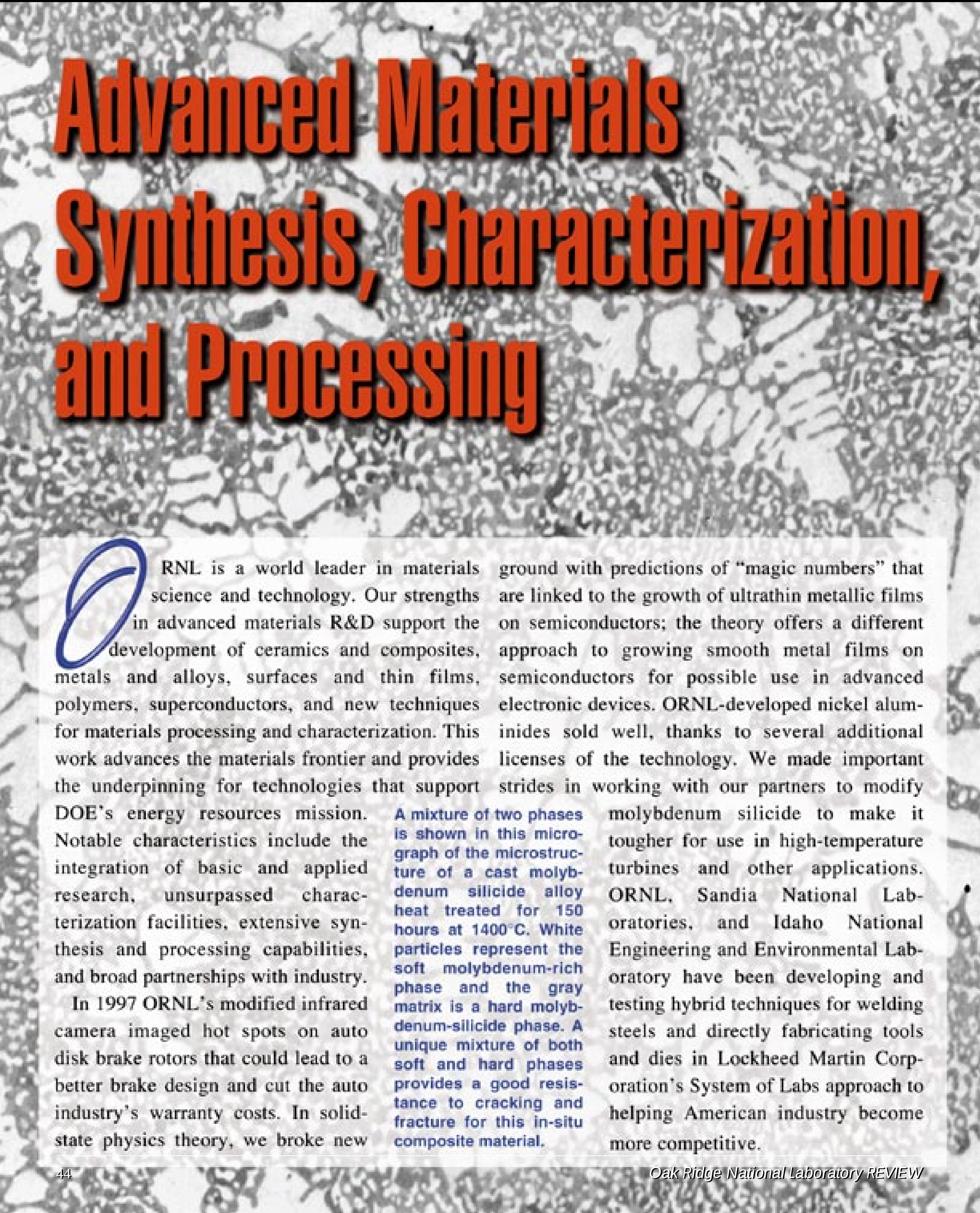
Advanced Materials Synthesis, Characterization, and Processing



