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Fundamental scientific research on interfaces in the US Department of Energy's Materials Sciences and Engineering program

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Abstract

This paper describes two facets of the Materials Sciences and Engineering program under the Office of Basic Energy Sciences at the US Department of Energy: (1) its organizational structure, mission, guiding principles, identification of national scientific user facilities, principal core research activities, identification of some unique portfolio activities, key focus areas, scientific challenges, and the linkage of these challenges to the mission of the Department of Energy; and (2) some recent accomplishments based on science funded under this program that relate to the atomic-level understanding and design of ceramic and metal interfaces.
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1. The US Department of Energy's Materials Sciences and Engineering program

The US Department of Energy (DOE) is the largest supporter of research in the physical sciences in the United States. Fundamental research in the physical sciences is funded under the Office of Science. The Director for the Office of Science is nominated by the President, and subject to confirmation by the US Senate. Dr. Raymond L. Orbach, a condensed-matter physicist, was sworn into this position on 14 March 2002.

With an annual budget of \$3.3 billion, the Office of Science is the principal funding agency of research programs in the United States in high-energy physics, nuclear physics, and fusion energy sciences. The Office also manages research programs in basic energy sciences, biological and environmental sciences, and computational science, all of which also support DOE's missions. The Office is responsible for the management of 10 DOE laboratories and for constructing and operating several large scientific user facilities.

While DOE supports various aspects of materials sciences and engineering under 19 different program offices spread throughout DOE, all fundamental scientific research in materials is grouped under the Office of Science, in the Office of Basic Energy Sciences' Division of Materials Sciences and Engineering. The Director of the Office of Basic Energy Sciences is Dr. Patricia M. Dehmer, and the Director of the Division of Materials Sciences and Engineering is Dr. Iran L. Thomas.

The mission of the Office of Basic Energy Sciences is twofold: (1) to foster and support fundamental research to provide the basis for new, improved, environmentally conscientious energy technologies; and (2) to plan, construct, and operate major scientific user facilities for "materials sciences and related disciplines" to serve researchers from academia, federal laboratories, and industry.

Virtually all fundamental scientific research in materials occurs under the Division of Materials Sciences and Engineering, which also has management and funding responsibility for the support of national user facilities involving neutron sources, synchrotron X-radiation, and electron beam microcharacterization. These facilities include:

- four neutron scattering sources (Intense Pulsed Neutron Source at Argonne National Laboratory, High Flux Isotope Reactor at Oak Ridge National Laboratory, Los Alamos Neutron Science Center at Los Alamos National

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Laboratory, Spallation Neutron Source—still under construction—at Oak Ridge National Laboratory);

- four synchrotron radiation sources (National Synchrotron Light Source at Brookhaven National Laboratory, Advanced Photon Source at Argonne National Laboratory, Advanced Light Source at Lawrence Berkeley National Laboratory, Stanford Synchrotron Radiation Laboratory at Stanford University);
- four electron beam microcharacterization centers (Shared Research Equipment Program at Oak Ridge National Laboratory, Electron Microscopy Center for Materials Research at Argonne National Laboratory, Center for Microanalysis of Materials at the Frederick Seitz Materials Research Laboratory at the University of Illinois, National Center for Electron Microscopy at Lawrence Berkeley National Laboratory); and
- the Materials Preparation Center at the Ames Laboratory at Iowa State University.

Furthermore, at least three new centers for nanosciences are now contemplated. Together, these national user facilities attract over 8000 users per year.

Much of the research pertaining to ceramic and metal interfaces and their control at the atomic level takes place under the Materials and Engineering Physics Team, one of two operational units under the Division of Materials Sciences and Engineering.

The guiding principles for this Team are as follows:

1. Advance fundamental understanding of materials through experimentation, theory, modeling, and simulation.
2. Ensuring scientific progress in materials topics central to basic energy sciences that may not have other federal support.
3. Focusing on five complementary and interrelated Core Research Activities (to be described later).
4. Breeding interactions via collaborative centers and "glue" funding.
5. Providing long-term support for key fundamental work.
6. Maintaining a dynamic program: retaining flexibility to start new projects to refresh the portfolio and stay at the forefront.

