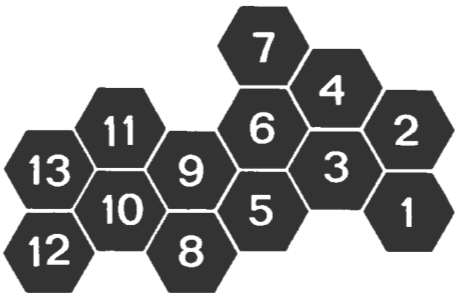
Oak Ridge National Laboratory
Fall 1983
review

Materials Research



Within the hexagons (or cubes) of the cover grid are examples of materials studied at ORNL or work performed by ORNL researchers. These materials and work are discussed in this special issue of the* Review *on materials research. For a more detailed explanation of the photos in the "hexes," see the cover caption on page 1.

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ARTICLES

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Editorial:

Materials Research at ORNL

By Alex Zucker, Associate Director for the Physical Sciences

This special issue of the *Review* is devoted to materials research at Oak Ridge National Laboratory. It is a fascinating issue. There emerges a picture of broad research capabilities from the exploration of very basic properties of matter as revealed, for example, by neutron scattering, to solutions of applied problems such as the development of particular graphites for missile nose cones. We cover a multitude of research areas: surface physics, corrosion, radiation effects, alloy theory, fracture, toughened ceramics, alloy design, nondestructive testing, welding and joining, magnetism, superconductivity, and others. We use some of the most advanced techniques: neutron and x-ray scattering, electron microscopy, particle accelerators, low-energy electron diffraction, Auger spectroscopy, laser annealing, ultrahigh vacuum methods, and sol-gel processing.

The Laboratory has national roles to play in the development of materials for fusion reactors, fossil energy, and nuclear power. A recent addition is our role as a center for development of ceramics for high-efficiency engines. The materials program is also responsible for the operation of user facilities in neutron scattering, ion and laser beam interactions with surfaces, analytical microscopy, and the low-temperature neutron irradiation facility. Literally hundreds of people a year come to Oak Ridge to conduct research and take advantage of the modern instrumentation and resident expertise. The High Temperature Materials Laboratory will provide yet another focus for residents and guests to do research in this rapidly evolving field.

At the heart of the Laboratory effort lies the recognition that greater understanding of the structure of matter—its inner workings, so to speak—will provide us with the means to tailor materials with specific properties for specific needs. New alloys, new ceramics, new surfaces, and new glasses come out of our laboratories. As this happens, we transfer them to industrial use as expeditiously as possible.

***THE COVER:** (1) inspecting for corrosion at Kentucky coal conversion plant; (2) studying radiation damage in alloys by electron microscopy; (3) high-temperature electrolytic treatment of an oxide crystal; (4) photomicrograph of anodized aluminum; (5) welding at ORNL; (6) photomicrograph of deformed zirconium; (7) high-temperature arc fusion crystal growth; (8) photomicrograph of aluminum-uranium alloy; (9) photomicrograph of partially oxidized tantalum; (10) high-temperature glass preparation; (11) neutron scattering facility at ORNL's High Flux Isotope Reactor; (12) analyzing material structure and composition in an electron microscope; (13) polished coke (carbon).*

The Review staff gratefully acknowledges the efforts of Jim Stiegler of ORNL's Metals and Ceramics Division and Fred Young of the Solid State Division, who helped to plan and solicit articles for this special issue. We also thank the many contributors to this issue for eloquently describing ORNL's exciting projects and developments in materials science and technology.

Bill Appleton (left) and Wayne Holland check the ion-implantation accelerator and laser system in ORNL's Surface Modification and Characterization Collaborative Research Center.

Fooling Mother Nature:

I-R 100

Ion Beam and Laser Techniques Improve Materials

By B. R. APPLETON

By using beams of ions and laser light to alter surfaces of materials and thus change their properties, ORNL scientists have produced semiconductor alloys for use in electronic devices, tougher ceramics for possible use in high-temperature engines, and a corrosion-resistant alloy for possible use in artificial hip joints. The supersaturated semiconductor alloy received an I-R 100 award in 1983.

Several years ago I was fascinated by a television commercial that extolled the virtues of a margarine by saying that it tasted so much like butter that even Mother Nature couldn't taste the difference. In the commercial, an actress dressed as Mother Nature was interrupted in the forest by a scientist in a white lab coat and asked to identify this particular brand of margarine. When she incorrectly identified the spread as butter, the scientist pointed out her error. "It isn't nice to fool Mother Nature," she replied, as she promptly summoned lightning, rain, and wind to punctuate her point.

As a materials scientist I identify by analogy with the plight of the scientist. Materials scientists are always trying to improve the materials given to us by Mother Nature; more often than not, however, we must resort to fooling Mother Nature to reach our goals, but Mother Nature usually has the last word.

A case in point is our work in using ion beams and laser beams to modify the surface or near-surface regions of materials to improve their properties. In this work we have changed materials into something better; for example, we have fabricated special semiconductor alloys that could be used for improved electronic devices, increased the hardness and fracture toughness of ceramics that could be employed in efficient heat engines, and produced a corrosion-resistant metallic surface alloy that could be used in artificial hip joints.

Materials Processing

Our primary motivation for using ion beams and pulsed lasers as processing techniques is that they can produce new properties in materials or, if you will, fool Mother Nature. Materials scientists learned from the alchemists of the Middle Ages who tried to change the individual base metals into gold that Mother Nature would not tolerate such drastic substitutions. However, they found that mixing various metals together to form alloys was a successful means of altering properties of materials and was a method acceptable to Mother Nature.

The most commonly used methods for making alloys are *equilibrium* processing methods in which two metals such as gold and silver are melted together and allowed to mix and cool slowly. Gold and silver are soluble in each other at all concentrations; in other words, any concentration of the two

Bill Appleton is head of the Particle-Solid Interactions Section of the Solid State Division of Oak Ridge National Laboratory. In pursuit of his Ph.D. from Rutgers, the State University of New Jersey, he explored the phenomenon of ion channeling in single crystals of silicon and germanium by using a tandem Van de Graaff accelerator. Thus began his career in using ion beams for solid-state physics research. After completing his doctoral studies, Appleton joined the staff of Bell Laboratories in Murray Hill, New Jersey, where he helped initiate an ion-implantation and ion-beam analysis program. When he came to ORNL in 1967, he continued pushing the use of ion beams for materials research. His research interests include ion-solid interactions, ion-channeling phenomena, and the use of ion-beam and laser techniques for materials research and surface modifications. The unconventional application of ion-beam and laser processing to alter the properties of materials has earned for Appleton and his colleagues a 1981 Department of Energy Award for Outstanding Sustained Research and a 1983 I-R 100 Award from *Industrial Research and Development* magazine. Appleton is associate editor of *Materials Letters* and *Applications of Applied Nuclear Science*, a Fellow of the American Physical Society, and vice-president of the Materials Research Society.

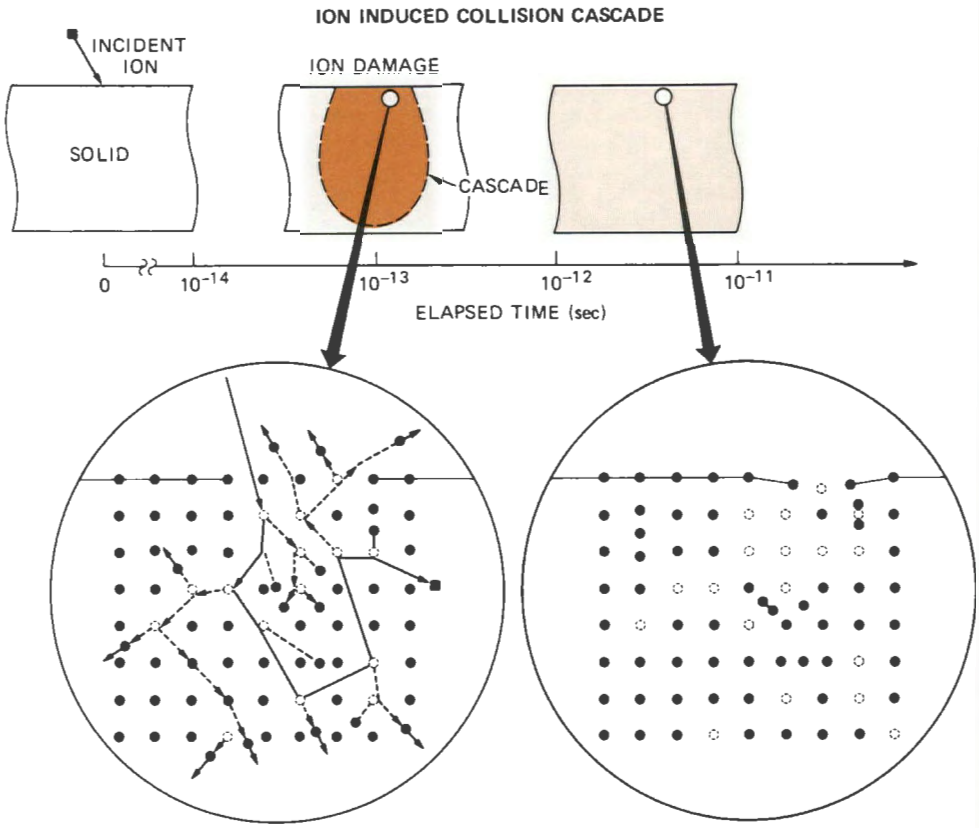
can be mixed and accommodated into a common ordered structure. Gold and copper also show similar behavior because they are both soluble in each other over all compositions.

However, Mother Nature is capricious in the case of silver and copper. This combination is anomalous because it shows only limited mutual solubility—that is, neither element is completely dissolved in the other at any concentration. But Mother Nature's anomalous silver-copper system can be "fooled" into mixing into a continuous solid solution such as the gold-copper system or the gold-silver system if the silver-copper system is cooled rapidly instead of slowly. This phenomenon was discovered in 1960 by P. Duwez and his co-workers at the California Institute of Technology; they found that by blowing molten mixtures of silver and copper onto very cold surfaces, complete solubility could be achieved. This rapid cooling process, or splat quenching, ushered in an era of *nonequilibrium methods*, which have been used for the development of a variety of metastable alloys.

In this article I will show that (1) ion beam and pulsed laser techniques are nonequilibrium processing methods that go beyond the capabilities of splat quenching and offer great versatility for altering properties of materials; (2) these techniques can lead to new and often unique changes in materials and thus can serve as ideal basic research tools; and (3) because they are capable of a wide variety of practical surface modifications, these techniques are rapidly becoming processing methods for commercial applications.

The techniques that we use in the Solid State Division (SSD) of Oak Ridge National Laboratory to modify the near-surface region of materials are ion implantation doping, pulsed-laser annealing, and ion beam and laser mixing. To understand why these techniques lead to alterations of materials in ways that are very different from equilibrium methods, we will also examine some of the ion-solid and laser-solid interactions that contribute to changing the properties of materials.

During ion implantation in a solid surface, the incoming ion dislodges atoms from their lattice sites, and these atoms in turn displace other atoms, and so on. Thus, thousands of atoms are set in motion along the track of each ion in what is called a "collision cascade" (left). These recoiling atoms stay in motion and interact for only a short time and then settle into new arrangements in the newly damaged solid (right).



Ion Implantation Doping

When charged atoms, or ions, produced in an accelerator bombard a target material, the ions penetrate into the near-surface layers of atoms in that material and become embedded there. This technique is called ion implantation doping. Ion implantation is a precisely controlled method for introducing impurities into solids. The depth to which an ion is implanted is controlled by regulating the energy of the ion beam; lateral uniformity is achieved by beam scanning; and a focused ion beam can even be used to "write" implanted patterns into solids with $<1 \times 10^{-6}$-m resolution. The implanted dose (concentration) is accurately controlled by measuring the charge accumulation in the target.

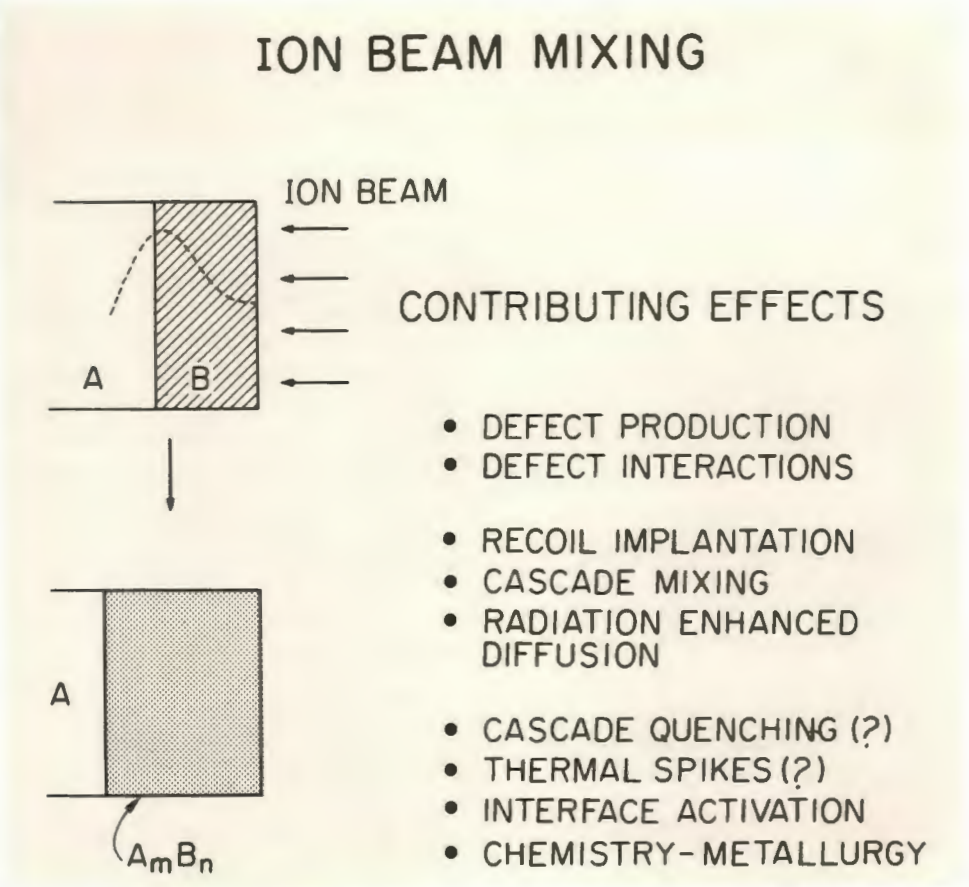
Ion implantation doping is a nonequilibrium method because the implantation of any ion species into any solid is unaffected by the normal constraints such as solubility limits and diffusion rates. Additionally, the detailed motion of the atoms in the solid contributes to a "rapid quenching" of the material's near-surface region. As each incident ion penetrates into the solid, it collides with the atoms of the solid and displaces them from their lattice sites; these recoiling atoms in turn collide with other atoms, causing more displacements. As a result of these collisions, thousands of atoms are set in motion along the track of each ion (the so-called "collision cascade"). However, these atoms remain in motion only for very short times ($\sim 10^{-13}$–10^{-10} s) before finding new configurations in the newly damaged solid. This rapid, short-lived movement of atoms leads to a mixing and rapid cooling ($\sim 10^{12}$–10^{14} K/s^{-1}), which can result in numerous nonequilibrium materials interactions such as amorphous structures (material whose crystalline order is completely destroyed), and new metastable alloy phases, as later examples will show.

All these attributes, coupled with reliability and reproducibility, have made ion implantation doping a premier processing technique in the semiconductor industry today. The tremendous explosion in handheld calculators, digital watches, video games, and personal computers can be traced directly to integrated circuit technology and ion implantation fabrication techniques.

In addition to its widespread use in the semiconductor industry, ion implantation is rapidly gaining acceptance as a materials processing technique for altering the near-surface properties of metals, ceramics, polymers, and a variety of other materials. The potential for fundamental materials research and ultimate practical applications will be illustrated later by some recent collaborative projects undertaken here at ORNL.

Ion Beam Mixing

A companion ion beam processing technique is ion beam mixing. In this process a thin film of one material is deposited on the surface of another material (substrate) by conventional means such as evaporation, sputter deposition, or electroplating. Then an energetic ion



In ion beam mixing, an energetic ion beam causes the atoms of a deposited thin film (B) to mix and interact with the atoms of the substrate (A), thus creating near-surface interactions (A_mB_n) that can lead to new properties.

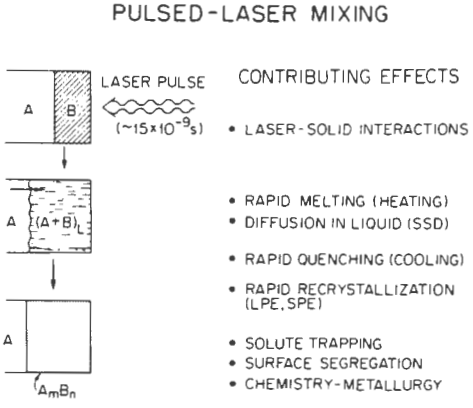
beam bombards this composite target, causing a variety of interactions to occur because the atoms of the deposited thin film are mixed with those of the substrate. The details of how this ion beam mixing process can lead to new materials properties are often not well understood, because the process involves a variety of complex interrelated ion-solid interactions and because it depends sensitively on the combination of materials and bombardment conditions. Nevertheless, the technique has resulted in some new and practical surface modifications.

We can obtain some insights into the nonequilibrium nature of the mixing process and understand why it leads to useful modifications by examining the consequences of some of the phenomena known to occur during ion bombardment. We have already pointed out that in ion implantation each incident ion initiates a collision cascade that wreaks havoc on the atoms of the solid. These atoms are knocked in all directions by the incident ion, dispersing like billiard balls on a pool table at the moment of the break. If more than one species of atom is present, such as at the interface of the deposited film and substrate, this atomic motion will result in intermixing similar to that of striped and solid-colored pool balls after the break. This mixing mechanism, called "ballistic mixing," depends only on the dynamics of the collision process; thus, mixing at the interface will occur whether Mother Nature likes it or not.

Ballistic, or interface, mixing has many uses. A major difficulty with all thin film deposition processes is that great care must be taken to properly prepare the substrate to ensure that the deposited film adheres to it. We have found that ion mixing almost always improves adherence and has been shown to work for metal/metal, metal/insulator, and even metal/polymer combinations. Other applications of ballistic mixing include fabricating graded composition interfaces to decrease detrimental thermal expansion problems or to improve epitaxial growth of a single crystal of one kind on another, normally incompatible one.

This ballistic mixing is not the only mixing mechanism. A common equilibrium mixing process is thermal diffusion, in which dopant atoms on the surface work their way into a solid by jumping into spaces vacated by atoms of the solid. During energetic ion bombardment of materials subjected to ion beam mixing, huge concentrations of defects are created by radiation damage, which can accelerate normal rates of heat diffusion by many orders of magnitude. This process of radiation-induced diffusion is just one of several mixing mechanisms that can result in extremely efficient mixing, and it gives rise to new properties in materials. The combined interactions initiated by ion bombardment can mix the near-surface species, induce atomic or molecular interactions in materials that lead to new properties, alter the near-surface microstructure, and initiate a variety of phenomena, depending on the exact conditions. What makes ion beam mixing complementary to ion implantation is its ability to fabricate a wider range of surface alloys and to alter the surface to greater depths.

In pulsed-laser mixing, unique surface modifications occur as the energy of the incoming laser light is absorbed into the electrons of material B and transferred to the atoms as heat. Rapid melting and mixing by liquid diffusion result at the surface (A + B), followed by rapid cooling and recrystallization as the heat is conducted away from the molten surface. The bottom line of this process is a new, uniform composition at the surface (A_mB_n) that has the desired properties.



Pulsed Laser Processing

Pulsed laser processing of solids is yet another way to "pull a fast one" on Mother Nature. It is a nonequilibrium method for selectively processing the surfaces of solids to achieve extremely rapid heating, even melting, and rapid cooling. It has numerous advantages over conventional thermal processing and is particularly compatible with ion implantation doping and ion beam mixing. The technique is more often called laser annealing or laser mixing, and like the ion beam processing methods already discussed, it is capable of a range of unique surface modifications. Recently, laser processes have been used at ORNL for fabricating high-efficiency silicon (Si) solar cells.

The relevant mechanisms associated with laser processing are a field of study in themselves. The annealing source usually consists of a powerful laser (such as a Q-switched ruby, Nd:Yag, or excimer laser), which emits an intense burst of coherent light in a pulse that lasts only a split second (10^{-9}–10^{-12} s). This laser light is absorbed initially into the electrons surrounding the atoms of the target solid, but is quickly transferred to the atom cores as heat. If enough energy is present in the pulse (e.g., 1–2 joules/cm^2 for a 15 × 10^{-9}-s duration pulse from a ruby laser on Si) the near-surface region will melt in times comparable to the pulse duration, according to findings by ORNL researchers. Because the vast bulk of the Si is still solid and still cool, the heat from this molten surface layer will be rapidly conducted away. This extremely rapid cooling catches Mother Nature unaware and makes possible a variety of new properties in materials.

New Properties

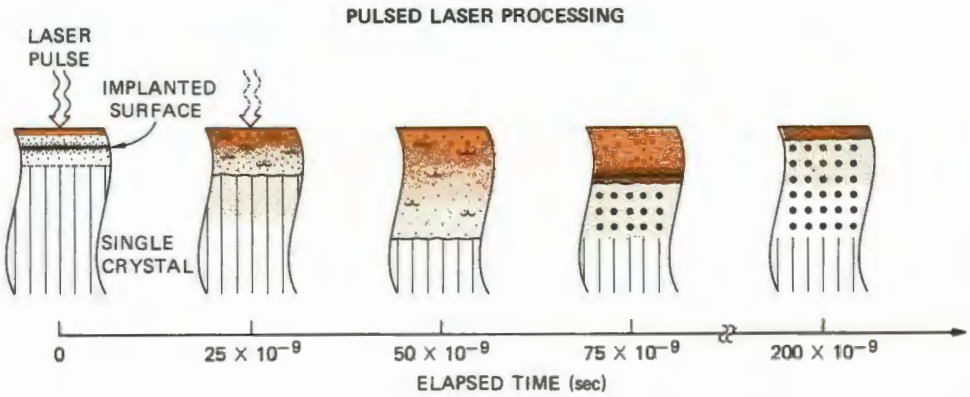
Ion beam and laser processing techniques are attractive for fundamental research on materials because they greatly expand the range of interactions that can be induced in materials, and in some instances they even provide new channels for interactions. Earlier, I suggested that the technique of splat quenching was a method of rapid cooling capable of fooling Mother Nature. The important parameter for this technique is the cooling rate, which is typically <10^7 K/s. Using a variety of pulsed lasers, we can obtain cooling rates from 10^9 to 10^{14} K/s in several ways: (1) by varying the pulse duration times (i.e., using nanosecond or picosecond lasers), (2) by tuning the wavelength of laser light to alter the absorption depth in the solid, and (3) by controlling the temperature of the substrate to increase or decrease heat conduction. Thus the hand of pulsed laser processing becomes quicker than the eye of Mother Nature.

The important consequences of rapid heating and cooling for fundamental research is that alloy systems can be made with a much wider range of compositions. For example, gold and silicon can be mixed and splat quenched to form an amorphous metglass only near the eutectic composition, which is 82% gold and 18% silicon; however, because the cooling rates of pulsed laser mixing are at least 100 times faster than those of splat quenching, these same metglasses can be formed at all compositions of gold and silicon.

Supersaturated Alloys

The development of a new class of supersaturated substitutional alloys of silicon is an excellent example of how basic research can lead to a practical development. Although the utility of these alloys was recognized in 1983 by an I-R 100 award given by *Industrial Research & Development* magazine to Woody White, Wayne Holland, Jagdish Narayan, and me, related research involved many researchers in the Solid State Division. We benefited greatly from the work of Ben Larson, Dave Zehner, Doug Lowndes, Fred Young, Rosa Young, Dick Wood, Jay Jellison, Jim Wang, and Syd Wilson (now at Motorola).

One type of these supersaturated alloys is fabricated by combining the nonequilibrium processing advantages of ion implantation doping and pulsed-laser annealing. Dopants of boron, phosphorus, gallium, arsenic, indium, antimony, thallium, or bismuth are first ion implanted into the near-surface region of silicon. This implantation severely damages the single crystalline silicon, turning the near-surface region completely amorphous. To make a semiconductor device, manufacturers must



When light from an intense laser pulse is absorbed in the near-surface region of an ion-implanted single crystal, its surface melts and recrystallizes very rapidly. As the molten layer resolidifies, the atoms in the liquid arrange themselves on the substrate crystal in perfect order, and the implanted dopants are similarly incorporated into substitutional sites.

anneal this damage to restore the crystalline perfection and to force the dopant into electrically active sites in the lattice. The semiconductor industry conventionally does this annealing by placing the implanted Si into an oven for an hour at a temperature of 900 to 1100°C.

Unfortunately, if this procedure is followed, the nonequilibrium edge that one gains on Mother Nature through ion implantation doping is lost to equilibrium thermal annealing. Under these circumstances, the maximum concentration of dopants that can be forced into the single crystal is limited by equilibrium solid solubility limits. In this case Mother Nature has the last word.

The rapid processing that is possible with pulsed laser annealing circumvents the limitations imposed by equilibrium thermal processing. When the ion-implanted Si is annealed with a single pulse from a Q-switched ruby laser (1–2 joules/cm^2, 15 $\times$ 10^{-9} s), the laser light is absorbed and the near-surface region melts beyond the implanted (damaged) depth in a very brief time (20 $\times$ 10^{-9} s). During these fleeting moments when this surface layer is molten (200 $\times$ 10^{-9} s), the dopant diffuses in the liquid Si. As the heat is conducted away to the cool substrate, the molten, doped surface layer begins to solidify. Because solidification occurs on a perfect single crystalline substrate that serves as a seed for regrowth, the melted layer resolidifies as a perfect single crystal (epitaxial growth).

This rapid, perfect recrystallization process is in itself an extraordinary result. During solidification the single crystal can be made to "grow" from the molten surface layer at velocities from 1–12 m/s by varying the laser annealing parameters. Furthermore, the regrown layer is completely free from any extended defects. To appreciate how truly remarkable this phenomenon is, one need only recognize that when single crystals of Si are grown from the melt under equilibrium conditions, it is necessary to limit growth velocities to <1.5 $\times$ 10^{-5} m/s to achieve comparable perfect crystalline order. If the pulsed laser parameters are adjusted for even more rapid cooling so that the liquid-crystalline interface velocity is >15 m/s, then resolidification is so fast that the Si atoms in the molten layer don't have time to arrange themselves in perfect order on top of the single crystalline solid. In this case the disorder of the liquid is frozen into the solid and an amorphous surface layer is formed. Mother Nature will make some concessions but she can be pushed only so far. These results illustrate why this is such a valuable tool for fundamental research.

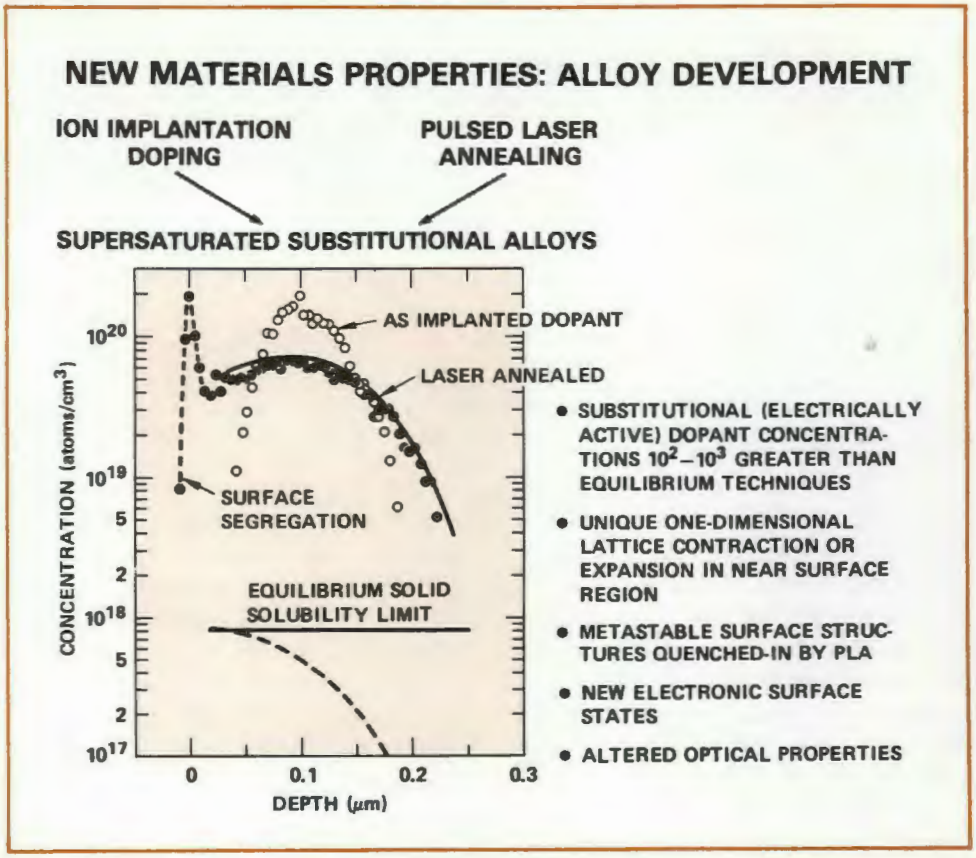
Now we can push studies of crystal growth, nucleation phenomena, interface kinetics, precipitation, and segregation phenomena to new bounds.

The new properties of these Si alloys are linked both to this very rapid (and perfect) recrystallization and to the phenomenon affecting dopant atoms during resolidification. Epitaxial regrowth occurs so rapidly that the dopant atoms in the melt are "trapped" into electrically active substitutional lattice sites (i.e., the same sites normally occupied by Si atoms) at supersaturated concentrations.

The concessions made by Mother Nature result in a class of alloys that possess a variety of new properties, which include:

- **Supersaturation**—The substitutional, electrically active dopant concentrations can exceed the equilibrium value for bismuth by more than a factor of 1300.
- **Unique lattice structure**—These alloys undergo a unique one-dimensional (non-cubic) lattice contraction (or expansion) in the near-surface region as a result of the substitutional incorporation of dopant atoms that are smaller (or larger) than Si atoms.
- **Metastable surface structures**—As a consequence of the rapid recrystallization, atoms on the surface are "quenched" into new atomic arrangements not normally possible.
- **Electronic properties**—The surface electronic properties are very different from Si prepared in the conventional manner.

New alloys with unique surface properties have been developed in ORNL's Solid State Division using ion implantation doping and pulsed-laser annealing. These supersaturated substitutional alloys, which received an I-R 100 award in 1983, can be used for high-power transistors, diodes, and advanced integrated circuit devices.



Improving Ceramics

Many of the problems that limit the use of materials originate at surfaces. Metal surfaces exposed to the atmosphere rust or corrode; friction and wear are related to the roughness and hardness of the surface; and even phenomena such as fracture (cracking), which is normally associated with bulk failure, starts as a surface crack. Surface modifications and coatings are thus used extensively to protect and extend the lifetime of materials. Some examples of recent collaborations using ion beam and laser processing may help to illustrate the potential practical use of these surface modification techniques.

Tailoring the surface properties of ceramics is one practical application of ion implantation doping. Several years ago Carl McHargue in ORNL's Metals and Ceramics (M&C) Division became intrigued with some of our ion beam and laser processing results and suggested that we initiate a joint seed money project to investigate the effects of ion implantation doping on the surface mechanical properties of ceramic materials. The Department of Energy is supporting efforts to toughen ceramics so that they can be used in highly efficient, high-temperature engines. We were granted some seed money, which we used to bring in a guest scientist, Hiroshi Naramoto of Japan, and along with Woody White and Jim Williams (SSD), we started research. Since then we have had invaluable contributions to this program from Marvin Abraham, Wayne Holland, and Gary Farlow (SSD), and Monte Lewis and Pete Angelini (M&C).

Using positive ion channeling, optical and electron microscopy, and electron spin resonance (ESR), we first found that it is impossible to turn the near-surface region of single crystals of alumina (Al_2O_3) amorphous by implanting chromium (Cr) at room temperature, even to very high doses ($>5 \times 10^{17}$ Cr/cm^2). However, this highly damaged Cr-doped surface is 40% harder and has 15% greater fracture toughness (resistance to cracking) than unimplanted Al_2O_3. These properties persist even when the sample is annealed in air to temperatures <800°C. Above 800°C the crystalline order is restored and the Cr acquires substitutional Al lattice sites (as determined from ion channeling), giving a valence state of Cr^{3+} (as determined by ESR), and the hardness drops to a value equivalent to an Al_2O_3-Cr_2O_3 solid solution.

The versatility of ion implantation and the importance of the implanted species to final properties are illustrated by the results observed when we implanted zirconium (Zr) into Al_2O_3. Unlike Cr, which is acceptable to Mother Nature as a substitute for Al because Cr is soluble and has the correct charge, Zr is insoluble in Al_2O_3. This implanted species also initiates a 40% increase in hardness and 20% increase in fracture toughness, but in this case the improvements persist to annealing temperatures as high as 1600°C.

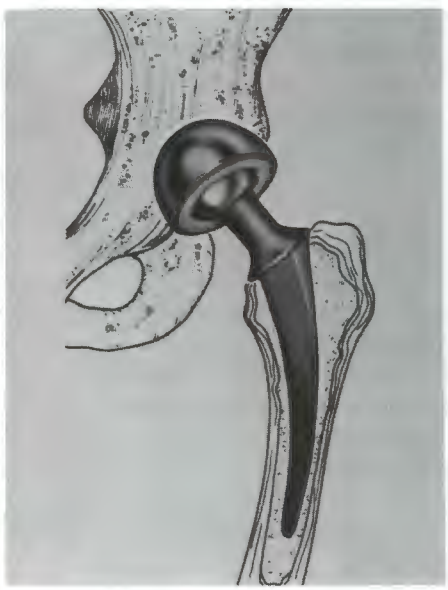
The importance of the properties of the material being implanted is illustrated by our related work on silicon carbide (SiC). This ceramic material has a covalent bonding structure like the semiconductor Si and thus damages

Surgical Implants

A limitation to the use of ion implantation doping is its relatively high cost—about \$0.10–\$0.50/cm^2. Consequently, it is usually most cost effective when applied to precision parts of high initial cost. This reasoning led Jim Williams of the Solid State Division to conclude that surface modification of materials used as supplemental or replacement parts in the human body is a promising application of this technique. Quite independently, Ray Buchanan at the University of Alabama was working to reduce the corrosion and wear of alloys used to replace hip joints. As fate would have it, Buchanan was a former teacher of Neil Thompson, who had done his thesis with Gene Kelly of the Chemistry Division and me here at ORNL on ion implantation of platinum in titanium (a technique that is less expensive than alloying to make titanium resistant to corrosion). The mutual connection led to a collaborative project to implant nitrogen (N) and chromium (Cr) in the titanium-aluminum-vanadium (Ti-6Al-4V) alloy used as the ball part of the hip joint and to evaluate the benefit, if any.

The hip joint operation involves replacing the natural hip joint with the Ti alloy ball, which moves in a high-density polyethylene socket. The most common failures occur because the body fluids attack the Ti, forming pits and releasing bits of metal. This metal becomes embedded in the polyethylene socket and abrasive wear removes even more metal. This causes mobility problems because of improper fit, and the metal particles can cause infection, inflammation around the joint, and other systemic effects when absorbed in the body fluids.

Williams and Buchanan found that by implanting the surface of the Ti alloy with N, the corrosive wear was reduced a factor of 400 to 1000. This work is still in its preliminary stages with experiments under way to identify the mechanisms involved, but it is clear that such improvements are very important. It is estimated that 75,000 to 100,000 hip joint operations are performed annually, and that the expected performance period of the artificial hip joints is 10 to 15 years. Thus, improvements in the performance length by a factor of 10 could eliminate the need for repeat operations and make this procedure available to young adults who need to replace defective joints. —*B.A.*



Appleton and Jim Williams work at the ion implantation accelerator where an alloy used for the stems and balls of artificial hip joints is implanted with nitrogen to make the alloy more resistant to corrosion and wear. The stem and ball (right) are made from the alloy as one piece, which is fitted into the bone. When the recipient of the artificial joint walks, the ball works inside the polyethylene cup. ORNL's process for ion implanting an alloy for surgical implants is being further developed and tested by at least one commercial manufacturer of hip prostheses.

much more easily. Consequently, room-temperature implantation of Cr or nitrogen (N) makes the near-surface region of SiC completely disordered (amorphous). As a result, the surface hardness actually decreases because the amorphous SiC surface expands and becomes much more flexible; however, the fracture toughness increases because cracks are much more difficult to initiate. We also discovered that Al_2O_3 could be made amorphous, with decreased surface hardness, by implanting it at liquid nitrogen temperatures.

These results are important to the materials needs of several programs of interest to DOE. Because ceramics are light, strong, wear-resistant and suitable for use at high temperatures, they are the materials of choice for bearing and wear materials in adiabatic diesel engines and for high-speed bearings in rotors and jet engines. Two serious limitations to their use are their mechanical properties and lubrication problems. Ceramics tend to crack under mechanical shock; thus, increased fracture toughness from implantation is important. Also, dry lubricants, which now must be used in high-temperature bearings, lead to a number of problems that limit the use of ceramic bearings. If implantation or some associated surface modification technique could improve mechanical properties and reduce the need for lubrication, it would be a significant advance. Such results appear quite possible.

These preliminary studies have shown that, within limits, we can tailor the surface properties of the ceramic by the choice of implantation conditions, ion species, and substrate material and that these alterations can persist to quite high temperatures. So far we have altered only the near-surface region while our mechanical testing procedure samples many times this altered depth. We believe that much greater improvements may be possible when greater surface depths are altered by high-energy ion implantation or ion beam mixing.

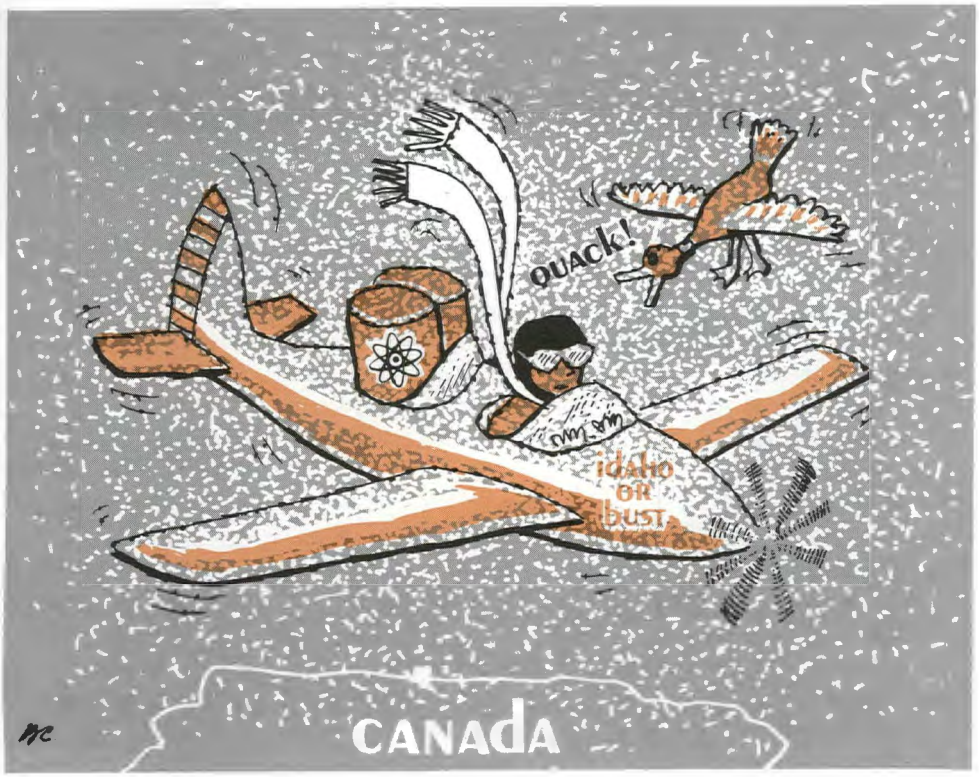
Looking Back and Ahead

Even though we are just starting to reap the fruits of ion beam and laser processing in materials research, the techniques themselves have deep roots at ORNL. Ion implantation was practically born in Oak Ridge with the use of the Calutron isotope separators at the Y-12 Plant to enrich uranium during the war years (1944–1945). The techniques and equipment developed there are still preeminent in the industry today. Similarly, many of the phenomena responsible for inducing beneficial alterations of materials during ion beam mixing were studied extensively at ORNL in the 1950s as part of the effort to characterize the effects of radiation on reactor materials. In fact, this was basically the charter under which the Solid State Division started. Finally, although lasers had been around a long time, it was not until 1977 that scientists from the Soviet Union recognized the benefits of lasers for annealing the damage in semiconductors. That same year, Rosa Young, Woody White, Jagdish Narayan, Greg Clark, Russ Westbrook, and Warner Christie at ORNL used ion implantation doping and pulsed-laser annealing to fabricate and characterize a high-efficiency solar cell.

The future of these techniques appears very promising. In fundamental studies, these techniques make it possible to test interactions of materials at limits not previously possible. In response to this potential, DOE has established a Surface Modification and Characterization Collaborative Research Center in ORNL's Solid State Division to make these capabilities available for collaborative fundamental studies to researchers in universities and industries.

The practical use of these techniques for surface modifications is also progressing rapidly. We have already noted the prominent role of ion implantation doping in the semiconductor industry, and several major manufacturers are now using ion beam mixing to form metal contacts and employing laser processing for selective annealing and shaping. The use of ion implantation for improving resistance to friction, wear, and corrosion in metal surfaces is also beginning to move from the laboratory to the marketplace. The Atomic Energy Research Establishment (AERE) in Harwell, England now does a sizable business in surface modification of metals for commercial firms in the United Kingdom. AERE has also licensed a commercial ion implanter for implanting nitrogen in metals. In the United States at least four small companies are now in the business of ion beam modification of surfaces.

Meanwhile, at ORNL we plan to continue to exploit the unique capabilities of ion implantation, ion beam mixing, and laser processing to create new or improved properties in materials. It isn't nice to fool Mother Nature, but we keep trying. ornl



lab anecdote

Materials scientists in Oak Ridge encountered a problem in 1947 after developing fuel elements for the Materials Testing Reactor (MTR), located at the Atomic Energy Commission's National Reactor Testing Station near Arco, Idaho. The fuel elements were each made of 18 flat plates consisting of enriched uranium sandwiched between aluminum cladding. Two aluminum side plates held the flat plates together, separating them enough to allow water to flow through and carry away the heat from the fuel. However, in preoperational tests, the Oak Ridge scientists found that differential stresses caused bowing of the plates in either direction. Thus, if two adjacent plates bowed toward each other, the coolant flow could be restricted and undesired hot spots could develop.

Several metallurgists described this problem to Eugene Wigner, the Laboratory's research director who later received a Nobel Prize in physics. He listened quietly and then left the room to ponder the problem. Later, he returned and proposed that the metallurgists change the design of the fuel element by curving the plates. Because the curved plates could bow in only one direction, he explained, the water coolant could still pass through. Wigner's simple, ingenious idea guided the development of the fuel elements that were used in the MTR.

Shipping the MTR fuel elements from Oak Ridge to Idaho was not free of problems either. In December 1951, the Metals and Ceramics (M&C) Division of Oak Ridge National Laboratory was trying to transport the MTR fuel elements as fast as possible in response to a request by Phillips Petroleum Company, which operated the MTR for the AEC. Because it would take a week and a half to ship the nuclear fuel by train (the usual mode of transportation), ORNL managers decided to send the 24 fuel elements by air.

Recalls Jack Cunningham of the M&C Division, "We loaded four tightly sealed shipping containers—each holding six MTR fuel elements—onto a commercial airplane in Knoxville. The attached shipping instructions described the contents as highly enriched uranium, with each fuel element containing 140 grams of uranium-235."

According to Cunningham, the fuel elements were flown to Chicago and then to Salt Lake City. Then they were loaded on a flight destined for Idaho Falls, but the pilot decided not to land because of heavy snow there. He flew to Butte, Montana, which was also snowbound. The only nearby place that he could find for a safe landing was Edmonton, Canada.

"You can imagine what a stir was created when Canadian customs officials found four boxes of bomb-grade material in the plane's cargo," Cunningham said. "High-level Canadian officials called the U.S. State Department to protest, and State officials reported the incident to the AEC.

"At 2:00 AM I was aroused from bed by a phone call from an AEC official who demanded to know why we had sent improperly safeguarded bomb-grade material to Canada. After a few phone calls, we finally explained to the satisfaction of all parties concerned how a few fuel elements destined for Idaho ended up in a foreign country."

It was a case of a big snowfall causing a little political fallout. ornl

High-Efficiency Beam-Processed Solar Cells

I·R 100

In the spring and summer of 1977, Rosa Young of the Photovoltaic Group in the Solid State Division of Oak Ridge National Laboratory was attempting to make solar cells that convert sunlight to electricity. She used silicon that had been implanted with ions, or dopants, to form the electrical junction needed to separate the charge carriers (electrons and holes) generated when the cell absorbs solar photons. Because ion implantation produces massive damage to crystal lattices, it is necessary to "anneal" the implanted silicon wafers at high temperatures to restore the crystallinity and electrically activate the implanted dopants. In Young's experiments, the standard procedures for annealing ion-implanted samples were yielding rather disappointing results.

Therefore, Young asked personnel at ORNL's Pure Materials Research Information Center (PMRIC) to compile a bibliography of all reported techniques for the annealing of ion-implanted silicon. The PMRIC's listing included several references in the Soviet literature to the "laser annealing" experiments of I. B. Khaibullin and coworkers. Intrigued by the reported results, Young set about locating a suitable laser at ORNL. Luckily, in the Fusion Energy Division she found a pulsed (Q-switched) ruby laser that had been used for temperature measurements of plasmas in the Impurity Study Experiment (ISX) device. Because this laser had the required characteristics for annealing silicon, Young's success was immediate, and the whole effort of laser processing of materials at ORNL was born in the fall of 1977.

Working with a number of collaborators in the Solid State Division, Young soon fabricated solar cells by ion implantation and laser annealing. The efficiencies of the first cells, though still well below those achieved by more conventional processing techniques, clearly demonstrated the potential for laser processing of solar cells. In the remarkably short time of five years, this technology has been developed at ORNL to the point where many of the best-informed experts in the field see laser processing as eventually supplanting techniques that have been under development for more than 30 years.

Concurrently, with the evolution of laser processing, a complementary program to develop a low-cost ion-implantation technique has been under way. This technique involves the use of a simple glow-discharge chamber to implant boron and phosphorus into the solar cell's front and back surfaces. Glow-discharge implantation is ideally suited for solar cell fabrication because it achieves very shallow, yet uniform, distributions of dopants; furthermore, it is inexpensive because it is not necessary to mass analyze the implanted species. Ion implantation and laser annealing together constitute an entirely new technology for solar cell fabrication—a technology frequently referred to as "beam processing."

A silicon solar cell is one of the simplest semiconductor devices imaginable. Basically, it consists of a single electrical junction near the front surface and the front and back contacts, which allow the current generated by absorption of solar photons to be conducted out of the device. The front contact must be made in the form of a comblike pattern designed to allow the maximum amount of sunlight to penetrate the cell while ensuring that the contact can carry the current generated without undue resistance losses. Two important embellishments on the basic structure are an antireflection (AR) coating, which sharply reduces the amount of light reflected from the front surface, and a so-called back-surface field, which is a built-in electrical field whose purpose is to reflect the charge carriers away from the back surface so that they may cross the electrical junction at the front surface and contribute to the external current.

In spite of the simplicity of the structure, very high efficiency cells have required complex processing techniques that are expensive and not easily automated. A typical cell fabrication sequence consists of the following steps: wafer slicing from large single-crystal ingots, surface preparation and cleaning, p-n junction formation by diffusion, contact metallization, and application of the AR coating. The thermal diffusion step in this conventional processing is carried out at approximately 1000°C for one hour in a large furnace and must be followed by carefully controlled cooling procedures; the method is energy-inefficient, costly, and difficult to automate. The metallization step usually involves photolithography, which is particularly time-consuming and expensive.

The laser-processing technology developed at ORNL completely circumvents the use of large high-temperature diffusion furnaces. The solar cells are fabricated in the following manner: A silicon substrate or cell blank suitably

The efficiency of this solar cell in converting sunlight to electricity is tested by Pam Fleming using special apparatus. ORNL has developed highly efficient photovoltaic cells by using laser processing.

doped during the growth process with either p- or n-type dopants is cut, cleaned, and polished. Formation of the p-n junction is then carried out by glow-discharge implantation (into the front surface region) of dopants having the opposite electrical charge of that of the substrate dopants. A high-powered, ultraviolet, xenon chloride (XeCl) laser is then used to electrically activate the dopant atoms and to repair the lattice damage created by the implantation process. A back-surface field is formed in the cell by the electron-beam deposition of 75 Å of antimony, which is then forced to diffuse into the silicon by irradiation with the XeCl laser. The solar cell is completed by forming electrical contacts to the front and back surfaces and by applying an AR coating.

In each of the steps involving lasers, the laser radiation produces ultrarapid melting and resolidification of the near-surface regions of the cell blanks. However, the energy deposition is so well localized (less than a few microns) and occurs in such a short time (approximately 10^{-7} s) that the temperature of most of the cell material is raised only a few degrees above ambient. Because of this localized, transient heating, most of the deleterious effects caused by high-temperature furnace processing are eliminated; thus, we sometimes refer to the laser techniques as "cold" processing.

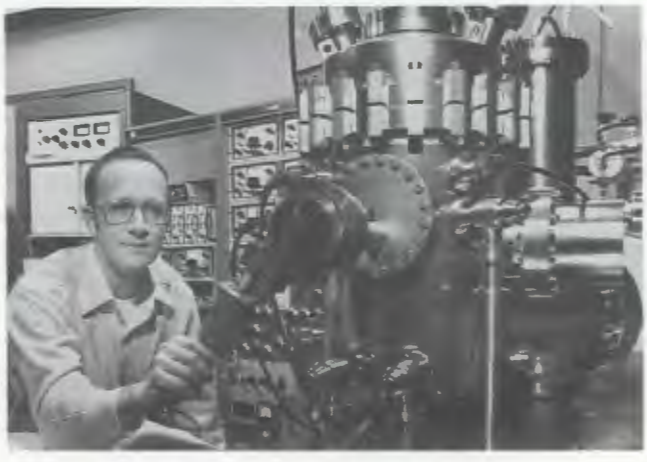
Moreover, because the laser energy is always used exactly where it is needed, laser processing is both energy-efficient and cost-effective. Indications are that the processing can be easily automated, something that has not been achieved in the solar-cell industry to date.

Our technique of using beam processing to develop high-efficiency silicon solar cells received one of the nine 1983 Materials Science Awards given by the U.S. Department of Energy. The award for significant implication for energy technology in the solid-state physics category was given to Rosa Young, Russ Westbrook, and me.

In a concerted effort at technology transfer, we are actively cooperating with Helionetics, Inc., a laser manufacturer that has designed and constructed a laser especially for processing semiconductors. It is the intention of Helionetics to commercialize the ORNL technology as rapidly as possible.

DOE's Solar Energy Research Institute (SERI) in Golden, Colorado, is the official agency for verifying the efficiencies of solar cells designed for terrestrial operation under one-sun conditions—that is, the solar energy is naturally diffuse rather than artificially concentrated. In November 1982 one of our laser-processed solar cells established what was then the highest efficiency recorded at SERI. Subsequently, apparently partly in response to our result but also with the active encouragement of SERI, a competition has developed to push solar-cell efficiencies to the limit. The highest efficiency that SERI had measured at the time of this writing was 17.1%, although reports of 18%-efficient cells are rumored. In our program we are now busily improving our fabrication facilities and techniques, fully expecting to break the 18% mark sometime this spring.—*Richard F. Wood, Solid State Division.*

On The Surface



John Wendelken at the electron-energy-loss spectrometer.

We interact with our three-dimensional world most often by seeing or feeling its surfaces. Moreover, many of the interactions of materials used by nature and man to shape and reshape the material world also occur at surfaces. Although the importance of surfaces is so obvious, the study of surfaces did not become popular until the last two decades. Because a surface reacts with its environment, the study of surfaces first requires the ability to control that environment. This ability has been acquired in the past 20 years as a result of the development of ultrahigh vacuum chambers and techniques for producing clean, well-characterized surfaces; since then the number of surface scientists and new surface-science techniques has grown explosively.

Research at Oak Ridge National Laboratory is no exception to these developments. Because the influence of surfaces in our world is so varied and widespread, it is not surprising that surface scientists are pursuing diverse activities in many ORNL divisions—namely, the Solid State, Chemistry, Analytical Chemistry, Metals and Ceramics, Health and Safety Research, and Fusion Energy divisions. Research projects range from the most applied to strictly basic. It would be impossible to survey all of these projects here, so I will focus on the more basic end of the spectrum with a few examples from the Solid State and Chemistry divisions involving the interaction of solid surfaces with foreign atoms and molecules.

When atoms and molecules such as oxygen, hydrogen, carbon monoxide, and nitric oxide stick to, or adsorb on, single-crystal metal surfaces, a variety of results can be expected. The adsorbed species may undergo catalytic reactions under the influence of a particular metal surface. Conversely, the metal surface may undergo structural changes under the influence of adsorbates. To understand these reactions on a fundamental level, we need to know where the atoms of both the host material and the adsorbed material are located and what the forces are that hold them together—or keep them apart. To unravel these details, we employ a variety of analytical techniques that use electrons, protons, and ions as surface probes.

An example of a surface that causes an adsorbate reaction comes from our study of nitric oxide (NO) on copper surfaces. Oxides of nitrogen are some of the pollutants discharged from automobile exhaust pipes. Although our principal motivation in this study is not concern about automobile exhaust, it is clear that the more complete our knowledge of the chemistry of any pollutant, the easier it is to devise a means for its control.

The study of NO on copper has been a team effort in which D. M. Zehner, R. S. Hathcock, P. A. Bruhwiler, G. R. Gruzalski, G. W. Ownby, and I used the techniques of electron-energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS). The first technique involves scattering very low energy electrons (less than 10 eV) from a surface and then measuring the energies of the scattered electrons. From the scattered-electron-energy spectrum we can learn the vibrational energies of molecules on the surface. Analysis of these vibrational energies can tell us the identity, location, and orientation of the molecules relative to the metal surface. XPS employs X rays impinging on the surface, which may cause electronic excitations that actually eject electrons into the vacuum environment of the experiment. The energy of these photoemitted electrons is dependent on the element from which they come; thus, their energy spectrum provides a "fingerprint" of the atomic species. And because an atom in a molecule has different electronic energy levels than the atom alone would, in many cases we can also identify the molecular as well as atomic species.

In the case of the copper and NO study, we found an exceedingly complex chemistry, especially when the copper crystals were chilled to -180° to -190°C. First, the crystal face, which determines the atomic arrangement of the copper atoms, is critically important to the NO chemistry. On the (110) face, EELS data indicate that small amounts of NO may be adsorbed and that the NO molecule stands on the surface neither parallel nor perpendicular to the surface but bent over. When too much NO is on the surface, it suddenly breaks apart into nitrogen and oxygen atoms. On the (100) and (111) faces of copper, some of the NO reacts at the lowest exposures to produce N_2O and O. With increasing NO exposure, EELS also showed that molecular NO was present at first in a bridge site—that is, bonded to more than one copper atom—and then in an "atop" site—that is, bonded to a single copper atom. Upon heating, the bridge-bonded molecules would convert to N_2O, which then left the surface, and the atop molecules just came off as NO.

If I could end the story here, it would sound as if everything is clear, but that is not the case. After larger exposures of the copper to NO, N_2O was no longer observed with EELS, but an unidentified vibration appeared. To try to understand this observation, we used the XPS technique and found N_2O present at high NO exposures, a result that agrees with the work of a British group. Unfortunately, the XPS was not sensitive enough to study the low-exposure cases in which EELS detected N_2O. Our hypothesis to explain the absence of N_2O in the high-exposure EELS data is that the N_2O molecule changes from standing up on the surface to lying down or parallel to the surface after the preferred adsorption sites are filled with atomic N and O from NO dissociation. EELS is less sensitive to vibrations parallel to the surface and the unidentified vibration could reasonably be a bending mode vibration, which is perpendicular to the surface when the molecule is parallel to the surface. In a new phase of this project, we plan to use synchrotron radiation to determine the orientation of the N_2O in the high exposure case.

A very different adsorption system, in which the adsorbate changes the substrate, is being studied by Gwo-Ching Wang and me. When hydrogen is adsorbed on a clean tungsten (100) surface, the diatomic hydrogen molecules split and the much more massive tungsten atoms are rearranged by the bonding forces between the hydrogen and tungsten atoms. The tungsten atoms are pulled together into pairs that may have two orientations at right angles to each other. From detailed angular studies of low-energy electron diffraction (LEED) beams scattered from a tungsten crystal cut at an angle to give an atomic-level stairstep effect, we know that the tungsten pairs occur in regions, or domains, of like orientation and that these domains nearly fill the steps but do not extend across step edges. The domains are about 30 Å (the step width) by 60 Å long at their maximum size. By studying the angular characteristics of the hydrogen vibration with EELS, we hope to determine next the effect of steps on the orientation of the tungsten pairs. The reward for this work will be a better understanding of a "classic" surface reconstruction problem, which has been studied by many surface scientists.

Certainly not all research involving adsorbate-surface interactions takes place in the Solid State Division. An outstanding example is the work of Steve Overbury and Ben Dekoven in the Chemistry Division. They are studying a variety of surfaces by scattering low-energy ions (fewer than 1000 eV) from these surfaces. The energy and angular distributions of the scattered ions permit one to "feel" the atomic ridges and bumps. Recently, they studied the adsorption of oxygen, oxygen and carbon together, and nitrogen on molybdenum (100) surfaces. They learned that both the oxygen and carbon reside at sites called four-fold hollow sites (at the center of a square formed by four molybdenum atoms) and that they are located approximately 0.3 Å above the average position of the molybdenum atoms. Although the nitrogen adsorption site is indefinite at this time, the ion scattering from a nitrogen-covered surface is similar to that from a carbon-covered surface.

Understanding the measurements derived from any probe technique requires understanding the probe itself, a particularly important part of Overbury and Dekoven's work. Their approach has been to make detailed comparisons of alkali and inert-gas ion scattering. The differences are complex, involving focusing effects, differing surface penetration, and neutralization of the probe ions so that they lose their charge and cannot be detected. It had been thought that a decrease in the intensity of helium ions ($He+$) scattered from molybdenum atoms exposed to oxygen resulted from the oxygen blocking the path of the scattered ions. Now, after comparing the scattering of helium ions to that of lithium ($Li+$) and potassium ($K+$) ions, they have shown that the effect is really caused by increased neutralization of the $He+$ by the oxygen rather than by blocking. This type of basic understanding is essential to increasing the range of problems that can be studied by ion scattering or any other surface techniques.—*John F. Wendelken, Solid State Division.*

Bernard Borie came to work at ORNL in 1949 and then left in 1953 to complete his doctoral studies with Professor B. E. Warren at the Massachusetts Institute of Technology. After studying with Andre Guinier at the University of Paris on a Fulbright Fellowship, he returned to ORNL in 1957. Since then he has been conducting x-ray diffraction research in the Metals and Ceramics Division. His research interests have centered on studies of most of the ways in which defects in crystal periodicity show up in the diffraction pattern. A native of Louisiana, Borie attended the University of Southwest Louisiana and Tulane University before coming to ORNL. Here, Borie, right, discusses diffraction research results with Harry Yakel.

Characterizing Materials by X Rays

I·R 100

By BERNARD BORIE

Ever since the pioneering contributions of Max von Laue and the two William Braggs—which were part of the great revolution in physics that spanned the first third of this century—diffraction crystallographers have known how to use X rays to determine exactly the repeating pattern of atoms that makes up a crystal. For many decades the classical business of crystallographers was to solve this puzzle: given the x-ray diffraction pattern from the three-dimensional periodic distribution of electron density that constitutes a crystal (X rays do not "see" nuclei), what are the shape and size of the repeat unit, and what are the positions of the various atoms within it? By now, scientists have determined literally tens of thousands of such "crystal structures." The structures constitute a fundamental part of the body of knowledge of modern science. Clearly, such atomic arrangements must be the starting point for the inference of physical and chemical properties—the business of metallurgists, solid-state physicists, chemists, mineralogists, and molecular biologists.

For many years the rules for "doing" a crystal structure were simple and fairly primitive. To be a cryptographer of nature required one to have much insight, intuition, and a good memory of the structures of other materials likely to be similar to the one under study. The study of diffraction crystallography in those days was perhaps as much an art as a science.

Included in the ingathering of scientific giants who populated the Manhattan Project in the wartime years was a house crystallographer. His job was to do the structures of the exotic new heavy elements and

The study of the atomic structure of matter by x-ray diffraction has a long and distinguished history at ORNL. Many contributions to the development of this discipline, including new ways to gather the data, new methods for their interpretation, and computer techniques for their manipulation and representation, had their origins in ORNL's crystallographic community. Many changes in our research lifestyle and the kinds of studies we will undertake are expected soon, mainly because of the availability of x-radiation from synchrotrons.