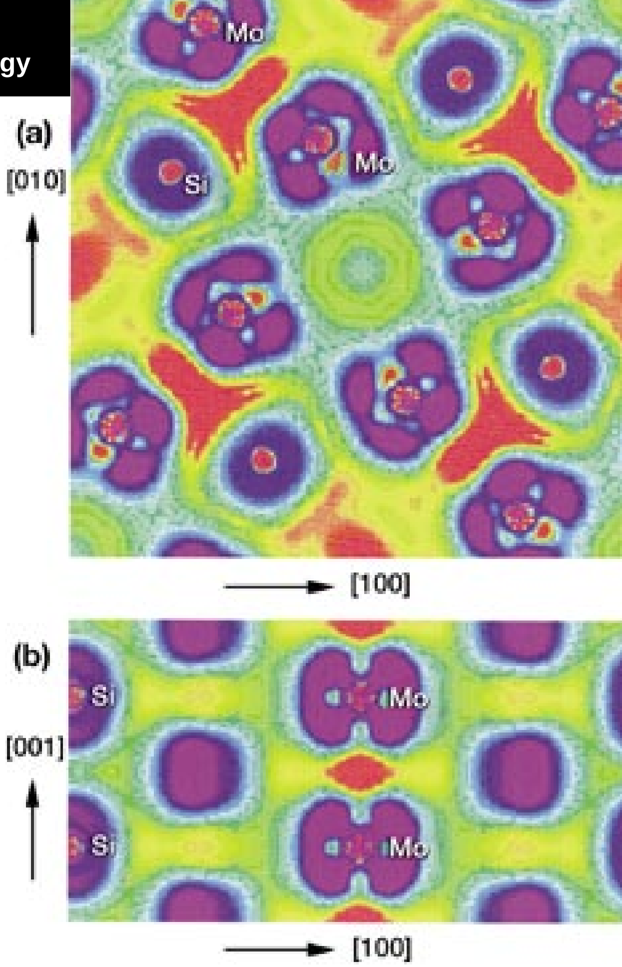
ORNL is a world leader in materials science and technology. Our strengths in advanced materials R&D support the development of ceramics and composites, metals and alloys, surfaces and thin films, polymers, superconductors, and new techniques for materials processing and characterization. This work advances the materials frontier and provides the underpinning for technologies that support DOE's energy resources mission. Notable characteristics include the integration of basic and applied research, unsurpassed characterization facilities, extensive synthesis and processing capabilities, and broad partnerships with industry.

In 1997 ORNL's modified infrared camera imaged hot spots on auto disk brake rotors that could lead to a better brake design and cut the auto industry's warranty costs. In solid-state physics theory, we broke new ground with predictions of "magic numbers" that are linked to the growth of ultrathin metallic films on semiconductors; the theory offers a different approach to growing smooth metal films on semiconductors for possible use in advanced electronic devices. ORNL-developed nickel aluminides sold well, thanks to several additional licenses of the technology. We made important strides in working with our partners to modify molybdenum silicide to make it tougher for use in high-temperature turbines and other applications. ORNL, Sandia National Laboratories, and Idaho National Engineering and Environmental Laboratory have been developing and testing hybrid techniques for welding steels and directly fabricating tools and dies in Lockheed Martin Corporation's System of Labs approach to helping American industry become more competitive.

A mixture of two phases is shown in this micrograph of the microstructure of a cast molybdenum silicide alloy heat treated for 150 hours at 1400°C. White particles represent the soft molybdenum-rich phase and the gray matrix is a hard molybdenum-silicide phase. A unique mixture of both soft and hard phases provides a good resistance to cracking and fracture for this in-situ composite material.

ORNL Successes in Intermetallics

ORNL-developed nickel aluminides are selling well, and ORNL is helping to make molybdenum silicide tougher for use in high-temperature turbines.



The calculated bonding charge density shows the depletion of density at the lattice sites (purple) together with an increase of density in the interstitial region. The bonding has pronounced covalent components (red), characterized by (a) the planar Mo-Si-Mo triangular bonding units on the (001) plane, and by (b) the unusually short Mo-Mo bond along the c axis. These covalent bonds give rise to the alloy's strength.

Now that some manufacturing firms recognize that nickel aluminide (Ni_3Al) alloys last much longer than commonly used materials under typical industrial conditions, commercial sales of Ni_3Al alloys based on ORNL compositions continue to rise. They exceeded 100 tons in 1997, and licensees expect sales to reach almost 250 tons in 1998. The chief reason for the climbing sales is the addition of six new licenses since 1995, bringing the total number of active nickel aluminide licensees to eight. (The total number of licenses signed is 13, but 5 have been terminated.)

