but without the addition of traditional melting-point depressants. Through this method, we expect to obtain joint compositions and properties approaching those of the parent material. It is particularly suitable for joining high-temperature materials, including intermetallics and ceramics, which have poor weldability by conventional fusion welding methods.

Prior to bonding, a stoichiometric composite interlayer consisting of elemental components is pre-placed on the parent material interfaces by a process such as vapor deposition, as illustrated in Fig. 3 for the joining of NiAl. The composite is then heated in vacuum to a suitable temperature above the melting point of the low-temperature constituent. The resulting liquid layer is allowed to react with the neighboring constituent and isothermally solidifies to form the high-melting-point parent compound. This process of stoichiometric interlayer bonding comprises two separate reactions:

- The accomplishment of metallurgical bonding by a wetting reaction between the transient liquid phase and the parent material.

- Isothermal solidification and homogenization to form the parent phase by reaction synthesis of the pre-placed films.

Both reactions are being evaluated, with emphasis on developing a predictive model of the isothermal solidification reaction kinetics.

Progress

In this newly funded project, we have selected an appropriate materials system (NiAl), arranged a collaboration with General Electric Aircraft Engines to produce single crystals for the experiments, prepared aluminum-coated nickel substrates for preliminary studies, initiated metallurgical bonding experiments, completed isothermal solidification experiments on nickel substrates that have verified our ability to use reaction synthesis to form NiAl, and identified several kinetic models to assess and, perhaps, improve.

The selection of the intermetallic phase, NiAl, as the matrix material was based on its phase diagram, its technological importance as a high-temperature structural material of the future, and its lack of conventional weldability. Advantages of the Ni-Al system include the low melting temperature of aluminum, the high solubility of nickel in liquid aluminum, and the ability to avoid intermediate phases in the aluminum-rich constituent at reasonable joining temperatures (above 1133°C). Single-crystal NiAl was selected to encourage a planar reaction front by avoiding enhanced reaction rates at grain boundaries.

Figure 3. Stoichiometric composite films are pre-placed between the components to be joined. In this case, films of nickel and aluminum on the NiAl parent material are illustrated.

Initial experiments of isothermal solidification were conducted on commercially pure nickel (Ni 201) substrates coated with high-purity aluminum. The coatings, applied by electron beam evaporation, adhered well and reacted with the nickel substrate upon heating. Complete isothermal solidification was successfully achieved for a 0.3-mm-thick aluminum layer in approximately 145 minutes at 1200°C. These results appear promising on a technological level, especially if one considers that thinner layers can be used to further decrease the reaction times.

Whereas the 0.3-mm and thicker layers increase the solidification times by increasing the transport lengths, they are being used to facilitate microstructural characterization. The intermetallic phases produced in these experiments were identified by EDX compositional analyses. Completed isothermal solidification treatments resulted in an outer layer of NiAl separated from the nickel substrate by a thin Ni_3Al interlayer. The nickel substrate, unlike NiAl, provides a semi-infinite source of nickel and therefore encourages Ni_3Al formation.

Interrupted isothermal solidification produced similar intermetallic layers extending from the original Ni/Al interface outward into the aluminum layer but terminating in a divorced eutectic layer near the surface of the aluminum coating. Defects produced during the reaction have been identified as Kirkendall voids and intermetallic stress fractures. The sensitivity of defect formation to processing methods will continue to be evaluated in future studies.

Continuing Work

Upon receipt of new material, our continuing experiments will focus on characterizing the evolution of intermetallic formation on coated single-crystal NiAl substrates for input into a kinetic model.

The second concurrent task is to evaluate the wettability of the mating interfaces. It is well known that wetting of a surface by aluminum requires special consideration of the need to disrupt the native surface oxide. In order of preference, methods being evaluated for this purpose are superheating, application of pressure, and the use of thin reactive coatings. These experiments are in progress.

Energetic Materials

R. L. Simpson, *Thrust Area Leader*

Overview

This thrust seeks to establish a fundamental understanding between the molecular structure of energetic materials and their sensitivity and performance. The effort consists of four activities. The first is an experimental and theoretical effort to determine energy-transport properties between crystal-lattice phonon modes (such as those generated in shocked materials) and vibron modes. In the second area, reaction kinetics and ignition sensitivity are being examined in terms of molecular structure and conformation. The third activity involves determining physical and chemical solid-state decomposition processes of energetic materials and correlating them to micromorphological changes caused by thermal cycling and characterized by atomic force microscopy (AFM). This activity has direct relevance to applied programmatic activities because material defects resulting from decomposition have a significant impact on sensitivity to mechanical loading. This project is a cooperative effort between the Lawrence Livermore and Sandia National Laboratories. Finally, new materials are being developed as part of our synthetic effort. One of these materials, LLM-101, has produced significant interest in the propellant community.

Experimental and Theoretical Studies of Energy-Transfer Dynamics in Energetic Materials

A. J. Ruggiero and L. E. Fried

Experimental and theoretical investigations of energy-transfer dynamics in explosive crystals and its role in determining shock and impact sensitivities continue to provide important insights into these complex issues.

Progress to Date

When a crystal receives an impact, low-frequency vibrations (called phonons) are excited. Typical phonon frequencies are 0 to 200 cm^{-1} . This energy must then be converted to the frequencies of molecular vibrations (vibrons) in the range of 1000 to 2000 cm^{-1} before bond breaking can occur.

We have refined a simple formula for the energy transfer rate in terms of the density of

vibrational states, the temperature, and the vibron-phonon coupling. Using this formula, we have estimated the temperature- and frequency-dependent phonon upconversion rates in widely varying materials such as TATB, HMX, and lead styphanate by examining existing inelastic neutron-scattering data. We find that phonon upconversion rates are strongly correlated with sensitivity: the most sensitive explosives having upconversion rates an order of magnitude greater than insensitive explosives.

Figure 1 illustrates the temperature and frequency dependence of the upconversion rates in beta-HMX and its more impact-sensitive conformational polymorph, gamma-HMX. These data illustrate the fact that subtle structural changes can have dramatic effects on upconversion rates and demonstrate the relationship between static structure and dynamics in determining overall shock and impact sensitivity.

During this period, software development for zero-background, gated, synchronous, photon-counting detection of single-channel, time-resolved Raman measurements and coordinated computer control of the detection monochromator and precision optical delay lines was completed. Components for single-channel detection were specified and procured along with additional optical components required for

constructing the femtosecond Raman microprobe spectrometer developed for this work.

Publication

L. E. Fried, and A. J. Ruggiero, "The Role of Energy Upconversion Rates in Determining Phonon-Induced Chemistry: a Comparison of Energetic Materials," submitted to *J. Propel. Explo. Pyrotech.*

Presentation

L. E. Fried, "Energy Transfer Dynamics and Sensitivity in Explosives," MRS Symposium, Boston, MA, Nov. 1992.

Figure 1. Energy-transfer rate as a function of frequency and temperature: (a) beta-HMX and (b) gamma-HMX

Chemistry of High-Pressure Reactions

M. F. Foltz

Observations of high-pressure-reaction rates are being interpreted as molecular conformation effects.

Progress to Date

Work continued in the interpretation of the high-pressure burn rate of the sensitive high explosive pentaerythritol tetranitrate (PETN) that had been measured in the diamond anvil cell (DAC) over the pressure range from 2 to 20 GPa. The burn-rate data showed that PETN burns one to two orders of magnitude faster in the DAC than does 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) or nitromethane (CH_3NO_2), respectively. The PETN burn-rate curve does not show simple pressure-dependent behavior like that of nitromethane, but has instead abrupt variations like that seen in the previously measured burn-rate curves of TATB and the four polymorphs of hexanitrohexaazaisowurtzitane.

In order to interpret these changes, static-pressure DAC mid-IR FTIR spectra were taken of micropellets of PETN embedded in KBr. Provisional identification has been based on (1) published assignments of the fundamental vibrations of the $\text{O}'\text{-NO}_2$ group determined from nitro compounds and nitrate esters, (2) comparison of PETN spectral features with those of pentaerythritol, pentaerythritol tetrahalides, *meso*-erythritol, and other nitrate esters, and (3) general normal-mode identification guidelines. More definitive identification is planned now that deuterated PETN, provided by K.-Y. Lee of Los Alamos National Laboratory, is available for infrared analysis.

Based on the preliminary spectral analysis, shifts and intensity changes in the infrared spectrum can be seen to suggest a pressure-induced molecular deformation in the pressure regime of the abrupt change(s) in the burn rate. Under static compression, PETN exhibits the greatest distortion in the CH_2 deformation, NO_2 symmetric stretch, and $\text{C-O}'\text{-N}$ deformation modes. Distortions other than deformation of the core carbon skeleton that are available to relieve pressure-induced strain are motions about the C-

C and $\text{C-O}'$ intramolecular bonds. Asymmetric deformation of the PETN molecules is suggested, possibly to a lower molecular symmetry conformation.

Progress has been made in setting up and using a data base for studying the relationship between crystallographic structural properties and impact sensitivity of high explosives. Based on sensitivity changes incurred by modifying the intermolecular hydrogen bonding of known systems, new molecular composites have been proposed that are expected to be more insensitive than the components individually. One proposed material, a complex between tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT) and dinitrobenzotriazole, attempts in its design to provide a stronger intermolecular network to produce a material that will have greater impact insensitivity than either material separately. The role of bond resonance in thermally insensitive explosives will also be addressed by the coupling of dinitrobenzotriazole with the stable TACOT. Work is under way to produce this and other proposed materials for testing.

Publication

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Condensed-Phase Thermal Decomposition of Energetic Materials Investigated by Atomic Force Microscopy (AFM) and Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS)

T. A. Land, R. Behrens, Jr.,* and W. Siekhaus

To gain a more detailed understanding of the issues of energetic materials decomposition and sensitivity, a collaboration between LLNL (Land and Siekhaus) and Sandia National Laboratories (Behrens) has commenced. The focus of our research is to gain an understanding of the important physical and chemical parameters that affect the thermal stability of TATB. One area of research is directed at understanding the physical changes that occur in the material as a function of heating, impact, and shock. The other area of our research focuses on understanding the chemical kinetics of the condensed-phase decomposition reactions. Since the decomposition of TATB occurs in the solid phase, both the physical and the chemical natures of the thermal reactions need to be understood and incorporated into any model that is developed to predict its response in abnormal thermal environments.

AFM

In experiments done so far, atomic force microscopy (AFM) has been used to observe the morphological changes that occur when TATB has been thermally cycled. The high-resolution capabilities of the AFM allow us to investigate the formation and growth of reaction centers or hot spots where reactions may have initiated and subsequently died out. It is important to correlate these observed physical changes with chemical changes in the material.

In our experiments, the AFM is used to investigate morphological changes on the surface and in the bulk of TATB crystals as a function of heating. Information about the bulk was obtained by cleaving crystals that have been heated and examining the exposed surfaces. After cleaving TATB crystals that were heated to 300°C and quickly recooled to room temperature, many patches of submicron-size holes were observed. This is the first time that such holes have been observed in the bulk of thermally cycled TATB. In contrast to holes previously observed to be concentrated on the surface of shocked and impacted TATB,³ these thermally produced holes have been observed throughout the crystal.

Figure 2 is a higher-resolution, 1.1- × 1.1-μm image of typical holes that were observed. The

larger holes are 100 to 140 nm in diameter, and the smaller ones are 25 to 50 nm. These holes may be remnants of hot spots of reactions that have started and died out. The AFM's high-resolution capability is being used to look for the beginnings of these reaction centers and to predict how they may change with time and temperature.

Figure 2. 1.1- × 1.1-μm image of typical holes created by heating a TATB crystal to 300°C. The larger ones are 100 to 140 nm in diameter.

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STMBMS

Simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and time-of-flight (TOF) velocity-spectra measurements^{1,2} are used to elucidate details of the solid-state decomposition reactions of TATB. The results from these measurements are used to identify the reaction products and to determine their gas formation rates. From this information, the reaction pathways are identified.

STMBMS is being used to investigate the chemistry of the thermal decomposition of TATB. The major decomposition products formed have been identified as the lower-molecular-weight species: H_2O , HCN , CO , NO , HNCO , CO_2 , and C_2N_2 . Another smaller, low-molecular-weight product is NH_3 . Significant higher-molecular-weight decomposition products include three furazan derivatives, mono-, di-, and tri-furazan that are formed by the loss of one, two, and three water molecules from the parent TATB molecule. This is the first time that the tri-furazan product has been observed in the decomposition of TATB.

STMBMS/TOF experiments aid in determining the identity of the products and also provide insight to the reaction mechanisms. Figure 3 shows the temporal behaviors of the ion signals associated with the furazan products formed during the isothermal decomposition of TATB. In these experiments, decomposition begins at about 275°C and rapidly increases as the sample reaches the isothermal temperature of 340°C . As shown in Fig. 3, the decomposition product signals have an induction period followed by an accelerating rate of product formation as the sample is depleted. This temporal behavior exemplifies the classic shape associated with solid-phase/autocatalytic decomposition. Further analysis of the temporal behavior of the ion signals in Fig. 3 suggests that the three distinct furazan products are formed by the stepwise loss of water.

An important step in determining the decomposition reaction pathways is to correlate products with similar temporal behaviors. It has been determined that the temporal behaviors of H_2O , CO_2 , CO , and HCN exhibit an early rise time and are correlated with the mono-furazan product, whereas cyanogen (C_2N_2), NO , HNCO , and NH_3 exhibit a later rise time and are correlated with the di- and tri-furazan products. The varied temporal behaviors of the ion signals associated with the decomposition of TATB

suggest a multiple-pathway decomposition mechanism. A detailed understanding of the reaction mechanisms requires further experiments that are presently being pursued.

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Figure 3. Ion signals associated with the furazan thermal decomposition products of TATB.

Synthesis of New Insensitive Materials

C. L. Coon

Research continued on the synthesis of heterocyclic compounds that contain both nitro and amino groups. Several interesting new target materials were prepared and are being evaluated.

Progress to Date

The main objective of this research is to prepare materials that are moderately energetic and are insensitive. The rationale behind the choice of target materials is to use heterocyclic substrates (which tend to increase density and heat of formation), which are substituted with nitro groups (to increase energy and oxygen balance), and amino groups (to increase stability through hydrogen bonding).

Pyridazine oxides and pyridine derivatives are of interest as new insensitive energetic mater-

ials because they should possess exceptional stability and have a relatively high heat of formation. Two moderately energetic pyridazines and one pyridine derivative were synthesized through procedures that can be amenable to scale-up, if necessary. These compounds are shown in Fig. 4, along with their estimated performances compared with HMX and TATB.

As shown in Table 1, Compound I appears to be the most promising of these three materials, and it is the most easily synthesized. It is being scaled up to prepare materials for sensitivity, stability, and heat-of-formation determinations.

Figure 4. Three compounds, two pyridazines and one pyridine derivative, were synthesized by procedures that can be amenable to scale-up. Compound I is the most promising and the most easily synthesized.

Table 1. Predicted performance of new compounds. Thermochemical predictions were drawn using the BKWR equation of state.

Material	% energy relative at $V/V_0 = 6.5$	
	TATB	HMX
Compound I	57	-7
Compound II	35	-20
Compound III	28	-24

The use of extensive hydrogen bonding to increase stability and density and to decrease sensitivity was extended to the synthesis of nitrohydroxyl compounds. Dinitrotetrahydroxycyclohexane (IV) is readily prepared from glyoxal and nitromethane and can then be treated with nitric acid in sulfuric acid to prepare the target material. This molecule has been given the LLNL designation LLM-101 and is of interest because of its easy and potentially inexpensive synthesis, its energy (which is estimated to be similar to that of HMX), and its exceptionally high CJ temperature. A heat-of-formation determination will be run soon so that the performance of LLM-101 can be determined with better accuracy. Current predictions indicate that the detonation performance is

59 to 81% better than TATB and -6 to +8% that of HMX. In addition, a sample of LLM-101 is being provided to Untied Technologies for evaluation as a propellant. The properties of LLM-101 are summarized in Fig. 5.

Research on dinitroimidazole (DNI) has continued, with emphasis being placed on its properties and performance. This work is being carried out in conjunction with Los Alamos National Laboratory and the Army Research & Development and Engineering Center (ARDEC). DNI is of interest because it appears to possess RDX-like energy with an impact sensitivity between that of TNT and TATB. Material has recently been obtained from ARDEC for larger-scale evaluation.

<u>Properties of LLM-101</u>	
Molecular formula:	$\text{C}_6\text{H}_8\text{N}_4\text{O}_{12}$
Molecular weight:	328.15
Melting point:	240°C
Density (by x ray):	1.865 g/cm ³
Impact sensitivity:	38.2 cm
Friction sensitivity:	8.4 Kg (1/10)
Spark sensitivity:	None (1 J)
DSC:	200°C (onset) 243°C (peak)

Figure 5. Synthesis, structure, and properties of LLM-101.

Weapons-Supporting Research Groups

Interface Science and Metal/Ceramic Interfaces Prepared Using Ultrahigh-Vacuum Diffusion Bonding

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We have designed and constructed and are operating an ultrahigh-vacuum (UHV) diffusion-bonding machine, a unique facility for producing highly controlled homophase and heterophase interfaces. Our machine is based on a previous design that is operating at the Max Planck Institut.^{1,2} In this machine, flat-polished single or polycrystals of materials with controlled surface topography can be heat treated up to 1500°C in UHV. Surfaces of annealed samples can be sputter cleaned and characterized prior to bonding. Then, samples can be precisely aligned crystallographically to obtain desired grain-boundary misorientations. Material couples can be bonded at temperatures and pressures up to 1500°C and 10 MPa. The capability to produce such interfaces, which is critical to further advancement of interface science and technology, previously did not exist in the United States.

Experimental Procedure

Figure 1 shows the design of the UHV diffusion-bonding machine. It has four chambers: a surface-analysis chamber, a diffusion-bonding chamber, an annealing chamber, and a surface-modification chamber (not shown).

First, a sample is introduced into the annealing chamber via an airlock chamber and then is annealed in UHV to 1500°C to stabilize the microstructure. After the annealing step, a rail system transports the sample to the surface-analysis chamber, to the surface-modification chamber, or to the diffusion-bonding chamber. In the surface-analysis chamber (Fig. 2a), sample surfaces are sputter cleaned with a 500-eV ion beam incident at 15°. The sample can be rotated during sputtering to ensure that material is removed uniformly and can be heated at the same time to about 700°C to purify its near-surface region. Surface cleanliness and levels of surface doping are assessed with Auger electron spectroscopy, low-energy electron diffraction, and static secondary-ion mass spectrometry.

