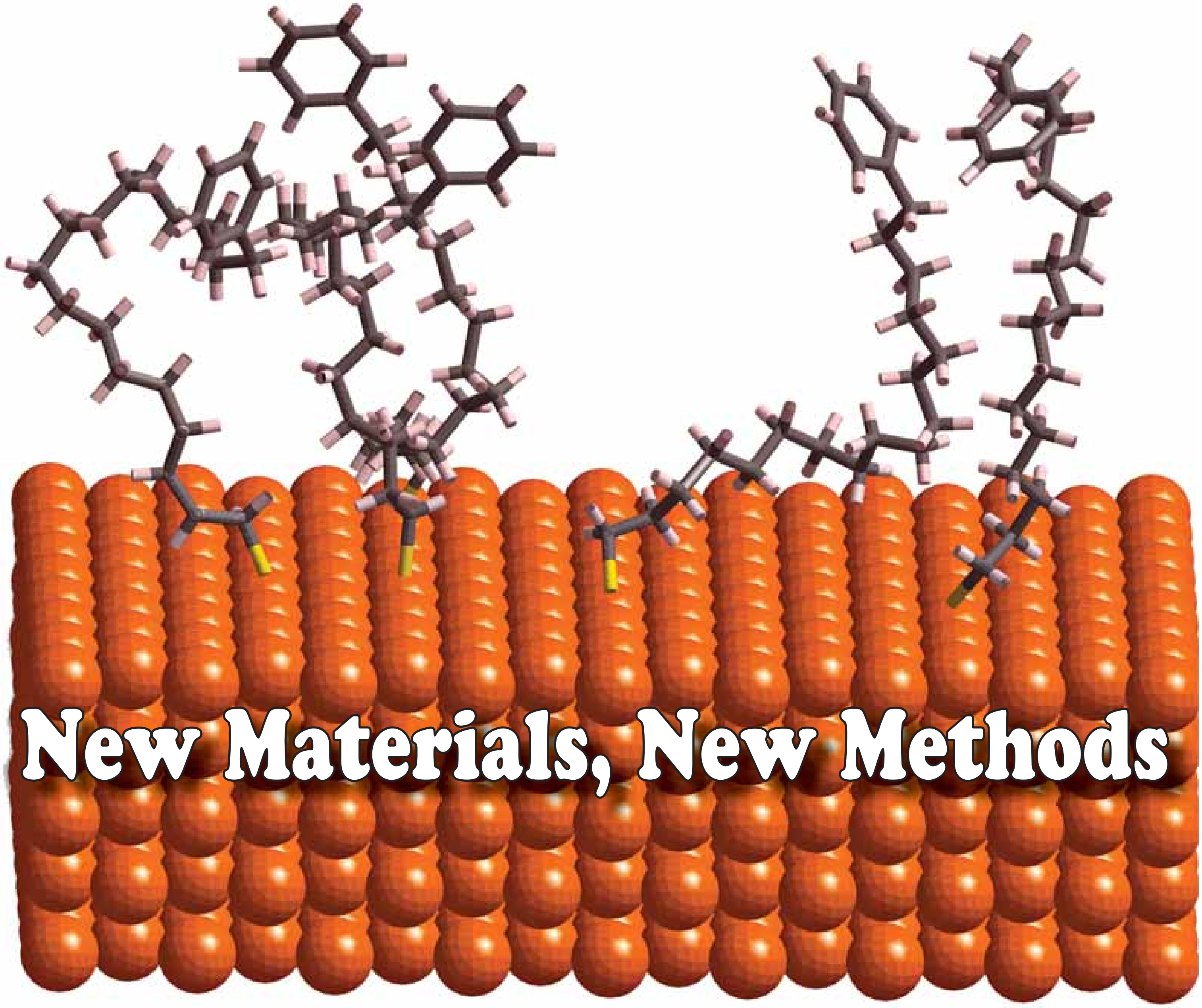
New Materials, New Methods



SwRI researchers are using advanced computational tools to develop and analyze nanomaterials

Using molecular dynamics theory, researchers can simulate the adsorption and surface structuring of boundary layer molecules (lubricant additive) on an ideal metal surface.