In 1966 Henri Levy worked at the console of the first x-ray diffractometer controlled by a minicomputer.

their compounds. For about six or eight years, the name of the famous W. H. Zachariasen from the University of Chicago disappeared from crystallographic research literature. His structure determinations of many compounds of the transuranics were to be published later after the war.

The Postwar Years

The early postwar years, the late 1940s and early 1950s, were exciting times in diffraction crystallography. In the hands of Ernie Wollan and Cliff Shull and their younger colleagues, Mike Wilkinson and Wally Koehler, the discipline of neutron diffraction was aborning in Oak Ridge. In those days, the interesting ways in which neutrons (which interact strongly with nuclei) could be used to supplement X rays dominated the interests of Henri Levy. He used neutrons to find hydrogen positions in crystals because hydrogen atoms with only one electron interact very weakly with X rays. Also active then in x-ray diffraction research was the well-remembered Max Bredig, who was my first boss in Oak Ridge.

That interval also saw the beginning of the use of diffraction techniques for purposes other than structure determinations. It was known that mechanical deformation broadened the diffraction maxima from crystalline solids; B. E. Warren and his students at Massachusetts Institute of Technology (MIT) first offered quantitative interpretations of this phenomenon in terms of distortions of the crystal-repeat pattern (strain) and crystal fragmentation (particle size). X-ray diffuse scattering as a measure of defects in crystalline periodicity was also of interest then to Warren and his students. John Cowley's famous study at MIT of short-range order in a copper-gold (Cu_3Au) crystal dates from then as does some of the early work with temperature diffuse scattering. The diffraction consequences of stacking faults, scattering from liquids, and small-angle scattering also interested Warren and his students and a contemporaneous school of thought led by Andre Guinier of the University of Paris. Warren used to like to say, "Everyone should do one crystal structure and then move on to something more interesting!" Our own diffraction program in the Metals and Ceramics (M&C) Division has some of its roots in the Warren-Guinier style of crystallographic research.

Much of the early work of Warren and his students was characterized by the use of the then new Geiger counter x-ray diffractometers. Guinier, however, has never forgotten the usefulness of photographic film in diffraction work. Even much of his later research shows his bias for that old-fashioned but still valuable two-dimensional position-sensitive radiation detector.

At that time it occurred to L. K. Jetter at ORNL that the new x-ray Geiger counter technology should greatly improve the methods then used by metallurgists to measure preferred orientation of crystallites in polycrystalline metals. Techniques developed by his group—which included Robin Williams, Jack Ogle, Carl McHargue, and me—were used not only for measuring preferred orientation but also for its representation. These techniques remain standard in many metallurgical diffraction laboratories.

At ORNL the 1950s also saw the appearance of Doug Billington's Physics of Solids Institute (ψ, or psi). Unfortunately for those who love acronyms, it fairly quickly evolved into the Solid State Physics Division. Much of the nonstructural neutron diffraction work and early studies of radiation damage were done there.

Recent Impacts

Two major impacts on x-ray diffraction crystallography in the 1960s were the application of computers and computer-controlled

automation to x-ray problems and the rediscovery of dynamical theory, which was first developed during World War I. Much of the early work with computers was done at ORNL by Henri Levy, Bill Busing, and their co-workers. Their famous least-squares program, which was used to find an optimum match between diffraction measurements and the resultant crystal structure, remains one of the most frequently cited items in the crystallographic literature. Their early computer-controlled x-ray diffractometer was literally the prototype of the modern diffractometers available commercially and in wide use today. Though obsolete, it is still being used to gather the diffraction data necessary for crystal structure determinations.

As is now widely recognized by organic and inorganic chemists alike and by biophysicists, the development of computers, computer-controlled diffractometers, and elaborate computer software has made single-crystal x-ray structure analysis the most powerful, most informative, and the least ambiguous method available for the determination of molecular structure. Considering the extraordinary current importance of the method, not many modern chemists would now agree with Warren's view that little interesting information is generated by doing crystal structures!

The dynamical theory is the oldest x-ray diffraction theory; it was worked out by P. P. Ewald while he was a lieutenant in Kaiser Wilhelm's army on the Russian front nearly 70 years ago. (How many second lieutenants have used their spare time so productively?) Interest in the theory fairly quickly faded, however, because it was found that nearly all crystals are sufficiently imperfect that their diffraction patterns are better described by the simpler kinematic theory. Dynamical diffraction theory requires a truly periodic medium for approximately the same kinds of reasons that the early forms of band theory do.

Two developments made the dynamical theory a very hot item around 1960: the general availability of truly perfect single crystals of silicon and germanium and the astounding discovery by G. Borrmann in Germany that if oriented to diffract, a perfect crystal becomes nearly transparent to X rays. This phenomenon, in which a crystal allows X rays to pass through because of diffraction, is explained by dynamical theory, although no one comprehended it until after Borrmann's work, which was lost to the West for some time due to World War II, became widely known. So extraordinary and unexpected was this phenomenon that some veteran crystallographers could believe it only after confirming it for themselves in their own laboratories.

Perfect Crystals

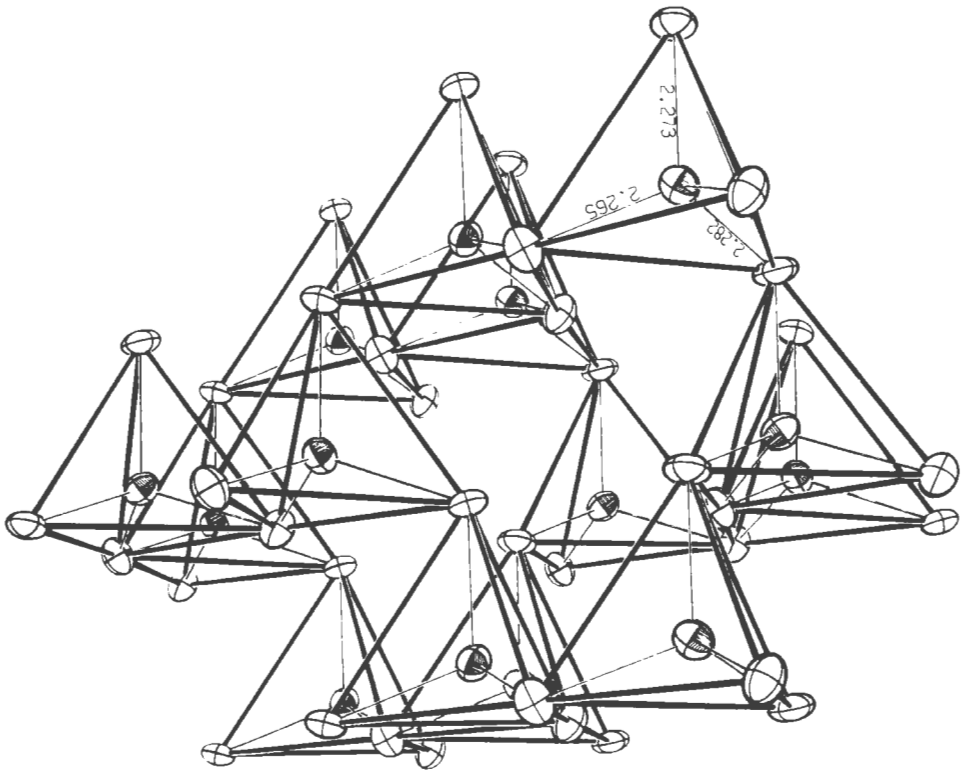
By means of some very careful and meticulous experimental work, Fred Young of ORNL's Solid State Division was the first to grow soft metallic single crystals so nearly perfect that the diffraction anomalies of the dynamical theory could be observed with them. In the 1960s, he and his co-workers, T. O. Baldwin and Alphonso Merlini, undertook some extraordinary experiments with these remarkable crystals—crystals so soft that drying Duco cement was found to strain them enough to turn off the Borrmann effect. A defect and its strain field—for example, a dislocation—will cast a shadow in the Borrmann transmission. The degree of contrast associated with the shadow for different Bragg maxima (x-ray diffraction peaks) was enough to find the relevant Burgers vector. In fact, methods were found to generate a stereo pair so that the depth of the dislocation in the nearly perfect crystal could be established.

The availability of these crystals allowed Ben Larson of ORNL's Solid State Division to test the theory of Peter Dederichs, who was then at ORNL on leave from the Kern Forschungs Anlage in Jülich, Germany. This theory predicts the effect of radiation-induced defects (and their strain fields) on Borrmann transmission and diffuse scattering.

Instrument Developments

Important instrument developments useful for x-ray diffraction research have evolved at our laboratory in the M&C Division. For many experiments it is desirable that the incident x-ray beam be monochromatic; this selection of a single x-ray wavelength is accomplished by first diffracting it from a special crystal monochromator. Of course, one pays a price in intensity for this method. To minimize the price, it is important that the composition and shape of the monochromator be optimized. This optimization has been achieved by Cullie Sparks in his development of curved hot-pressed pyrolytic graphic crystals. These crystals are generally recognized as the best way to produce a focused beam of single-wavelength radiation—either for X rays or neutrons.

The special research interest of Bob Hendricks, formerly of the M&C Division diffraction group, was small-angle x-ray scattering—a kind of diffraction experiment of use to professional disciplines from metallurgy to biology. In his efforts to create an optimum instrument for such measurements, he recognized that it should be large enough to magnify the small pattern around the direct beam and should



This drawing of the crystal structure of orthorhombic zinc chloride was generated by the Oak Ridge Thermal Ellipsoid Program (ORTEP), a universally used computer program developed at ORNL by C. K. Johnson for drawing crystal structure illustrations with a mechanical plotter. This crystal structure is based on a hexagonally close-packed array of corner-sharing $ZnCl_4$ tetrahedra, three layers of which are shown here. Zinc atoms are those with shaded octants. Three Zn-Cl distances in one tetrahedron are labeled in Angstrom units. ORTEP can accept output from another program, such as ORNL's Busing-Levy program, which uses least-squares procedures to estimate atomic coordinates and thermal vibration parameters from x-ray or neutron diffraction data. The $ZnCl_4$ structure shown above was determined from x-ray diffraction data collected with W. R. Busing's automated diffractometer. ORTEP is a good example of the degree to which the manipulation of diffraction data and the representation of results derived therefrom have become dependent on the computer.

be equipped with a powerful, carefully collimated, monochromatic x-ray beam and with a detector system more sophisticated and quantitative than is the traditional photographic film. For several years his prize-winning 10-m instrument has been used by visitors who come to ORNL expressly for small-angle x-ray scattering studies. Its incident beam is generated by a Sparks graphite monochromator and a powerful rotating anode source. Its detector is a novel two-dimensional position-sensitive proportional counter—one of the first of its kind—which was developed by Cas Borkowski and Manfred Kopp of ORNL's Instrumentation and Controls Division.

X-ray Physics

Though one often thinks first of diffraction as the phenomenon used in x-ray research to characterize solids, X rays are used for other types of research. Because of the powerful, focused beams of X rays that can be obtained from his new monochromator, Sparks has long been interested in detecting trace amounts of elements by measuring the intensity of the fluorescence excited by such beams. He has found that by combining his monochromator with the enormous x-ray intensity of synchrotron sources, detection limits as low as a few parts per billion in concentration are attainable. Luis Alvarez of the University of California at Berkeley is interested in possibly using this fluorescence detection method having an ultrahigh sensitivity to test his theory that a giant asteroid struck the earth about 65 million years ago, causing many catastrophic changes, including the extinction of the dinosaurs. This work has stimulated others to attempt the construction of an x-ray microprobe with resolution on the order of a micron.

An unexpected consequence of the fluorescence development research was a significant advance in x-ray physics—the discovery of anomalous Raman resonance scattering, normally an optical and not an x-ray phenonemon. In this phenomenon the outgoing X rays have less energy than the incident radiation, and the X rays produced are not phase related to the X rays doing the excitation. The scattering pattern is thus inelastic and incoherent. This phenonemon was first observed by Sparks and interpreted for us by Sam Faulkner. This part of the scattered radiation, like the Compton scattering, contains no information about the atomic array. However, we expect that it will provide valuable new insights into the details of atomic structure itself.

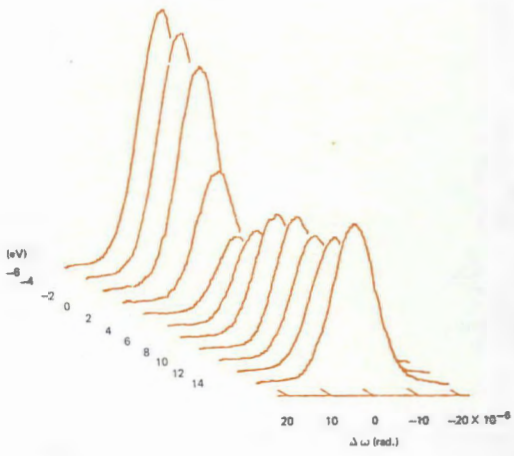
New Directions

What does the future hold for x-ray research in general and for our research community here at ORNL in particular? Clearly, the next big event for us will be access to an extraordinary new x-ray source—synchrotron radiation. This radiation, which is produced by

high-speed electrons constrained to a circular path by magnetic fields, is perhaps three to four orders of magnitude more intense than is radiation from conventional sources; unlike conventional X rays, synchrotron radiation is a continuum rather than a set of spectral lines and is nearly completely plane polarized.

Certain preliminary experiments have been completed at the synchrotrons at Stanford and Cornell universities; however, the real metamorphosis from the good old days to the strange new times for us at ORNL will begin when the light is turned on at the National Synchrotron Light Source at Brookhaven National Laboratory later this year. Unlike the Stanford source, the Brookhaven source will be totally dedicated to x-ray research and will provide access to more useful radiation than does the synchrotron at Cornell. We at ORNL are instrumenting our own radiation beam line at the light source; much research either previously impossible or impractically difficult will soon be easily accessible to us.

Larson and his co-workers in the Solid State Division plan to extend their time-resolved (on the order of nanoseconds) studies of laser annealing already begun at the Cornell synchrotron. Their earlier Cornell studies had revealed transient phenomena, mainly split-second melting and resolidification in silicon after annealing. Another possible experiment of interest to this group—one requiring the enormous intensity advantage available at a synchrotron—is a dynamic study of phase transformations. With so much intensity, a good diffraction pattern may be quickly recorded so that a number of closely spaced (in time) measurements should yield a diffraction "motion picture" of a crystal changing rapidly during a transformation. Synchrotron studies of radiation damage and ion implantation as well as very high energy resolution (in the microvolt range) experiments, necessary for elastic and inelastic x-ray scattering studies of lattice statics and dynamics, are also likely.

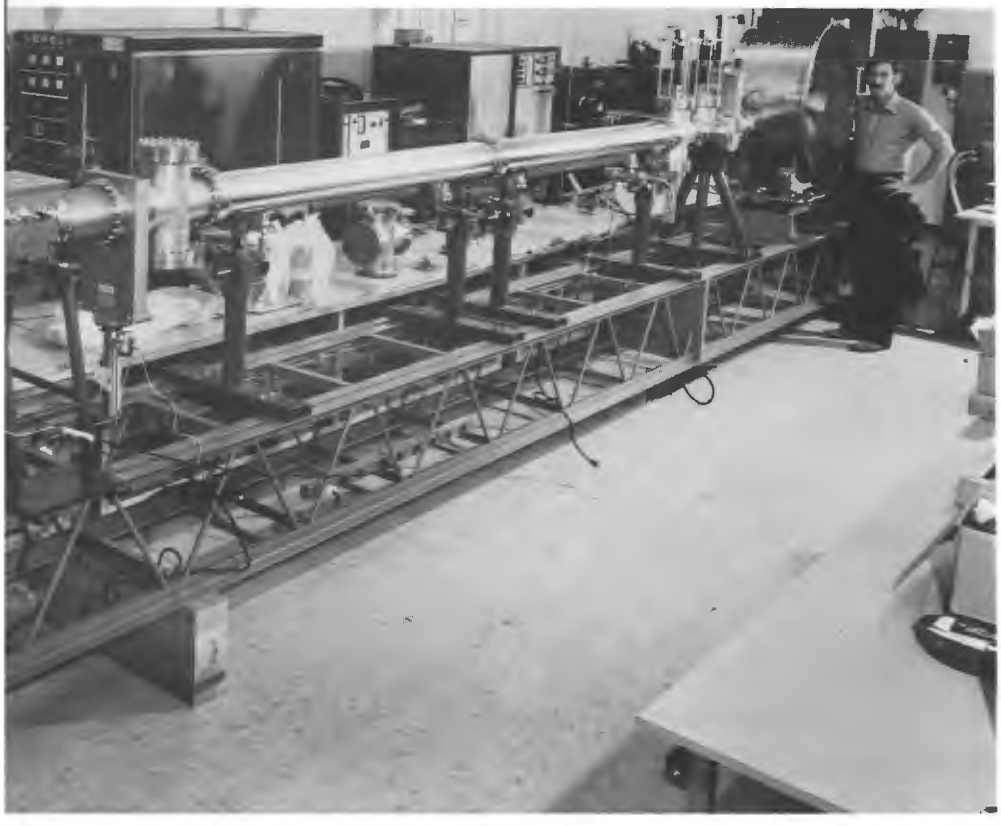


These rocking curves show how dramatically the intensity of a Bragg maximum of gallium arsenide can be altered by small changes—a few electron volts—in the energy of the incident radiation near an absorption edge of the sample. Synchrotron radiation is particularly convenient to show this effect because closely spaced energies for the incident beam can be chosen from its continuum with a monochromator.

Our own group in the M&C Division is interested in the distribution among the positions in structures of atoms of similar atomic number. Such studies are not only scientifically challenging but also of considerable practical importance. Alloy systems in which iron is combined with its near neighbors in the periodic table are of major engineering significance. Practically nothing is known about order among the different kinds of atoms in these systems because the relative x-ray scattering strengths of atoms are approximately proportional to the atomic number. However, by a proper choice of energy for the incident beam, the resonance phenomenon of anomalous dispersion can be used to enhance greatly the contrast between such atomic pairs in the diffraction pattern. Unlike the line spectrum from conventional sources, the continuum intensity distribution from a synchrotron allows such a choice.

Our efforts to this end are off to a good start with Harry Yakel's measurements of the average distribution of iron and several of its neighbors in various sets of atomic sites of the complex intermetallic compound called the sigma phase. This work was done partly at the synchrotron at Stanford and partly on Busing and Levy's obsolete equipment.

We are currently developing software for our Brookhaven beam line to analyze diffuse x-ray scattering, which reveals fluctuations about the average atomic composition. With the synchrotron, the diffuse intensity may be con-



This 20-m x-ray beam line developed by Gene Ice (left) and others at ORNL will be powered by beams 10,000 times more intense than conventional sources when it is moved to the National Synchrotron Light Source nearing completion at Brookhaven National Laboratory. Scientists from all over the nation will use this special x-ray facility to study arrangements of atoms in metal alloys and defects in crystalline structures. ORNL and Oak Ridge Associated Universities personnel will operate the beam line and collaborate on research with industrial and university users. More useful x-radiation will be available at this one station than from all of the conventional x-ray sources used in the United States for research. The ORNL beam line received an I-R 100 award in 1983.

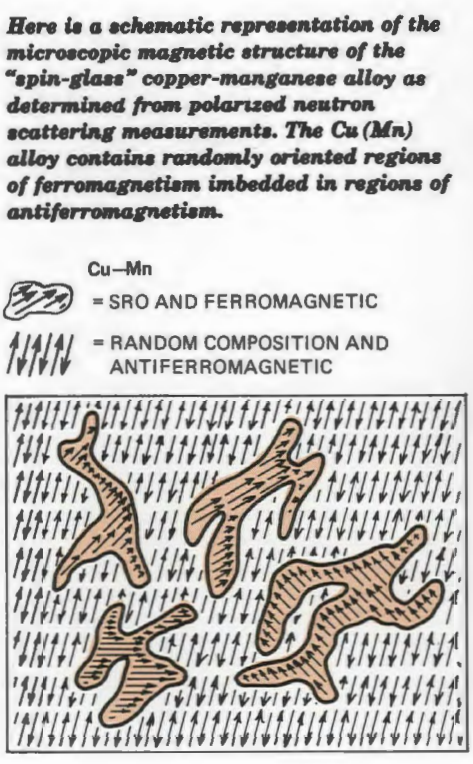
trast enhanced by the phenomenon of anomalous dispersion. Such measurements have never been attempted before. We think that we have found some novel methods for manipulating the diffuse intensity (appropriate only for synchrotron measurements) that will give insights on a new scale of detail into the short-range structure of substitutional alloys. We are eager to try our new tools to see how they work. Al Narten of ORNL's Chemistry Division plans similar contrast-enhanced studies of x-ray scattering from liquid metallic alloys.

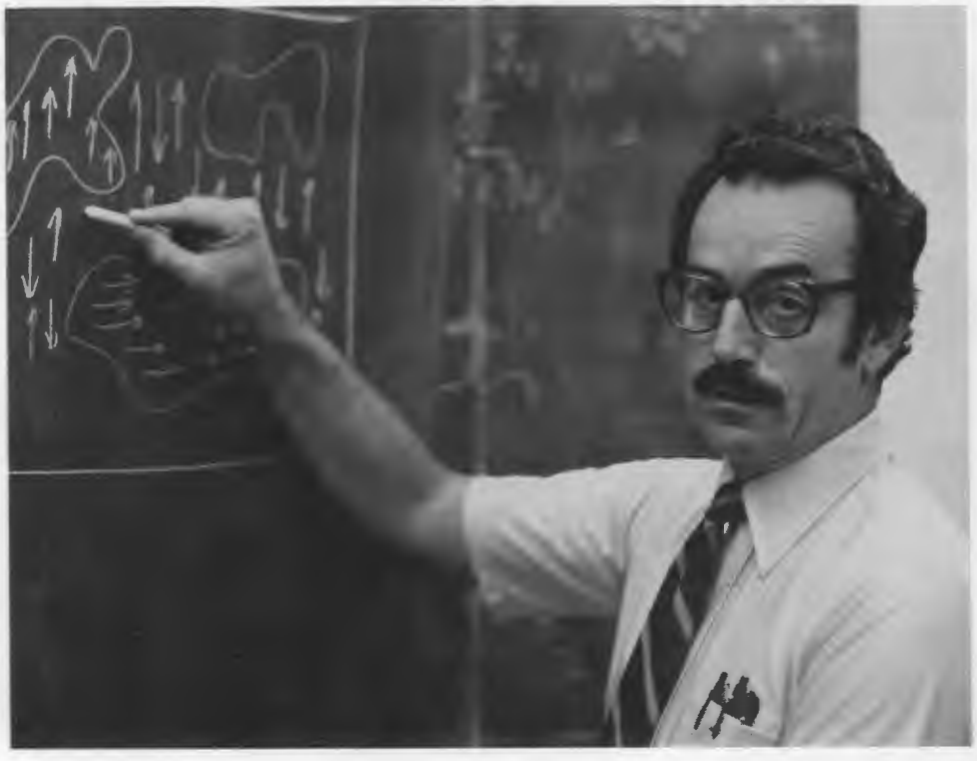
Of course, access to the synchrotron will provide many other research opportunities that various members of our x-ray research community will probably exploit in the future. Surface studies and the weak scattering of X rays from monolayers, partial monolayers, or thin oxide films will no doubt attract the attention of crystallographers. Two relatively new phenomena—extended x-ray absorption fine structure and near-edge structure—have already been used to help resolve structural questions. Such studies are particularly appropriate for synchrotron work. It is likely that new dynamical diffraction experiments will occur to us as we settle into our new research lifestyle imposed on us by the synchrotron.

It will be a very different style of work from what many of us old hands are used to. In the first place the station will not be exclusively ours (in the same sense that our laboratory source is). A group of university and industrial scientists which was organized through Oak Ridge Associated Universities has participated in the design and construction of our station. Members of this group and others will have their turn at the station. There will be much scheduling, submitting to research proposal reviews, and "waiting in line," all of which many of us are not used to. Also, because access to the synchrotron is so valuable, we must work around the clock during our assigned time slot. Because of the great quantity of quickly gathered data and the need not to waste time, much instrumental automation and computer manipulation of the data will be necessary.

New radiation sources, new ways to tailor the radiation for particular experimental goals, powerful new detectors to measure in detail the scattered intensity distribution, and computers to manipulate both the components of the experiment and the resultant data are all at hand. All these will no doubt yield important insights into the exotic new materials that will affect the lives of us all. ornl

Here is a schematic representation of the microscopic magnetic structure of the "spin-glass" copper-manganese alloy as determined from polarized neutron scattering measurements. The Cu (Mn) alloy contains randomly oriented regions of ferromagnetism imbedded in regions of antiferromagnetism.





Bob Nicklow is head of the Crystal Physics Section in ORNL's Solid State Division. He came to ORNL in the fall of 1963 after completing work for a Ph.D. degree in physics at Georgia Institute of Technology. During his career at ORNL, he has applied neutron scattering methods to the study of atomic vibrations in solids and to the measurements of the energy spectra of spin oscillations in rare-earth metals, compounds, and alloys. He has served as group leader in neutron spectrometry and is the author or coauthor of about 80 publications.

Neutron Scattering in Materials Research

By ROBERT M. NICKLOW

Since the availability of significant fluxes of low-energy (thermal) neutrons from research nuclear reactors in the late 1940s, neutron scattering research has grown tremendously and has become perhaps the most fruitful single source of experimental information about the structural, magnetic, and dynamical properties of materials on the microscopic level. The first application of neutron scattering to the study of solids was carried out at Oak Ridge National Laboratory by E. O. Wollan and C. G. Shull in 1946. Their use of neutron beams at the Graphite Reactor opened up a whole new field of research that continues to be active throughout the world. Because the history of the field has been presented previously by my colleague Wally Koehler of the Solid State Division (see W. C. Koehler's "Neutron Scattering at ORNL," ORNL *Review*, Spring 1976), I will focus on the technical

method of neutron scattering, reasons for using it instead of x-ray scattering, research projects currently being carried out at ORNL, and speculation about future directions in the field.

Neutron Properties

The neutron has several special properties that make it a particularly valuable tool for research on problems of condensed matter (liquids and solids). Perhaps the most basic is its wave property. For condensed-matter studies, it is a fortunate coincidence that the most abundantly available neutrons, those from thermal-neutron reactors such as ORNL's High Flux Isotope Reactor (HFIR), possess wavelengths of the same size (1 Å) as the typical distance between atoms. Thus, these "slow neutrons" are ideally suited for studies of the spatial arrangement of atoms because of the interference between neutron waves elastically scattered by different atoms.

The neutron possesses a magnetic moment—that is, it behaves somewhat like an atomic-scale magnet and interacts with the atomic moments existing within magnetic solids. The resulting neutron scattering pattern contains just that information needed to determine both the spatial arrangements and the orientations of the atomic magnetic moments. No other experimental technique can provide such information.

In comparison with X rays or electrons, the neutron interaction with most materials is very weak. Thus, neutrons are highly penetrating, thereby providing information on bulk properties rather than surface properties and allowing a sample to be studied quite conveniently in extreme environments provided by cryostats, furnaces, or high-pressure cells, which can have walls made nearly transparent to neutrons.

And, finally, it is (almost incredibly) fortunate that, in addition to the above highly desirable properties, the energy spectrum of neutrons from nuclear reactors overlaps nearly ideally the energy spectrum associated with the motion of atoms and their magnetic moments as a result of their thermal excitations. Consequently, the relative energy change of a neutron scattered inelastically is large and can be measured accurately and easily by neutron spectrometry, thus providing the most detailed information available experimentally about the bonding and magnetic forces between atoms in condensed matter.

Neutron scattering experiments at ORNL have shed light on the structure of water, the way in which water reduces the performance of solid electrolytes in experimental batteries, the magnetic ordering of copper-manganese crystals, atomic bonding forces in crystals, and the structure of uranium crystals at a very low temperature.

For structural studies, neutron scattering is similar to x-ray (or electron) scattering in many respects. Typically, a well-collimated beam is directed onto a sample and the intensity of the scattered radiation is measured. The variation of the intensity with scattering angle is determined by the spatial arrangement of the atoms and by the relative scattering cross sections of different elements in the sample—that is, the probability that a given element will scatter neutrons at certain angles and intensities. Almost all of the structurally important scattering from crystalline samples is concentrated into relatively few diffracted beams that are sharply peaked in scattering angle (Bragg peaks or reflections). Usually, the intensity of each beam is measured separately with a small radiation detector that at one setting intercepts a small portion of the range of possible scattering angles. Samples that are not crystalline (e.g., liquids and amorphous solids) or are quasi-crystalline (e.g., plastics and some metal alloys) scatter radiation over rather large angular ranges. For these situations it is sometimes possible to use detectors that can intercept at one setting a large portion of the scattering pattern. The relatively recent development at ORNL by Cas Borkowski and Manfred Kopp of position-sensitive, large-area detectors for both neutrons and X rays has contributed to a rapid growth in research on such materials.

Neutrons vs. X Rays

A brief examination of the differences between neutron and x-ray scattering methods provides a convenient means for illustrating the significance of the neutron experiments. The differences in experimental procedures are largely dictated by differences in source intensities, source energy spectra, and the origins of unwanted background radiation. Until recently, x-ray experiments typically involved a spectrometer and source that fit on top of a table. By contrast, most neutron experiments, at least at ORNL, are carried out on very large spectrometers, some of which could hardly fit into a typical laboratory room. Furthermore, the neutron source itself occupies a much larger space. The large size of the neutron equipment is necessary because of the low source intensity (large samples and large beams help to increase the signal-to-noise ratio) and because of the massive

Hal Smith (left) adjusts the orientation of a crystal in the neutron beam as Jack Davidson looks on. The diffraction pattern is being measured with the neutron-sensitive scintillation detector and television intensifier system (behind the crystal in this photo) and is displayed instantaneously on two TV monitors.

amounts of shielding required to keep unwanted reactor radiation (gamma rays and high-energy neutrons) from the experimental space.

The energy spectrum of reactor thermal neutrons is very broad with no sharp peaks in contrast to the characteristic line radiation from an x-ray tube. The single-wavelength (monochromatic) beams that are required for scattering studies are already present in the x-ray source, but for neutron experiments beams of a desired wavelength must be obtained by isolating a slice of the reactor spectrum with a monochromating device. Typically, this device is a crystal oriented to produce a diffracted beam that is directed onto the sample and that has a wavelength, λ, given by the familiar Bragg law: $\lambda = 2d\sin\theta$. Although the resulting monochromatization ($\Delta\lambda/\lambda$) is good, it is typically ten times worse than that of characteristic x-ray radiation, and the neutron intensity at the sample is one-hundredth that available from an x-ray tube, even for neutron experiments carried out at HFIR, which has the highest neutron flux in the world!

Why, then, do scientists use neutrons, especially for structural studies for which X rays have proven to be so valuable for 70 years? Actually, x-ray scattering is, and may always be, the preferred method for most such studies. However, because neutrons are much more penetrating in most materials than are X rays, a neutron sample can have more than 100 times the volume of an x-ray sample of the same compound. Therefore, in the scattered neutron radiation, we compensate for much of the relative intensity deficiency of the neutron source. But, more importantly, neutrons are more effective than are X rays for analyzing some atomic structures. This advantage stems from the fact that neutrons and X rays interact with atoms very differently; in essence, neutrons "see" the atomic nucleus, while X rays "see" atomic electrons. Neutrons are therefore used as a probe whenever the scattering cross sections are more favorable for neutrons—as is always the case for magnetic studies and sometimes the case for certain atomic structures.

Because X rays interact with the atomic electrons, the x-ray scattering cross sections are approximately proportional to the atomic number of the scattering element. The scattering thus varies in magnitude in a regular, monotonic way by almost two orders of magnitude from hydrogen to uranium. Elements that are adjacent in the periodic table have almost the same x-ray scattering cross section. Neutrons interact with the atomic nucleus (except for magnetic interactions) in a complicated way, thus leading to scattering amplitudes that fluctuate in magnitude widely and in an irregular manner from element to element. Different isotopes of an element will usually have different neutron scattering properties. Neutron scattering is therefore particularly useful in the study of structural problems that involve combinations of light and heavy atoms or combinations of atoms with nearly equal atomic number. Of course, there are many such problems.

Hydrogen Studies

Hydrogen plays an extremely important role in determining the properties of a wide variety of condensed systems, including metal hydrides, organic molecules in plastics and in biological systems, and liquids ranging from water to electrolyte solutions. Consequently, a significant accomplishment of neutron scattering has been the determination of the location in liquids and solids of hydrogen, which is

Ralph Moon (left) and Bob Nicklow make adjustments on the two triple-axis neutron spectrometers located at the HB-1 beam port of the High Flux Isotope Reactor. The spectrometer on the left provides a beam of polarized neutrons used for studies of the magnetic properties of materials. In this experiment the sample is being studied while in a high magnetic field provided by the superconducting magnet located on the neutron spectrometer.

nearly invisible to X rays because it has only one electron. The first such neutron scattering experiment (to find the positions of hydrogen atoms in crystals) was performed by Henri Levy at the Graphite Reactor in the late 1940s.

Not only does hydrogen (H) possess a rather large neutron scattering amplitude compared to other elements but also its scattering amplitude is very different from that of its isotopes, such as deuterium (D). The success of a recent study of the structure of water by Al Narten and Bill Thiessen of ORNL's Chemistry Division depended largely on the use of samples prepared with different mixtures of light (H_2O) and heavy (D_2O) water. By intercomparing data obtained for the different mixtures, the researchers made an unambiguous and direct measurement of the oxygen-oxygen, oxygen-hydrogen, and hydrogen-hydrogen interatomic distances and coordination numbers. Similar studies of the electrolyte neodymium trichloride in water by Narten and Dick Hahn involved the use of samples prepared with D_2O and with three different neodymium isotopes.

Solid electrolytes are also under intensive study at ORNL for possible use in long-lived batteries needed for electric cars and storage of electricity at power plants. Neutron scattering experiments are providing essential structural information for this study. For example, the positions of water molecules within the ionic conducting planes of hydrated lithium-beta (Li-β) alumina have been determined in a collaboration study involving George Brown of the Chemistry Division and John Bates, Nancy Dudney, and Jim Wang of the Solid State Division. Their results have led to a better understanding of the atomic mechanism by which exposure to water causes a serious deterioration of the ionic conduction in this technologically important material.

Spin-Glass Magnetism

For decades materials scientists have studied the properties of solid solutions or mixtures (alloys) of two or more elements with the aim of producing materials that possess either a combination of, or an enhancement of, the desirable properties of the individual constituents. Usually, the alloy properties depend on the spatial arrangements of the constituent elements. Often these elements have nearly equal atomic numbers—examples are manganese, nickel, iron, and chromium in steels—or the alloy is magnetic. Sometimes an alloy possesses a property not found in any chemical compound or elemental solid. One example is the peculiar "spin-glass" magnetism of copper crystals that have 25% (or less) of the copper (Cu) atoms replaced by manganese (Mn) atoms, i.e., crystalline Cu(Mn). These have been studied extensively by Joe Cable and N. Wakabayashi of the Solid State Division.

On the basis of neutron scattering studies and other types of magnetic measurements, it is generally accepted that at very high temperatures the orientations of the moments on the magnetic atoms (the Mn atoms in this example) in solids are changing very rapidly: at any instant the various atomic moments are oriented randomly. Usually when the temperature is lowered, a magnetic freezing (or ordering) temperature is reached below which the atomic moments become aligned either parallel (ferromagnet) or antiparallel (antiferromagnet) to each other, because of their mutual magnetic interactions. The unusual property of Cu(Mn) is

that even below the ordering temperature, the atomic moments (sometimes called spins) retain their random orientations. In other words, the atomic spins freeze into a random or glassy state (spin-glass), which is loosely analogous to the random arrangement of the atom positions occurring in glass—or so it was believed until the neutron scattering experiments of Cable and Wakabayashi.

By using an incident beam of polarized neutrons (e.g., all the neutron spins oriented up) and by making a polarization analysis of the scattered beam, they were able to separate the magnetic scattering by the Mn spins from the scattering by the Cu and Mn nuclei. The ORNL results showed that neither the Mn atoms nor their spin orientations are distributed truly randomly on the sites of the underlaying copper crystal lattice. Instead, inhomogeneities in the Mn distribution produce regions of short-range atomic ordering (SRO) in which a Mn atom has fewer Mn neighbors than the average value expected for a random distribution. In alloys SRO is quite common and even expected. However, in this case it led to an exceedingly complicated magnetic ordering—that is, a ferromagnetic ordering within crystal regions that possessed SRO was superimposed on antiferromagnetic ordering in regions where the Mn distribution is approximately random. This microscopic connection between the atomic and magnetic ordering, suggested by the results of neutron scattering experiments at ORNL, will undoubtedly lead to new physical pictures of spin-glasses.

Ferromagnetism and superconductivity (electron flow without resistance) are two forms of long-range order that may exist in a material at low temperatures. When both are present, they compete with and may destroy one another. Many physicists have wondered under what conditions they might coexist. Recently, at HFIR, Argonne National Laboratory scientists in collaboration with Herbert Mook of ORNL's Solid State Division discovered that superconductivity and ferromagnetism can coexist in a material chilled to less than one degree above absolute zero. The material is a crystal of erbium rhodium boride grown at Argonne—the only such crystal in existence. A report on the discovery of this unusual phenomenon of coexistence in this and another rare-earth material appeared in *Physics Today* in March 1982.

Vibrational Frequencies

The atoms in solids are not stationary. Because of their thermal energy, they are in constant motion. However, because the atoms are strongly bound to each other, they do not move far. Rather, they move back and forth, or vibrate, around their equilibrium positions. The frequency of vibration depends on the strength of these bonds: for strong bonds, as in diamond, the frequency is high; for weak bonds, as in lead, the frequency is low. However, in no solid is there only one vibration frequency. If we imagine the atoms bound to each other by springs, we can understand that the motions are not independent. The movement of one atom affects its neighbors, and they in turn move, affecting their neighbors, and so on. Imagine the many different kinds of jiggling patterns possible in a collection of trillions of atoms (even a crystal 1 mm on a side contains 10^{20} atoms) in a three-dimensional array. In fact, there are trillions of different vibration frequencies. This problem may appear to be hopelessly complex; however, a remarkable ordering to the "allowed" frequencies exists. Rather than look at the motion of individual atoms, we must look at the possible modes of collective motion of groups of atoms. Many years ago theoretical physicists had concluded that these collective motions were most easily described in terms of vibration waves and that the complicated vibration patterns of the atoms in crystals were simply a collection (or superposition) of many such waves, each having a particular wavelength and frequency. Under certain simplifying, but realistic assumptions, the frequency ω and wavelength λ are connected according to a simple equation [$\omega = A\sin(\pi d/\lambda)$] known as the dispersion curve, or dispersion relation. This equation relates frequency to wavelength in terms of the distance (d) between neighboring atoms and the strength of the bonding force (A). Because the wavelength can vary in increments of interatomic distances from a minimum value of a few angstroms (10^{-8} cm) to a maximum value comparable to the dimension of the crystal (a few centimeters), trillions of vibration frequencies can all be related by this dispersion relation.

A major triumph of neutron scattering research has been the direct and unambiguous experimental determination of the atomic bonding forces by measuring the dispersion relations for hundreds of crystallized compounds and elements. At ORNL these measurements are carried out on triple-axis spectrometers capable of analyzing the energy distribution of the neutrons scattered by a sample. A peak in this distribution determines frequency, and the scattering angle determines wavelength. Such measurements, here and elsewhere, have led to many discoveries. For example, the above equation is usually much too simple to describe measured dispersion curves, thus indicating that the forces between atoms in solids are more compli-

cated than is a collection of springs. In metals, particularly superconductors, the electrons that are responsible for electric currents produce effective forces between atoms separated by large distances. In some compounds (such as samarium sulfide and thulium selenide) a fluctuation of the number of valence electrons occurs. Mook has discovered that such fluctuations strongly perturb the atomic vibrations. In addition, the influences on vibrations of impurity atoms, radiation damage, and phase transitions, to name a few effects, have been studied in detail at ORNL.

Typically a phase transition involves an abrupt change in the spatial arrangement of atoms at a particular temperature. Sometimes this change occurs when a vibration wave with a particular wavelength ceases to vibrate. The corresponding vibration pattern freezes in place as the vibration frequency falls to zero (a "soft" vibration mode) as the transition temperature is approached. The new atomic structure normally can be identified easily through measurements of the diffraction pattern before and after the transition. The Bragg diffraction peaks of one structure are replaced by new peaks of the other structure. An interesting exception to this situation was found in an ORNL study of uranium crystals.

For many years it had been known that abrupt changes in certain physical properties of uranium (heat capacity, elastic constants, and thermal expansion coefficient) occurred at a temperature of 43 K. The observed behavior was typical of that often found at structural phase transitions, but neutron and x-ray diffraction studies had failed to detect any significant changes in the scattering pattern of uranium. A clue leading to the explanation of this puzzling situation was first obtained by Harold Smith of the Solid State Division through his study of the dispersion curves of uranium by neutron scattering. He found that one of the dispersion curves possessed a peculiar shape; a deep anomalous "dip" in frequency occurred in a very narrow range of vibration wavelengths. Although the first measurements were obtained at room temperature, which is far removed from 43 K, this behavior was indicative of a soft vibration mode. Indeed, further measurements at lower temperatures showed that the frequency at the dip approaches zero near 43 K. The new, previously undetected Bragg diffraction peaks of the transformed structure were then easily found, thus allowing a description of the new structure to be made for the first time.

Outlook

Although these examples of recent applications of neutron scattering at ORNL to the study of materials are typical, by no means do they represent the breadth of materials properties under investigation here. Other typical studies, to name a few, include magnetic forces and the energy spectra of spin oscillations; magnetic moment distributions within individual atoms; hydrogen motions in biological systems; the structural, magnetic, and dynamical properties of noncrystalline (amorphous) materials; energy distributions of atoms in liquids; and, of course, small-angle scattering (SANS) studies of polymers, fluxoid lattices in superconductors, precipitates and voids in metals, and the structure of macromolecules in biological systems previously discussed by Wally Koehler in the Summer 1980 issue of the *Review* and by V. R. Ramakrishnan in the Spring 1983 issue.

In addition, the variety of ORNL facilities available for neutron scattering research is expanding. Recent developments include a neutron-sensitive scintillation detector and television intensifier system, which was designed by Jack Davidson of ORNL's Instrumentation and Controls Division and which will allow scattering pattern measurements to be made very rapidly and viewed on a television monitor. This instrument permits sample characterizations to be carried out quickly and certain time-dependent changes in sample properties (e.g., a phase transition) to be studied while they occur. A U.S.-Japan collaboration in neutron scattering will provide ORNL with an additional spectrometer for studies of time-dependent sample properties as well as with new sample environment equipment for achieving extremely low temperatures (less than 0.005 K), high temperatures (2100 K), and high pressures (30,000 atm).

Much of our research involves collaboration with scientists in other divisions at ORNL and with scientists from universities and other laboratories. We encourage such collaborations, and we welcome proposals for new research problems. In fact, our involvement with outside users of ORNL neutron scattering facilities has grown significantly in recent years. All of the facilities are now formally included in a users' program, and experimental time on our spectrometers is made available to anyone who submits a proposal that, in the judgment of a review committee, has sufficient scientific merit. During the past year approximately 130 experiments (including 100 SANS experiments) proposed by outside users were carried out. The future of neutron scattering research at ORNL promises to be just as exciting as was the past. Discoveries of new materials with interesting and important properties seem to be never ending. ornl

Jim Bentley is group leader of the Electron Microscopy Group in ORNL's Metals and Ceramics Division. A native of England, he received his Ph.D. degree in physical metallurgy from the University of Birmingham, England. He joined the ORNL staff in late 1974. His research interests center on structure-property relationships in materials. Here, he checks an x-ray spectrum of a material at the analytical electron microscope.

Characterizing Materials by Analytical Electron Microscopy

By JIM BENTLEY

When an electron beam interacts with a solid material, an array of signals is produced that provides information about the material's composition and structure. At ORNL analytical electron microscopy is used to understand how microstructure affects properties. The goal is to develop principles for the design of alloys that have superior properties, such as high resistance to radiation damage.

Through an understanding of the relationships between properties and microstructure, principles can be developed for the design of advanced materials that have superior properties. Analytical electron microscopy (AEM) is probably the most important technique that provides detailed microstructural characterization used in making these structure-property correlations. What is AEM? According to *Introduction to Analytical Electron Microscopy* (Plenum Press), "When electron beams interact with a solid, it is well known that a bewildering number of possible interactions follow. AEM attempts to take full qualitative and quantitative advantage of as many of these interactions as possible while still preserving the capability of high-resolution imaging." Most current AEM systems are converted transmission electron microscopy (TEM) systems with accelerating voltages of from 100 to 200 kV. Usually specimens are restricted to electron-transparent films.

In the late 1950s and throughout the 1960s, TEM of thin crystalline foils came to preeminence in the study of arrangements of dislocations, grain boundaries, and submicrometer precipitates. Of central importance was the ability to obtain a selected area diffraction pattern from a 1- to 2-μm-diameter region of the specimen. With a specimen titling stage and reference to the diffraction patterns, images could be formed under spe-

PHOTO/JOHN RICHARDS

Jerry Lehman of Oak Ridge Associated Universities studies the microstructure of materials using the high-voltage electron microscope, one of several SHaRE facilities used by both ORNL and university researchers.

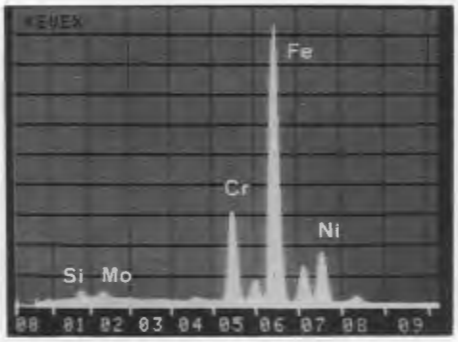
cific diffracting conditions. The kinematical and dynamical theories of electron diffraction could then be used to interpret the image contrast.

In the early 1970s, TEM was being used under the leadership of Jim Stiegler in the Metals and Ceramics (M&C) Division of Oak Ridge National Laboratory to study radiation damage in metallic structural alloys for breeder and fusion reactor applications. Although the 1-MV high-voltage electron microscope (HVEM) considerably enhanced TEM capabilities, it became clear that conventional TEM was insufficient to analyze and understand radiation-induced alloy phase instability and swelling. About this time attachments for scanning transmission electron microscopy (STEM) became available, and energy-dispersive x-ray spectrometers (EDSs) were successfully interfaced to TEMs. A TEM so modified constitutes a simple AEM. In early 1975 Ray Carpenter was responsible for the acquisition of ORNL's first AEM, which operates at 120 kV. In 1978 ORNL obtained two more instruments (also 120 kV)—one equipped with a field emission gun (FEG). This type of electron gun, which requires an operating pressure of 10^{-10} torr (10^{-8} Pa), uses as an electron source a single-crystal tungsten tip with a radius of ~50 nm. The brightness is more than 1000 times that of a conventional tungsten thermionic emission electron gun and allows the formation of small high current-density electron probes necessary for the highest sensitivity in microanalysis experiments. Illumination from such a gun is also highly coherent and enhances the high-resolution imaging performance.

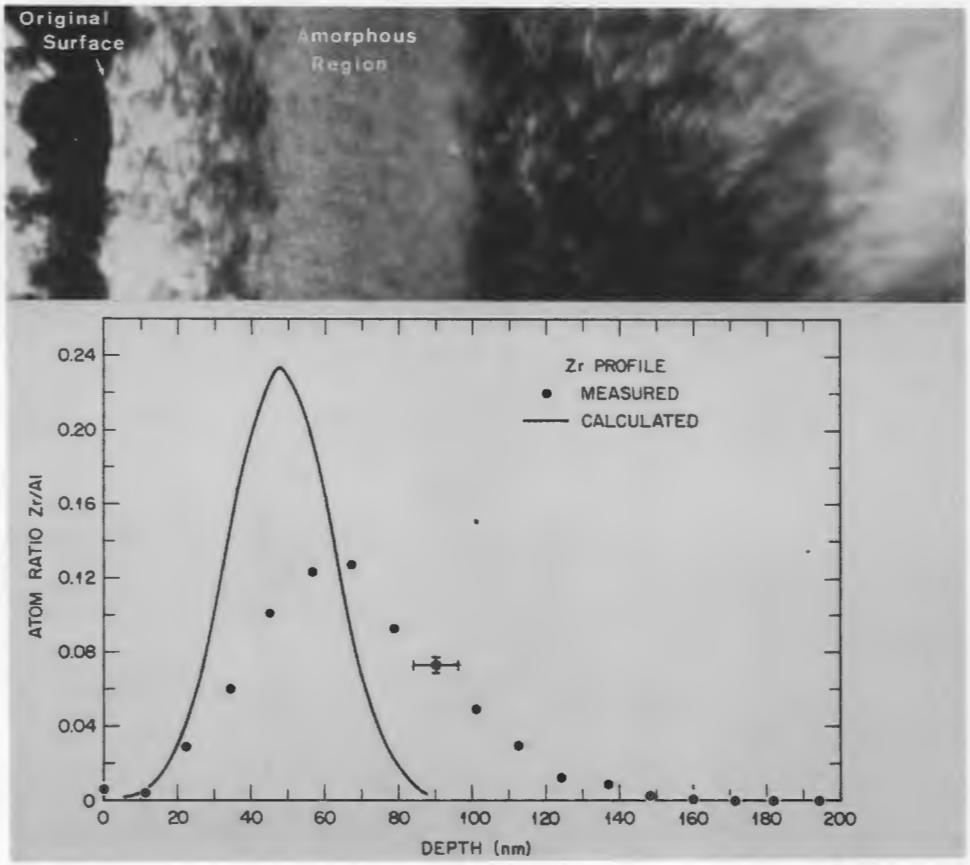
However, the forte of AEM is small-probe work. For structural metals and ceramics, the techniques used most often are energy-dispersive x-ray microanalysis and electron energy loss spectroscopy for elemental compositions and convergent-beam electron diffraction for crystallographic information.

X-ray Microanalysis

The basis of the technique of x-ray microanalysis is that elements present in the specimen are identified from the characteristic fluorescent X rays emitted from atoms ionized by the incident electron beam. The x-ray detector is typically a 30-mm^2 silicon [Si(Li)] crystal, 15 mm from the specimen, cooled by liquid nitrogen and protected by a thin beryllium window. The manufacturers, who had much more experience interfacing such detectors to conventional scanning electron microscopes, originally claimed that the detected X rays came only from the specimen vol-



Energy-dispersive x-ray spectrum from type 316 stainless steel showing the characteristic peaks from chromium, iron, and nickel.



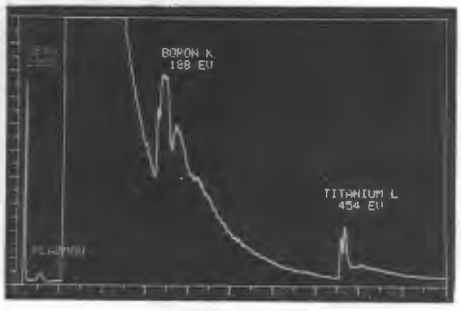
Cross-sectional micrograph of a specimen of alumina (Al_2O_3) ion-implanted with zirconium. The affected region extends to a depth of 200 nm from the surface, with an amorphous region centered at about 70 nm. The measured and calculated zirconium profiles are plotted in the lower part of the figure at the same scale as the micrograph.

ume excited by the electron probe; these claims turned out to be false. Ed Kenik and I worked for some time to understand and correct the situation. We found that apertures in the illumination system of the microscope act as an efficient x-ray generator as they collimate the beam. X rays so produced have energies up to 120 keV and fluoresce the specimen and holder so that the spatial resolution is on the order of millimeters, not nanometers. Our modifications, including non-beam-defining apertures, have now been adopted as standard by instrument manufacturers so that indeed the spatial resolution is approximately equal to the size of the electron probe—5 nm is achievable.

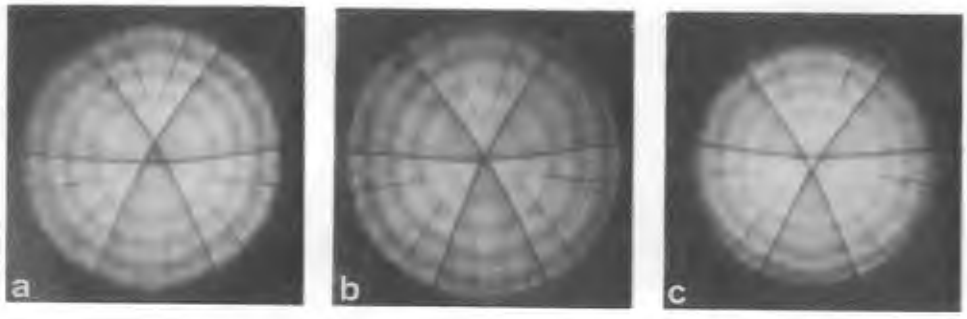
Once a reliable spectrum is obtained, the peak intensities are measured and converted to concentrations. Rather than standards, we use calculated ionization cross sections, based on semiempirical fits to selected data. The cross-section formulations were developed by Nestor Zaluzec while at ORNL on a Wigner fellowship. The fluorescent yield and detector efficiencies also enter into the calculations. This standardless technique produces an accuracy of better than 2%. Although there remain some problems with secondary fluorescence and beam spreading (which is currently being studied by Kenik, using Monte Carlo techniques), x-ray microanalysis remains the easiest and most used analytical technique.

The technique played a key role in understanding the physical metallurgy of swelling and in developing swelling-resistant austenitic stainless steels. Eal Lee and Phil Maziasz have identified elements that undergo radiation-induced solute segregation and have established the compositions of radiation-induced and radiation-enhanced precipitates. The compositions and microstructures of the alloys were adjusted to reduce segregation, improve phase stability, and trap transmutation-produced helium on a fine scale. In this way void nucleation is delayed, and the swelling caused by void formation is reduced. Many of the specimens were bombarded in a Van de Graaff accelerator to simulate radiation damage produced in a reactor, and the damaged volume of material is limited to a surface layer approximately 1 μm thick. No other technique was capable of analyzing, even for screening purposes, the phases present.

Another example of the use of x-ray microanalysis is the recent work of Pete Angelini and Phil Sklad on the measurement of concentration profiles in ion-implanted ceramics. The specimens are prepared in cross section (no mean achievement in itself), and a fully quantitative composition profile is measured by scanning the electron probe in the STEM mode. This pro-



Electron energy loss spectrum from a 10-nm region of titanium diboride (TiB_2). The spectrum shows the zero-loss peak, and the plasmon peak, and the boron K ionization edge. Note the fine structure on the boron edge and the splitting of the titanium L_2 and L_3 edges.



Fine structure (HOLZ lines) in the central disk of convergent beam electron diffraction patterns from $(Ni, Fe)_3V$ alloy. Note the movement of the HOLZ lines as the accelerating voltage is changed: (a) 103.22 kV, (b) 104.22 kV, and (c) 105.22 kV. These voltage changes are used to measure the degree of long-range order in the alloy.

file can be compared to the theoretically modeled one and, perhaps even more importantly, to the damaged microstructure in the form of dislocations, voids, and amorphous layers.

Electron Energy Loss Spectroscopy

The second technique for elemental microanalysis is electron-energy-loss spectroscopy (EELS), which permits us to look at the ionization process directly. The energy of electrons transmitted through the specimen is analyzed by passing them through a double-focusing, 90° magnetic sector spectrometer, which disperses electrons having different energies. Electrons that have lost energy, for example, in the excitation of plasmons or ionization of atoms in the specimen, are bent more by the magnetic field. The magnet current is ramped, and the electrons of different energies pass sequentially through slits (typically 2 μm wide) to a scintillator-photomultiplier tube detector operated both in the analogue and single electron counting modes to cover the wide dynamical range of intensities of 10^6 or more.

Although EELS can be used for any element, it is particularly useful for elements of low atomic number ($Z < 11$) whose characteristic X rays are absorbed in the beryllium window, gold contact layer, and silicon dead layer of the EDS detector. Also, the fluorescence yield (the fraction of ionized atoms that decay by x-ray emission rather than by emission of Auger electrons) is very small for low-Z elements. Finally, the collection efficiency of EELS can exceed 50% compared to the 1% or less collection efficiency of EDS.

Quantification of EELS data, however, is more complex than for EDS spectra. The peak-to-background ratio is much worse, and the background decreases rapidly with increasing energy loss. An accuracy of 5% or better can be achieved but appears to be limited by approximations in the cross-section calculations.

Two EELS spectrometers were designed by Zaluzec and built at ORNL. More recently, high-performance commercial spectrometers became available, so we replaced one of our home-built instruments with a commercial one.

In structural ceramics, the low-Z elements, particularly boron, carbon, nitrogen, and oxygen, are important constituents. Intergranular phases (regions of different composition or crystal structure at the boundaries between crystalline grains) may reduce the mechanical properties of materials subjected to high temperatures. EELS has proven invaluable in identifying such microphases in complex ceramics, thus allowing changes to be made in the composition or processing treatments to mitigate the adverse effects of the microphases.

To date, EELS has been used only for microanalysis from ionization-edge intensities. Potentially, however, there is a wealth of information on valence and bonding from near-edge fine structure. Also, extended electron-loss fine structure, which is analogous to the x-ray case of extended x-ray absorption fine structure, can provide information on the atomic environment of a particular elemental species. All of this information on valence, bonding, and atomic environment should be obtainable from 10-nm-size regions.

Electron Channeling

A recent development in microanalysis by EDS and EELS uses electron channeling in crystal lattices to good effect. Near a Bragg reflecting orientation, the electrons propagate in a standing wave pattern with the periodicity of the Bragg reflecting planes and with the maxima either on the crystal planes or between them. The apparent composition from spectra

Ed Kenik, ORNL director of the SHaRE program, uses an analytical electron microscope that is part of the Metals and Ceramics Division facilities available for collaborative research with outside users.

obtained from the same region of the specimen under different diffracting conditions can be used to determine the specific sites within the crystal lattice of a particular element. The spatial resolution is not as high as in normal microanalysis because of the requirement of a nearly parallel electron probe, but regions much less than 1 μm in diameter can be easily analyzed.

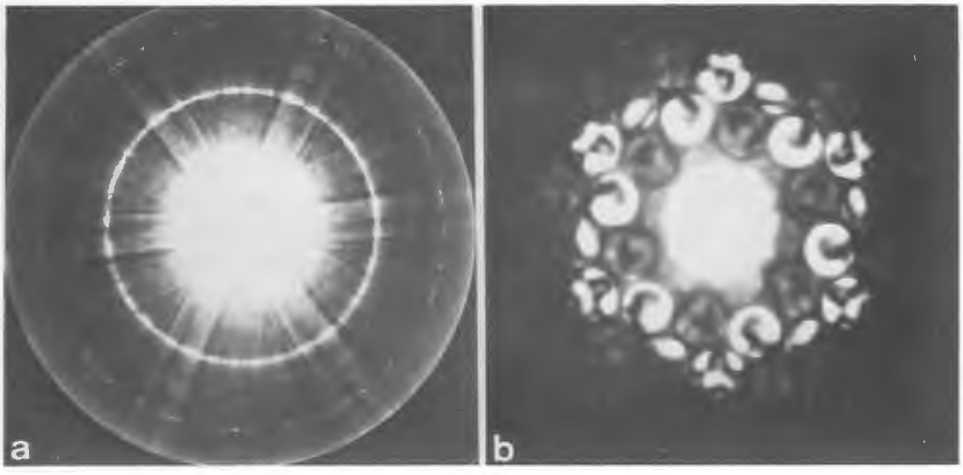
Steve Pennycook of ORNL's Solid State (SSD) Division has been applying this technique to doped semiconductors, in particular antimony in silicon; he has measured the fraction of antimony that substitutes for silicon in silicon lattice sites. Comparisons to ion channeling showed good agreement, but the measurements made in the electron microscope of the role of precipitates and their state of coherency allowed a better understanding of the results.

Convergent-Beam Electron Diffraction

The small electron probes so necessary for STEM imaging and microanalysis also allow one to obtain a microdiffraction pattern from a region of the specimen approximately the size of the probe, which may be less than 10 nm. This resolution is far superior to that of selected area diffraction, which uses an aperture in the first image plane to define the "selected" area and is limited by spherical aberration of the objective lens to approximately 1 μm. The Bragg reflected beams in these diffraction patterns formed with almost parallel illumination (beam divergence $<10^{-2}$ mrad) become disks with the convergent beam (~10 mrad) conditions necessary to form a small probe. The technique is therefore most generally known as convergent-beam electron diffraction (CBED). CBED literally adds another dimension to the information in electron diffraction patterns. Three-dimensional information is present as fine structure in the Bragg disks and in the intensity distribution at large scattering angles. Most distinctive and useful are fine dark lines that can be thought of as arising from intensity diffracted into Bragg reflections on high-order Laue zones—hence, "HOLZ" lines.

The HOLZ lines are extremely sensitive to changes in lattice parameters—in fact, changes of a few parts in 10^5 can be detected. This property was put to use by Dave Braski (M&C), Joe Cable (SSD), and me to measure the long-range-order parameters in nickel-iron-vanadium [$(Ni, Fe)_3V$] alloys, ordered alloys developed at ORNL. We found about a 0.5% reduction in the lattice parameter as this alloy develops long-range order from the disordered state. Instead of measuring the relative movement of HOLZ lines caused by different lattice parameters in specimens with different degrees of order, we adjusted the accelerating voltage to compensate for the change in lattice parameter. Neutron diffraction was used to generate calibration curves by measuring the degree of order from superlattice-to-fundamental intensity ratios on a set of "standards." Braski then used the technique to quickly and inexpensively measure the degree of order in irradiated specimens and in weldment heat-affected zones—measurements not possible by neutron diffraction because of the small specimen size. Joe Horton is also using the technique to study rapidly solidified, ductile nickel aluminides based on Ni_3Al that have boron additions.