In the bonding chamber (Fig. 2b), samples are stacked on the lower ram of the diffusion-bonding press. First, a spacer is placed on the ram and fixed with a set of fingers on a precision crystal-orientation device. The first sample is stacked onto the spacer, and another set of fingers is driven in to hold the sample. The next sample is placed on top of the first sample and fixed with a third set of fingers. Finally, a second spacer is stacked atop the samples and positioned by a final set of fingers.

Figure 1. The Lawrence Livermore National Laboratory UHV diffusion-bonding machine.

A laser beam is then reflected off the edge of the bottom sample in the stack. The sample is rotated with the precision crystal-orientation device until a pre-polished optical flat reflects the laser beam through a port of the diffusion-bonding chamber onto a screen. The position of the reflection is noted, and the laser beam is then raised to intersect the upper sample. This sample is rotated so that the reflection from its optical flat coincides with the reflection from the bottom sample. The

Figure 2a. Cutaway view of the surface-analysis chamber. SIMS ion gun is at top left. SIMS quadrupole mass spectrometer is at top right.

Figure 2b. Cutaway view of the diffusion-bonding chamber. Bonding chamber and press are at top left.

rotation gears of the precision crystal-orientation device are locked, and the upper ram is brought to bear on the sample stack. A small load is added, and the fingers are withdrawn. The entire stack is then raised into the furnace for bonding. An airlock is also incorporated in the diffusion-bonding chamber to facilitate removal of bonded samples.

Results and Discussion

Bonding Kinetics of Copper with Sapphire

To determine the conditions under which completely dense interfaces form, we are studying the evolution of bonded interfacial area as a function of bonding temperature and time. The system under investigation is copper/sapphire. Insight will be gained from this study into the appropriate bonding conditions for copper/alumina mechanical test specimens, and data will be obtained on a model system in diffusion bonding.

In the surface-analysis chamber, the surfaces of the specimens to be bonded were cleaned by sputtering with Xe^+ ions at 1 keV. The samples were rotated during sputtering to maintain an even surface finish. The cleaned surfaces were placed together in the bonding chamber, and high-purity alumina spacer blocks were inserted between the specimens and the rams of the hydraulic press. To ensure proper alignment of the specimen stack so

that the applied force is distributed as an uniform pressure on the bond area, a spherical radius of curvature was ground on one end of the top spacer block to allow point contact with the top ram. The applied force resulted in a pressure of 1 MPa at the bonding interface in all cases studied here.

The bonding temperature and times were varied to study their effects. The temperatures chosen were 800, 900, and 1000°C, and the times were 1, 2, and 4 hr. During the diffusion-bonding heat cycle, the pressure in the bonding chamber never exceeded 1×10^{-8} Torr. The heating and cooling rates were 20 and 15°C/min, respectively.

Characterization of the bonded area at the interface was done by optical microscopy through the sapphire. With light at normal incidence, the bonded areas are light in contrast because the copper conforms to the polished surface of the sapphire and reflects light back into the objective. The micrographs were digitized and, for each micrograph, a brightness threshold was chosen that corresponded to the bonded area. The number of pixels above this brightness was summed, and an area fraction was calculated.

Some results are shown in Figs. 3a and 3b. The average measured bonded area is shown along with the high and low measures, indicating the variability in bonded area density across the entire interface. The results indicate that achieving a fully dense interface in the copper/alumina system at a pressure of 1 MPa requires lengthy bonding times, probably 6 to 12 hr, at 1000°C or higher.

Figure 3a. Fractional bonded area as a function of time for constant temperature and pressure.

Figure 3b. Fractional bonded area as a function of temperature for constant time and pressure.

Copper/Titanium/Alumina Interface

In this experiment, ~ 50 Å of titanium was sputter deposited onto a piece of sapphire and then covered with ~ 2 μm of copper. The samples were removed from the sputter-deposition machine and loaded into the UHV diffusion-bonding machine. Bulk, polycrystalline, oxygen-free, high-conductivity (OFHC) copper was bonded to the coated sapphire. Surfaces of the copper and coated sapphire were sputter cleaned *in situ* prior to bonding. Bonding was carried out at 800°C for 1 hr at a bonding load of 1.0 MPa. The resultant bonded sample was cut into the appropriate geometry for analytical electron optical observation. Figure 4 is a cross-section electron micrograph of the bonded interface overlaid with the x-ray energy-dispersive spectroscopy profile.

Figure 4. X-ray energy-dispersive spectroscopy trace of aluminum, titanium, and copper $K\alpha$ x rays as a function of position relative to the interface between copper (left in the electron micrograph) and sapphire (right).

Fracture of the Cu/Al Interface

We have fabricated copper/alumina bonded samples intended for fracture testing. These samples were ~ 200 - μm -thick foils of polycrystalline high-purity copper, diffusion bonded to 2.0-cm-long, high-purity, polycrystalline alumina rods. The foil geometry was selected to minimize the contribution of bulk plasticity to the fracture-resistance measurements. Surfaces of the copper foils and alumina rods were sputter cleaned *in situ* prior to bonding. Bonding was carried out as a function of temperature (800, 875, or 960°C) and time (1 or 2 hr) at a bonding load of 1.0 MPa. The yield was seven 4-point samples for bend testing.

Figure 5 shows how this geometry was fabricated such that it could be bonded in UHV, where the samples are handled remotely without sample holders. The pieces at left are the starting materials, flat-polished alumina rods, a thin copper foil, and a support ring for the copper foil. Two support rings are spot welded to the rim of the copper foil. This support ring facilitates the remote handling of the samples in UHV. The bonding process proceeded as follows:

- An alumina rod was loaded into the surface-analysis chamber of the UHV diffusion-bonding machine.
- The alumina was sputter-cleaned using $\sim 2 \times 10^{18}$ Xe^+ ions/ cm^2 . To reduce the hillock formation that is typical in sputtering, the ion beam was incident at 15° from horizontal, and the sample was rotated during sputtering.

Figure 5. Fabrication of 4-point bend samples. (a) Alumina rod, copper foil, and copper ring (left); as-bonded samples (center); one of seven bend-test samples cut from a single sample (right). (b) Magnified image of bond line, shown with a human hair for comparison.

- After cleaning, the alumina was transferred to the diffusion-bonding chamber and loaded onto the lower ram of the diffusion-bonding press.
- The copper foil was then sputter cleaned on both sides by means of a procedure similar to that used for the alumina, except that the copper was heated to $\sim 400^{\circ}\text{C}$ during sputtering.
- The copper foil was stacked atop the first alumina rod in the diffusion-bonding chamber.
- The second alumina bar was cleaned, completing the sample stack.
- A load of 1.6 MPa was applied to the stack, which was then raised into the radio-frequency heater in the diffusion-bonding chamber.
- The temperature was ramped to the set point over 25 min, maintained for the required soak time, and then ramped back to room temperature over 15 min.

During the bonding process, the vacuum in the diffusion bonding chamber typically did not exceed 5×10^{-9} Torr. The samples at center in Fig. 5a show the as-bonded configuration. It is possible to produce one to two samples per day of this type. After removal from the bonding machine, each sample was cut into seven $3 \times 3 \times 40$ -mm bars for 4-point bend testing. This bend-test sample configuration is shown at right. Figure 5b is a

micrograph of the copper foil bonded between two alumina bars. A human hair shown in the micrograph illustrate how thin the copper foil is.

With a high-speed saw, samples were notched for 4-point bend testing. Notches were 0.5 mm deep with a kerf of $\sim 87 \mu\text{m}$. Samples were loaded on a 4-point bend fixture. The midpoint deflection was monitored by means of a spring-loaded probe fitted with two opposing clip gauges. Load and midpoint displacement were monitored as a function of time for a constant crosshead displacement rate.

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Advanced Synchrotron Radiation Study of Materials

J. Wong, P. A. Waide, and J. W. Elmer

Overview

Our objective is to advance and develop state-of-the-art synchrotron radiation (SR) methods to investigate and elucidate the role of atomic and electronic structures in determining the physicochemical properties of materials and their processing.

The activities defined in this program take advantage of the various unique characteristics of SR such as high intensity, high collimation, high polarization, and broadband tunability from VUV to hard x ray in order to probe the structure of matter on an element-selective basis in real time as well as in real space down to the second and subsecond time scales. The research areas include an expansion of our existing SR capabilities in material characterization using these powerful photon sources and development of new capabilities to (a) investigate the phase transformation *in situ* in fusion welds; (b) develop and implement a novel, quick-scanning EXAFS capability on our PRT x-ray beamline at SSRL to study time-dependent phenomena; and (c) develop new soft x-ray capabilities to study low-Z materials containing silicon, aluminum, and magnesium that are of technological importance.

Some highlights of our technical accomplishments are as follows:

- Designed and built a diffraction chamber to study phase transformation in fusion welds.
- Achieved the first high-resolution EXAFS spectra of silicon, aluminum, and magnesium with a YB₆₆ double-crystal monochromator.
- Defined and evaluated the critical experimental parameters in QEXAFS in both the time and energy resolution domains.

From 6/15/92 to 11/15/92, J. Wong worked at HASYLAB in Hamburg to complete the second and last five months of his Humboldt Award fellowship work on QEXAFS investigation and YB₆₆ characterization at the BESSY synchrotron laboratory in Berlin.

Welding-Induced Solid-State Phase Transformations: Problem Definition

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We are using time-resolved diffraction to investigate the solid-state phase transformations that occur during the rapid thermal cycling of materials in the heat-affected zone (HAZ) and fusion zone (FZ) in a fusion weld.

Introduction

Solid-state phase transformations often occur during the rapid thermal cycle produced by a weld. Examples of such phase transformations that occur during welding include allotropic transformations such as bcc/hcp elemental titanium, transformations in two-phase alloys such as fcc/bcc stainless steels, and martensitic transformations such as the fcc/bcc transformation that occurs in iron-based steel alloys. Most of the phase transformations of interest will involve deviations from equilibrium microstructures, resulting in partial transformations and/or the creation of metastable phases. These types of phase transformations receive a considerable amount of attention in welding research, development, and application studies.

Discussion

Figure 1 is a thermal profile that surrounds a quasisteady-state weld in a material that undergoes a solid-state phase transformation at a temperature T_T and melts at a temperature T_L . If the material is titanium (which has a low-temperature hcp phase and a high-temperature bcc phase) and the equilibrium phase relationships are maintained, then the HAZ depicted in Fig. 1 denotes regions between T_T and T_L . Material in this region has the microstructural history hcp/bcc/hcp. The region depicted FZ has been heated above the liquidus temperature. Material in this region has the microstructural history hcp/bcc/liquid/bcc/hcp. Regions outside the HAZ do not reach the transition temperature and would not be expected to form any new phases, although

Figure 1. Thermal profile surrounding a weld moving at a velocity V . The region between the boundaries marked "start" and "finish" is the region where the allotropic phase transformation takes place.

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grain growth may occur during the thermal treatment. The region between the start and finish locations in the weld is the region of activity, and knowing the relative fraction of phases as a function of distance between these boundaries yields the information that is needed to model the nucleation and growth characteristics of the hcp phase from the bcc phase.

We propose to use pure titanium as a first test system for the feasibility of our experimental approach. This material is allotropic, bcc to hcp on cooling, and can transform martensitically at high cooling rates. It also has an advantageously large temperature differential between the bcc/

hcp transition temperature (882°C) and the melting point (1670°C). Therefore, a correspondingly large region should contain the bcc phase, which would facilitate mapping out its location around the weld pool. Further, commercial applications for titanium and titanium alloys center about the aerospace industry, and DOE interest centers around defense applications.

Figure 2 is the conceptual design of the diffraction-welding stage that will monitor the phases in the weld region. Fabrication was scheduled for completion by mid-April, followed by laboratory test and diagnostics before performing the first synchrotron run at SSRL in early May.

Figure 2. Schematic of the diffraction-welding apparatus used for phase-transformation study by TR-XRD.

First EXAFS Spectra with a YB₆₆ Monochromator

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We used a YB₆₆ double-crystal monochromator to measure, for the first time, high-resolution XAFS spectra of magnesium (K-edge, 1303 eV), aluminum (1559 eV), and silicon (1839 eV) in a number of compounds and minerals.

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Technical Activity

The measurements were performed on the JUMBO beamline at SSRL during a run in January 1993, with SPEAR operating at an

electron energy of 3 GeV, injection current of ~100 mA, and a lifetime of over 20 hr. A YB₆₆ boule was grown using an indirect-heating, float-zone technique. A sister pair of (400)-oriented crystals ($2d = 11.72 \text{ \AA}$), each $18 \times 10 \times 0.7 \text{ mm}$ thick, were cut and polished from this boule. Areas of high homogeneity, as revealed by white-light synchrotron radiation topography and by a single peak in rocking curve measurements, were carefully mapped out for each crystal. These areas were found to be located along the growth axis of the crystal closer to the zone end. The crystal pair was configured in a nondispersive mode and with a fixed exit-beam height, sending a monochromatic beam from the UHV monochromator chamber to a vacuum sample chamber (10^{-5} Torr or better) through a $0.4\text{-}\mu\text{m}$ -thick CVD diamond window. The energy position of the monochromator was initially calibrated by means of its own transmission curve from the position of the L₃ and L₂ edges of yttrium at 2080 eV and 2156 eV, respectively, assuming no chemical shift in YB₆₆ from the metal values. X-ray absorption spectra were recorded by monitoring total electron yield with a channeltron.

In Fig. 3, the "raw" experimental EXAFS spectrum of aluminum metal is shown. This spectrum, the first EXAFS scan ever made with YB₆₆, was recorded with a SPEAR current of ~50 mA. The integration time from each data point was 1 s. Traditionally, aluminum K-edge EXAFS spectra have been recorded with quartz (1010) monochromator crystals, which undergo radiation damage in a synchrotron beam in a matter of hours, thus degrading the resolution. The use of a quartz monochromator would yield

Figure 3. Experimental EXAFS scan of aluminum metal—the first ever recorded with YB₆₆.

an upper energy limit to just below the silicon K-edge at 1839 eV. With YB₆₆, aluminum EXAFS spectra can now be routinely recorded to 2060 eV, some 500 eV above its K-edge, to give a much more useful EXAFS data range to $11 \text{ \AA}^{-1}$.

Figure 4 is an experimental EXAFS scan of sillimanite, an aluminosilicate mineral having a chemical composition of Al₂SiO₅, from 1525 to 2060 eV. This spectrum was recorded at a SPEAR current of ~79 mA. A fine step size of 0.2 eV/point was used over both the aluminum and silicon edges to register the high-resolution features in the XANES region. The integration time for each data point was 2 s. The whole spectrum was recorded in just over an hour. Positive chemical shifts between 5 and 6 eV from the corresponding aluminum metal and elemental silicon values were measured in this and other aluminosilicate minerals and compounds.

Figure 5 is the EXAFS spectrum of magnesium in MgO recorded from 1250 to 2000 eV. The scanning parameters were similar to those used for the sillimanite sample. Note again the high-resolution features in the XANES region. A positive edge shift of 3 to 4 eV with respect to magnesium metal (1303 eV) was observed. With this monochromator, EXAFS data can now be collected to over 700 eV above the magnesium edge to yield a $k_{\text{max}} \approx 13.5 \text{ \AA}^{-1}$, vs $k_{\text{max}} \approx 8 \text{ \AA}^{-1}$ for a beryl monochromator, which limits data to just below the K-edge of its aluminum constituent.

The new data clearly establish the performance of YB₆₆ as both a high-resolution and *synchrotron radiation*-stable soft x-ray monochromator in the 1- to 2-keV region. Over a continuous experimental run of two weeks on the JUMBO

Figure 4. Experimental EXAFS scan of sillimanite (Al₂SiO₅).

Figure 5. An experimental XAFS spectrum of MgO. Insets: normalized XANES and k -weighted Fourier transform of the extracted EXAFS signal showing radial structure to 8 Å.

line, the energy calibration of the monochromator was stable to within ~ 1.5 eV. The drift may largely be due to thermal effects on the first crystal at high SPEAR current in the beginning of each fill. This was anticipated because YB₆₆ has a low thermal conductivity. More systematic characterizations of the thermal load effects are being planned. As monitored periodically by rocking-curve measurements, the monochromator resolution remained essentially unchanged during the two-week run. This again had been speculated because YB₆₆, being a semiconductor like silicon and germanium, is less prone to radiation damage in a synchrotron radiation beam than are insulating materials such as quartz and beryl.

Thus, besides opening up new EXAFS investigations of three relatively spectroscopic "silent" elements—magnesium, aluminum, and silicon—which are constituents in a large variety of important technological materials such as zeolites, silicate glasses, and high-performance alloys, the YB₆₆ monochromator also enables L-edge spectroscopy of some 4p elements such as gallium to strontium and M-edge spectroscopy of elements from lanthanum (including all rare earths) to iridium. These L-edge and M-edge spectroscopic measurements will provide the data needed for understanding the electronic structure and, hence, chemical bonding of materials containing these elements, because the final states are associated with the valence levels of

interest. Also, since the Bragg angle for the YB₆₆(400) reflection varies from 80 to 20° in the 1- to 2-keV range, this monochromator may be used to preserve circularly polarized light above and below the orbit plane to study magnetic dichroism in the soft x-ray above 1800 eV. Finally, YB₆₆ may also have a significant impact in catalysis, mineralogy, and possibly environmental and biological sciences.

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Theory, Modeling, and Computation

A. Gonis

Overview

This year a new group on theory, modeling, and computation (TMC) was created. The TMC Group focuses on the major elements of theory, modeling, and computation that previously were within other thrusts and groups. Combining all these elements into a single group will improve focus and coordination and will make it possible to plan theoretical and computational development to address problems of increasing complexity.

The purpose of the Theory, Modeling, and Computation Group is to

- Investigate the electronic origins of the physical, chemical, and mechanical properties of materials by means of electronic structure calculations.
- Develop modeling capabilities for studying microscopic, mesoscopic, and macroscopic properties of materials.
- Apply these models to analyze, guide, and support related experimental activities.

These three areas of activity support ongoing experimental work in the Chemistry and Materials Science Department. Over the last year, the Group was involved in a number of projects, as reported in the following sections.

Electronic Structure of Metallic Alloys

P. P. Singh and A. Gonis

The aim of this project is to develop theoretical and computational frameworks for describing the electronic structures of ordered, partially ordered, and disordered alloys. Based on our study of light-element alloys such as Al-Li, we have modified our codes to include the effects of charge transfer in disordered alloys.

Progress

We have successfully resolved the controversy^{1,2} regarding the stability of ordered and disordered Ni-Pt alloys. Calculations done by other researchers^{1,2} in the field indicated conflicting origins of long-range order in these alloys. Since we can treat ordered as well as disordered alloys on an equal footing, we are able

to provide a better understanding of the electronic origins of long-range order in Ni-Pt alloys. Based on our calculations, we find that the mass-velocity and the Darwin shifts—the so-called scalar-relativistic terms—play an important role in stabilizing the Ni-Pt alloys. Figure 1 shows the effects of the relativistic terms on the densities of states of ordered and disordered Ni-Pt alloys.