By Kwai S. Chan, Ph.D., Michael A. Miller, Ph.D. and Wuwei Liang, Ph.D.

Southwest Research Institute (SwRI) has strong technical programs in materials integrity and characterization, probabilistic mechanics, biomechanics, surface engineering, materials chemistry, environmental effects and failure analysis. These program areas all employ some combination of experimental and numerical investigations to understand and predict material behavior and performance. In situations where fundamental material behavior is needed but cannot be measured in the laboratory because conditions are too severe — or the material does not yet even exist —SwRI researchers turn to the emerging field of computational material science, where underlying material properties and behavior can be predicted using computer simulations.

Computational material science uses theoretical calculations to develop the scientific basis for exploring, selecting and designing materials as well as for optimizing and predicting material properties at various length scales ranging from atomic, molecular and microscopic to macroscopic scales. The key idea behind computational material science is to accelerate the discovery process, shorten the time, and reduce the cost of developing and inserting advanced materials into the design of new products. Using computational methods departs from the traditional empirical approach, which relies on experimental observations and trial-and-error for material development and is more costly and time-consuming.

One area where computational material science is increasingly being applied is the field of nanomaterials. The emergence of nanotechnology has created a new class of materials with unique structures and properties that are not adequately addressed by existing theories. Because of the small size, *ab initio* methods— also known as first-principles methods because they rely on basic and established laws of nature — and molecular dynamics codes are required to predict or simulate the properties of nano-scaled materials. In first-principles methods, material structures and properties are predicted on the basis of electronic bonding and quantum mechanics computations with limited use of empirical data. In molecular dynamics, materials are presented as a system of atoms with interactions that are treated classically and governed by interatomic potentials that may be either obtained semi-empirically or computed directly from first-principles methods. In many instances, the experimental difficulties associated with measuring the properties of nano-scaled or small-volume materials are overwhelming, and it becomes more advantageous to compute the relevant material properties on the basis of first-principles or molecular dynamics methods or both. In other instances, theoretical computations can predict, verify or optimize experimental measurements. Similarly, there are situations where the properties to be measured are beyond the detection limits of current technologies. They can only be computed using theoretical means, thus providing the impetus for the emergence of computational material science as a scientific discipline. A recent National Research Council study identified "the integration of materials information, captured in computational tools, with engineering product performance analysis and manufacturing-process simulation" as an emerging engineering discipline and a national need.

SwRI researchers are involved in a wide range of activities concerned with computational material science and engineering. Because the problems being addressed are diverse, a variety of computational methods are being used including *ab initio*, molecular dynamic, thermodynamic and diffusion codes. In a number of research projects, SwRI scientists and engineers have applied computational material science and engineering to solve practical problems for government and industry clients.

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Dr. Michael Miller (left) is a staff scientist in the Materials Engineering Department in SwRI's Mechanical and Materials Engineering Division. Miller, a physical chemist, specializes in experimental and theoretical methods of analyzing organic, inorganic and polymeric compounds in complex systems. Dr. Kwai Chan (center) is an Institute scientist in the Materials Engineering Department. Chan, recognized internationally for his work in materials science, has more than 25 years experience in materials research including modeling the mechanical behavior of materials and developing life-prediction methods. Dr. Wuwei Liang is a research engineer in the Materials Engineering Department. Liang's research focuses on computational mechanics and materials science, with an emphasis on fracture, fatigue, nanomaterials and probabilistic analysis and design. Background: 76-node parallel computer cluster dedicated to computational materials science.