Ni_3Al alloys are being used in dies for making truck brake parts and tools like pliers and wrenches. A major steel company is replacing its steel transfer rollers with Ni_3Al rollers, which are used to move steel plates through a furnace where they are softened for shaping into structural components. The steel and automotive industries are beginning to show interest in replacing their radiant burner tubes with tubes made of Ni_3Al. These tubes of burning gas are used in industrial furnaces for heat-treating parts to harden their surfaces. Because Ni_3Al lasts much longer in a furnace's carbon atmosphere than conventionally used materials, it is expected to be used increasingly in industrial heat-treating equipment.

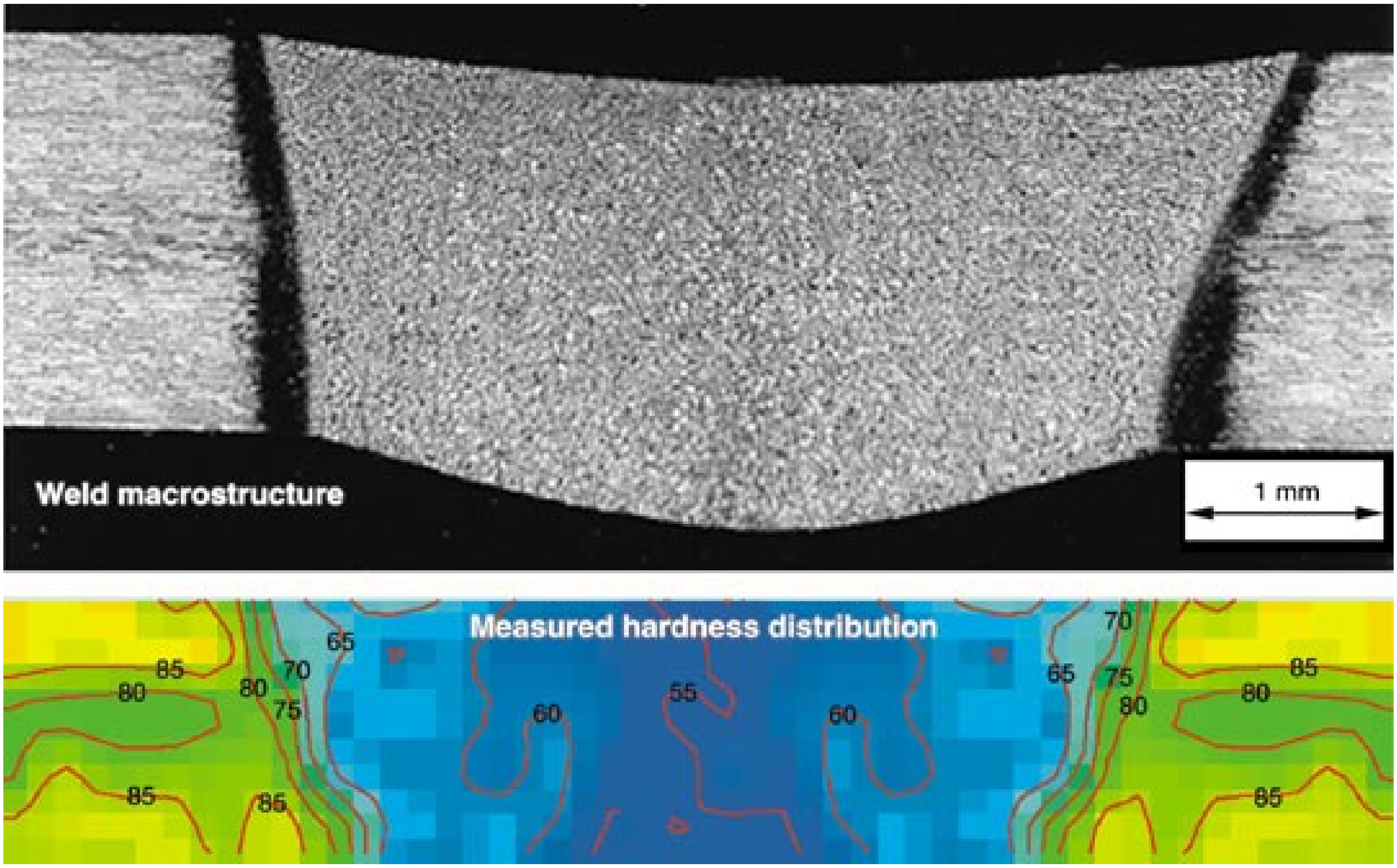
The success of ORNL's intermetallics research and development programs and the commercialization of this technology under DOE's Office of Energy Efficiency and Renewable Energy, Office of Industrial Technology, Advanced Industrial Materials Program, was confirmed in a recent evaluation by the National Materials Advisory Board of the National Research Council. This report acknowledges the quality of both the research and the management of the intermetallics program.