By far the most common use of CBED is to determine crystal symmetry. The crystal point group and space group describe the symmetry of the shape of the crystal and of the atomic arrangements on the crystal lattice, respectively. The crystal point group can be obtained from the observed symmetry of the diffraction pattern. The presence of three-dimensional information is what often allows an answer to be obtained. From the behavior of dynamical absences in the patterns, glide planes and screw axes can be identified in a fairly straightforward manner. Thus, it is possible to determine space groups from 10^{-15}-g quantities of material! X-ray crystallography usually requires single crystals with millimeter dimensions. The crystallographic data, along with unit cell dimensions, play a vital role in phase identification. Dave Stephenson (M&C) and I have used CBED to determine crystal symmetry of pre-



Convergent-beam electron diffraction patterns from 100-nm precipitates of $Al_{12}Mo$ formed in aluminum ion-implanted with molybdenum. (a) Angular range of view is approximately 20°. The pattern has threefold rotational symmetry. (b) Higher magnification view of the center of the pattern shows sixfold rotational symmetry. Such patterns provide positive identification of the precipitates.

cipitates in aluminum implanted with molybdenum ions.

Finally, in a Shared Research Equipment (SHaRE) program study on catalyst-support interactions, Ashok Dhere (University of Kentucky) and I obtained microdiffraction patterns by scanning a 2-nm probe across catalyst particles in the STEM mode and recording the diffraction patterns with a videocamera system developed by Joe Horton. Frame-by-frame examination of the videotape thus allows crystallographic data to be obtained from 2-nm regions of the specimen in <0.02 (1/60) s. Such information cannot be obtained by normal photographic techniques because of the problems of specimen damage during the exposure of the film.

Combined Techniques

The real power of AEM is demonstrated most effectively when the various capabilities of an instrument are used in combination to give a complete description of the microstructure of a material or the absolute identification of a second phase. Many of our applications make use of the availability in one instrument of high-resolution imaging and high spatial resolution microanalysis and microdiffraction capabilities. In a study of second-phase particles in austenitic stainless steels, the combination of AEM techniques proved invaluable. Convergent-beam electron diffraction was used for precipitate identification and determination of orientation relationships, x-ray microanalysis and EELS were employed for compositional measurements, and high-resolution imaging (weak beam and lattice imaging) was used for the determination of the interphase boundary dislocation structure.

In another example, Sklad, Angelini, and I used AEM to identify intergranular phases in liquid-phase sintered ceramics made of titanium boride and nickel (TiB_2-Ni). Both Ni_3B and a complex face-centered cubic τ boride (approximately $Ni_{20}Ti_3B_6$) have been identified. X-ray microanalysis and EELS were used to determine compositions (EELS particularly for boron), and CBED was used to determine crystal point groups and lattice parameters. High-resolution imaging was then used to investigate the structure of TiB_2 grain boundaries where microanalysis revealed appreciable segregation of nickel and iron.

Future Prospects

Although the above examples of recent applications of analytical electron microscopy at ORNL indicate what is achievable today, a number of exciting developments are planned. First, within the next year we expect delivery of a 300-kV instrument. The specifications indicate improved performance in all areas. The higher energy electrons allow for greater penetration so that thicker specimens may be imaged. Some of the experiments now performed in the HVEM, which has no analytical capabilities, could be carried out more productively in a 300-kV AEM. The interpretable point resolution is ~0.2 nm compared to the 0.4 nm of our 120-kV instruments; the sensitivity of EDS is improved, and beam spreading is reduced; and for EELS the allowable specimen thickness (which is a very practical limitation at 120 kV) is increased by more than a factor of 2.

A related exciting development is the acquisition of a field-ion microscope—atom-probe system with both a high-resolution "Poschenrieder" analyzer and imaging-atom-probe capabilities. In this technique the specimen is in the form of a sharp needle with a tip radius of ~100 nm. In addition to single-atom resolution of the surface atoms, field evaporation allows single specific atoms to be identified. The imaging-atom-probe mode allows distribution "maps" of a particular element with near atomic resolution to be obtained. Under the leadership of Mike Miller we plan to use this system for microanalysis when the required spatial resolution is less than the 5- to 10-nm limit of AEM. An important feature of the proposed research will be the use of AEM both for specimen screening and comparative microanalysis on the same specimen. ornl

BOOKS

Tales about Metals, *S. I. Venetsky, Translated from the Russian by N. G. Kittell, Mir Publishers, Moscow (1981). 211 pp. Reviewed by Carolyn Krause,* Review *editor.*

Many metals such as copper, gold, iron, lead, mercury, silver, tin, and zinc have been known to mankind for thousands of years. Other metals such as platinum, titanium, and uranium have been put to use only in recent decades. Although the 80 metals in the periodic table vary greatly in weight and properties, they belong to the same family and have fascinating histories. How fascinating? To find out, read Venetsky's book.

This informative, entertaining book intersperses humorous and tragic stories with colorful facts about 24 metals—including their discovery, the origin of their names, their properties and uses, and the location of large deposits. On every page spread are charming colored drawings, often of human figures labeled with elemental symbols.

Tales about Metals was recently translated from the third edition of the 1970 book, which received the best-book-of-the-year diploma in the science journalism contest of the Moscow Journalists' Organization and a diploma in the USSR Znaniye Society's annual contest for writers of popular science. As an editor, I found the quality of its science writing good, but the translation itself could have benefited from more editing and proofreading. Some of the stories are sketchy and raise questions about their credibility or the consequences of some actions. Also, though rich in facts, the book unfortunately is not useful for quick reference because it lacks an index and has a table of contents whose chapter titles omit the names of the elements discussed in the text.

Even so, when read from cover to cover, *Tales about Metals* is a valuable source of information and anecdotes about metals and their compounds. Here are some examples of facts and stories that I found particularly useful and interesting.

- *Lithium*, the lightest metal, reduces the solubility of glass in water, an important fact for tea drinkers who like only sugar, not glass, in their beverage. Venetsky tells the story of how American physicist Robert Wood used lithium chloride in 1891 to reveal his landlady's cooking habits. It was suspected that the morning stew that this Baltimore boardinghouse matron fed her tenants consisted of leftovers collected from plates at dinner the night before. To test this idea, Wood sprinkled harmless lithium chloride on a few hunks of steak that he purposely left on his dinner plate. The next day he collected some pieces of breakfast meat, examined them through a laboratory spectroscope, and spotted the tell-tale red line of the spectrum produced by lithium.
- *Beryllium* minerals include emeralds, which were first mined 2000 years ago by slaves of Cleopatra, queen of Egypt, and which were shipped to palaces in the Middle and Far East. During World War II, the Germans managed to tap into the American supply of beryllium by inducing "watchmakers" from neutral Switzerland to order large quantities of it from the United States for watch springs. Indeed, beryllium parts turned up in the Germans' aircraft machine guns.
- About 2000 years ago a stranger presented the Roman Emperor Tiberius with a cup made from a light metal that was shiny like silver and obtained from clay. Legend has it that the emperor ordered the stranger beheaded because he feared that the new metal—*aluminum*—might devalue the gold and silver in the royal treasury. The Emperor Napoleon III gave his most illustrious guests aluminum spoons and forks while his less honorable guests had to settle for silver and gold utensils. Aluminum became less of a precious metal after 1886 when an American (Charles Hall, a student at Oberlin College at the time) and a Frenchman independently developed an electrolytic method of aluminum production.
- Henry Ford learned about the lightness and hardness of *vanadium* steel when he picked up a fragment of a crashed car during a French motorcar race in 1905. He was so impressed that he instigated the development of a superior American vanadium steel that he could use to make lighter, cheaper cars.
- The 16th-century chemist Paracelsus performed a magic trick that his audiences deemed a miracle. He would show a painting of snow-covered trees and hills and then transform the winter landscape into a summer one complete with foliage and grass. All he did was to move a lit candle closer to the back of the canvas to heat up the paint. The paint used was *cobalt* chloride with a bit of nickel or iron chloride. It is normally colorless; however, if heated, it turns green.

In the Middle Ages Venetian craftsmen used cobalt to make a blue glass of unsurpassed beauty and popularity. To guard the secret of the process, in the 18th century the government of Venice moved all glass factories to an island and permitted no outsiders to visit and no glass-makers to leave without permission. When an apprentice fled the island and set up his own glass shop in Germany, he met a predictable fate: his shop was burned down and he was stabbed with a dagger.

• *Copper*, which was alloyed with zinc to make bronze for thousands of years, was used to make coins in Russia in the 17th century. When the copper coins replaced silver money, food prices began to rise. As a result, an uprising, known in Russian history as the "copper riot," occurred in Moscow in 1662. The riot was ruthlessly suppressed, but the copper money was replaced by silver to appease the people.

• Venetsky tells several interesting stories about *silver*. The Greek army under Alexander the Great became ill with a gastrointestinal disease, although the military commanders were generally not sick. The explanation for this oddity was that the soldiers drank from tin cups, whereas the commanders' cups were made of silver, which kills bacteria when it is dissolved in water. The spendthrift Emperor Nero of Rome had thousands of mules shod with silver. Although many treasure hunters have tried diving in ocean waters where Spanish galleons were known to have sunk, they could have found silver recently just below the land surface in Gotland, a Swedish island. Some archeologists believe that 1000 Arab silver coins found at the island's surface were dug up by a rabbit!

• When *tin* is subjected to freezing temperatures, it disintegrates into powder—a phenomenon known as "tin plague." This metallic disease caused the death of Captain Robert Scott, the British polar explorer, and his comrades following an expedition to the South Pole in 1910. They had left caches of food and kerosene for their trip back, but when they returned, they found that their fuel had leaked out of its cans. The reason: the kerosene cans had been soldered with tin, which "caught a cold" and disintegrated.

• *Gold*, the beautiful yellow metal that has caused wars, murders, and immense suffering in the name of greed, is the subject of many anecdotes in this book. Some stories concern the search by alchemists in the Middle Ages for the "philosopher's stone" to transmute baser metals into gold and the plundering of gold from the Aztecs and Incas by Spanish and Portuguese conquistadors. I like the story about the man who bought the roof of an ancient church across from the Philadelphia Mint. The church parishioners gladly sold him the roof because the church was being renovated at the time. It never occurred to them that the buyer would scrape paint off the roof, burn it, and recover 8 kg of gold—of much greater value than the roof itself. The source of the gold dust was the pipe of the Mint's smelter. Another of my favorite stories concerns Nobel Prize winner Niels Bohr. Before fleeing Nazi-occupied Copenhagen in 1943, he left behind his gold Nobel medal, which he had dissolved in a retort of aqua regia (a mixture of nitric and hydrochloric acids). When he returned after the liberation of Denmark, Bohr chemically extracted the gold from the solution and had a replica of the medal made.

• *Mercury*, the only metal that is liquid under ordinary conditions, is a well-known poison but is safely found in human mouths. Mercury has the ability to dissolve metals and form amalgams, such as silver-mercury amalgams used to fill our teeth. Early in this century one scientist thought he saw evidence that he had obtained gold from mercury by passing electricity through mercury vapor. What happened was that mercury droplets on his fingers had dissolved gold from the rims of his glasses which he touched; thus, he had inadvertently transferred gold from his glasses to the mercury he was studying.

• *Lead*, which is used largely for electric batteries, is both a poison and a protector—against radiation and against knock in gasoline engines. Some American toxicologists attribute the decline of the Roman empire to lead poisoning; they believe that the 25-year lifespan of Roman aristocrats resulted from their heavy use of lead dishes and lead cosmetics.

In his chapter on *zirconium*, Venetsky twice mentions the importance of separating hafnium from zirconium to produce pure zirconium, which is used in nuclear reactors because of its transparency to neutrons and its resistance to high temperatures. But Venetsky fails to note that the difficult process of separating the two elements was developed in Oak Ridge.

Venetsky mentions alternatives to conventional prospecting and mining for locating and developing valuable mineral deposits. He suggests that dogs can be used as ore-seekers to sniff out deposits of beryllium and nickel; that certain sea animals, plants, and bacteria can extract metals such as copper, gold, and vanadium from the environment; and that rockets could pull asteroids into the earth's orbit for production of iron and nickel. If scientists and engineers succeed in using these methods on a large scale, there may be many more interesting tales about metals for Venetsky and others to tell. ornl

Solid State Physics Theory

Everyone has heard an ethnic joke or two, but few have been told a physicist joke. Here is a good example of the genre. A farmer was not getting good egg production from his hens. He tried remedies suggested by neighboring farmers, by his local co-op, and even by the agriculture department at the state university, all to no avail. Finally, in desperation, he decided to ask a theoretical physicist about his problem because he had heard how smart they were (probably from another theoretical physicist). The theoretical physicist came to the farm, visited with the hens for a while in the chicken coop, and then went home and worked on the problem late into the night. Early the next morning, he rushed back to the farm and announced excitedly that he had the solution. "To start with," he told the farmer, "assume that we have a spherical chicken."

The theorists in the Solid State Division of Oak Ridge National Laboratory try to refrain from such fowl invention. This is because they work closely with the experimentalists in the division, who rarely experiment on systems for which the "spherical chicken" approximation is valid. Because a wide range of experimental programs exist in the division, there is a correspondingly broad spectrum of theoretical activity. At present, this research may be grouped into four areas: surfaces; electronic, magnetic, and vibrational properties; particle-solid interactions; and laser annealing. Much overlap exists among these areas, and any one theorist may work in several of them concurrently.

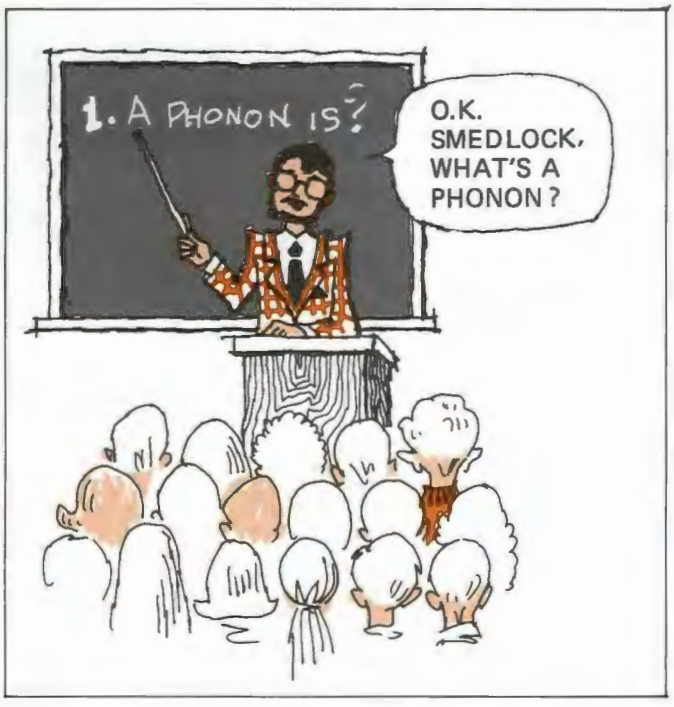
The study of surfaces has grown rather dramatically in recent years because surface properties are decisive in many material problems encountered in the development of advanced energy systems. A first question to ask about a surface is, "Where are the atoms in the surface region located?" One of the methods commonly used to study the crystallography of surfaces is low energy electron diffraction (LEED). In the past, it was usually assumed that only the atoms in the very outermost layer were displaced or "relaxed" from the positions they would have occupied in the bulk crystal, and there was some disagreement about the accuracy of surface structures deduced from analysis of LEED data. Recently, a painstaking experimental and theoretical investigation of several copper and silver surfaces has established that LEED can provide surface crystallographic information accurate to about 2 pm (2×10^{-12} m), provided that sufficient care is taken both in the data collection and in the theoretical analysis. Moreover, this study also showed conclusively that the relaxation of several atomic layers must be considered to explain the data.

Research on the electronic, vibrational, and magnetic properties of solids encompasses a variety of subjects. The materials studied may be metals, semiconductors, or insulators; they may be perfectly ordered pure crystals or amorphous solids with short-range order but no long-range periodicity, or they may contain point defects such as substitutional impurities or extended defects such as grain boundaries.

Theoretical work within this broad area frequently is closely tied to the strong neutron scattering program in the Solid State Division. A recent collaborative effort on ferromagnetism in nickel and iron provides a good example of the interplay between theory and experiment. Unusual results found in neutron scattering measurements on ferromagnetic nickel motivated further theoretical calculations; these then suggested new experiments that verified the theoretical prediction of a new type of magnetic excitation in nickel.

Neutron scattering is also the best method available to study "phonons," the collective atomic vibrations in solids. Comparison of predictions with experimental phonon data provides information about the validity of theoretical models for the forces that hold the solid together. In the early and middle 1970s, anomalies were discovered in the phonon data for certain transition metals and transition metal compounds. These anomalies in the data gave rise to a plethora of models and explanations, most of which were phenomenological and involved some sort of anomaly in the electronic response function, which describes how the electrons respond to ionic motion. First principles calculations for phonons in the 4d transition metals (e.g., molybdenum and niobium) performed at ORNL have now shown that the phonon anomalies can be explained without invoking any peculiar behavior in the electronic response.

Particle-solid interactions may be of intrinsic interest, or they may be used as tools to study other phenomena. An example in the first category is radiation damage in metals, which has direct relevance to

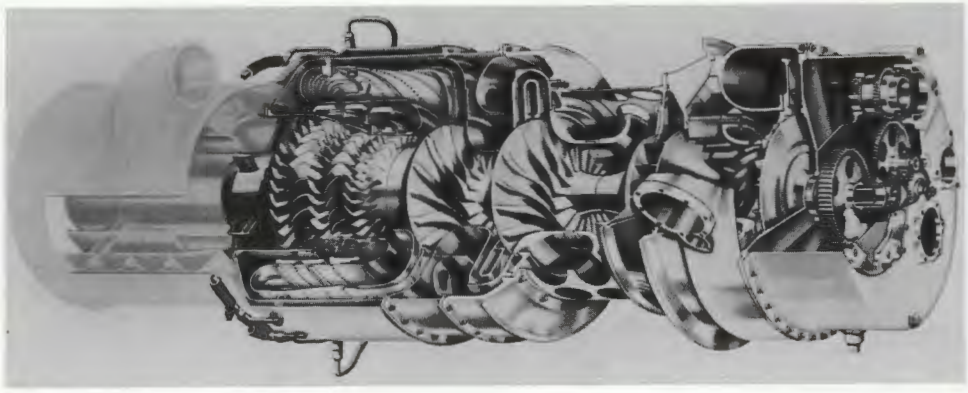


technological problems in both fission and fusion reactors. Numerical methods developed to study this problem have recently been extended to displacement damage in monazite and related minerals, which may prove to be suitable hosts for the isolation of long-lived nuclear wastes. A second example is fast ion conduction in solid electrolytes such as β and β'' alumina; fast ion conductors may be used to develop a new generation of storage batteries.

When a beam of ions is projected onto a solid, the scattering and absorption of the ions depend on the direction of the beam relative to the crystallographic axes of the target. For certain special orientations of the beam, the ions are "channeled" through open regions in the solid without much loss. The pioneering work on channeling, both theoretical and experimental, was done in the Solid State Division in the early 1960s. Now, through comparisons of numerical simulations with experimental data, channeling has become a tool to probe atomic positions and potentials in solids. More recently, it has been used to complement other techniques such as LEED to study surface crystallography.

Laser annealing is a hot research subject, primarily because of its potential for the processing and manufacture of semiconductor devices such as solar cells. When a semiconductor such as silicon is illuminated by a short pulse of high-intensity laser light, then, under suitable conditions, all crystallographic imperfections are removed down to some depth, and any electron donor or acceptor impurities present are redistributed much more uniformly. It is even possible to exceed the normal solubility limits for the electrically active dopants by subjecting the silicon to ion implantation and then laser-annealing the sample. It is virtually certain now that these phenomena occur because the near-surface region of the crystal melts when the laser pulse is applied; the crystal then regrows epitaxially (and perfectly) as the melt front sweeps back to the surface. The dopants can diffuse rapidly in the liquid phase, thus ensuring their more uniform distribution after the annealing process is completed. Results from calculations based on the melting model agree with a wide variety of experimental data taken at ORNL and elsewhere.

At the beginning of this Cook's tour of theoretical research in the Solid State Division, it was made clear that the days of the spherical chicken are numbered. So too are the days of the back of the envelope on which theoretical physicists were once wont to make calculations. The kinds of problems being studied and the need to generate accurate numerical predictions for real systems from nonsimplistic theories have forced the theorists to rely more heavily on large, high-speed computers. The ever-increasing computing demands of theorists and other scientific users have taxed the Laboratory's mainframe machines. Several ways currently under consideration to solve this problem include purchasing so-called super-mini computers for relatively small communities such as the Solid State Division and providing time on Class VI supercomputers such as the Cray 1 to users throughout the Laboratory.—*Mark Mostoller and John Cooke, Solid State Division.*



This auxiliary power unit of a turbine engine could use ductile nickel aluminides, such as those developed at ORNL, for its turbine disks and other components. (Photograph courtesy of Garrett Turbine Engine Company.)

Design of Ordered Intermetallic Alloys

By C. T. LIU

Many advanced heat engines and energy conversion systems must be operated at reduced temperatures because of inadequate performance of current structural materials at high temperatures. Thus, these engines and power plants are not as efficient as they could be. Current heat-resistant alloys, such as stainless steels and superalloys, are ductile and fabricable but are not strong enough at elevated temperatures. Structural ceramics, on the other hand, have excellent high-temperature strength but are extremely brittle and have very low fracture toughness. Hence, in an age when energy efficiency and fuel conservation are highly valued, a pressing need exists to develop innovative materials for structural service at elevated temperatures. Recently, significant achievements have been made in the Metals and Ceramics Division of Oak Ridge National Laboratory in the design and development of a new class of stronger structural materials based on ordered intermetallic alloys.

These alloys are a unique class of materials with an atomic arrangement distinctly different from conventional metallic alloys. Below the critical ordering temperature (T_c), alloying atoms in ordered intermetallic alloys arrange themselves periodically and form a superlattice crystal structure. Unlike standard alloys, which have weak atomic bonds, ordered intermetallic alloys have a strong chemical arrangement that reduces the mobility of atoms and results in good structural stability and resistance to high-temperature deformation. The major difficulty with these materials, however, is their tendency to exhibit brittle fracture and low ductility; in other words, they crack or break easily when stressed at ambient temperatures. This poor fabricability and low fracture toughness have limited the use of ordered intermetallic alloys as engineering materials.

We have conducted a systematic design study to understand the brittle fracture behavior and to overcome the brittleness problem in ordered intermetallic alloys. We have used two approaches to design ductile intermetallic alloys. One is to control the ordered crystal structure by "macroalloying"—that is, by adding a controlled amount of elements to the atomic lattice to stabilize ductile superlattice structures. The other is to control grain-boundary chemistry by "microalloying"—that is, by adding tiny amounts of elements that tend to concentrate in the grain boundaries (defect regions between periodically arranged atoms) to enhance grain-boundary cohesion.

The bulk material of the ordered nickel-vanadium alloy [Ni_3V (75 at.% Ni-25 at.% V)] and the cobalt-vanadium alloy (Co_3V) is brittle because of a limited number

C. T. Liu shows Maggie Winsbro some shiny samples of ductile nickel aluminide designed and made at ORNL. The new alloy's high-temperature properties have been determined at the Instron testing machine shown here.

By adjusting the composition of nickel aluminide and adding small amounts of boron and manganese and large amounts of iron, ORNL metallurgists have produced a new intermetallic ordered alloy that is stronger than conventional structural materials at elevated temperatures. An I-R 100 award winner in 1983, the alloy is also ductile enough to be used in automobile valves, turbine disks, and other components of high-temperature heat engines and power plants.

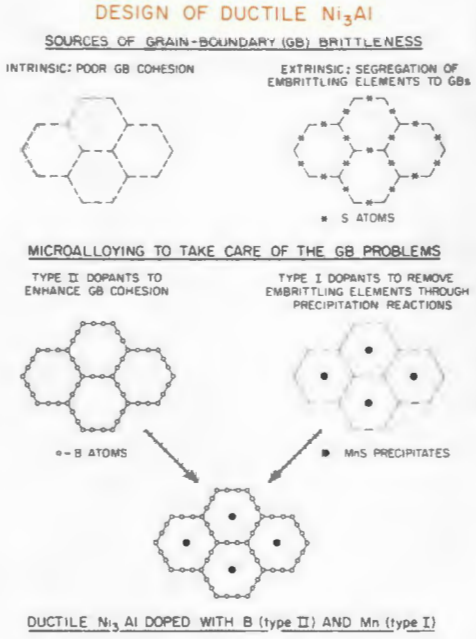
of slip systems available in their tetragonally or hexagonally ordered crystal structures; by contrast, cubically ordered structures have more slip systems and are more ductile. We found that such tetragonally or hexagonally ordered structures can be altered systematically to cubically ordered structures by controlling the concentration of "free" electrons in the alloys. This shift from a hexagonally to a cubically ordered structure can be achieved by partial replacement of nickel and cobalt with iron (Fe) atoms, which lowers the free electron content and stabilizes the cubically ordered structure. Controlling the free electrons stabilizes the cubically ordered structure in the $(Fe,Ni)_3V$, $(Fe,Co,Ni)_3V$, and $(Fe,Co)_3V$ alloy systems.

In testing, we found that all the cubically ordered alloys having extensive slip systems are ductile, with tensile elongation exceeding 35% at room temperature. By comparison, hexagonally ordered alloys such as Co_3V and $(Co,Ni)_3V$ are all brittle and have very little ductility (<1%) at room temperature. We consider this modification to be a major achievement in the design of ductile alloys.

Ordered Aluminides

Recently, our efforts in high-temperature alloy design have focused on ordered nickel aluminides (Ni_3Al). Although single crystals of Ni_3Al are ductile, polycrystals are extremely brittle and have little or no ductility at ambient temperatures. The brittleness is associated with poor grain-boundary cohesion, resulting in intergranular cracking and very little plastic deformation within grains. For example, a Ni_3Al cast ingot hot rolled at 1200°C at ORNL was almost pulverized because of extensive cracking along the grain boundaries, vividly demonstrating the grain-boundary brittleness in Ni_3Al.

To solve the problem of embrittlement in grain boundaries in Ni_3Al, we adjusted the composition of the polycrystals by adding a small amount of dopants (usually <1%) for controlling the chemistry and cohesion of grain boundaries. A series of dopants, including titanium (Ti), cerium (Ce), manganese (Mn), boron (B), and carbon (C), were added to Ni_3Al; the selection of these dopants was based on empirical experience and theoretical consideration of atomic bonding among alloying elements. Of the dopants added, boron was found to be the most effective in improving the ductility and fabricability of Ni_3Al, provided that the alloy contains less than 25% Al. Manganese additions further improve the fabricability and formability of boron-doped Ni_3Al. In short, we found that by making nickel aluminide that is 76% nickel and 24% aluminum and by microalloying it with boron and manganese, we produced a material that can be cold fabricated readily into sheets, foils, rods, and wires. The outstanding form-



In designing ductile nickel aluminide (Ni_3Al), ORNL metallurgists have overcome brittleness caused by poor grain-boundary cohesion by adding boron (B) to improve the grain-boundary cohesion and manganese (Mn) to remove sulfur, an embrittling element that concentrates in grain boundaries.

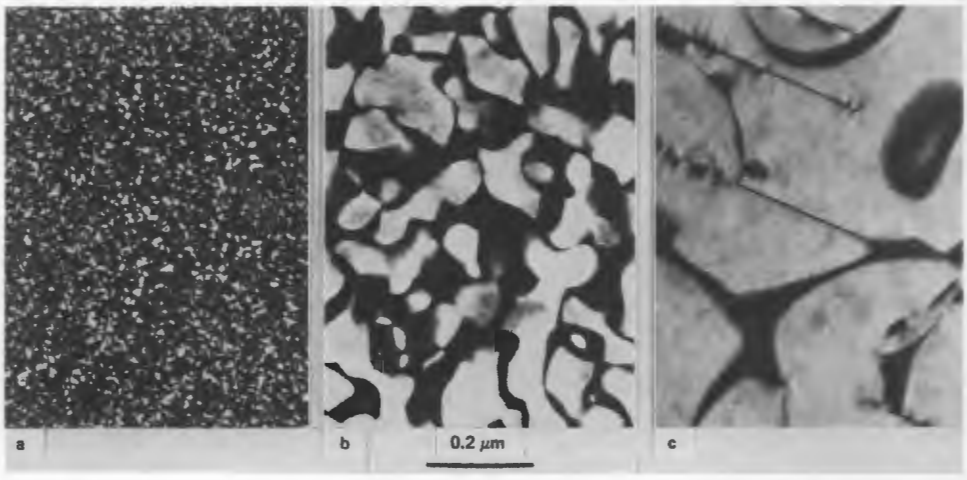
ability of the aluminide stems from a combination of excellent ductility and stretchability. Microalloyed Ni_3Al exhibits a room-temperature tensile elongation of above 50%—the highest ductility ever achieved by polycrystalline aluminides.

Carl Koch and I have also developed a nickel-iron (NIFE) aluminide composed of 10 to 12% Al, 9 to 14% Fe, 0.5 to 1.0% Mn, 0.5 to 1.0% Ti, 0.03 to 0.07% B, with the balance being Ni. The NIFE aluminide, which in 1983 received an I-R 100 award from *Industrial Research & Development* magazine, is very ductile and strong and resistant to oxidation and deformation at high temperatures.

Role of Dopants

Microanalytic tools, including the transmission electron microscope (TEM), Auger electron spectroscope (AES), and scanning electron microscope (SEM), have been used to study the function of microalloying elements. No borides were detected in boron-doped Ni_3Al, indicating that boron additions essentially remained in solution instead of forming second-phase particles. AES is an ideal tool to analyze the composition of atomic layers on surfaces or interfaces such as grain boundaries. AES analysis by Cal White revealed that boron has a strong tendency to concentrate in grain boundaries in boron-doped aluminides. Furthermore, recent quantum-mechanical modeling studies on electronic effects indicate that boron atoms may enhance atomic bonding, improve grain-boundary cohesion, and reduce the tendency toward brittle intergranular fracture.

Sulfur (S), an impurity in Ni_3Al, also tends to concentrate in grain boundaries. But unlike boron, sulfur is harmful; it promotes embrittlement of grain boundaries and intergranular fracture in nickel-base alloys. We suspect that the beneficial effect of manganese in Ni_3Al is to remove sulfur from grain boundaries by forming second-phase particles, such as MnS.



Transmission electron micrographs show the growth of ordered domains (dark fields) over time in the long-range-ordered alloy $(Fe, Co)_3V$ at 700°C after (a) 3.6 ks (1 h); (b) 60 ks (16.7 h), and (c) 0.96 ms (266.7 h).

Property Tests

Mechanical properties of the aluminides were determined by pulling specimens until they cracked or broke as the test temperature rose. Unlike conventional metallic alloys, the yield strength of boron-doped Ni_3Al increases with increasing temperature, reaching a maximum around 600°C. In other words, this material can be subjected to increased mechanical stresses at higher temperatures without deforming. The aluminide is, thus, much stronger than commercial alloys at elevated temperatures.

Furthermore, the strength of the aluminide can be substantially increased by solid solution hardening and particle strengthening with alloy additions. The advanced aluminide alloys we developed display a yield strength at 600°C as high as 830 MPa (120,000 psi), which is more than six times that of type-316 stainless steel and four times that of Hastelloy X, a commercial nickel-base, solid-solution superalloy. The advanced aluminides are also stronger than particle-strengthened superalloys such as Waspaloy. For instance, at 870°C the tensile strength of the

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Liu checks a printout at a high strain-rate Instron testing machine used to determine properties of alloys at high temperatures.

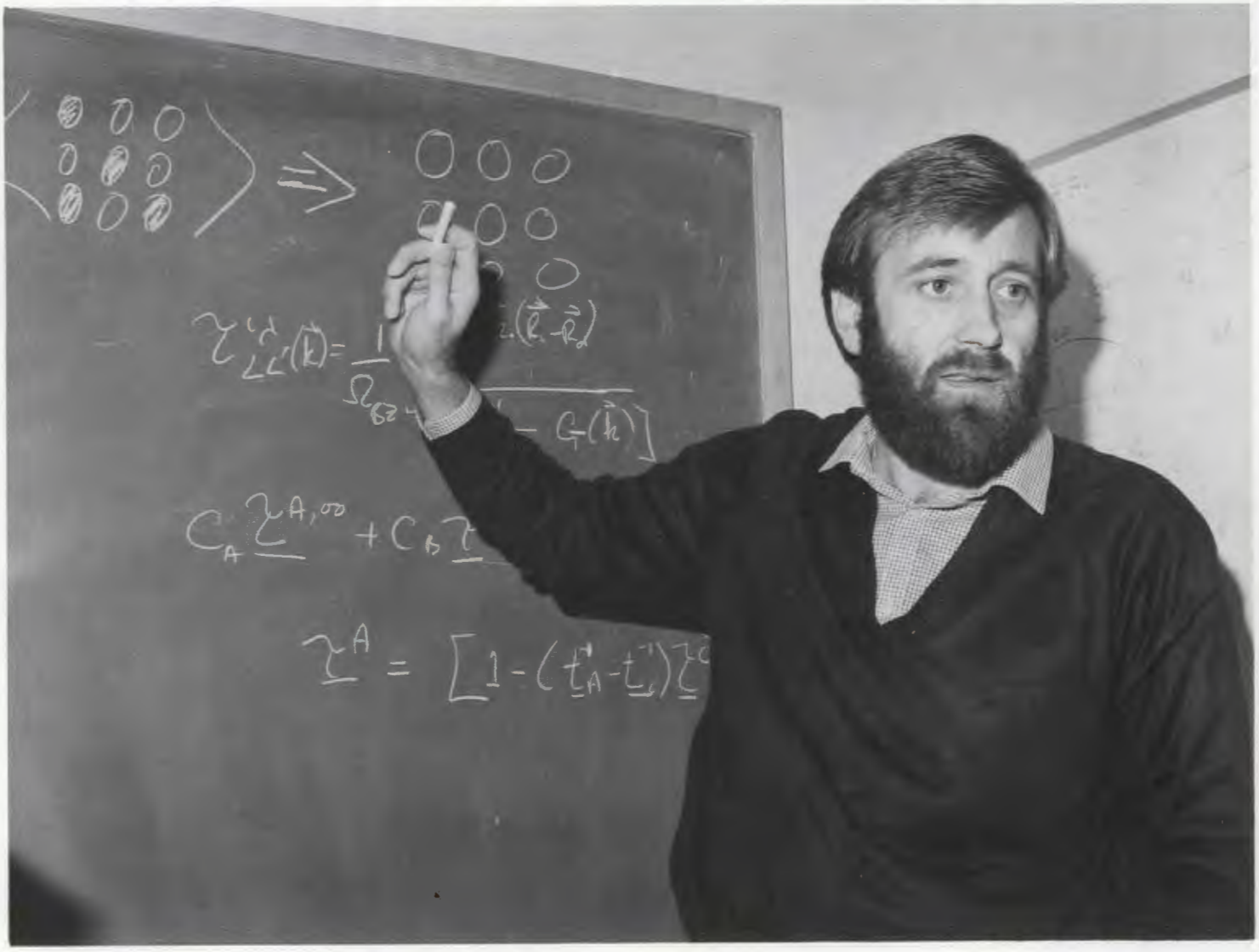
Nickel aluminides based on Ni_3Al can be made ductile by microalloying. At left is an unmodified nickel aluminide alloy; at right is Ni_3Al doped with boron and manganese. The aluminides are much stronger than stainless steels and superalloys at elevated temperatures.

advanced aluminides is 840 MPa, and the strength of Waspaloy is only 530 MPa.

In contrast to the ordered intermetallic alloys based on V, Fe, Ni, and Co, the advanced aluminides that we developed resist oxidation in air at temperatures ranging up to 1000°C. The aluminide samples displayed no apparent spalling (chipping when cooled down), and their weight gain due to oxidation is significantly lower than that of austenitic stainless steels. The low oxidation rate is attributed to the formation of a thin layer of aluminum oxides that protects the base metal from excessive oxidation. The exposed samples remain ductile after oxidation, thus indicating that no embrittlement of the aluminides occurs in oxidizing environments.

In summary, ductility and fabricability of Ni_3Al containing less than 25% Al can be dramatically improved by microalloying the material with a small quantity of boron and manganese. The improvement stems from the enhancement of grain boundary cohesion, thereby reducing the tendency toward brittle intergranular fracture. Mechanical and metallurgical properties of the aluminide can be further improved by macroalloying it with alloy additions. The structural aluminides that we developed based on Ni_3Al possess a unique combination of high-temperature strength, engineering ductility, and oxidation resistance. Furthermore, they constitute a new class of high-temperature structural materials that contain no critical strategic elements such as chromium and cobalt. The successful design of structural aluminides could therefore reduce the nation's dependence on these imported critical elements, which are extensively used in heat-resistant alloys in heat engines and power plants as well as for vital industrial and defense needs.

Industrial interest in the ductile aluminides is high. ORNL has received more than 200 requests for information on the material, and more than 20 companies have asked us to provide test specimens so that they can evaluate in their laboratories the material's properties, such as resistance to corrosion and wear. Cabot Corporation has allocated money for scaling up production of large batches of the alloy and for assessing the market for the material. Several companies see ductile nickel aluminides as promising materials for use in automobile exhaust valves and turbine disks. Someday, modified aluminides based on those first made at ORNL may be used in high-temperature automobile and jet engines as well as advanced power plants and coal conversion facilities. ornl



The Theory of Alloys:

From the Schrödinger Equation to the Rolling Mill

By MALCOLM STOCKS

In the approximately 5.5 millennia that have passed since humans first discovered that the unique properties of bronze (an alloy of copper with tin) could be turned to advantage, metallic alloys have been used in every facet of human life. Bronzes are still used by sculptors; alloys of iron and aluminum are employed in thousands of everyday applications; more advanced alloys are used in hostile environments such as chemical process plants, power stations, and spacecraft; and plutonium alloys form the core of weapons of mass destruction.

The reasons for the ubiquitous use of metallic alloys are simple to understand. By varying the constituents and the ratio of one con-

Malcolm Stocks was born and educated in England, where he obtained a bachelor's degree in applied physics from the Technological University of Bradford and doctoral degree in theoretical solid state physics from the University of Sheffield. After two years of postdoctoral work in the Theory Group in ORNL's Metals and Ceramics (M&C) Division and four years on the staff of the Physics Department of the University of Bristol in England, he returned in 1976 to the M&C Division, where he is a senior research scientist. His work at ORNL has focused on developing the theory of alloys.

stituent to another, metallurgists can improve the characteristic properties of metals—e.g., high strength and ductility, high electrical and thermal conductivities—and supplement them with other desirable characteristics, such as corrosion resistance, resistance to damage caused by radiation, high strength-to-weight ratio, and enhanced high-temperature properties. The goal of these modifications is to produce low-cost alloys that are specifically engineered to meet the demands of a wide range of technological applications.

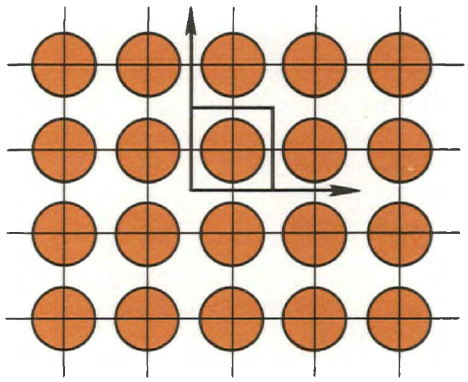
Used in its broadest sense, the term *alloy* simply refers to a substance composed of a mixture of two or more metals; and, as such, it covers a multitude of sins. Indeed, most alloys used commercially contain several different elements; are for the most part polycrystalline; usually contain several distinct phases (regions of distinct chemical composition and/or atomic arrangement); and are highly defected, having undergone elaborate heat treatments and varying amounts of rolling and shaping.

The development of new and useful alloy systems and the elucidation of their properties are the domain of metallurgy. Traditionally, the search for new alloy systems has been conducted largely on a trial-and-error basis, guided by the skill and intuition of the metallurgist, large volumes of experimental data, the principles of 19th-century thermodynamics, and *ad hoc* semiphenomenological models. Recently, this situation has begun to change as a result of developments in alloy theory that are making it possible to calculate the properties of alloys. For the first time, it is possible to understand the underlying mechanisms that control the formation of alloys and determine their properties. Today theory can offer guidance in understanding the properties of alloys and in developing new alloy systems.

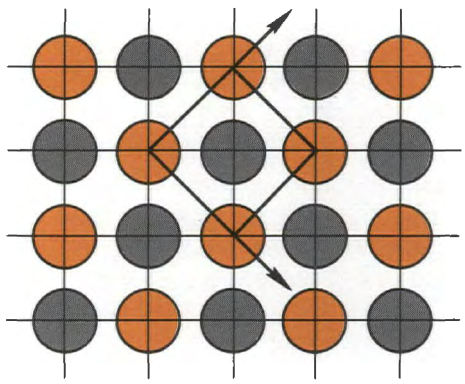
Although calculation of the properties of most complex commercial alloys is still well outside the realm of alloy theory, theoretical methods have been developed whereby the properties of individual phases can be calculated from first principles—that is, without recourse to adjustable parameters or parameters obtained from experiment. Indeed the properties of the electron glue that holds together an alloy's atomic building blocks can now be calculated to such a precision that many of the physical and metallurgical properties of alloys can be calculated about as accurately as they can be measured.

For pure metals and ordered alloys the theoretical techniques required to perform these calculations were developed during the 1960s and 1970s at a number of institutions, including Oak Ridge

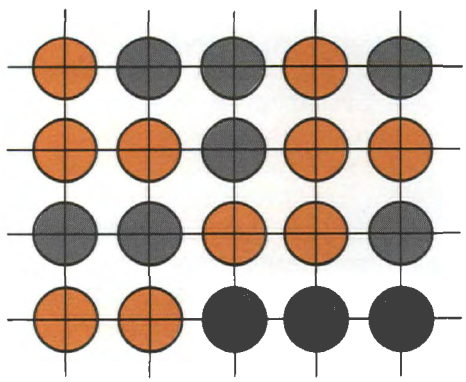
Recent developments in alloy theory are making it possible to calculate alloy properties, understand mechanisms that control properties, and guide the development of superior alloys for technological applications such as high-temperature energy systems.



In a pure metal, the lattice sites are occupied by atoms that are all of the same type, and the whole crystal can be generated by the replication of a basic unit cell.



In an ordered AB alloy, the two different atomic species are arranged in a regular manner. Again the whole crystal can be generated by the replication of a basic unit cell.



In an A_cB_{1-c} random alloy, the two different atomic species are distributed randomly over the available lattice sites. Consequently, there is no basic unit cell from which the rest of the crystal can be generated.

National Laboratory. The development of the first principles theory of random alloys has occurred more recently, and in this development ORNL has played a leading role. The description of the modern theory of random alloys and the new perspectives that theory provides on the rich and varied properties of alloys are the subject of this article.

Electron Glue

In an isolated atom the positively charged nucleus is surrounded by a neutralizing charge of electrons, each of which is confined to its own orbit and endowed with a characteristic energy. This energy, which may be thought of as the negative of the energy that would have to be supplied to remove an electron from its orbit and take it infinitely far from the nucleus, is greatest for the orbitals near the nucleus, the most tightly bound electrons, and smallest for those far away from the nucleus, the least tightly bound electrons. When atoms are brought together to form a solid, the separation between adjacent nuclei, which is typically the order of a few Angstrom units (1 Å = 10^{-8} cm), is sufficiently small that electrons in the least tightly bound orbitals on neighboring atoms overlap. As a consequence, these electrons are no longer confined to orbit a single nucleus; instead, they are free to move throughout the crystal; furthermore, they can take on any one of a *band* of energies. These delocalized, or *conduction*, electrons (so called because they are free to carry electrical current) form the electron glue that holds the crystal together. Thus, the way these *conduction band* electrons distribute themselves with respect to the fixed array of nuclei is of central concern in the theory of the metallic state.

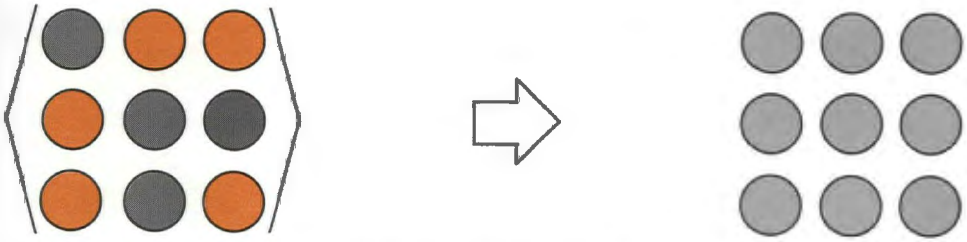
Most modern first principles calculations of the electronic structure of metals are performed within the context of a theory called "density functional theory." This theory, which is exact in principle though not in practical application, gives a *modus operandi* for calculating the way the electronic charge distributes itself in a crystal. In a macroscopic sample of a metal there are approximately 10^{23} nuclei and electrons, all interacting with one another. In density functional theory this impossibly complicated, many-particle problem is mapped into a much simpler model of a single electron interacting with the nuclei and other electrons through an effective interaction or potential. The way in which the electrons respond to this effective potential is described by the solution of a second-order differential equation called the "Schrödinger equation," in which the effective potential occurs. The solution of this equation, named after one of the founding fathers of modern physics, becomes the central task of the first principles theory of condensed-matter physics.

Pure Metals and Ordered Alloys

Despite the simplicity of the density functional theory, the mathematical problem of solving the Schrödinger equation is still a formidable one. However, for pure metals and ordered alloys, the fact that the electronic charge density (which describes the way that the electrons are distributed) and effective crystal potential are the same in each unit cell greatly simplifies the solution of the equation. During the last 30 years, a whole battery of techniques called "band theory methods" have been developed to effect its solution. At ORNL, work on band theory methods began in the mid-1960s with the development in the Metals and Ceramics (M&C) Division of the so-called "Korringa-Kohn-Rostoker" (KKR) method by Sam Faulkner, Harold Davies (now in ORNL's Solid State Division) and Hugh Joy (no longer at ORNL). Indeed, Jan Korringa, the first to discover this method, has for many years been an ORNL consultant. The KKR method and its progeny have been used extensively in recent years to calculate the properties of pure metals and ordered alloys. The KKR method also forms the basis for the development of the modern theories of random, or disordered, alloys.

Using modern band theory methods in conjunction with density functional theory, first principles calculations of the properties of pure metals and ordered alloys can be performed with relative ease. For such properties as the cohesive energy and the equilibrium lattice spacing, which give measures of the energy required to form the solid from isolated atoms and the separation between atoms on the lattice, respectively, as well as for several other properties, the results are generally within a few percent of those measured experimentally.

Recently, in collaboration with W. M. Temmerman of the Daresbury Laboratory of the United Kingdom's Science and Engineering Research Council (SERC), I looked at the nickel and iron aluminides, (Ni_3Al and Fe_3Al), ordered alloys which are technologically very interesting. Modifications of Ni_3Al are currently being developed for high-temperature applications by C. T. Liu and his co-workers in the M&C Division in collaboration with Cabot Corporation. The Ni_3Al alloy forms in a metallurgically favorable crystal structure called $L1_2$ that is basically face-centered cubic—that is, the basic unit cell is a cube that has one atom at each of the eight corners and one atom at the center of each face. In Ni_3Al the corner atoms are aluminum, and the atoms on the cube faces are nickel.



The basic idea behind the coherent potential approximation (CPA) is that for the purposes of calculating the configurationally averaged properties of a random alloy, the random array of real atoms can be replaced by an ordered array with the same effective "atom" on each site. The properties of the effective atom and, hence, of the random alloy are determined from a requirement that the properties of the ordered array of effective atoms give the "best" representation of the average properties of the real alloy.

Unfortunately Fe_3Al does not normally form in the $L1_2$ crystal structure; rather, it forms in a structure called DO_3, which—from the metallurgical point of view—is undesirable. The structure is basically body-centered cubic, having atoms at cube corners and at the cube center. Alloys that are basically body centered are generally less ductile than those that are face-centered cubic and as a result are less metallurgically useful. From the point of view of high-temperature technological applications, it would be enormously important if Fe_3Al or some modification of it could be produced in the $L1_2$ structure. Recently, it has been reported that Fe_3Al can be stabilized in the $L1_2$ crystal structure by the addition of carbon.

For Ni_3Al, theory gives the lattice spacing within 1.5% of the experimental value. Theory also predicts that at a temperature of absolute zero ($T = 0$ K), the system is weakly ferromagnetic; on the other hand, calculations performed on Fe_3Al in the $L1_2$ crystal structure show it to be strongly ferromagnetic. The fact that Fe_3Al does not form in this structure does not stop us from finding out what its properties would be if it did.

Our calculations also show that the addition of one carbon atom per Fe_3Al unit cell results in a decrease in the equilibrium lattice spacing and a loss of the ferromagnetism. This finding suggests that the stabilizing effect of carbon is associated with increased iron-carbon bonding and the consequent loss of magnetism.

Random Alloys

As I remarked previously, because the crystal potential that enters the Schrödinger equation is the same in each unit cell, the solution of the Schrödinger equation for pure metals and ordered alloys is relatively straightforward. In random alloys, no similar simplification exists. In random alloys, the effective potential in every unit cell, defined in terms of the region of space immediately surrounding each lattice site, is different from every other because every atom is surrounded by a different arrangement of other atoms. This complexity is further compounded by the fact that we do not know how the atoms are distributed among the available lattice sites; we know only the concentrations of the species. Thus, to calculate properties of an alloy, we must average the properties of the alloy over all possible arrangements or configurations of the atoms that are consistent with their concentrations. It is these configurationally averaged properties of alloys that are measured by experiment. Because of this great complexity, we must resort to approximation schemes.

The modern development of the theory of alloys began in 1967 with the discovery by Paul Soven, then at Bell Laboratories, of a new approximate method for calculating the electronic structure of random alloys. This method is called the "coherent potential approximation" (CPA). Soven suggested that to calculate the configurationally averaged properties of the disordered alloy, we should replace the potential seen by an electron at each site in the crystal, which is different at every site in the crystal, by some effective potential, which is the same at each site. Within the CPA, the effective potential that best represents the properties of the system is selected according to some reasonable criterion for which Soven provided a specific prescription.

The importance of the CPA as a theory of the disordered state was almost immediately recognized by many different groups throughout the world. In 1971, Sam Faulkner, Ron Williams (now a professor at the University of Vermont), and I used a simple model appropriate to copper-nickel (Cu_cNi_{1-c}) alloys to show for the first time that the CPA was capable of giving a detailed understanding of the electronic properties of a real alloy system. Although our calculations were very limited and could not be extended very far beyond the Cu_cNi_{1-c} alloy system, they did encourage me to pursue the further development of the CPA.

At this point, Balazs Gyorffy, Walter Temmerman (then a research student), and I, while at the University of Bristol in England, began to develop a completely general method in which the random crystal potential of disordered alloys is treated in the same way as in the theory of ordered systems. These developments have led to a method we now call the "Korringa-Kohn-Rostoker–coherent potential

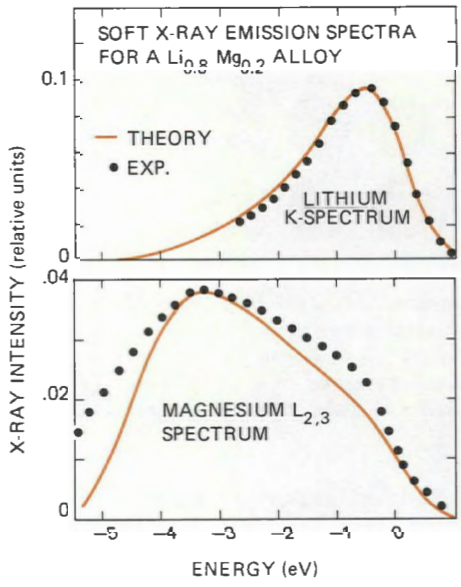
approximation" (KKR-CPA). The development of the KKR-CPA took place in two stages. At the first level, for a given random crystal potential, we solved the equations involved in the CPA and from these solutions calculated a number of interesting physical properties. Even at this stage we were able to make sufficiently sophisticated guesses of the crystal potential to allow us to explain the results of a large number of experiments. In the second stage of the development, following a number of theoretical and technical innovations, Herman Winter of the Kernforschungzentrum in Karlsruhe, Germany, and I succeeded in implementing methods that allow us to perform fully self-consistent calculations. Within density functional theory, the electronic charge density determines the crystal potential; and through the solutions of the Schrödinger equation, the crystal potential determines the charge density. Thus, in a complete theory, the Schrödinger equation must be solved many times for various guesses of the potential until one is found that produces a charge density that is the same as the one from which it was generated. At this level, the KKR-CPA is a proper first principles theory of the electronic structure of random alloys. Other than the CPA itself and density functional theory, essentially no approximations in the calculations of properties of an alloy exist. The inputs required are a knowledge of the atomic numbers of the constituent species, the crystal structure, and the lattice spacing—the last of which we will soon be in a position to calculate. The theory of random alloys has almost caught up with the theory of ordered alloys.

Although the computer codes used to perform fully self-consistent KKR-CPA calculations were largely developed on an IBM-3033 computer at ORNL, their efficient utilization requires a capacity not available on this type of machine at reasonable cost. Consequently, the self-consistent KKR-CPA calculations done so far have been performed on the CRAY-IS, a supercomputer at SERC's Daresbury Laboratory. Although the CRAY-IS can run the KKR-CPA codes about 25 times faster than an IBM-3033, these modern-day theories of the properties of alloys are so complex that they tax even the world's most advanced computer.

By using the KKR-CPA theory, we can now explain many physical and metallurgical properties that were previously outside the realm of theoretical discussion. This great predictive/"postdictive" power of the KKR-CPA theory and the picture it provides of the distribution of electronic states in a random alloy can best be illustrated by a few examples.

Band Structure Spectroscopies

A number of experimental methods can probe the electronic structure of random alloys by indirectly measuring the conduction band *densities of states*, $n(\epsilon)$. For each energy ϵ in the conduction band, $n(\epsilon)$ measures the number of electrons that have that energy. In an x-ray photoemission experiment, it is the total densities of states that are measured; in the soft x-ray emission experiment, the component densities of states on the different atomic species are measured. The results of KKR-CPA calculations have been used as a basis for understanding spectroscopic measurements on a number of alloy systems, including Cu_cNi_{1-c}, Ag_cPd_{1-c}, and Li_cMg_{1-c}. In all cases, the calculations offered detailed explanations of the major structure in the measured spectra. Furthermore, the calculations often pointed to the failings of previous



On the basis of existing theory, the peak at an energy of −3.5 eV observed by ORNL experimenters in the magnesium $L_{2,3}$ soft x-ray spectrum (bottom frame) was unexpected. Calculations of the spectra based on the KKR-CPA theory provide an overall understanding of the shape of both the lithium and magnesium spectra. They also allow us to identify the mechanism that gives rise to the peak in the magnesium spectrum. This results from negatively charged electrons gathering around magnesium atoms in order to neutralize the excess unit of positive nuclear charge that the magnesium sites possess.

attempts to understand the properties of alloys in terms of simple alloy theories. For example, calculations on Ag_cPd_{1-c} alloys showed that two models—the rigid band model and the virtual crystal approximation—which had previously been used to describe the electronic structure of random alloys were totally incorrect. This finding was surprising because the rigid band model, first proposed by Sir Neville Mott in 1935, has been used extensively by physicists and metallurgists to understand experimental results in numerous alloy systems, including Ag_cPd_{1-c} alloys. This demonstration of the invalidity of the rigid band model shows that the ability of a theory to explain the results of an experi-

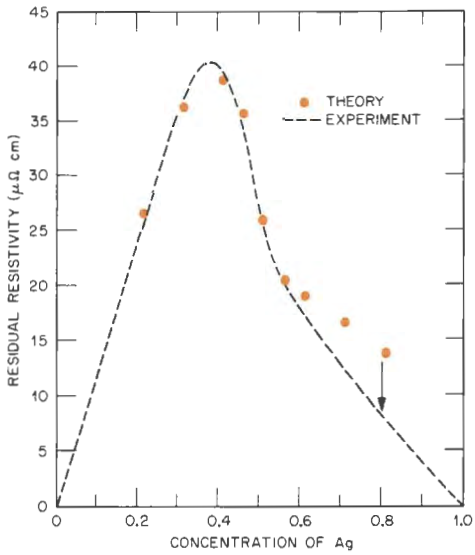
ment does not necessarily mean that it provides an understanding of the physics.

Residual Resistivity

At finite temperatures all metals, except superconductors, have a finite electrical resistivity because the current-carrying electrons are scattered by the thermally induced vibrations of the atoms in the solid. Unlike the case in pure metals and ordered alloys, the resistance to the flow of electricity in a random alloy does not disappear as the temperature approaches absolute zero. The remaining resistivity results from the intrinsic disorder in the system and is called "residual resistivity."

In many homes, the high residual resistivity alloys Nichrome and Canthal (nickel with chromium and iron with aluminum, respectively) are used in heating elements for stoves. More exotic alloys of platinum with tungsten have been used at ORNL to make high-flux heaters that could be used to simulate reactor conditions in reactor safety studies.

Despite the obvious technological importance of this property, theory was essentially silent on microscopic mechanisms that control the size of the residual resistivity in a particular alloy. Indeed Bob Williams (Physical Properties Group in the M&C Division) has on occasion been known to point this out. Bob has long made important experimental measurements of the transport properties of alloys, including their residual resistivity. It was therefore particularly satisfying when for Ag_cPd_{1-c} alloys, Bill Butler and I could reproduce in detail the unusual way that the residual resistivity depends on the concentrations of silver and palladium. We determined this relationship from a knowledge of only the atomic numbers of silver and palladium and the measured crystal



Based on the results of KKR-CPA calculations and a simple theory of electronic conduction in metals, the unusual concentration dependence of the residual resistivity of Ag_cPd_{1-c} alloys can be reproduced in detail, using only the atomic numbers of the constituent species and the alloy's measured lattice-spacing.

structures and lattice spacings of the alloys. Furthermore, not only did we show that the qualitative understanding of the residual resistivity of these systems—which had been provided by a model called the "sd-model" (again proposed by Mott)—was incorrect but we also substituted for this model one based on the KKR-CPA.

Ordering and Phase Stability

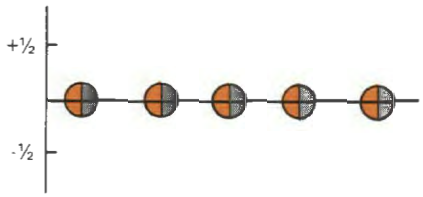
Although it is important to understand the intrinsic properties of the conduction electrons in an alloy and to offer detailed explanations of experimentally measured results like those documented above, such interpretations are not the major goal of theoretical studies of alloys. Having gained confidence in the correctness of our theoretical methods, we must then use this knowledge to pursue our true goal: to understand how the electron glue determines the structural arrangement of the atoms in an alloy and, hence, its metallurgical properties.

Even in an alloy that is nominally random, there is usually some residual order in the way the different species arrange themselves with respect to one another. In some alloys such as Cu_cNi_{1-c}, like atoms tend to cluster together; in other alloys such as Cu_cPd_{1-c}, atoms of one species prefer to have near neighbors of the opposite species. Alloys of the former type are said to show clustering; the latter are said to exhibit short-range order (SRO). At the lowest temperatures, alloys that cluster tend to separate into immiscible regions of pure A and pure B, whereas SRO alloys tend to form ordered compounds. Using the KKR-CPA, we have begun to study the question of whether a particular alloy system will exhibit clustering or SRO; in examining this question we are developing two rather different methods.

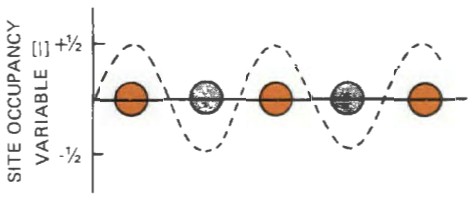
Concentration Waves

In the first approach, which we call a "concentration functional method," we focus on the way in which the atomic species of completely random alloys attempt to arrange themselves in response to the electronic structure. By using this approach, which was developed in collaboration with Balazs Gyorffy, we explained the existence of concentration waves in Cu_cPd_{1-c} alloys. A concentration wave may be thought of as a long-lived periodic variation in the site concentration about the average homogeneous value. For a completely random A_cB_{1-c} binary alloy, the probability of occupancy of each site by the A species is c. In a system with a concentration wave along some direction, the average concentration of the A species at sites along that direction is different from c and varies in a periodic manner. The period of this variation may not be

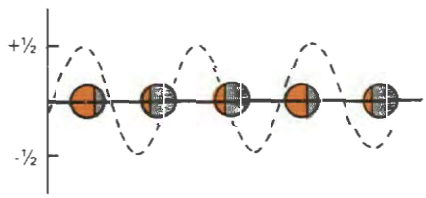
A concentration wave may be thought of as a long-lived periodic modulation of the average site occupancy in an alloy. Consider an $A_{0.5}B_{0.5}$ binary alloy and let Ξ describe the occupancy of each site in the crystal.