There are five core research areas under the Materials and Engineering Physics Team:

1. *Structure and Composition of Materials*, which includes such topics as the arrangement and identity of atoms and molecules in materials; development of quantitative characterization techniques; theory and modeling of atomic and magnetic structure; specialized tools for spatial resolution, quantitative imaging, and spectroscopy; mechanisms by which atomic arrangement are created and evolve; structure and composition of inhomogeneities, defects, and morphology of surfaces, interfaces, and precipitates; and advancing the state of the art of electron-beam microcharacterization methods and instruments.
2. *Mechanical Behavior of Materials and Radiation Effects*, which includes behavior of materials under static and dynamic stresses; deformation and fracture over all length scales, temperatures, and environments; relations among internal stress, crack nucleation, and crack tip shielding; response of materials to radiation resulting in atomic displacements; radiation-damage mechanisms and degradation modeling; and surface modification by ion implantation.
3. *Physical Behavior of Materials*, which includes response of materials to temperature, pressure, compositional gradients, and magnetic and electric fields; and corrosion, electronic, magnetic, dielectric, semiconducting, and superconducting behaviors, including the role of defects and interfaces.
4. *Synthesis and Processing Materials Science*, which includes atomic and molecular self-assembly; nanostructured materials that mimic the structure of natural materials; welding and joining; and new materials-processing approaches to improve properties and reduce wastes.
5. *Engineering Sciences*, which includes materials engineering; nanotechnology and microelectromechanical systems; multiphase fluid dynamics and heat transfer; nonlinear dynamic systems; and nondestructive evaluation and early warning of impending failure.

The Materials and Engineering Physics portfolio is a significant and—in some cases—the only source of federal support in the United States for *fundamental scientific research* in the following energy-mission relevant topics: radiation damage, welding and joining, aqueous and galvanic corrosion, high-temperature gaseous corrosion, photovoltaic semiconductors, high-temperature mechanical behavior, nondestructive evaluation, granular and multiphase fluid transport, and nonlinear behavior of engineering systems.

Key focus areas and scientific challenges include:

1. *Quantitative Nanoscale Characterization*: Maintaining the nation's instrumentation infrastructure (in conjunction with the Condensed Matter Physics and Materials Chemistry Team under the Division of Materials Sciences and

Engineering) is necessary to enable leading-edge science on radiation damage, welding and joining, corrosion, and photovoltaics, all of which require an atomic-scale understanding of structure and composition.
2. *Fundamentals of Mechanical Behavior*: Linking fundamental aspects of materials structure, processing, and behavior at various length scales is necessary to achieve the fundamental understanding of deformation over many length scales. This understanding is required to make advances in structural materials and processing and to understand how defects and interfaces control mechanical and physical behavior.
3. *Science-Based Materials Design*: Devising accurate models and key tests of materials theories to allow predictive design of next-generation materials is necessary for the rational development of next-generation materials with enhanced functionality and unprecedented resistance to radiation, environmental degradation, and failure.

2. Some recent accomplishments under the Materials and Engineering Physics Team

Recent accomplishments under the Materials and Engineering Physics Team that relate to the atomic-level understanding and design of ceramic and metallic interfaces are described below.