Designing fracture-resistant composites

Considerable efforts have been made to develop new niobium (Nb)-based alloys and composites for potential application as turbine blade materials in military engines. These efforts have been motivated by the desire to increase the thrust-to-weight ratio by increasing the operating temperature of the engine. The Nb-based multiphase alloys are seen as possible high-temperature materials of the future because their melting point is greater than that of current blade materials made of nickel-based alloys. These Nb-based alloys are processed to exhibit a multiphase microstructure containing a significant amount of one or more intermetallic phases embedded in a metallic matrix or an intermetallic matrix containing ductile metallic particles. In many instances, the alloys exhibit low fracture resistance because substantial amounts of intermetallic phases in the microstructure cause the Nb matrix to behave in a brittle manner.

Depending on the alloy composition, as many as six intermetallic phases in alloyed forms can exist in the microstructure of Nb-based alloys and *in-situ* composites, which often contain six or more elements such as Nb, chromium (Cr), titanium (Ti), silicon (Si), aluminum (Al), hafnium (Hf) and others. These intermetallic phases provide high-temperature creep strength and oxidation resistance, while the Nb solid solution improves the ambient-temperature fracture resistance. The large number of potential combinations of alloying elements, however, makes the discovery of beneficial alloy additions a daunting task if undertaken by empirical means alone.

In a project funded by the U.S.

New alloys are being evaluated for high-temperature applications such as aircraft turbine blades.

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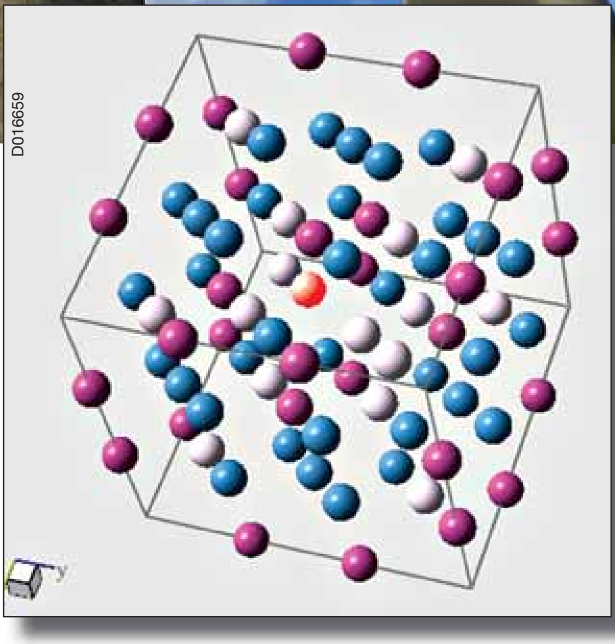
Air Force Office of Scientific Research, SwRI materials scientists developed a set of computational tools and extended an internally developed *ab initio* code for designing Nb-based alloys and composites with desired composition, microstructure and performance. The SwRI team used the computational results to identify beneficial alloying additions that would increase crack-tip plastic deformation and therefore fracture toughness. The SwRI approach allowed a systematic evaluation of the alloying effects on fracture resistance of individual elements. Adding titanium enhanced fracture toughness and reduced the barrier against crack-tip plastic deformation, while adding Cr and Al reduced fracture resistance by decreasing plastic deformation. These computational tools provided an effective means for optimizing alloy composition, microstructure, and fracture properties for Nb-based alloys and composites.



A supercell is used to compute the migration energy of a Cr atom (single atom shown in red, at center) toward a vacancy in a Ni-Mo-Cr alloy (Ni: purple; Mo: blue; Cr: white).

Nuclear waste disposal and management

Nickel-based alloys such as Alloy 22 are candidate materials for applications such as the outer containers of waste packages for the disposal of high-level nuclear waste. During fabrication processes and long-term storage, Ni-based alloy outer containers can undergo microstructural changes caused by the formation of ordered Ni$_2$ (chromium, molybdenum) and brittle intermetallic phases. The precipitation temperature of these brittle intermetallic phases and the ordering temperature of Ni$_2$(Cr, Mo) are in the range of 773 to 1,073 degrees Kelvin, and both reactions are sluggish. Because of slow reaction kinetics, the formation, morphological evolution, and properties of the Ni$_2$(Cr, Mo) and brittle intermetallic phases cannot be measured confidently using short-term tests over a reasonable time frame. Similarly, the mechanical properties of Ni$_2$(Cr, Mo) and brittle intermetallic phases are largely unknown because they have not been measured due to the fact that specimens are difficult to prepare and heat-treat.