In a random alloy, $\Xi = 0$ at all the sites; and, on average, each site is occupied equally by the A- and B-species.



An ordered AB compound can be described in terms of a periodic variation in Ξ that is in phase with the lattice such that the sites are alternately either always A, $\Xi = +1/2$, or always B, $\Xi = -1/2$.

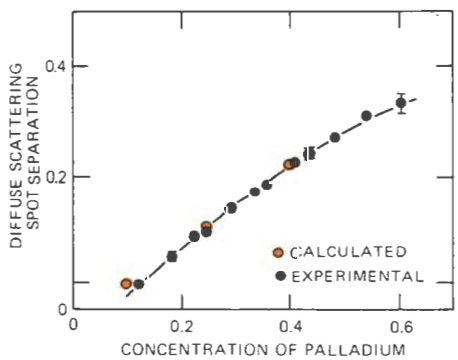


In some alloys, while Ξ varies periodically, it does not have the same period as the underlying lattice. This situation describes an incommensurate concentration wave of the type seen in Cu_cPd_{1-c} alloys.

related to the periodicity of the lattice; such a concentration wave is said to be incommensurate with the lattice.

Experimentally, concentration waves show up in conventional x-ray, electron, and neutron diffraction experiments. When, for example, an x-ray beam is directed on a perfect crystal, it is diffracted by the atoms that compose the crystal. The diffracted beams of X rays emerge from the crystal at specific angles; these angles are called "Bragg angles," and the scattered x-ray intensities at these angles are called "Bragg maxima." It is from the position of the Bragg maxima that the crystal structure and spacing between atoms on the crystalline lattice are inferred. For a system that has a concentration wave, extra peaks called "diffuse scattering spots" occur in the scattered intensity. The position of the diffuse scattering spots is related to the wavelength of the concentration wave.

Electron diffraction pictures from Cu_cPd_{1-c} clearly reveal the existence of concentration waves. Furthermore, it is clear from the variation with concentration of the positions of the diffuse scattering spots that the wavelength of the concentration waves varies substantially with alloy concentration. By using a result of our concentration functional theory that allows us to calculate the diffuse scattering intensity, we were able to accurately reproduce the concentration variation in the diffuse scattering spot position that was measured experimentally. We were also able to identify a mechanism involving the behavior of the conduction band electrons that gives rise to the formation of concentration waves.



In Cu_cPd_{1-c} alloys, concentration waves are seen as diffuse scattering spots in conventional electron diffraction patterns. The separation between these diffuse scattering spots is related to the wavelength of the concentration waves. Results of KKR-CPA calculations reproduce in detail the rapid concentration variation in the diffuse scattering spot separation seen in this alloy system.

While the calculations were specific to the Cu_cPd_{1-c} alloy system, it was clear that the explanation for the existence of the concentration waves is transferable to a large number of other systems that show similar behavior. Thus for a whole class of alloy systems, we now understand the origins of these effects that occur as precursors to the formation of ordered phases.

Ordering Energies

In the second approach, we examine the question of ordering in alloys by using a *cluster method*. In this method, we calculate directly the energy associated with particular local arrangements of atoms in the otherwise random alloy. These arrangements are chosen to represent various situations ranging from clustering to SRO. The arrangement that the actual system will prefer to adopt is the one of lowest energy. By using this method, Tony Gonis of Northwestern University, Bill Butler, and I calculated the electronic structure of near-neighbor clusters in an $Ag_{0.5}Pd_{0.5}$ alloy. From these calculations we predicted that this system would exhibit SRO. For this particular alloy, measurements made by Bob Williams of how much the electrical resistivity varies with heat treatment taken together with various thermodynamic measurements suggest that this tendency toward SRO is the case.

However, for a definitive experimental test of this prediction, we await the fruits of the latest developments in x-ray diffraction. These developments are being undertaken at the National Synchrotron Radiation Source at Brookhaven National Laboratory by a group led by Cullie Sparks of the M&C Division. They will make it possible to measure the diffuse scattering for alloys whose atomic species are near neighbors in the periodic table, as are silver and pal-

Bill Butler (working at the terminal) and Sam Faulkner exchange ideas at the Data General MV 10,000 "supermini" computer. This new computer in the Metals and Ceramics Division will be the workhorse for further developing the theory of alloys.

ladium. Diffuse scattering is proportional to the difference in the x-ray scattering powers of the individual species. For alloys whose atomic species are near neighbors in the periodic table, this difference is too small to be measured conventionally. By using the energy tunability of X rays produced by the synchrotron source, however, scientists can change the apparent scattering power of one species and, hence, accentuate the diffuse scattering so that it can be measured.

Although the developments of the last decade have taken us far toward a detailed theoretical understanding of the properties of metallic alloys, it is clear that we have merely scratched the surface. Further theoretical developments are required just to be able to predict the *stable equilibrium phases* of alloys—that is, for each temperature, to predict the way the atomic species that comprise the alloy are arranged. To be able to accomplish this in the most straightforward way, we must be able to calculate the total energies associated with the pure metals, the possible ordered compounds, and the disordered solid solutions. Furthermore, the precision of our calculations must be enough to make a distinction between the various crystal structures we may wish to consider—face-centered cubic, body-centered cubic, hexagonal close-packed, etc. At present it is possible to do total energy calculations at T = 0 K for pure metals and ordered compounds and just about possible for random alloys, though not with sufficient precision to calculate the very small energy differences among the various crystal structures.

Of course, an ability to predict the stable equilibrium phases that an alloy assumes at various temperatures is still only a very limited perspective. At some time it will be necessary, for example, to develop an understanding at the microscopic level of how macroscopic defects such as grain boundaries, dislocations, and voids affect the properties of metallic systems. ornl

Mechanical Properties of Metals and Alloys

Material failure by fracture is one of the most serious technological problems encountered in energy systems. For example, if a pressure vessel or steam generator tube in a nuclear or coal power plant should begin to crack, the plant must be shut down for reasons of safety and protection of plant components—a costly action. It is not yet well understood which of the material parameters are most important in influencing the rate at which structural damage is accumulated and the stage at which failure finally occurs. Research programs at Oak Ridge National Laboratory have emphasized the understanding of the basic mechanisms of material failure, and our approach has been primarily the characterization of microstructure and the relationship of microstructure to bulk mechanical behavior of materials.

Why does a material that is normally ductile fracture in a brittle manner in a harsh nuclear or chemical environment? That question is the focus of an ORNL program in the Solid State Division. Structural materials are normally ductile—that is, when a crack starts to form in such materials, a permanent change in shape (plastic deformation) occurs at the crack tip. This deformation allows energy to dissipate, making it more difficult for the crack to grow. Brittle fracture occurs when plastic deformation at the crack tip does not occur, thus allowing the crack to propagate through the material. It is not known what prevents deformation in the case of brittle fracture.

Our electron microscope observations of crack tip behavior made during the in situ deformation of various metals and alloys have shown that under ductile conditions, there is a zone that is free of dislocations, which are line defects in the crystal structure of a solid or boundaries between plastically deformed and undeformed areas of the material. This dislocation-free zone implies that the crack tip area is responding elastically, although the larger volume of the material is undergoing plastic deformation. Hence, the stress field at the crack tip can be described in terms of a stress-intensity factor, which describes how long a metal can resist cracking or breaking under prolonged or repeated stress.

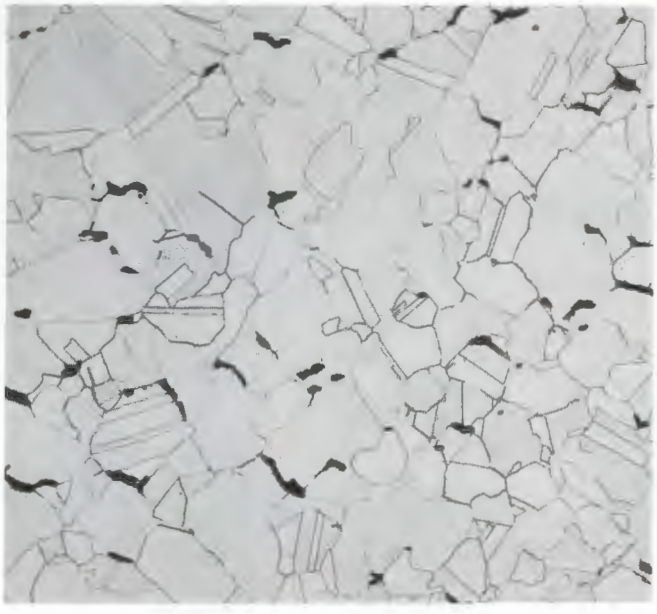
The dislocation-free zone reflects an impediment to the generation of dislocations at crack tips. This impediment has been expressed in terms of the critical stress intensity factor for dislocation generation; because this stress intensity factor is lower for materials that are ductile than for materials that undergo brittle fracture, it has been proposed that the size of the dislocation-free zone be used as a criterion for screening out ductile materials that will resist brittle fracture under stressful conditions. The smaller the dislocation-free zone, the lower the critical stress intensity factor will be; thus, a material with a relatively small zone will generate more dislocations at crack tips, thereby keeping it ductile even in harsh environments.

The impediment to dislocation generation at crack tips increases with increasing flow stress, the stress level required for plastic deformation. Thus, when the flow stress rises to a critical value, dislocation generation ceases at the crack tip and further stress leads to brittle fracture. In many structural materials (such as steels), the flow stress decreases with increasing temperature, so brittle fracture is not normally a problem at room temperature. However, the flow stress of structural materials is observed to increase as a result of neutron irradiation; consequently, the temperature at which the flow stress reaches the critical value for fracture rises with increasing doses of radiation. In a nuclear reactor, for example, when the temperature at which brittle fracture occurs is equivalent to the reactor ambient temperature, material that is normally ductile can fail in a brittle manner. This proposed micromechanical mechanism of the ductile-brittle transition of structural materials may give insight into the costly and long-intractable problem of brittle fracture.

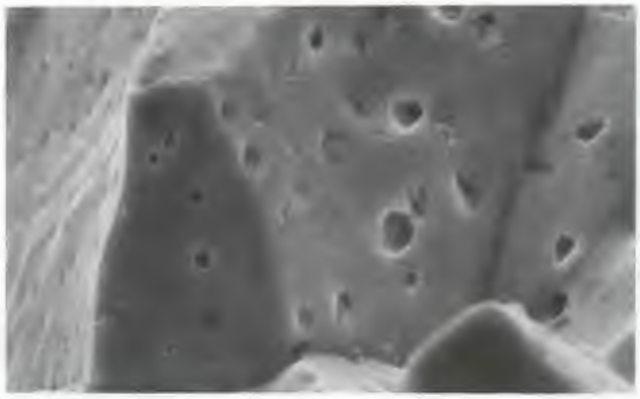
Most structural metals and alloys exhibit their lowest ductility at specific ranges of temperature near one-half of their absolute melting temperatures and at applied stresses well below their yield stresses (stresses at which the material actually deforms plastically). This minimum ductility results from nucleation, growth, and interlinkage of microcracks and cavities on the grain boundaries, which are planar defects between clusters of periodically arranged atoms. This phenomenon in which a material deforms and then cracks at interfaces between its atomic lattices is called intergranular creep fracture. Because intergranular creep fracture often limits either the life or service of structural components of energy systems such as nuclear power plants, several of us in ORNL's Metals and Ceramics Division are studying the physical mechanisms responsible for this phenomenon.

When polycrystalline metals are deformed under applied stress at temperature ranges 0.4 to 0.7 times the

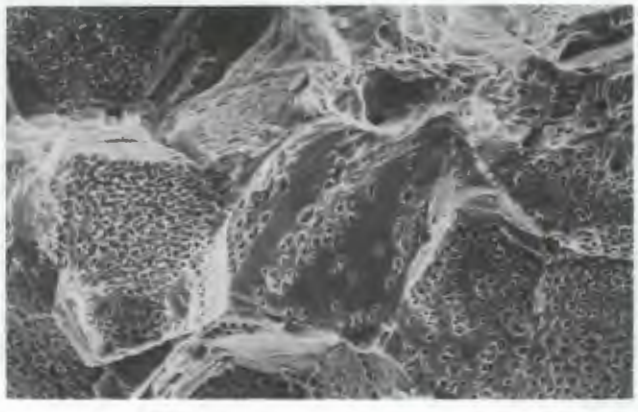
A scanning electron micrograph of creep cavities on fracture surface of nickel-tungsten alloy (Ni-4% W). Intergranular cavities in their early growth stage were revealed using a liquid-metal (lead) embrittlement technique.



A scanning electron micrograph (SEM) of creep cavities on fracture surface of Type 304 stainless steel. The whitish areas represent individual grain boundaries (center and lower left) or inclined grain facets (upper half). About ten grain facets are shown with individual cavities (tiny dark holes).



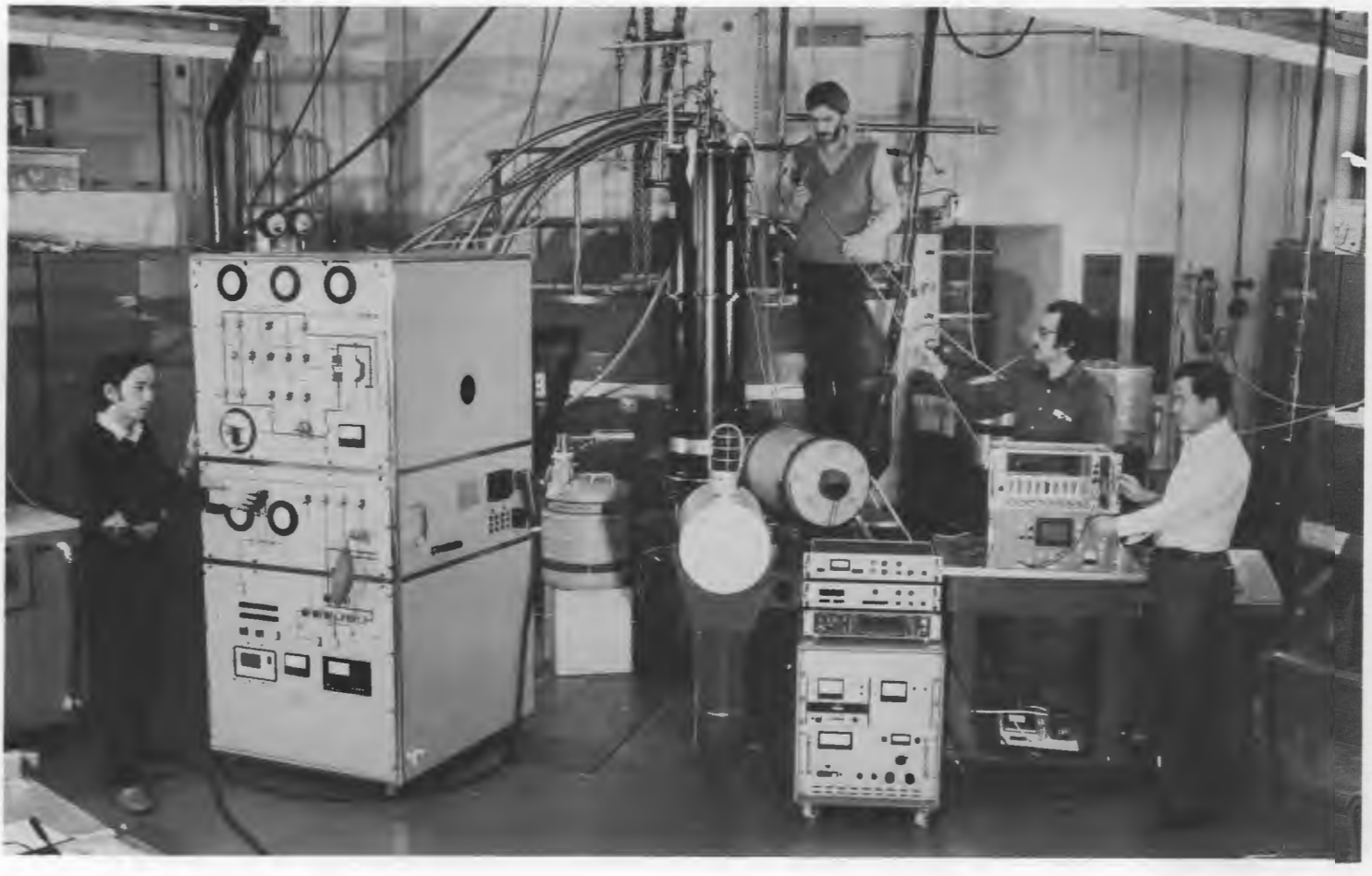
An optical metallograph of intergranular creep cavities in a nickel-chromium (Ni-20% Cr) alloy. The black dots are individual cavities and the long black streaks are microcracks resulting from interlinkage of cavities.



absolute melting temperature, one of the necessary conditions for microcrack or cavity nucleation is the development of internal stress concentrations. We developed theoretical models to calculate both the evolution of stress concentrations at a variety of microstructural sites and the rate of nucleation and growth of intergranular cavities. We used cyclic creep and fatigue tests to verify these theoretical estimates of the stress concentration required for cavity nucleation. We then characterized the distribution of different sizes of intergranular cavities by using small-angle neutron scattering (SANS) and high-voltage electron microscopy (HVEM); these techniques can detect and measure the size of intergranular cavities with greater accuracy than conventional techniques such as scanning electron microscopy. We were among the first to use SANS and HVEM techniques for investigating intergranular cavitation in structural metals and alloys. In fatigued nickel, we resolved the volume fraction of cavities on the order of 10^{-5} with the SANS technique and confirmed the presence of intergranular cavities by HVEM observation.

Metallurgists have known for many years that certain trace impurities in a material can induce or greatly enhance intergranular cavitation, dramatically reducing a material's creep ductility in temperature regimes where the inherent minimum ductility already exists. Using high-resolution, scanning Auger electron spectroscopy (AES), we found that detrimental trace elements such as sulfur and antimony concentrate in grain boundaries and cavity surfaces in nickel and its alloys, thereby enhancing the nucleation and growth of intergranular cavities. However, we also found that a small addition (0.11%) of zirconium to a nickel-base alloy improves the alloy's creep strength and ductility by reducing grain boundary diffusivity, a kinetic factor involved in intergranular cavitation.

Our improved understanding of the mechanisms for intergranular cavitation and of the role of different trace impurities in promoting or inhibiting this cavitation process will increase our capability of predicting mechanical properties of candidate alloys for structural materials. Such a theoretical tool should reduce the need for costly trial-and-error methods normally used to design new or improved alloys for use in energy systems.—*Mike Ohr, Solid State Division, and Man Yoo, Metals and Ceramics Division.*



Marketing ORNL-made Materials

I·R 100

By CAROLYN KRAUSE

The development and application of new energy-related materials at Oak Ridge National Laboratory has a long tradition. One ORNL alloy that has been used commercially for years is INOR-8, which was developed in 1956–58 to withstand the high operating temperatures and corrosive fluids characteristic of the Molten Salt Reactor Experiment. The nickel-base alloy, which contains 11 to 13% molybdenum and 6 to 8% chromium and many trace elements, was developed by Henry Inouye, Bill Manly, and Tom Roche. The alloy has been manufactured as HASTELLOY ® N by Cabot Corporation, where Manly is now senior vice president. Its principal use is for components of jet aircraft engines.

More recently, ORNL has developed several new materials for energy applications. Actions have been taken to facilitate the flow of information about development of these materials to the commercial sector. In response to many requests by universities and industries, ORNL has sent samples of its materials for testing. Several companies are now manufacturing, or intending to fabricate, materials using the technology developed at ORNL.

Four ORNL-developed materials are examples of technology transfer. They are a low-swelling steel alloy for breeder and fusion reactors; a modified, microalloyed, chromium-molybdenum steel alloy for use in steam boilers, in breeder reactor piping, and in multiple components of coal-to-oil conversion plants; a modified nickel aluminide alloy for use in turbine disks and automobile valves; and laser-processed solar cells for the efficient conversion of sunlight to electricity. The latter three of these

The neutron scattering facility at the High Flux Isotope Reactor is a user facility. Three of the four people shown above have come from elsewhere to use ORNL's specialized research equipment and to provide apparatus of their own for special experiments. Present are, from left, S. Kawarazaki of Osaka University, Japan; P. Hilton, Oxford Instruments, Ltd.; Robert Nicklow, ORNL's Solid State Division; and N. Kunitomi, Osaka University. In this case, the Japanese have provided a dilution refrigerator as part of the U.S.–Japan Cooperative Program on Neutron Scattering. In this refrigerator (the cabinet at left plus the vertical cylinder in the center), a mixture of helium isotopes (^{3}He and ^{4}He) in the liquid state provides a means for achieving temperatures below 0.0005 K. This ultralow temperature (one of the coldest on Earth) together with neutron scattering measurements is used to study nuclear magnetism. (See sidebar on user facilities on p. 58.)

materials have received I-R 100 awards from *Industrial Research & Development* magazine, which annually recognizes 100 laboratory innovations that show promise for making or being used in commercial products.

Low-Swelling Steel

In the mid-1970s ORNL researchers in the Metals and Ceramics (M&C) Division developed a stainless steel that is highly resistant to swelling and embrittlement—undesirable effects normally induced in other steels by neutron radiation in a fast breeder reactor environment. Arthur Rowcliffe, Jim Stiegler, Everett Bloom, and Jim Leitnaker developed the low-swelling steel by analyzing why certain heats of steel swell while others do not. They found that relatively small amounts of certain elements suppress the swelling and that others enhance it. Based on this information, they devised specifications for a low-swelling steel (see Arthur Rowcliffe's "Design of D9: A Radiation Damage-Resistant Steel" elsewhere in this issue).

In breeder reactor environments such as the Experimental Breeder Reactor-II (EBR-II) in Idaho, energetic neutrons wreak havoc on materials in at least two ways: they dislodge atoms from their lattice sites, forming vacated lattice sites that collect as voids; and they react with steel constituents to form helium bubbles that act as nuclei for the voids. This void formation increases the volume and reduces the density of the material, causing swelling.

To prevent the smaller helium bubbles from coalescing into larger bubbles that could expand into voids, ORNL researchers added titanium to the steel. ORNL's titanium-modified steel trapped the bubbles on fine-scale titanium carbide particulates formed by reaction of the titanium with carbon in the steel. The effect of this trapping of small bubbles and voids was to reduce the swelling significantly. This trapping of helium bubbles also prevented them from migrating to the grain boundaries and thus causing the steel to become less ductile.

To reduce swelling even further, ORNL researchers added small amounts of silicon to the titanium-modified steel. It is believed that silicon decreases swelling by trapping radiation-induced point defects and promoting their recombination. To improve the material even more, the ORNL metallurgists increased the nickel content and decreased the chromium and molybdenum content of the steel to avoid the formation of undesirable precipitate phases.

Based on tests at EBR-II, ORNL researchers found that stainless steels that contain controlled levels of titanium and silicon are superior to type 316 stainless steel (now used in breeders) because they exhibit reduced swelling, increased creep strength, and enhanced resistance to helium embrittlement. Because this material known as the D9 alloy swells by less than 5% of its original size while type 316 stainless steel exhibits 50% swelling in an equivalent neutron environment, the alloy could be a better material for fuel cladding and ducts in liquid metal fast breeder reactors; because ducts and cladding made from the D9 alloy would swell less, reactor designers can achieve a greater efficiency in breeding new fuel.

In recent years, ORNL has developed a low-swelling steel, a modified chromium-molybdenum alloy, a modified nickel aluminide, and highly-efficient, laser-processed silicon solar cells. Now, these materials are moving from the laboratory bench to the marketplace.

Hanford Engineering Development Laboratory (HEDL) in Richland, Washington, is working on optimizing alloy chemistry, improving fabrication procedures, and establishing a statistically sound data base for the D9 alloy. Commercial vendors—Allvac, Cartech, Inc., and Superior Tube, Inc.—have fabricated fuel pin assemblies and flow ducts from the D9 alloy. These components are currently undergoing extensive irradiation testing in the Fast Flux Test Facility (FFTF) at Hanford. Successful performance in these tests could lead to the gradual replacement of type 316 stainless steel by the D9 alloy as the structural material for the FFTF core. The new alloy is also being considered for use in fusion reactors whose 14-MeV neutrons can produce 10 times as much transmuted helium in the alloy as breeders.

Chrome-Moly Steel

"Seldom if ever has a new steel been introduced which has been accompanied with such a plethora of property data. This accumulation of data should result in an early market acceptance of the steel." So wrote Robert Irving in his article "What's This Steel They're Raving About Down in Tennessee?" in the June 25, 1982, issue of *Iron Age*. The steel that Irving is writing about is an alloy developed by ORNL and Combustion Engineering, Inc., of Chattanooga.

This modified alloy, which contains 9% chromium and 1% molybdenum, was developed for the U.S. Energy Research and Development Administration (ERDA), the predecessor of the U.S. Department of Energy, for piping liquid sodium in breeders. In 1974 ERDA set up a task force to identify a reference material for the fast breeder. ORNL was asked to examine ferritic steels with chromium contents ranging from 8 to 14%, types 304 and 316 stainless steels, and various nickel-bearing, solid-solution alloys. ORNL selected the standard 9-Cr—1-Mo steel developed years ago by the Timken Company of Canton, Ohio. To improve the alloy's properties, ORNL worked with a subcontractor, Combustion Engineering, to modify the steel.

By 1979 Vinod Sikka and fellow researchers from the M&C Division and Combustion Engineering had investigated the properties of 120 laboratory melts and had determined the recommended composition and heat treatment. The microalloyed chrome-moly steel contains 9% chromium, 1% molybdenum, and controlled trace amounts (less than 1%) of carbon, manganese, phosphorus, sulfur, and silicon that are equivalent to or smaller than the amounts used in the standard alloy. The modified steel differs from the standard one in that it contains trace amounts of niobium, vanadium, nickel, nitrogen, and aluminum. According to Sikka, the niobium and vanadium improve the strength of the alloy at elevated temperatures.

Phil Sklad works at the electron microscope, which is part of the SHaRE facilities ***(see p. 58.)***

The new steel has several advantages over the standard ferritic and other steels. It has better tolerance of design stresses with no loss of ductility, higher resistance to thermal stress, and immunity to stress corrosion cracking in chloride-bearing water. In addition it is resistant to radiation-induced swelling, and it conserves strategic materials because it uses only half the chromium present in type 304 stainless steel.

This improved ferritic steel is also superior to austenitic steel in several ways. The new ferritic steel costs less than do austenitic steels and exhibits an increased resistance to thermal stress and to stress corrosion cracking during fabrication, shipment, and operation.

Steam generator pipes are normally made of a ferritic steel that contains 2.25% chromium and 1% molybdenum. The heat-exchanger tubes within the steam generators, however, are made of austenitic steel. Joining the two types of steel requires a transition joint—a difficult joint to make because the properties (such as thermal expansion coefficients) of the two different steels are so dissimilar. The problem of the transition joint would be eliminated if a modified ferritic steel could be used throughout for both the steam generator and tubing. It is now considered possible to replace austenitic stainless steels with the ORNL–Combustion Engineering ferritic alloy; such a substitution would allow an all-ferritic system, thus eliminating the need for and uncertainty of austenitic-to-ferritic steel-weld transition joints.

The new alloy is favored for use not only for piping liquid metal in breeders but also for coal conversion plants, particularly in such components as advanced superheaters and steam supply sys-

tems, fluidized-bed heat-exchanger tubing, and liquefaction-plant pressure boundaries.

Under Sikka's leadership, ORNL researchers have extensively studied the properties of the new alloy. They have obtained much data on its resistance to corrosion, its mechanical properties, engineering code requirements, design costs, and its ability to be welded and fabricated into castings, bar, plate, and tubing using commercial processes.

Nine private American firms have participated in developing fabrication processes either under contract or using private funds. The Japanese firms Sumitomo and Nippon Kokan K.K. have melted large heats on company funds; a United Kingdom company, Tube Investments, Ltd., has fabricated boiler tubes on company funds. Four American universities have participated in studies of the alloy. Five utilities (two foreign) have installed

Two Types of Technology Transfer

Transferring the technology of fabricating modified aluminide alloys will not be as easy as transmitting the word on how to make the modified chrome-moly steel. So says Jim Weir, director of ORNL's Metals and Ceramics Division. He argues that ORNL will become more involved in transferring the aluminide technology to the private sector and that the industry adopting the technology may want an exclusive patent right. This has not been the case for the new chrome-moly steel.

"Manufacturing standard chrome-moly steel is a big business," Weir says. "All competent steelmakers can easily make our modified microalloyed chrome-moly steel using their rolling mills and standard equipment; once their equipment is set up, all they need from us is the composition and heat treatment. Because the industry is receiving many orders for the steel and because no special equipment is required to make it, steel fabricators are taking no risk in making this new alloy.

"But," Weir observes, "the situation is different for our aluminide alloy. It will probably have to be stirred while it is molten to make sure that the composition is uniform throughout the melting and solidification. If the material is not melted properly, it won't be homogeneous and ductile; instead, parts of it may become so brittle that it can't be rolled into sheets or forged into shapes. In fact, it could easily break forging equipment used, say, to make automobile valves. Industry will have to learn how to melt and fabricate it.

"As I see it," Weir continues, "a potential aluminide fabricator will want an exclusive patent right to the fabrication technology because there is a risk in making the material. Money may have to be spent on capital equipment to stir the molten alloy or otherwise make the composition uniform. The fabricator will have to invest in scaled-up manufacturing technology and will therefore want guarantees that no one else will compete in the fabrication and marketing of the alloy."

Weir says that ORNL plans to work with industry in properly melting the aluminide material so that it can be used for components of energy-producing systems. Several companies—Garrett Turbine Engine Company, Ford Motor Company, and Cabot Corporation—are interested in using, making, or marketing aluminide materials for turbine disks, automobile exhaust valves, and other applications.

In these instances, the companies are using their own funds to make batches of the aluminide material or to purchase material from ORNL. In the case of the modified chrome-moly alloy, however, ORNL allocated some DOE funds to industry through subcontracting to scale up equipment for making the ferritic steel.

What is exciting about modified aluminides, according to Weir, is that they are less dense and yet stronger than current superalloys used to make turbine blades. Thus, the new aluminides could be used in power plants and jet engines for turbine blades. Valves are another possible use, says Weir.

"In the case of engines," Weir says, "modified aluminides can lighten the turbine. If the lighter aluminides are used to make valves, then the springs and cam shafts needed to push those lighter valves can be smaller. Thus, use of a lighter-weight material affects the whole engine design. Because the engine uses less material, it costs less, weighs less, and uses less fuel. In addition, because modified aluminides are so strong, they can make an engine perform more reliably and last longer, improving the economics of operating the machine."

It may be hard to transfer the technology of making aluminides, but the national need for less costly, energy-efficient devices suggests that the extra effort is worth the time and money.

In this ion-implantation chamber, superconducting alloys are being made by ion-implantation doping and ion-beam mixing. The experimenters are Bill Appleton (left) and guest scientists from the Federal Republic of Germany. They are working at ORNL's Surface Modification and Characterization Collaborative Research Center, which is a user facility for academic, industrial, and national laboratory scientists. (See sidebar on user facilities on p. 58.)

experimental superheater tubes of the alloy in fossil-fired power plants. Babcock and Wilcox, Inc., is manufacturing 8230 m (27,000 ft) of boiler tubing for an application.

In the academic sector, Northwestern University, the University of Connecticut, the University of Tennessee, and the University of Iowa are studying such aspects of the material as its weldability and resistance to embrittlement and fatigue.

Many American firms have spent their own funds on testing the material's resistance to corrosion and other properties, fabricating it into tubes or pipes, or developing welding procedures for it. They include Atlas Foundry and Machine Company, B&W, Cameron Iron Works, Climax Molybdenum, Chicago Bridge and Iron, Combustion Engineering, General Electric, Struthers Wells, Timken Company, Rockwell International, and Westinghouse Advanced Reactor Division. In addition, TRW, Inc., is forging the alloy into automobile valves, and Gulf Oil is studying its resistance to sulfur at high temperatures for possible use in oil-drilling equipment. Utilities such as the Tennessee Valley Authority, Detroit Edison, and American Electric Power are using the alloy for reheaters and superheaters in coal-fired power plants. Studies of the alloy's fracture toughness, resistance to radiation damage, and compatibility with lithium and sodium are being studied by ORNL, Argonne National Laboratory, Battelle Columbus Laboratory, and HEDL. Obviously, there are numerous people in industry and academia who are raving about this new steel alloy and want to know more about it.

Vinod Sikka examines modified 9 Cr-1 Mo tubes after three years of operation at about 590°C in the Tennessee Valley Authority's Kingston Steam Plant. ORNL will examine these tubes after an additional three years of operation. The modified 9 Cr-1 Mo tubes seen here are those with small transition pieces, easily identified by two adjacent weld seams.

Nickel Aluminides

In November 1981 ORNL approved seed money for a project to make normally brittle aluminide alloys into ductile materials for use in high-temperature energy systems. Ordinary aluminide alloys are very strong and resistant to oxidation at elevated temperatures but are extremely brittle at all temperatures. In 1982, however, Chain Liu and Carl Koch of the M&C Division adjusted the composition of nickel aluminide by replacing some of the nickel with iron and by adding trace amounts of boron and manganese. The result was a strong, very hard, oxidation-resistant alloy that is also quite ductile. (See C. T. Liu's article on "Design of Ordered Intermetallic Alloys" elsewhere in this issue.)

Industrial interest in this new alloy is high. ORNL has received 200 letters requesting information on the ductile aluminides, and 20 companies have asked for samples that they want to test and evaluate in their laboratories. Cabot Corporation has committed its own funds for preparing large heats (batches) for evaluation of the alloy's wear and corrosion resistance and is conducting a market analysis to determine demand for the material. Cabot plans to make turbine disks from the modified aluminides for gas-turbine applications. Garrett Turbine Engine Company has expressed interest in working with ORNL on aluminides for turbine blades, and Ford Motor Company has requested test material for automobile exhaust valves (see box).

ORNL's Solar Cells

ORNL's Solid State Division has used lasers to implant ions and to anneal ion damage in silicon cells that convert sunlight to electricity. Some of these laser-processed solar cells have achieved efficiencies of 16.5%—that is, 16.5% of the incoming solar energy was converted to electrical energy. Such a high efficiency was certified to be a record by DOE's Solar Energy Research Institute. Since then, only one commercial solar cell company has topped that record, having made solar cells with an efficiency of 17.1%.

Now, in an effort to outdo this company and to get the ORNL technology into the marketplace, the Solid State Division is working with a commercial firm, Helionetics, Inc. In this arrangement, Helionetics has provided ORNL researchers with a high-power industrial laser to test ion implantation, surface modification, and annealing techniques on silicon semiconductor materials. The information obtained from these experiments in fabricating improved solar cells will then be available to Helionetics and other interested concerns.

In conclusion, ORNL materials scientists have developed new alloys and semiconductor materials for energy applications that are of great interest to industry and academia. Technology transfer activities are now under way to smooth the path for moving these promising materials into the marketplace. ornl

Unique ORNL Facilities Used by Academic and Industrial Scientists

Besides technology transfer to industry, ORNL also encourages the exchange of information between its researchers and those who work in the laboratories of industry and academia. Attracted by the results of ORNL basic research and by the unique array of research facilities at the Laboratory, a number of companies and universities send people to ORNL to conduct research on materials. This type of interaction is expected to increase with the completion of the High-Temperature Materials Laboratory later this decade. ORNL also sends researchers to visit and to guide companies and universities doing subcontracted work for the U.S. Department of Energy.

In all these sectors, researchers seeking to understand the behavior of materials must be able to characterize them, both structurally and chemically, on as fine a scale as possible. Several years ago, ORNL researchers recognized that the technology was in hand, or nearly so, to develop probes for measurements that would allow precise and quantitative descriptions of the internal makeup of materials. ORNL management supported efforts to develop a broad range of state-of-the-art capabilities for characterizing materials, including analytical electron microscopy, x-ray and neutron scattering, and particle-beam techniques for surface analysis. All are described in detail in articles in this issue of the *Review*.

These facilities and techniques represent a set of characterization capabilities unsurpassed anywhere in the world, and as such they are a major national resource. ORNL realized the value and broad appeal of these facilities to the materials community and quickly developed a number of approaches to make them available to university and industrial collaborators. The opportunity for collaboration presents the double advantage of making sophisticated equipment available to a wide spectrum of the materials community and of multiplying research achievements made at ORNL through the contributions of our collaborators.

Some examples of ORNL–university and ORNL–industry interactions follow.

ORNL's Metals and Ceramics (M&C) Division has assembled and maintained a complete, modern microanalysis facility for materials research. It includes state-of-the-art capabilities in transmission and analytical electron microscopy, surface analysis, and nuclear microanalysis. This equipment is made available to outside users under the auspices of the Shared Research Equipment (SHaRE) program administered by Oak Ridge Associated Universities for DOE. Ed Kenik, manager of the SHaRE program in the M&C Division, estimates that university researchers use SHaRE equipment 20% of the time for materials research. The SHaRE program allows outside users an opportunity to conduct research using sophisticated microanalytical facilities not available in their own institutions.

Participants in SHaRE projects in 1983 have included researchers from Auburn University, Dartmouth College, Georgia Institute of Technology, Kansas State University, the National Bureau of Standards, North Carolina State University, Vanderbilt University, and the universities of Florida, Kentucky, Missouri, Texas, Virginia, and Windsor.

Because ORNL is the lead laboratory for developing ceramics for DOE's advanced heat engines program, researchers here are working closely with several companies to develop ceramics for use in advanced gas turbines and adiabatic diesel engines. The companies include Garrett, Cummins, General Motors, and Ford Motor Company as well as major ceramic manufacturers such as Carborundum, GTE, and Norton.

ORNL's M&C Division is collaborating with industries and universities to develop and qualify an improved steel alloy for use in the pressure vessels of coal conversion plants. Institutions involved include Carpenter Technology Company, Climax Molybdenum Company, Cornell University, Lukens Steel Company, the University of California at Berkeley and at Santa Barbara, the University of Tennessee, and Westinghouse Research Center. Researchers at ORNL and the University of Kentucky have worked together to understand how chlorides in coal cause corrosion in fractionation vessels of coal liquefaction plants.

When ORNL's beam line is installed in 1984 at the Synchrotron Light Source now being completed at Brookhaven National Laboratory, more useful x-radiation will be offered from this station than can be obtained from all of the conventional x-ray sources available for research in the United States. ORNL's 20-m

A researcher from Japan, Hiroshi Naramoto (left), checks data from ion-scattering analysis of solids. With him are Bill Appleton (center) and Woody White (right). This work is performed at ORNL's Surface Modification and Characterization Facility.

x-ray beam line will be 10,000 times more intense than conventional sources. Scientists from all over the nation will use this special x-ray facility to study arrangements of atoms in metal alloys and defects in crystalline structures.

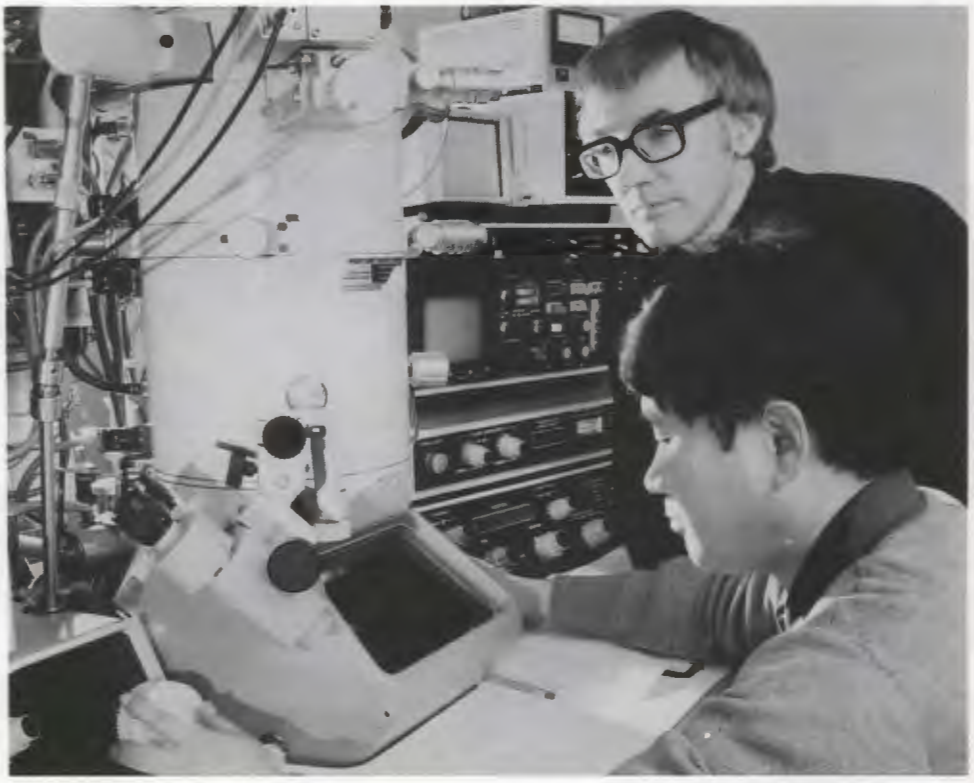
Already at least 15 universities are signed up to use the ORNL beam line for their research. They include Georgia Tech, North Carolina State University, Pennsylvania State University, Purdue University, Rice University, Vanderbilt University, Virginia Polytechnic Institute and State University, and the universities of Florida, Houston, Kentucky, Puerto Rico, Tennessee, Texas, Utah, and Virginia. Industrial users include Allied Chemical and IBM Research Laboratory.

ORNL's Solid State Division has several research facilities that are used by scientists from universities, industries, and other laboratories in the United States and abroad. ORNL's Surface Modification and Characterization Collaborative Research Center, where ion and laser beams are used to modify the surface and near-surface regions of materials to improve their properties, has been or is being used by 15 companies. They include Bell Laboratories, Corning Glass, Exxon, IBM, Motorola, Texas Instruments, Union Carbide, and Westinghouse. National laboratories in addition to ORNL that use the surface research facility are Argonne and Lawrence Livermore. Surface sciences at ORNL have drawn researchers from 17 universities in states such as Alabama, Arizona, California, Illinois, Maryland, Ohio, New York, Pennsylvania, and Tennessee. Seven foreign institutions in Australia, Austria, Germany, and Japan have also sent scientists to Oak Ridge to use this special facility.

When a researcher at the Forsyth Dental Center wanted to learn the positions of minerals in wet bones and the effect of water on those positions, he undertook a collaborative study with an ORNL physicist at one of the Laboratory's neutron scattering facilities. ORNL's neutron scattering and small-angle neutron scattering facilities have been used by 90 people from 38 institutions for materials research in a recent 12-month period. The institutions include 17 universities and eight U.S. companies. Scientists come from several foreign countries to pursue their studies here. ORNL has hosted representatives from Canada, England, France, Germany, Israel, and Japan. U.S. scientists have come to ORNL's neutron scattering facilities from such institutions as Iowa State University, the Massachusetts Institute of Technology, Northwestern University, Rice University, Yale University, and the universities of Illinois, Massachusetts, Pittsburgh, Wisconsin, and California at San Diego.

In short, ORNL's user facilities have proved to be of "material" benefit to researchers from all over the world.

Arthur F. Rowcliffe is group leader of the Structural Materials Group in ORNL's Metals and Ceramics Division. He obtained his bachelor's degree in metallurgy at the University of Wales and began working in the field of nuclear materials at the Culcheth and Harwell Laboratories of the United Kingdom Atomic Energy Authority (UKAEA). He left the UKAEA in 1966 to pursue doctoral studies at the universities of Cambridge and Manchester and earned his Ph.D. degree from the latter. After emigrating to the United States in 1970, Rowcliffe served as a materials consultant with a Boston-based company and as a senior engineer at Westinghouse Electric Corporation's Advanced Reactor Division near Pittsburgh. In 1975 he joined ORNL where his research interests have included developing and studying radiation-resistant alloys for fast breeder reactors and fusion devices.



Arthur Rowcliffe (right) and Eal Lee at the transmission electron microscope.

Design of D9:

A Radiation Damage–Resistant Alloy

By ARTHUR ROWCLIFFE

The development of breeder reactors in the United States, Europe, Japan, and the Soviet Union has stimulated an intense interest in the behavior of materials subjected to neutron radiation at high temperatures. A goal of materials development programs throughout the world has been to generate improved materials that will extend the lifetimes of reactor core components and hence reduce fuel cycle costs and improve breeding characteristics.

In a liquid metal fast breeder reactor, the fuel pellets are contained in long narrow tubes (fuel pins, or cladding). A regularly spaced array of several hundred fuel pins is contained within an outer, hexagonal cross-section flow duct, which channels the sodium flow for most effective cooling of the fuel pins. The sodium carries away heat, which is transferred to steam generators; the steam turns a turbine to generate electricity.

Cladding and Ducts

Materials for the fuel pin cladding and for the ducts are subjected to temperatures ranging from 350°C to 650°C coupled with intense irradiation by neutrons having energies from 0.01 to 1.0 MeV. The fuel cladding must withstand stresses from internal pressurization from fission products and from mechanical interactions with the fuel. It must maintain its integrity for several years in spite of attack from fission products on one side and from liquid sodium on the other. To maintain the geometry of the core and to ensure easy removal for refueling, the ducts must have good long-term dimensional stability—that is, they must retain their shape and size. The ducts must also be able to withstand impact loadings that could occur during refueling operations or during seismic events.

The neutron energy spectrum in a fast reactor causes large numbers of atoms to be displaced from their lattice sites in materials making up

the reactor core. How many times a single atom is displaced depends on how long its host component remains in the core. Economic considerations require that core components for commercial breeders have lifetimes of about 900 full-power days. Translated to the microscopic scale, this lifetime requirement means that in some regions of the core, each atom in a component will be displaced, by collisions with energetic particles, approximately 150 times.

ORNL has developed a steel alloy that is resistant to neutron-induced swelling. It could prove useful in ducts and cladding in fuel assemblies of breeder reactors and as a structural alloy for fusion reactors.

In the mid-1960s, when design work on many of the world's current breeder reactors began, no information existed on the behavior of materials under these exacting conditions. However, data were available on the effects of radiation on materials properties at low displacement levels. This limited information, together with proven fabrication technology, led to the almost universal selection of conventional austenitic stainless steels of the AISI 316 type for cladding and ducts. This material is currently used, for example, for fuel assemblies in the recently commissioned Fast Flux Test Facility (FFTF) at Hanford, Washington, which is designed to test breeder reactor fuels and components.

Void Swelling

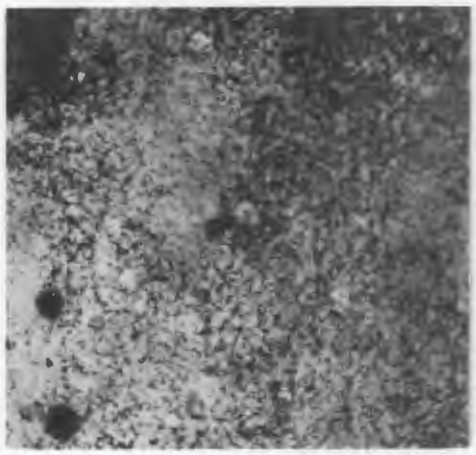
During the late 1960s when irradiation experiments in fast reactors achieved increasingly high displacement levels, a new radiation phenomenon was discovered in the United Kingdom—namely, void swelling. Subsequently, metallurgists realized that two other phenomena—irradiation creep and radiation-induced solute segregation—were closely coupled with void swelling.

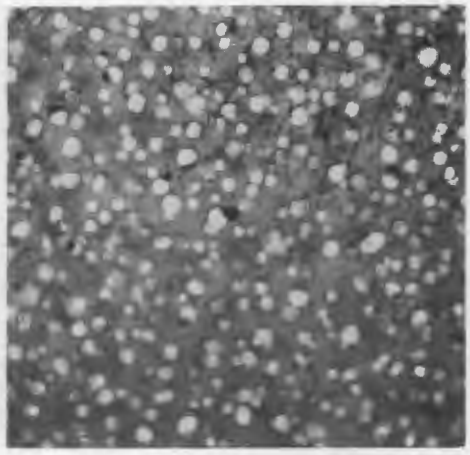
The atoms displaced from their sites during neutron irradiation are known as interstitials, and the resulting empty lattice sites are known as vacancies. Vacancies and interstitials are defect regions of high energy. These so-called point defects must be eliminated to reduce the energy of the system. Vacancies and interstitials migrate rapidly and either recombine with each other or become absorbed at various favored locations, or sinks, within the metal structure. The phenomena of void swelling and irradiation creep (stress-induced growth) have their origins in the way in which point defects are absorbed at internal sinks. Under certain circumstances, vacancies agglomerate and form tiny, three-dimensional voids in the metal lattice. The corresponding displaced atoms collect into extra platelets of atoms known as dislocation loops. The voids grow continuously during irradiation, and the dislocation loops expand and move through the metal lattice, eventually giving rise to macroscopic dimensional changes. In other words, the material swells and its density decreases.

As data became available at increasingly higher levels of displacement damage, the void swelling phenomenon came to dominate considerations of reactor core design. As a result of swelling, ducts undergo both a radial and an axial growth. Because of neutron flux and temperature gradients, the rate of swelling varies across the duct wall and induces a bowing along the length of the duct. Eventually, these shape changes cause significant reactivity changes, lower the efficiency of breeding plutonium fuel from uranium-238, and create difficulties in removing individual fuel assemblies from the core.

Recently, it has been shown that the original material selected for breeder reactor cores—type 316 stainless steel—undergoes a volume increase of 50% to 70% when irradiated to a level equivalent to the goal fluence of a commercial breeder reactor. The serious design problems created by this phenomenon and its potential impact on breeding performance and economics led to the launching of a major experimental effort in this country in 1974 to explore all aspects of core materials performance and to seek a solution to the swelling problem. This program—the national Clad/Duct Alloy Development Program—involved several national laboratories, universities, and the principal reactor manufacturers. It was coordinated by Hanford Engineering Development Laboratory (HEDL).

Several different classes of alloys were considered in the search for low swelling materials, most notably nickel-based superalloys and ferritic stainless steels. However, the AISI 316 stainless steel, in spite of its poor resistance to radiation-induced swelling, was heavily favored because of these assets: excellent mechanical properties, resistance to corrosion, and the existence of a well-developed technology to fabricate the material. The approach advocated by Oak Ridge National Laboratory's Radiation Effects Group, then led by Jim Stiegler and Everett Bloom of the Metals and Ceramics (M&C) Division, was to seek improvements in the swelling resistance of type 316 stainless steel by slightly modifying the alloy composition while





Here is the microstructure of stainless steels (magnified 50,000 times by transmission electron microscopy) after irradiation in EBR-II to a neutron dose of 60 dpa at 500°C. Microscopic voids developed in the type 316 stainless steel shown at left. The structure of the low-swelling D9 alloy (right) consists of dislocations and fine precipitates.

preserving the other advantageous properties of the alloy class.

Type 316 stainless steel is a member of a class of austenitic stainless steels. (Austenitic steels differ from ferritic steels in many ways; for example, they are nonmagnetic and do not undergo changes from ductile to brittle behavior in certain critical temperature ranges.) The austenitic stainless steels are based upon the iron-chromium-nickel-carbon alloy system—that is, these elements are the primary constituents. These steels also contain some half a dozen minor alloying elements such as silicon, molybdenum, and manganese, which make essential contributions to alloy properties. In addition, the steelmaking process contributes a host of impurity or residual elements such as oxygen, nitrogen, phosphorus, sulfur, and boron, which the manufacturer tries to keep at low levels in the range of <0.01 wt %.

Despite their small concentrations, these minor and impurity elements can greatly influence an alloy's tendency to swell. The first indications of their influence came from ORNL experiments in the early 1970s at the Experimental Breeder Reactor-II (EBR-II) in Idaho. It was observed that the radiation exposure at which alloy swelling started varied significantly among stainless steels having minor differences in compositions. ORNL researchers who made this observation were Jim Stiegler, Everett Bloom, and Jim Leitnaker.

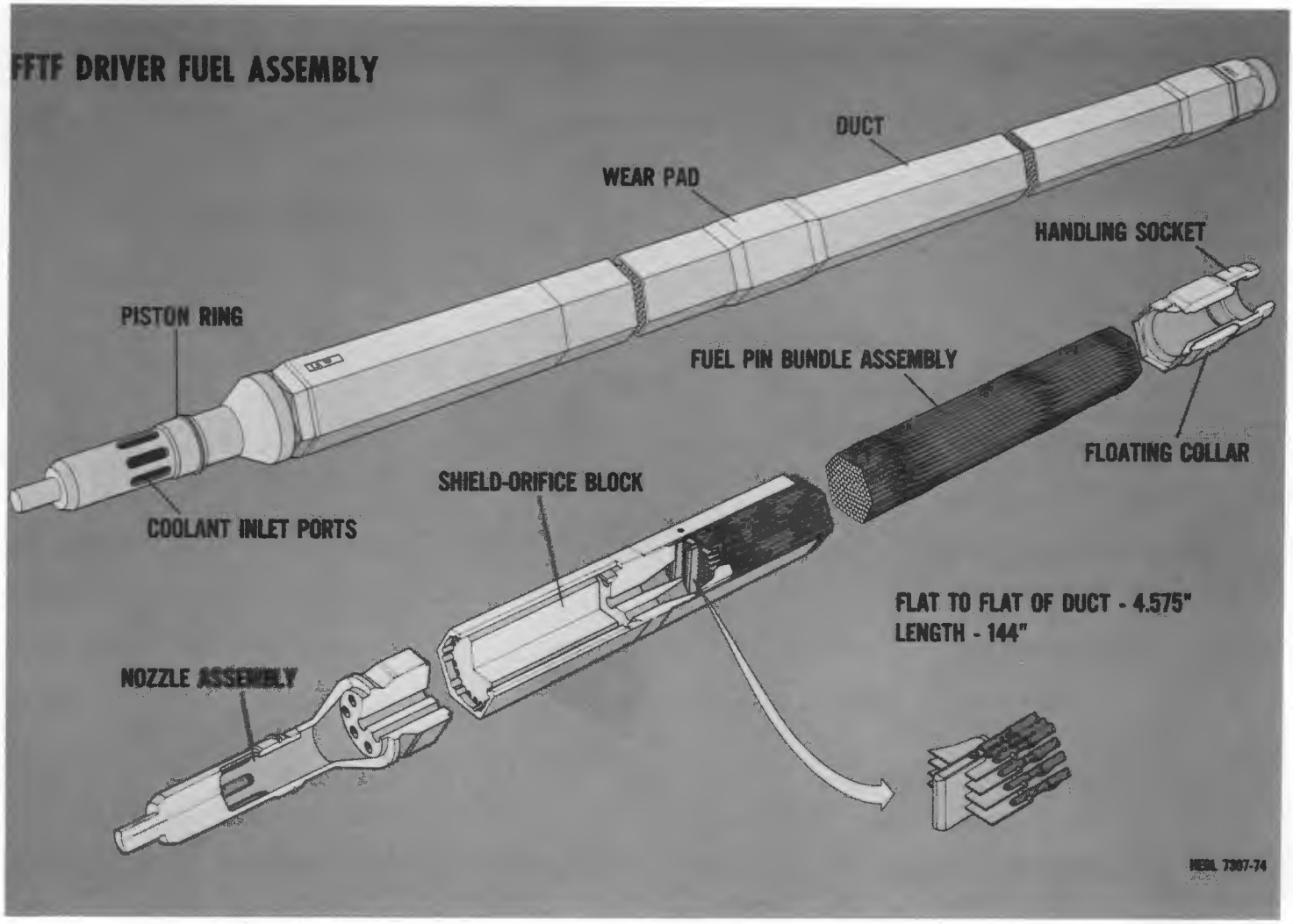
At about this time, it was demonstrated by researchers in the United Kingdom that void swelling in metals and alloys could be produced by bombarding specimens of these materials with beams of heavy ions from particle accelerators. The high-particle fluxes from these machines produce atomic displacements at rates 1,000 to 10,000 times as high as those achieved in a breeder reactor. Thus, use of accelerators instead of reactors in attempts to simulate reactorlike radiation damage reduces the time scale of an irradiation experiment from years to hours. (It was subsequently shown by Eal Lee, Phil Sklad, and me that data obtained at these high damage rates may not be used to predict accurately and quantitatively the actual behavior of materials in operating reactors. However, the technique does provide a versatile means of exploring damage mechanisms and characterizing general behavior of various alloy classes in a well-controlled environment.)

Titanium-Modified Steel

The 5-MV Van de Graaff accelerator operated by the M&C Division's Radiation Effects group was used by Greg Gessel and me in a series of experiments on both simple iron-chromium-nickel (Fe-Cr-Ni) alloys and on complex stainless steels. We showed that swelling is highly sensitive to the concentrations of certain minor alloying elements, notably titanium (Ti), silicon (Si), and niobium (Nb). (Titanium is useful in other ways, too. In 1968 Jim Weir, now director of ORNL's M&C Division, and W. R. Martin discovered that the addition of titanium reduces irradiation embrittlement in stainless steel; for this work, Weir received an E. O. Lawrence Award in 1973.)

This early work in 1972–75 focused our attention on the potentialities of steels having optimized Ti and Si concentrations and led to the specification of alloy LS1, which proved to be highly resistant to swelling in heavy-ion irradiation experiments. Subsequently, the Cr, Ni, and Ti concentrations of this alloy were adjusted to prevent the formation of certain second-phase particles, which developed during exposure to reactor operating temperatures and which were known to aggravate embrittlement problems. The resulting composition was given the designation D9. This designation has since become a generic term that covers a class of titanium-modified steels under development by the United States Breeder Program.

In 1977-78 the national Clad/Duct Alloy Development Program embarked upon a series of irradiation experiments in EBR-II to explore the full range of D9 properties—i.e., resistance to irradiation creep and swelling, stress rupture behavior, tensile properties,



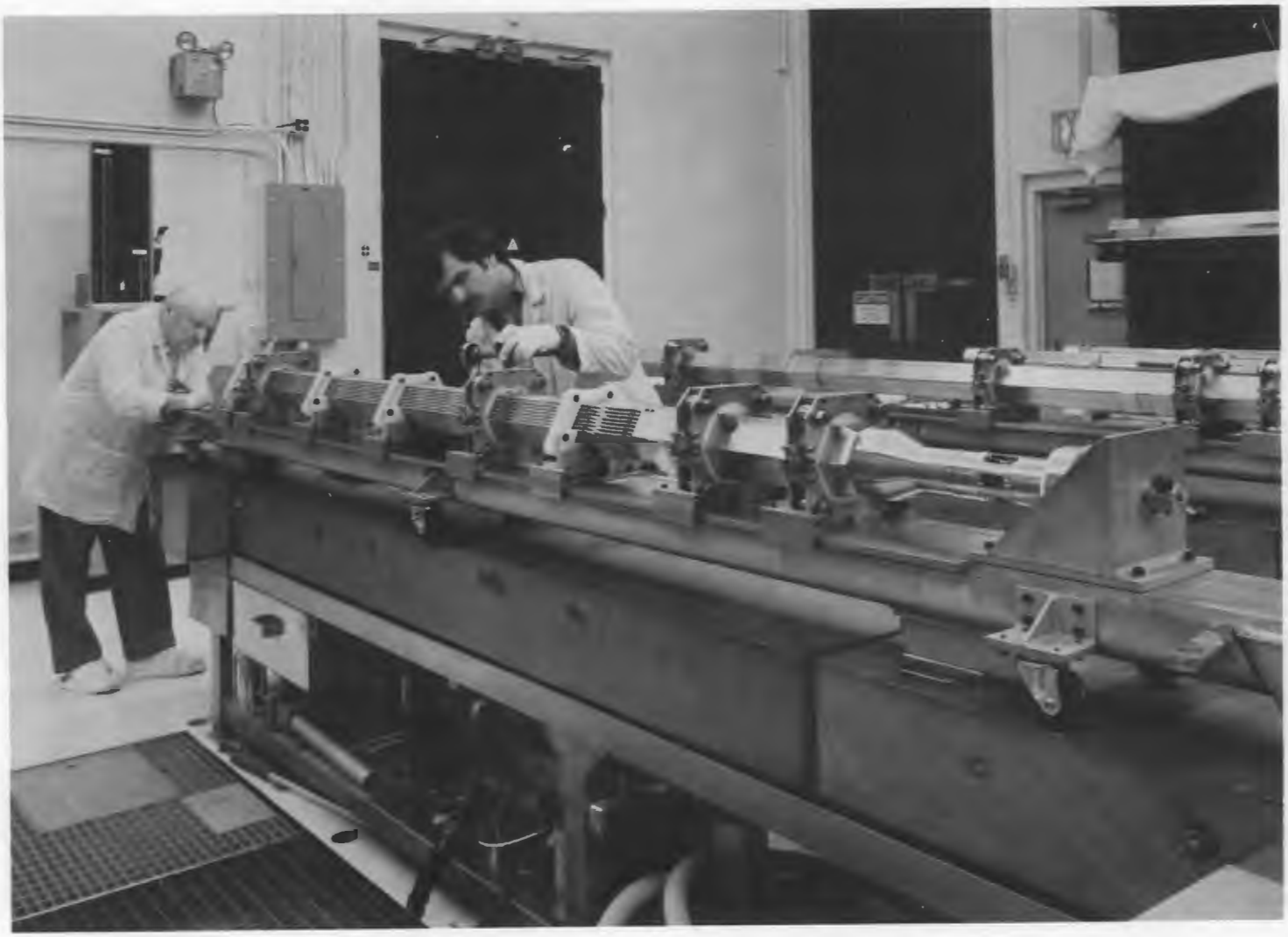
The D9 alloy developed and tested by ORNL and later by Hanford Engineering Development Laboratory (HEDL) will be used in the ducts and fuel pins designed for the driver fuel assemblies of the Fast Flux Test Facility at HEDL.

fracture toughness, corrosion properties, and fuel pin behavior. Early data from this comprehensive effort showed that the D9 alloy has promising properties. Since then the development effort has divided into three distinct but interactive activities, each with its own time scale.