Figure 1. The scalar-relativistic (solid line) and the nonrelativistic (dashed line) total densities of states for (a) $L1_0$ NiPt and (b) substitutionally disordered $Ni_{0.5}Pt_{0.5}$ calculated at their equilibrium lattice constants. The details are given in Ref. 3.

Our calculations so far result in the effective one-electron potentials that are spherically symmetric. As these potentials are fairly close to the real potentials in the solids, the full charge densities calculated from these potentials are expected to be reliable. The result of such a calculation is shown in Fig. 2, where the valence charge density of silicon is plotted in the (110) plane. The silicon charge density compares very well with the results of full-potential calculations, which are rather computer-intensive. As a further

Figure 2. The valence charge density of silicon in the (110) plane calculated as described in Ref. 4.

Figure 3. The differences in valence charge density between $L1_0$ AlLi and the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane, as described in Ref. 4. The charge density for the disordered $Al_{0.5}Li_{0.5}$ corresponds to an aluminum atom at the central site and CPA atoms at all other sites. The contours are in units of 10^{-2} electrons/(a.u.)³.

illustration of the usefulness of this approach, Fig. 3 shows the differences in the valence charge density between $L1_0$ AlLi and the substitutionally disordered $Al_{0.5}Li_{0.5}$ in the (001) plane with the aluminum atom at the central site.

We also developed the formalism for applying the coherent potential approximation (CPA) to the tight-binding linear muffin-tin orbital method, which was consistent with the single-site nature of the CPA.

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Development of New Thermoelectric Materials with Exceptional Figures of Merit (Theory Part)

P. E. A. Turchi

A better understanding of the relationships between electronic properties and crystalline structure in materials that possess interesting thermoelectric properties will be achieved by a synergistic effort between (1) atomistic characterization and measurements of the transport properties and (2) modeling by state-of-the-art approaches. This acquired knowledge will support and guide the experimental effort in designing and processing new, advanced thermoelectric materials. The development of new theoretical tools that combine, on one hand, accurate knowledge of microscopic material parameters and, on the other hand, experimental determination of transport coefficients should provide a more accurate evaluation of the figure of merit, ZT , which characterizes the efficiency of thermoelectric materials.

Purpose of the Work

This work is a thorough study of structure-properties relationships for a class of materials

that *a priori* exhibit interesting transport properties for thermoelectric applications. The study will be based on electronic-structure calculations in the framework of first-principles and semi-

phenomenological methods. The role played by alloying, pressure, and anisotropic distortions on these relationships will be examined for this class of materials, either in the bulk form or in multilayer configurations.

From experimental studies of the kinetic characteristics of metals and alloys, the conductivity and thermopower are known to have singularities associated with so-called electronic topological transitions (ETTs). These ETTs are related to the shape and size of the Fermi surface and are induced by such factors as uniform compression, anisotropic deformation, and changes in the alloy concentration.

In the late 1950s, Lifshitz noticed that such topological transitions manifest themselves as certain anomalies in thermodynamic and kinetic electron characteristics that are relevant to improving the thermoelectric properties of materials. This work will predict whether a gap exists in the density of states of a selected class of materials. It will also yield estimates of the effective masses—quantities of importance for the evaluation of the figure of merit.

Work in Progress

This project is expected to expand our knowledge of thermoelectrics to new classes of materials by a synergistic effort between experimental studies, including both material fabrication and characterization, and theoretical work. During the evaluation, materials found to have promising thermoelectric properties will be optimized for high-temperature applications. Since the bulk of this proposed work has a high degree of risk and is still in its exploratory stage, effort will be put on trying to select materials that possess other interesting properties as well, and for which the C&MS Department foresees potential applications in other fields (e.g., uranium-based materials and magnetic multilayers).

First-principles electronic structure studies are being performed for a series of silicon- and germanium-based transition-metal compounds. The calculations are based on the scalar relativistic linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) within the local density approximation of the density functional theory. Obviously the electronic structure is iterated, in this scheme, to charge self-consistency for all electrons in the system. The

only input parameters are the atomic numbers of the various species and the crystalline structure.

In order to (1) treat more-complex structures such as the Nowotny "chimney-ladder" structures (and even the amorphous state) that thermoelectric materials exhibit and (2) examine the role played by alloying on the electronic properties of these compounds, a more versatile method based on the tight-binding approximation (TBA) and the recursion method will be used. The alloying effect itself will be treated within the single-site coherent potential approximation (CPA), which accounts appropriately for chemical disorder effects. The electronic parameters that enter this semiphenomenological model are obtained either from a fit to first-principles band structure calculations or directly from the so-called TB-LMTO scheme, which reduces the basis set to a tight-binding one, so that an accurate description of the electronic properties can still be achieved.

As an example of the immediate information one can obtain from such calculations, it is instructive to examine the band structure of B2 (or cP2, of CsCl-type)-based MSi-ordered compounds (where $M = \text{Fe, Ru, or Os}$) at their equilibrium lattice parameter along symmetry lines in the first (simple cubic) Brillouin zone, as computed with the LMTO-ASA method. Although these compounds have an overall metallic character, it is interesting to note that the Fermi surface is confined only around the R point—i.e., $\pi/2a(111)$ —of the Brillouin zone. Hence, one immediate question is, what kind of atomic distortions in the bcc lattice or alloying (doping) can affect this feature and make an ETT (in particular, a metal-semiconductor transition) possible?

Work Plan

From either LMTO-ASA or TB (TB-CPA)-based calculations, one can obviously deduce the electronic band structure, the Fermi surface (if any), the total and partial densities of states, and the equilibrium properties of the material under investigation (i.e., total and formation energies, equilibrium lattice parameter, and bulk modulus). In addition, using the Birch-Murnaghan expression for the energy as a function of volume, one can deduce the equation

of state and therefore study the effect of pressure on these properties.

The class of materials selected for this study includes MX , MX_2 , and M_2X_3 , where $X = \text{Si}$ or Ge and M is a transition metal belonging to the VIA-VIIIA series (i.e., Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, or Ir), with special emphasis on Fe-, Ru-, and Os-based materials. Note that the crystalline structures and properties of these three metal-based silicides are very similar, at least at high-silicon composition (above 50 at.% Si).

In this study, the following questions will be addressed:

- Semiconducting vs metallic character.
- Influence of the crystalline structure, M or X substitution, and pressure on stability and electronic structure properties of these materials (e.g., width of the band gap in the case of a semiconductor). In particular, the

coupling of the band-edge states in the band structure to the lattice must be investigated in a systematic way by analyzing the shifts in the energies induced by small changes in the atomic positions because most complex structures displayed by silicon- or germanium-based compounds can be derived from simple ones by the solid-state analog of Jahn-Teller distortions. Such analysis should provide insights in selecting the appropriate doping for achieving an appropriate band-gap "tuning."

- Influence of bulk vs multilayer configuration on these properties.

Note that such study may be extended to other systems of technological interest—including Bi-Te, Bi-Se, and Sb-Te—in order to optimize material parameters.

Electronic-Structure Calculations

J. van Ek, P. A. Sterne, and A. Gonis

Our long-term goal is to develop an ab initio capability to predict the influence of clusters or layers of actinide atoms on the properties of the surface of a refractory metal. This is a very ambitious goal, and the current effort is to develop and validate the required calculational tools. The final goal is to describe these systems by techniques suited for describing surface phenomena without introducing artifacts that lack physical reality, such as periodic slabs or supercells. The construction of such codes is currently under development. In the meantime, existing computational technology is being used to study the electronic structure of various phases of plutonium and of plutonium surfaces.

The Electronic Structure of α , δ , and Hexagonal Plutonium

Results of the first relativistic, fully self-consistent electronic structure calculations on monoclinic α -plutonium have been completed and analyzed. Also, energy-volume curves for fcc δ -plutonium and three forms of fictitious hexagonal plutonium were calculated. Comparing the results for the different phases of plutonium, at the experimental α -plutonium density, led to the following main conclusions.

Plutonium in close-packed fcc and hexagonal crystal structures is a metal with a strongly itinerant 6d band and a much more localized 5f band. In α -plutonium, the atomic positions are rearranged in such a way that the formation of short (f) bonds has become feasible. This gives rise to a widening of the f band in α -plutonium (see Fig. 1). In addition, a downward shift of the 5f band relative to the 7s and 6d bands causes a narrowing of the valence band in α -plutonium of about 0.5 eV. This effect should be observable in a photoemission experiment.

The stability of the complicated α phase with respect to δ -plutonium can be viewed as a consequence of maximized 5f bonding. Because of the electrostatic repulsion, overlap between 5f states in twelve-fold coordinated fcc δ -plutonium is normally excluded. Reducing the number of nearest neighbors from 12 to between 3 and 5 allows formation of 5f bonds in δ -plutonium. The empirical observation that brittleness correlates with f-bonding and ductility with d-bonding seems to hold for plutonium. Differences found between the electronic structure of α and δ -plutonium (or hexagonal plutonium) show that it is not valid to simulate the α phase by a plutonium allotrope with much higher lattice symmetry.

Plutonium on Selected Surfaces

At the moment, electronic structure calculations for atoms, small clusters, or layers of pluto-

nium on refractory metal surfaces are being prepared. Again, the computational effort involved will be great. Fortunately, the electronic-structure code has been adapted to run in parallel mode on a cluster of workstations in the context of the previously mentioned α -plutonium calculations. This means that results can be obtained within a reasonable amount of time.

Publication

J. van Ek, P. A. Sterne, and A. Gonis, "Phase Stability of Pu," submitted to *Phys. Rev. B*.

Presentation

J. van Ek, "Comparison of α - and δ -Pu Electronic Structure," American Physical Society Meeting, Seattle, WA, Mar. 1993.

Figure 1. Total density of states (DOS) for δ -plutonium (a) and α -plutonium (b) at the experimental α -plutonium density. Energies are given relative to the Fermi level (E_F).

Real-Space, Multiple-Scattering Theory

E. Sowa and A. Gonis

We have developed a first-principles method, the real-space multiple-scattering theory (RSMST), for charge-self-consistent total-energy calculations of the electronic structure of systems with extended defects, e.g., grain boundaries and other interface systems. We have applied this method to selected grain boundaries.

Purpose

We are interested in predicting and explaining materials properties using a theoretical approach based on condensed-matter physics: i.e., computational materials science. Although simulations with classical interatomic potentials (e.g., EAM) can treat larger systems than first-principles electronic-structure calculations, there are some important unresolved issues (transferability of interatomic potentials, directional bonding, etc.) associated with these simulations which only fully quantum-mechanical calculations that explicitly treat the electrons in the material can address. Ultimately, such calculations are expected to shed light on some of the problems encountered while simulating these systems using interatomic potentials. To be fully understood, any mechanical property that depends on chemical bonding will also require a quantum treatment of the electrons.

The presence of an interface in an otherwise perfect crystal breaks the translational invariance upon which standard electronic-structure techniques rely. Since interfaces often dominate the properties of real materials, it is important to have an appropriate technique for studying their electronic structure. The RSMST is such a method. By taking advantage of the invariance properties that survive in a semi-infinite system, it provides a way to compute the electronic structure of bicrystalline materials without resorting to artificial boundary conditions such as slabs and supercells.

Accomplishments

This year, RSMST development proceeded to the point where we now have a charge-self-consistent code that can compute total energies,

densities of states, etc., for commensurate metal grain boundaries. We have used this code to study $\Sigma 5(310)$ tilt grain boundaries in copper and niobium, including the comparison of total energies of different structures.

Although this work demonstrated the suitability of the RSMST approach for handling extended defects in materials, it also showed us that the geometries encountered in interface work often involve potentials that are poorly represented by shape-approximate methods such as the muffin-tin approximation (MTA) that we have used to date.

This problem is not unique to the interface program. Many of the complex materials of interest to the C&MS Department share the same problem, yet the MTA is still part of most of the Department's electronic-structure tools (RSMST, LMTO, KKRC-CPA, etc.).

Plans

Using the new TMC Group structure, we plan to make a concerted effort to solve the problems associated with full-potential electronic-structure methods, which will give us the tools to tackle a wider array of interesting materials problems. We will take full advantage of the presence of Dr. James MacLaren of Tulane University, who will be spending his sabbatical with us.

We also plan to investigate the possibility of deriving interatomic potentials from our first-principles calculations. We hope to place on firmer physical grounds the simulations that use these kinds of potentials. We require physical explanations, which may be provided by a clear connection between the interatomic potential and the first-principles calculation that produced it.

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Weapons-Supporting Research

Individual Projects

Properties of Carbon Fibers

R. M. Christensen

The mechanical properties of carbon fibers are determined in terms of the elastic moduli of single-crystal graphite. This is done for the two basic fiber microstructures, radial and onionskin. The final results are found through a transformation from cylindrically orthotropic to transversely isotropic properties. The procedure is synthesized in a two-step process. First, a general set of nine cylindrically orthotropic properties is transformed into a set of five equivalent transversely isotropic properties. Second, these results are specialized to the two separate cases of radial and onionskin microstructures. This process is easily accomplished for four of the five transversely isotropic properties, but the fifth property—the transverse shear modulus—is a particularly difficult case that must be treated separately. Some consequent practical considerations for carbon fibers may be of considerable utility in optimizing these types of materials for high-performance applications.

Description

Carbon fibers exhibit a wide spectrum of properties, which are consequences of the intimate details of the manufacturing process conditions. These properties' variations are probably best viewed as being dependent on microstructure variations, which themselves tie back to the processing conditions. The present investigation is concerned with the two most common idealizations of microstructure because these are probably the two most critical forms. Specifically, this investigation determines the consequences in terms of mechanical properties of the two fundamental types of microstructure for carbon/graphite fibers.

The basic planar graphitic structure is shown in Fig. 1. Covalent bonds provide the atomic forces within the basal planes, whereas the forces acting between basal planes are of much weaker origin, such as van der Waals forces. These in-plane and out-of-plane forces, which can differ by orders of magnitude, are the source of the extreme anisotropy found in graphite fibers. The two standard geometric conformations of the basal planes that can exist in circular cylindrical fibers (see Fig. 2), radial and onionskin, admit easy idealization for analysis.

Fibers communicate behavior to an overall composite medium through their interfaces or by integrated effects over their cross sections. In this sense, then, a nonhomogeneous fiber and a homogeneous fiber can have the same overall effect on a composite medium if the properties of the homogeneous fiber are properly adjusted. This is exactly the process that is developed. Equivalent homogeneous and transversely isotropic fiber properties are determined such that the corresponding fiber would have the same composite material effect as would the nonhomogeneous radial or onionskin cylindrically orthotropic fiber types in Fig. 2. Thus, the properties so determined for the equivalent homogeneous fiber will differentiate the two basic microstructures.

Relative to the coordinate axes shown in Fig. 1, the five independent properties for a graphitic single crystal are taken as

$$\begin{aligned} C_{11} \\ C_{22} = C_{33} \\ C_{12} = C_{31} \\ C_{23} \\ C_{66} \end{aligned}$$

The effective longitudinal modulus (E_z) is the same for both microstructures and is given by

$$E_z = C_{22} - \frac{C_{12}^2 + (2C_{22} + \sqrt{C_{11}C_{22}} - 2C_{23})C_{12}^2 + (2\sqrt{C_{11}C_{22}} + C_{23})C_{12}C_{23} + (2\sqrt{C_{11}} + \sqrt{C_{22}})\sqrt{C_{11}C_{23}^2}}{(\sqrt{C_{11}} + \sqrt{C_{22}})^2(\sqrt{C_{11}C_{22}} + C_{12})} \quad (1)$$

Figure 1. Ideal crystal graphite structure. Basal planes.

Figure 2. Typical fiber types: radial (left) and onionskin (right) structures.

Three of the other properties also are identical for the two microstructures and have reasonably simple solutions. The behavior of the fifth property, the transverse shear modulus (μ_T) is distinctly different from the other four. The solution for μ_T , when specialized to the two

microstructures, remains quite different in the two cases. This is shown through both the exact solution and some asymptotic forms.

In addition to the effect of the two microstructures on the properties of equivalent homogeneous fibers, there are other significant

differences. Failure characteristics would be expected to be very different for the radial and onionskin fiber types. The singularities at the origin are different for the two microstructures, and in general, the state of stress throughout the single fiber would be drastically different in the two cases. The solutions found here in connection with the equivalent-properties problem could also be used to investigate for a failure mechanism. In general, the stress singularities occur in the radial microstructure case and not the onionskin case. The exception to this is the transverse shear property, in which singularities occur for both microstructures.

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Thermoelectric Materials with Exceptional Figures of Merit

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L. Hicks,* D. Makowiecki, D. O'Brien, M. Olsen, R. Otto, P. Turchi,
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After a thorough review of the literature on thermoelectric materials and extensive consultation with leading researchers in the field, we have concluded that it may be possible to achieve high figures of merit with thermoelectric quantum wells. Such materials and devices are now being fabricated at LLNL and will be evaluated in the foreseeable future. Bulk materials with unusual promise, such as pseudo-binary alloys of FeSi_2 and OsSi_2 , are also being synthesized, evaluated, and modeled. Funding sources for continuation of this effort are being pursued aggressively.

Background

The relative efficiency of a thermoelectric material is measured in terms of the dimensionless figure of merit, ZT . The best known thermoelectric materials are heavily doped, mildly degenerate semiconductors with $ZT \leq 1$. If materials with $ZT \leq 3$ could be found or developed, thermoelectric devices could be made that would have thermodynamic efficiencies close to that of an ideal Carnot engine. In fact, such materials would make it possible to completely replace conventional heat engines and mechanical refrigeration systems with solid-state devices. We are pursuing two parallel approaches to high- ZT thermoelectric materials: thermoelectric quantum wells and new pseudo-binary alloys. The theoretical basis for thermoelectric quantum wells has already been developed (2-D case by MIT, 1-D case by LLNL). Quantum theory predicts that thermoelectric devices fabricated as 2-D quantum wells or quantum wires could have $ZT \leq 3$ at relatively low temperature. We are using novel LLNL technology to make thermoelectric multilayer films (2-D quantum wells) that should have enhanced performance. From collaborative work with an industrial partner, we have come to believe that bulk $(\text{Fe},\text{Os})\text{Si}_2$ may have an exceptional figure of merit at high temperature.