To circumvent these experimental limitations, SwRI researchers used a first-principles, quantum-mechanical computational code (WIEN2K) based on the full potential linearized augmented plane wave (FLAPW) method to compute the energy of formation of potentially brittle intermetallic phases in a Ni-base alloy. The thermodynamic data were incorporated into an existing database for Ni alloys and used in conjunction with Thermo-Calc® software to compute the binary Ni-Cr phase diagram and to predict the formation of ordered phases in Alloy 22 (Ni-21.2Cr-15.5Mo-4Fe-3W, in weight percent) at various temperatures. In addition, they used WIEN2K to compute the elastic constant, theoretical stress-strain curve, tensile ductility and fracture toughness of Ni$_2$Cr and Ni$_2$Mo. With these results, researchers were able to assess the long-term stability and potential degradation of Ni-base alloys in a nuclear waste repository environment.

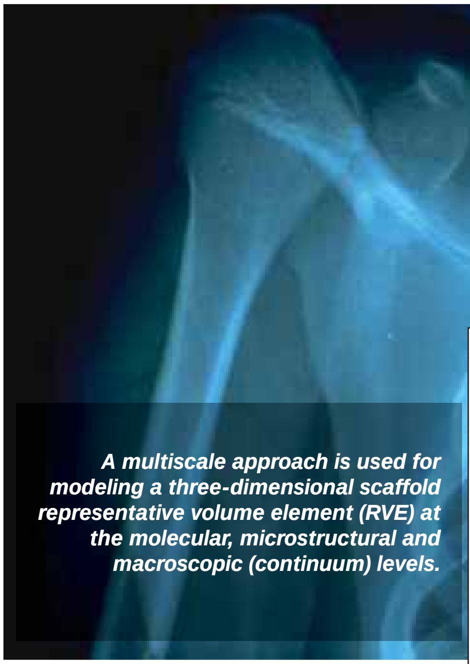
SwRI researchers used computational methods in an internal research project to compute the mobility database for Ni-Mo-Cr-Fe-W alloys. Again using the WIEN2K code, they computed the electronic structure and total energy of an n-atom supercell, which comprises multiple unit cells of the crystal lattice, with atom positions designed to simulate the desired diffusion processes. The computational procedure involved calculating the energy for vacancy formation, the energy barrier for solute migration and the correlation factor of individual diffusive species in the host metal. Using first-principles computational results of the energy of vacancy formation, they computed migration energy for solute self-diffusion and activation energy for diffusion of Mo, Cr, Fe, W, and Ni in Ni-Mo-Cr-Fe-W alloys such as Alloy 22, to expand the existing mobility database required for long-term diffusion kinetics computations for these alloys.

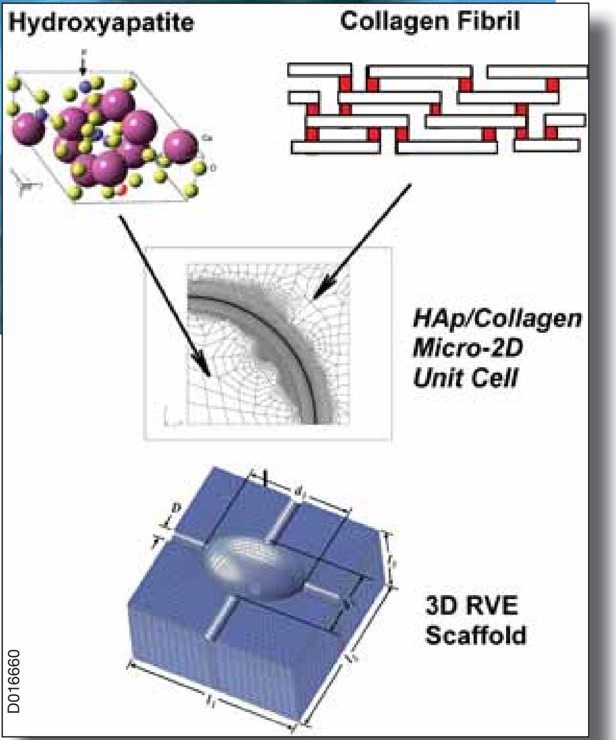
Developing nanocoatings for power generation applications