Design Data Base

To allow core designers to explore the full implications of a new material and to meet the requirements for commercial acceptance of that material, a complete design data base has to be established. The first stage of the data base project is to make measurements on commercially manufactured heats of D9 to determine the effects of irradiations on the alloy's physical and mechanical properties. Experiments placed in EBR-II about five years ago are now approaching neutron exposure levels that are typical of a commercial breeder reactor. They show that the early D9 composition is 50 times as resistant to swelling as type 316. All other properties (including those altered by exposure to radiation) have been found to be at least equal to those of type 316. Based on these data, we estimate that the use of the D9 alloy for core components in the Fast Flux Test Facility would double the lifetime of the existing core.

The second stage of establishing a design data base is to gain



D-9 alloy, which was originally developed at ORNL, is used throughout this test assembly being readied by Westinghouse Hanford Company personnel at Richland, Washington. Pellets of mixed uranium-plutonium oxide fuel are sealed inside 217 long thin tubes called fuel pins. The fuel pin tubing and the hexagonal duct that would later be placed around the pin bundle are both fabricated from D-9 alloy. The test assembly is now undergoing irradiation testing in the Fast Flux Test Facility at Hanford.

operating experience with full-scale assemblies of fuel pin bundles and ducts fabricated from D9. Such a program was started by HEDL in the FFTF when it went into full-power operation early in 1983.

In addition to the design data base activity, a parallel effort to optimize alloy performance is in progress at HEDL. For example, a series of D9 alloys having a range of Si and Ti concentrations is being irradiated to determine the most effective combination of elements for swelling resistance. This work will also allow metallurgists to specify the acceptable ranges of critical element concentrations for commercial production of large heats of D9. Another effort examines how varying the concentrations of minor impurities affects the resistance of D9 alloys to creep rupture. Because of its high neutron flux, the use of the FFTF as an irradiation facility has halved the time required for irradiation experiments. It is expected that these optimization studies will define compositions that have properties superior to those alloys of the principal current composition. In addition, these studies will allow the definition of composition and fabrication specifications to ensure reproducible component performance.

Basic Studies

Simultaneously, during the large-scale effort to ready D9 for

A 12-foot-long fuel assembly is prepared for insertion into the reactor vessel region of the reactor containment building of the Fast Flux Test Facility. The large machine that transfers fuel and test assemblies in and out of the reactor vessel is shown in the background of this "fisheye" view.

commercialization by obtaining information on how to produce the alloy composition with the best properties, an understanding has been developing of the basic mechanisms involved in the swelling behavior of complex alloys. This understanding has evolved in the first place from the application of new analytical electron microscopy techniques to investigate the structure of damage in neutron-irradiated austenitic steels. In ORNL's M&C Division, for example, the Structural Materials group is currently using these techniques to examine about 10 compositional variants of the D9 alloy. Secondly, irradiation experiments using heavy ion beams in various laboratories around the world have yielded a wealth of new information on high-temperature radiation damage mechanisms. At ORNL the Defect Mechanisms group led by Lou Mansur is using theory and computer modeling to predict precipitation behavior and helium effects in D9 alloys (see Mansur's "Radiation Effects in Metals and Alloys" elsewhere in this issue). The success of these efforts at ORNL depends heavily on the developments in analytical electron microscopy pursued by the Electron Microscopy group led by Jim Bentley (see Bentley's "Characterizing Materials by Electrons" elsewhere in this issue).

The importance of these activities is not only to understand the behavior of the existing commercial alloys but also to suggest new directions for further development. As such, this activity lags behind the design data base phase by at least six to eight years. However, the achievements of these programs will form the springboard for the development of a second generation of advanced alloys based upon a much deeper understanding of the mechanisms involved in the swelling phenomenon.

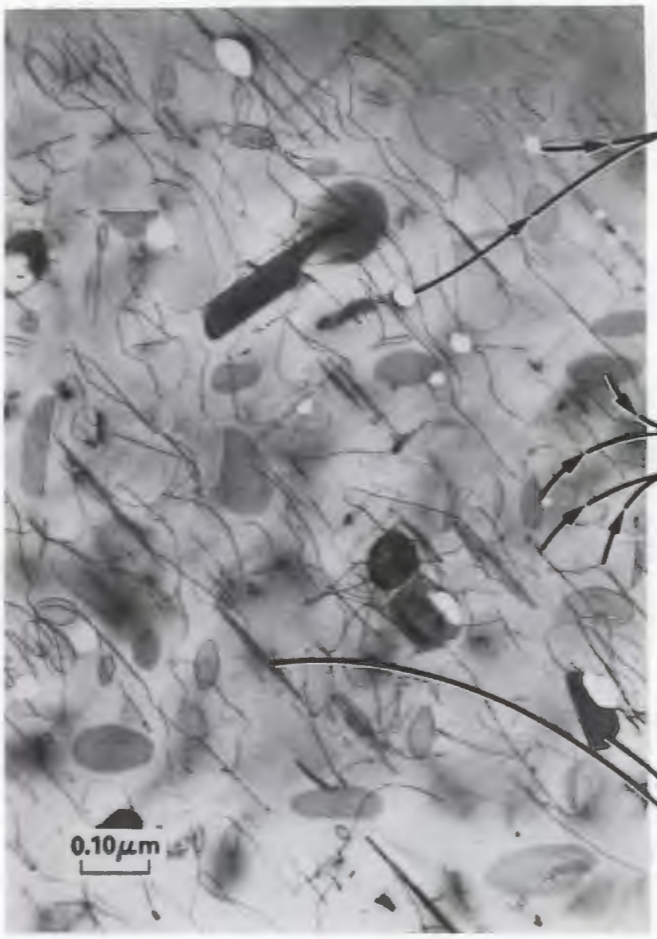
The improvements in alloy performance achieved in the Breeder Program are also significant to the development of magnetic fusion energy devices. Stainless steels are included among several materials under development for the first wall and blanket structures of fusion reactors. These materials, which are being studied at ORNL, must perform under radiation conditions not unlike those in a breeder reactor core except that the fusion materials will be exposed to neutrons having energies of 14 MeV. The phenomenon of void swelling could produce dimensional changes that could limit the lifetime of these devices. Thus, both breeder reactors and fusion devices of the future are likely to benefit from the development of new swelling-resistant materials. ornl

Materials for Fusion

The plasma to be magnetically confined in commercial fusion power devices can be exceedingly hostile to its immediate surroundings—the materials making up the "first wall" and the structure holding the blanket used for breeding new fuel. At the same time, materials can have the effect of quenching the hydrogen plasma, thus preventing it from producing the sustained heat required to make steam for generating electricity. This interaction of materials and plasma is being studied at Oak Ridge National Laboratory.

Nuclear fusion reactions that occur in the high-temperature, ionized hydrogen gas produce neutrons with energies of 14 MeV—much higher than the neutron energies in fission reactors. These high-energy neutrons can severely affect materials through intense heating and radiation damage. Unless appropriate materials are found or developed that can resist these effects, the desired lifetime of five to ten years for fusion reactor components may be unattainable. For this reason, the National Research Council's Energy Engineering Board recently identified the materials issue as one of the most critical engineering problems in fusion energy development.

Researchers in ORNL's Fusion Materials Program are examining a limited range of materials that promise not only to withstand neutron radiation and heat fluxes but also to allow a sufficient number of neutrons to be absorbed by the blanket of lithium for breeding the fusion fuel, tritium. These materials were selected because they present a minimal environmental impact—that is, they do not become excessively radioactive as a result of inter-



This electron micrograph, made by Bill Wiffen, Jim Stiegler, and Everett Bloom of ORNL, shows the neutron-radiation damage that materials in a fusion reactor will undergo. The radiation damage was simulated by placing a sample of stainless steel in the core of a fast breeder fission reactor at a temperature of about 590°C and exposing it for a year to a high flux of neutrons. The total flux (1.9×10^{26} neutrons/m^2) displaced each atom in the lattice of the steel an average of 10 times. Although most of the point defects from neutron irradiation recombined and annihilated each other, a small fraction of the defects cluster with others of their own type. Some vacated sites in the lattice (vacancies) aggregated into empty spaces called voids (white areas); some displaced atoms coalesced into regions called dislocation loops (medium gray areas), and the chemical elements in the steel segregated (dark gray areas). As a result the steel swelled and became less ductile.

actions with neutrons and thus do not pose a serious waste disposal problem.

ORNL materials scientists have also looked at the effects of neutron radiation on electrical insulation for the plasma-confining superconducting magnets. In this small effort, the scientists established the irradiation lifetimes of epoxies and polyimides and provided data on the increased resistivity in copper used to carry the current in the magnets in case the superconductor transforms to a normal conductor. If the resistivity is too high, the magnet becomes unsafe.

Materials that appear promising for use as the first wall are beryllium, graphite, aluminum alloys, and refractory carbides. One goal of ORNL's Fusion Materials Program is to examine the extent to which these materials, in interaction with the energetic plasma, introduce impurities to the plasma. Such wall-generated impurities are a problem because they cause energy losses in the plasma. Using laser-induced fluorescence spectroscopy, physicists from ORNL's Solid State Division have measured the density and distribution of impurities such as aluminum and neutral hydrogen in hydrogen plasmas. These results have provided new insights into the first-wall environment and materials requirements.

Another goal of ORNL's Fusion Materials Program has been to identify and improve alloys that can qualify as blanket structural materials. Front-runners include ferritic steels and austenitic stainless steels; vanadium alloys and long-range-ordered alloys have been selected for a long-term investigation. Because no fusion test reactor exists, the next best option is to expose test materials to fusionlike environments to determine which materials are the most resistant to radiation damage. Simulation tests have been done on nickel-containing alloys such as austenitic stainless steels at ORNL's High Flux Isotope Reactor (HFIR) and the Oak Ridge Research Reactor (ORR), which are designed to produce great numbers of neutrons having a wide spectrum of energies. Recognizing the excellent fusion materials testing capability of the ORNL reactors, the Japanese Atomic Energy Research Institute recently signed a five-year, $10-million agreement with the U.S. Department of Energy to collaborate on tests of alloys in the HFIR and ORR. From the results of the simulation tests, metallurgists have predicted that the unique radiation damage of 14-MeV neutrons in most materials would include (1) the formation of defects and high concentrations of helium and hydrogen in the metal lattice, causing embrittlement, and (2) the displacement of atoms from their lattices 10 to 20 times, forming voids that result in swelling.

Our results also have shown that both the austenitic stainless steels and ferritic steels (including the chromium-molybdenum steel alloy developed by ORNL and Combustion Engineering, Inc.) retain their ductility and strength below 600°C even with several hundred parts of helium per million in the lattice. These encouraging results suggest that the lifetimes of improved materials can be made long enough to meet the requirements of fusion reactor designers.—*James L. Scott, Metals and Ceramics Division.*

Breeding Tritium at ORNL

Recently, ORNL and Argonne National Laboratory collaborated on a three-month experimental run to demonstrate that tritium could be bred and recovered from a lithium-containing blanket material. The experiments were performed at the Oak Ridge Research Reactor under the leadership of ORNL's Engineering Technology Division; the five other divisions that participated were the Analytical Chemistry, Chemical Technology, Engineering, Instrumentation and Controls, and Operations divisions. ANL designed and supplied the miniaturized breeder blanket assembly and the tritium gas analysis system. ORNL designed and built the test facility and capsule test assembly and carried out the experiments.

The material used to breed tritium was a ceramic, lithium aluminate. After the lithium aluminate was irradiated with neutrons, the newly bred tritium was swept out by a gas consisting largely of helium. The tritium was collected for analysis by the gas analysis system.

The experiments demonstrated that 99% of the tritium released from the lithium aluminate was in the gaseous form, that essentially all the tritium produced was recovered, and that the tritium release could be accelerated by increasing the temperature and by making the sweep gas 0.1% hydrogen. The containment system also worked well; no radioactive tritium was released to the environment.

Radiation Effects in Metals and Alloys

By LOUIS K. MANSUR

Fission power plants and future fusion devices can be reliable sources of electricity if they have components that last a long time before being replaced. Because many metals and alloys are vulnerable to radiation damage at high temperatures, it is critical that materials researchers first understand how radiation affects materials in order to select, modify, or design alloys that are resistant to radiation damage.

At Oak Ridge National Laboratory, materials researchers have

Louis K. Mansur, group leader of the Defect Mechanisms Group in ORNL's Metals and Ceramics Division, came to ORNL in 1974. His previous experience includes five years with the U.S. Atomic Energy Commission (predecessor of the U.S. Department of Energy) in reactor physics and engineering. He holds a Ph.D. degree in engineering physics and materials science from Cornell University. His current area of interest is the mechanistic understanding of atomic and microstructural processes in metals and alloys and the application of this understanding to materials problems in energy technology. At ORNL he is developing the theory of microstructural evolution–a theory based on point defect reactions and integrating experimental and theoretical activities in the area of radiation effects on materials. Mansur's group received DOE's 1983 Materials Sciences Award in the category of significant implications for energy technology for "the effect of helium gas and pulsed irradiation on materials behavior in fusion reactors." This and other work are described in the article.

Neutrons from fission and fusion power plants can lead to profound changes in metals and alloys. At ORNL theorists and experimentalists work together to understand how radiation alters the properties of these materials. Their ultimate goal is to determine the mechanisms underlying these changes and to select and design alloys that resist radiation damage.

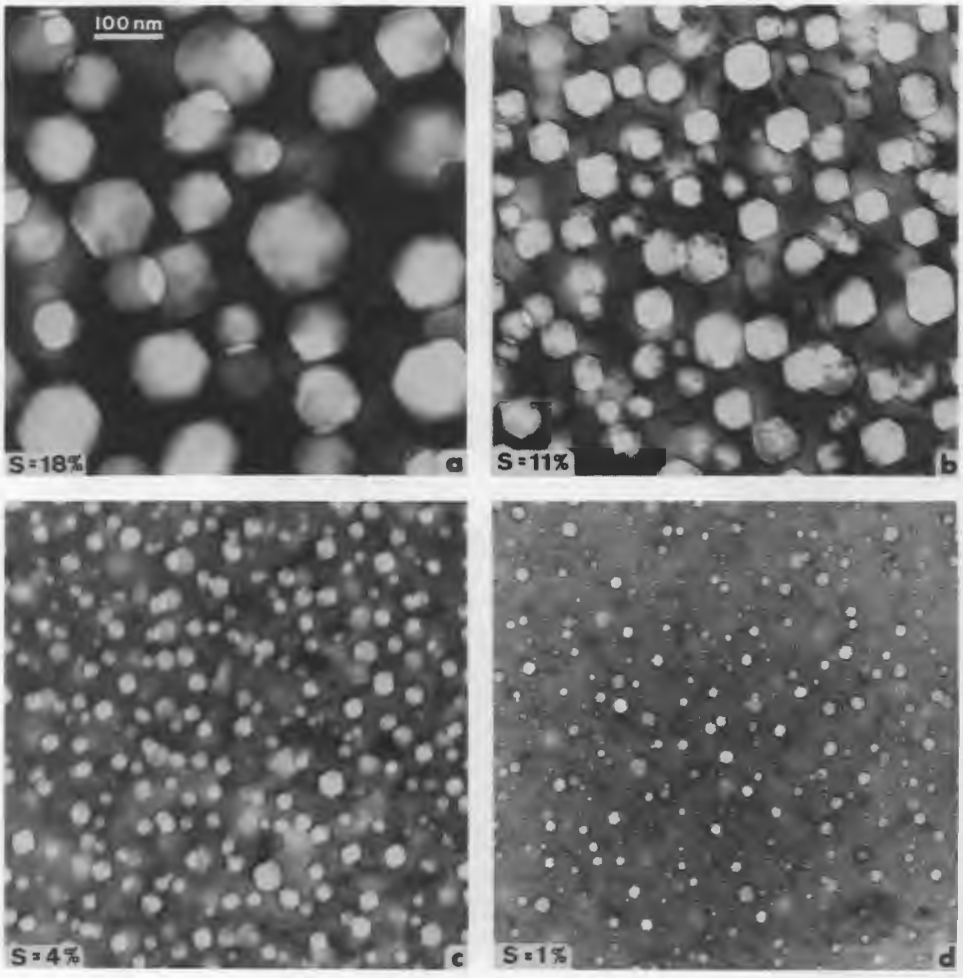
been working on such problems for more than 30 years; in fact, ORNL is regarded as a world leader in the field of radiation effects in structural metals and alloys. Research in ORNL's Metals and Ceramics (M&C) Division embraces both the basic science of radiation effects and the design of radiation-resistant structural materials for fission and fusion reactors. The interaction of these programs is an outstanding example of the mutual benefits attainable when both applied and basic research efforts are focused on a common problem area.

ORNL's basic researchers in defect mechanisms work with applied researchers in structural materials to understand underlying atomic and microstructural mechanisms of radiation effects. This information guides the applied researchers in designing improved alloys for possible use in fission and fusion reactors. These researchers interact heavily with electron microscopists and receive extensive support from specialists in specimen preparation and laboratory techniques. All this research is supported by the U.S. Department of Energy.

The field of radiation effects in materials is a vital area of reactor technology as well as an important area of materials science. In the United States, DOE spent about $25 million in fiscal year 1983 on radiation effects research and development, excluding the large cost of operating materials testing reactors and accelerator-based neutron sources. Additional research is supported by the U.S. Nuclear Regulatory Commission. Besides ORNL, other national laboratories involved in radiation effects R&D re Argonne National Laboratory, Battelle Pacific Northwest Laboratory, Brookhaven National Laboratory, Hanford Engineering Development Laboratory, and Los Alamos National Laboratory. Corporate research laboratories and divisions of companies such as the Westinghouse Electric Corporation and the General Electric (GE) Company also participate in this research as do a number of prominent universities. In addition to the United States, France, the United Kingdom, Germany, Japan, and the Soviet Union have major research programs in radiation effects.

Property Changes

That radiation affects the properties of materials has been known for at least 150 years—ever since



The method of introducing helium strongly influences swelling in a test specimen of a stainless steel alloy irradiated at 625°C with nickel ions to a high dose representative of that accumulated in a reactor over several years. At right are micrographs of specimens (a) irradiated with nickel ions only, (b) irradiated with nickel ions while simultaneously being injected with helium to simulate neutron-induced transmutation, (c) preinjected at 625°C with helium and then irradiated with nickel ions, and (d) preinjected at room temperature with helium and then irradiated with with nickel ions. The symbol S indicates the amount of swelling.

the discovery that some minerals exhibit anomalous properties because of exposure to the (then unknown) internal radiation from decay products of the naturally occurring radioactive thorium and uranium in the minerals. ORNL consultant Eugene P. Wigner is generally credited with the first suggestions in the 1940s that energetic neutrons in reactors would displace significant numbers of atoms and lead to changes in properties. However, the profound changes in physical and mechanical properties that radiation could cause in materials were fully appreciated only after the development of nuclear fission reactors in the 1950s and 1960s. In these reactors, neutrons from the fissioning fuel core displace atoms in structural materials. Because highly energetic neutrons displace more atoms than do "slow" neutrons, fast spectrum reactors such as the liquid metal fast breeder reactor (LMFBR) undergo more radiation damage than do thermal spectrum reactors. Thus, when fast spectrum reactors were first operated, the magnitude of possible radiation effects began to become apparent.

Radiation effects is a broad term encompassing all the phenomena that occur in materials exposed to radiation. In reactors, energetic neutrons collide with metal atoms, which are geometrically arranged in lattices; these collisions knock out atoms from their lattice sites, thus creating interstitial atoms, which are accommodated in the interstices between normal lattice sites. The empty lattice sites are called vacancies. Interstitials and vacancies are referred to collectively as point defects. These radiation-induced point defects are ultimately responsible for progressive changes in microstructure and macroscopic properties of materials in reactor environments.

When the vacancies agglomerate as empty spaces called voids or cavities, the material begins to increase in volume and decrease in density; in other words, it starts to swell. *Swelling*, which can cause the volume of structural alloys to increase by tens of percent when subjected to high doses of radiation, is one of the most important effects of radiation. Designers of fusion reactors and fast breeder reactors must take this effect into account. For example, design must ensure that dimensional limits are not exceeded.

Neutron-induced reactions of alloying or residual impurity elements in alloys can also be impor-

Monty Lewis adjusts bombardment parameters for a triple-beam irradiation using the system he pioneered. The beam line on the left carries heavy ions such as nickel or iron for producing displaced atoms in the target. The beam line on the right carries ions of hydrogen or helium, which cause important changes in the response of metals and alloys to radiation.

tant. When neutrons react with the compositional elements of steels (including nickel, iron, and chromium), helium is formed. This insoluble rare gas is an important transmutation product that affects swelling and causes the material to become brittle and more vulnerable to cracking. *Irradiation embrittlement* is exacerbated when impurities and alloying elements are forced by the point defect fluxes to concentrate in grain boundaries (interfaces between individual crystallites) and when the alloy is hardened by changes in the microstructure of the grain interiors.

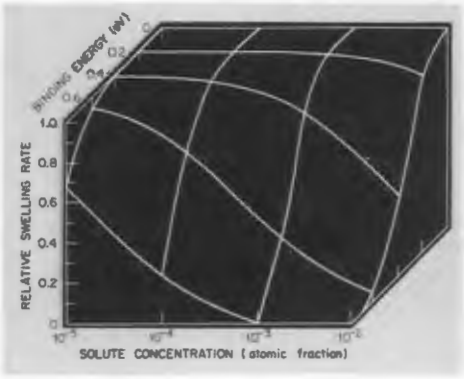
When an irradiated material is examined in the electron microscope, high densities of cavities ranging in diameter from 1 nm to more than 100 nm are found. The cavities can be so numerous that their average spacing is only a few times their diameter. These cavities, which represent a new phase of empty space, are generally not gas-filled bubbles. However, helium and other gases are responsible for stabilizing the cavities and allowing swelling to begin. Without the gases, very small cavities would shrink by evaporation of the vacancies. Once the cavities reach a critical size because of the presence of helium, they will grow inexorably, driven by the point defect fluxes. On a microscopic scale, the material resembles Swiss cheese; the volume of empty space contained in the cavities is equal to the overall swelling of the material.

Another radiation effect is called *irradiation creep*, the permanent deformation that results when a material is irradiated while a mechanical stress is applied. This stress-directed deformation may be many orders of magnitude larger than the more familiar thermal creep of materials subjected to stress at elevated temperatures. *Irradiation-induced solute segregation and precipitation* cause local inhomogeneities in the alloy composition because of the demixing of the solid solution resulting from the flows of point defects. These local variations in composition lead to macroscopic changes in physical and mechanical properties of materials. For example, precipitates may interact with cavities, thus leading to higher swelling. Also, precipitation may either harden or soften the material, depending on the detailed structure and composition of the material.

Basic Studies

Under Jim Weir the M&C Division has been contributing to the characterization and understanding of these phenomena for many years. Investigations into both basic mechanisms and applications for

The theory predicts reduced swelling when impurities are introduced. Impurities and certain alloying elements trap point defects, thereby increasing the fraction of point defects that recombine and consequently reduce swelling. High concentrations of impurities and strong binding of point defects to impurities are predicted to reduce swelling drastically. These predicted trends agree with experimental observations of impurity and alloying effects on swelling.



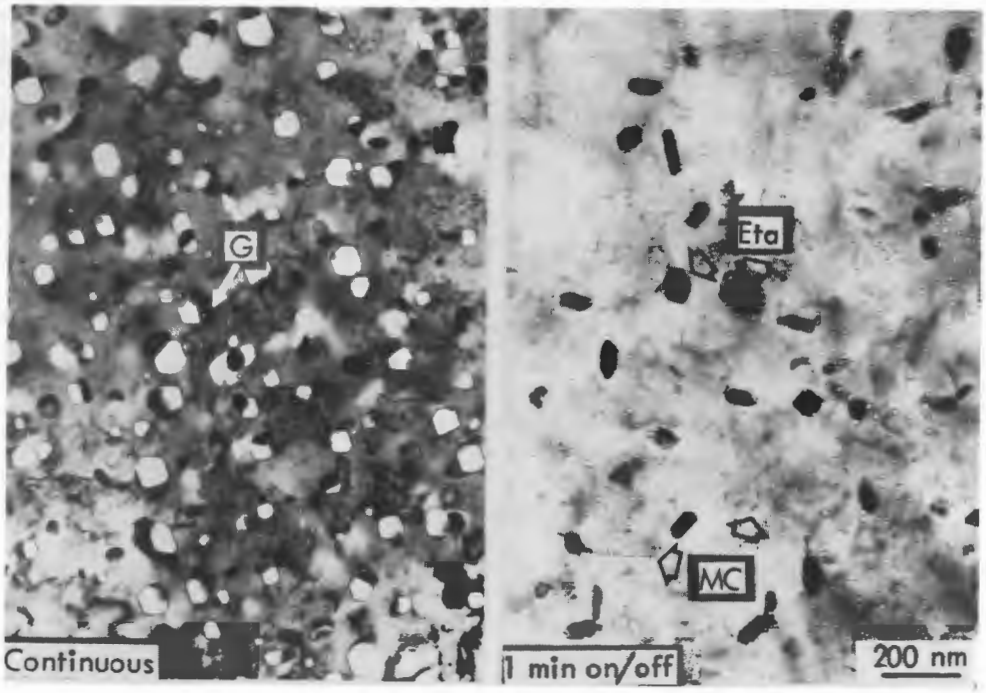
fast reactor materials were supported initially by the U.S. Atomic Energy Commission. These programs evolved and grew along with the funding agencies and later were incorporated into the U.S. Energy Research and Development Administration and now into DOE. In 1974 a large program of basic radiation effects research was established in the M&C Division under the direction of Jim Stiegler. Shortly after this a large program on alloy development for fusion reactor materials was also begun in Stiegler's group.

In the Defect Mechanisms Group, theorists work with experimentalists to investigate mechanisms of radiation damage in materials considered for use in fusion devices and in fast breeder reactors. This combined effort has helped to develop principles used for designing radiation-resistant materials. By employing electron microscopy as the main tool of observation as well as other modern techniques and equipment, ORNL scientists have characterized defects approaching the atomic scale and localized regions of compositional inhomogeneities on the order of tens of nanometers in materials before and after irradiation.

To simulate the radiation damage likely to occur in materials in breeder and fusion reactors, ORNL scientists subject various materials to neutron radiation from two DOE fast reactors, the Experimental Breeder Reactor II in Idaho and the Fast Flux Test Facility in Washington, and from ORNL's mixed thermal and fast spectrum reactors—the High Flux Isotope Reactor and the Oak Ridge Research Reactor, respectively. In addition, charged particles from accelerators are used extensively to produce radiation damage. For example, using an accelerator to irradiate stainless steel with nickel ions of several million electron volts produces radiation effects qualitatively similar to neutron irradiation from a reactor. At ORNL a dual accelerator system is used; a 5-MeV Van de Graaff accelerator bombards the material with heavy ions, and a 400-keV Van de Graaff accelerator injects light ions such as helium and hydrogen into the region damaged by the heavy ions. The injection of these gases is intended to mimic the production of important neutron-induced transmutation products. The development and routine operation of this important facility are the responsibility of Monty Lewis. Aided by Roy Buhl and Sylvester Cook, Lewis has developed a wide variety of ion sources, pioneered simultaneous triple ion-beam bombardment, and developed beam-pulsing capabilities.

ORNL has contributed extensively to the worldwide effort to characterize the microstructure and properties of materials exposed to neutron radiation. The M&C Division's development of a center for state-of-the-art electron microscopy, which is headed by Jim Bentley, stemmed directly from the need to examine the microstructural and microcompositional changes induced by radiation. The use of charged-particle techniques as a faster, less expensive, and more controllable method for producing radiation effects was pioneered by ORNL and several other laboratories. ORNL's accelerator laboratory from organizations such as GE, Westinghouse, the Harwell Laboratory in England, many organizations in Japan, and many universities. ORNL researchers at the accelerator laboratory are also developing advanced techniques for ion-beam microanalysis and ion implantation.

ORNL has recently conducted experiments in which the ion beam is interrupted to subject the specimen to pulsed radiation. Because materials in some fusion reactors designed for the future would be subjected to pulsed irradiations, a need exists for data in this area. Until recently, nearly all radiation effects data pertained to the effects of steady irradiation. ORNL researchers were among the first to anticipate the need for and to obtain data on pulsed radiation effects. The theory of radiation effects suggests that pulsing is also a powerful technique for understanding the mechanisms of radiation effects. The physics of the development of various microstructural defects during irradiation can be dissected with respect to the different relaxation times and complex interdependencies of the various processes, such as cavity development, dislocation evolution, helium diffusion, and solute segregation and precipitation.



Pulsing of irradiation affects the development of swelling and precipitates in a stainless steel alloy. The effects of pulsing are relevant to materials used for pulsed fusion reactors and important for revealing the basic physical processes underlying microstructural development. Here, it is shown that pulsed irradiation results in much less swelling and in different precipitates than are found in specimens subjected to the same dose of continuous radiation. The symbols G, eta, and MC refer to three precipitates of different structure and composition.

Applications

In the mid-1970s M&C staff members led by Everett Bloom, Arthur Rowcliffe, and Jim Stiegler, together with researchers in other laboratories, developed new alloys of type 316 stainless steel that are resistant to swelling. Intended for use in fast breeders and experimental fusion devices, these steels have received very high doses of radiation in test reactors and yet show minimal swelling—only about 1%. By contrast, ordinary type-316 stainless steel, which was not tailored to resist swelling, expands to up to 1.5 times its original volume (50% swelling) at the same doses. For comparison, values of 3 to 5% represent the upper limit acceptable in reactor designs.

Other accomplishments of ORNL's fundamental experimental program in radiation effects deserve mention. Our extensive studies of the effects of helium on swelling and microstructure have influenced the development of alloys for possible use in fusion reactors, where very high levels of helium generated by neutron-induced transmutation reactions must be accommodated. Ken Farrell and Nick Packan's work on the effect of helium on microstructure in simple alloys is recognized as a major contribution in this field. Our comparative studies have helped to demonstrate that ferritic materials are much more resistant to radiation effects than are austenitic alloys. Linda Horton's doctoral dissertation and subsequent research on ferritic iron-chromium alloys is providing the microstructural characterization necessary to understand the differences. We have recently begun work in the relatively new field of radiation-induced phase instability (the appearance of various precipitates under irradiation that do not occur to the same extent without irradiation). Eal Lee's extensive and insightful work in this area, together with that of collaborators such as Phil Maziasz in the applied programs, is setting the standard by which other work in this field is judged. The effect of helium and solute segregation and precipitation on embrittlement is a new area of study at ORNL, requiring coordination between applied and basic programs. Bob Clausing and Lee Heatherly are applying the M&C Division's extensive interface analysis capabilities to this problem.

Theory Development

I have been actively involved with collaborators within and outside ORNL in developing the theory of radiation effects. This is an extensive mathematical framework that helps make possible the understanding of radiation effects in a mechanistic way. One of our early contributions showed how swelling depends sensitively on the competition between dislocations and cavities as sinks for point defects and how this sensitivity depends on dose. (Dislocations are the terminal lines of extra planes of atoms within the material.) We also developed the theoretical description of the coalescence of smaller cavities to form larger cavities—an important phenomenon at high doses.

Similarly, we have made progress in understanding how charged-particle irradiations differ from neutron irradiations. We have developed a theory of impurity and precipitation effects on swelling and creep and predicted that point defect trapping by impurities could drastically reduce swelling and creep; these theoretical conclusions agreed with experimental observations. The group also described a

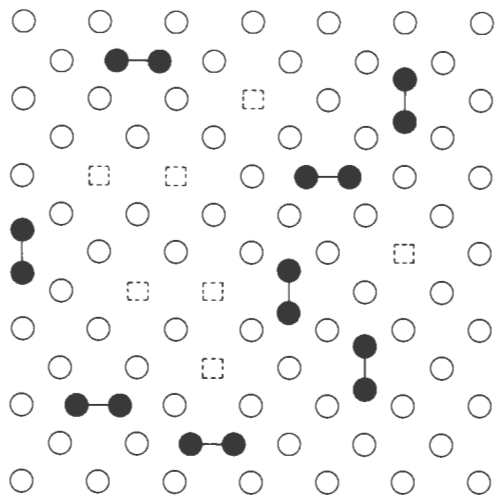
mechanism of increased cavity swelling in the presence of irradiation-induced precipitation and formulated the theory underlying this mechanism. The theory holds that, during irradiation, point defects are absorbed on precipitate-matrix interfaces and diffuse along the interface to the attached cavity, thus causing it to swell. The existence of the mechanism has been verified experimentally. The effects of helium gas on swelling are now being investigated. Recently, we derived a more comprehensive description of helium interaction mechanisms, which is of particular use in both swelling and helium embrittlement studies.

We are now constructing a new type of theoretical framework. This method, which is termed *cascade diffusion theory*, provides a better tool than does the conventional theory for understanding radiation effects. A cascade is the disturbed local region of material that results from one collision of a neutron with a lattice atom. This initial energetic collision displaces many atoms in the region by a cascading process in which the struck atom transfers its energy to other atoms. The traditional theory has ignored the fact that point defects are generated in discrete bursts initiated by neutron collisions and lost at spatially discrete sinks (cavities, dislocations, and grain boundaries); it has modeled the processes by constructing an "equivalent" homogeneous medium in which everything is treated according to its average value. This description, by definition, eliminates the possibility of understanding important processes that can occur only during point defect concentration fluctuations caused by point defect production in collision cascades. The identification of a new mechanism of irradiation creep has been made possible by ORNL's new theory, and initial indications are that the new mechanism may account for a significant fraction of the high irradiation creep rates observed experimentally.

Future Directions

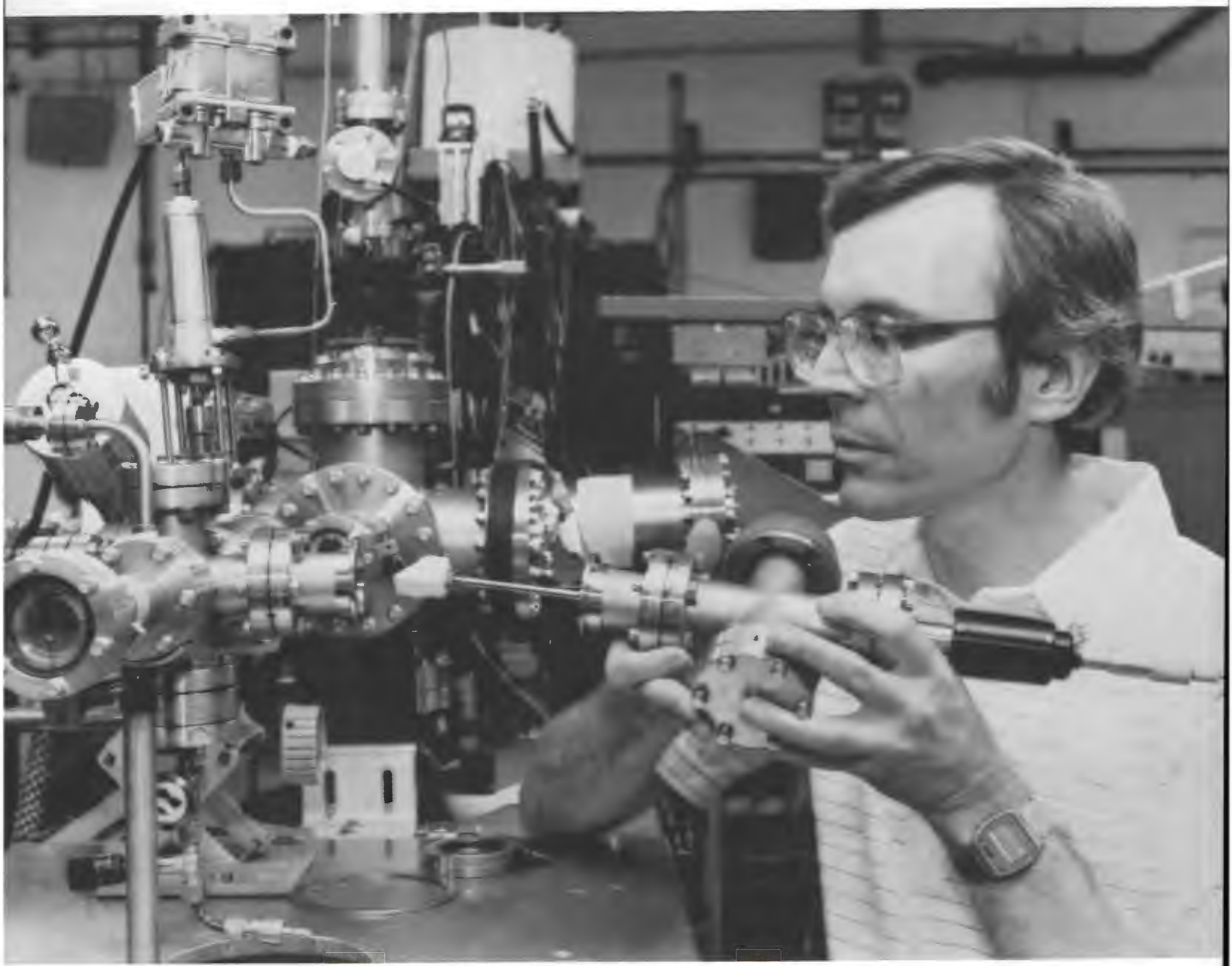
For the future, the M&C radiation effects researchers plan to conduct in-depth studies of the processes leading to embrittlement. Based on many observations of different materials under various irradiation conditions, helium and solute segregation are strongly implicated in embrittlement. The object of the research is to learn more about the role of helium and solute segregation—on a fundamental or mechanistic level—in making materials brittle.

The complex issue of phase instability during irradiation will be the subject of continuing investigations at ORNL. We plan to study new materials, including ferritic alloys and new model austenitic alloys of various compositions, to understand how radiation induces phase changes. We also plan to begin studies of radiation effects on ceramics. Comparatively little is known about the behavior of these materials under irradiation even though they are candidate materials for fusion reactors. Some fusion reactor designs, for example, include the use of a ceramic to breed tritium by neutron-induced transmutation reactions; such a material should withstand high doses of displacement-producing radiation. Ceramics are also needed for electrical insulators in fusion reactors. We view radiation effects in ceramics as a great challenge at the basic scientific level because of the more complex structure and different electronic configurations that are responsible for differences in basic microstructure and in the kinetics of defect formation.



A plane of atoms in the face-centered cubic structure of metals such as copper, nickel, and stainless steel alloys is shown here. In this simplified representation of the displaced atoms from a cascade resulting from a low-energy neutron collision, the open circles are atoms on lattice sites, the dashed squares represent vacancies, and the shaded circles represent interstitials. The interstitials, named for the interstices between lattice atoms, actually take the form of two atoms sharing the same lattice site, so that each is displaced from the site by an equal amount, forming a "dumbbell." Mark Robinson, Dean Oen, and other scientists in ORNL's Solid State Division have made important contributions to understanding the collision process leading to atom displacement.

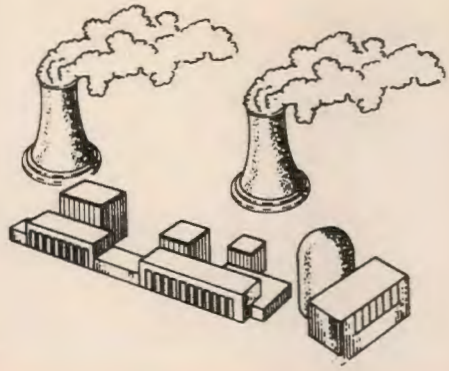
Knowledge of radiation effects is also important because it contributes to an understanding of the physics of materials and of the basic aspects of materials behavior. Radiation is a unique tool because the point defects and changes in microstructure produced by irradiation often cannot be achieved by conventional thermal or mechanical treatments. For example, vacancies can be produced thermally only at high temperatures but can be produced by radiation at low temperatures. Because vacancies can diffuse and engage in many complex reactions at low temperatures, the use



of radiation to produce vacancies opens up a new field of study of vacancy behavior and properties. In conventional thermal and mechanical treatments, interstitials are not generally produced; however, radiation produces interstitials in large quantities, thus permitting the study of their properties and those of the materials interacting with them. Such information sheds light on the fundamental behavior of materials.

The radiation effects program at ORNL has a broad charter and challenging future. It embraces the development of new experimental and theoretical tools and techniques for studying defect and material properties as well as the discovery of principles useful in designing new alloys that may make fission and fusion reactors more efficient and reliable sources of energy. ornl

Lewis works on the environmental ion-beam microanalysis and ion bombardment chamber systems that he is developing. The microanalysis chamber (foreground) will be used to probe specimens irradiated in the ion bombardment chamber (background) to determine the locations of atoms injected by the triple-ion-beam accelerators (right) or introduced by chemical diffusion.



Aging Trends in Nuclear Power Plants

By the year 2000, eight nuclear power plants that have the combined capacity to generate over 5000 MW of electricity will be approaching their design lifetime of 40 years. Concerned about the aging of nuclear power plants, the U.S. Nuclear Regulatory Commission (NRC) has been sponsoring aging studies, some of which are being conducted at Oak Ridge National Laboratory. The purposes of these studies are to determine what the aging effects are, how to detect and mitigate them, and how to establish a safety basis for operating nuclear plants beyond their design lifetimes.

The Nuclear Operations Analysis Center of ORNL has obtained aging effects data from the reports that NRC requires of utilities whenever a nuclear power plant has an abnormal operating event. Of the more than 35,000 operating events reported in 1969 through 1982, about 5900 events had age-related causes. About 2800 events resulted from instrument "drift"—the setpoint, or calibration, of a safety-related instrument was found outside acceptance criteria contained in the plant's technical specifications. The remaining 3100 events were attributed to other age-related causes such as wear, corrosion, oxidation, crud, and fatigue. These age-related effects caused degradation or catastrophic failure in a variety of components.

According to ORNL's George Murphy, of the components that failed due to age-related causes, 20% were valves; 14% pipes; 9% radiation monitors; 8% pumps; 5% diesel generators; 3% steam generator tubes; 3% heat exchangers; and less than 1% each for about 120 other components.

Although the failure rate for steam generator tubes appears relatively low at 3%, Murphy notes that of all the components listed, tube failure is probably the most expensive to repair. Another type of age problem now getting considerable attention from NRC is the embrittlement of reactor pressure vessels. This potential cause of vessel failure is a worry because of the reactor safety problems it might pose and because of the high cost of replacing a reactor vessel.

The following two articles focus on ORNL's efforts to solve the age-related problems of steam generator tube failure and reactor vessel embrittlement. This work is sponsored by NRC.

Eddy-Current Inspection of Energy-System Components

I·R 100

A 1000-MW power plant costs billions of dollars to build and operate. Over the plant's 40-year life, even a small increase in efficiency can make a big difference in profitability—for example, a 6% improvement can increase lifetime revenues from the plant by a billion dollars. Reliability is also crucial because equipment failures can shut down a power plant and force a utility to replace its electricity with higher-priced power from other sources; shutting down a 1000-MW plant costs about $50,000

Julia Bishop checks the data being collected during operation of ORNL's multifrequency eddy current instrument from inside a mobile laboratory. The instrument, which received an I-R 100 award in 1983, has been tested for inspecting steam generator tubes for flaws.

per hour for replacement power at normal consumer rates. Motivated by economics of this scale, today's energy systems are achieving higher performance by using improved materials and component designs.

As important as the material performance and component design are, it is equally important to have a method of periodically monitoring the performance of the components throughout their operating life. Like people, power plants age; over time, their components may decline in performance, become unreliable, or threaten the health of the whole system. Thus, a monitoring method is needed to permit detection of defects in components, such as tubes in steam generators and closure welds in superconducting magnets, before the components fail and consequently cause large financial losses.

A nuclear reactor's steam generator is required not only to produce electricity but also to remove decay heat from the reactor after the control rods have been inserted, as in a shutdown. If some tubes in a steam generator fail, the operator can see indications of the problem on the control panel instruments and shut down the reactor. But the steam generator must continue to function to remove the decay heat from the core. Simultaneous failure of many tubes in the steam generator would impair the generator's ability to remove decay heat and protect the fuel elements from damage.

Ginna Incident

A dramatic case that points up the need for good inspection techniques occurred not long ago at the Ginna nuclear power plant near Ontario, New York. In January 1982, a steam generator tube ruptured, allowing 1900 liters (500 gallons) of primary-system coolant per minute to enter the secondary side of the steam generator. The leak forced a rapid, difficult shutdown of the reactor and the declaration of a "site emergency," the second-most-serious class of nuclear plant accident (the most serious is a "general emergency," an accident of the scale of the one at Three Mile Island in 1979). The Ginna plant's well-trained operators quickly brought the reactor under control, thus preventing an accident that could otherwise have reached TMI proportions. Still, the tube failure added 4 to 6 weeks to the length of a maintenance and inspection shutdown and forced the plant's owner, Rochester Gas and Electric Company, to spend millions of dollars on replacement power (besides the cost of the repair). Ginna is by no means alone in having steam generator problems; in fact, the steam generator has become the Achilles heel of the nuclear power plant.

To prevent such failures, frequent monitoring of steam generators is required by NRC to attempt to accurately identify tubes that are flawed and in need of replacement. Monitoring involves an inspection at various intervals—either while the plant is operating or when it is shut down for maintenance. This inspection must accurately measure the component and material properties of interest while ignoring property variations that are of no interest. Furthermore, if the inspection is delaying a plant's restart, it must be fast (Remember—$50,000 for each hour of delay!).

One method currently being used to inspect steam generator and condenser tubes (in both nuclear and fossil plants) and being further developed for inspection of future energy systems is an electromagnetic induction, or eddy-current

examination. Eddy currents, which flow in circular patterns like those of water in a stream, are induced in the conducting component by alternating currents flowing in coils of wire near the conductor and are affected by a number of properties of the conductor. These properties include the electrical conductivity; magnetic permeability; conductor thickness (or thickness of various layers of one conductor on others); distance of the coil from the conductor; and the size, shape, and location of any defects in the conductor. When all these property variations occur at the same time, the results are very difficult to interpret.

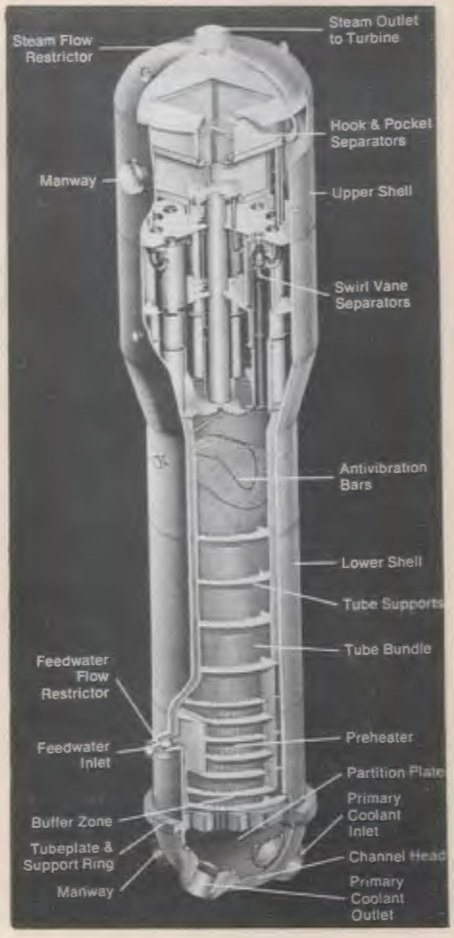
Unfortunately, the commercially manufactured eddy-current devices used for these inspections are not yet sufficiently developed to detect all types of flaws that can occur in steam generator tubing. Furthermore, these devices are not reliable enough to determine with high confidence the presence and extent of flaws. At some power plants, generator tube failures have occurred just weeks after an in-service inspection indicated no problems.

ORNL's Technique

In the ORNL program aimed at improving eddy-current devices for in-service inspection for steam generator tubing, Robert McClung, Gerry Scott, L. D. Chitwood, Jim Smith, Ed Deeds, and I have developed multifrequency-multiprobe devices that can detect several different types of flaws in a single pass through a tube. During recent blind round-robin examinations of flawed steam generator tubing, the ORNL measurements averaged within 0.5% of the "true" values obtained by measuring the percent of wall thickness penetrated by stress corrosion cracking. The accuracy of the ORNL measurements was outstanding in comparison with the round-robin measurements of five other organizations, all of which used commercially available eddy-current equipment. Some of these measurements obtained with commercial equipment missed the true values by as much as 40%.

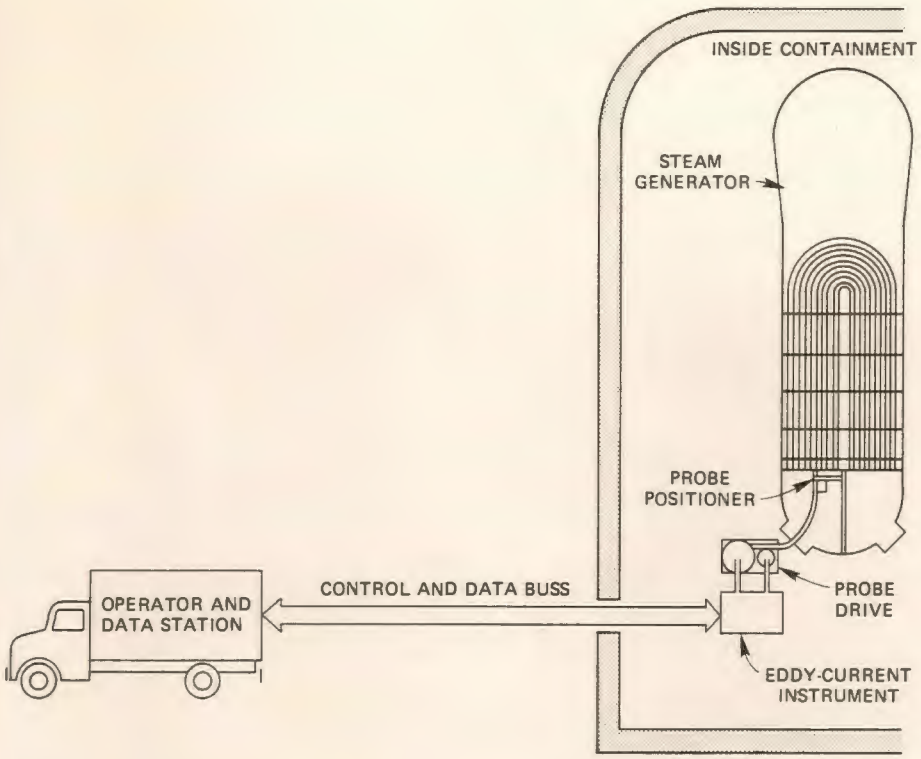
By using multiple frequencies (or pulses) and multicoil positions, we can obtain different responses from the different types of property variations. If we make enough independent instrument readings, we can compute the value of each property independently of the other test-property variations. This type of "multiple-property" test is much more complex to design and perform than were earlier eddy-current examinations. Fortunately, the rapid advances in digital computer technology have allowed us to develop the capability to do the necessary design, calibration, and performance of these inspections. A single steam generator tube can be scanned and the data can be analyzed in two to three minutes.

In the initial design, mathematical models based on Maxwell's equations are used to calculate the changes in the magnitude and phase of the eddy currents (related to the instrument readings) as functions of the test properties. During the computer phase of the instrument design, we can maximize the predicted instrument response to various property variations (such as defect size or material conductivity) by changing the test properties that we can control (e.g., coil size, shape, location, and operating frequencies).



A schematic of the Westinghouse steam generator used in nuclear power plants.

We then "invert" the equations—usually by statistical, least-squares processes—so that we can obtain the properties from the computed instrument readings and thus can predict the accuracy and sensitivity of the test. The optimized instrument and coils are then assembled and "calibrated" by measuring several thousand different combinations of property values at different frequencies. This procedure involves our using computer-controlled positioners to move the standard samples relative to the coils.



After being set up inside the radioactive containment, the eddy current instrument and probe positioning equipment are remotely controlled from a distance of several hundred feet.

After the calibration step, a microcomputer in the instrument can be programmed to perform a series of complex tasks: (1) control the probe scanning, (2) make between 100 and 1000 measurements per second of eddy-current magnitude and phase at each of three frequencies, (3) convert to digital signals and correct for instrument drift, (4) compute the properties from the readings using polynomial algorithms, and (5) record data in real time in both digital and analog forms as the component is scanned. Components with problems can be automatically called to the inspector's attention. A microcomputer-aided inspection of this type, for example, would have spotted the worn tube in the steam generator of the Ginna plant and allowed a repair before the costly accident occurred.

Laboratory tests of our equipment and techniques have been quite encouraging. For one model of Westinghouse steam generator (Model D), our instrument's error rate for predicting fretting wear (external rubbing of tubes, caused by vibration) was calculated at only 1%; this figure compared with 11% for a multiple-frequency instrument that lacks our digital data-reduction techniques. Better accuracy in detecting degradation gives utilities the confidence to operate reactors closer to the maximum power levels because further generator degradation is unlikely if no other signs of wear have been spotted.

Promising Field Tests

Field tests at two nuclear power plants have also been promising. The accident at Ginna occurred about six months after a visit we made there; unfortunately, our tests did not include the tube that later failed. We have also visited the Point Beach plant in Wisconsin, which—like Ginna—has a history of steam generator problems. Future field trials of our instrument will focus mainly on a steam generator test facility at Battelle's Pacific Northwest Laboratories in Richland, Washington, where a failed steam generator from a commercial nuclear plant was shipped for examination. Other field tests at operating nuclear plants may be scheduled if NRC thinks there are serious problems that warrant such inspection.

In addition to steam generator inspections, the multiple-property technique has also been successfully used to inspect superconducting-magnet cable for advanced fusion energy research machines. The U.S. Department of Energy's Large Coil Program is aimed at the building and testing of superconducting magnets one-third to one-half the size needed for electricity-producing fusion reactors in the future. In one of the experimental magnets, stainless-steel-clad cables will contain a superconducting alloy, copper, and liquid-helium coolant. By having a technique to inspect and ensure the integrity of the cable's critical 100-m-long closure weld, the fusion researchers can safely double the magnet's field strength.

Soon, we hope, commercially manufactured versions of our equipment will be available. In September our technique received an I-R 100 award as one of the year's 100 most significant technical achievements; we hope that this recognition will help convince instrument manufacturers of the commercial potential of the technique. One system on the market already uses digital data reduction to assist the operator, but, unlike our system, it does not yet automatically call defects to the operator's attention.

The three-frequency eddy current instrument developed at ORNL for nondestructive testing.

The multiple-property, eddy-current techniques developed at ORNL permit the performance of many inspections that were formerly considered impossible. The design and construction of these high-speed, multiple-property tests have been expensive, but the savings resulting from the more nearly accurate measurements, the additional test information, and the more reliable components have been much greater than the development cost.—*Caius V. Dodd, Metals and Ceramics Division.*

Reactor Vessels and Safety

As water-cooled nuclear power reactors age, several materials problems may occur that could adversely affect the safety of these commercial power plants. Such problems involve the vessel that contains the nuclear fuel core.

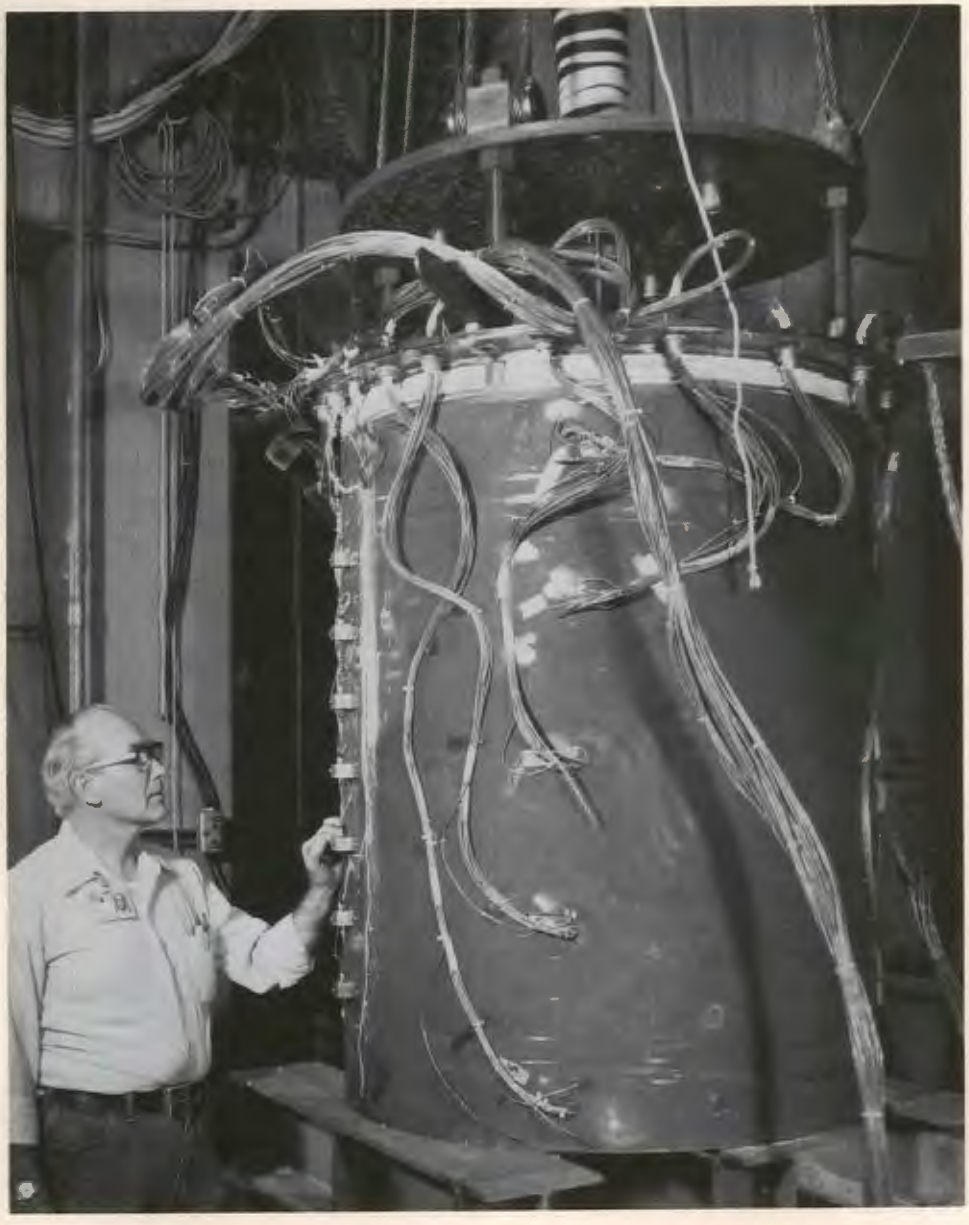
In pressurized water reactors (PWRs), the steel alloys that make up the pressure vessel normally accommodate neutron radiation from the reactor core and loadings imposed by high temperature and by high-pressure water. However, after long-term exposure to radiation, this material may become brittle, and the tendency to crack is enhanced if tiny flaws were originally present.

In the 1970s researchers in Oak Ridge National Laboratory's Heavy Section Steel Technology (HSST) Program under the leadership of Grady Whitman in the Engineering Technology Division tested several scaled-down pressure vessels that were deliberately flawed and then pressurized until the vessels failed by leaking or rupturing. They found that the vessels failed only after being subjected to pressures two and a half to three times as great as the design pressure even when large flaws were present. The results were interpreted to mean that flaws below a certain size that could be detected would not pose a safety problem under normal operating conditions. Thus, ORNL's work has verified that the Pressure Vessel Code of the American Society of Mechanical Engineers (ASME) provides for a large margin of safety.

Thermal Shock Studies

More recently at ORNL, overcooling accidents in PWR vessels have been investigated both analytically and experimentally to evaluate the integrity of older vessels under conditions where high thermal stresses are induced from sudden injection of colder water to cool the core. Some vessels that have high levels of copper and other impurities have been determined to be more susceptible to the effects of neutron bombardment and are becoming embrittled at a rate faster than expected. Under these conditions of "thermal shock," small flaws might propagate suddenly in this material. The behavior of flaws under thermal loading and combined thermal-pressure loading is being intensively studied at ORNL.