New research directions at ORNL in intermetallics include development of ultrahigh-temperature intermetallic silicides. Today, intermetallic alloys such as Ni_3Al alloys can be used in devices that operate at 1200°C, but alloys that can operate above 1300°C are needed for advanced turbine blades, heat exchangers, advanced coal conversion plants, and high-temperature glass-molding devices. Molybdenum silicides have excellent strength and creep resistance above 1300°C, but they are brittle at ambient temperatures and not resistant enough to fracture to be used as structural engineering materials. Research to improve the properties of silicides was approved in April 1997 as a project of the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials sponsored by DOE's Division of Materials Sciences. Center projects involve collaborative research among a number of national labs. The project also has support from DOE's Fossil Energy Materials Program and Advanced Industrial Materials Program.

ORNL has the technical lead for developing molybdenum silicide alloys with Ames Laboratory, which discovered that the addition of boron improves the alloys' oxidation resistance. Rod Judkins is project coordinator and C. T. Liu is technical coordinator for the ORNL part of the effort.

At ORNL C. L. Fu is leading the theoretical effort on first-principles calculations for the electronic and structural properties of molybdenum silicides. Collaborating theorists at ORNL and Ames Laboratory have already investigated phase stability, bonding strength, elastic properties, and thermal expansion coefficients in the alloy. The bonding in this alloy was found to be covalent, which gives rise to the strength of this material. The calculated elastic constants agree with experimental measurements at Los Alamos National Laboratory.

ORNL experimenters Liu, Joachim Schneibel, and Easo George studied multiphase alloys based on Mo_5SiB_2, which shows good creep resistance and oxidation resistance at high temperatures. They found that the alloy's oxygen resistance is sensitive to its silicon level. They studied the effects of oxygen and carbon impurities on the silicide and determined the alloy's microstructure, alloying effects, mechanical behavior, interfacial properties, and criteria for material processing. In this multiyear project, they hope to solve technical problems such as making the alloy less brittle and tougher by incorporating additives in the right proportions, controlling interfacial structures and properties, making the cast structure less porous, optimizing the alloy's microstructure to get good mechanical properties, and improving the alloy's oxidation resistance at high and low temperatures. Already the experimental program's multiphase alloying approach has resulted in improved fracture strength of the molybdenum silicide. Such successes in improving molybdenum silicide could help the material join nickel aluminide alloys as strong candidates for a high-temperature materials hall of fame.



Weld macrostructure of an aluminum alloy and its associated hardness profile. ***Electronic file enhanced by Allison Baldwin.***

System of Labs Approach to Welding, Direct Fabrication

ORNL, SNL, and INEEL are developing and testing hybrid techniques for welding steels and directly fabricating tools and dies.

In 1996 Al Narath, who then managed Lockheed Martin's Energy and Environment Sector, had a bright idea: Why not apply the unique expertise and capabilities of the sector's three DOE national laboratories to meeting critical national needs, such as improving industrial competitiveness? Why not focus the talents of groups from the three different labs on difficult, important problems through a "system of laboratories" approach? He proposed that such an approach would (1) speed the development of advanced technologies and their transfer to the commercial sector, (2) avoid duplication and competition among the laboratories while expanding their capabilities, and (3) make more efficient use of limited funding.