The U.S. Department of Energy (DOE) and power generation companies are interested in achieving greater power plant efficiency by increasing steam temperature to 760 degrees Centigrade and steam pressure to 35 Mega Pascals. This combination of high steam temperature and pressure, referred to as the ultra super-critical (USC) condition, has been shown to promote coal ash corrosion and increase corrosion rates. To improve reliability and availability of fossil-fired USC boilers, it is essential to develop advanced nanostructured coatings that provide excellent corrosion and erosion resistance without adversely affecting other properties of the component materials, such as toughness and thermal fatigue strength.

For a project funded by DOE through EPRI, SwRI scientists applied computational methods to design and assess potential Fe-Cr-Ni-Al systems to produce stable nanostructured coatings that form a protective, continuous scale of alumina or chromia. They used the Thermo-Calc® software to generate phase diagrams for the design of Fe-Cr-Ni-Al nanocoatings and performed computational modeling of the grain growth process and sintering of voids to assess microstructural stability. Researchers used the DICTRA® diffusion code for interdiffusion of Al, Cr and Ni to maximize the long-term stability of the nanocoatings.

The computational results identified a new series of nanocoatings that maintain long-term stability and corrosion resistance by forming a diffusion barrier layer at the coating/substrate interface that prevents Cr or Al loss from inward diffusion. Fabrication and characterization of these new nanocoatings are currently in progress.



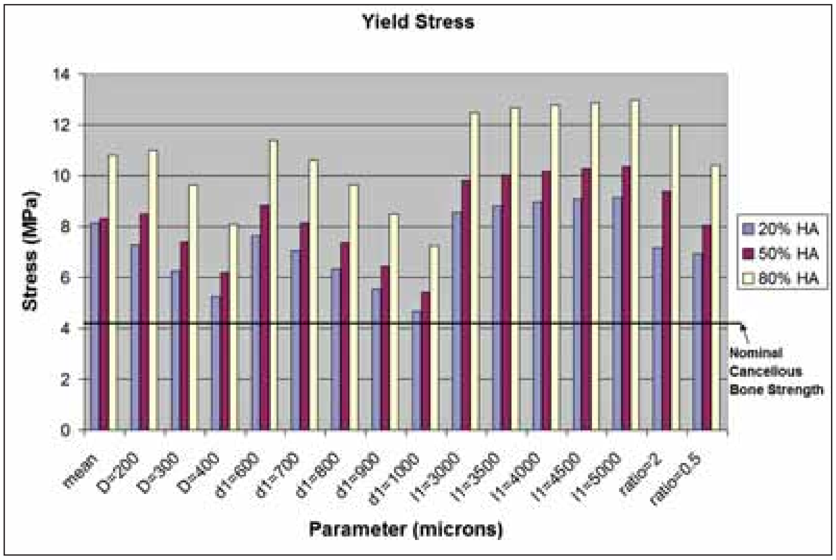


A multiscale approach is used for modeling a three-dimensional scaffold representative volume element (RVE) at the molecular, microstructural and macroscopic (continuum) levels.

Designing tissue engineering scaffolds

Bone-tissue engineering scaffolds are used to heal large defects caused by trauma or disease, or by therapies directed toward mitigating disease. To promote bone formation, vasculature-inducing pore geometry is critical in scaffold design, because bone tissue regeneration does not proceed without vascular invasion. The optimum scaffold architecture for bone tissue regeneration is a porous structure with a narrow range of pore sizes and density, and a high degree of interconnectivity among pores. To achieve such a design, the microstructure of the scaffold material must be optimized to satisfy both biological and mechanical function requirements. The limitations of many existing scaffold fabrication methods have required biology to adapt to the scaffold geometry, rather than designing the scaffold geometry to accommodate the biological imperatives of bone-wound healing.