Whether a crack would stop growing near the outer surface or would proceed through the entire vessel wall in such an overcooling accident depends on the severity of the transient, the extent of radi-

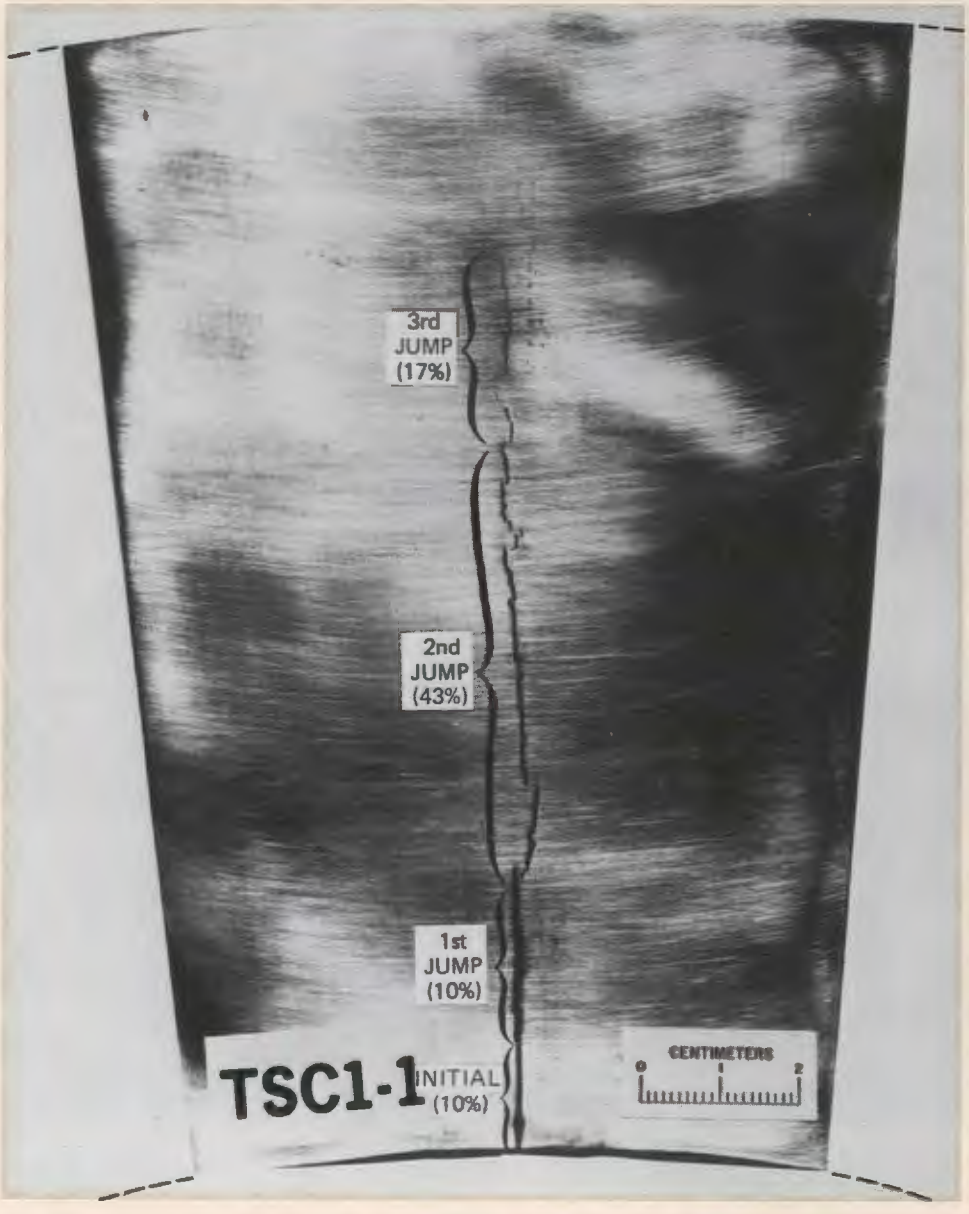


A typical test cylinder assembly in ORNL's thermal shock program includes a 3800-kg, thick-walled (152-mm) steel test cylinder that is purposely flawed on the inner surface and is instrumented with 15 thermocouple thimbles, 9 crack-opening displacement gages, 3 ultrasonic crystals, and 4 acoustic emission transducers. Checking the instrumentation is Tom King.

ation damage, and the material's ability to arrest the advance of a rapidly growing crack. Recent ORNL experiments under the direction of Dick Cheverton in ORNL's Engineering Technology Division show that thermal shock alone will not drive a crack through the wall—that is, substantial pressure loading is needed to complete crack penetration. Other experiments and analyses indicate that (1) thermal shock may cause short flaws to extend on the surface to become long flaws, thus increasing the potential for deep propagation; (2) propagating cracks can arrest in a rising stress intensity field; and (3) a phenomenon referred to as warm prestressing occurs during many of the postulated pressurized thermal shock transients and tends to limit crack growth.

ORNL researchers are developing computer codes to predict the behavior of flaws in PWR reactor vessels during overcooling accidents. Additional testing is required to verify these computer models. In 1984, experiments will be conducted at the new Pressurized Thermal Shock Test Facility, located in the old power plant building at Oak Ridge Gaseous Diffusion Plant. This facility will subject scaled-down test vessels, made of the same type of material used in commercial PWR vessels, to simulated overcooling transients. Because the test facility allows independent control of pressure and temperature, it can simulate a range of overcooling accident conditions. The test vessels are each 1 m in diameter with walls 150 mm thick and have shallow flaws that will propagate during the test and that presumably will arrest in the tougher material deeper in the wall. Extensive instrumentation will accurately monitor temperature distributions in the vessel wall and crack growth characteristics; such information is needed to evaluate the validity of the calculational models.

Materials investigations are continuing to evaluate the effects of neutron bombardment on the fracture toughness of materials used in reactor vessels. Fracture toughness reflects a flawed material's ability to resist the growth of a crack when a load is applied. Many vessel materials covering a range of susceptibility to the effects of irradiation are being studied at ORNL. Currently, plans have been completed to irradiate large fracture specimens in the Oak Ridge Research Reactor to extend the



During a typical thermal-shock experiment, the initial flaw propagates in several steps deep into the 152-mm-thick wall of the test cylinder.

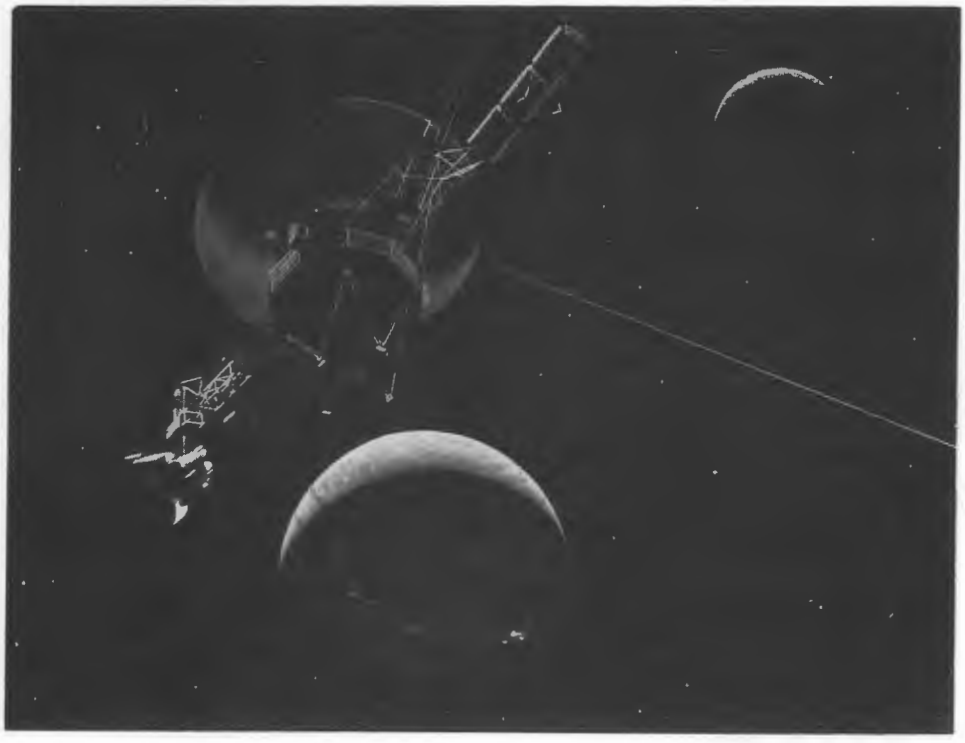
data base that is required to accurately predict flaw behavior.

Evaluating Predictions

In a related pressure vessel simulation study performed in cooperation with other organizations and partially supported by the Electric Power Research Institute, ORNL will evaluate the uncertainties in predictions of neutron fluence and steel embrittlement in PWR pressure vessels. ORNL researchers will determine the accuracy of calculated values of neutron fluences and steel embrittlement by comparing these estimates with actual measurements made on dosimeters and steel samples placed in a research-reactor "benchmark facility." These results will help check the methods used to estimate the radiation damage in commercial reactor vessels. The behavior of neutron-irradiated materials during postulated overcooling transients can then be modeled with the techniques developed under the HSST Program.

If it is determined that a commercial vessel wall will be extensively embrittled before the end of the planned reactor lifetime, then certain options can be considered to reduce the effects of an overcooling accident. Remedial measures that could be taken are (1) reducing the reactor's power, (2) changing its fuel arrangement to reduce leakage of fast neutrons, (3) increasing the temperature of the emergency core coolant, (4) altering the operating procedures, or (5) annealing the vessel.

ORNL materials research sponsored by the Nuclear Regulatory Commission is integrated with work performed by other NRC contractors to take maximum advantage of available experimental facilities and staff capabilities. The ORNL research is focused primarily on resolving high-priority safety issues and providing NRC staff with the data and analyses needed to make decisions about specific power plants well before a safety-threatening condition develops. (*This article was written by the* Review *staff based on information supplied by Frank Homan, Metals and Ceramics Division, and Grady Whitman and Dick Cheverton, Engineering Technology Division.*)



This painting shows Voyager 2 *as it looks back upon Neptune and its moon Triton seven hours after the spacecraft's closest approach to the distant planet on August 24, 1989. Aboard are radioisotope thermoelectric generators clad with a special iridium alloy developed at ORNL.*

Alloys for Nuclear Power Systems in Space

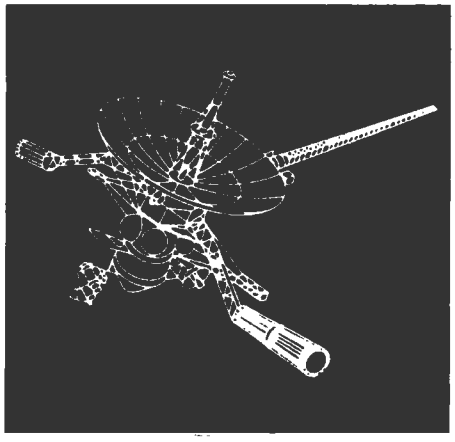
By ROY COOPER and HENRY INOUYE

ORNL developed the iridium-tungsten alloy used to contain the nuclear fuel for the recent Voyager missions to Jupiter and Saturn. Now, ORNL is planning to test different alloys for possible use in small reactors being designed for advanced civilian applications such as an orbiting space station and for national defense applications including radar and laser systems in outer space.

Going on a space mission is analogous to taking a long ocean voyage in a small boat. Both spacecraft and boat are constructed of high-quality materials but have only limited space for gear and onboard components. One of the more critical components is the power supply to provide electricity for the instruments that navigate, communicate, and explore. Because power-supply systems on unmanned spacecraft cannot be repaired, they are designed for high reliability by making the system redundant and by eliminating as many moving parts as possible.

Depending on the mission, different types of compact power sources have been used on spacecraft. Brief trips (such as those made by the space shuttle) rely on storage batteries and fuel cells, while orbiting earth satellites depend mainly on solar cells. However, if the mission takes a long time and is in a direction away from the sun, solar cells become progressively inefficient. Thus, for long, planetary missions, systems that convert nuclear energy to electricity are required.

Nuclear sources of electricity for applications in outer space require special materials. In the 1970s Oak Ridge National Laboratory developed special alloys for cladding radioisotope thermoelectric generators (RTGs) that were used



aboard the *Pioneer* (Jupiter), *Viking Lander* (Mars) and *Voyager* (Jupiter and Saturn) spacecraft. In the 1980s RTGs will be employed in the *Galileo* (Jupiter) and Solar-Polar missions.

Also in the 1980s, further exploitation of space is anticipated for both civilian and military applications that require high power levels. To this end, three U.S. government agencies—namely, the Department of Energy (DOE), National Aeronautics and Space Administration (NASA), and the Department of Defense (DOD)—are sponsoring the development of space nuclear fission reactor systems designed to generate electricity at power levels ranging from 100 kW to 100 MW. Compact nuclear reactors are needed because these power levels are much higher than are currently obtained from photovoltaic solar panels (approximately 10 kW) and RTGs (approximately 0.3 kW). Such high-power reactors could be used aboard an orbiting space station whose microgravity vacuum may be exploited for processing certain metal alloys and crystals for electronics. In addition, these reactors could be used for powering ion propulsion systems for trips to the outer planets and for defense applications such as surveillance satellites, large radar systems, laser-based communications equipment, and laser or particle-beam weapons designed to destroy enemy missiles in flight.

ORNL has a lead role in the development of refractory alloys for these compact reactors. Because these reactors must operate at a high temperature to ensure efficient power production, alloys having high melting points will be needed for the nuclear fuel cladding and as structural materials.

Radioisotope Generators

RTGs are the nuclear devices currently used to provide electricity for space voyages to the outer planets. In RTGs, the heat liberated by the decay of a plutonium radioisotope (^{238}Pu) is converted to electrical power in special thermocouples called thermoelectric elements. Electricity is generated when one end of the thermoelectric element [such as a silicon-germanium (SiGe) compound] is heated and the other end is kept cooler (the Seebeck effect). These nuclear generators have two advantages: they have no moving parts to wear out, and the power decreases only a few percent after several years because of the degradation of the thermoelectric elements and the reduced heat-generation rate of the decaying fuel (the half-life of the ^{238}Pu isotope is 87 years).

The space probes to Mars in 1975 (*Viking Lander*), to Jupiter in 1972 (*Pioneers 10* and *11*), and more recently to Jupiter and Saturn in 1977 (*Voyagers 1* and *2*) had several RTGs on board. The 100-W RTG units on *Voyagers 1* and *2* consist of a graphite cylinder about the size of two 4-L (1-gal) cans stacked end to end. Twenty-four golf-ball size spheres of $^{238}PuO_2$ inside the graphite cylinder produce 2400 W of heat, thus raising the temperature of the assembly of several hundred Si-Ge thermoelectric elements to about 1100°C.

ORNL's Metals and Ceramics (M&C) Division was responsible for developing a cladding alloy to contain the hazardous nuclear fuel that is capable of withstanding the searing heat of reentry into the atmosphere and the impact of falling on the Earth. The cladding is heated to 1300°C under normal design conditions. However, if the spacecraft fails to escape the Earth's gravitational pull because of a rocket malfunction, the total heat produced by the nuclear fuel and the aerodynamic friction of the air on the generator as it reenters the Earth's atmosphere would momentarily raise the generator temperature to 1800°C. The generator then cools at lower altitudes because of the denser air there and then impacts at 90 m/s (200 mph) at a temperature of 1300°C. Thus, the task of the M&C Division in the mid-1970s was to develop a cladding alloy that could withstand the possible thermal and mechanical abuse of reentry heating and impact. In addition, the cladding also had to resist reactions with the $^{238}PuO_2$, graphite, and air.

For this application, C. T. Liu and Henry Inouye developed several precious metal alloys based on platinum and iridium. These rare metals were not inexpensive; they have cost as much as $1000 per troy ounce. Liu and Inouye worked with 100 or more ingots, each having the value of a Cadillac. One of their six patented alloys, an iridium-tungsten (Ir-W) alloy, was selected for the *Voyager* missions.

They found that iridium became stronger and more brittle as the material was made more pure. Thus, by restricting the tungsten content of the alloy to 0.3% of the alloy composition and by doping it with about 50 ppm each of thorium and aluminum, they made an alloy strong enough but with sufficient ductility (ability to deform without

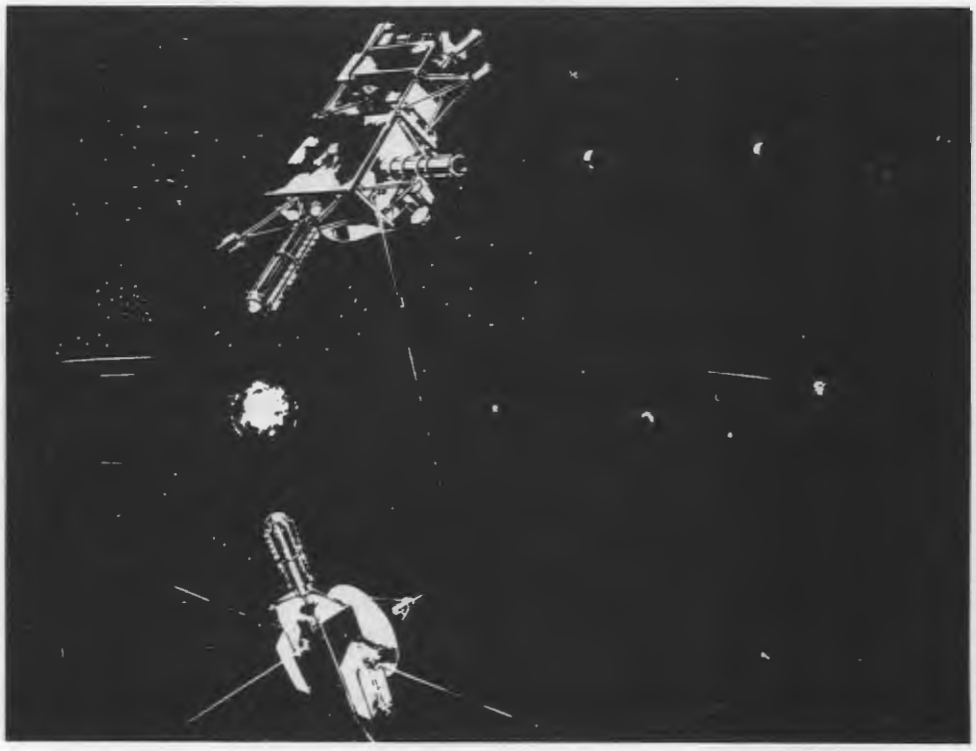
Roy Cooper (right) is manager of the Technology for Space Nuclear Projects effort at ORNL. A native of Illinois who was raised in Alabama, he holds a master's degree from the University of Tennessee in metallurgical engineering. He worked at the Y-12 Plant before joining the staff of ORNL's Metals and Ceramics Division in 1975. His research interests center on high-temperature materials. Henry Inouye has worked as a metallurgist and chemist in ORNL's Metals and Ceramics Division since 1952. Born and raised in Colorado, he received a master's degree in materials science from the Massachussetts Institute of Technology. Before coming to Oak Ridge, he worked for American Brake Shoe in Denver, the National Bureau of Standards in Washington, D.C., and the U.S. Department of Defense in Ogden, Utah. At ORNL Inouye was a group leader from 1952 to 1973. Since then he has continued his work in developing alloys and understanding high-temperature gas corrosion. Inouye is a Fellow of the American Society for Metals and a recipient of an I-R 100 award. He has received many honors for his work in developing alloys for use in spacecraft. These honors include the Viking Mission Pin Award, Space Nuclear Systems (1973); the NASA Pioneer/Jupiter Group Achievement Award (1974); the ERDA Mariner/Jupiter Saturn Program Commendation (1975); the ERDA Voyager Mission Citation (1977), and the NASA Pioneer XI Group Achievement Award (1977). The article that follows covers ORNL's efforts in developing materials for two kinds of nuclear power systems for spacecraft: those that run off the heat of radioactive decay in planetary missions and those that will be driven by controlled chain reactions in weapons-carrying supersatellites and space laboratories lofted into orbit by the space shuttle.

breaking) to meet the mission requirements.

How did ORNL qualify the experimental alloys for service on space missions? At Los Alamos National Laboratory (LANL), a $^{238}PuO_2$ fuel sphere clad with the Ir alloy was heated to 1300°C and then fired out of a surplus Navy gun at 90 m/s (200 mph) at a granite block. The alloy passed if the assembly, although squashed, released no fuel. At ORNL a stainless steel bullet was fired from a gas gun at the hot alloy test piece. The alloy passed if the ductility exceeded a specified minimum value.

Improved RTG systems are currently being built to support the *Galileo* space mission now being planned by NASA and the Solar-Polar space mission being planned as a joint endeavor by NASA and the European Space Agency. The *Galileo* mission will send a satellite to explore Jupiter and its moons and will launch a probe into Jupiter's atmosphere. The Solar-Polar mission will harness the gravitational pull of Jupiter to loft a satellite into an orbit around the poles of the sun.

The primary power source for each satellite will be an improved RTG, which can deliver three times more electricity than the RTG units now in space. This RTG system will use an improved iridium-tungsten-



The international Solar-Polar mission now being planned by NASA and the European Space Agency will use improved radioisotope thermoelectric generators (RTGs) in a satellite to be lofted into orbit around the poles of the sun. The RTG fuel will be clad with an iridium-tungsten-aluminum-thorium alloy developed at ORNL. The RTGs will also be protected from the heat associated with accidental re-entry into Earth's atmosphere by thermal insulation sleeves made of bonded carbon fibers by a process developed at ORNL.

aluminum-thorium alloy developed at ORNL (Ir-0.3% W-50 ppm-Al-60 ppm Th) for the fuel cladding. In addition, the ORNL carbon technology program under Walt Eatherly and J M Robbins in the M&C Division has made bonded mattes of carbon fibers for thermal insulation sleeves in these RTGs. These sleeves will protect the RTGs from the searing heat of the atmosphere and from impact on Earth in case of an accidental re-entry.

For RTGs the next materials frontier will be the development of thermoelectric modules that more efficiently convert radioactive decay heat into electricity. Bob McClung's group in the M&C Division is developing nondestructive inspection methods to assess the integrity of these new thermoelectric converter concepts.

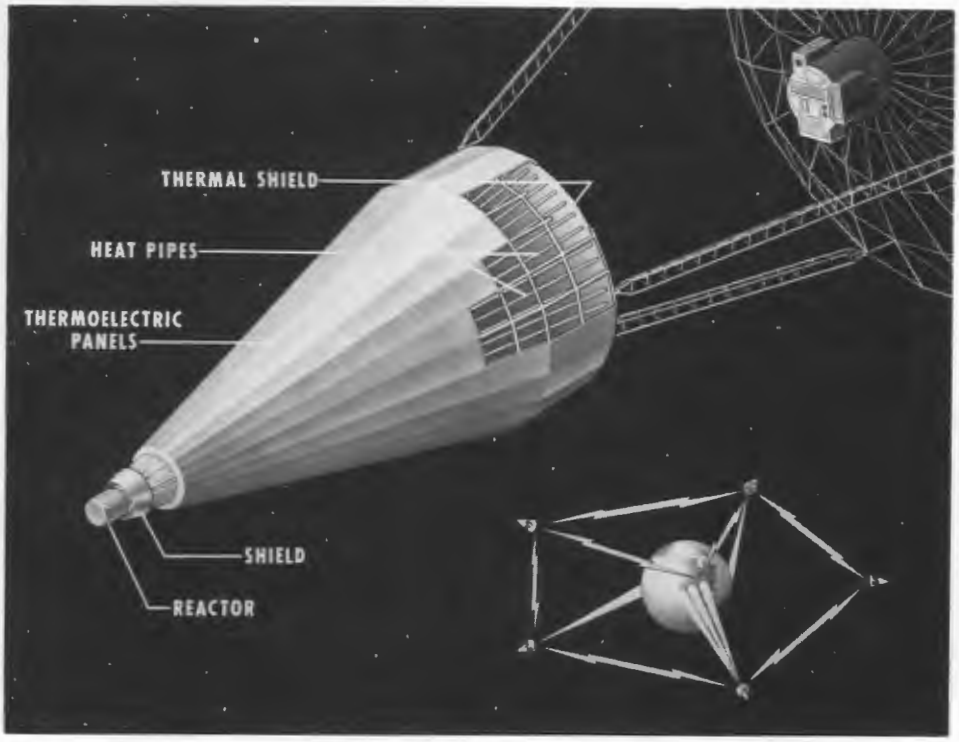
Space Reactor Alloys

In the 1960s, ORNL first became involved in materials development for space fission reactors for NASA in the Systems for Nuclear Auxiliary Power (SNAP) programs. The M&C Division developed and characterized advanced structural alloys and cladding alloys for proposed SNAP systems. In work for NASA's project to develop an advanced lithium-cooled space power reactor in the 1970s, ORNL constructed and operated refractory alloy and stainless steel systems for liquid-lithium and boiling-potassium pumped-loop corrosion experiments. More recently, ORNL has assisted LANL in fabricating and characterizing molybdenum alloy heat pipes for use in the core of a space reactor based on a LANL concept.

Only one test reactor (SNAP-10A) has been lofted into orbit by the United States. Since the 1960s the space reactor program has been virtually inactive in the United States, even though the Soviet Union has used a number of small reactors to power its surveillance satellites (including *Cosmos 954*, which failed and crashed in Canada about five years ago, and Cosmos 1402, which failed and reentered the atmosphere in February 1983). The U.S. space reactor program was revived after President Reagan announced his new space policy on July 4, 1982, while welcoming home the crew of the final test flight of the Columbia space shuttle.

Comparing the fourth landing of the *Columbia* to the "golden spike which completed the first transcontinental railroad," President Reagan suggested that the shuttle opens up space to human activities just as regular railroad service opened up the West to settlement and commerce. The goals of these activities, he added, should be to establish a permanent orbiting laboratory and space telescope, to strengthen the nation's security, and to obtain economic benefits through exploitation of space.

In 1983 in response to the administration's new space policy, DOE sponsored a space reactor study in which ORNL participated. The results of the ORNL studies appear in a February 1983 ORNL report entitled *Space Nuclear Power Reactor Studies*. This report was summarized by William O. Harms, director of ORNL's Nuclear Reactor Technology Programs, in his testimony presented May 24, 1983, to the subcommittees on Energy Research and Production and on Space Science and Applications of the Committee on Science and Technology of the U.S. House of Representatives.



This space probe contains a heat pipe space reactor system designed at Los Alamos National Laboratory. Materials used in the system include a molybdenum-rhenium alloy, molybdenum, beryllium, beryllium oxide, zirconium oxide, and boron carbide. Uranium oxide is the nuclear fuel. Such a reactor would be turned on or shut down while in orbit by a radio signal beamed from Earth.

The ORNL study team selected two reactor concepts: (1) the liquid-metal-cooled fuel-pin reactor and (2) the direct-Rankine-cycle, boiling-liquid-metal-cooled fuel-pin reactor. For the near term (early 1990s), the nuclear fuel selected is uranium oxide clad with stainless steel and, for the long term (after 1995), uranium nitride clad with a tantalum alloy. For the near term, both concepts use potassium as the coolant and stainless steel as the structural material; for the long term, the first concept uses lithium as the coolant and a tantalum alloy as the structural material, and the second concept uses potassium as the coolant (and working fluid) and a tantalum alloy as the structural material.

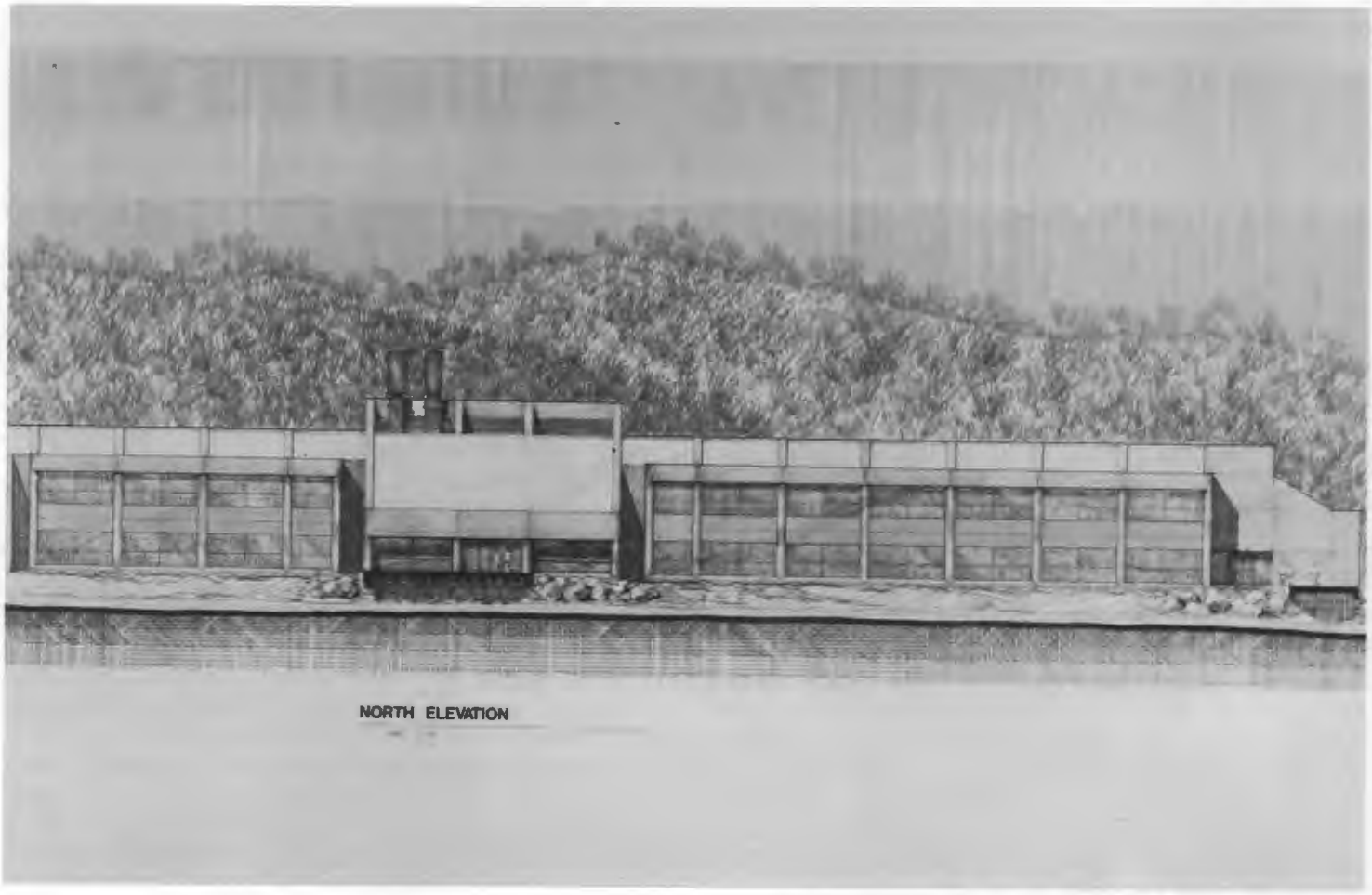
The advanced materials development required for the long-term space reactor concepts is now being planned by the Technology for Space Nuclear Projects team managed by Roy Cooper of the M&C Division. The alloys being considered for possible use as cladding for nuclear fuel and as structural materials are nickel-based and cobalt-based superalloys and refractory alloys—materials that have high melting points such as those based on niobium, molybdenum, tantalum, and tungsten.

Refractory alloys have the ability to retain high strength and other key properties at the elevated operating temperatures required for space nuclear reactors. Because space reactors will be designed for the long term to be compact, lightweight, and capable of efficiently converting nuclear heat to electricity at relatively high power levels (100 kW to 100 MW), they will operate at a temperature well above 800°C, thus precluding the use of stainless steels.

To supply the needed data for advanced materials required for the higher-performance space reactors envisioned for launch as early as 1995, Cooper's team and others are planning to test refractory alloys. These tests would add to the results obtained in the 1960s and 1970s by ORNL and other laboratories to determine the maximum reactor outlet temperature that these respective alloys can tolerate.

Guidance regarding ORNL's future role in this program is forthcoming following an August 1983 workshop and symposium on Refractory Alloy Technology for Space Nuclear Power Applications conducted by ORNL and DOE's Oak Ridge Operations. In the interim ORNL has assembled unique high-temperature, high-vacuum creep and fatigue test machines, an inert gas welding chamber, and alkali metal corrosion testing facilities, all of which are ready to support refractory alloy development needs.

In summary, future space missions will need prime power systems with much higher electrical energy per system weight than those currently used for space applications. For these more efficient power systems, metallurgists must develop alloys that can resist increasingly higher temperatures and hostile environments. Alloys based on niobium, molybdenum, tantalum, and tungsten are candidates for use in the more critical parts of the newer generators. The expertise gained by our work on these metals beginning in the mid-1960s uniquely qualifies ORNL as the organization that can understand, design, develop, qualify, and fabricate refractory alloys for use in advanced space exploration and defense applications. ornl



An artist's conception of the High-Temperature Materials Laboratory.

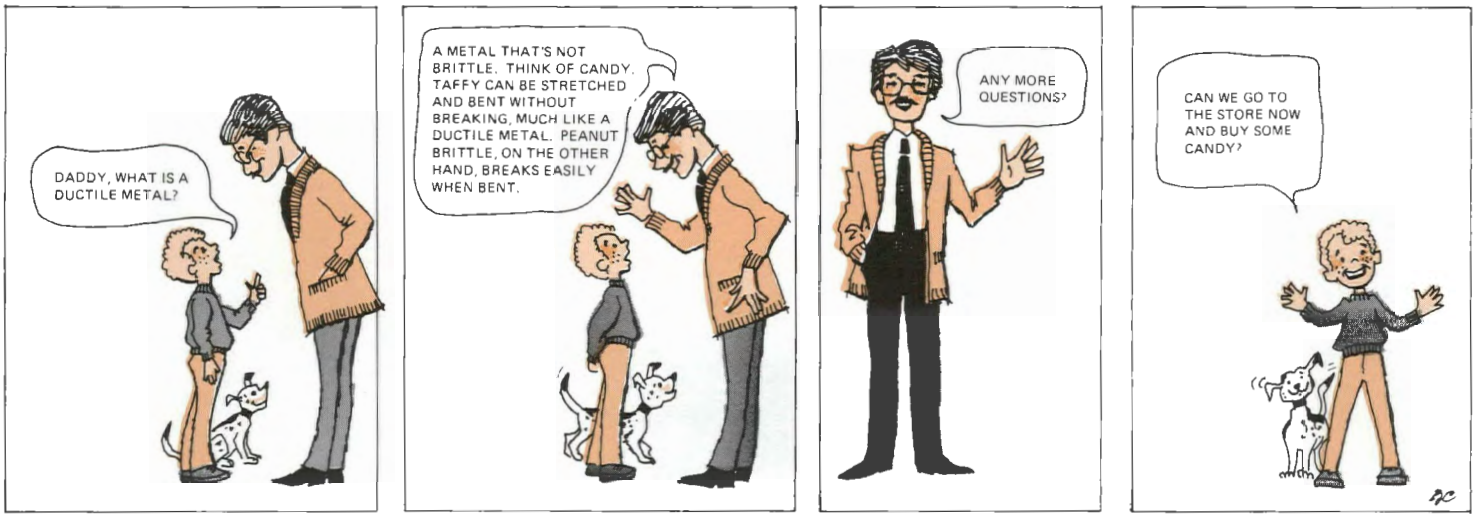
Toward a High-Temperature Materials Laboratory

By V. J. TENNERY

Materials that can withstand high temperatures are needed in energy-efficient heat engines for automobiles and airplanes, in advanced power plants, and in facilities that convert coal to liquid and gaseous fuels. For this reason, Oak Ridge National Laboratory has proposed that the U.S. Department of Energy establish a national research center at ORNL devoted to research on and development of heat-resistant materials for applications to energy production and conservation.

The High-Temperature Materials Laboratory (HTML), which was included in DOE's fiscal year (FY) 1984 budget, is scheduled to be built at ORNL by 1988 or 1989. ORNL received the first actual funds, in the amount of $1 million for FY 1983, and $9 million for FY 1984. We anticipate receiving the remaining $10.6 million in the FY 1985 budget. An architect-engineer has been selected to design the facility, and the design process will be completed by September 1984.

Our present concept of the HTML includes four basic ideas: (1) a central building of about 4,645 m^2 (50,000 ft^2) will contain offices and laboratories where ORNL staff of various disciplines can conduct multidisciplinary research on high-temperature materials; (2) the HTML's special



research equipment, estimated to cost about $3 million, will support the research; (3) laboratory and office space will be available to industrial and university researchers who periodically conduct research in the HTML, which will be a national user facility; and (4) about half of the annual research budget for the HTML will be oriented to basic materials research (such as understanding the behavior of dislocations and vacancies in a material at high temperatures), while the other half will support applied research (such as development of new ceramics and alloys, compositions that have superior strengths at high temperatures). We think that having basic and applied research specialists working closely together can provide substantial benefits to achievement of the goals of both types of research.

ORNL's proposed High-Temperature Materials Laboratory has been in the federal budget cycle since fiscal 1978. But after several frustrating years of having funds for the HTML deleted, it looks as if the national user facility will become a reality by 1989.

From Idea to Reality

The sequence of events that finally leads to a new research facility typically requires about ten years. Once the idea is conceived, an analysis must be performed to show that the conceptual facility is needed and that the research to be carried out in it is justifiable and important. Next, people in the supporting agency (in our case, DOE) must be so convinced of the need and importance of the facility that they will include the facility in their budget requests. Following this step, a private firm is contracted to prepare the conceptual design, which consists of considerable detail, including the floor plan for all laboratories and offices, utilities, and the heating and air-handling system. In addition, the firm proposes a construction schedule and estimates the total cost for the building. This cost estimate is the basis of the formal budgetary request to the supporting agency.

If the building request survives the budget processes of the supporting agency and Congress, the first actual funds are made available. Achieving this goal, however, is no small matter, as will be illustrated in the story of the HTML. After Congress appropriates funds, the next step is the final architectural design and the engineering design in which numerous engineering drawings are prepared that will be used later by the construction contractor in building the structure. The design work is performed by a private firm under contract to the supporting agency. For the HTML, the architectural and engineering design contractor is the firm Deeter Ritchey Sippel (DRS), located in Pittsburgh, Pennsylvania. The A. M. Kinney (AMK) firm in Cincinnati, Ohio, is a subcontractor of DRS and is responsible for various engineering aspects of the design.

The architectural design of the HTML, started in November 1983, is expected to require about a year. Following the architectural design work, a construction contract will be established by DOE, and building construction will actually begin. We plan for construction of the HTML to start during FY-85 and be essentially completed in about two years. We expect to occupy the building about three years following the start of construction.

Wilbur Warwick inserts bend fixture containing silicon carbide into the Instron mechanical test machine. This machine is used to measure fracture strengths of ceramics at temperatures as high as 1500°C.

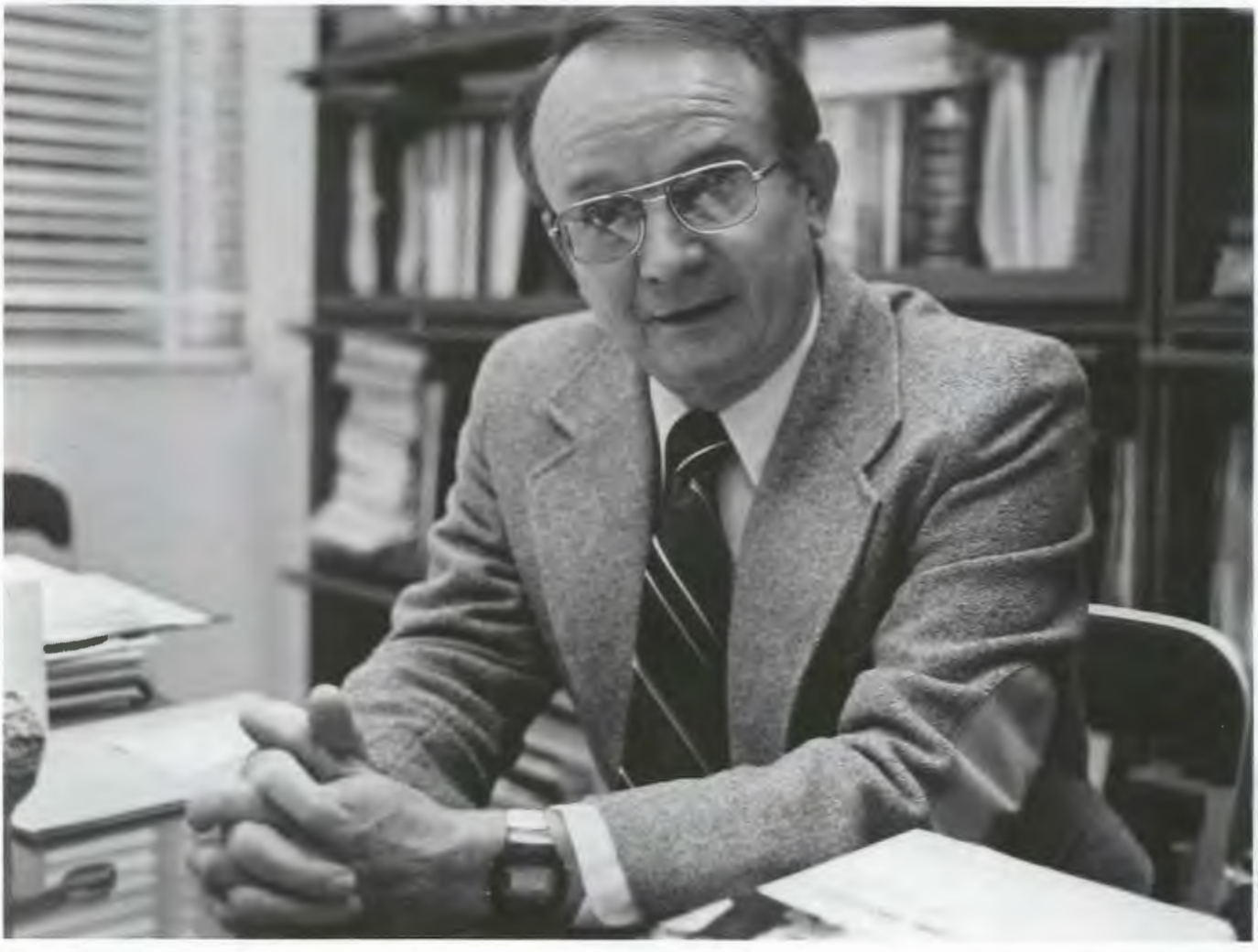
In the case of the HTML, the conceptual and architectural design steps and the anticipated construction have involved and will require extensive participation by staff members of the Union Carbide Engineering Division. John Murray is serving as the liaison officer for ORNL and two organizations—DOE's Oak Ridge Operations, where Bill Gilbert is the responsible party, and the Engineering Division. Murray is responsible for ensuring that all engineering aspects of the building are planned, coordinated, and conducted in a timely and cost-effective fashion.

HTML's Evolution

The HTML concept evolved in the mid-1970s during discussions in the Metals and Ceramics (M&C) and Solid State (SS) divisions. The idea was sharpened and brought into focus as a result of a series of nine national workshop meetings held in the spring of 1977 for university and national laboratory representatives and organized by what was then the Division of Physical Research of the Energy Research and Development Administration (ERDA), the predecessor of DOE. These meetings, hosted by four national laboratories (Argonne, Lawrence Berkeley, Brookhaven, and Oak Ridge), were held to identify new directions and priorities for future basic materials research relevant to advanced energy systems. ORNL was the site for three of these meetings, which were largely organized by ORNL staff members Carl McHargue (M&C) and Mike Wilkinson and Fred Young (SS).

One conclusion emerged from several of these workshop meetings: an increased emphasis on high-temperature materials research was warranted and, in some cases, would be critical to the future successful operation of several energy systems being pursued by ERDA (and now DOE) as a means for reducing the dependence of the United States on imported oil. Examples of such energy systems include advanced heat engines, coal-to-oil conversion plants, fluidized-bed combustion systems, high-temperature gas-cooled reactors, liquid-metal fast-breeder reactors, and fusion power devices. Because it was recognized that many alloy and ceramic materials may have insufficient strength and fracture toughness, be prone to corrosion, or have other property limitations at high temperatures, materials science experts agreed at the DOE workshop meetings that it was of national importance to develop new materials or learn how to modify conventional materials for the harsh environments of advanced high-temperature energy systems.

Shortly after the last of these meetings, Alex Zucker, ORNL Associate Director for Physical Sciences, organized a committee of ORNL staff members to decide what response, if any, ORNL should make as a result of the conclusions and recommendations of the DOE workshops. The committee, which was chaired by Tim Riley (then in the M&C Division and now with IBM), concluded that a new centralized national facility is needed to bring together the materials experts who can conduct the required research. The committee considered ORNL to be a good site because of its extensive, ongoing basic and applied materials programs. By August 1977, a proposal describing such a facility and the general types of research to be con-



Vic Tennery is the director of ORNL's High-Temperature Materials Laboratory, which is now being designed. As a staff member of ORNL's Metals and Ceramics Division for 11 years, he headed the Ceramic Technology Group from 1976 to 1979 and directed the research of the Structural Ceramics Group from 1979 to 1981. His areas of research have included oxide and nitride ceramic fuels for fast breeder reactors, potential radiologic impacts of breeder fuel systems, ceramic materials for high-temperature heat exchangers, and high-temperature corrosion of refractory materials used in industrial furnaces to process materials. Before coming to ORNL in 1972, he was a professor of ceramic engineering at the University of Illinois at Urbana where he earned his Ph.D. degree in ceramic engineering in 1959. Tennery served on a committee that reviewed the national magneto-hydrodynamics program for the U.S. Department of Energy, is a Fellow of the American Ceramic Society, and recently became a member of the advisory editorial board of a new international journal, *High-Temperature Technology*.

ducted was prepared, and a construction request was forwarded to ERDA. A conceptual design based upon a 7,400-m^2 (80,000-ft^2) building was completed. Ted Lundy (M&C), serving as ORNL's liaison officer, interacted with Union Carbide Engineering Division and the conceptual design contractor.

In October 1977, John Cathcart (M&C) was appointed coordinator of the HTML initiative and assumed the roles formerly held by Riley and Lundy. Early in 1978, the HTML Advisory Committee was formed to provide ORNL management with objective assessment and guidance in the quest for the

HTML. This committee, which includes both university and industrial representatives, has met several times at ORNL and has been particularly helpful to ORNL management.

In July 1980, we received a formal request from the Office of Basic Energy Sciences (OBES) to reduce the size of the HTML from about 7,400 m^2 (80,000 ft^2) to about 4,600 m^2 (50,000 ft^2). A second conceptual design to meet these new requirements was completed that December. Hanna Shapira of ORNL's Energy Division then prepared sketches of alternate architectural treatments for the building.

In December 1980, an important event occurred—the formation of the HTML's Industrial Users' Committee. Its purpose is twofold: to advise ORNL management of possible mechanisms for industry-ORNL interactions, such as assigning industrial researchers to the HTML, and to make recommendations to ORNL management on future important areas for high-temperature materials research.

In April 1981, ORNL hosted a special meeting of the Industrial Users' Committee. About 50 senior industrial R&D executives attended and heard our ideas for the HTML. We described selected examples of ORNL materials research to them (such as our work in developing stronger alloys and tougher ceramics) and solicited their support for the proposed facility. As a result of this meeting, we received strong support for the HTML from the industrial community. Some of our new industrial contacts requested information on how to start and organize research programs in which interested companies could collaborate with ORNL materials scientists and engineers.

The HTML budget fortunes were looking very favorable during the FY 1982 budget cycle in 1981. The project was included in the President's Budget and was formally authorized by congressional and presidential action; unfortunately, at the last moment, the HTML funds were deleted during House-Senate conference action on the appropriations bill. Also during 1981, I was appointed director of the HTML, replacing Cathcart, who returned to full-time research in the M&C Division. In the same year, two major ORNL review committees again strongly endorsed the HTML concept.

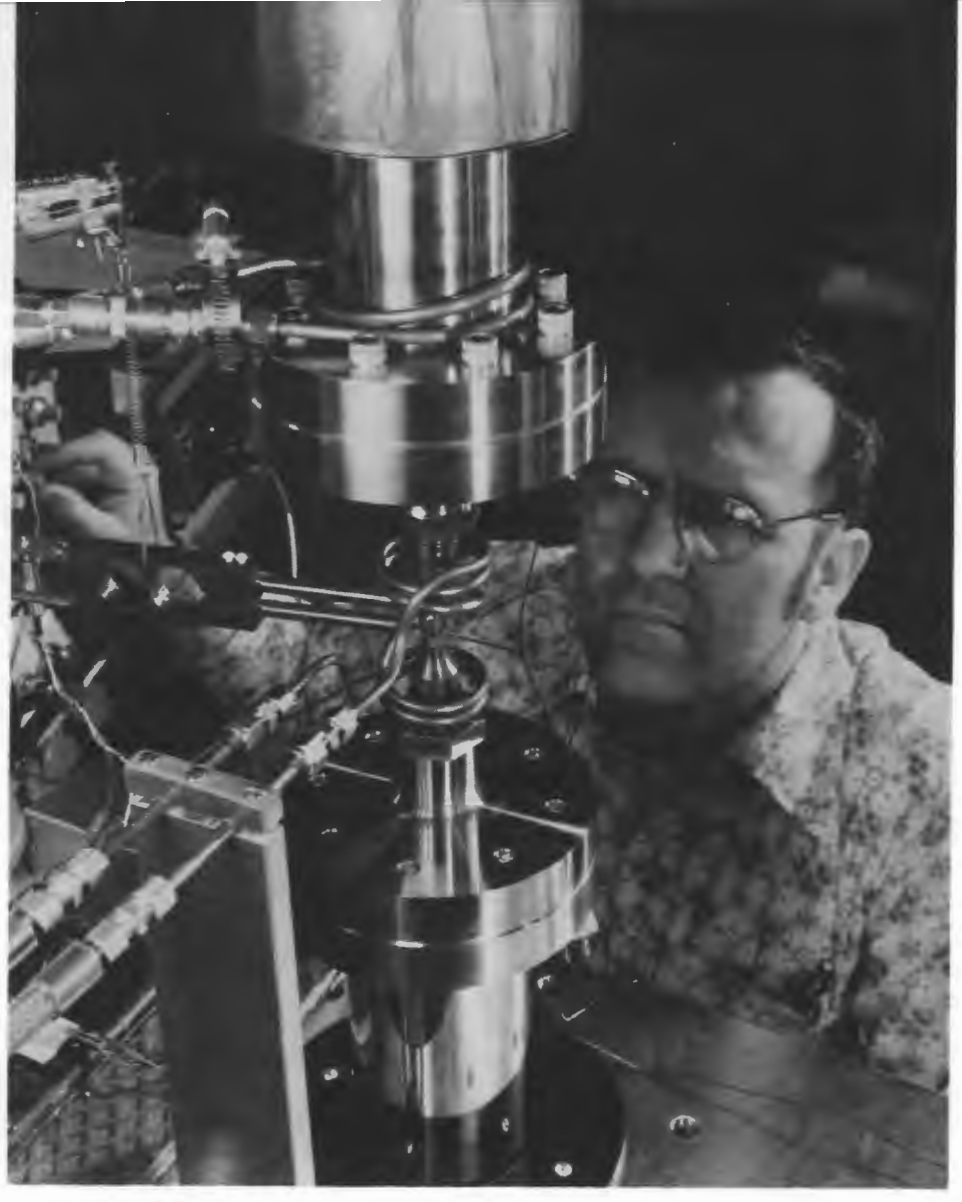
During 1982, in an effort to bring the HTML into being, we analyzed ORNL's research program supported by the Division of Materials Sciences of OBES and identified certain research activities within the Solid State, Metals and Ceramics, Chemistry, and Chemical Technology divisions that would be consolidated into a high-temperature materials program. After several months of effort, Carl Koch (M&C), Paul Becher (M&C), and I, aided by the many researchers involved in this work, completed our first set of research plans.

Perseverance Pays

We persevered and, in preparation for the FY 1984 budget cycle, undertook to strengthen the support base for the HTML. For example, we provided documents that support the HTML concept to the Office of Management and Budget (OMB), which conducted an independent analysis of the project in late 1982. Then, one day in December 1982, I was informed that the project was deleted from the DOE/OBES budget by OMB. We were very discouraged, for this news seemed to be the death knell for the project. However, the following morning I learned that the project had been transferred in the FY 1984 budget to the Office of Vehicle Engine Research and Development (OVERD) within the DOE's Conservation Program. This action meant that an entirely different set of House and Senate Committees would now be responsible for judging the project.

In February 1983, I made a presentation on the HTML concept, the proposed building, and details of some of ORNL's ongoing materials research to the Solid State Sciences Committee of the National Research Council. This committee is often asked by Congress to provide advice on whether a proposed research facility is justifiable and suitable. In March, Zucker testified before the Subcommittee on Energy Development and Applications, Committee on Science and Technology, U.S. House of Representatives. During his testimony, he presented recent results of ORNL's materials research program and explained why the HTML is needed.

Since that time, the project has survived the FY 1984 budget markup process in the Appropriations Committees of both the House and Senate, and the President signed the appropriations bill on November 4. The FY 1983 budget reprogramming has been completed, and the FY 1984 budget for the project was received in January 1984. The architectural engineering contractor has been selected, the contract for this work was signed this past November, and the design work is under way. During November and December 1983, work by DRS and AMK resulted in determination of the location of the HTML (immediately south of Building 4508), selection of the HTML structure type (reinforced concrete), the architectural treatment, and general details for the floor plans. We expect to start actual construction in early 1985. For us, 1984 was the year when our sponsor in Washington gave the green light to the project that we believe can truly benefit the nation. ornl



Larry Egner of the Metals and Ceramics Division calibrates an extensometer to measure deformation in stainless steel during a high-temperature fatigue test.

Materials Technologies for Advanced Nuclear Energy Concepts

In the 1950s, it was predicted that nuclear power would be so cheap that electric meters would not be required. By 1973 the cost of nuclear electricity was greater than had been anticipated, but it was still needed because the Arab embargo ended the United States' presumption of a cheap, ever-increasing oil supply. However, even though the demand for electricity continued to grow in the United States, the era of nuclear plant cancellations and deferrals began. Erratic economic growth, skyrocketing interest rates, and long construction times and licensing delays had essentially destroyed that early dream of cheap nuclear power, and alternative means for energy production and conservation were being pushed. Since then, higher-performance, advanced nuclear plant concepts have emerged with major emphasis on lower capital costs, inherent safety, and increased reliability. What are some of the materials problems posed by these concepts, and how are scientists and technologists at Oak Ridge National Laboratory addressing them?

In materials and structures research at ORNL, our goal is to provide a technological basis for ensuring that reactor components

and systems for advanced concepts such as the liquid metal fast breeder reactor (LMFBR) and the high-temperature gas-cooled reactor (HTGR) will perform efficiently and reliably during their design lifetimes. Like their predecessors, these higher-performance machines must last for 30 to 40 years in potentially corrosive environments and in high-radiation fields but at much higher temperatures. Construction and operation of LMFBRs and HTGRs worldwide have already provided a great deal of information on the behavior of structural materials, but the higher temperatures proposed for advanced systems and the several reported failures of structural components in operating plants point out the need for improved materials technologies.

In nonnuclear applications, design of pressure-boundary components using the rules of the American Society of Mechanical Engineers (ASME) dates back 40 years. The ASME approach is referred to as design-by-rules and is used for home water heaters and fossil fuel plants and has been used for some older nuclear plants. In this approach, the critical dimensions for a component are based on allowable stress criteria, which consider resistance to rupturing when stressed (stress-to-rupture properties), resistance to breaking when subjected to tension (tensile properties), and resistance to a permanent change in the material's shape after prolonged exposure to relatively small external forces at high temperature (creep).

Although use of design-by-rules has generally proven successful for nonnuclear systems, a material failure that can be tolerated in a water heater or a fossil-fired plant may prove to be extremely costly and totally unacceptable in a nuclear plant. The ASME recognized that additional considerations were needed for nuclear components exposed to high-temperature cyclic loading and thermal shock conditions. Therefore, the ASME formulated a design-by-stress analysis requirement where fatigue (the tendency of a material to break under cyclic or repeated alternating stress and strain) and creep-fatigue properties must also be considered.

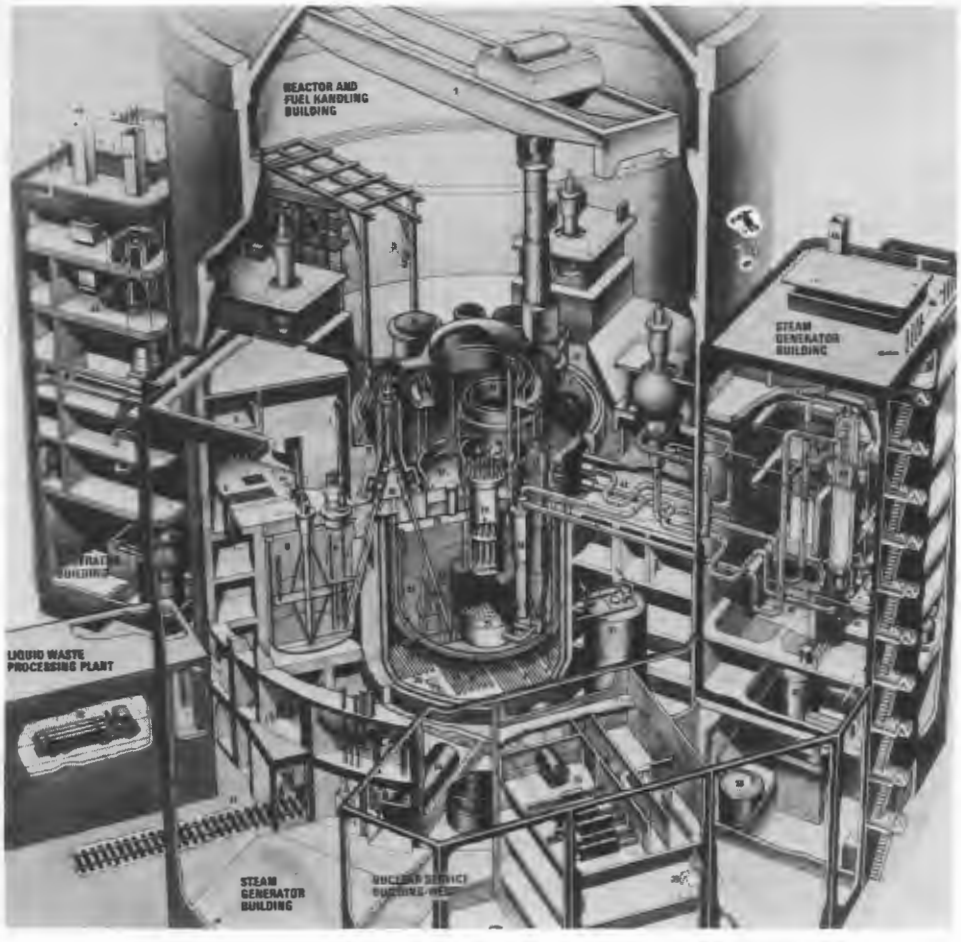
In LMFBRs, several structural failures in piping, heat exchangers, and steam generators have been reported. The steam generator is a particularly critical component in an LMFBR because its tubes form the boundary between sodium and water (or steam); thus, the possibility exists that highly corrosive sodium hydroxide would be produced as the result of a structural failure. Failures of this type have occurred in type 304 stainless steel welds in the French Phenix, the niobium-stabilized, chromium molybdenum (2.25% Cr and 1% Mo) steel superheaters in the Prototype Fast Reactor (PFR) in the United Kingdom, and the superheaters (made of the same material as those in the PFR) in the Russian BN-350. These failures were attributed to fatigue, improper heat treatment, and undetected defects in welds.

The cracking of the type 304 stainless steel welds in Phenix was clearly associated with a deficiency in the design-by-rules method. Jim Corum and his coworkers in the Engineering Technology Division are attempting to establish a high-temperature design methodology that addresses the deficiencies in this method. Some of the key problems they are studying are mathematical descriptions of inelastic behavior, criteria and rules for time-dependent deformation and failure, confirmatory structural assessments, and simplified methods for minimizing the cost and time of design analysis. Although the ORNL High-Temperature Structural Design Program was developed for application to LMFBRs, it is in many respects equally applicable to HTGRs.

Implementation of either design-by-rules or design-by-stress analysis requires a good data base on material properties. Chuck Brinkman and his Mechanical Properties Group in the Metals and Ceramics (M&C) Division provide baseline design data on tensile, creep, fatigue, creep-fatigue, and crack-growth properties, and they determine the effects of environment and microstructure on these properties for specific design applications.

Fabrication and service defects are generally unavoidable in any system, and, as mentioned above, they have led to component failures in a number of reactor systems. Thus, the ability to nondestructively characterize defects, especially during service life, is critically important. The M&C Division's Nondestructive Testing Group led by Bob McClung has made considerable progress in several difficult problem areas, including in-service inspection of stainless steel welds and advanced techniques for the in-service eddy-current inspection of ferritic steels to check for flaws.

Standard eddy-current techniques have been found unacceptable for in-service inspection of the double-wall tubes proposed for use in an advanced LMFBR steam generator. The standard technique cannot overcome two problems: (1) the need for boreside magnetization of the 2.25 Cr-1 Mo steel to allow penetration of the eddy currents through the tube wall for evaluation of the outer surface and (2) the high heat generation in the tubing caused by magnetization. McClung, Gerry Scott, and Cas Dodd have achieved the level of



Schematic of the Superphenix, a 1200-MW(e) fast breeder reactor under construction in France.

magnetization required for this application with a boreside probe that contains both the eddy-current coil and magnetic coils. They are developing a pulsed technique to provide adequate signal intensity and magnetization; because the current is pulsed, less heat would be generated.