As a result of this System of Labs initiative, ORNL, Sandia National Laboratories (SNL), and Idaho National Engineering and Environmental Laboratory (INEEL) are working together on welding science and the direct fabrication of structural components using rapid manufacturing technology. The initial funding for these collaborations came through the Laboratory Directed Research and Development Program of each lab.

The welding collaboration (ORNL, Oak Ridge Y-12 Plant, SNL, and INEEL) has resulted in a successful proposal to DOE's Office of Industrial Technology on developing a process to combine laser welding and arc welding to weld steels for automotive applications. This proposal will bring $100,000 a year to each site for three years (DOE is supporting 70% of the program, and the steel industry is funding the remaining 30%).

In the past year, the welding groups worked on developing a combined process for welding aluminum alloys, lightweight materials needed to make automobiles and aircraft operate more efficiently. They showed that it is possible to combine the processes to exploit the advantages and eliminate the weaknesses of each process.

Arc welding, in which a hot plasma produced by electrodes supplies the heat to melt and join two pieces of metal, has several advantages. It is commonly used, easy to control, and inexpensive. However, arc welding cannot be used at high speeds because it does not melt the metal enough to make a good joint. Laser welding can be used at high welding speeds with good penetration. However, it works well only when the pieces to be welded fit together neatly and when the surface is very clean. Also, laser welding does not penetrate aluminum alloys well because of poor coupling between the laser light and the material.

The three-lab welding group has demonstrated that combining laser and arc welding allows the laser to penetrate aluminum alloys better because of the presence of the arc plasma. It was also shown that the coupled laser-arc welding process is capable of achieving the desirable high welding speeds.

In the development of laser-assisted plasma arc welding and laser-assisted gas-metal arc welding, the three labs are playing distinct roles based on their strengths. SNL is developing each process by combining the two welding tools. INEEL is determining how best to control and automate each process. And ORNL's welding group, led by Stan David (including John Vitek, Suresh Babu, and Ed Oblow), is conducting properties measurements on welding samples and developing computer models (e.g., a neural network) to relate the samples' microstructures to their properties (e.g., hardness and ability to withstand loads). For example, the model can predict the shape of the weld based on parameters such as welding speed and power.

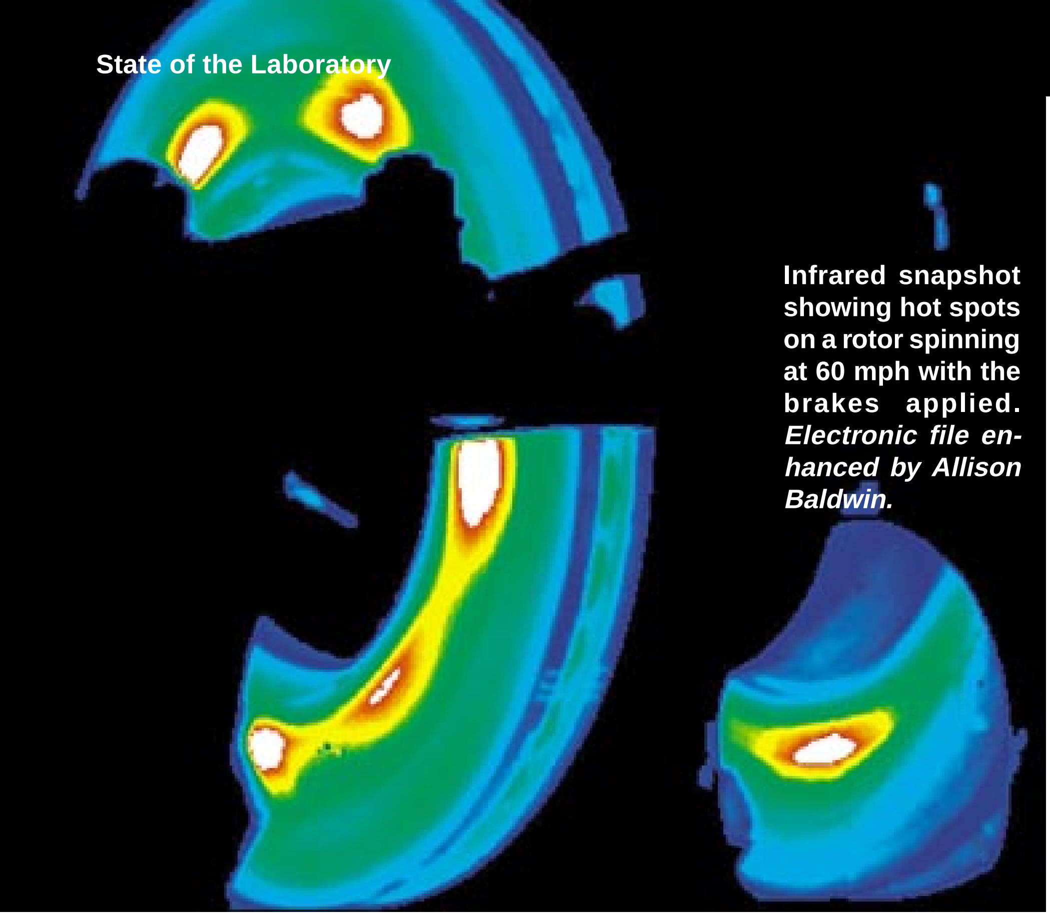
In research on direct fabrication, the goal is to produce a die (e.g., a mold for stamping out a product such as a beverage can) from a material in a single step instead of the usual multiple steps involving melting, casting, quenching, cutting, and machining, with various heat treatment steps in between. The idea is to form the die by depositing material using computer control. Researchers are comparing the performance of materials fabricated by conventional forming, spray forming (by INEEL), and laser-engineered net shape (LENS) technology (by SNL). The goal is to modify alloy compositions to improve performance of materials that could be used in the $100-billion tool-and-die industry. Direct fabrication is expected to dramatically reduce the time and cost for developing complex dies and tools and to make a major impact on rapid prototyping.