As part of an internally funded program, SwRI researchers applied computational material science to develop a multiscale modeling approach for designing a scaffold made from a two-phase composite of brittle hydroxyapatite (HAp) particles embedded in a ductile collagen matrix. Property optimization is essential because a highly porous structure that promotes cell growth may lack the strength and toughness required as a load-bearing scaffold. SwRI researchers calculated the elastic properties and theoretical strengths of nanoscaled HAp particles from first principles. They then used the finite element method to predict the constitutive properties of the HAp/collagen composites for several HAp contents. These constitutive relations of the composite were



This bar chart shows parametric results for scaffold property optimization.

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Two-dimensional friction maps and the structural ordering (e.g., island formation) that occurs for a lubricant additive on an ideal surface are measured using atomic force microscopy (AFM). Molecular dynamics simulations are performed in parallel to explain or verify the AFM-measured friction at the scale of molecular distances. This tactic enables one to engineer and evaluate novel lubricant additives by making appropriate modifications to the chemical structure of the additive depending on the specific application.

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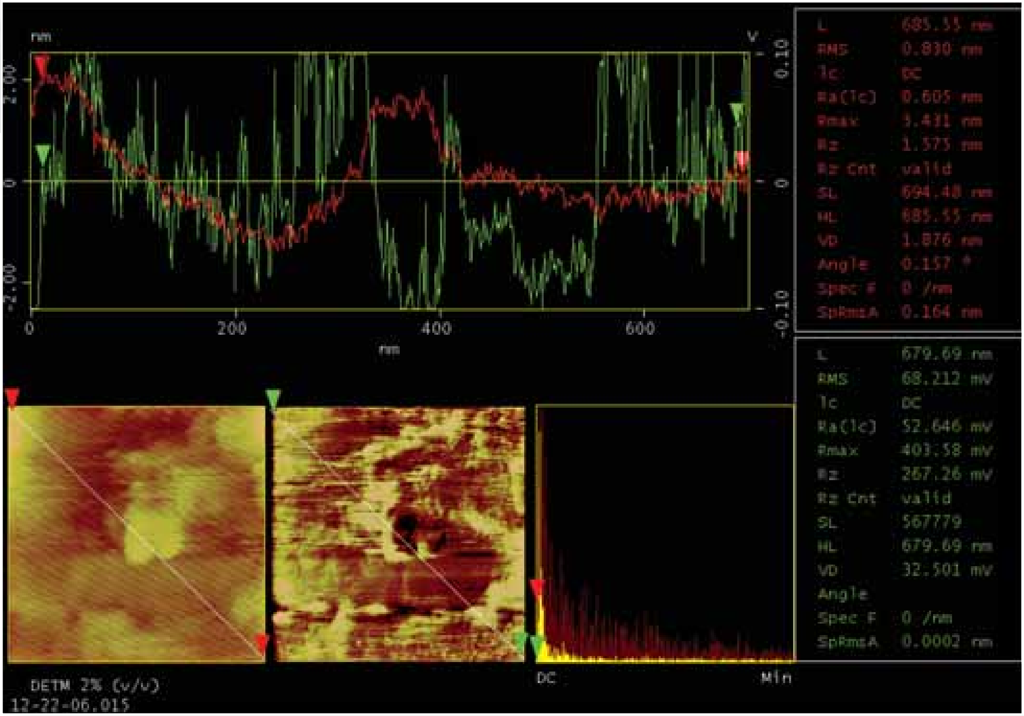


used to optimize the mechanical properties of a three-dimensional scaffold with respect to pore size, pore density and volume fractions of HAp in the composite so that the scaffold properties exceed or match those of bone tissue.