Fabrication of New Thermoelectric Materials

2-D Quantum Wells

Unfortunately, molecular beam epitaxy is too expensive for producing practical thermoelectric materials. We are producing thermoelectric multilayer films (2-D quantum wells) by alternately sputtering quantum-well and barrier layers onto a moving substrate from dual magnetrons. The quantum-well layer has a very narrow band gap and is sandwiched between two barrier layers made of a material with a relatively large band gap. Bulk materials for sputtering targets have been produced by melting zone-refined elements together under vacuum, grinding ingots into powders under argon, and pressing and sintering powders under vacuum or argon. Targets also have been purchased.

Transmission electron microscopy (TEM) shows individual Bi_2Te_3 layers that are 100 Å thick, separated by B_4C layers that are 20 Å thick (see Fig. 1). We have demonstrated that we can produce Bi_2Te_3 layers that are less than 30 Å thick. Attempts have also been made to use low-angle x-ray diffraction to determine layer thickness, but results were ambiguous. Crystal structure and orientation of layers have been investigated with both electron diffraction and x-ray diffraction.

We have demonstrated the feasibility of making alternating layers of Bi_2Te_3 (quantum well) and B_4C (barrier) with dual-magnetron sputtering. In the future, we plan to explore annealing as a possible means of controlling

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Figure 1. Multilayers of B_4C/Bi_2Te_3 ; 60,000 $\times$ enlargement of full multilayer region.

crystal structure and orientation of layers. We also plan to deposit $Bi_{0.9}Sb_{0.1}/PbTe_{0.8}Se_{0.2}$, a system now believed to have much better performance than Bi_2Te_3/B_4C .

Bulk Thermoelectric Materials for High Temperature

Pseudo-binary alloys of $FeSi_2$ and $OsSi_2$ are believed to have unusually high ZTs at 1000 K. The electronic structures of these silicides now are being modeled by Turchi.¹ We are preparing promising high-temperature thermoelectric materials, including doped $(Fe,Os)Si_2$, by pressing and sintering powders at high temperature. The necessary processing techniques were developed by preparing samples of doped $Si_{80}Ge_{20}$, which has well-known thermoelectric properties.

These materials were characterized by x-ray diffraction. As expected, the diffraction pattern of $Si_{80}Ge_{20}$ indicates a diamond-type structure. The lattice parameters of two p-type samples were determined to be 5.465 and 5.463 Å, respectively. These lattice parameters correspond to silicon concentrations of 75.7 and 85.8 at.%, respectively.

We are now producing doped samples of $FeSi_2$ by the same technique. We have also used powder metallurgy to make bulk samples of low-temperature thermoelectric materials, $(Bi,Sb)_2(Te,Se)_3$, and $Pb(Te,Se)$. These materials serve as standards for x-ray diffraction and thermoelectric measurements, as well as sputtering targets. Relevant properties are now being determined.

Evaluation of Materials

The ZT of a given thermoelectric material depends on its Seebeck coefficient (α), electrical conductivity (σ), electronic thermal conductivity (κ_{el}), and lattice thermal conductivity (κ_{ph}):

$$ZT = \frac{\sigma \alpha^2}{\kappa_{ph} + \kappa_{el}} T \quad (1)$$

In the case of bulk materials or free-standing thin films, the Harman technique will be used to measure ZT as well as α , σ , κ_{el} , and κ_{ph} .²

A prototype quantum-well device will be made by depositing both n- and p-type multilayer films onto a dielectric substrate. One end of the device will be heated while the other is cooled. Current generated by the device will be determined by monitoring the voltage across a thin-film load resistor. Performance will be compared to that of a standard device made from thermoelectric single-layer films.

A high-temperature test stand for evaluating bulk thermoelectric materials at temperatures as high as 1400 K has been constructed. This instrument is installed in a glove box and has fully automated data acquisition.

Pursuit of Funding

A credible project has been started at LLNL with WSR funding to achieve profound improvements in thermoelectric materials and devices. The future of this important effort depends on the availability of continued support. A great deal of effort has been expended in the pursuit of funding. Our efforts include proposals to the National Institute for Science and Technology Advanced Technology Programs (NIST ATP), DOE Technology Transfer Initiatives (TTI), DOE Conservation Energy, DOE Office of Basic Energy Sciences (OBES), and an LDRD Director's Initiative at LLNL.

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Laboratory Directed Research and Development

Director's Initiatives

Aerogel-Based Electronic Devices

R. W. Pekala, S. T. Mayer, J. L. Kaschmitter, R. L. Morrison,
L. W. Hrubesh, R. J. Contolini, and A. F. Bernhardt

Aerogels have open-cell structures with interconnected colloidal-like particles (~10 nm in diameter), high surface area (400–1000 m²/g), and ultrafine cell/pore sizes (<50 nm). Aerogels have been synthesized from both inorganic and organic precursors. Recently, it was recognized that silica aerogels have low dielectric constants ($\epsilon < 2$) and carbon aerogels have high electrical conductivities (~20 S/cm) as a result of their intricate nanostructure. Our research explores the fundamental chemistry, engineering, and physics issues involved with tailoring the structures and properties of aerogels for applications in capacitors, batteries, and integrated circuits.

Double-Layer Capacitors

Several methods are used to produce carbon foams or aerogels that have possible applications as electrodes in double-layer capacitors:

- Phenolic microballoons are stabilized with an appropriate binder and pyrolyzed to form syntactic carbon foams.
- The partial oxidation and pyrolysis of phase-separated polyacrylonitrile foams result in microcellular carbon foams.
- Reticulated vitreous carbon (RVC) foams are produced by pyrolyzing an open-cell polyurethane foam that has been infused with a reactive monomer such as furfuryl alcohol.
- Replica carbon foams result from the pyrolysis of a phenolic resin within a sacrificial substrate that is subsequently removed.
- The sol-gel polymerization of resorcinol with formaldehyde leads to carbon aerogels after pyrolysis.

In each of these cases, processing parameters control the morphology, density, and cell size distribution of the final foam.

The LLNL Aerocapacitor is an electrochemical double-layer capacitor that uses carbon aerogels as both the positive and negative electrodes. Carbon aerogels are the ideal double-layer electrode material because they have very high volumetric surface areas (>500 m²/cm³) with controllable pore sizes and density (0.1 to 1.0 g/cm³). Particularly important is their very low electrical resistivity (< 25 m Ω ·cm) as

compared to electrodes fabricated from activated carbon-black particles or fibers.

As shown in Fig. 1, two aerogel electrodes are separated by an electrically isolating, ionically conductive separator (e.g., a polypropylene membrane) that is flooded with electrolyte. Each electrode is polarized with opposing charges when a charging voltage is applied. For example, during charging of the Aerocapacitor, application of a bias at the positive electrode will cause migration and electrostatic adsorption of hydroxyl anions at the carbon/electrolyte interface. All of the aerogel surface area contributes to the double-layer capacitance, except where the micropores are too narrow (<10 Å).

The high usable surface area of the carbon aerogel accounts for demonstrated capacitances up to 35 F/cm³. The high conductivity of the aerogel electrodes leads to power densities greater than 5 kW/kg for aqueous-based devices. Aerocapacitors are currently being fabricated in low-voltage bipolar stacks. Future efforts are being directed at developing new potting techniques for packaging these devices.

Significant achievements to date:

- Evaluation of aerogel capacitance as a function of formulation, pyrolysis temperature, and chemical activation.
- Development of casting techniques to produce carbon aerogels with thicknesses less than 500 μ m and diameters of 35 mm.
- Analysis of the pore-size distribution and surface area of carbon aerogels synthesized under different conditions.

Figure 1. Schematic of the Aerocapacitor.

- Development of new processes for air-drying or subcritical drying resorcinol-formaldehyde gels.
- Fabrication of a 5-V, 5-F Aerocapacitor using bipolar stacks.
- Development of a method for bonding nickel mesh collector plates to a carbon aerogel

Lithium-Ion Batteries

Rechargeable lithium-ion batteries use a lithium-metal oxide cathode and a carbon anode. These batteries are often referred to as "rocking chair" batteries because of the back-and-forth motion of the lithium ions during charging and discharging. The battery is charged when lithium ions released from the cathode (e.g., LiNiO_2) flow to the anode and intercalate themselves between the graphite layers of the carbon. During discharge, the reverse process occurs. Lithium-ion batteries have high energy densities ($\sim 120 \text{ W}\cdot\text{h/kg}$) and are inherently much safer than rechargeable cells that use lithium metal as the negative electrode.

We have investigated the use of LLNL-developed carbon foams and aerogels as anodes in such batteries. In general, this application requires a low-surface-area foam with some local order (i.e., microcrystalline domains). We have

tested carbon aerogels and find that they intercalate to a very low level and experience a large amount of formatting (a parasitic side reaction) during the charging operation. The large surface area of the aerogels is a detriment in this particular application. As such, we have developed new carbon foams from the phase-separation, freeze-drying, and pyrolysis of a polyacrylonitrile/solvent mixture. The resultant carbon foams have an anisotropic cell structure (1 to $10 \mu\text{m}$) and low surface area ($< 50 \text{ m}^2/\text{g}$). These carbon foams intercalate lithium at $\sim 60\%$ of the theoretical value, LiC_6 .

Recently, we demonstrated that polyacrylonitrile (PAN) foam can be doped with a solution of phosphoric acid and subsequently pyrolyzed to give a carbon foam with increased intercalation capabilities. We have tested these PAN carbons as electrodes by immersing them in electrolyte with a lithium metal electrode and a reference electrode. The PAN carbon electrode is then cycled versus the lithium metal potential. In this test, a small, 70-mg electrode was charged at a constant current of 1.3 mA to 5 mV and then held at 5 mV for 10 h. It was then discharged at a constant current of 1.3 mA to 1.5V and held for 6 h. The electrode was cycled at a low rate to prevent any possible ambiguities due to ohmic effects and to stabilize the material between charge and discharge. Symmetrical charge and

discharge profiles were observed, indicating good reversibility of the carbon.

Significant achievements to date:

- Synthesis of PAN carbon foams with densities ranging from 0.1 to 0.5 g/cm³.
- Evaluation of phosphorus doping levels on the intercalation and formatting of the resultant carbon foam.
- Demonstrated the improved cyclability of the P-doped carbon foam

Thin-Film Dielectrics

We are fabricating thin-film silica aerogels for use as an insulator with a low dielectric constant ($\epsilon < 1.2$) in high-speed electronic circuits. We are developing processes to seal, pattern, and metallize both bulk and thin film aerogels. Thin-film aerogels ~10 μm thick recently have been fabricated and currently are undergoing electrical, optical, and mechanical tests. Qualitative tests show that the aerogels can be sealed from subsequent semiconductor process liquids so that conventional photoresist techniques can pattern these materials. Aerogels have been patterned for the first time with plasma etching techniques. We have sputtered thin (<0.5- μm) gold metal layers onto the aerogel surfaces and electroplated thicker (>1.0- μm) layers.

Our silica thin-film aerogels are made from a silica solution (with the consistency of oil) to which water, a solvent, and a base catalyst are added, forming a gel. The ungelled solution is first spun on a silicon wafer in a manner similar to that used to spin on conventional photoresists in semiconductor processing. Then, it is allowed to gel while being exposed to an atmosphere designed to minimize the evaporation of the solvent from the gel. Multiple layers with controlled thicknesses are made in this manner. The gel is then dried by supercritical extraction of the solvent, leaving the aerogel attached to the silicon wafer. The process takes only a few hours, whereas other methods can take days.

Significant achievements to date:

- Demonstrated the first-ever thin film (<10 μm thick) of silica aerogel attached to a silicon substrate and characterized its thickness and index of refraction.
- Demonstrated the sealing of aerogel thin film using a plasma-deposited polymer coating (i.e., CHF_3).
- Demonstrated the compatability of liquid photoresists with polymer-coated aerogel films and deposited photoresist patterns on silica aerogels.
- Demonstrated metallization of silica aerogel surfaces by achieving coating thicknesses and quality comparable with other dielectric substrates used for this purpose.

Publications

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Presentation

S. T. Mayer, R. W. Pekala, and J. L. Kaschmitter, "The Aerocapacitor: A Carbon Aerogel Based Supercapacitor," 2nd International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 7-9, 1992.

Molecular-Level Studies of Energetic Materials

P. C. Souers

This project consists of three integrated tasks dealing with high-explosive predetonation:

- *Molecular hydrodynamics, J. Belak, Physics.*
- *Doorway-mode spectroscopy, A. J. Ruggiero and L. E. Fried, C&MS.*
- *Structure and sensitivity, M. F. Foltz, C&MS.*

The first two will have a large impact in about five years, with the creation of frequency-specific initiation being the most important goal. This would be the ultimate protection device in preventing accidental explosions. The structure program will have an immediate effect; this area is on the verge of a major breakthrough that will result in the creation of a new, insensitive, high explosive of potential interest to the DoD. The issues of initiation and sensitivity are foremost, and the often-used, solid, high explosive HMX (high power, moderate sensitivity) and TATB (low power, low sensitivity) are used as baseline materials throughout.

Molecular Hydrodynamics

Objective

The objective of this task is to describe explosive predetonation using a computer model running on a massively parallel system. The model is a "hydrocode"; i.e., each element is a molecule linked to the others for energy and momentum flow. The intent is to model the flow of shock-wave energy from the lattice vibrations (phonons) to the molecular vibrations (vibrons) using the real world of molecules instead of averaged bits of matter. The goal is to discover what frequencies cause maximum energy flow and start the initiation process, given the particular structure of the solid explosive.

Accomplishment

The point atom has been converted to a complete molecule in the simulation code. Bonded intramolecular potentials and local environment models have been obtained. Both are empirical: the first describes the excited solid explosive; the second has the capacity to dissociate into products to be determined.

Milestones

- 1/93–6/93. Test the code and the two potential forms on small compounds for which data are available. These include nitromethane, benzene, fused silica, and graphite.

- 3/93–9/93. Develop the framework to track energy flux from phonons to vibrons. Extend local environment potentials (the chemistry potentials) using experiment and quantum-mechanical calculations.
- 6/93–12/93. Simulate a weak shock in crystalline HMX and TATB using bonded potentials.
- 12/93–3/94. Simulate a strong shock in HMX and TATB using local environment potentials.
- 10/93–9/94. Simulate tight binding of the shock response of HMX and TATB. This is much more of a quantum-mechanical model than either of the previous empirical models.
- 3/94–9/95. Add defects to the best of the models and rerun.

Doorway-Mode Spectroscopy

Objective

The objective of this task is to experimentally measure the actual flow of predetonation energy as it flows from phonons to vibrons. A femtosecond laser Raman spectrometer is almost complete that will carry out this work. Molecular-dynamics (MD) calculations show that the lattice energy flows in two steps: a fast (femtosecond) dephasing followed by the actual (picosecond) energy flow. Additional new theory has shown that a likely frequency for energy flow is about

400 cm^{-1} , as caused by the motion of the nitro groups. The faster the energy flows at this frequency, the more sensitive the explosive.

Accomplishments

The laser equipment has been procured and installed. Production of optical-quality HMX crystals is under way. HMX has been simulated, both in and out of equilibrium, and phonon-vibration conversion has been obtained. A theory of energy upconversion, as related to the density of phonon states, has been derived.

Milestones

- 3/93–6/93. The total laser-system performance is optimized and ready for data collection. MD simulations will concentrate on obtaining spectroscopic variables that will correspond to the experiments.
- 7/93–10/93. Properties of HMX will be measured as functions of temperature, and simulations will be completed. TATB's electronic structure will be calculated in order to develop the force field. An analytical theory directly linking phonon upconversion rates to a chemical reaction rate will be developed. Finally, defects will be incorporated into the existing phonon upconversion theory.
- 11/93–10/95. HMX vibrational dynamics will continue, in collaboration with C.-S. Yoo, using diamond anvils to study the behavior under pressure, thereby measuring the anharmonicity of the phonon-vibron interaction. Experimental work will begin on TATB. Non-equilibrium MD calculations on HMX and TATB at various shock strengths will be done.
- 1/95–10/95. Infrared pump/probe spectroscopy based on a new difference-mixing adjustment to the femtosecond source will be used to study HMX and TATB.

Structure and Sensitivity

Objective

This task is to create an algorithm to predict explosive sensitivity based on composition, which, in turn creates the three-dimensional crystal structure. The algorithm is intended to search through various organic compounds to predict an insensitive high-performance candi-

date, which will then be synthesized and tested. The resulting explosive should be attractive to the DoD, given the increased interest in safety.

Accomplishments

Our entire plan is based on the recent observation that only a few graphitic structures exist and that all are insensitive, whereas almost all explosives have herringbone (angled) structures and are sensitive. This observation yielded the prediction that a hydrogen-bonded complex of one part DNBT and two parts ANTA would be graphitic and insensitive, although only ANTA, a weak explosive, is insensitive by itself. The resulting complex proved to be one of few insensitive graphitic explosives with more energy than ANTA by itself. A large data base has been started, using rare and fragmentary information not previously available. A computer graphing program illustrates the crystal structure and the hydrogen bonding structure that confers insensitivity. The algorithm will be based on properties of the hydrogen-bonding arrangement.

Milestones

- Second half, FY93. The data-base/graphing system will be filled with data, many collected from the most obscure sources. The data base will be divided into categories, from which illustrative samples will be taken from inventory and drophammer tested for sensitivity. Small-scale quantities of at least one new explosive, built off the TATB hydrogen bond structure, will be synthesized and tested.
- First half, FY94. Thermal-sensitivity testing of TATB will be projected to other hydrogen-bonding arrangements, with algorithm predictions verified by drophammer, differential scanning calorimetry, and infrared spectroscopy. Studies of heating in weakening the hydrogen bond network will begin. Results will be used to upgrade the data base and the algorithm.
- Second half, FY94. The algorithm will be used to predict an insensitive explosive more powerful than TATB. Studies of bond-network weakening with temperature will continue.
- The winning material will be scaled up for performance testing. Other sensitivity tests appropriate to advanced analysis will be run. The material will enter the cycle of presentation as a candidate for production.

Laboratory Directed Research and Development

Individual Projects

Nanoscale Lithography Induced Chemically or Physically by Modified Scanned Probe Microscopy

M. Balooch, W. J. Siekhaus, and A. V. Hamza

We are investigating (1) chemical reactivity on the atomic (or nanometer) scale as it occurs naturally or as it is induced by phenomena occurring between the tip and the substrate in a scanning tunneling microscope (STM) and (2) physical modification of the substrate by the tip of an atomic force microscope (AFM). The ultimate goal is to generate nanoscale patterns, such as narrow trenches and ultrathin oxide masks, to be used in advanced electronics. The STM is an attractive instrument for nanoscale lithography because its characteristics (i.e., its low voltage and its high, localized electric field) cause minimal damage to nearby structures and to the substrate. Moreover, it is a compact and flexible processing tool, capable of operating over a wide range of environmental conditions. In this project, various electronic-material substrates such as Si, SiO₂, and SiC are examined.