A metal piece showing logos of ORNL, INEEL, and SNL made by direct fabrication—spray forming by INEEL and LENS by SNL. ***Electronic***

In spray forming, metal from a molten ingot is sprayed and deposited layer by layer at a rate of 1000 pounds per hour. In LENS a light beam from a computer-controlled laser melts and deposits powder point by point to make any shape at a deposition rate of 2 pounds per hour. Although spray forming lays material down much faster than LENS, it cannot form certain desired shapes, such as tubes.

ORNL researchers led by Everett Bloom are searching for materials that could be deposited by a combined spray-forming–LENS process to produce any shape at greater speed. Studies show that dies made of carbide-strengthened H-13 steel are sufficiently strong and stable at low temperatures, but dies made of this material lose their strength when the temperature is in the range of 450 to 550°C. To extend the life of dies, ORNL researchers led by Phil Maziasz have modified the carbide composition of H-13 steel to make it more stable in dies used to make aluminum parts at temperatures up to 600–700°C. C. T. Liu's group has also developed a new nickel aluminide alloy for die—and tool—applications at temperatures up to 1000°C. Tests at SNL and INEEL are in progress to show that the new nickel aluminide alloy can be deposited by LENS- and spray-forming without technical difficulty. Liu, Dewey Easton, and Lee Heatherly have also been experimenting with making an iron-based-bulk-amorphous metallic glass, which is very hard and tough but low in friction and excellent in wear resistance. Such a shiny metallic glass would contain iron, titanium, and other elements. This material, which would withstand temperatures in the 400 to 500°C range, could be fabricated from a supercooled liquid, using less energy than is required by other forming methods.

These projects are only about a year old, but progress on both suggests that the System of Labs approach produces results that no one lab could achieve by itself. This new kind of national lab collaboration should help industry jump to the next level in economic competitiveness.



Infrared snapshot showing hot spots on a rotor spinning at 60 mph with the brakes applied. ***Electronic file enhanced by Allison Baldwin.***

Auto Disk Brake Hot Spots Seen By Infrared Camera

ORNL's modified infrared camera has imaged hot spots on auto disk brake rotors, which could lead to a better brake design and cut the auto industry's warranty costs.