Nanotribology and surface structure of lubricant additives

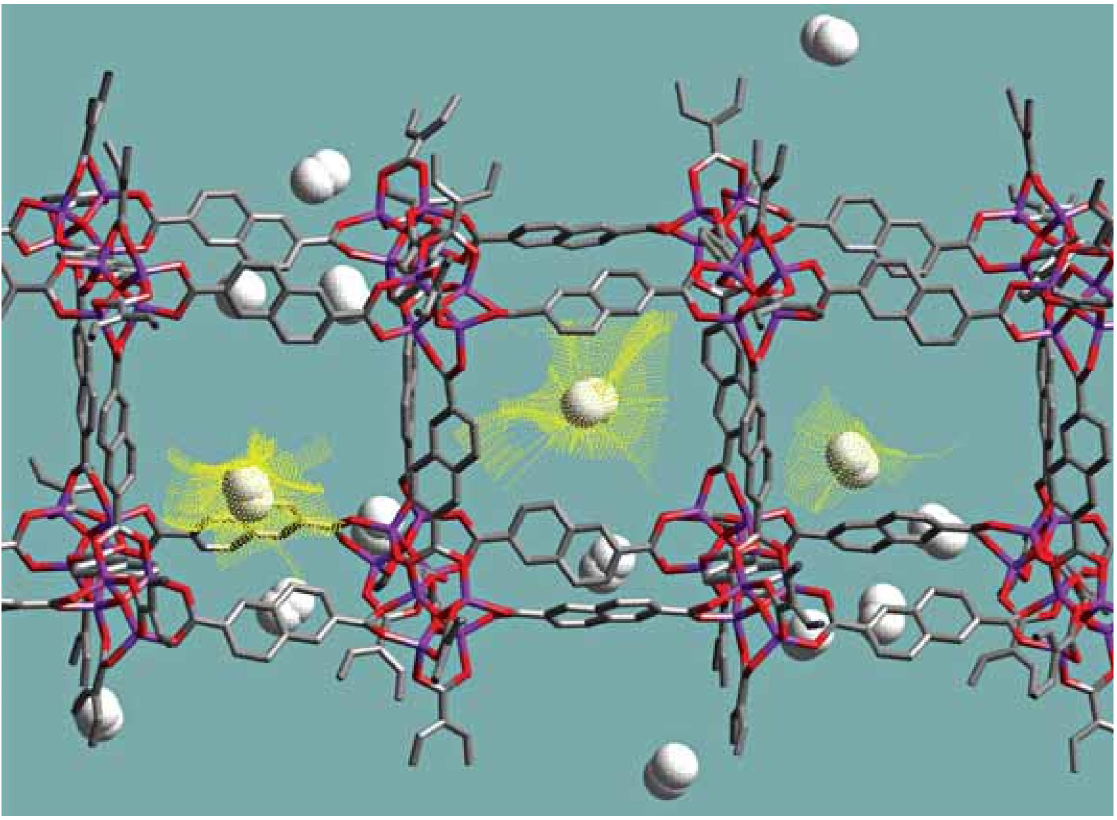
Tribology is the science and technology of interacting surfaces in relative motion. Molecules such as detergents or lipids, which generally constitute various classes of lubricant additive packages, have remarkable tribological properties when used as interfacial boundary layers between two contacting metal surfaces under dynamic loads. The current understanding of the tribological behavior of such boundary-layer additive molecules is incomplete at the fundamental level because the mechanisms of adsorption or chemisorption, surface structure and phase state, and tribology over molecular-distance scales remain poorly understood. This lack of fundamental understanding has hindered the development of new additives, or improvements in existing ones.

In a project funded by a commercial client, SwRI researchers used molecular dynamics theory to predict the surface structure and tribological properties of boundary-layer molecules (lubricant additives) between two metal surfaces. They then correlated the molecular dynamics predictions with the surface structure and friction maps derived using atomic force microscopy techniques. The results established a tactic for assessing the relationship among molecular adsorption, surface structure and tribological properties, leading to a better understanding of existing lubricant additives and to developing strategies for synthesizing new ones with improved properties.