2.1. New Interferometric electron-beam technique (Y. Zhu, L. Wu, J. Tafto, M. Suenaga, and D.O. Welch; Brookhaven National Laboratory)

A new interferometric electron-beam technique has been developed that measures atomic displacements in crystals across interfaces in a bismuth-based superconductor to an accuracy of 1 pm, i.e. one-hundredth of the diameter of an atom. Imperfections in atomic packing, such as interfaces and crystal boundaries, often determine the properties and behavior of materials, particularly in nanostructured devices, and can lead to new insights about chemical bonding and electronic structure at structural imperfections and subsequent changes in materials performance. A critical example is the effect of lattice expansion at the interface between crystallites on current flow in superconductors. This accomplishment was made possible by a new interferometric technique that coupled electron diffraction with imaging by using a highly coherent electron beam in an electron microscope. The key to the accuracy of the measurement is its independence of the wavelength of the electrons. This was achieved by quantitative analysis of interference patterns produced by electron waves, which are scattered by structural imperfections. The result is a greatly enhanced capability to map imperfections and their resulting strain fields in materials ranging from superconductors to multilayer semiconductor devices.

2.2. Use of electron holography for grain-boundary measurement (V. Dravid; Northwestern University)

V. Dravid has used electron holography to measure, image, and map the grain-boundary potential across a single grain boundary in strontium nitrate. Thin-film dielectrics, photovoltaics, ferroelectrics, high T_c superconductors, and semiconductors often have excess charges, with associated boundary potentials, at various internal boundaries. More recently, Dravid went a step further and found that the grain-boundary potential, which blocks current flow at low fields, decreases as the applied field increases. This result shows how high fields switch on the current in electroceramic devices. Electron holography uses the sensitivity of a modern electron microscope's highly coherent electron waves to electrical fields to image the field from excess charges within a range of less than one nanometer around a grain boundary. Using a technique roughly equivalent to visible light holography, electron holography pushes resolution to the size of an atomic unit cell (~0.5 nm); at this resolution a grain-boundary potential can be imaged.

2.3. Detailed image of gallium nitride (C. Kisielowski, M.A. O'Keefe, C. Nelson, and R. Kilaas; National Center for Electron Microscopy, Lawrence Berkeley National Laboratory)

An image of the semiconductor gallium nitride that clearly distinguishes columns of nitrogen from their heavier gallium neighbors has been produced by full reconstruction of the electron wave after it passes through the material in an electron microscope. The image was achieved by computer processing of a through-focus series of 20 images to unscramble the amplitudes and phases of the electron wave. The resulting phase image shows that gallium and nitrogen columns are unambiguously distinguished by their contrast, and are clearly resolved at their separation of 0.113 nm. This result demonstrates that crystallographic defects such as inversion domains, dislocation core structures, or bonding at interfaces could be characterized with truly atomic resolution even if light elements are involved. Understanding the complex defect structure of gallium nitride is critical to controlling electronic behavior and achieving the material's ultimate performance potential: to revolutionize lighting with an energy-conversion efficiency at least five times better than that for a conventional lightbulb.

2.4. Behavior of liquid metals on ceramic surfaces (E. Saiz, A.P. Tomsia, and R.M. Cannon; Lawrence Berkeley National Laboratory)

A centuries-old problem in understanding the behavior of liquid metals on ceramic surfaces has been solved. The classical Young–Dupre thermodynamic equation that predicts the equilibrium contact angle for a liquid droplet on a solid substrate does not accurately describe all wetting behavior. One of the most widely encountered exceptions is the observed hysteresis when a molten metal wets a surface at high temperature; in this case the contact angles created between the droplets formed by advancing (growing) and receding (evaporating) liquids may be different. The Berkeley group studied the structure of the triple junction formed where a molten metallic liquid droplet, a solid alumina substrate, and the vapor from the droplet are in contact. To do this they removed the metal droplets by acid etching and then imaged the topography of the region with atomic force microscopy. They discovered that in cases where hysteresis was observed, the surface of the substrate in the region of the triple junction had not remained flat. Instead they found small ridges ranging in height from a few to several hundred nanometers. Since the Young–Dupre equation assumes that the substrate is rigid and insoluble, the presence of ridges could be the basis for hysteresis in high-temperature wetting. The group further determined that the ridges are formed by diffusion of substrate material under the metal droplet, and that the rate of this diffusion increases with temperature. The Berkeley group calculated that deviations from the Young–Dupre equation could be expected whenever the temperature is above one-fourth of the melting point of the substrate. They then further showed that the shapes of the ridges formed by advancing and receding metal fronts are different, and they developed a quantitative theory of high-temperature wetting that correctly accounts for substrate diffusion and explains why spreading rates are often orders of magnitude slower than those found in low-temperature systems. Understanding this phenomenon is of both fundamental interest and practical value in controlling many important industrial processes, including soldering, brazing, coating, and composite processing.