You're driving fast when a deer crosses the road ahead. You slam on the brakes, avoiding a collision. That's the good news. The bad news is that the steering wheel shakes violently when you apply the brakes. Annoyed by the wobble, you take the car to the dealer and learn that the problem is "disk brake judder" and that the brake rotor may have to be refaced or replaced (at a cost as high as $200). Fortunately, the dealer will cover the cost because your car is under warranty, but that may not be true the next time you get brake judder. Because brake repairs cost the automobile industry and consumers billions of dollars, the U.S. industry is trying to determine the causes of brake judder and ways to prevent it.

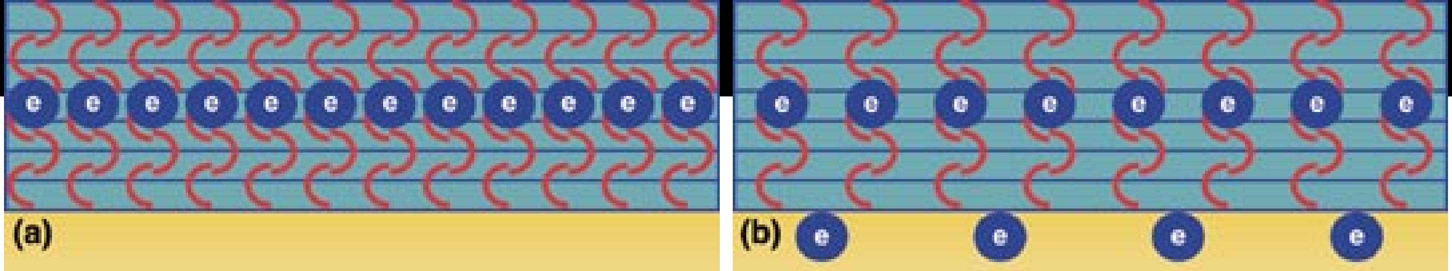
Using a high-speed, high-sensitivity digital infrared (IR) camera, ORNL researchers led by Ralph Dinwiddie have located and measured the temperature of brake disk "hot spots"—valuable information that may steer automakers toward a better brake design. The IR camera, obtained in 1996 from Amber, a Raytheon Company, has a temperature resolution of 0.015°C and takes 142 images per second (compared with a 0.2°C resolution and 30 images per second for a conventional IR camera). Through reverse fellowships and user projects with Ford Motor Company, General Motors Corporation–Delphi Chassis Systems, and Bosch Braking Systems, ORNL researchers have taken the IR camera to these companies' Michigan and Ohio sites for brake studies. But first they had to make the camera setup portable by configuring it to operate with a laptop computer. They also developed the interface circuitry to enable synchronized time-lapse thermography; thus, they can capture images of hot spots on a spinning brake rotor every three revolutions over a four-minute period.

A disk brake is a disk-shaped rotor that spins until pads rub against its surface when you depress the brake pedal, slowing or stopping the car. Using the IR camera, ORNL researchers were the first to image hot spots, or localized expansions, that develop in gray cast iron rotors when brakes are applied at high speeds. As the brakes heat up, areas of the rotor surface are raised, like turning an ordinary potato chip into a Pringle®. These raised areas drag more aggressively against the brake pads when pressed against the rotor, causing steering wheel vibrations.

By capturing multiple images of a spinning rotor, the infrared camera records temperature changes in hot spots that are observed to drift around the rotor. From this information, auto industry researchers have learned that the amount of friction (coefficient of friction) between the pads and rotor, their ability to conduct heat (thermal conductivity), and the amount they expand (thermal expansion) in response to heat cause distortions in the rotor at or above a "critical speed." This critical speed for the hot spots to develop is often below highway speed limits, so the auto industry would like to find ways to significantly increase the critical speed.

To achieve this goal and reduce the probability of brake judder, changes will have to be made in the design of the rotor and composition of the brake pads, which now are made of graphite, copper wires, brass fibers, kaline (clay), and even nut shells. ORNL's infrared camera is being used to determine whether design and composition changes are minimizing the evolution of hot spots. If the auto industry is successful in selecting the right design and materials, it could slow down an annoying drain on its profits.

This research is sponsored by the DOE's Office of Transportation Technologies as part of the High Temperature Materials Laboratory Programs. Funding to purchase the camera was provided by the Advanced Turbine Systems Program of DOE's Office of Industrial Technology to determine how well ceramic coatings on turbine blades hold up in a high-temperature environment.