Hydrogen storage materials

The principal obstacle to implementing a hydrogen-based economy remains storage under ambient conditions of temperature and pressure. While most approaches to this problem have focused on physical adsorption, wherein useful uptake is realized only at low temperatures (77 degrees Kelvin, for example), recent experiments have suggested the possibility of chemically adsorptive strategies based on nanostructures consisting of catalyst particles on, or caged within, a highly porous structure.

Under funding from DOE and SwRI's internal research program, researchers are currently applying *ab initio* and molecular dynamics theories to design novel nanoscale architectures for solid-state hydrogen storage, providing important insights into the underlying mechanism for hydrogen uptake in new structural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Molecular dynamics simulations combined with ab initio *calculations are being used to study the hydrogen adsorption (known as physisorption) and hydrogen addition reactions involved in an isoreticular metal-organic-framework (IRMOF-8) for hydrogen storage applications. This image shows the surface field for non-bonded interactions of select hydrogen molecules trapped in the small, though highly ordered, voids of the framework. IRMOFs of similar structure have been measured by SwRI scientists to adsorb up to 68 percent of the equivalent liquid density of hydrogen, requiring only 60 bars of pressure and 77 degrees Kelvin.*

motifs. Using *ab initio* computations, SwRI scientists are exploring the electronic and catalytic properties of nanometer-sized metallic compounds of unique elemental combinations useful in facilitating the binding and dissociation of hydrogen molecules in highly porous substrates. Some of these are isoreticular metal-organic-frameworks, single-wall carbon nanotubes and new forms of carbon materials. They are further combining these levels of theory with molecular dynamics simulations to critically assess the thermodynamic and kinetic viability of hydrogen storage materials predicted on catalytically doped porous structures.

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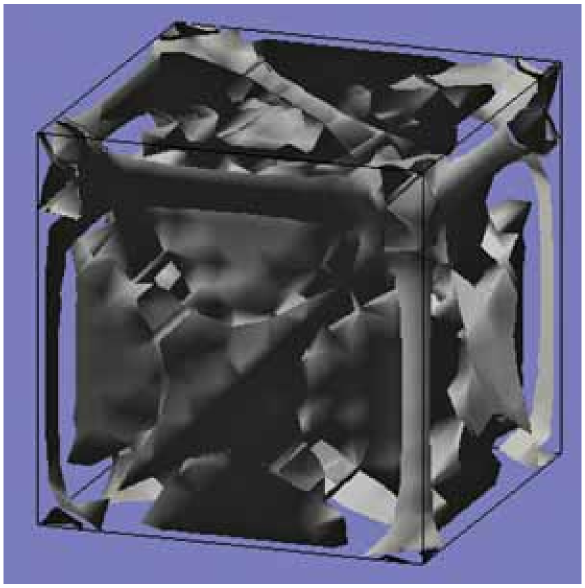

This image shows an ab initio *calculation of the electronic Fermi surface of an* $AuAl_2$ *unit cell. Clusters of this metal compound are being explored as dissociation catalyst for hydrogen storage applications.*

Future applications

Computational material science provides an important avenue for accelerating the development of advanced materials and for turning them into new products. By validating theories with critical experiments, computational material science can speed up the discovery process, develop scientific understanding at the atomic or molecular levels, and solve engineering problems in a wide range of disciplines where conventional approaches have proved inadequate. There are continuing efforts by SwRI researchers to apply the computational material science approach to designing new nanocoatings for power generation. Efforts are also continuing to develop unique nanostructured materials for tissue engineering scaffold applications. There is also a plan to apply this emerging technology to novel cathode and anode materials for lithium batteries and other devices for energy conversion.

In the future, the proliferation of computation-based material design may evolve into an integral part of the component and structure design process as scientists and engineers face increasingly more complex problems that require fundamental solutions in shorter times. v

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