Introduction

To study the etching and deposition processes that occur between the tip and the substrate in a proper environment, a reaction chamber capable of handling a variety of gases of interest has been designed and constructed to accommodate our existing STM and AFM. This chamber has been used to study the STM-induced oxidation of silicon substrates with nanometer resolution, and the results were reported in detail last year. Our main goals this year are to study the thermal, ion-enhanced, and tip-induced etching of silicon in the presence of XeF₂ as a reactant at atomic resolution.

Progress to Date

Our main effort has been to modify the reaction chamber to perform STM imaging with atomic resolution by installing vibration isolation components and lowering the base pressure of the system to avoid contamination. Since XeF₂ is an extremely corrosive gas, we decided to first examine the performance of the system by studying C₆₀/Si(111) interaction.

The silicon samples are outgassed for 12 h at about 1000 K prior to removing the surface oxide. The (7 × 7) surface is prepared by annealing the sample to 1375 K for 30 s. The sample is then slowly cooled to 600 K, at which point the power

supply is turned off. STM data recording commences 2 h after surface preparation in order to minimize the thermal drift. The C₆₀ powder is placed in a gold foil envelope fastened to a button heater. Many pinholes are made in the foil to allow uniform deposition. Deposition is accomplished by heating the envelope to over 800 K to allow C₆₀ molecules to evaporate from the envelope and deposit on the silicon substrate.

We have directly observed the "cage opening" of C₆₀ on Si(111)-(7 × 7) by STM and correlated the opening with global surface characterization such as AES and TPD spectroscopy. Isolated C₆₀ clusters are observed on Si(111)-(7 × 7) after annealing the surface to 620 K (see Fig. 1a). Annealing the surface to 1020 K causes the C₆₀ cages to open and thereby cover more of the surface (see Fig. 1b). The opening of the C₆₀ cage correlates with an increase in the amount of silicon-carbon bonding and with the increase in the carbon-to-silicon AES peak height ratio, which increases with annealing temperature. The ratio increases because the opened cages cover more of the substrate silicon atoms, thus reducing silicon Auger emission from the substrate. The same area imaged after annealing to 1150 K reveals that most of the adsorbed molecules disappeared from the surface (see Fig. 1c). Larger-area scans collected after annealing to 1150 K showed that no cup-like fragments remain after this high-temperature annealing.

Figure 1. Same-area STM images of C_{60} on Si(111) annealed to different temperatures.

In silicon etching, we have been able to use the STM tip as a means to generate craters on silicon surfaces that were cleaned from native oxide and then hydrogen terminated. This is accomplished by pulsing the tip to a few volts in the XeF_2 environment. Different crater diameters and depths can be obtained by varying the pulse width and height. Figure 2 shows a typical crater generated in a 0.3-Torr, XeF_2 partial pressure with a 5-V, 2- μ s tip pulse.

Figure 2. STM-induced etching of silicon in XeF_2 gas.

Milestones for FY93

Even though thermal and ion-assisted etching of silicon by fluorinated gases has been studied for more than a decade, the detailed

mechanism involved in this process has never been determined. The site adsorption, surface mobility, and the process involved in induced reactions (by ions, electrons, or electric field) to remove silicon atoms are of great interest. For example, the ion-enhanced reactivity reported in the literature could be the result of the creation of defect sites on the surface that are more reactive than the rest of the surface atoms. On the other hand, the role of ions could be mainly to assist the surface intermediates to become a volatile product.

During the remainder of FY93, we will use STM to study in detail the adsorption, diffusion, and reaction of XeF_2 molecules on Si(111). The effect of a damage site (induced by ion bombardment) on reactivity will be studied by creating defect sites first, followed by adsorbing XeF_2 and examining the site in real time as the reaction proceeds.

The detailed kinetics of STM-induced etching will be studied by applying voltage pulses to the tip. The effects of the polarity and the intensity of the field between the tip and the substrate, and the effect of the tunneling current density will be investigated to find optimum conditions for enhanced etching. A model for STM-induced etching will be proposed.

Finally, nanoscale etching of silicon by the STM tip in XeF_2 reactant gas will be demonstrated.

Proposed Work for FY94

- Modify the STM to operate at high temperature. This will enhance our capabilities to study the reaction kinetics by imaging the surface at different temperatures at or near the atomic scale.
- Explore the formation of SiC film growth by C_{60} cage opening to investigate the possibility of growing single-crystal SiC at lower temperature and with no hydrogen incorporation, as opposed to the conventional CVD method.
- Produce F_2O_2 (a.k.a. FOOF) as a reactant gas for etching SiC and study the kinetics of etching by STM and molecular beam mass spectrometry.

Prospects for Future Funding

The development of STM with the capability to operate over a wide temperature range and with atomic resolution opens great opportunities to investigate kinetic processes that could not be studied before. For the first time, the reaction rate on a specific site can be measured in real time as a function of temperature.

Strong interest in SiC films exists, in electronics for high-temperature semiconductors, and in mechanical engineering for hard and corrosion-resistant coatings.

At the end of this project, we will pursue appropriate industry connections for developing SiC coatings and for nanoscale lithography.

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Nanoscale Magnetism

J. G. Tobin, G. D. Waddill, A. F. Jankowski, and S. Y. Tong*

We are working to ascertain the structure-property relationships of reduced-dimensionality magnetic systems. The samples are ultrathin films and multilayers, and the fundamental measurements probe the geometric, electric, and magnetic structures on an atomic scale and with elemental specificity. Using circularly polarized x rays, the x-ray absorption, photoelectron spectroscopy, and photoelectron diffraction measurements give us a sensitivity to the elementally specific magnetic moments, level-dependent exchange splittings, and local magnetic structure. These measurements will provide us with previously unavailable details of structures and properties and provide benchmarks for state-of-the-art calculations of such reduced-dimensionality systems. These fundamental studies will ultimately impact technologically critical areas such as magnetic information storage and chemical analysis of actinide materials.

Introduction

We are moving toward spin-dependent measurements using photoelectron diffraction. By means of our new data-collection mode and analysis method,¹ we hope to use a variant of imaging with photoelectron diffraction to elementally resolve not only the source atom but also scattering atoms. This would directly address and resolve the ongoing controversy in such systems as Fe/Cu(001), where it is essentially impossible to differentiate surface alloys (copper around iron) from overlayer clustering (iron and iron). The key is to use the spin-specific scattering calculations of S. Y. Tong and circularly polarized x rays as the excitation. We would also be able to directly measure local magnetic ordering with this technique.

Recent Progress

We present a combined experimental and computational study that demonstrates direct wave-front reconstruction to obtain surface structure with atomic resolution using spatially resolved imaging of energy-dependent photoelectron diffraction (SRI-EDPD). The theory behind this method was presented earlier by Tong et al.,² but this is the first experimental investigation using this particular approach.

Additionally, a new, rapid data-collection mode was introduced. Moreover, while Fourier transformation of experimental data provides a direct image of the surface structure, detailed multiple-scattering simulations and transformation of calculated intensities are used to verify the analysis.

The crucial results are shown in Fig. 1. Both the first in-plane nearest neighbors (copper) and second in-plane nearest neighbors (gold) are imaged with atomic resolution, *without the intrusion of artifact peaks*. The system studied—1/2-monolayer, c(2 × 2) Au/Cu(001)—is a particularly severe test of this imaging technique because of the complexity of this system, which exhibits competing growth modes involving surface-alloying, bulk-alloying, and overlayer formation. The c(2 × 2) surface alloy is clearly observed, and the surface alloy is easily differentiated from a c(2 × 2) overlayer. However, such a non-model-dependent discrimination of a surface alloy from an overlayer is impossible using more-conventional diffraction techniques.

Thus, the reconstruction formula for inverting EDPD spectra has been applied to experimental data. This direct method, based on the intersection of contour arcs associated with each measurement direction, can provide vectorial atomic positions with atomic resolution. First results for the c(2 × 2) Au/Cu(001) system are encouraging, demonstrating two-dimensional vectorial imaging. By achieving atomic resolution of less than 1 Å, the reconstruction image shows

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directly and conclusively that the Au/Cu(001) system involves alloying in the surface layer. Further work is in progress using both regular photoemission spectra and spin-dependent photoemission with circularly polarized x-ray beams.

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2. S. Y. Tong, H. Huang, and C. M. Wei, "Method for Spatially Resolved Imaging of Energy-Dependent Photoelectron Diffraction," *Phys. Rev. B* **46**, 2452 (1992).

Experiment

Theory Alloy

Theory Overlayer

Figure 1. Images reconstructed from experimental spectra (top), calculated spectra for the surface alloy model (middle), and overlayer model (bottom). In each picture, the thick cross marks the gold emitter's position, thin crosses and the circle mark the expected atom positions of neighbors in a $\pi/4$ sector. The plane of view passes through the nuclei of surface layer atoms (see insets for surface models). [gold = solid circle, and copper = hollow circle.] The experiment clearly agrees with the surface alloy model.

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Inorganic and Organic Aerogels

L. W. Hrubesh, T. M. Tillotson, F. M. Kong, and R. W. Pekala

We are investigating the synthetic conditions necessary to tailor the structure and properties of organic and inorganic aerogels at the nanometer scale. Our synthetic approach involves the sol-gel polymerization of (1) multifunctional monomers or (2) molecular building blocks in dilute solution. The resultant aerogels have high surface areas (400 to 1000 m²/g), small pore sizes (<50 nm), and a solid matrix composed of interconnected spherical particles or fibers with characteristic diameters of 10 nm. We are developing a fundamental understanding of the chemistry-structure-property relationships in these unusual porous materials.

Inorganic Aerogels

We have synthesized new aerogels of pure zirconia and tantalum at densities lower than previously achieved for these mid-Z metals. We modified our formerly developed, two-step, sol-gel chemistry to make prehydrolyzed precursors from which we made low-density aerogels of both zirconia and tantalum. Our monolithic zirconia aerogels have densities as low as 38 kg/m³, but they are extremely weak, and tantalum aerogels have densities as low as 60 kg/m³, which is within a factor of 4 of the theoretical limit.

In addition to our synthetic efforts, we have completed the characterization of new pure erbium, praseodymium, and neodymium aerogels and published the results. These aerogels were made from sol-gel chemistry, with the metal chloride as the starting material. The metal chloride was dissolved in alcohol and reacted with water. Propylene oxide was added to scavenge the liberated hydrochloric acid and to help induce gelation. These reactions intentionally were slowed by mixing at slightly above 0°C. The resulting gels were supercritically dried using both the high- and low-temperature methods. The high-temperature extracted aerogels were monolithic, translucent, hydrophobic, and very weak. The low-temperature extracted aerogels were transparent and hydrophilic, but not monolithic.

Mixed aerogels were made by adding the rare-earth chloride-alcohol solution directly to prehydrolyzed tetramethoxysilane (condensed silica) in a two-step gelation process. The resulting solution was also partially condensed and served as a precursor to making gels and aerogels. When these gels are supercritically extracted

at high temperature, they result in transparent monoliths that are quite stable to atmospheric moisture.

Other significant achievements:

- Developed a model to predict the optimum density for minimizing the thermal conductivity of aerogels and prepared results for publication.
- Completed measuring the thermal conductivity of ultralow-density silica aerogels, both pure and loaded with carbon particles.
- Completed analyzing the frequency dependence of the attenuation of sound by aerogels and completed measurements at ultrasonic frequencies.

Organic Aerogels

Whereas much research has been conducted on the production of large monolithic aerogel samples, we have developed a new method for forming organic aerogel microspheres (0.1 to 3.0 mm in diameter) in a cost-effective manner. This method involves stirring an aqueous sol in mineral oil at elevated temperature until the dispersed phase has reacted to form nonsticky gel spheres. No other chemicals or surfactants are required to stabilize the dispersion.

The size of the spheres formed depends on the collision rate of the liquid droplets and the reaction rate of the monomers. The collision rate is governed by the volume ratio of the aqueous solution to mineral oil and by the applied shear rate. The reaction rate depends on the aerogel formulation and the curing temperature. After the crosslinked spheres have been formed, they

are washed with acetone, and then supercritically dried from carbon dioxide.

We have produced aerogel microspheres from both resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF). The RF microspheres can be pyrolyzed at 1050°C to form carbon microspheres.

We are continuing to characterize the structure and transport properties of carbon aerogels, using Raman spectroscopy as a sensitive method for monitoring the local order. For disordered carbons, two broad Raman lines are observed: the line in the vicinity of 1580 cm^{-1} is associated with local crystalline order, whereas the line at 1360 cm^{-1} results from disorder-induced scattering that is forbidden in a perfect crystal. Sample characterization of aerogels has involved the measurement of central frequencies, line widths, line shapes, and integrated scattering intensities for each of these lines, obtained from the fits of the spectra to the Breit-Wigner-Fano (BWF) equation. From the ratios of the integrated intensity of the disorder-induced line to that of the Raman active line (I_{1360}/I_{1580}), the in-plane microcrystallite size (L_a) is determined according to Knight's formula, which is valued for a laser excitation wavelength of 4880 Å:

$$L_a = 44 (I_{1580}/I_{1360}) \quad (1)$$

Figure 1 shows Raman spectra for carbon aerogels synthesized at $R/C = 200$. The observed spectra are almost identical, but a small reduction in line width is seen with increasing density. Of interest is the in-plane microcrystallite size of 25 to 30 Å for all samples. Raman measurements are not very sensitive to L_a in this size range, but we can safely conclude that all L_a values measured for carbon aerogels are much smaller than the particle size (~120 Å). This indicates that the width and structure of the carbon ribbons within each particle are similar and independent of the bulk density. These results agree with conclusions reached from TEM and BET characterization measurements.

Other significant achievements:

- Measured the magnetic susceptibility and magnetoresistance of carbon aerogels as a function of temperature.
- Measured the photoconductivity of carbon aerogels.
- Completed a light-scattering and fluorescence study of the RF polymerization.

Figure 1. Raman spectra for carbon aerogels synthesized at $R/C = 200$.

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Structural Transformation and Precursor Phenomena in Advanced Materials

P. E. A. Turchi, L. T. Reinhard, and S. C. Moss*

Local chemical order and atomic displacements are the major precursors of alloy transformations. Their effects on transformations are studied both theoretically, with modern electronic-structure theory of alloy phase stability and Monte Carlo simulations, and experimentally, with scattering and surface techniques in the case of the transformation from a simple bcc-based FeCr alloy to a complex σ phase upon cooling.

Progress to Date

We have developed codes in collaboration with A. Traiber to study the electronic-structure and phase-stability properties of ternary alloys in order to address the question of complex phase formation. The methodology represents an extension to multicomponent alloy systems of the tight-binding (TB) description of the electronic structure, and of the generalized perturbation method (GPM), which describes order-disorder phenomena. Chemical disorder effects are taken into account within the coherent potential approximation (CPA). The electronic-structure parameters that enter the TB model have been fitted to results from first-principles calculations to accurately determine the electronic properties and the phase diagrams of the binary alloys.

The first system selected was Fe-Ti-V. To provide an insight into the role played by atomic orbital directionality in the stability of complex phases, the TB approach was also used. The electronic parameters that enter the model were obtained from the first-principles linear muffin-tin method, in the atomic sphere approximation (LMTO-ASA). The TB-LMTO parameters obtained for the Fe-V alloy, which exhibits stability properties similar to those of Fe-Cr, are currently being tested to check their transferability to various topological configurations and to address the question of complex phase formation.

Precursor phenomena are also important in the context of the temporal evolution of a system. Here, the case of an energetic competition between an ordered state and phase segregation is especially interesting because of the different

time and length scales involved (ordering is much faster than segregation) and the evident structural differences between the competing phases. In our previous studies on FeCr alloys, it was shown that the alloying effect (favoring phase separation) and the local chemical order may compete. In the case of equiatomic TiV, the local order alone favors segregation, with the B32 ordered structure being only slightly unstable with respect to phase decomposition.

The energetic quantities obtained from our first-principles electronic-structure calculations for TiV were used in Monte Carlo simulations based on the kinetic Ising model. This study shows for the first time that, for such alloys prepared in the high-temperature disordered configuration and subsequently quenched inside the miscibility gap, an ordered B32 phase first spontaneously forms before evolving toward phase separation. A detailed analysis of this remarkable evolution indicates that, even in the final stage (i.e., near thermodynamic equilibrium), the ordered phase wets the interface between the two disordered decomposition products. Calculations are ongoing to estimate which ternary additions would favor the experimental observation of such an unusual kinetic path.

The Monte Carlo study was also performed on two-dimensional model systems to assess the effect of the parameters of the problem (e.g., the energy differences between the competing phases) on the time evolution and to examine the role played by extended defects such as antiphase boundaries. A typical time evolution of a two-dimensional equiatomic AB system (based on a square lattice) is shown in Fig. 1, after an instantaneous quench from high temperature to a temperature well below the miscibility gap. Note that

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the fast, homogeneous, ordering reaction is followed by phase separation, mostly initiated at antiphase boundaries. In the late stage of transformation, it is clearly apparent in Fig. 1 that the interface between the A-rich and B-rich solid solutions is ordered.

On the experimental side, FeCr, a basis of many commercially interesting alloys, has been selected for the study of precursor phenomena. This alloy exhibits a bcc-solid solution above 1094 K near equiatomic composition and transforms into a σ phase upon cooling. Due to a favorably slow kinetics of transformation, single crystals with the high-temperature crystalline structure, around 47 at.% Cr, could be grown.

In addition to the previously reported x-ray diffuse-scattering work, we have performed low-energy electron diffraction (LEED) experiments of the possible surface-induced bcc-to- σ transformation in oriented FeCr single crystals with surfaces perpendicular to (110) or (111). These studies were done in collaboration with Dr. J. E. Houston of Sandia National Laboratories,

Albuquerque, NM. Several *in situ* heat-treatment experiments inside the σ stability field were performed. No change in the symmetry of the LEED patterns was observed within the available time scale.

We are currently evaluating the I(V) data to obtain information about possible deviations from the bulk bcc structure that may correlate with the incipient σ formation. Further experiments with available high-purity single crystal-line samples (recently produced by L. L. Jones, Ames Laboratory, Ames, IA) are scheduled in the near future.

An x-ray grazing-incidence diffraction experiment was performed on FeCr single crystals on beam line X10A at the National Synchrotron Light Source at Brookhaven National Laboratory in collaboration with Dr. K. S. Liang (Exxon). Data were collected in high-symmetry, in-plane directions above and below the σ transition temperature, T_σ . Whereas no clear indications for a diffuse intensity buildup above T_σ could be detected, the transformation from bcc

Figure 1. Time evolution of the microstructure of an equiatomic model system based on a square lattice, instantaneously quenched from high temperature to $T = T_\sigma/3$ (where T_σ corresponds to the top of the miscibility gap). The number above each plot denotes the elapsed time, after the quench, in units of attempted Monte Carlo steps (MCS) per site.

to σ was indeed observed below T_σ . The transformation kinetics exhibited a pronounced incubation time, indicative of a strongly first-order transition.