Schematic representation of the "electronic growth" concept. In (a), as a metal (blue) is added onto a semiconductor substrate (yellow) layer by layer, the motion of the conduction electrons in the metal film is confined by the two vacuum-metal and metal-semiconductor interfaces, forming electronic standing waves (red). These waves resist being squeezed any further, helping to stabilize the film. In (b), some electrons leak into the semiconductor, weakening the stabilizing force. These two competing effects determine the critical thickness for smooth film growth. *Drawing by Allison Baldwin.*

Metallic Thin Films and Magic Numbers

Theoretical studies at ORNL provide new understanding of the metal-semiconductor interface and of a different approach to growing smooth metal films on semiconductors.

For decades it has been known that certain nuclei are more stable than others and that certain atoms are inert while others are active. In the 1980s, physicists at the University of California at Berkeley discovered that, when atoms form clusters, certain clusters are also more stable than others. These systems are particularly stable when they each contain a "magic number" of constituent particles: protons and neutrons for the nuclei, electrons for the atoms, and atoms for the clusters. Now, an ORNL team is finding evidence for magic numbers in a new territory—the growth of metal films on semiconductor substrates.

Metals in contact with semiconductors are essential components in electronic devices ranging from small computers to smart cards. Because of the trend of device miniaturization, it is often desirable to form two-dimensional, atomically flat metal overlayers. Unfortunately, because of strain effects, most metal atoms deposited on a semiconductor surface naturally form three-dimensional clusters, leading to a rough film. Recently, a University of Texas group showed that an atomically flat silver film could be grown by depositing silver atoms on a gallium arsenide (GaAs) surface at 140 K and then annealing it to room temperature. The atomic flatness of the film was verified using a scanning tunneling microscope. The Texas study showed that smooth film growth could be achieved, but only above a critical thickness of seven layers of atoms (15 angstroms thick). The existence of such a critical thickness was unexpected, given commonly recognized growth mechanisms involving individual atomistic processes or strain effects.

How the critical thickness is attained was explained in 1997 by Zhenyu Zhang, a solid-state theorist at ORNL, in collaboration with the Texas group. Their theoretical work on deposition of metals on semiconductors has resulted in the formulation of a conceptually new mechanism for smooth film growth. The theory, which shows the importance of quantum effects in thin-film growth, can be explained by textbook-level quantum mechanics (particles in a box). When a metal film is thin, the moving conduction electrons within the film are confined in the film thickness direction—on one side by the vacuum and on the other by the metal-semiconductor interface. This "squeezing" of the electronic motion leads to quantized energy levels for the electrons, increasing the total energy of the system. However, because many more conduction electrons are in the metal than in the semiconductor, some electrons will spill from the film into the substrate, decreasing the system's energy. The competition between the two effects—quantum confinement and charge spilling—determines the observed critical thickness.

Within this "electronic growth" mechanism, Zhang and collaborators predicted that a critical thickness of a few atomic layers should also exist for the growth of two other noble metals (copper and gold) on GaAs and that only the first atomic layer of any alkali metal can be grown smoothly. For some other metals, smooth metal films can be formed only at certain magic numbers of atomic layers. Therefore, this theory promises to predict what amount of which elements should be deposited on which substrates at what temperatures to obtain the smoothest metal films.

In studying the transport properties of metal films, Zhang and his postdoctoral research associate Jun-Hyung Cho predicted an unexpected phenomenon related to depositing one antimony layer at a time on GaAs. If the film has one layer, it is insulating (electrically nonconducting), but if a second layer is added, the film becomes metallic (electrically conducting). Conventional wisdom says that adding another layer of metal to a metallic film can only make the thicker film more metallic. But Cho and others predict that with three layers of antimony, the film becomes insulating again and only when the film contains four or more layers of antimony will it maintain its metallic property. This prediction is being investigated experimentally by an ORNL surface physics group.

This theoretical work provides new understanding of the metal-semiconductor interface and of a different approach to growing smooth films. It also suggests that it may be possible to do quantum engineering of metallic overlayers down to the atomic scale, enabling the fabrication of perfect films needed for developing next-generation electronic devices.

The research was sponsored by ORNL's Laboratory Directed Research and Development Program and the U.S. National Science Foundation.