Although existing materials for LMFBRs are regarded as adequate, meeting the goal of cutting costs requires improved materials that have better overall properties. A major achievement of the LMFBR Materials and Structures Program at ORNL has been the development of an improved ferritic steel that potentially can be used in a variety of component designs at lower costs in advanced nuclear plants. The new alloy, called modified 9 Cr–1 Mo steel, was developed by a team from M&C led by Vinod Sikka, in cooperation with Combustion Engineering, Inc., Chattanooga (see article entitled "Marketing ORNL-made Materials" elsewhere in this issue). The addition of small amounts of niobium and vanadium and the more precise control of chromium and carbon (as compared to standard 9 Cr–1 Mo steel) has resulted in an alloy that has the mechanical strength of type 304 stainless steel at temperatures ranging up to 550°C but whose resistance to stress corrosion cracking in halide and caustic environments is much greater. *Industrial Research & Development* magazine awarded one of its prestigious I-R 100 awards in 1982 to ORNL for development of the modified 9 Cr–1 Mo steel on the basis of its "importance, uniqueness, and usefulness to mankind."

Important advances in radiation-resistant fuel cladding and duct alloys for LMFBR applications are described in Arthur Rowcliffe's "Design of D9: A Radiation Damage-Resistant Alloy" elsewhere in this issue.

In the case of the HTGR concept a technical issue of concern is the ability of the graphite fuel elements to remain intact, especially under severe thermal transients during reactor shutdown. Cracks were observed recently in two graphite fuel blocks removed from an operating HTGR at Fort St. Vrain, Colorado. Working with graphite manufacturers, Walt Eatherly and Ray Kennedy of the M&C Division have developed material and processing modifications that resulted in an improved grade of graphite, which is stronger than the material now used yet is still sufficiently resistant to oxidation and radiation damage.

The current *de facto* moratorium on the sale of nuclear power plants marks the end of a nuclear era. If we are to have a second nuclear era, as former ORNL director Alvin Weinberg has termed it, improvements must occur in designs of future nuclear systems. Our challenge is to develop highly reliable, inherently safe, and environmentally acceptable systems that are economically competitive. This is a large order, to be sure, but one to which ORNL is dedicated and, in fact, significantly contributing through improvements in materials and materials technologies.—*Jim DiStefano, Metals and Ceramics Division, and Bill Harms, Central Management Offices.*

Paul Becher (standing) and Matt Ferber confer over a micrograph at the scanning electron microscope.

Advanced Structural Ceramics

By PAUL F. BECHER

Ceramics—materials made by heating inorganic, nonmetallic powders to high temperatures—are not commonly thought of as structural materials capable of supporting high loads or stresses as do steels. Mention of the word "ceramics" conjures up an image of something fragile, such as chinaware, pottery, and glass. Of course, some ceramic materials such as concrete (when reinforced with steel rods) are known for their structural uses, even though they are obviously brittle.

In spite of their brittleness, though, ceramics are strong and hard at high temperatures. Thus,

they are useful in a wide variety of energy conversion applications. Some ceramics have optical uses, such as glass lenses, potassium chloride laser windows, and alumina and beryllia microwave windows. Electrical applications have been found for ceramics in insulators, piezoelectric transducers, semiconductors, and capacitors.

Ceramics are strong when compressed, but, as we will see shortly, high tensile strength ceramics require very careful processing so that the cracks or defects that control strength are kept quite small—well under 100 μm. These properties result from the absence of any plastic deformation in most ceramics at temperatures below

Ceramics are very hard materials and can be quite strong at high temperatures but because they are brittle, they have had only limited use in energy conversion devices. However, ORNL researchers have found that incorporating zirconia particles or silicon carbide whiskers into ceramics such as alumina substantially increases the material's toughness, or resistance to cracking under stress. Ceramics made of polycrystalline titanium diboride can also be made to have high fracture strengths and toughness by careful control of the microstructure.

Ceramics possessing chemical or wear-resistant properties are used as abrasives and in pump and valve components used in the chemical industry, while those resistant to high temperatures are found in refractory insulation and may be used in components of heat engines such as valve lifters, piston caps, cylinder liners, and bearings. In fact, Oak Ridge National Laboratory is the U.S. Department of Energy's lead laboratory for developing ceramics for advanced heat engines such as the adiabatic diesel engine.

In each of these cases, the ceramics are subjected to some type and magnitude of tensile loads or stresses. Many times the design of components has to be modified to minimize these stresses; and, as a result, full advantage often cannot be taken of the material's desirable properties. Ceramics often do break quite readily when subjected to bending or tension; many college students learned about this phenomenon in their respective chemistry laboratories when they tried to break a glass rod cleanly, only to have it splinter into several pieces.

1000°C; thus, often only modest tensile-type stresses are necessary to make inherent cracks grow.

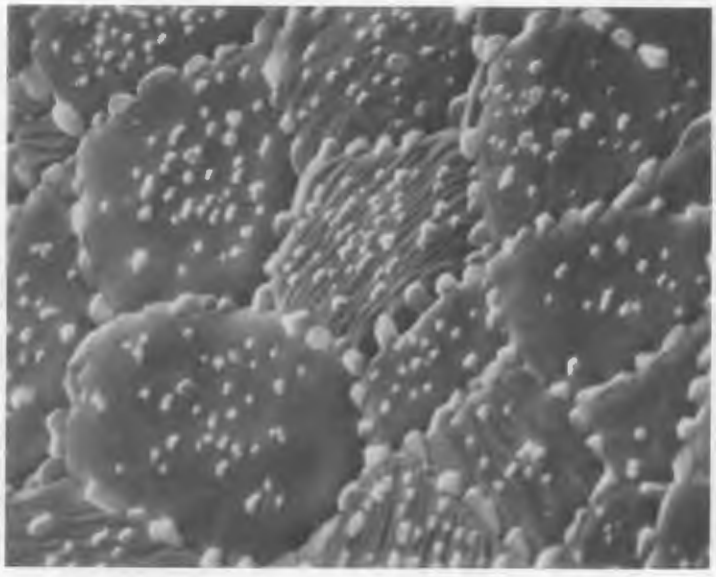
The failure of ceramics under tensile stresses such as bending stems from the motion of cracks under stress; usually, each crack advances by the elastic stretching and breaking of the chemical bonds at the sharp tip of the crack. Because virtually no plastic deformation occurs at crack tips in ceramics as it does in metals, little energy is required to advance the crack. Thus, ceramics have values of fracture toughness, or resistance to cracking, of only about one-tenth those of metals.

The result of the low fracture toughness values of ceramics is a strong sensitivity of the tensile fracture strength (resistance to breaking when bent) to the size of flaws such as cracks or cracklike defects that are always present. To improve its tensile fracture strength, a ceramic's fracture toughness must be increased or the flaw sizes decreased. For ceramics that have typical critical fracture toughness values, one must keep the flaw sizes below 20 μm in order to achieve tensile fracture strengths of 700 MPa (100,000 psi). Flaw sizes can be minimized during the fabrication of ceramics by the use of techniques that eliminate pores and porelike defects and cracks. However, in making a large number of ceramic components, it is very difficult to ensure that the flaws are small enough and that they will remain so throughout the life of a component in service.

Another approach would be, of course, to increase the fracture toughness of the ceramic and thus allow larger flaws. We could improve fracture toughness by identifying mechanisms that can increase the amount of energy that must be applied to cause cracks to grow. The question then arises: what are the processes that can be used to dissipate additional energy in the crack tip region?

Toughened Ceramics

To dissipate more energy at a crack tip, some process must be triggered by the tensile stresses localized there to increase the fracture toughness of the material. At ORNL the Structural Ceramics Group has prepared ceramics that contain particles that undergo stress-induced transformations (changes in crystal structure) which involve both an increase in the volume and a change in the shape of the particle. Such features are characteristic of the tetragonal-to-monoclinic phase transformation in zirconia (ZrO_2) and hafnia (HfO_2). The nature of this particular phase transformation is also such that the stress required to initiate it can be controlled by both certain chemical additions (e.g., small amounts of yttria, or Y_2O_3) and changes in temperature. By decreasing both the amount of additive and the temperature, the level of stress needed to initiate the phase transformation



Alumina (Al_2O_3) with 20 vol % zirconia (ZrO_2) particles is shown in this micrograph (magnification ×4000).

Alumina (Al_2O_3) with 20 volume % silicon carbide (SiC) whiskers appears in this micrograph (magnification × 5000).

decreases. The net effect of decreasing additive and temperature, then, is that particles undergo a phase transformation in a larger region around the crack tip and the fracture toughness increases as desired.

That substantial increases in fracture toughness are obtained by such stress-induced phase transformations has been demonstrated by research conducted at ORNL by Matt Ferber, Shirley Waters, and me. We have found fracture toughness increases in a polycrystalline alumina matrix in which tetragonal ZrO_2 particles are dispersed. In this case the stress-induced phase transformation in the ZrO_2 particles increases the toughness of the alumina by a factor of 2 to 4 and raises the amount of energy dissipated during crack growth by up to a factor of 10. The key here is to make alumina ceramics in which the ZrO_2 particles are well dispersed, the ZrO_2 particle size is small (<1 μm), and the amount and uniformity of the Y_2O_3 additive are controlled. Whether alumina can be toughened depends upon our ability to trigger the phase transformation of the ZrO_2 particles under stress. We have found that large (>1 μm) tetragonal ZrO_2 particles or particles with low Y_2O_3 content will change phase automatically before we apply an external stress. At the other extreme, if the Y_2O_3 content is too high (>3 mole %), the ZrO_2 does not change phase even under stress. In these cases the phase transformation is not available for toughening when it is needed; thus, the toughening effect is lost. The desired microstructural and compositional control is possible, however, if the dense ceramics are fabricated with powders derived from carefully controlled sol-gel techniques such as those developed by Walt Bond, Bill Arnold, and G.D. Davis of ORNL's Chemical Technology Division.

The Payoff

What is the payoff obtained by improving fracture toughness in a ceramic? One benefit is that it is now possible to fabricate a ceramic material that can have a tensile fracture strength of 700 MPa (100,000 psi) even though it contains relatively large flaws. Normally, to achieve such strengths the critical flaw size must be kept very small (<20 μm). By increasing the fracture toughness threefold, the allowable critical flaw size is increased ninefold (to sizes approaching 200 μm).

Increasing the allowable flaw size in turn makes inspection easier. Techniques currently used to detect flaws and defects in materials are capable of locating such large flaws but are now only capable of resolving certain types of small flaws approaching 20 μm in size—and then only in components having very simple shapes. Thus, if the toughness of certain ceramics is increased, current inspection techniques can ensure that components made from these materials will have high tensile strengths.

The second benefit of toughening ceramics will depend upon further advances in flaw detection techniques. If flaws that measure 50 μm could be readily observed, then toughened components that pass inspection would have fracture strengths in excess of 1340 MPa (>190,000 psi). I should point out that current experimental results show that fracture strengths in bending in excess of 1000 MPa

Shirley Waters slides a capsule of alumina-zirconia powder on a thermocouple prior to operating the thermal analysis system used to characterize ceramic powders and obtain information on phase transformations and the amount of heat absorbed or released by reactions as a function of temperature in a particular atmosphere.

(145,000 psi) can be obtained in the ZrO_2-toughened alumina ceramics.

Whisker Reinforcement

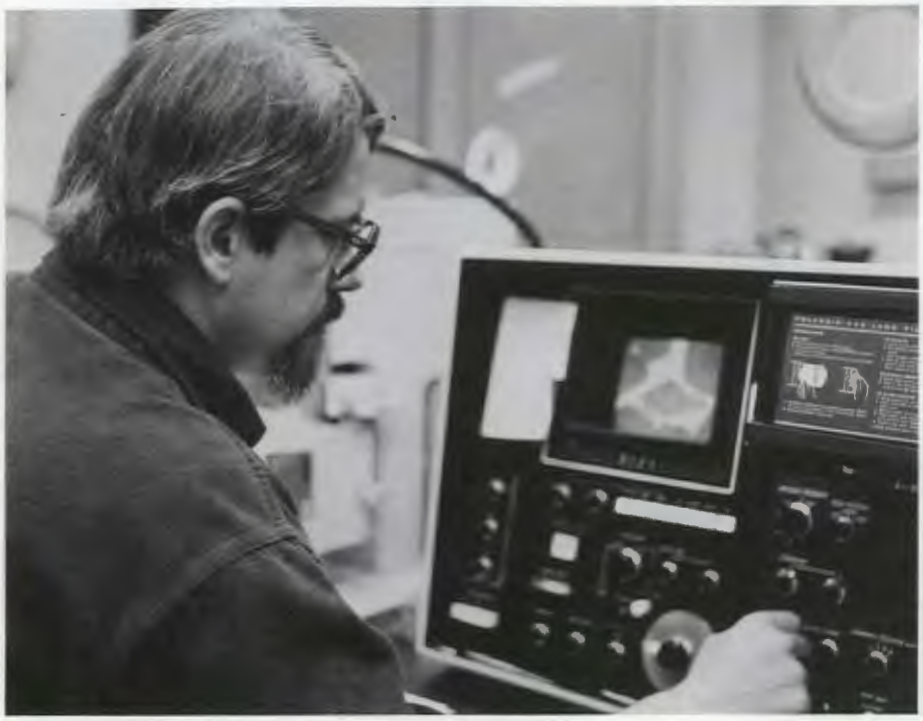
Other processes tested at ORNL can be used to toughen ceramics. One that offers considerable promise involves the incorporation of high strength whiskers, tiny (<1 μm diam) rodlike single crystal or polycrystalline materials that are extremely rigid. In this case, the whiskers as well as the ceramic matrix resist the growth of the cracks under applied tensile stresses. By controlling the amount and strength of the whiskers and how well the whiskers are bonded to the ceramic matrix, we can obtain a material in which the whiskers essentially hold the ceramic together in the crack tip region. For the crack to advance, it must pull the whiskers out of the ceramic matrix. Because this process requires more energy, the whiskers inhibit the crack's growth.

Results of a cooperative research program involving George Wei of the Ceramic Technology Group and me show that the fracture toughness of alumina more than doubles as a result of the addition of silicon carbide (SiC) whiskers. As in the case of the ZrO_2-toughened aluminas, such improvements in fracture toughness will substantially increase both the allowable flaw size in ceramic components and their tensile fracture strengths.

Slow Crack Growth

So far we have focused on the "critical" tensile fracture strength of ceramics where failure occurs instantly; however, failure also can occur, after some time, even when the applied tensile stress is less than the material's tensile fracture strength. In fact, these processes of slow crack growth often limit the use of some ceramics because they can withstand only very low applied stresses and still avoid failure within some specified time. In other words, applying a stress that is kept lower than the tensile fracture strength will cause fracture in the ceramic—but it takes a longer time.

The logical question then is, Can we increase the time before failure occurs by increasing the fracture toughness? If we consider the processes that occur during crack growth, we can show that toughening processes, such as phase transformation toughening and whisker reinforcement, should occur over a range of applied stresses. For example, increasing the applied stress (and stress intensity) causes an increase in the transformation zone at the crack tip in the



Paul Becher has been group leader of the Structural Ceramics Group in ORNL's Metals and Ceramics Division since 1981. Prior to coming to ORNL in 1980, he worked for 10 years at the Naval Research Laboratory. In 1970 he earned his Ph.D. degree in ceramics engineering from North Carolina State University. An expert on the mechanical behavior and processing fundamentals of ceramics, Becher has authored 70 technical papers and served as program chairman and exhibit chairman of the Basic Science Division of the American Ceramic Society of which he was made a Fellow in 1979.

ZrO_2-toughened alumina; thus, the material effectively gets tougher with increasing applied stress. The toughening process then requires the application of greater stress intensity to achieve crack growth rates comparable to those in the nontoughened ceramic matrix. In practice, this procedure would allow the use of such toughened ceramics under much higher stress conditions and still obtain a very long time before failure would occur.

Work at ORNL provides the first evidence that toughening processes, such as those found in the ZrO_2-toughened alumina and the SiC whisker reinforced alumina, do impart greater resistance to slow crack growth. Data derived from these experiments show, in fact, that toughened ceramic components can resist failure from the application of these subcritical stresses hundreds or thousands of times longer than conventional ceramics do.

The problem of slow crack growth may also be attacked in other polycrystalline ceramics by examining the effect of the matrix microstructure. In noncubic ceramics, internal stresses are introduced during fabrication as a result of the nonuniform contraction of adjacent grains during cooling. The dense material will thus consist of a distribution of grain interfaces subjected to either residual tensile or compressive stresses. The nature of the crack growth is such that the crack will be influenced more by the local residual tensile stresses than by the residual compressive ones. Analysis of the local stress intensity that results from these residual stresses indicates that it increases with increasing grain size.

Modeling studies by Ferber show that the stress intensity acting on a crack tip must include the contribution of both the applied stress intensity and the local stress intensity. When the latter is included, these modeling studies show that decreasing the grain size increases the ceramic's resistance to slow crack growth. These predictions are substantiated by experiments conducted by Ferber and me on polycrystalline titanium diboride (TiB_2), a very anisotropic material. Our results show that the lifetime before failure occurs in fine-grained (6 μm) TiB_2 is many orders of magnitude longer than that of a coarse-grained (12 μm) material in which the residual stresses are much higher. In fact, predictions indicate that the fine-grained TiB_2 can endure for many years, even when the applied stresses approach 80% of its critical fracture strength. The coarser-grained material, on the other hand, fails instantly at such levels.

Fabrication

Finally, we need to consider how such ceramics are fabricated. The processes most often used to pro-

duce ceramic materials involve the consolidation of ceramic powders at high temperatures (typically >1200°C). During consolidation, the powder particles are joined together; they grow and change shape as voids, or pores, are removed by diffusion processes that allow atomic species to move. In this way a dense body containing many grains is produced. The critical requirements include both minimizing the growth of the powder particles and of the subsequent grains that are formed during consolidation and elimination of voids and pores. Particle and grain growth can be lessened by minimizing the temperature required for consolidation.

Several techniques are used to lower the consolidation temperatures. One is to add small amounts of selected chemical compounds that speed up diffusion during the consolidation process; another is to start with ultrafine (up to 0.1 μm) powder particles that can be closely packed together so that the atoms need move only a small distance to form grains and remove voids. In the case of the TiB_2 ceramics, Carlos Bamberger, Jorulf Brynestad, Dale Heatherly, and Fred Land of the Chemistry Division's High Temperature Chemistry Group are studying high-temperature reactions that could be used to synthesize ultrafine, pure powders. Results to date have shown that TiB_2 powders produced by processes based on the Chemistry Division studies can be used to form dense fine-grained (<2 μm) TiB_2 ceramics at modest temperatures. Additional studies by Cabell Finch and Pete Angelini of the Structural Ceramics Group reveal that when only coarse (5 μm) powders are available, small amounts (<10%) of metals having low melting points can be added to produce dense TiB_2 ceramics at temperatures below 1500°C. When this technique is used, the resultant grain size is about the same as the starting powder size. Both techniques, then, allow us to produce the fine-grained TiB_2 ceramics, which have high fracture strengths and are extremely resistant to time-dependent failure under stress.

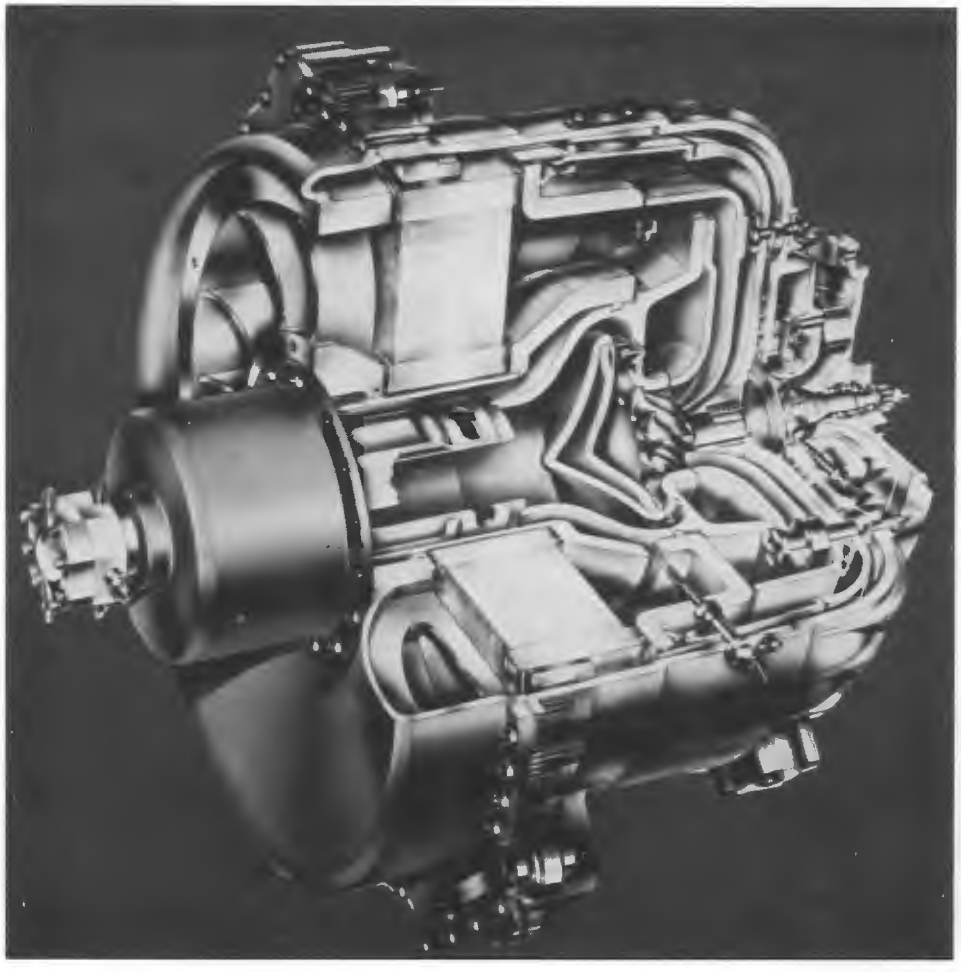
In conclusion, several means exist to tailor the mechanical properties of ceramics so that they are much less likely to fracture. We at ORNL have found that incorporating ZrO_2 particles or strong SiC whiskers into the ceramic during the fabrication process substantially increases its fracture toughness. This increased fracture toughness allows the ceramic fabricator to use inspection techniques now available to verify that the cracks or flaws in components are small enough to ensure that components will have high fracture strengths. In addition, these toughening techniques greatly reduce the likelihood that failure will occur with time as a result of slow crack growth when the component is subjected to in-service tensile stresses. In the case of noncubic ceramics, we can also use processing techniques that produce dense, fine-grained ceramics. This processing will minimize the internal stresses in the ceramic and thus result in a high-strength ceramic with greatly increased service life. Thus, materials such as the fine-grained TiB_2 ceramic can be used under service conditions in which high strength [500 MPa (70,000 psi)] must be maintained for many years. As understanding and application of toughening techniques continue to advance, the image of ceramics as brittle and fragile may gradually be displaced by their growing reputation as durable structural materials. ornl

Materials for Energy Conservation

Our perception of energy conservation has changed within the last decade. During the "energy crises" of the mid-1970s, most people associated energy conservation with curtailing energy use and changing lifestyles by lowering thermostats, driving less, and reducing industrial production. This curtailment suggested that a lower standard of living was inevitable. Recently, energy conservation has taken on a more positive meaning—that of using energy more efficiently by getting more useful energy from the same amount of fuel and by reducing wasteful energy losses. The efficient use of energy is thus a cost-effective energy source. Many consumers are now reducing their energy consumption by using available conservation technologies (additional insulation, lighter automobiles) without making sacrifices in their lifestyles or standard of living. Likewise, industry has cut its energy usage and maintained its level of production by using improved industrial processes and controls.

Although additional energy conservation can be achieved by a more widespread use of available technology, significant future gains in energy efficiency will require new technology developments for advanced energy conservation systems. Many of these advanced systems (more energy-efficient buildings, industrial process equipment, and automotive engines) can be

Dave McElroy leans on an evacuated insulation panel made in France by L'Air Liquide and gages the thickness of a stack of three fiberglass batts. The stack has the same resistance to heat flow as the French insulation. The French panel is 5.7 cm thick, almost one-fifth the thickness of the stack of fiberglass batts (26.7 cm). The panel is made of aluminized plastic, evacuated to 0.01 atm, and filled with ultrafine particles of silica. Because of its vacuum and the small particles, this thin insulation has an R-value of 33 and is potentially useful in refrigerators and water heaters. ORNL is evaluating alternative particles that could be used to make this type of insulation less expensive.

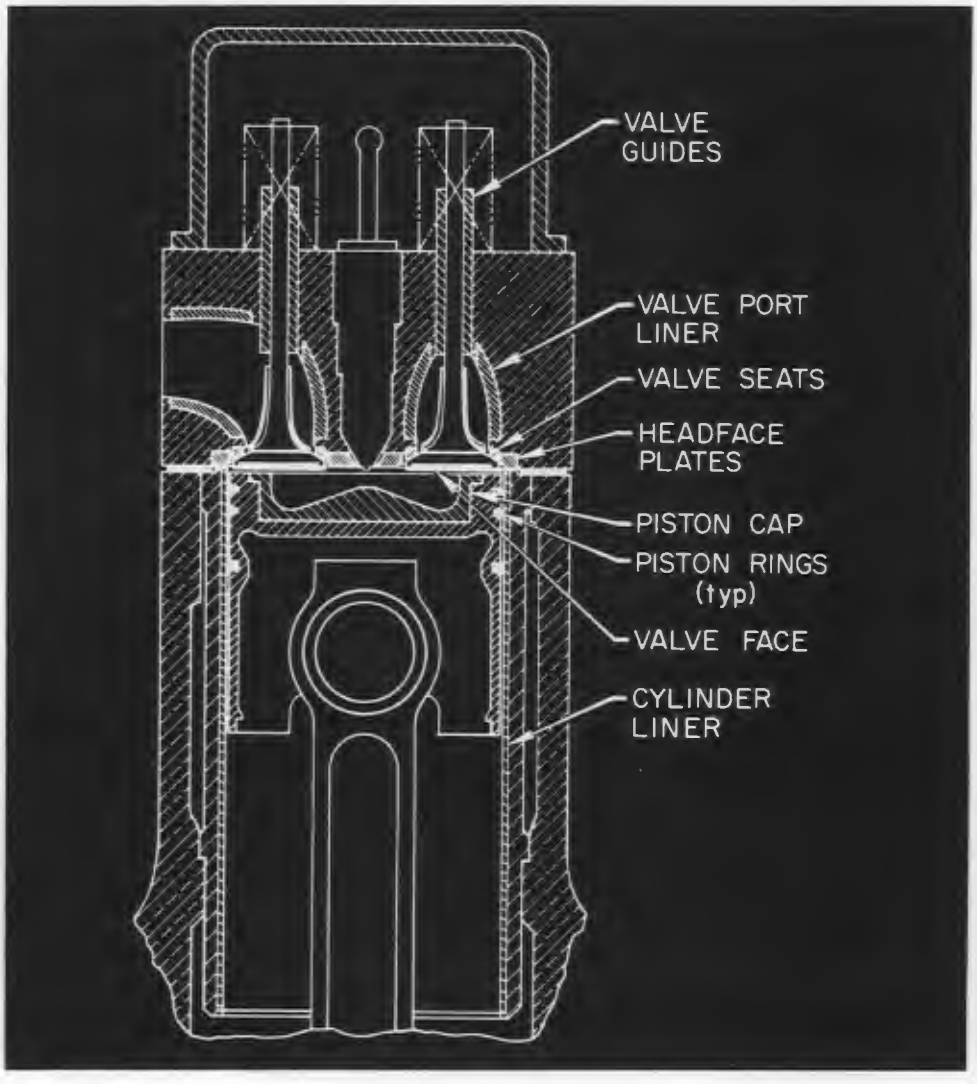


A fuel-efficient automotive gas turbine engine requires extensive use of high-strength ceramics in the hot sections of the engine. DOE is supporting two teams for the development of a ceramic gas turbine engine (Garrett Turbine/Ford and Allison Turbine/Pontiac). The new DOE/ORNL program is aimed at increasing the reliability of the ceramic components. (Photography courtesy of Garrett Turbine Engine Company.)

built and operated at a much lower capital cost and with less environmental impact than developing new energy sources and generating capacity.

A major impediment to achieving greater energy efficiency is the lack of reliable, cost-effective materials for advanced energy conservation systems. Such systems require special materials that permit increased temperatures and pressures and that reduce heat losses, friction, and wear. Energy can also be saved by using lightweight materials and recycling energy-intensive raw materials. Industry is doing much to improve state-of-the-art materials; however, long-term, high-risk development of new materials for advanced systems requires government support in many areas. The Metals and Ceramics (M&C) Division at Oak Ridge National Laboratory is responsible for four major research and development programs on materials for the Department of Energy's Assistant Secretary for Conservation and Renewable Energy. These programs cover the major energy-consuming sectors—buildings, industry, and transportation.

Research on the mechanisms that control heat transfer in building insulation materials, plus development of improved insulations that further reduce heat losses from buildings, is being carried out by Dave McElroy's Physi-



This schematic of an adiabatic diesel engine being developed by Cummins Engine Company shows the use of ceramic parts and coatings in the hot sections of the engine. The insulating ceramic components reduce the heat loss and allow the recovery of this thermal energy through a turbocompound unit or other energy conversion device. This mechanical energy can be fed back to the transmission, thus increasing the overall engine efficiency by up to 30%. (Photograph courtesy of Cummins Engine Company.)

This slag deposit on silicon carbide tubes is the result of five months of exposure to corrosive combustion products from a steel reheat furnace (soaking pit) at the Babcock and Wilcox plant in Beaver Falls, Pennsylvania. ORNL is testing ceramic materials that are candidates for tubing in recuperators, devices that recover heat from industrial flue gases for use in preheating combustion air. Silicon carbide was selected for testing because it is a good heat conductor that is highly resistant to thermal shock.

cal Properties Group. This group is part of the Building Thermal Envelope Systems and Insulating Materials Program, which was established in 1977 and is managed by Ted Lundy. McElroy's development of improved models for heat transport and simple and reliable test methods has helped industry and other government programs determine more nearly accurate insulation values for existing materials and devise methods for improving the effectiveness of new insulations.

For example, radiation heat transport in building insulations at room temperature was not thought to be significant. However, the development of improved models and testing at ORNL showed that radiation transport can account for 30 to 45% of the total heat conducted in low-density insulations. Application of this information to current industry test methods helped resolve serious discrepancies in advertised "R-value" data from insulation manufacturers and was important in reducing the burden and cost of additional insulation testing by industry. This information is also being used to develop an insulation that will contain opaque particles of the correct size and distribution to block radiation heat transport; thus the particles will lower the apparent thermal conductivity by 25 to 30% at little or no additional cost.

Our industrial conservation program, also started in 1977, emphasizes the development of technology to make improved materials for industrial insulation, for use of alternate fuels, and for the recovery of waste heat from industrial furnaces. Our current work focuses on ceramic recuperators for recovering waste energy from high-temperature (~1000°C) industrial flue gases for preheating combustion air in industrial furnaces. Such recuperators could reduce the use of fuel by 30 to 50%. This project, led by Irv Federer, involves testing and analyzing potential ceramic tube materials in high-temperature industrial furnaces, as well as developing new materials and processes. Both ORNL and industrial subcontractors are participating in the project.

A major concern is whether ceramic materials will be reliable when subjected to corrosive industrial gases, such as those in aluminum remelting and steel reheat furnaces. We are determining the corrosion mechanisms and effects on properties of ceramics exposed to corrosive gases simulating those of the industrial environment. Our goal is to help industry select the most corrosion-resistant ceramic materials and to predict their long-term reliability.

In 1981 at the request of DOE's Office of Vehicles and Engines Research and Development, Vic Tennery and I assessed ceramic technology needs and developed a long-range plan for using ceramics in advanced automotive engines. We arrived at a seven-year, $100-million, joint laboratory-industry-university program to meet those critical technology needs. DOE assigned ORNL the lead role in implementing the program, which is being managed by Ray Johnson of the M&C Division.

Replacing metal parts in engines with ceramic ones is desirable because ceramics, unlike metals, maintain their strength at high temperatures. In current heat engines, only about one-third of the energy from burning fuel can be used to drive the engine. The remaining two-thirds of the energy escapes through friction losses, the exhaust, and the coolant, which is used to remove heat to prevent the metal parts from melting. If metal parts in automobile engines and other heat engines were replaced by heat-resistant ceramic materials, these engines could use fuel 30 to 40% more efficiently and save the nation an estimated 8×10^7 m^3 (5×10^8 bbl) of oil annually.

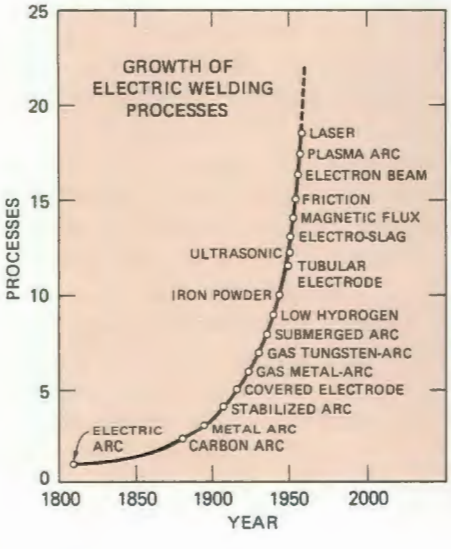
Although ceramics have many desirable properties—high strength at elevated temperatures, low density, and resistance to thermal shock, wear, and corrosion—they also have a serious limitation as a structural material. Most metals usually bend when stressed, but ceramic materials are so brittle that they often crack or break under stress. However, ceramicists at ORNL have found ways to add fibers and particles to create composite ceramics that are resistant to fracture. (See Paul Becher's article "Advanced Structural Ceramics" elsewhere in this issue.) Further work on these ceramic materials could make them suitable for use in uncooled engines and gas-turbine engines.

Uncooled engines, such as adiabatic (no-heat-loss) diesels, will be designed to use the exhaust heat to drive turbine blades for additional power; such engines will be made of ceramic parts or coatings and may be available in the late 1980s. For the longer term (1990s and beyond), gas-turbine engines made of ceramic components are envisioned. These engines will use fuel more efficiently because they will operate at much higher temperatures than conventional heat engines and recover exhaust-gas heat. Because the gas-turbine engine is an external combustion device, it can easily use a wide range of alternate fuels (for example, synthetic liquids and gases made from coal or biomass), which may be required in the future.

The Energy Conservation and Utilization Technology Program was established by DOE in 1980 to provide base technology and innovative approaches for all advanced conservation systems. The Materials and Tribology Projects, managed by Joe Carpenter, involve long-range research in high-temperature materials, lightweight materials, and tribology (the science of friction and wear in materials). The materials project is focused on developing ductile ordered alloys for use in heat exchangers, valves, and turbine disks (see C. T. Liu's article "Design of Ordered Intermetallic Alloys"); finding ways to join ceramic components with metal parts or other ceramic components in engines and heat exchangers; and recycling the increasing amount of plastic scrap in lighter weight automobiles to reduce the amount of petroleum used for making plastics. The tribology project, led by Charles Yust, examines mechanisms controlling the wear and friction of ceramic materials, with the goal of increasing their resistance to wear and lowering their friction.

This basic research program is aimed at solving the materials problems for a wide range of advanced conservation systems, thus paving the way for the increased energy efficiency and industrial productivity needed to keep the United States competitive with other countries.—*Anthony Schaffhauser, Metals and Ceramics Division.*

Growth of processes of welding since its beginning (C. Jackson, Welding Journal, Vol. 42, 1963, p. 216).



Welding Metals and Alloys

By S. A. DAVID

Welding is the art and science of joining metals, usually by heating them to a suitable temperature. In the broadest sense, welding includes the formation of metallurgical bonds in various kinds of welded, brazed, and soldered joints and rules out joints by mechanical means or adhesives. Welding goes back to prehistoric days when people were soldering with copper-gold and lead-tin alloys. Evidence indicates that artisans were joining iron and steel to form weapons as early as 1000 B.C. However, the

only sources of heat for joining in those days were wood and coal. The development of modern welding technology began in the latter half of the 19th century when electrical energy became more easily available. The growth of modern welding technology in the last 30 years has been phenomenal, and the development of new heat sources such as beams of electrons and laser light has provided further impetus to this growth.

ORNL is recognized worldwide for advancing the science and technology of welding. Recently, ORNL researchers have done pioneering work in producing improved weld metals, optimizing their properties, and developing welding processes and procedures to make better transition joints.

Welding encompasses a wide spectrum of physical and applied sciences. Because of its complexity, for years welding technology has seen growth more as an art than as a science. However, in recent years the trend has been changing. The field has been receiving the attention and recognition of experts in physical sciences and engineering, and more funding has been made available to support research, including basic research. Since its formation in 1950, the Welding and Brazing Group at Oak Ridge National Laboratory has played a significant role in advancing the science and technology of welding and is recognized worldwide for its contributions. ORNL has made major contributions in the development of welding procedures for critical nuclear and space components, pipes, refractory metals, and filler metals and brazing procedures for metals and ceramics. Our strong points include a highly skilled and experienced staff, a multidisciplinary approach to problem solving, and unique capabilities, including a multikilowatt continuous-wave carbon dioxide (CO_2) laser.

Stainless Steel Welds

In welding, metallic parts are united by heating, which causes the parts to flow together. The material being welded interacts with the heat source as it is subjected to temperatures from ambient to above its *liquidus* (temperature above which the material is 100% liquid). Based on the temperature distribution and associated metallurgical phase changes, the weldment may be divided into three distinct parts—the fusion zone (FZ), the heat-affected zone (HAZ), and the base metal (BM). Regardless of the welding process, welding may be carried out with or without the addition of filler metal and, depending on the thickness of the material, the weld may consist of one or many welds (single or multiple pass).

Although welding activities at ORNL involve both austenitic and ferritic steels, significant contributions have been made to the basic understanding of the welding of austenitic stainless steel, a corrosion-resistant alloy steel that contains 6–26% chromium, 6–22% nickel, and 0.08% carbon.

Two of the most important microstructural constituents of austenitic stainless steel welds are austenite and ferrite phases. Depending on the composition, the weld may be fully austenitic or contain austenite with varying amounts of ferrite, which has a higher chromium content. Fully austenitic stainless steel weld metal is known for its tendency to crack at high temperatures during welding. This "hot-cracking" phenomenon is known to be caused by the segregation of constituents such as sulfur and phosphorus which remain molten during solidification. These "low-melting" constituents are present in steels as residuals from the steel-making process.

Various theories have been offered to explain the role of ferrite in preventing hot cracking, but none is very convincing. The problem of hot cracking can be overcome by slight adjustments in steel chemistry to obtain a small percentage of retained ferrite in the microstructure. Although the ferrite may prevent hot cracking in the weld metal, it has been found to promote corrosion susceptibility, reduce cryogenic toughness, and lead to embrittlement at elevated temperatures because of the transformation of ferrite to the brittle sigma phase. Hence, because austenite lacks the drawbacks of ferrite, it would be highly desirable to produce a fully austenitic stainless steel weld without hot cracks. To achieve this type of weld, John Vitek and I have sought to understand the solidification behavior of these alloys and the role of ferrite in preventing hot cracking.

In the past five years, our basic research funded by the U.S. Department of Energy's Basic Energy Sciences Program has made significant contributions in this area. Using controlled solidification experiments such as interrupted solidification and sophisticated electron microanalytical tools such as scanning transmission electron microscopy (STEM), Vitek and I have been able to identify the origin of ferrite in austenitic stainless steel weld metal. Interrupted solidification experiments involve heating alloy specimens to various temperatures between the points where liquid and solid coexist in the alloy, rapidly cooling the specimen, and characterizing the phases that exist when the temperature is held at

Stan David received his B.S. and M.S. degrees in metallurgical engineering from the Indian Institute of Science of India and earned a Ph.D. degree in the same field from the University of Pittsburgh. From 1972 to 1977 he served on the faculty of the university's Department of Metallurgical and Materials Engineering; he is now Adjunct Professor of Metallurgical and Materials Engineering there. In 1977 he became a staff member of ORNL's Metals and Ceramics Division. Since then he has continued to make significant contributions to the field of welding. Because of these contributions he received the McKay-Helm Award in 1980 and the Lincoln Gold Medal in 1981 from the American Welding Society. As task leader of the Basic Energy Sciences welding program at ORNL, he has developed new areas of research in welding. He served as the general chairman of the 1981 conference, "Trends in Welding Research in the United States," sponsored by the American Society for Metals, and he is editor of the recently published conference proceedings.

one point. The STEM analysis, which obtains solute profiles at submicron intervals, is essential to understand how various elements partition, or separate out, during the transformation, either from liquid to solid or solid to solid.

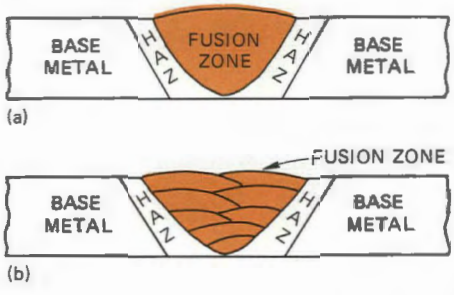
Using the information gathered, we have been able to attribute the origin of ferrite in austenitic stainless steel weld metal to (1) incomplete transformation to austenite of the ferrite that forms from the liquid during solidification of the weld metal and (2) the transformation of the same ferrite, depending on the cooling rate, to Widmanstatten austenite, which leaves behind some residual ferrite. In both cases the transformation of ferrite to austenite has been identified as a solid-state reaction that is diffusion controlled.

As previously mentioned, the most desirable austenitic stainless steel weld metal is the one that contains a fully austenitic microstructure that does not crack at high temperatures. We have achieved this goal through controlling the process variables such as the heat source and welding speed and have obtained some exciting results. Using a high-power, continuous-wave CO_2 laser as a heat source at welding speeds in excess of 2.54 cm/s, we have been able to produce a fully austenitic weld that does not crack in an alloy that would normally have a duplex ferrite plus austenite microstructure. We have achieved such a modification in microstructure in a typical type-308 stainless steel weld. Further confirmation of these promising results has been obtained through rapid solidification, or splat cooling, experiments. In short, what we found was that high cooling rates encountered during laser welding and rapid solidification by splat cooling resulted in a ferrite-free austenitic material that does not crack at high temperatures.

Residual Elements

A good weld should be ductile and have strength properties comparable to those of the base mate-

Inserting a pipe into the internal bore welding machine.



Schematic of a weldment showing various regions—namely, base metal, heat-affected zone (HAZ), and the fusion zone. Figure A is a single-pass weld, and Figure B is a multi-pass weld.

rial. That is, it should be able to deform plastically without cracking or breaking. Earlier work at ORNL by Norman Binkley and Gene Goodwin has revealed that austenitic stainless steel welds made with electrodes containing titania and lime-titania coatings had higher creep strength and ductility than welds made with lime-coated electrodes. Also, further work has shown that small additions of titanium (Ti), phosphorus (P), and boron (B) to austenitic stainless steel weld metal improved its ability to resist creep rupture at elevated temperatures. These additions are known as controlled residual elements (CRE).

Although steel properties have been improved because of CRE additions, the role of titanium, boron, and other elements in improving the properties has long been a mystery. Recently, however, Vitek and I unraveled partially, if not fully, the mystery of CRE additions. In particular, we have explained the role of titanium in improving the resistance of stainless steel to creep rupture.

We have studied welds with and without CRE additions during long-term exposure to elevated temperatures to determine the stability of phases in the weld metal. We found that the ferrite in both types of welds is unstable and dissolves, accompanied by an extensive amount of solute redistribution that results in chromium enrichment within the ferrite, which eventually transforms to the brittle sigma phase. We also found a continuous network of metal carbides ($M_{23}C_6$) at prior austenite-ferrite interfaces in the welds that lacked CRE additions, but no such observation was made in the welds that had CRE additions. Evidently, titanium in the CRE weld ties up the carbon in the alloy as TiC and prevents the precipitation of $M_{23}C_6$ carbides. We propose that the absence of the carbide network is responsible for the improved creep rupture properties of steels that have CRE additions. We are now trying to ascertain how boron improves the properties of austenitic steel used in welding.

Transition Joints

For purposes of improved design and economics, dissimilar metal welds, or transition joints, are used in many transportation and energy systems. The Welding Group at ORNL has played, and continues to play, a significant role in developing improved transition joints for energy systems. Transition joints are required in several energy systems. For example, in fossil-fired power plants, the primary boilers and heat exchangers operate at temperatures low enough that the economical ferritic steels are the best choice of material for construction. However, because of their higher operating temperatures, the superheater and reheater tubes require more expensive austenitic steels. Hence, transition joints are required for these two different types of stainless steels.

Although general experience with transition joints between austenitic and ferritic steels has been satisfactory, industrial experience (both domestically and internationally) has shown a disturbing number of failures within these joints in fossil-fueled power plants. Preventing such failures can make power plants more reliable and save several hundred thousand dollars per day—the cost of a power plant shutdown.

ORNL welding researchers Jim King, Gene Goodwin, and Gerry Slaughter have led international efforts to determine the cause of failure of these joints and to design better joints. They have led an internationally constituted Task Force on Dissimilar Metal Welding to facilitate cooperation and information exchanges among laboratories, utilities, commercial fabricators, and universities, and they

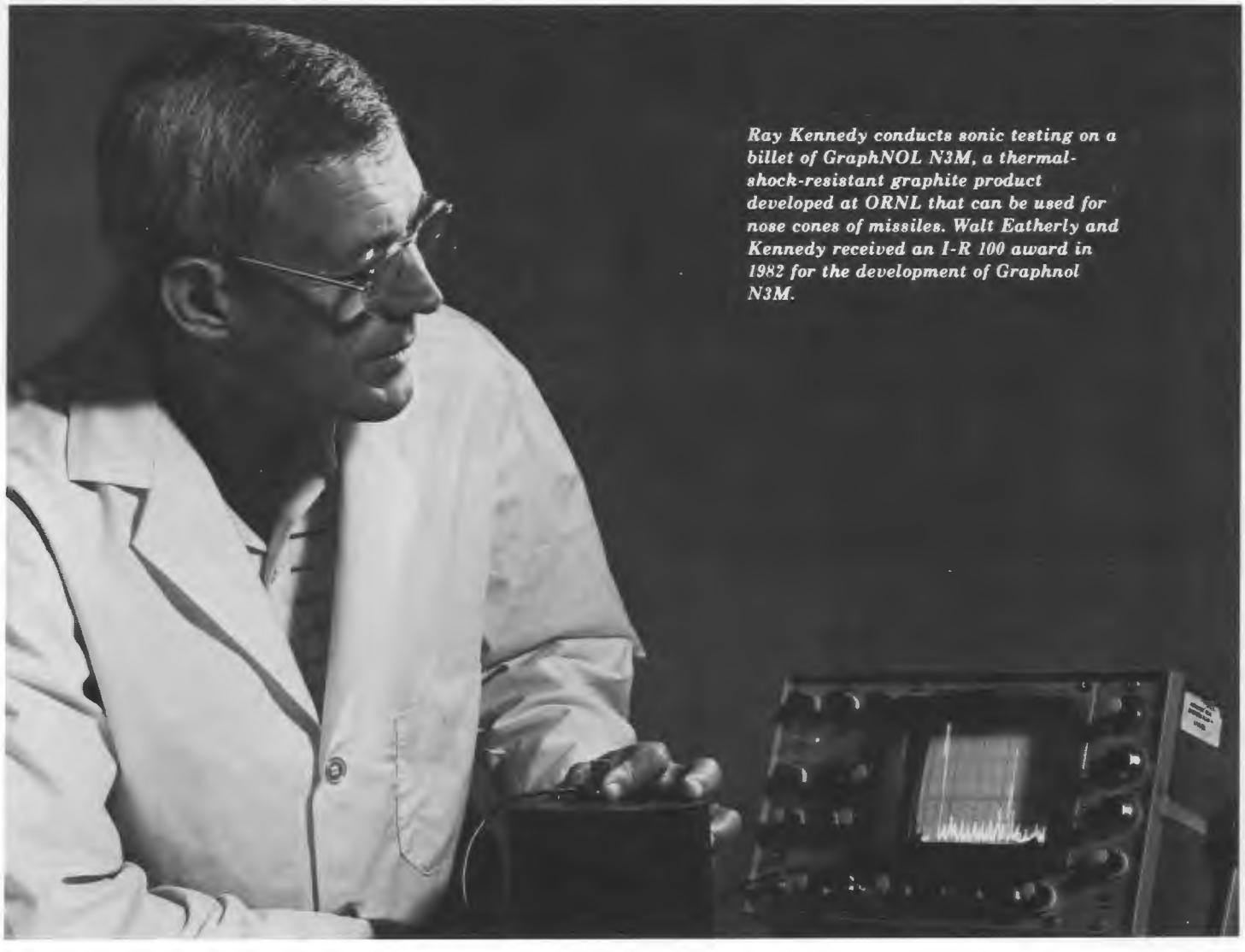
This transition joint configuration has been studied at ORNL. Mean coefficients of expansion from 20 to 540°C (70 to 1000°F) are noted below each material.

Robbie Reed inserts a metal specimen into the Gleeble 1500 thermomechanical simulator, which reproduces thermal and stress conditions undergone by metals during welding.

have studied the early methods that used austenitic stainless steel filler metals to join low-alloy ferritic steels to austenitic steels. Cyclic stresses and high temperatures caused failure in the ferritic material parallel and adjacent to the weld metal. They have identified the major cause for the failure to be high stresses at the interface because of differences in the coefficient of thermal expansion in the weld metal and base metal—that is, differences in the constant amount that each material expands when heated to a specific temperature. In addition, certain other metallurgical problems such as carbon migration and stress cycles have been found to aggravate the problem.

King and Slaughter also studied the more recently used ferritic-to-austenitic steel joints that use nickel-base austenitic filler metal. The nickel-base weld metal greatly reduces undesirable metallurgical reactions and also has a thermal expansion coefficient nearer that of ferritic material. Although experience with this particular joint has been found to be more favorable than that with stainless steel weld metal, occasional failures still occur. To overcome this problem, ORNL's Welding Group and the General Electric (GE) Company collaborated in developing an improved transition joint. The joint was made by combining the dissimilar metal with a material or series of materials whose coefficients of thermal expansion lie between those of the materials to be joined. The effect of this development is to distribute the mismatch in the coefficients of thermal expansion over several interfaces so that the difference at any one interface is reduced. We are continuing our efforts to understand the mechanism of transition joint failure and to extend joint lifetimes. Meanwhile, transition joints based on the ORNL–GE design are being used in two coal-fired power plants—a plant operated by the American Electric Power Company in Ohio and the Kingston Steam Plant (near Oak Ridge) operated by the Tennessee Valley Authority.

In welding technology, it is clear that ORNL is engaged in a wide variety of both basic and applied research activities. In addition to some of the activities described above, work is also being carried out in the welding of ferritic steels, advanced alloys for space applications, titanium alloys, long-range ordered alloys, and aluminides. Brazing alloy development for metals and ceramics is also under way. In addition, some of our staff members serve on several national professional society committees and advisory boards related to welding and joining. Also, the welding facilities at ORNL are being updated to keep up with the rapidly growing technology. The recently acquired thermomechanical simulator, which is capable of simulating thermal and stress cycles encountered by the weldment during welding, adds another unique capability to ORNL, which continues to be one of a handful of laboratories at the forefront of developments in the 3000-year-old technology of joining metals and alloys. ornl



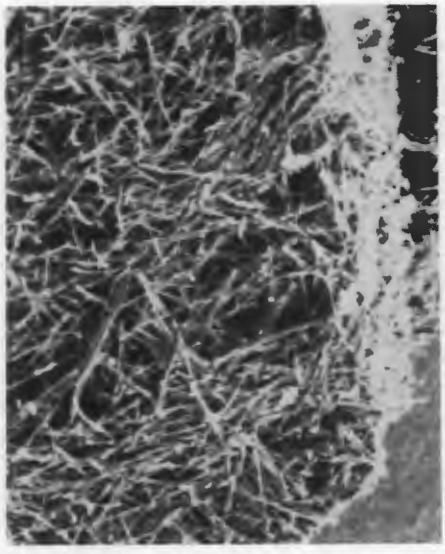
Ray Kennedy conducts sonic testing on a billet of GraphNOL N3M, a thermal-shock-resistant graphite product developed at ORNL that can be used for nose cones of missiles. Walt Eatherly and Kennedy received an I-R 100 award in 1982 for the development of Graphnol N3M.

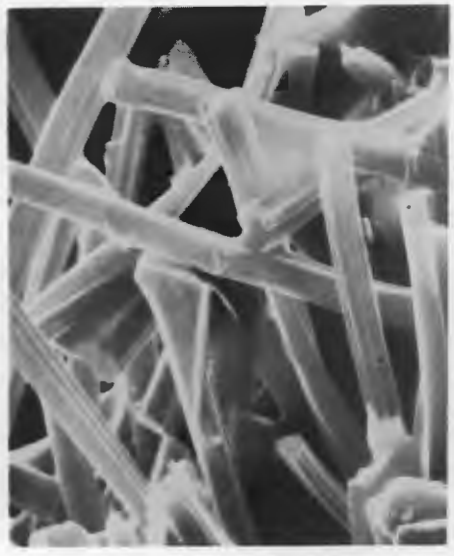
Graphites for Space and Defense

I·R 100

Graphite, like diamond, is crystallized carbon. However, in diamond the carbon atoms bond in tetrahedral fashion (four directions in three dimensions) to three nearest neighbors, whereas in graphite the carbon atoms bond in three directions to three nearest neighbors in the same plane. These three-directional (trigonal) bonds are the strongest known in nature, yet their planar nature allows the carbon atoms to slide by each other. Thus, graphite is in a sense both harder and softer than diamond. By judiciously mixing these properties, scientists can obtain a material that can be designed specifically to meet hundreds of applications. Diamonds may be a girl's best friend, but in the world of industry and commerce, graphites surpass diamonds in usefulness and economic value.

Oak Ridge National Laboratory researchers have experimented with graphite and carbon since the beginnings of nuclear energy in the 1940s. Because of its ability to grow stronger at high temperatures, to resist radiation damage, and to slow neutrons, graphite has been used as a moderator in nuclear reactors. The name of the world's first operating thermal reactor—the Oak Ridge Graphite Reactor—gives recognition to these desirable properties. Graphite is also the moderator for high-





Carbon fibers matted with a phenolic resin (left) are employed to make a carbon-bonded carbon fiber insulation now used in heat sources aboard satellites. Under higher magnification (right) the crenolated carbon fibers and carbonized phenolic bridges are apparent, along with the open structure that makes the composite an excellent thermal insulator.

temperature gas-cooled reactors (HTGRs). In recent years, the ORNL graphite program in the Metals and Ceramics Division has developed special forms of carbon and graphite for use in HTGRs and for possible aerospace, defense, and high-technology applications.

For example, under contract to the U.S. Naval Surface Weapons Center, Ray Kennedy, Fred Jeffers, and I have developed a process to make a new artificial graphite product called GraphNOL N3M. This new process and product received an I-R 100 award in 1982 from *Industrial Research & Development* magazine, which annually recognizes 100 promising innovations. GraphNOL can resist radiation damage from intense neutrons and can withstand extreme thermal shock and stress. Thus, it can be used not only for heat exchangers, turbine blades, and piping in fission and fusion power plants but also in missile and space rocket nose cones. Missile components of GraphNOL recently passed tests in actual flights across the Pacific Ocean missile range.

The new manufacturing process that we developed to produce GraphNOL is an application of the theories of fracture mechanics (understanding why materials crack or break). This process can be modified to produce high-quality graphites tailored to meet special needs.

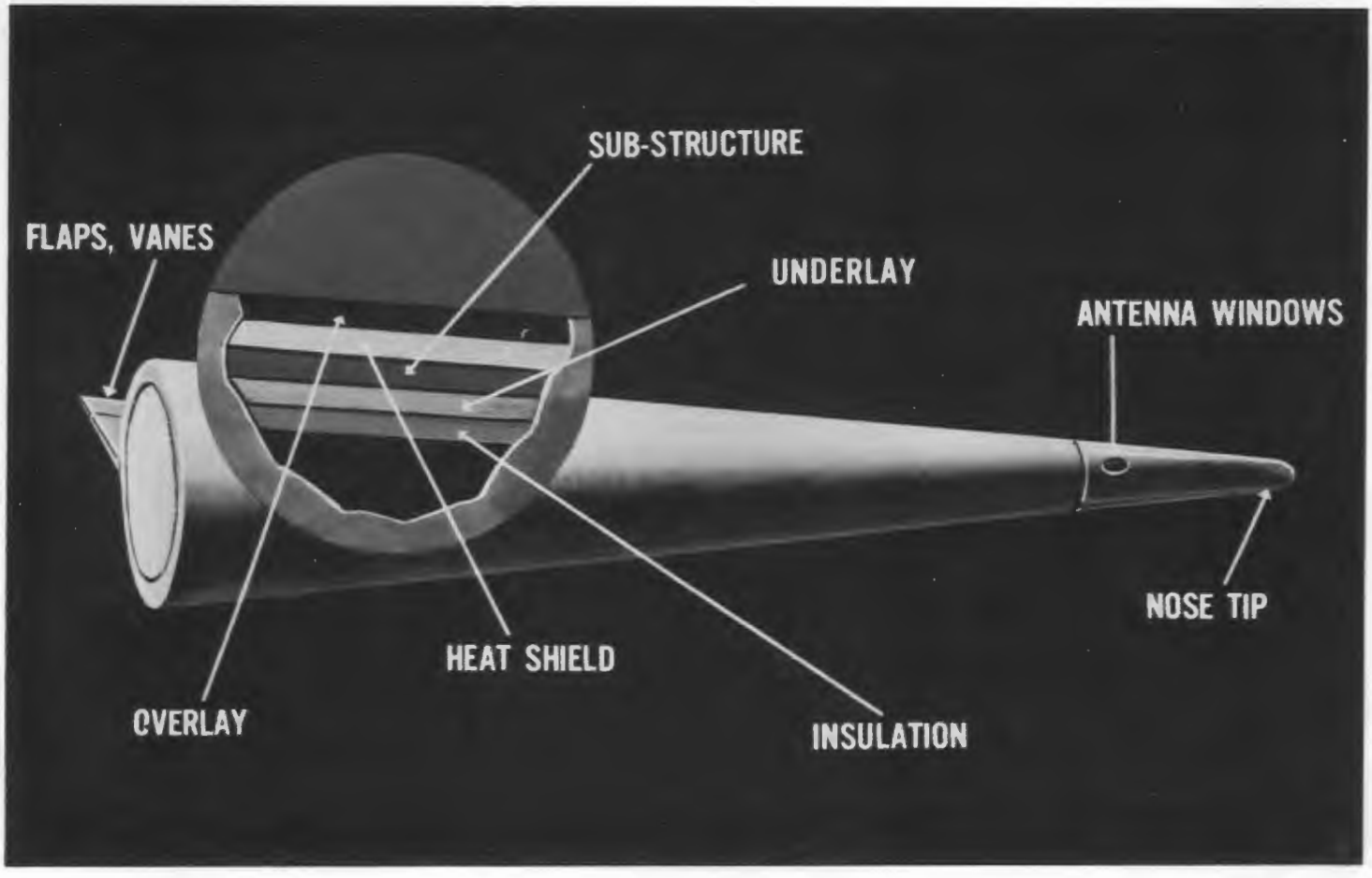
Although graphite can be obtained from natural deposits for such uses as lubricants and pencils, high-quality graphite designed for specific industrial purposes is usually made by heating organic precursors (generally pitches and tars) in furnaces to temperatures hotter than those of the sun's surface. At these temperatures graphite crystals are formed. Many different types of graphites exist; how each one is made depends on the raw materials, fabrication methods, and heat treatment used. Because graphites vary in crystalline degree and orientation, they can have vastly different mechanical properties. Thus, making a graphite to meet a specific need is a complex process that remains in part a black art.

To fabricate carbon and graphite materials of interest, it is necessary to have high-pressure autoclaves to fill the voids in normally porous graphites with carbon (impregnation). ORNL has developed special equipment for impregnation and for carbonaceous, metallic, and ceramic coating of graphites, primarily by vapor deposition. With this capability, we can transform organic structures into crystalline graphite that is in the form of finished products of usable size and shape.

Over the years, our research has focused on relating graphite's large-scale physical and chemical properties to its microstructure and single-crystal behavior. Because graphite is extremely anisotropic—that is, because its properties have different values along different crystal axes, these properties must be treated as tensors rather than as scalars (numbers). In other words, the properties of polycrystalline graphite depend very sharply on the relative orientations of the individual crystallites that make up the whole.

For example, if graphite is fabricated to have one highly preferred direction, it may be slippery; with other directions, it may exhibit considerable friction. This directional property of graphite holds true also when neutrons damage it; the displaced atoms form new interstitial planes that cause the crystals to grow in one direction while their volume remains the same. By studying the effects of this radiation damage on the microstructure of graphite, we and others have obtained the information needed to help us develop graphites that are highly resistant to radiation damage. The keys to this damage resistance are highly dispersed pores and macroscopic isotropy—uniform behavior in all directions.