Future Work

This program provides new insights into the formation and the stability of complex phases by a synergistic effort between atomistic characterization of the early stage of transformation and modeling by a state-of-the-art approach. This is increasingly important because novel materials with promising properties are being synthesized. Work is now being performed to

- Define accurate and transferable potentials that can be used in molecular-dynamics simulations to provide additional insight into the formation and stability of complex phases.
- Study the effect of ternary addition on the occurrence and the stability of complex phases.

Fundamental questions are being addressed on

- Surface reconstruction and segregation in the bcc phase prior to the bcc-to- σ transformation.
- Orientation relationships between bcc and σ near the surface.
- Kinetics of transformation near the surface.

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Ductile-Phase Toughening of Refractory-Metal Intermetallics

G. A. Henshall and M. J. Strum

Brittle, intermetallic compounds based on refractory metals could satisfy needs for high strength and creep resistance at extremely high temperatures if they can be toughened by the dispersion of a ductile second phase. Beginning with the V-V₃Si system, in situ synthesis methods are being explored as a way of producing these ductile-phase toughened intermetallic matrix composites (IMCs). Room-temperature fracture-toughness tests have been performed on specimens of varying ductile-phase fraction synthesized using three methods: (1) arc melting (AM) with commercially pure vanadium, (2) AM with high-purity vanadium, and (3) directional solidification (DS) with high-purity vanadium. The results show that toughness increases as the V(Si) fraction increases, from 1.3 MPa√m for pure V₃Si to 31 MPa√m for V(Si). For the 50% V₃Si composite, DS improves the toughness over AM from 10.5 to 18.5 MPa√m, nearly the industrial target value of 20 MPa√m. This improvement appears to be associated with greater debonding between the two phases, leading to improved ductility in the V(Si). In addition to these experiments, an innovative approach is being used to study the effects of interphase debonding on toughness using the finite-element method (FEM). Use of a parametrically varied critical energy-release rate at the interface crack tip shows that higher interface toughness increases constraint in the ductile phase, which would decrease toughness. FEM analyses of creep in composites with creep-resistant matrices have shown that, because of stress redistribution within the material, the composite creep rate is much less than would be predicted from simple analytical models.

Detailed Description

The continuing search for improved light-weight structural materials for high-temperature service has led to the investigation of intermetallic compounds based on the Group VB and VIB refractory metals. The major barrier to their use is the lack of ambient-temperature toughness required for damage tolerance. The approach we are considering to solve this problem is "ductile-phase toughening," in which a high-melting-point ductile phase is dispersed within the intermetallic matrix. The ductile phase may increase toughness by "bridging" the crack faces, thereby inhibiting crack opening, or by blunting the crack tip. To produce these composites, *in situ* synthesis methods are being investigated in which the two components of the composite form by phase separation during solidification.

Our first objective is to develop synthesis and processing techniques that optimize the

chemistry and microstructure of the composites. The next objective is to develop a mechanistic understanding of ductile-phase toughening and, in particular, to assess the dependence of fracture toughness on the distribution and properties of the constituent phases and the interface behavior. The final objective is to characterize the high-temperature creep behavior of ductile-phase toughened composites as a function of their microstructure and to develop a micromechanical understanding that provides predictive capabilities. The major goal will be to identify the microstructures that best maintain the superior creep properties of the intermetallic while providing sufficient low-temperature toughness.

Three different synthesis methods have been used to date in preparing the V-V₃Si *in situ* composites. During previous reporting periods, conventional vacuum arc melting (AM) was performed, first using commercial-purity vanadium plate and then using high-purity vanadium chips as stock. During the first half of FY93,

directionally solidified (DS) ingots were made, in collaboration with B. P. Bewlay of GE Corporate R&D Lab, using the high-purity vanadium stock. In all cases, electronics-grade silicon was used for alloy preparation.

For all of the alloys studied, the V_3Si was the discontinuous phase.^{1,2} The eutectic microconstituent consists of V_3Si rods or ribbons with aspect ratios of up to 10. In the AM eutectic, the rods form packets that are randomly oriented, whereas in the DS materials, the V_3Si rods are strongly aligned in the growth direction. Studies by Bewlay et al.² have shown that a crystallographic orientation relationship exists between the two phases in the DS eutectic; the $\langle 111 \rangle$ direction in $V(Si)$ is parallel to the $\langle 001 \rangle$ direction in the V_3Si . This directionality has a pronounced effect on mechanical properties. For compositions other than the eutectic, but in the two-phase regime, "islands" of either $V(Si)$ or V_3Si are present in a "sea" of the eutectic microconstituent previously described.

To assess the influence of processing and ductile-phase fraction on toughness, room-temperature fracture toughness tests have been performed on specimens of varying composition that were synthesized using the three different techniques.

As shown in Fig. 1, the V_3Si has a fracture toughness of only about $1.3 \text{ MPa}\sqrt{\text{m}}$ (estimated from indentation tests), and the $V(Si)$ phase has a toughness of about $31 \text{ MPa}\sqrt{\text{m}}$. The industrial target for advanced turbine engine materials is $20 \text{ MPa}\sqrt{\text{m}}$. The $V-V_3Si$ composites have intermediate toughnesses that increase as the ductile-phase fraction increases. (The exception is the DS alloy with 90% ductile phase; investigation of this anomaly is in progress.)

For the eutectic—or 50% intermetallic—composite (near the ratio likely to be of practical use), the two AM techniques result in a toughness of about $10 \text{ MPa}\sqrt{\text{m}}$. The DS process produces a more optimized microstructure and/or chemistry and increases the toughness of the 50% V_3Si composite to $18.5 \text{ MPa}\sqrt{\text{m}}$, nearly that targeted for practical use.

Based on examinations of the fracture surface using scanning electron microscopy, improved toughness in the DS eutectic is associated with greater ductility of the $V(Si)$ and a greater tendency for delamination of $V(Si)$ ligaments from the V_3Si rods. Plastic stretching of the $V(Si)$ was observed over approximately 85% of the fracture surface in the DS material

Figure 1. The average fracture toughness, K_Q , of $V-V_3Si$ composites as a function of ductile-phase fraction.

and over only 40% of the surface in the AM alloys. Cleavage of both the V_3Si and the $V(Si)$ was observed in the other regions of the fracture surfaces. Using an available model for toughening by ductile bridging³ and using the fraction of fracture surface exhibiting ligament stretching as a weighting factor, we developed a model of the effects of directional solidification on fracture toughness that is consistent with the data.⁴ More fundamentally, the difference in fracture behavior between the two eutectics suggests that cleavage in one or both of the phases is sensitive to crystallographic orientation.

Additional experiments are under way to improve our understanding of the effects of directional solidification on the toughness of $V-V_3Si$ composites. In addition, since it may be desirable to study a system in which the intermetallic is the continuous phase, exploration of another materials system is being considered.

To study the mechanisms of ductile-phase toughening, numerical crack-growth simulations using the NIKE2D FEM code have begun. One major goal is to quantify the influence of interfacial debonding on the stress-displacement behavior and, hence, the overall fracture toughness of idealized composites.

In collaboration with E. Zywicki of LLNL Engineering, an innovative approach is being implemented. Debonding between the phases is modeled by release of interface nodes once the energy-release rate at the interface crack tip

reaches a prescribed critical value. Results to date⁵ reveal that increased interface toughness reduces debonding, thus increasing both the composite peak strength (see Fig. 2) and the ductile-phase constraint predicted by the model. This increased constraint would decrease the overall toughness of the composite either by accelerating internal void formation and growth or by elevating stresses above the cohesive strength, causing cleavage. These predictions are consistent with our experimental results.

Finally, our understanding of the micro-mechanics of creep in composites with creep-resistant matrices has progressed using NIKE2D. The NIKE2D results suggest that ductile-phase toughening additions used to improve low-temperature toughness may not severely degrade high-temperature strength and creep resistance. Simple analytical models, which cannot account for stress redistribution within the material, predict a much poorer performance of the composites. These simulations are continuing in an effort to validate this hypothesis.

Figure 2. NIKE2D predictions of the effect of interface toughness, J_{crit} , on the stress-vs-crack-opening-displacement (COD) response of a lead-glass composite.

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Fundamental Studies of Particle-Solid Interactions

T. Diaz de la Rubia and M. W. Guinan

The aim of our research is to improve our understanding of nonequilibrium processing of materials with energetic beams. Our goals are to develop models of defect production and transport in materials in order to help industry develop improved macroscopic modeling tools for manufacturing next-generation electronic components and other advanced materials. The project focuses on two topics: (1) ion implantation and beam processing of semiconductors and (2) radiation effects in novel, bulk, nanophase materials.

Introduction

As the dimensions of integrated circuits shrink and the cost and complexity of manufacturing increases, empirical approaches to industrial process design cease to be practical. Hence, process modeling of device manufacturing becomes critical.

However, process modeling currently is not predictive, the main limitation being a lack of complete understanding of the physical processes involved. For example, an understanding of defect production during ion implantation, as well as dopant diffusion and activation, is vital to supporting shallow junction technology. Addressing these limitations is one of the critical factors that will determine the future success of the semiconductor industry.

We are developing a unique capability in the area of atomistic simulation of energetic particle interactions with solids. Our molecular-dynamics (MD) codes use massively parallel computers to provide the physical insight (otherwise lacking) that will allow us to describe the defect production and diffusion processes common to beam-assisted processing of materials. Our atomistic simulation codes—together with modern 3-D visualization tools and continuum-transport simulation programs—will lead the way to a comprehensive total computer-aided design (TCAD) tool. This TCAD tool will provide a predictive process-modeling package for manufacturing the next generation of semiconductor integrated circuit components.

Code and Graphics Development

In association with the massively parallel processing (MPP) applications group at the National Energy Supercomputing Center (NERSC), our code for semiconductor materials studies is currently being developed to use MPP capabilities such as the Cray C90, the connection machine CM5, and networks of workstations. The code implements the message-passing programming paradigm on these machines and will therefore be easily portable as new computers come on line at LLNL or elsewhere.

With the help of the graphics group at NERSC, we have developed visualization methods to effectively display the atomistic dynamics simulated by the code. Our results of 5-keV displacement cascades in Cu_3Au were shown by LLNL at the November 1992 supercomputing conference in Minneapolis and will be showcased by LLNL's National Storage Laboratory to display the capabilities of their high-performance parallel interface (HiPPI).

Semiconductor Device Processing with Ion Beams

We are presently carrying out MD studies of ion implantation in silicon at recoil energies from threshold (15 eV) up to 15 keV. The simulations employ crystallites with up to 216,000 atoms at 10 K interacting through semiempirical, three-body, interatomic potentials. The simulation cells

have periodic boundaries in all three dimensions and can contain a free surface in a given direction. To date, all simulations have been performed with the Stillinger-Weber potential for silicon. Comparisons of the results obtained so far with simulations employing a Tersoff-like potential developed by Rockett in Illinois will proceed in the near future.

We have obtained detailed information on the threshold energy required to produce a stable Frenkel pair in the silicon lattice. This energy has been found to vary with orientation, in good agreement with experimental information. Along the [111] direction, the minimum energy required to form a stable Frenkel pair is 23 ± 2 eV. In this case, a vacancy at the original recoil site and a tetrahedral interstitial are formed. At a recoil energy of 30 eV, a $\langle 110 \rangle$ dumbbell self interstitial is formed along with the vacancy. Quenching of the samples to nearly zero kinetic energy reveals that the $\langle 110 \rangle$ interstitial is the stable form. The vacancy- $\langle 110 \rangle$ interstitial pair has an energy 1.25 eV lower than that of the vacancy-T interstitial configuration. Moreover, we have annealed our samples at temperatures up to 750 K for 15 ps. These isochronal annealing runs reveal that the tetrahedral interstitial first transforms into a $\langle 110 \rangle$ dumbbell before recombining with its own vacancy. These results are in excellent agreement with first-principles *ab initio* MD studies of point defects in silicon that predict the $\langle 110 \rangle$ split to be the lowest-energy interstitial configuration. Along the [111] direction, the threshold drops to 18 ± 2 eV, with the $\langle 110 \rangle$ split interstitial being produced at a recoil energy of 25 eV.

For recoils in the [100] direction, the situation is very similar to that of the [111] direction but simpler since no tetrahedral interstitial has been found at any energy. Only the low-energy-configuration vacancy- $\langle 110 \rangle$ split pair has been found. The threshold for this defect to be produced was found to be 23.5 ± 1 eV.

Along the [110] direction, the situation is more complicated. The threshold appears quite high (>35 eV). However, at recoil energies of 35 eV, we have found a closed chain of four replacements with no defect production. We are presently carrying out the simulations at 40 eV as well as along [110] to discern the mechanisms of defect production along these directions.

The observation of a $\langle 110 \rangle$ split as the stable interstitial resulting from low-energy recoils in a silicon lattice may help explain the fact that, for 30 years, electron irradiation studies of silicon

have not been able to identify the form or even find the interstitial. *Ab initio* MD results show that the $\langle 110 \rangle$ split interstitial has no states in the gap and therefore does not give rise to EPR signals that may be used to identify it. We are presently trying to determine the migration enthalpy of this interstitial configuration. This will help us to better understand diffusion in silicon following ion irradiation.

At higher recoil energies, we have so far obtained results for displacement cascades in silicon initiated by 3- and 5-keV gold recoils moving near a (001) direction. Fifteen-keV events are currently under way in crystallites containing a free surface. These events have shown a surprisingly large shock-wave component in the energy-dissipation mechanism. Such shock-wave processes are not usually taken into account by simpler descriptions of the implantation process. Significant consequences that could help understand some of the fundamental processes associated with beam interactions in semiconductors are being explored. For example, the large amount of coherent energy dissipated by the shock wave may be partly responsible for the low activation energy observed during the ion-induced recrystallization of amorphous-crystalline (a-c) interfaces in silicon. A cascade in the crystalline side of a pre-existing a-c interface may induce substantial atomic diffusion at the interface, even if the cascade does not precisely overlap it.

Radiation Effects in Nanophase Materials

Our collaborator, Prof. Hahn, recently moved from Rutgers University to the Technische Hochschule Darmstadt in Germany, and synthesis of silver and lead nanophase samples was delayed for about two months. Consequently, irradiation of these specimens is only now starting at the GSI in Darmstadt. Our ongoing plans to build a new beamline in the Chemistry and Materials Science Department's 4-MV ion accelerator for in-house irradiations have been put temporarily on hold. Dr. Winterer, a postdoctoral associate of Prof. Hahn, will be spending several months in Livermore working on the MD simulation studies of radiation effects in these materials. For this, he will be using our MD code for metal systems that was developed

during last year's LDRD funding cycle and runs on the MPP platforms.

Summary

As a result of our efforts to date in the area of MD simulation studies of beam-solid interactions, AT&T Bell Laboratories has become very interested in collaborating with us to develop new computational tools for process modeling of semiconductor devices. We have submitted a proposal abstract to ARPA to get funds under the NCAICM call. In addition, we plan to submit a proposal to DOE's recent HPCCI call to build, in collaboration with AT&T, an MPP computer

optimized for performing classical, tight-binding and *ab initio* MD. This machine would be unique, in that the architecture would be designed to best perform the neighbor-finding algorithms that are key to the performance of MD codes. We also plan to submit a technology-transfer initiative with AT&T to DOE before the end of this fiscal year.

Presentations

1. T. Diaz de la Rubia, AT&T Bell Laboratories, Murray Hill, NJ, January 1993.
2. M. W. Guinan, International Conference on Evolution of Microstructure in Metals During Irradiation, Sep.–Oct. 1992, Minett, Canada.

Electronic-Structure Evolution of Metal Clusters

V. V. Kresin, M. J. Fluss, R. H. Howell, and W. D. Knight*

We are investigating the properties of alkali metal clusters, emphasizing electronic structure and collisional properties. We are interested in the development of electronic energy levels with increasing cluster size and the correlation between electronic structure and collisional properties of free metallic clusters. These properties can be studied as the cluster size grows atom by atom. We have been conducting a detailed study of collisions involving metal clusters. This research has been extended to study alkali-cluster collisions with sodium atoms and with carbon fullerenes. This direction is of interest to both experimentalists and theorists in the field. It represents a way to map out the step-by-step development of the interaction of a metallic system with atoms and molecules, a question of interest in surface science and catalysis.

Technical Activities and Results

After a detailed study of elastic and inelastic collisions between alkali clusters and noble gas atoms and halogens completed last year, we recently performed experimental measurements of collision cross sections for interactions between a beam of neutral sodium clusters and (1) sodium atoms and (2) C₆₀ and C₇₀ clusters. The experiment was performed by passing a tightly collimated beam of sodium clusters through a heated scattering cell. By precisely controlling the temperature of the cell (and thus the vapor pressure of the scattering gas) and by measuring the corresponding depletion of the cluster beam, we were able to determine absolute scattering cross sections of the collisions. Data analysis and comparison with available theoretical calculations are now in progress.

This project is of considerable interest to researchers in the field. Collisions between alkali and fullerene clusters represent a convergence of intense experimental efforts in two fields. We were able to take advantage of recent work carried out at LLNL by Abrefah, Olander, Balooch, and Siekhaus,¹ who measured the temperature dependence of the vapor pressure of buckminsterfullerenes. The possibility of applying our results to the recently discovered alkali-cluster doping of bulk fullerenes is intriguing. In turn, collisions between alkali clusters and atoms are of considerable fundamental value.

Understanding the interactions involved is an important and actively discussed theoretical issue because it reflects such cluster properties as electromagnetic response, fission barrier formation, and evaporation dynamics. It is also important for practical applications such as particle formation and cluster film growth.

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Presentations

1. A. Scheidemann and V. Kresin, "Scattering Experiments and Spectral Response Properties of Metal Clusters," Meeting of the American Physical Society, Seattle, Mar. 1993.

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2. V. Kresin, "Electrons in Metal Clusters," Condensed Matter Seminar, Department of Physics, University of California, Berkeley, Feb. 1993.
3. V. Kresin, "Scattering of of Alkali Clusters and Their Response Properties," Sixth International Symposium on Small Particles and Inorganic Clusters, Chicago, IL, Sep. 1992.
4. V. Kresin, "Electron Distribution and Collective Resonances in Nonspherical Metal Clusters," International Workshop on Electronic Excitations and Magnetism in Clusters, East Lansing, MI, Sep. 1992.