2.5. Sub nanoscale investigation of segregation at CdO/Ag(Au) heterophase interfaces by three-dimensional atom probe (J.T. Sebastian, O.C. Hellman, and D.N. Seidman; Northwestern University)

The three-dimensional atom-probe (3DAP) allows for the atom-by-atom reconstruction of a small volume (typically $10\times10\times100$ nm which contains approximately 5×10^5 atoms) of a material with respect to both position and chemical identity. It is therefore ideally suited to the study of solute segregation at internal heterophase interfaces. They investigated solute segregation in several ceramic/metal (C/M) heterophase interface systems, including CdO/Ag(Au) (where Au is the segregating species). Samples were prepared by internal oxidation leading to a fine distribution of nanometer-size ceramic precipitates (CdO) formed within the metal [Ag(Au)]. The presence of the precipitates on the surface of the 3DAP specimens was confirmed by field-ion microscopy, and 3DAP analysis was performed on the ceramic/metal interface regions. In the 3DAP atomic reconstructions, the interfaces of the nanometer-size CdO ceramic particles were delineated as isoconcentration surfaces. The distribution of the segregating species (i.e. Au) as a function of distance to the isoconcentration surfaces was determined via the proximity histogram (proxigram) method. This method allows for the direct determination of the Gibbsian excess (Γ) of a segregating species at such interfaces, independent of their specific topology. The Gibbsian interfacial excess of Au at the CdO/Ag(Au) interface ($\Gamma_{\mathrm{Au}}^{\mathrm{CdO/Ag}}$) determined in this manner was 1.65 nm^{-2} at 650 °C. This calculated Γ represents the thermodynamic equilibrium value of Au segregation at the temperature of internal oxidation, 650 °C.

Another CdO/Ag(Au) interface examined in the exact same manner did not exhibit significant segregation of Au. Thus for this system, some interfaces exhibit segregation, while other do not. A reason for this observed disparity is the relationship of segregation behavior to interfacial dislocation structure. They suggested that the interface that exhibits segregation was part of a larger CdO precipitate than was the interface that did not exhibit segregation. A larger precipitate would contain an array of misfit dislocations to accommodate the lattice parameter misfit between Ag and CdO, which is $\sim$15%. These misfit dislocations produce a strain field that contains atomic sites where the segregating gold atoms are bound attractively to the interface.

2.6. Ordering at liquid/solid interfaces (R.C. Birtcher, C.W. Allen and S.E. Donnelly; Argonne National Laboratory)

The ordering of liquid xenon at an interface with solid aluminum was observed in real space. Faceted cavities containing fluid xenon were created in aluminum by ion implantation. High-resolution electron microscopy revealed three well-defined layers of xenon atoms proximate with each liquid/solid interface. The degree of interfacial ordering varied with fluid density and cavity size. Although such interfacial layering had been predicted theoretically, previous experimental observations were ambiguous. Computer simulation yielded additional insight. Three-dimensional ordering can occur in a sufficiently small cavity, i.e. the “liquid” orders in compliance with the geometry of the surrounding solid. For example, liquid in a 2-nm wide cavity condenses into a body-centered-cubic atomic arrangement rather than the face-centered-cubic atomic arrangement expected for unconfined solid xenon. Hence these findings provide a natural explanation for several previous reports of unexpected structures in confined systems. This observation of liquid ordering is of fundamental importance for many important technological phenomena that occur at liquid–solid interfaces. The stronger interactions implied by such ordering will modify friction coefficients between lubricated components, as well as metal corrosion rates in liquid environments.

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