Our studies of the effect of radiation on microstructure have also helped us and others improve the

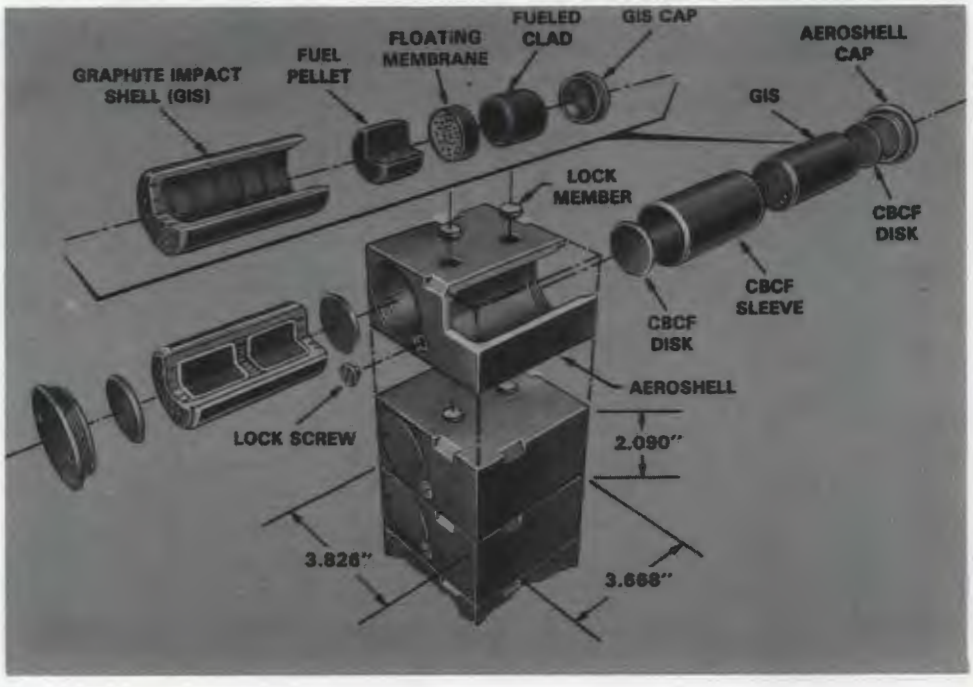


The nose tip of this missile is made of GraphNOL N3M to protect it from the searing heat of reentry. The arrows point to areas on the reentry vehicle where critical heat-resistant materials are required.

mechanical properties of graphite. To fabricate most artificial graphites, a mixture of sized particles and an organic binder are formed into a body and heat-treated to reduce the particles and binder to carbon. We have found that by making the particles chemically active during the forming process, the finished material will withstand the high degree of internal strain generated by the crystal anisotropy. This ability to withstand strain is an essential key to the material's resistance to radiation damage and thermal shock. This approach led to the development and commercialization of GraphNOL, which is particularly resistant to thermal shock.

Currently, we are developing criteria for graphite so that we can predict under what conditions it will fail structurally—that is, develop cracks that lead to fracture. We are studying fracture initiation and growth in graphite and developing statistical techniques and mathematical models to establish tolerance limits—that is, to determine the probability that failure will occur as a function of stress encountered in any application. We are also developing nondestructive test methods to predict mechanical behavior under various conditions.

Our studies of fracture mechanics have demonstrated that at least two types of flaws account for the failure of graphite under ordinary conditions. One flaw is found in the raw materials, the other is introduced in the fabrication process. Once the type of flaw is understood, we may use this information to improve graphites for both reactor and aerospace applications. On the theoretical side, classical fracture mechanics appears quite adequate to describe and predict graphite's behavior if the theories are modified to include the pseudoplastic nature of graphite's mechanical properties. Nondestructive sonic techniques appear most promising in fracture-mechanics research and in production quality control; qualitatively at least, fracture-mechanics parameters can be predicted by measuring the velocity of sound waves in the material and the decay of the wave energy as it passes through the graphite.



This general-purpose heat source designed by General Electric Company for satellites uses graphite and carbon materials to protect the heat source in the event of an accidental reentry. The fuel pellet is clad in a graphite impact shell, which in turn is clad in a carbon-bonded, carbon fiber (CBCF) thermal insulation sleeve. The process for making the CBCF sleeves and disks was developed at ORNL.

The use of graphite is limited by oxidation. When oxygen reacts with graphite, it consumes the material, thus converting it to the gases carbon monoxide or carbon dioxide. Thus, a goal of graphite researchers has been to find ways to protect graphite from oxidation. Various approaches have included coating the graphite with an oxidation-resistant material and introducing an oxidation-inhibiting chemical agent into the graphite.

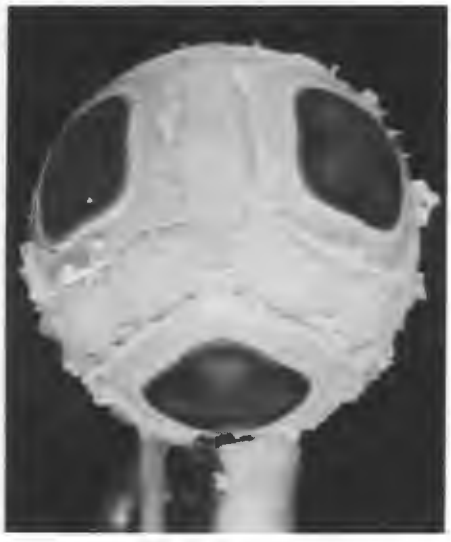
The study of graphite oxidation has been plagued historically by insufficient characterization of the material under study. Our current work in this area involves relating oxidation mechanisms to both the pore and surface microstructure by using "active-site" concepts as a working hypothesis. An active site is a surface defect which acts as a catalytic center that promotes chemical reactions such as oxidation. So far, we have demonstrated that the increased tendency of oxidized graphite to crack can be attributed either to binder oxidation or to active sites generated by impurities. This finding has encouraged our belief that the oxidation mechanisms can be related quantitatively to microstructure. We therefore plan to alter the microstructure by introducing trace elements as oxidation inhibitors (doping) and by eliminating crystalline defects (active sites) in the binder.

As previously stated, graphite structures can be altered to match specific applications. For example, we have made carbon fibers for thermal insulation by deliberately inhibiting the crystalline development to prevent good thermal conductivity. Bonded mattes of carbon fibers are currently used in satellites' isotope-powered electric generators, which convert the heat of radioactive decay directly into electricity. This thermal insulation is being made at ORNL by J M Robbins and Clyde Hamby for the U.S. Department of Energy. This fibrous matte insulation can be used for high-temperature applications on Earth as well as in space; for example, it can be employed at remote, inaccessible sites where maintenance-free sources of electricity are required for instrumentation. This process of manufacturing insulation is now being readied for commercialization.

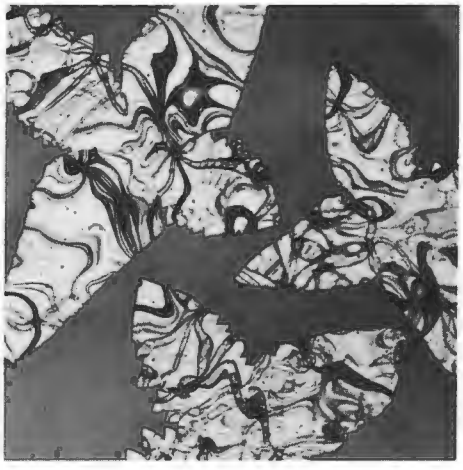
From a theoretical standpoint, we have determined that this carbon-bonded–carbon-fiber material conducts heat because of three mechanisms that are equally responsible for the thermal conductance; these mechanisms involve the transport of phonons (atomic vibrations), photons (light particles), and gas molecules. This type of carbon material is thus an intriguing object of study that may help us develop the theory of thermal conduction in such common applications as house insulation.

The study of carbon and its various forms has had a long and proud history at ORNL. Developing new high-temperature forms of carbon, finding applications for these forms, and elucidating the theory of carbon materials will continue at ORNL, thus keeping us on the frontier of carbon and graphite research. Diamonds may be forever, but graphite and other forms of carbon will surely be around for a long time to serve our special needs.—*Walt Eatherly, Metals and Ceramics Division.*

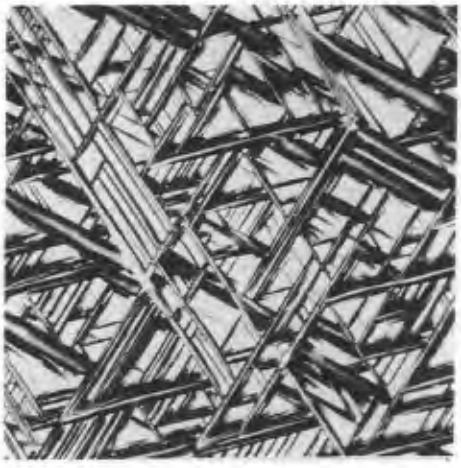
(Editor's note: Eatherly recently received the George Skakel Memorial Award from the American Carbon Society in recognition of his contributions to the science and technology of carbon. He is the third American to receive this international award, which has been presented biennially since 1969.)



It looks like E.T., the Extraterrestrial, but it's actually a niobium single-crystal sphere oxidized for 24 hr at 400°C. Where the sphere is dark, the layers of oxidation are thin; where it is light, the oxidation layers are thick. Oxidation rates vary greatly over different crystallographic orientations on the sphere.



Amorphous anodically formed oxide stripped from tantalum and crystallized in the beam of an electron microscope. The patterns shown represent strain contours in the crystalline oxide.



Traces of oxide platelets formed on a tantalum single crystal oxidized for 30 min at 500°C. These needlelike features represent the intersection of platelets of oxide with the surface of the metal.

Corrosion Studies at ORNL

No matter how strong the alloy or how fracture-resistant the ceramic, such materials are useless unless they can be made reasonably compatible with their operating environments in high-temperature energy systems. Thus, it is not surprising to find a long tradition of corrosion studies—both applied and fundamental—at an energy research facility like Oak Ridge National Laboratory. From the beginning, ORNL has had a program dedicated to studying ways of reducing corrosion and to selecting materials that are resistant to corrosion, the gradual wearing away of a material by chemical action.

In 1951, when I first came to work at the Laboratory, the Aircraft Nuclear Propulsion Program, known locally as the ANP project, was the center of attention. It took me a couple of weeks to realize that the project had nothing to do with the Great Atlantic and Pacific Tea Co., and by that time I was caught up in studies of liquid-metal and fused-salt corrosion.

These two areas of corrosion research in support of the Nuclear Energy for the Propulsion of Aircraft (NEPA) and ANP projects were rooted in the need for exotic new heat transfer media to cool the small, high-energy-density reactors envisioned as aircraft power plants. In 1960, however, national leaders became disenchanted with the idea of a nuclear reactor circling overhead; consequently, the Laboratory's attention shifted toward nuclear power for civilian uses. At this time two other corrosion research areas gained ascendency—aqueous corrosion studies in support of the Homogeneous Reactor and gas-metal interactions in connection with the Experimental Gas-Cooled Reactor.

Fundamental corrosion research had its beginning in the 1950s. Aqueous corrosion studies included G. H. Cartledge's demonstration that iron loses its reactivity in the presence of pertechnetate ions and thus is less prone to forming iron oxides. This finding came at a time when technetium was a newly discovered man-made element. At about the same time, Fred Young and his co-workers in the Solid State Division initiated an investigation of the effect of radiation on the reactivity of metals, and we in the Metals and Ceramics Division began a long-term study of the effect of oxidation-induced stresses on the oxidation process.

Out of these early studies came the expertise needed to attack the diverse corrosion problems that cropped up later.

- The ANP-inspired studies of molten salt corrosion by Gene Hoffman, Jim DiStefano, and Jack DeVan provided the basis for DeVan's work in the qualification of the ORNL-developed alloy INOR-8 (later renamed Hastelloy® N when it was marketed) as the structural material for the Molten Salt Reactor Experiment. This reactor, incidentally, is listed in the *Guinness Book of Records* as the holder of the world's record for the longest period of continuous operation (20 months).
- The aqueous corrosion work on the Homogeneous Reactor by Ed Bohlmann, Glenn Jenks, Ed Compere, and John Griess led to a "fix" (through the adjustment of the pH of the cooling water) for the deterioration of the thermal conductivity of the fuel element cladding in the High Flux Isotope Reactor. Oxide scale buildup was identified as the cause of the reduced heat transfer.
- This tradition of aqueous corrosion studies has been continued by the Chemistry Division's Franz Posey, Gene Kelly, and their coworkers. Particularly notable has been Kelly's theory of the effect of magnetic fields on corrosion processes and his studies of the corrosion of iron, titanium, and cobalt. His paper describing the Kelly-Bockris mechanism of iron dissolution was recently designated a "citation classic" because of the number of times it has been referenced in other papers.
- Our studies of oxidation-induced stresses combined with the x-ray measurements by Bernard Borie and Cullie Sparks of strains in oxide films from 1 to 25 nm thick provided the basis for an explanation of the marked oxidation rate anisotropy (different values when measured from different directions) exhibited by many metals. In a related piece of this research, Dick Pawel and Hank Inouye developed the understanding of oxygen solution effects in tantalum and its alloys during oxidation; with this knowledge they certified the spaceworthiness of the tantalum-alloy-clad isotopic power sources on *Pioneer 10*. A grateful National Aeronautics and Space Administration (NASA) rewarded Dick and Hank with tie tacks, but recognition from NASA pales in comparison to the satisfaction of knowing that these power sources are still working 10 years later as *Pioneer 10* crosses the orbit of Pluto!
- Corrosion problems related to the use of lithium-cooled nuclear reactors as power sources for satellites and spacecraft prompted the classic study by Hoffman, DiStefano, and Ron Klueh of corrosion by liquid lithium. In this study they demonstrated that oxygen in niobium and tantalum components of the reactor greatly accelerated lithium corrosion. Their "fix" was to add small amounts of very reactive metals such as hafnium or zirconium to the niobium and tantalum alloys to tie up the oxygen.
- Concern about the safety of light-water reactors led to the extension of our gas-metal reaction studies to the Zirconium-Water Oxidation Kinetics (ZWOK) Program. In this work we investigated the effects of steam oxidation on the Zircaloy cladding of fuel rods under loss-of-coolant conditions. Our goal was to provide the oxidation rate data needed to predict how hot the cladding could get and how long it could do without cooling before becoming embrittled by steam oxidation. Largely through the efforts of Dick Pawel, Rodney McKee, Ray Druschel, and others, we were able to develop a reliable set of high-temperature oxidation rate data for Zircaloy-4 that confirmed the conservatism of the Baker-Just correlation used by the Department of Energy to predict safe temperature-time limits for "off-normal" reactor conditions. These results, which are an extension of earlier work by Marion Picklesimer, Dave Hobson, and Phil Rittenhouse, have been incorporated into DOE's "best-estimate" computer codes for describing off-normal reactor behavior, but I'm afraid that our data are of little help in accidents such as the one at Three Mile Island, where the reactor core was reduced to rubble.

In more recent times, consonant with the broadening of ORNL's mission, corrosion research has moved in several new directions. Emphasis on the use of fossil fuels has led to studies of sulfidation processes and hot corrosion, such as the investigation by DeVan and Pete Ficalora of corrosion in fluidized-bed coal combustors. The possibility of using ceramics as structural materials at very high temperatures prompted the efforts of Vic Tennery, Matt Ferber, and their co-workers to characterize the reactions of silicon carbide with combustion gases at elevated temperatures. New techniques such as ion implantation and laser mixing for modifying surfaces and the steadily increasing use of electron optics and other sensitive means for characterizing the microstructure and microchemistry of corrosion specimens are adding new dimensions to corrosion research.

An old field is taking on a new appearance, and new opportunities for understanding corrosion mechanisms are in the offing. However, corrosion is such a complex phenomenon that it will probably defy an ultimate solution. After all, in the corrosion business Mother Nature is on the side of the Black Hats, and I suspect that, like the poor, rust will be with us always!—*John V. Cathcart, Metals and Ceramics Division.*

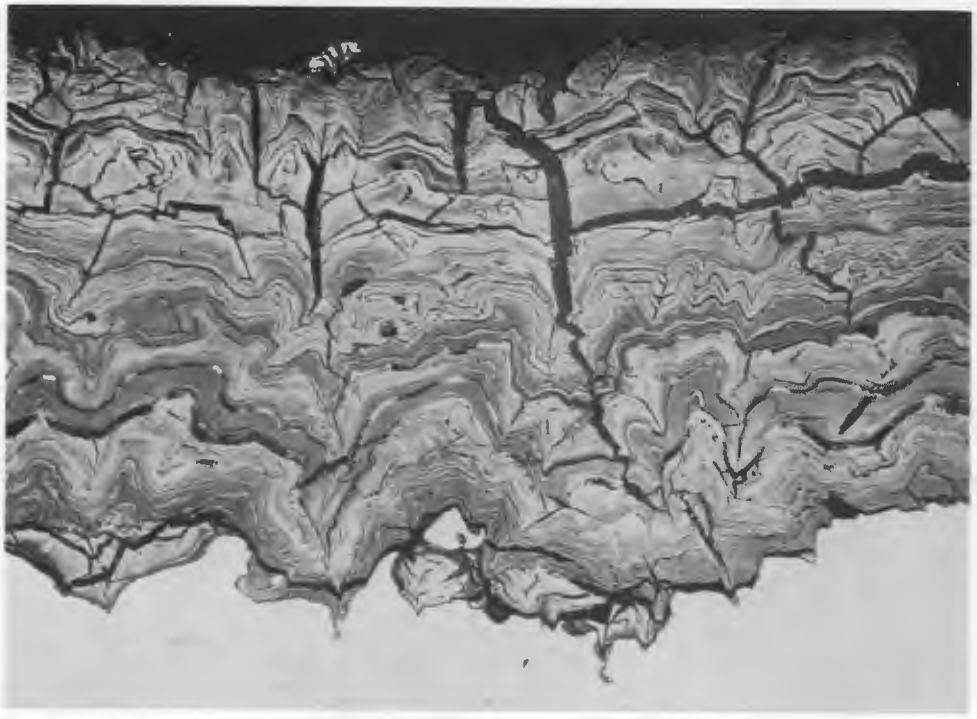
Jim Keiser (left) and Rod Judkins inspect a reactor effluent separator for corrosion at the H-Coal Plant in Catlettsburg, Kentucky.

Fossil Energy Materials Research

Many processes that convert coal to liquid or gaseous fuels or that burn it directly expose the materials of construction to hostile environments, including high temperatures and pressures under highly corrosive, erosive conditions. Several researchers in Oak Ridge National Laboratory's Metals and Ceramics Division are studying the behavior of materials in such environments. The aim of the research is to provide an understanding of the performance of existing materials in coal conversion and coal combustion systems and to develop new materials, where needed, for use in these systems.

In coal liquefaction, a coal-oil slurry prepared by mixing finely ground coal with a process-derived oil may be heated to about 450°C at 14 to 21 MPa (2000–3000 psi) to dissolve the coal and add hydrogen to the coal liquids. Pressure vessels of the size anticipated for commercial plants will require the use of heavy-section steel about 30 cm (12 in.) thick. New steels are needed for coal liquefaction to provide greater strength and resistance to hydrogen attack than are provided by the steels currently accepted by the Boiler and Pressure Vessel Code of the American Society of Mechanical Engineers.

Bob Swindeman of ORNL is leading a combined ORNL–



Sulfide scale, a type of corrosion, developed on this section of Type 316 stainless steel during exposure to a coal liquefaction environment at the Solvent Refined Coal (SRC-II) plant in Fort Lewis, Washington.

industry–university effort to develop and qualify an improved pressure-vessel steel for coal conversion. The development of this steel has already involved Climax Molybdenum Company, Lukens Steel Company, and Carpenter Technology, in addition to researchers at the University of California (Berkeley and Santa Barbara campuses), the University of Tennessee, Cornell University, and Westinghouse Research Center. The new steel will be useful not only for coal liquefaction and coal gasification pressure vessels but also for the hydrocracker and hydrotreater vessels used by the petrochemical industry.

After the coal has been dissolved and hydrogenated, coal-derived liquids containing undissolved mineral ash flow through pressure let-down valves into separator vessels where gaseous by-products are separated from the liquids. As the hot, ash-containing coal liquid flows through the restricted orifice of the pressure let-down valve at near-sonic velocities, it severely erodes the valve trim and seat, even though they are made of cemented tungsten carbide.

ORNL researchers in the Fossil Energy Materials Program are actively engaged in developing more erosion-resistant materials for pressure let-down valves. In the early stages of this effort, Ernie Long worked with commercial suppliers of cemented carbide, with the liquefaction pilot plants, and with Battelle Columbus Laboratories to identify the most erosion-resistant commercially available materials. More recently, Tony Caputo and Jack Lackey have been using chemical vapor deposition to coat the most erosion-resistant materials with titanium diboride (TiB_2), a material whose hardness approaches that of diamond. This technique has produced TiB_2-coated valve materials that show no measurable erosion; however, additional work is necessary to understand the process sufficiently to be able to control it and make high-quality coatings reproducibly.

Following pressure let-down, the coal liquids go to a series of vessels where the liquids are distilled, or fractionated, into the various product fractions, such as naphtha, fuel oil, and recycle solvent oil used to dissolve the coal. In this fractionation area, there has been a severe problem with corrosion caused by the chlorides in the coal. Jim Keiser, Rod Judkins, and Vivian Baylor, working with metallurgists from the liquefaction pilot plants and researchers from the University of Kentucky, developed an understanding of the corrosion mechanism and provided suggestions for preventing it.

ORNL has also provided assistance in the analysis of failures and in materials testing at the liquefaction pilot plants. Because coal liquefaction processes are still under development, process engineers are continually changing process conditions, resulting in changes in the environment to which materials are exposed. To understand the performance of materials in these environments, ORNL provides racks of material test specimens to operating pilot plants for insertion in process streams and vessels. After extended exposure, often thousands of hours, corrosion rates are determined, corrosion scales are analyzed to provide insight on the cause of corrosion, and alloy compositions to resist corrosion are recommended to the operators of pilot plants and to the designers of demonstration plants. Arni Olsen is responsible for reviewing the materials selected by the industrial designers of demonstration and

Four ORNL staff members and a Wilsonville, Alabama, engineer examine four sections of a fractionation column taken out of service at the Advanced Coal Liquefaction Research and Development Facility because of severe corrosion. The men are, from left, Bill Leslie, Jim Newsome, Pat Barnett (Wilsonville engineer), Maurice Allen, and Jim Keiser.

commercial liquefaction plants and for ensuring that the knowledge gained in the pilot plant testing program is properly factored into the selection of materials for the large plants.

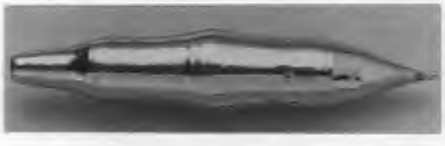
Although ORNL has emphasized materials for coal liquefaction, we have also been involved in materials for coal gasification. Joe Hammond has assisted coal gasification pilot plants in the solution of some of their materials-related problems and published reports on experience with materials in the Westinghouse, Bi-Gas, and Combustion Engineering gasification systems.

Materials for fluidized-bed combustion (FBC) is another research area of the Fossil Energy Materials Program. In an FBC system, crushed coal is burned in a fluidized bed containing limestone. Because the limestone captures most of the sulfur released by the burning coal, extensive use of FBCs in the eastern half of the United States instead of conventional coal-fired plants may help reduce the amount of acid rain in that region. Heat for raising steam for industrial processes or electrical generation is removed from the fluidized-bed combustors by heat exchanger tubes immersed in the bed. Because of the many instances of erosion and corrosion of these heat exchanger tubes in FBC test beds, a need exists for understanding the performance of materials in this environment. Researchers at ORNL and other laboratories have observed that the in-bed tubes become coated with a thin, apparently impermeable layer of calcium sulfate produced by the reaction of sulfur in the coal with the limestone in the bed. Pete Ficalora and Jack DeVan have studied the reaction of calcium sulfate with the metallic elements commonly found in heat exchanger alloys—that is, chromium, iron, and nickel. They concluded that the corrosion often seen in fluidized-bed combustors containing limestone sorbent may be caused by the calcium sulfate deposit on the tubes rather than by the sulfur oxides in the gas phase.

For advanced fossil energy systems, engineers have proposed incorporating devices that recover energy or convert it into useful forms more efficiently. Examples of such devices include high-temperature heat exchangers and gas turbines. For these systems, the Fossil Energy Materials Program is supporting the development of advanced alloys (such as iron-nickel aluminides) and structural ceramics described by C. T. Liu and Paul Becher in articles elsewhere in this issue.

In addition to the in-house research described above, the Fossil Energy Materials Program at ORNL is responsible to the Oak Ridge Operations of the U.S. Department of Energy for the technical management of national research programs on materials for fossil energy systems. In this role, ORNL is responsible for identifying needs for research and development, for developing research plans to address those needs, and for implementing those plans (after approval by DOE) at other national laboratories, universities, and industrial research centers. About 75% of our work is devoted to managing the subcontracted work performed for DOE, and the remaining 25% focuses on in-house research. The combination of our in-house research and technical management of the national program has earned ORNL respect as a leader in fossil energy materials research.—*Ron Bradley, Metals and Ceramics Division.*

Lynn Boatner has been the leader of the Crystal Growth and Characterization Group in ORNL's Solid State Division since October 1977, when he came to the Laboratory. Before that, he was a research scientist at the École Polytechnique Federale in Lausanne, Switzerland. A native of Texas, he holds a Ph.D. degree in physics from Vanderbilt University. His research interests include crystal growth and characterization, nuclear waste form development, electron paramagnetic resonance studies, and ferroelectric materials. In 1982 he cochaired the international meeting of the Materials Research Society and shared an I-R 100 Award with Marvin Abraham for the development of monazite ceramics as a nuclear waste form. Here, he is using a small chisel to split, or cleave, single crystals of magnesium oxide into smaller symmetric pieces.



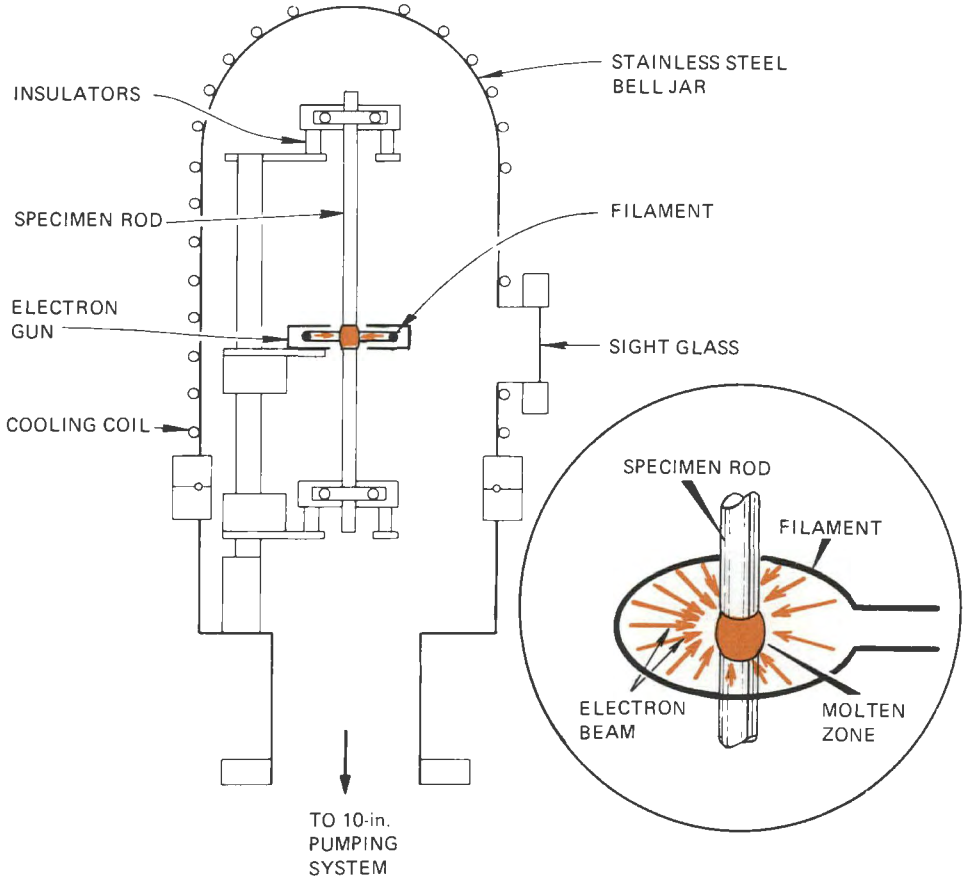
This ORNL-grown single crystal of an alloy of iron, nickel, and chromium is typical of 300 series stainless steel.

Growing Single Crystals of Refractory Materials

I·R 100

By LYNN BOATNER

Many special physical, chemical, and electronic properties of matter have their origins in the symmetric, repetitive structure of crystals. Some of these properties of crystalline materials—their abilities to reflect and refract light—led to our ancestors' earliest fascination with natural crystals that they extracted from the earth's crust, polished, and eventually faceted into gemstones. When humans pulled the first glittering crystals from the dirt, they found themselves holding a material produced by natural processes that had occurred over millions of years. Although our ancestors' initial



In electron beam float zone growth, a molten region is formed by electron beam bombardment and held in place between two solid pieces of the material by surface tension. The electron gun is mechanically translated along the "feed" rod so that the molten "floating" zone moves from one end of the rod to the other. Even though several crystals may initially nucleate, frequently one crystal "grain" dominates and outgrows the others, so the entire cross section of the rod consists of one single crystal.

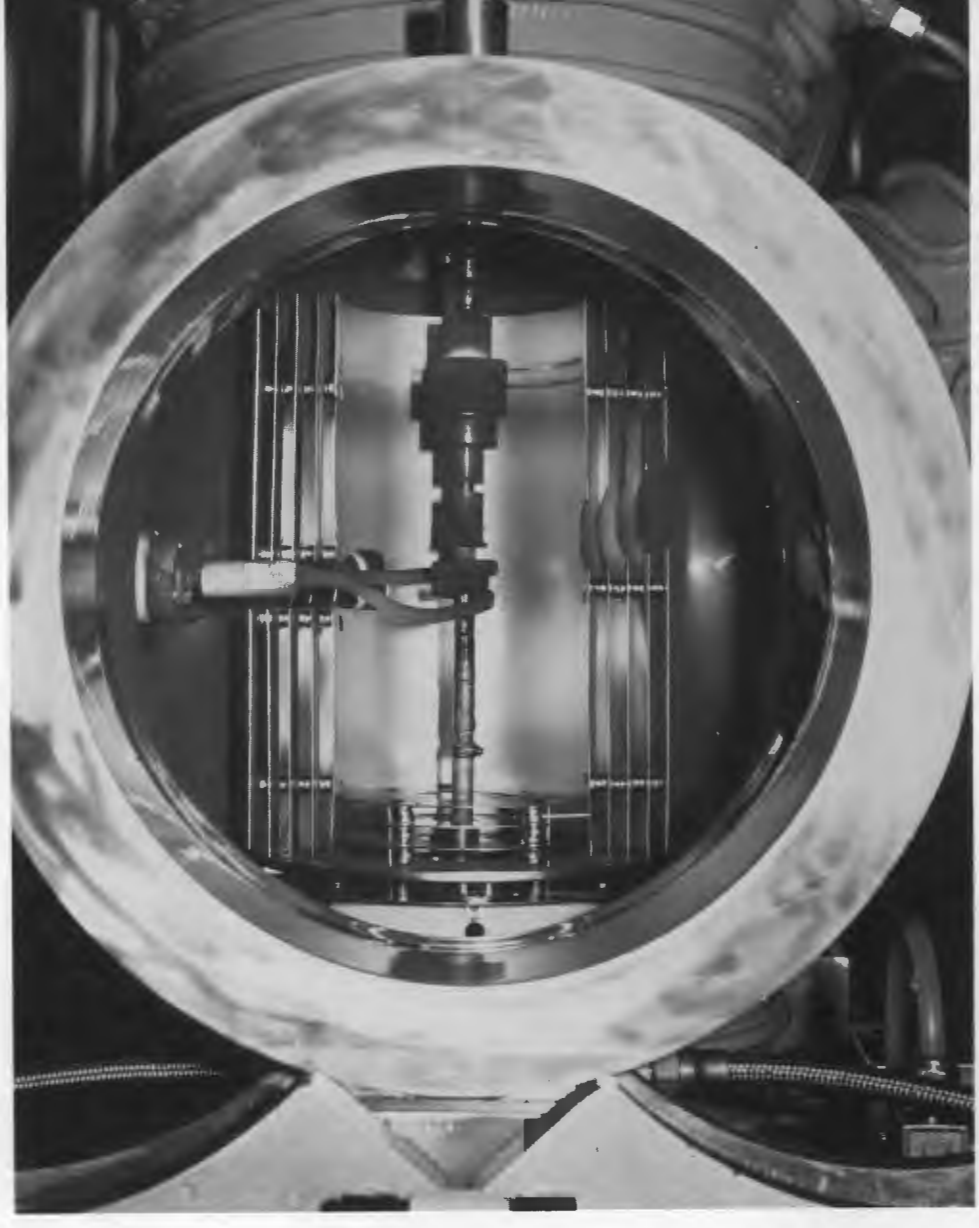
interest in crystalline substances was stimulated by optical effects, these effects and many other often unique properties are responsible for the more recent technological importance of this fascinating form of matter.

Today the revolutionary changes resulting from the use of man-made crystals in modern solid-state electronic devices are apparent almost everywhere. At Oak Ridge National Laboratory, however, we have found, and continue to seek, uses for crystals made from materials that melt only at very high temperatures. Crystals grown from refractory materials can be used in systems for energy production, the storage of nuclear wastes, and visual and digital information storage. In this article I will describe some of the methods used at ORNL to produce single crystals of high-temperature materials. Fortunately, these methods do not require the millions of years used by nature—a feature that is greatly appreciated by Laboratory management.

Man-made single crystals are commonly used for electronic devices, lasers, gemstones, and structural materials. At ORNL, crystals are grown from hard-to-melt materials for possible use in systems to produce energy, transmit electricity, store nuclear wastes, and process optical signals.

Crystals are a highly ordered state of matter in which the fundamental units—ions, molecules, or atoms—are arranged to form identical microscopic structural blocks called cells. In principle, an infinitely large single crystal can be generated from these units by joining them together in an ordered repetitive way—a little like stacking bricks to form a wall. This systematic building up of a macroscopic solid from identical microscopic structural units produces a crystal lattice that is characterized by an important property called long-range order. Ideally, long-range order means that by displacing a cell an arbitrary but integral number of cell lengths along special directions in the crystal, a situation can be produced in which each atom of the displaced cell lies on top of an identical atom in the new cell position.

Because the first use of natural crystals appears to have been in the nonutilitarian role of beautifying human possessions, it is not surprising that the earliest examples of synthetic crystal growth represent efforts to duplicate natural crystalline materials that are used as gemstones. Attempts to grow synthetic gems were, in fact, made by the English chemist Robert Boyle before 1672, and in 1891, a French scientist named Auguste Verneuil developed a process for growing single crystals of ruby (i.e., crystals of aluminum oxide, Al_2O_3, doped with chromium).



Radiofrequency (rf) zone techniques are used to grow single crystals of the highly refractory transition metal carbides and nitrides. The float-zoned carbide rod can be seen in the center; the rf-induction coil is positioned near the top of the rod. The multilayered structure visible on either side of the central rod is the back half of a tantalum heat shield used to reduce radiative heat losses, which become significant at very high temperatures.

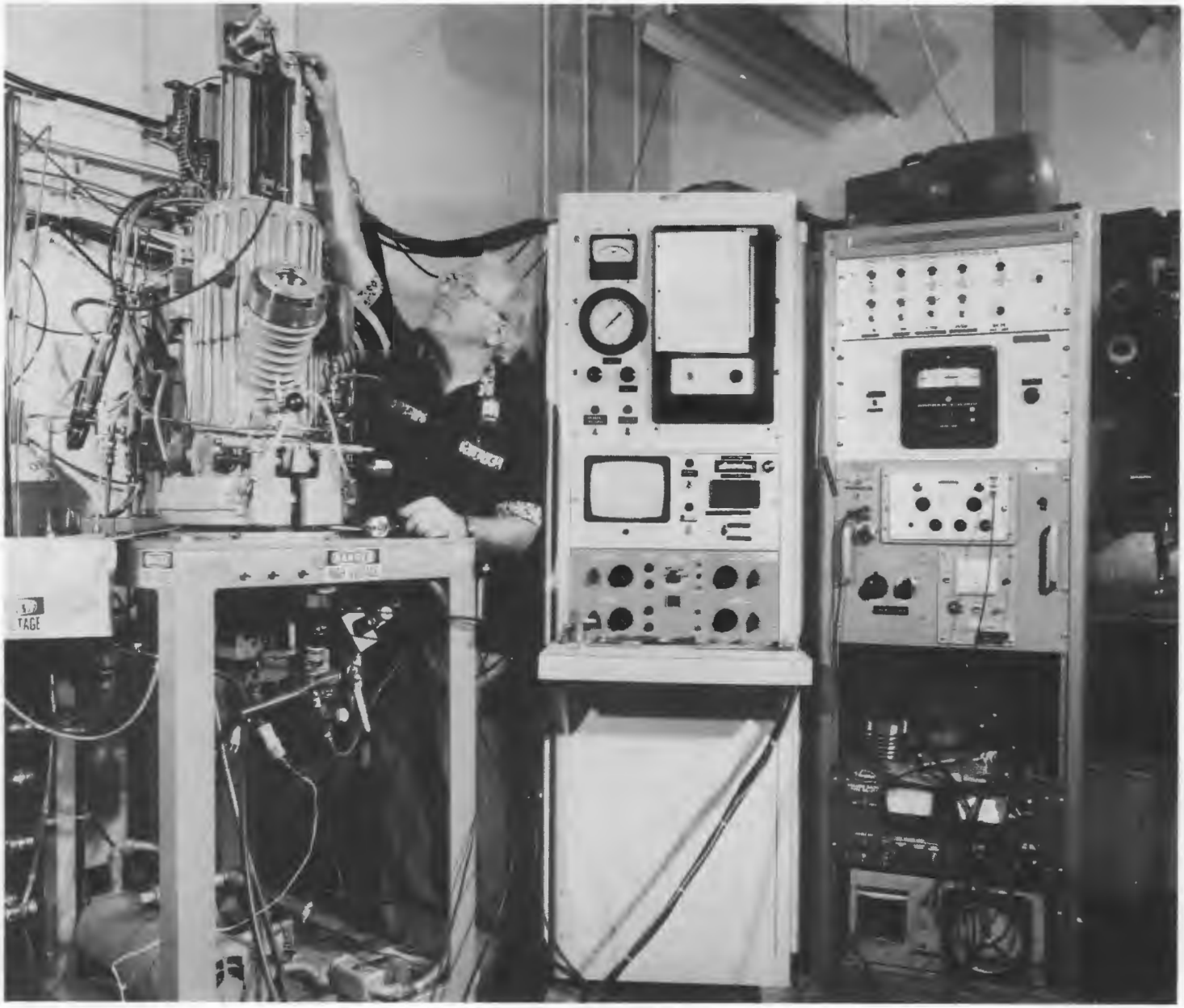
Crystals in Science and Industry

Although the earliest efforts to grow crystals attempted to duplicate natural gems, similar activities today represent a very small percentage of the resources devoted to single-crystal production. The most striking examples of the impact of devices based on single crystals of silicon, germanium, and gallium arsenide are in the solid-state electronics field. There are, however, less well-known but increasingly important technological and industrial applications of single crystals. Today, man-made single crystals are used in lasers, optical modulators, strain gages, bearings, and even turbine blades.

Even if large single crystals had no industrial or technological importance, they would still be of interest to the research scientist. The symmetric structure of crystals is responsible for numerous distinctive intrinsic properties such as high thermal conductivity, the ability to transform electrical energy into mechanical energy (and vice versa), and anisotropic mechanical properties. Crystalline symmetry also leads to interesting phenomena that occur when crystals interact with external perturbations such as X rays, neutron beams, light, and sound.

Depending on the characteristics of a given material and the type of growth process employed, single crystals are grown in the temperature range from below 1 K to over 4000 K. The article by Vic Tennery that appears elsewhere in this issue discusses the importance of high-temperature materials in energy-related systems; the emphasis here will also be on those ORNL crystal-growth activities that are specific to refractory (i.e., hard to melt) materials. Generally, we will deal with growing crystals of materials that melt at temperatures above 1200°C and will focus on those methods that were, and continue to be, central to the history and tradition of working with high-temperature materials at ORNL.

During the mid-1960s, research on the growth of single crystals of three types of high-temperature materials was conducted in ORNL's Solid State Division and Metals and Ceramics (M&C) Division. In the Solid State Division, Dick Reed applied the technique of electron-beam, float-zone (EBFZ) growth to the purification and preparation of single crystals of niobium—an elemental metal that melts at about 2470°C. The EBFZ technique is a variation of the basic float-zone method first conceived by W. G. Pfann of Bell Laboratories. In this technique, liquid surface tension holds a relatively narrow liquid zone of melted material in place between two solid rods of the substance being treated. This molten zone is then moved along the mate-



Bill Brundage makes adjustments on a high-pressure crystal growth system. Equipment of this type is necessary for the growth of crystals of materials whose components are volatile at elevated temperatures.

rial by moving either the heating source or the material itself. Repeated passing of the molten zone along the rod purifies the material by a fractional crystallization process, and a single crystal can be grown by either moving the molten zone very slowly or by using a seed crystal at one end of the rod. In the variation of the float-zone technique used by Reed, a beam of electrons melted the material and formed the narrow molten zone.

Reed went on to apply the EBFZ technique to the purification and growth of single crystals of vanadium, nickel, titanium, tantalum, zirconium, and a host of refractory binary alloys such as rhenium-tungsten, molybdenum-zirconium, and niobium-tantalum. The resulting specimens were used both at ORNL and many other laboratories in research on crystal perfection, mechanical properties, superconductivity, radiation effects, and various other research topics.

While Reed was working on the EBFZ growth of metal single crystals in the Solid State Division, Cabell Finch and Wayne Clark of the M&C Division were using a sophisticated process called the flux technique to grow single crystals of thorium dioxide (ThO_2) and cerium dioxide (CeO_2). Having a melting point of 3390°C, thorium dioxide is the metal oxide that has the

Homer Harmon adjusts the electrodes on a Czochralski crystal growth system in which an electric arc is used to melt the material from which the single crystal is "pulled."

highest known melting temperature. The beauty of the flux technique used by Finch and Clark is that it permits the growth of crystals of refractory materials at temperatures significantly below their melting points. In the case of thorium dioxide, Finch and Clark were able to grow high-quality single crystals at a temperature of only 1280°C instead of the ThO_2 melting temperature of 3390°C. This type of growth is accomplished by dissolving the material to be crystallized in a molten salt (or flux), thereby avoiding the brute force approach of first melting the material and then carrying out the slow, controlled solidification process used for the growth of large single crystals. The flux technique is similar to the familiar method of growing crystals of table salt or copper sulfate from a water solution except that a molten salt, or flux, is used as the solvent instead of water.

Finch and Clark eventually extended the flux technique to the growth of single crystals of thorium and zirconium silicates. (Zirconium silicate, or $ZrSiO_4$, occurs in nature as the mineral zircon and is often used as a gemstone. The growth of these materials illustrates another positive feature of the flux crystal-growth technique. Some materials melt incongruently—that is, they change form or decompose at their melting point. Zirconium silicate is such a material, and the lower growth temperature associated with the flux technique avoids the decomposition that occurs at the $ZrSiO_4$ melting point.

The third high-temperature crystal growth effort initiated at ORNL in the mid-to-late 1960s involved the growth of the refractory oxides of magnesium (MgO), calcium (CaO), and strontium (SrO), which are structurally identical to common table salt. The equipment for a crystal-growth process called the submerged arc fusion technique was assembled by C. T. Butler of the Solid State Division and used in the growth of MgO single crystals. In this approach to crystal growth, a three-phase electric arc is buried or submerged in a large mass of oxide powder. The powerful arc is used to melt a pool of MgO that is contained by a sintered mass of the same material. The novel "self-containment" aspect of this method enables one to grow crystals of materials that are so reactive at their melting points that no dissimilar crucible material can be found that will not react with the molten liquid.

Butler left ORNL in 1972 for an academic position and the submerged arc fusion equipment was taken over by Marvin Abraham and

Yok Chen. Abraham and Chen used this apparatus in developing a technique for the growth of large, clear crystals of MgO. This work was patented and recognized in the form of an I-R 100 Award that Abraham and Chen received from *Industrial Research & Development* magazine in 1975. The availability of large single crystals of these simple model oxides formed the basis for much of the work that eventually gave ORNL a leading position in the area of research on defects in insulating solids.

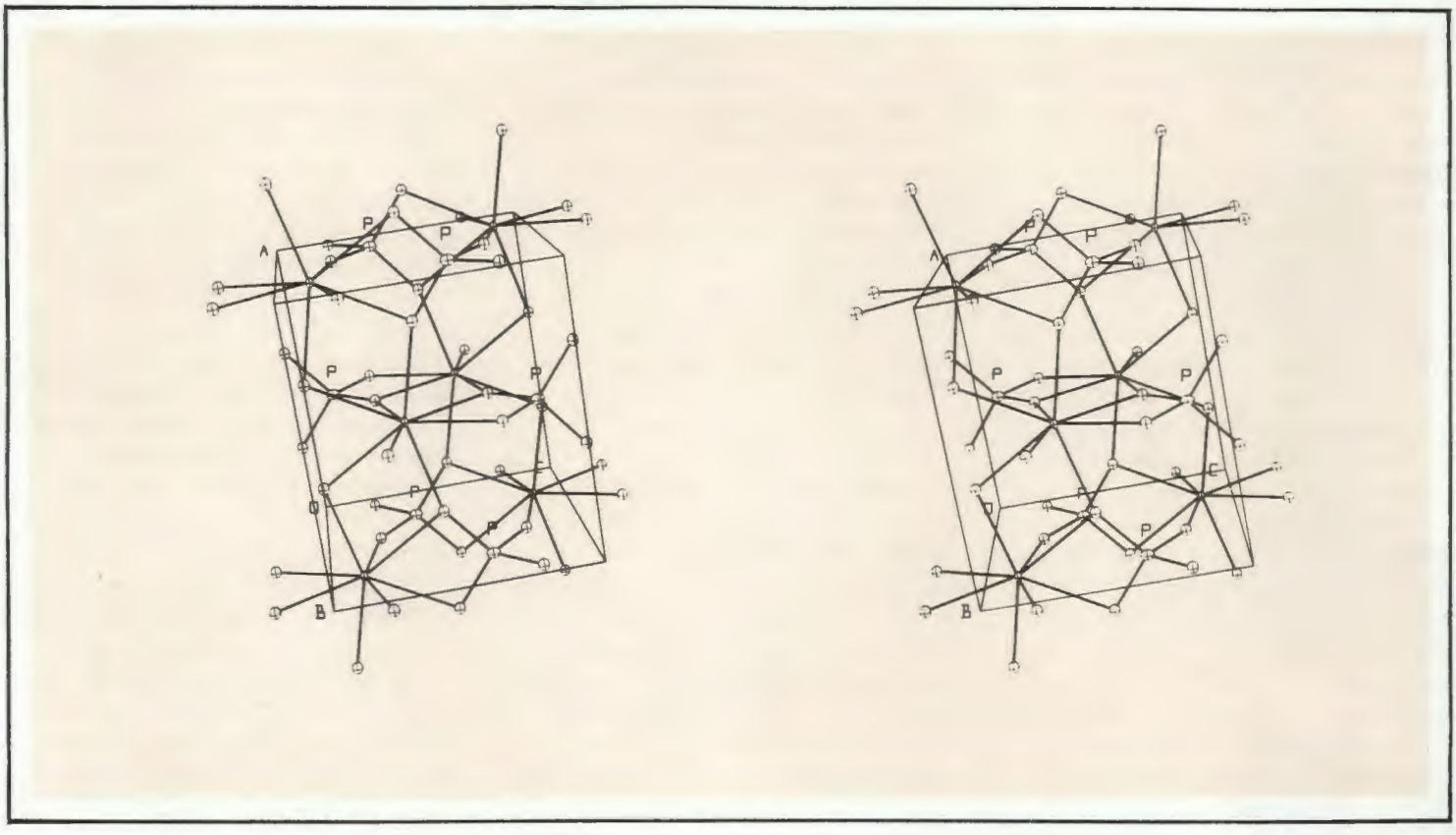
Although the previously mentioned three examples of earlier ORNL efforts in the high-temperature crystal growth area date back almost 20 years, none of these earlier capabilities have been lost. Instead, in the evolution of this type of work at ORNL, the researchers have continually built onto and extended these early capabilities while adding techniques and the ability to grow single crystals of other energy-related, high-temperature materials. Currently, almost all of the ORNL single-crystal growth efforts are carried out by members of the Solid State Division. Some examples of the more recent activities in the area of high-temperature crystal growth are found in the work of Larry Darken, Bill Brundage, Mike Chang, and me.

Recent Research

Larry Darken is growing single crystals of the transition-metal carbides using a radiofrequency (rf)-induction, float-zone technique (like the electron-beam counterpart described earlier except that rf-induction heating replaces the electron beam). Transition-metal carbides such as vanadium carbide (VC) and titanium carbide (TiC) are some of the hardest and most refractory known materials. They are also corrosion resistant in various hostile environments, and their combined properties have led to their use in numerous industrial and technological applications. Several investigations of these substances currently under way at ORNL are motivated by the outstanding potential of carbides for energy-related applications in electrical heating elements, in resistors, and as high-temperature structural materials. Transition-metal carbide single crystals are central to these ongoing studies, which include work on the effects of impurities and defects as well as research on electronic and optical properties. Specifically, carbide single crystals are being used in studies of vacancy ordering, thermionic emission, fluxoid lattices in superconductors, and neutron scattering. Thus far, Larry Darken has grown single crystals of VC, TiC, zirconium carbide (ZrC), and niobium carbide (NbC) and is preparing to grow tantalum carbide, which has a melting point of over 3800°C. The growth of these very refractory carbides is facilitated by a recently installed 100,000-W rf generator, and special radiation shields are employed around the growing crystal to minimize the large radiative heat losses occurring at these very high temperatures.

Single crystals of two distinctly different, but nonetheless interesting and important, materials are being grown by Bill Brundage in the Solid State Division. First, Brundage is using a crystal-pulling technique to grow large single crys-

Joanne Ramey (left) and Lynn Boatner hold a set of monazite single crystals that were grown in the furnaces visible in the background. These specimens were donated by ORNL to the mineralogical collection of the Smithsonian Institution in Washington.



tals of ternary alloys of iron, nickel, and chromium. The ratios of these constituents are chosen so that the resulting crystals are analogs of commercial 300 series stainless steels. These specimens can be used in studies of the intrinsic mechanical and defect properties of the stainless-steel alloy in the absence of grain boundary effects that are present in normal polycrystalline commercial stainless steels.

In the crystal-pulling (Czochralski) technique used by Brundage, molten feed material is contained in a crucible and its surface is contacted by a cooled seed crystal. The meniscus (curved surface) caused by the surface tension of the molten liquid permits a solid–liquid interface to be established slightly above the level of the liquid feed material. By carefully controlling the thermal conditions and slowly raising the solid seed crystal, this solid–liquid interface can be maintained at a constant height relative to the liquid surface and a solid crystal is effectively drawn or pulled from the liquid. This crystal-pulling technique is currently the dominant method for growing the large silicon single crystals so important in today's solid-state electronics industry.

A variation of the flux technique described earlier is being used by Brundage to grow large single crystals of sodium β''-alumina [e.g., 0.9 Na_2O · 0.6 MgO · (5 Al_2O_3)]. Because it exhibits a high ionic conductivity at temperatures significantly below its melting point, this inorganic material is a candidate for use as a solid electrolyte in sodium-sulfur batteries, which may someday be used to power electric cars and store off-peak electricity at power plants. The sodium β''-aluminum crystals grown by Brundage are being extensively investigated by a Solid State Division group led by John Bates. Brundage's specimens are currently the largest such single crystals ever grown.

Sometimes the low-temperature properties of refractory materials are more interesting and important than their characteristics at high temperatures. Mike Chang is using an rf-induction, float-zone technique to grow single crystals of a family of materials that falls into this category. Vanadium silicon (V_3Si), vanadium germanium (V_3Ge), titanium platinum (Ti_3Pt), and niobium germanium (Nb_3Ge), which are generally referred to as A-15 compounds based on the metallurgical notation for their particular cubic structural type, are of interest because they become superconductors at cryogenic temperatures ranging up to 23 K. Chang is growing a series of vanadium silicon single crystals in which the vanadium-to-silicon ratio will be varied in the region around the V_3Si composition. These samples are being used in studies of

Stereo view of the structure of an ORNL flux-grown lutetium orthophosphate crystal. The structure can be seen in three dimensions using a small stereo viewer such as that found in an old slide viewer. Don Mullica and W. O. Milligan of Baylor University in Waco, Texas, are collaborating with ORNL in structural determinations of the entire lanthanide orthophosphate transition series by means of x-ray diffraction techniques.

structural phase transitions and of magnetic flux pinning in the superconducting state. Work of this type can have important and far-reaching implications for the application of superconducting devices to producing and conserving energy and transmitting electricity.

A final example of how single-crystal growth can make contributions in even a highly applied and diverse research area such as the development of nuclear waste forms is provided by some of the crystal-growth efforts of Joanne Ramey and me. Working with Ramey, Abraham, and Brian Sales, I have been trying to develop advanced ceramic materials for the permanent disposal of nuclear wastes. In particular, we have evaluated a polycrystalline ceramic that is chemically analogous to a phosphate mineral called monazite as a potential primary radioactive waste form. Natural monazite crystals are made up of a rather complex mixture of rare-earth orthophosphates ($REPO_4$). Ramey and I have grown orthophosphate single crystals of every member of the rare-earth transition series (except for radioactive promethium phosphate) for use in research on nuclear waste forms. A complete set of these crystals was recently donated to the Smithsonian Institution in Washington, D. C., for inclusion in its mineralogical collection.

Natural monazite crystals often contain the actinide elements thorium and uranium, but synthetic ORNL monazite crystals have been grown that incorporate most of the actinide elements produced during nuclear power reactor operation such as americium, curium, neptunium, plutonium, and uranium. We have also grown and investigated crystals containing many of the other elements such as iron and zirconium that are found in certain types of nuclear waste. The Solid State Division's work on monazite-based nuclear waste materials was recognized in 1982 by the I-R 100 Award that Marv Abraham and I received.

As an example of how research in one area can stimulate new investigations in another, it turns out that in addition to their potential use as a nuclear waste form, the rare-earth phosphates are interesting new high-temperature ceramics in their own right. Rare-earth orthophosphate compounds do not melt until heated to a temperature of approximately 2000°C. Furthermore, the powder-forming and compaction processes developed in the Solid State Division can be used to produce high-density ceramic bodies. Because the chemical stability of the rare-earth orthophosphates is high under many conditions, these ceramics may find a variety of energy-related, nonnuclear applications as specialized refractories, insulators, processing components, and high-temperature structural ceramics.

Future Directions

With the advent of ORNL's High Temperature Materials Laboratory, demand is increasing for samples of single crystals of refractory substances. This increased research emphasis on properties of high-temperature materials will require the development of new techniques for the growth of single crystals. Members of the Solid State Division's Crystal Growth and Characterization Group are currently implementing a research program that will focus on the development of these new crystal growth methods.

Additionally, we are continuing to experiment with the growth of potassium tantalate niobate crystals because of their potential ability to store vast amounts of visual and digital information in the form of laser-produced, three-dimensional holographic images. These images can be "written" into and "read" out of the crystal by means of laser beams. We are trying to find the best method for growing crystals that have high optical quality and the ability to store holographic images for a long time.

The relationship between the preparation and growth of single-crystal research specimens and many advances in solid-state science is largely symbiotic. Each research area simultaneously feeds off and nurtures the other in the sense that the availability of new research materials stimulates new characterization research, and the results of this research, in turn, are fed back into the efforts to produce higher quality materials. In the absence of the continuing development of new or improved research materials, solid-state science would soon stagnate, and without solid-state science, we might still be using crystals only as glittering stones to wear around our necks. ornl

awards and appointments

Liane B. Russell has been designated a Corporate Fellow of Union Carbide Corporation. She is the second woman in the corporation and the first woman in the Nuclear Division to be so honored.

As was the case in 1982, ORNL received 6 of the 100 awards presented this year by *Industrial Research & Development* magazine for innovative developments. The winning entries and developers were: nickel-iron aluminides for structural use at high temperatures, by **C. T. Liu** and **Carl C. Koch**; vacuum ultraviolet spectrometer, by **John C. Miller**, **Robert N. Compton**, and **C. Dewey Cooper**; supersaturated semiconductor alloys, by **C. W. White**, **Jagdish Narayan**, **Bill Appleton**, and **O. Wayne Holland**; multiple-frequency, eddy-current testing instrument for detecting defects in metal components such as steam generator tubes, by **C. V. Dodd**, **L. D. Chitwood**, and **W. E. Deeds**; processes for recovering silver from photographic and photoreproduction effluents, by **Franz A. Posey** and **Al Palko**; and an x-ray monochromator for focusing and analyzing synchrotron radiation, by **Cullie Sparks**, **Gene Ice**, and **Melvin Willey**.

J. T. Thomas has been elected a Fellow of the American Nuclear Society.

The U.S. Department of Energy has presented three of its nine 1983 Materials Science Awards to members of ORNL's Metals and Ceramics, Solid State, and Chemical Technology divisions. In the metallurgy and ceramics category, the award for significant implication for energy technology went to **Louis K. Mansur**, **Ken Farrell**, **Linda Horton**, **Eal Lee**, **Monty B. Lewis**, and **Nick Packan** for "the effect of helium gas and pulsed irradiation on materials behavior in fusion reactors." In the solid state physics category, the award for significant implication for energy technology was received by **Rosa T. Young**, **Russ Westbrook**, and **Richard F. Wood** (with G. A. van der Leeden from Helionetics, Inc.) for "high-efficiency silicon solar cells by beam processing." In the materials chemistry category, the award for significant implication for energy technology was given to **T. B. Lindemer**, **E. C. Beahm**, and **T. M. Besmann** for "thermodynamic investigations and modeling of energy-related chemical systems."

Mike Saltmarsh has been appointed coordinator of the Development and Technology effort of the ORNL Fusion Program and of the Plasma Technology effort of the Toroidal Program Planning Office at Princeton Plasma Physics Laboratory.

The National Society of Professional Engineers has presented a certificate to Union Carbide Corporation's Nuclear Division in recognition of its "progressive professional employment practices" in relation to engineers who work at the four UCC-ND plants.

ORNL researchers recently elected as fellows of the American Association for the Advancement of Science are **Charles C. Coutant**, **Melvin I. Dyer**, **Chester W. Francis**, **Robert V. O'Neill**, **Henry Shugart**, **Robert Van Hook**, **Webster Van Winkle**, and **Michael Wilkinson**.

Roy Cooper has been named manager of the Technology for Space Nuclear Projects, and **M.M. Martin** has been appointed manager of Technology for Special Nuclear Projects. Both efforts, part of ORNL's Nuclear Reactor Technology Programs, aim at developing radioisotopic and fission-reactor power systems for use in space.

William R. Laing has been named head of the new Radioactive Materials Analysis Section in the Analytical Chemistry Division.

Robert J. Gray was presented the President's Award by the International Metallographic Society and was selected to judge an international photographic competition at Nikon House in New York City.

Joseph A. Carpenter was selected by the Cooperation Committee of the Indian Institute of Metals and the American Society for Metals to be a guest lecturer for 1983.

Benjamin F. Hobbs, Ralph B. James, and **George Sugihara** have received Eugene P. Wigner Fellowships established and sponsored by ORNL.

Martin S. Lubell has been chosen program chairman for the 1985 Cryogenic Engineering Conference, which will be held at the Massachusetts Institute of Technology.

John Storer, M.D., has been presented the Distinguished Scientific Service Award by the University of Chicago's Medical Alumni Association.

At the request of the U.S. State Department, **William L. Russell** served as a scientific adviser to the U.S. Delegation to the 32nd Session of the United Nations Scientific Committee on the Effects of Atomic Radiation.

Van D. Baxter received the Willis H. Carrier Award from the American Society of Heating, Refrigeration, and Air Conditioning Engineers for the best scientific paper by a young author.

A. P. Malinauskas has been named director of the Nuclear Regulatory Commission Programs at ORNL, replacing **A. L. Lotts**, who went to Oak Ridge Gaseous Diffusion Plant to head its Atomic Vapor Laser Isotope Separation work.

Susan Whatley is second vice-president of the Society of Women Engineers.

The University of Pittsburgh has appointed **Stan A. David** to be Adjunct Professor of Metallurgical and Materials Engineering.

Rowena O. Chester is now the head of the Dosimetry and Biophysical Transport Section of the Health and Safety Research Division.

D. P. Stinton and **N. M. Atchley** placed first in the Different or Combined Techniques Category of the Ceramographic Contest held by the American Ceramic Society. Their winning entry was a poster that describes hydrofracture grout.

P. F. Tortorelli received the President's Citation of the Oak Ridge Chapter of the American Society for Metals.

Gerald M. Slaughter has been elected to a three-year term as a trustee of the American Society for Metals.

Walter P. Eatherly received the George Skakel Memorial Award from the American Carbon Society in recognition of his contributions to the science and technology of carbon.

Paul S. Rohwer has been named head of the Health Physics Department of the Industrial Safety and Applied Health Physics Division.

Everett Bloom has been appointed to the Metals Engineering Institute Committee of the American Society for Metals.

Ivan Sellin, ORNL consultant, has been named a Distinguished Service Professor by the University of Tennessee at Knoxville.

Dan Robbins has been elected a director-at-large of the Board of Directors of the American Society for Information Science.

Nancy P. Norton was awarded a Sigma Xi certificate in recognition of her work as a librarian who has provided "noteworthy support" to ORNL research scientists and engineers.

Julian Dunlap has been appointed head of the Tokamak Experimental Section in the Fusion Energy Division.