Osteoporosis Research

J. H. Kinney, N. Lane,* and G. A. Henshall

Osteoporosis, which is characterized by abnormally low bone density that results from loss of both mineral and matrix from bones, manifests itself clinically as fractures, and on noninvasive quantitative imaging tests as low bone density.¹ Osteoporosis is a common public health problem in the United States; hundreds of thousands of postmenopausal women annually suffer fractures of the hip, distal forearm, and vertebrae. Complications of these fractures are estimated to cost over \$6 billion annually.² We are developing x-ray tomographic microscopy for in vivo measurement of bone mineral concentration and developing the framework for relating bone mineral concentration to mechanical properties and to etiologic factors. A method that can microscopically image bone mineral content in vivo would be a major advance in this field.

Background

Osteoporosis refers to excess fragility of bone, such that when bone is exposed to normal or minimally increased stresses, it fractures.^{3,4} Although several techniques developed over the past 10 years—such as single and dual photon densitometry, digital x-ray absorptiometry, and quantitative computerized tomography⁵—can measure bone mineral content and density in different areas of the body, only a fair correlation exists between densitometry measurements and bone material properties or fragility. Even people who have normal bone mineral density for their ages still suffer osteoporotic fractures. Therefore, although densitometry can measure bone density in large populations and bone mineral changes from interventional trials, it is not sensitive enough to detect abnormalities in bone material properties that would result in fragility.

Project

Our project consists of two elements:

- Using x-ray tomographic microscopy to image, three-dimensionally and *in vivo*, bone mineral concentration in rat tibias and femurs.
- Determining structure-property relationships.

X-ray tomographic microscopy (XTM) is a non-invasive imaging technique that is ideally suited to quantitative mapping of mineral concentration

gradients in calcified tissues.⁶ *In vivo* experiments using live rats will be conducted to demonstrate the ability to monitor the progression of bone mineral loss and structural changes in an individual animal. The rate of bone mineral loss, as well as the nucleation sites for this loss, in normal rats will be compared with bone mineral loss in ovariectomized rats. The measured bone-mineral-density gradients will be used in a 2-D, finite-element model to qualitatively estimate the effects of bone mineral loss on the mechanical response of these tissues to applied loads.

Progress

Ever since this project began in 1993, the work has focused on developing the XTM scanner for live animal research and developing analytical methods for quantitatively analyzing the 3-D images of bone structure.

In preliminary experiments at Stanford Synchrotron Radiation Laboratory (SSRL), we determined the radiation dose required for imaging a rat tibia *in vivo*. The dose was 90 Rads—higher than we had anticipated, but well below that required to induce bone damage (>400 Rads). With the new CCD camera system that we intend to install this summer, this dose can be reduced by half, and it should be possible to reduce it much further with an optimized experimental design. We also tested a fast x-ray shutter that prevents animals from being exposed except during actual data acquisition.

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The stage for holding and positioning the rat during scanning has been built and tested. The experimental procedure is to anesthetize the rat, cast its hind limb in an epoxy wrapping, and fixture the limb into the XTM field of view. After a scan is performed, the cast is removed. As a result of improved experimental design, scan times have been reduced from 1 hr to 30 min. We anticipate that scan times of a few minutes will be achieved by using the faster electronics package scheduled for installation this summer.

Results from the first rat experiments are excellent. Figure 1 shows a cross-sectional slice of the proximal tibia just below the growth cartilage metaphyseal junction. The trabecular bone is the small, spongy structure surrounded by the cortical shell.

Our initial approach in analyzing the XTM data has been to obtain the metric stereological parameters (histomorphometry)—volume fraction of trabecular bone, surface area of trabecular bone, trabecular plate separation, and trabecular plate width—that are the standard parameters quoted in osteoporosis studies. We tested the sensitivity of XTM for making these measurements and, in an initial study of three ovariectomized rats, were able to show differences in these parameters consistent with trabecular platelet loss. In Fig. 2, we show the results of XTM measurements of trabecular volume and separation in the greater trochanter of the three rats that had been fed different diets.

Figure 1. XTM cross section of the proximal tibia below the growth plate.

To assess the effects of bone mineral loss on mechanical strength, it is necessary to incorporate bone structure. To do this, we must begin by describing the 3-D data in terms of texture (i.e., nonscalar representations of the microstructure). Feldkamp⁷ proposed using the method of secants for determining anisotropy of trabecular bone. In this method, the line intercept length is calculated for all angular rotations of a single slice plane.

Figure 2. Histomorphometric parameters of cancellous bone structure obtained noninvasively from three rats on different diets.

The results for three orthogonal sections are plotted as line intercept length vs angle. An isotropic structure traces out circles, whereas an anisotropic structure generates an ellipse. The major and minor axes indicate the degree of anisotropy, and the angle between the axes indicates the orientation of the trabeculae with respect to a known orientation. This method, however, is a simple, straightforward extension of 2-D analyses and does not take full advantage of the 3-D data.

Our approach takes full advantage of the 3-D obtained with the XTM. A mesh is fit to the 3-D surface of the trabecular bone. Surface-normal vectors are calculated for each position on the mesh, and the angles with respect to the long axis of the bone are projected stereographically onto a plane. The result is a stereographic projection of surface normals similar to an x-ray pole figure. The actual 3-D orientations of the trabeculae are then determined by measuring the great circles on the stereographic projection.

Figure 3 is a 3-D XTM image of the trabeculae 1 mm distal from the growth cartilage. The image is oriented along the long axis of the tibia. The trabeculae are plate-like and are oriented approximately 20° with respect to the long axis. Figure 4 is a 3-D XTM image of the same bone but approximately 3 mm distal from the growth cartilage. Here, the trabeculae are more rod-like and oriented 55° with respect to the long axis.

Figure 3. XTM image of the 3-D trabecular bone structure in the proximal tibia.

Figure 4. XTM image of the trabecular structure distal to that in Fig. 3. Note the change in shape and orientation.

The pole figure (orientation distribution function) for the trabecular bone in Fig. 4 is shown in Fig. 5. With these data, it may be possible to identify preferential resorption of trabecular bone as a result of osteoporosis and to develop better risk assessment and treatments.

Figure 5. Orientation distribution function of the trabecular bone structure in Fig. 4.

Another approach to 3-D analyses is taken from topology. Odgaard and Gundersen⁸ have developed techniques for obtaining the Euler-Poincaré characteristic from 3-D networks. The weighted Euler-Poincaré characteristic can be related to the first Betti number and provides an indication of the degree of interconnectedness. We intend to incorporate this approach in future work.

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Solid-State Amorphization at a Crystalline Interface

A. F. Jankowski

Experimental observations and theoretical assessments of solid-state amorphization (SSA) have been limited by spurious conditions. The objective of this investigation is to create the proper experimental conditions with which to observe and control the nucleation of an amorphous phase. It is logical to assume that nucleation of a disordered phase should occur at locations in a crystalline system that have the greatest degree of disorder, such as internal interfaces. Multilayer thin films will be used to synthesize samples with crystalline interfaces. An attempt to regulate the driving force behind the SSA nucleation mechanism will be approached by systematically varying the crystalline interface spacing, i.e., the layer-pair spacing. Lattice strains produced at interfaces in short layer-pair spacings may affect the critical temperature (T_c) of SSA as a consequence of altering the interfacial elastic-energy barrier to the transformation.

Introduction

Experimental observations of solid-state amorphization (SSA), the crystalline-to-amorphous phase transformation, often are complicated by complex process conditions. For example, large plastic strains are generated during external loading in the ball milling process.

Theoretical assessments of SSA have been limited by the use of an amorphous parent phase. Specifically, SSA is treated simply as interdiffusion at an interface of an ordered phase with a highly disordered phase, which really is not SSA.

If amorphization of a material system progresses without an amorphous parent phase, then nucleation of an amorphous phase is first necessary. The objective of this investigation is to create the proper experimental conditions with which to observe and control the nucleation of an amorphous phase.

Technical Activities

The Ni-Ti system is selected for the study of SSA during FY93. Multilayer thin films are prepared using magnetron sputter deposition under the condition that the sputtered neutrals are in a near-thermalized state. High-resolution electron microscopy of Ni/Ti samples prepared in cross section reveals the Ni-Ti and Ti-Ni interfaces to

be crystalline¹ and the Ni/Ti structure to be a face-centered-cubic (fcc) superlattice.² Auger electron spectroscopy (AES) has been used to confirm sample composition through the process of generating concentration profiles.

An asymmetry is revealed between the Ni-Ti and Ti-Ni interfaces in an AES depth profile for a 26-nm Ni/Ti sample (see Fig. 1). The gradual

Figure 1. An Auger depth profile of a 26-nm layer pair Ni/Ti superlattice reveals a more gradual composition transition between nickel and titanium than does a Ti-Ni interface. This indicates that nickel preferentially interdiffuses into the titanium layers.

change in composition at the Ni-Ti interface indicates that nickel preferentially interdiffuses into the titanium layers. X-ray diffraction is being used to characterize the layer pair spacings and composition profile (at grazing incidence) as well as the lattice distortions (at high angle).

Analysis of copper $K\alpha$ scans in the $\theta/2\theta$ mode reveals a square-wave composition profile with strained layers of nickel (in tension) and titanium (in compression).³ Differential thermal analysis (DTA) is used to measure the critical transition temperature (T_c) of SSA. A characteristic endotherm (i.e., decrease in temperature) indicates an order-disorder transition.

DTA results show a T_c that appears to depend on the multilayer pair spacing, $d_{\text{Ni/Ti}}$. SSA of a 26-nm Ni/Ti sample is shown to occur at 325°C via *in situ* atomic imaging.⁴ The DTA scan (see Fig. 2) confirms this by the characteristic endotherm, measured at 308°C, and also shows an endotherm for a 3-nm Ni/Ti sample at 412°C. The change in $d_{\text{Ni/Ti}}$ has mitigated an apparent change in the T_c of SSA. A future explanation rests in the examination of the microstructure and modeling of the nucleation mechanism.

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Figure 2. The differential thermal analysis (DTA) trace is a plot of the difference in temperature ΔT between an alumina standard and the Ni/Ti multilayer as a function of increasing temperature T . The endotherms, marked by a sudden decrease in temperature at T_c , indicate solid-state amorphization.

Hydrogen Chemisorption on Diamond Surfaces

R. S. Daley and R. G. Musket

We have demonstrated the ability to measure submonolayer quantities of surface hydrogen on insulating glasses by ion-beam techniques. We extend this ability to an analysis of the diamond (100)-(1 × 1) and -(2 × 1) surfaces. The difference between mono- and dihydrated diamond (100)-(1 × 1) surfaces is 0.5 monolayer (ML) of hydrogen (1 ML = two hydrogen atoms per surface carbon) and is easily resolvable by forward recoil spectroscopy (FRS), which permits measurements of <0.05 ML. By measuring surface hydrogen concentration, the correct surface structures can easily be deduced for the (1 × 1) and (2 × 1) surfaces. If an intermediate coverage (1 ML > θ > 0.5 ML) is found for the (1 × 1) surface, then a combination of mono- and dihydrated surface states is indicated, as predicted by theory. For the (2 × 1) surface, the absolute difference between monohydrated and hydrogen-free surfaces is again 0.5 ML. A finding near 0.5 ML suggests that the carbon atoms have formed dimers and are predominately monohydrated, whereas coverages below 0.25 ML would indicate that most of the surface carbons are dehydrogenated and that carbon-carbon π -bonds have formed.

Background

The advantages of ion-beam techniques over other conventional surface analysis tools are

- The technique is nondestructive.
- Elemental specificity is easily obtained.
- Quantitative measurements at submonolayer coverages are possible.
- Surface hydrogen can be detected.

Our proposal builds on our previous work by examining hydrogen coverages on another insulating material: the technologically important diamond (100) surface. The information obtained in this study will allow us to deduce the correct structures for the diamond (100)-(1 × 1) and (2 × 1) surface phases as well as provide information on the kinetics of hydrogen desorption from the (100) surface. These quantitative results are essential if a complete understanding of the role of surface hydrogen during the chemical vapor deposition of thin diamond films is to be completely understood. In particular, this research will help bridge a gap that has recently been created between experiment and theory on the structure of the diamond (100)-(1 × 1) and (2 × 1) surfaces. To date, hydrogen coverages have only been inferred by indirect measurement techniques.

Technical Activities and Results

To measure surface hydrogen coverages under controlled conditions, an ultrahigh-vacuum (UHV) chamber attached to the accelerator beamline is required. An existing Varian-designed UHV chamber has been modified and equipped with the appropriate surface-analysis equipment required for the experiment. A UHV manipulator with heating and cooling capabilities is also required.

To date, all the planning, design, and hardware purchases for the project have been made. The detector and other surface-analysis systems have been built and installed in the UHV chamber. An existing Vacuum Generators manipulator has been modified to handle small samples (5 × 5 × 0.25 mm) and provide heating to 1200°C and cooling to -125°C. This manipulator has been tested and performs very well. The UHV chamber (see Fig. 1) has been equipped with the following items:

- A 168° Rutherford backscatter (RBS) detector for bulk and surface elemental impurity analysis.
- A detector for forward recoiled hydrogen atoms.
- An ion sputter gun for surface cleaning and modification.

- Low-energy electron diffraction (LEED) optics for monitoring changes in surface structure.
- A gas manifold and filament system for dosing the surface with atomic gas species.
- A retractable faraday cup for monitoring the ion beam current.

The chamber is ready to be moved to the 4-MeV ion-accelerator beamline, where it will be placed directly behind our current analysis chamber. Therefore, we will have all our current materials-analysis capabilities plus the use of a UHV system for surface analysis. The first experiment will involve a detailed investigation of how atomic hydrogen interacts with diamond surfaces.

Summary

The UHV analysis system is almost ready to go on line. When it becomes operational, we will

analyze the surface hydrogen coverages on diamond under controlled and reproducible conditions. The data and results should lead to a better understanding of the role of chemisorbed hydrogen in determining surface structure and in the growth of CVD diamond films.

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Figure 1. Top view of the UHV chamber, showing the layout of the ion detectors, gas doser/filament assembly, LEED optics, sputter gun, and retractable faraday cup.

Laboratory Directed Research and Development

**Glenn T. Seaborg Institute for
Transactinium Science**

Glenn T. Seaborg Institute for Transactinium Science

D. C. Hoffman, *Director*

Overview

During the first half of FY93, five LDRD projects were funded under the auspices of the Glenn T. Seaborg Institute for Transactinium Science (ITS).

The largest of these involves studies of actinides in the environment and includes the ongoing project entitled "Plutonium Solubility and Speciation in Carbonate Solution." These carbonate solutions are typical of the groundwater at the proposed national nuclear waste repository site at Yucca Mountain, Nevada, and the studies are relevant to the potential for migration of plutonium. Measurements are made in a controlled-atmosphere glove box using optical fibers to carry light from a state-of-the-art, laser-induced, photoacoustic spectrometer (LIPAS). The method is significantly more sensitive than conventional ultraviolet/visible spectroscopy. This research forms the basis for graduate student M. Neu's Ph.D. dissertation, which will be completed in FY93.

Also included is a new interdisciplinary project entitled "Bacterial Remediation of Actinide-Contaminated Sites," which was initiated by ITS Senior Postdoctoral Fellow A. Happel in February, 1993.

Another project relevant to actinide speciation is N. Hannink's dissertation research on "Cation-Cation Complexes of Actinides," again using the LIPAS technique. The novel interactions of actinyl (V) cations with other multiply charged cations are being investigated.

The ongoing research of J. Sytsma, an ITS Postdoctoral Fellow on "Two-Photon Spectroscopy of the Actinide Ions Cm^{3+} and Am^{2+} ," will yield valuable information about the electronic properties of the 5f elements, such as crystal field effects and site symmetries in solids. This information is not accessible by conventional, linear laser spectroscopy.

In a project to be completed in FY93, "Fully Relativistic Surface Green Function and Its Applications: Theoretical Study of Uranium on Pt (111) Surface," Senior Postdoctoral Fellow E. Tamura is comparing his theoretical results with experimental findings for ultraviolet photoemission spectra.

Plutonium Solubility and Speciation in Carbonate Solution

M. Neu, D. Hoffman, R. Silva, K. Roberts,* and H. Nitsche*

The solubility-limited speciation of ^{242}Pu as a function of time in near-neutral carbonate solutions is being measured to better understand the chemical behavior of plutonium in groundwater. Plutonium, in a single oxidation state, is added to an aqueous solution, and aliquots of the resulting solution are removed over a period of weeks to measure the solubility and investigate the nature of the soluble species. To simulate a natural groundwater, all experiments are performed at $\text{pH} = 6.0 \pm 1$, $T = 30.0 \pm 2$, $P_{\text{CO}_2} = 5.71\%$, with 0.100M sodium perchlorate as an electrolyte. Laser-induced photoacoustic spectroscopy (LIPAS) and extraction methods are used to identify and quantify the plutonium species present. Plutonium(V) is the most stable oxidation state under these conditions, independent of the initial concentration and oxidation state (IV, V, or VI). Plutonium(VI) exhibits the most complex solution behavior, reflecting the equilibria involving soluble and insoluble forms of both Pu(V) and Pu(VI).

Introduction

In order to assess the potential for migration of plutonium in groundwater, it is crucial to understand the influences of environmental conditions on solubility, chemical speciation, and kinetic and thermodynamic behavior. Concentrations of individual species are being measured as a function of time to investigate which species may be stable in natural waters and will, therefore, dominate the environmental chemistry. Plutonium solubility in solutions relatively rich in carbonate is being measured using liquid scintillation counting; the speciation is investigated using extraction methods and laser-induced photoacoustic spectroscopy. This method yields the same information but is significantly more sensitive than conventional ultraviolet/visible spectroscopy.

Progress

A remote, fiber-optic, laser-induced photoacoustic (LIPAS) spectroscopic system was built, and a small-volume cuvette was designed to minimize the amount of plutonium used. A computer-linked system for solution control and monitoring provided temperature and pH control. Plutonium solutions of a single oxidation

state were prepared electrochemically, and separate aliquots were added to individual pre-equilibrated carbonate solutions and monitored.

Solutions were maintained for several weeks under an overpressure of a CO_2 /argon mixture. Liquid scintillation counting was performed on aliquots of the plutonium-carbonate solutions, and spectral regions containing characteristic absorbance bands for Pu^{4+} , PuO_2^+ and PuO_2^{2+} were scanned. All experiments were performed at $\text{pH} = 6.0 \pm 1$, $T = 30.0 \pm 2$, and $P_{\text{CO}_2} = 5.71\%$, with 0.100M sodium perchlorate as an electrolyte. Initial concentrations of plutonium were 4.75×10^{-5} , 2.51×10^{-5} , and $3.68 \times 10^{-4}\text{M}$, for Pu^{4+} , PuO_2^+ , and PuO_2^{2+} , respectively.

Most of the plutonium(IV) initially came out of solution, dropping from $4.75 \times 10^{-5}\text{M}$ to $\sim 5 \times 10^{-8}\text{M}$ after 5 days, then appeared to resolubilize over the next 5 days. From day 10 to the end of the experiment at day 22, the concentration of soluble plutonium was $(1.0 \pm 3) \times 10^{-6}\text{M}$. Spectroscopic identification and quantification of the soluble species were not possible at this low concentration; spectra over the regions of interest for Pu^{4+} and PuO_2^+ were indistinguishable from background.

The plutonium(V) solution had a soluble plutonium concentration of $(2.1 \pm 1) \times 10^{-5}\text{M}$ over a period of 53 days. The soluble plutonium was determined to be $>95\%$ PuO_2^+ from spectroscopic data.

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which valences are bound and if microbial retention is linked to reduction. We will identify both the cellular components that are required for actinide binding and the corresponding genes that encode proteins required for actinide binding. Our long-term goal is to use molecular genetic techniques to engineer bacteria for high-specificity binding of individual actinides and for maximal actinide accumulation.

Technical Activities Proposed

The overall goals of our research are to

- Quantify the microbial binding and retention of actinides.
- Determine the specificity of metal binding.
- Identify the cell components that bind actinides.
- Define the genes and gene products responsible for binding transactinium elements.
- Bioengineer bacterial strains for maximal actinide binding and high-specificity metal binding.
- Test these strains for remediation of waters and soils from contaminated sites.

During FY93, we will complete the microbial binding assays with Tc, U(VI), Np, Pu, and Am. We will determine the valence states of the bound elements and investigate whether microbial binding is linked to reduction. The maximal load (grams of actinide bound per gram dry weight of cells) will be determined, along with the stability constants of these complexes. Bioaccumulation of actinides will be assayed under a variety of conditions to measure the influence of pH, ionic strength, and the presence of inorganic and chemical complexing agents. We will also determine the specificity of actinide-microbe binding. Other metals and anions will be included in the binding assays to test for inhibition of actinide binding: Fe, Mo, Pb, Se, V, Mg, Mn, Ni, Cu, Co, Zn, nitrate, and sulfate.

By the end of FY93, we plan to identify bacterial components that are responsible for actinide binding via three separate approaches—by using electron microscopy to determine which cell structures are binding the actinide, by assaying actinide binding to bacterial mutants that lack specific cell structures, and by biochemically analyzing cell fractions for bound actinide.

Cation-Cation Complexes of Actinides

N. Hannink, D. Hoffman, R. Silva, and R. Russo

We are investigating the complexation of actinide(V) cations with other actinide cations. The previously discovered complex, $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$, was investigated using laser-induced photoacoustic spectroscopy (LIPAS), a spectroscopic technique yielding basically the same information as absorption spectroscopy, but with greater sensitivity. Although this technique had not been applied to the study of cation-cation complexes among the actinides, preliminary results indicate that the method and equipment are working, and we are planning to look at other cation-cation complexes.

Introduction

Actinyl(V) cations form complexes with a variety of other cations, including other actinides; this cation-cation complex formation is unique to the +5 oxidation state. In 1961, Sullivan, Hindman, and Zielen discovered the

$\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$, cation-cation complex.¹ Since then, the cation-cation complexes of NpO_2^+ have been studied extensively, but these complexes of PuO_2^+ remain virtually unstudied. The formation constants for cation-cation complexes are small, ranging from 0.095 to 16.0. Small formation constants and radioactive species, some of which are

which valences are bound and if microbial retention is linked to reduction. We will identify both the cellular components that are required for actinide binding and the corresponding genes that encode proteins required for actinide binding. Our long-term goal is to use molecular genetic techniques to engineer bacteria for high-specificity binding of individual actinides and for maximal actinide accumulation.

Technical Activities Proposed

The overall goals of our research are to

- Quantify the microbial binding and retention of actinides.
- Determine the specificity of metal binding.
- Identify the cell components that bind actinides.
- Define the genes and gene products responsible for binding transactinium elements.
- Bioengineer bacterial strains for maximal actinide binding and high-specificity metal binding.
- Test these strains for remediation of waters and soils from contaminated sites.

During FY93, we will complete the microbial binding assays with Tc, U(VI), Np, Pu, and Am. We will determine the valence states of the bound elements and investigate whether microbial binding is linked to reduction. The maximal load (grams of actinide bound per gram dry weight of cells) will be determined, along with the stability constants of these complexes. Bioaccumulation of actinides will be assayed under a variety of conditions to measure the influence of pH, ionic strength, and the presence of inorganic and chemical complexing agents. We will also determine the specificity of actinide-microbe binding. Other metals and anions will be included in the binding assays to test for inhibition of actinide binding: Fe, Mo, Pb, Se, V, Mg, Mn, Ni, Cu, Co, Zn, nitrate, and sulfate.

By the end of FY93, we plan to identify bacterial components that are responsible for actinide binding via three separate approaches—by using electron microscopy to determine which cell structures are binding the actinide, by assaying actinide binding to bacterial mutants that lack specific cell structures, and by biochemically analyzing cell fractions for bound actinide.

Cation-Cation Complexes of Actinides

N. Hannink, D. Hoffman, R. Silva, and R. Russo

We are investigating the complexation of actinide(V) cations with other actinide cations. The previously discovered complex, $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$, was investigated using laser-induced photoacoustic spectroscopy (LIPAS), a spectroscopic technique yielding basically the same information as absorption spectroscopy, but with greater sensitivity. Although this technique had not been applied to the study of cation-cation complexes among the actinides, preliminary results indicate that the method and equipment are working, and we are planning to look at other cation-cation complexes.

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$\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$, cation-cation complex.¹ Since then, the cation-cation complexes of NpO_2^+ have been studied extensively, but these complexes of PuO_2^+ remain virtually unstudied. The formation constants for cation-cation complexes are small, ranging from 0.095 to 16.0. Small formation constants and radioactive species, some of which are

oxygen sensitive, require special handling and sensitive techniques.

Laser-induced photoacoustic spectroscopy (LIPAS) is a relatively new spectroscopic technique that uses the nonradiative relaxation of the absorbing species, thereby generating heat and an acoustic wave. Because LIPAS and conventional absorption spectroscopy use the same physical phenomena for the initial process (absorption of light by a species), the information derived by each method is the same; therefore, the same analysis methods can be used. By analyzing the shifts in spectral absorption peaks during complexation, formation constants can be calculated.

A remote LIPAS system, set up at LLNL in an inert-atmosphere glovebox, allows containment of the radioactive species, provides an oxygen-free environment, and uses a sensitive measurement technique, all of which are needed for this project.

During the course of this study, PuO_2^{2+} , complexation with UO_2^{2+} , and NpO_2^{2+} will be examined. PuO_2^{2+} is important because this plutonium species has been shown to be present in many environmental waters. We not only will learn more about cation-cation complexes but also will learn more about the behavior of PuO_2^{2+} in the presence of other actinides in acidic solutions.

Progress

By the end of FY92, various preliminary items were completed. For instance, the remote LIPAS apparatus was constructed, installed in the inert-atmosphere glovebox, and tested using stable lanthanides. The spectral data analysis program SQUAD was tested using LIPAS data.

During the first part of FY93, preliminary experiments using the previously discovered $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex were started. This complex was chosen for the initial studies using the LIPAS system and analysis using SQUAD to test the method and equipment for application to these types of complexes. These studies were performed at two ionic strengths, 0.5 and 6M. At 0.5M, no evidence for the complex was seen; at 6M, however, evidence for complexation was seen. Figures 1 and 2 show data for 0.5 and 6M ionic strengths, respectively. Based on the initial data, which have a fairly large error, an equilibrium constant of 4 was obtained. This

agrees favorably with previously reported values of 2.45 (Ref. 2), 2.50 (Ref. 3), and 3.7 (Ref. 4), for ionic strengths from 6 to 7M.

Figure 1. Spectra of $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ experiment at 0.5M ionic strength. Spectrum 1 is a 0.000248M NpO_2^+ standard, and spectrum 2 is an experimental solution containing 0.000248M NpO_2^+ and 0.260M UO_2^{2+} . Both spectra are background subtracted.

Figure 2. Spectra of $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ experiment at 6M ionic strength. Spectrum 1 is a 0.000248M NpO_2^+ standard, spectrum 2 is an experimental solution containing 0.000248M NpO_2^+ and 0.0867M UO_2^{2+} , spectrum 3 is a 0.0867M UO_2^{2+} standard, and spectra 4 and 5 are blanks.

Summary

The methodology and equipment are functioning as expected. A preliminary result for the $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ complex has been obtained; however, in order to obtain a more precise value for this constant, the experiment has been repeated and the data are currently under analysis. As a continuation of this project, we will look for the $\text{PuO}_2^+ \cdot \text{UO}_2^{2+}$ and $\text{PuO}_2^+ \cdot \text{NpO}_2^{2+}$ complexes and determine their equilibrium constants.

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Two-Photon Spectroscopy of the Actinide Ions Cm^{3+} and Am^{2+}

J. Sytsma and N. Edelstein*

We seek to better understand the electronic properties of the actinide ions Cm^{3+} and Am^{2+} , especially in relation with Gd^{3+} and Eu^{2+} . New insight into the electronic structure of these actinide ions should come from comparing the two-photon excitation data with those measured for the analogous lanthanides. In two-photon excitation, the energy of the excitation light is not resonant with the transition; instead, two photons provide the energy matching.

Introduction

Two-photon laser spectroscopy (TPS) complements conventional linear laser spectroscopy in solids. A significant advance has come from experimental and theoretical results of TPS studies of Gd^{3+} and Eu^{2+} . The enormous progress in understanding the intensities of intra $4f^7$ transitions of these ions led to the idea of TPS studies on the actinide analogues of Gd^{3+} and Eu^{2+} , Cm^{3+} , and Am^{2+} , respectively. Important differences in the electronic structure of the actinide analogues (i.e., much stronger spin-orbit coupling) should provide a stringent test of the new theories that have arisen from TPS studies of the $4f^7$ ions.

Progress

After testing the cryogenic part and electronic detection system on Ce^{3+} in LuPO_4 , we had to move the laser laboratory. Therefore, no experimental work could be done from early December 1992 to mid-February 1993.

After the move, we first performed measurements on Gd^{3+} in LaF_3 . The $^8s_{7/2} \rightarrow ^6p_{7/2}$ transition was observed, at room temperature as well as at liquid-helium temperature, by tuning the dye laser wavelength through 618 to 622 nm. Downer et al. published extensively on this system.¹ We repeated part of their measurements in order to test our new setup and normalize our detection sensitivity to that in Ref. 1.

Linear spectroscopy of $\text{LuPO}_4\text{:}^{248}\text{Cm}^{3+}$ was performed to measure the optical properties of

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this system. The following measurements were taken:

- Absorption spectra
- Emission and excitation spectra
- Decay measurements.

Absorption Spectra

The absorption data show approximate 75 transitions, all starting from the ground state (G.S.). This state is a nominal $8s_{7/2}$, but the large spin-orbit coupling accounts for considerable mixing of levels with nonzero angular momentum. The total crystal-field (c.f.) splitting induced by this mixing amounts to $\sim 10 \text{ cm}^{-1}$. The splitting between the lowest c.f. component and the next c.f. component of the G.S. is only 3 cm^{-1} .² This is insufficient to freeze the Cm^{3+} population into one energy component, even at liquid helium temperature. Most of the absorption bands do show a structure with maxima separated by 3 and 10 cm^{-1} from the maximum at lowest energy.

The absorption spectra show a weak polarization dependence. This significantly helps the symmetry assignments of the transitions. The positions and the respective symmetry assignments are fit to a phenomenological c.f. Hamiltonian. Preliminary results are consistent with data obtained from electron paramagnetic resonance (EPR).²

Emission Spectra

Emission spectra of $^{248}\text{Cm}^{3+}$ in LuPO_4 were taken to find the exact positions of the emitting $^{248}\text{Cm}^{3+}$ energy levels. It is essential to understand the emission pattern in detail. The two-photon excitation is detected by monitoring the emission of $^{248}\text{Cm}^{3+}$. It is imperative that these emission energy levels be known accurately.

Emission is observed only from the first excited J-level ($6d_{7/2}$). Emission from higher levels is obviously quenched by nonradiative transitions; such transitions occur by interactions of the electronic system with the lattice, mainly via the $[\text{PO}_4]^{3-}$ vibration of $\sim 1000 \text{ cm}^{-1}$. All of the intensity of the radiative transition is contained in the electronic transition. No vibronic side bands are observed.

Not all c.f. components of the excited states show up in the absorption spectra. Excitation measurements were used to determine the positions of the c.f. components of the $6d_{7/2}$ state. In contrast with the emission spectra, vibronic tran-

sitions are now observed. We do not understand this phenomenon.

Decay Measurements

Decay measurements are used to experimentally determine the transition probabilities of the radiative transition. The decay time is long, about $450 \mu\text{s}$, as is expected for a parity-forbidden transition.

From the absorption data, the optical intensity parameters Ω_l ($l = 2, 4, 6$) are deduced. With the wavefunctions obtained from the c.f. fit, these parameters can be used to predict the transition probabilities. Up to now, however, many energy levels have still been excluded from the c.f. fits. The wavefunctions are consequently not accurate enough to justify transition probability calculations. TPE experiments are now in progress.

Our collaborators have succeeded in growing LaCl_3 single crystals doped with $^{248}\text{Cm}^{3+}$. Since the optical properties of this system are very well known, TPE experiments can be started directly on this system.

Summary

Conventional optical spectroscopy techniques have been used to determine energy levels of $^{248}\text{Cm}^{3+}$ in LuPO_4 . The information is used in TPE experiments and theoretical calculations. The experiments are in progress.

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Fully Relativistic Surface Green Function and Its Applications: Theoretical Study on Uranium on Pt(111) Surface

E. Tamura and A. Gonis

Theoretical angle-resolved UPS spectra are presented for uranium monolayers on Pt(111) and for fcc U(111) surfaces. We find that uranium island formation can occur if a peak in the UPS spectra appears just below the Fermi level as soon as uranium is deposited on platinum. We suggest an experimental procedure for testing this prediction.

Introduction

There are at least two advantages in studying the chemical properties of materials by means of surface spectroscopies. First, one can easily control the geometrical arrangement of atoms on the surface by choosing suitable substrates and their chemical components. Second, one can directly apply well-established surface spectroscopic techniques, such as low-energy electron diffraction (LEED).

We are studying, theoretically and computationally, angle-resolved vacuum ultraviolet photoemission spectra (UPS) from uranium monolayers on Pt(111), under the assumption that uranium can be grown epitaxially on the Pt(111) substrate. We also are studying the fcc U(111) surface regarding a possible island-growth on the substrate. Since platinum and uranium are both high-Z elements, we have to treat their scattering properties relativistically. Our photoemission computer code is based on the fully relativistic spin-polarized layer Green function method, and it yields layer-projected densities of states (DOSs) of initial states, which is helpful in analyzing photoemission spectra.

Theory and Numerical Results

A semi-infinite crystal model may be viewed as a stack of atomic layers extending infinitely in two dimensions parallel to the surface. The effective electron-solid interaction is approximated by muffin-tin (spherically symmetric) cell potentials, which are obtained through an application of the linearized muffin-tin orbital (LMTO) method. The layer Green function is constructed in terms of the solutions of the Dirac equation, taking into

account scattering by other crystal atoms in the layer under consideration and by the adjacent layers.

Figures 3 and 4 show the angle- and orbital-angular-momentum-projected layer DOSs for U/Pt(111) and U(111) in the direction normal to the surface, which are obtained directly from the imaginary part of the Green functions. In this calculation, we assume an inverse lifetime of 0.2 eV so that we can regard the electronic states as holes of excited electrons (corresponding to Lorentzian broadening). Since f-electrons (thick solid line) are rather localized and, therefore, are relatively insensitive to the substrates, we find the f-state DOS for a pure uranium surface to be similar energetically to that of a uranium monolayer on platinum (upper panels). However, f-electrons are more localized in the U/Pt(111) system than in U(111), simply because there is no way for f-state electrons to penetrate into the platinum substrate (Fig. 3b). This can be seen very easily by switching off the lifetime broadening in the calculation. While the f-electron DOS approaches the d-function-type features (uranium-layer-induced surface states) in U/Pt(111), it keeps the (narrow)-band features in U(111).

In Fig. 5, the spin-resolved UPS spectra for U/Pt(111) and U(111) obtained by normal incident positive helicity (circularly polarized) light are shown. Spin-resolved spectra immediately give us an additional piece of information; the symmetry type of the initial states of photo-excited electrons. For a (111)-surface normal, the crystal has C_{3v} (three-fold rotation and three mirror operations) symmetry, and it is known that there are two types of symmetry groups, L_{4+5} and L_6 . In our spectra, spin-up and spin-down intensities correspond to L_{4+5} and L_6 symmetry, respectively.

Figure 3. Layer DOS of U/Pt(111) surface: uranium overlayer (a), platinum bulk layer (b). Total DOS is drawn with thin solid line, d-state with thick dashed line, and f-states with thick solid line. The Fermi-level is referenced to zero.

Investigating the dipole matrix elements computationally (it is impossible experimentally), we can trace back from the excited (final) states to the initial states and identify the physical origin of all spectra. In UPS for U/Pt(111) (Fig. 5a), all peaks are of electrons excited from the platinum substrate (mainly from d-states), while only f-state electrons are exclusively excited from U(111) surfaces (Fig. 5b). These are rather surprising results because the main contribution to UPS spectra usually originate from the topmost layer due to the short escape length of excited electrons (3 eV is assumed for excited states in terms of inverse lifetime) whose DOSs are similar for both U/Pt(111) and U(111).

Checking the matrix elements closely, we find that final-state d-waves in U/Pt(111) are very weakly excited in contrast to U(111), where

Figure 4. Same as Fig. 3, but for U(111) surface.

there are dominant dipole-allowed states in transitions from f-initial states. This type of complication has been found in UPS analysis, so that UPS spectra do not directly reflect the DOS of initial states. Furthermore, we predict that island formation takes place if a peak appears just below the Fermi level immediately as uranium is deposited on platinum substrate.

Summary

We theoretically and computationally investigated UPS spectra from U/Pt(111) and U(111) surfaces. The results obtained are consistent with the experimental findings of Gouder and Colmenares,¹ who performed experiments with polycrystalline platinum substrates. Further investigation, using single-crystal substrates, seems necessary in order to compare with the theoretical analysis.

Figure 5. Spin-resolved normal emission UPS from U/Pt(111) (a) and U(111) surfaces (a) by circularly polarized light of 21 eV: spin-up intensities (thick solid line), spin-down intensities (thick dashed line) and total intensities (thin solid line).

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