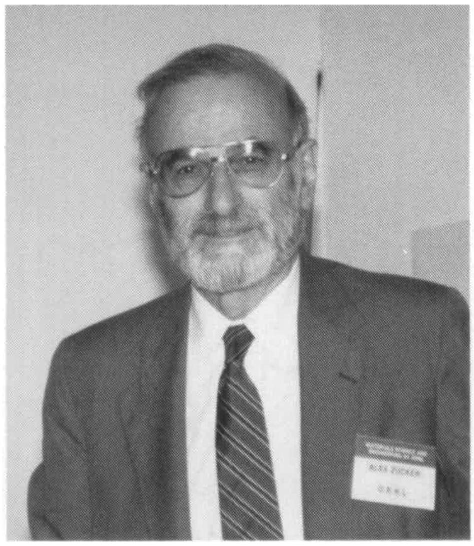
ORNL Materials Programs Highlighted

Oak Ridge National Laboratory hosted a three-day meeting May 14-16 to report on ongoing research in four separate divisions at the Laboratory. According to Alexander Zucker, associate director of Physical Sciences at ORNL, this meeting, "Materials Science and Engineering at Oak Ridge National Laboratory," was the first time a joint multidivisional program had been arranged. Work originating in and among the Metals and Ceramics, Solid State, Chemistry and Chemical Technology Divisions was described to an audience from a variety of U.S. university, government and industrial labs that filled the Pollard Auditorium of the Oak Ridge Associated Universities in Oak Ridge, TN.

Zucker's introductory remarks included some figures which put funding of materials research and development at ORNL in perspective. The total budget is approximately $57 million, of which $9 million is applied to programs that are subcontracted out, but where ORNL maintains the lead role. The remaining roughly $48 million is expended in-house, principally on individual research programs with about $4 million devoted to support of some user facilities such as the Bulk Shielding Reactor, the Surface Modification facilities, and ORNL beam-line facilities at Brookhaven National Laboratory.

About 40% of the $57 million figure is funded by the U.S. Department of Energy's Office of Basic Energy Sciences (OBES, Materials Sciences Division), the rest coming from applied DOE programs such as Energy Conservation, Fossil Energy, Nuclear Fission and Nuclear Fusion programs. This picture does not include approximately $8 million in support of the High Flux Isotope Reactor by the Physical Sciences side of OBES, nor some $20 million in construction and equipment money allocated to the new High Temperature Materials Laboratory. Many of the fruits of this research investment were described in the technical sessions which followed Zucker's remarks.



Alexander Zucker, ORNL associate director of Physical Sciences.

Sessions were chaired by Bill R. Appleton, director of the Solid State Division, James O. Stiegler, director of the Metals and Ceramics Division, and Vic J. Tennery, director of the High Temperature Materials Laboratory. A broad spectrum of research topics were covered in areas of both materials processing or synthesis and materials characterization. Unique capabilities at ORNL can be traced to a combination of facilities such as the Surface Modification Center, the High Flux Isotope Reactor, and the National Center for Low Temperature Neutron Irradiation. Summaries of the three days of talks are given below. Readers of the BULLETIN who are interested in more details on particular research projects or who are interested in the user facilities described should contact ORNL directly.

Surfaces and Interfaces

The session on surfaces and interfaces began with several papers on the use of ion beam and laser techniques for materials processing and analysis. The utility of ion beam and pulsed-laser processing in basic materials research is that these are non-equilibrium processing methods that impose extreme constraints on materials interactions. Consequently, they often lead to new and sometimes unique materials properties or offer new insights into the nature of the nonequilibrium interactions themselves. One such experiment involved the use of subnanosecond pulses from a synchrotron to study undercooling and overheating in silicon that occurs during melting and recrystallization induced by 20 nanosecond laser processing. By synchronizing the firing of a 20 nanosecond pulsed laser with 0.15 nanosecond x-ray pulses from the synchrotron, the temperature of the rapidly moving liquid-solid interface could be monitored through measurements of thermal-expansion-induced-strain. Measurements performed on <111> Si during 11 meters/second melting and during 6 meters/second regrowth showed that the interface temperature was 110 K lower during regrowth than during melting and that most of the temperature change was associated with the regrowth phase.

Similar measurements utilized time-resolved reflectivity and transmission measurements with nanosecond resolution to study the melting of amorphous Si

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Bill R. Appleton, director of the Solid State Division.

James O. Stiegler, director of the Metals and Ceramics Division.

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induced by rapid pulsed-laser processing. Combining these optical measurements with TEM and ion scattering and comparing to theoretical model calculations permitted the researchers to study explosive crystallization, phase changes, interfacial growth kinetics, and nucleation and solidification phenomena under conditions of large undercooling.

Ion implantation doping, ion beam mixing, ion beam deposition, and pulsed-laser processing are also capable of inducing a wide range of surface modifications in a variety of materials. Ion implantation was used to tailor the hardness, fracture toughness, and flexural strength of a variety of ceramic and insulating materials. By combining ion scattering/channeling, cross-sectional TEM, and optical and mechanical property measurements, it was possible to deduce the microscopic change associated with these induced changes and to trace their evolution during annealing. These studies were furthered by the development of a new ultra-low-load microindentation system for mechanical property measurements of near-surface modified materials.

Controlled surface alloys were made by implanting Ru into Ti electrodes for the purpose of studying the electrocatalysis of Cl_2 and O_2 evolution. The mechanisms of the electrocatalyzed Cl_2 evolution reaction were established by determining the effects of electrode potential and chloride ion concentration on the rate of the reaction, and by correlating the rate with the Ru-implant profiles measured by ion scattering.

Direct ion beam deposition was used to fabricate isotopic heterostructures of ^{30}Si and ^{74}Ge and to study the mechanisms controlling low-temperature epitaxy of Si and Ge. By decelerating isotopically pure ion beams from an implantation accelerator to energies of 20-40 eV in an ultrahigh vacuum chamber, epitaxial crystals of ^{30}Si were grown on Si(100) at temperatures as low as 400°C, ^{74}Ge films were grown on Ge(100) at 400°C, and ^{57}Fe was grown epitaxially on Ag(100) at 200°C.

A scanning electron microscope was modified to perform *in-situ* studies of erosion and erosion-corrosion by analyzing the effects of single-particle impact on ductile materials. This apparatus was used to compare current models of erosion. Results show that multiple particle impacts change the surface properties of a material. For nickel-base alloys, work hardening dominates any annealing effect of the impacts.

Model calculations based on fractals were successfully applied to explain the ac response of rough electrode interfaces in electrochemical measurements. The small signal ac impedance of the interface between a blocking electrode and an aqueous or solid electrolyte often contains a constant-phase-angle element whose impedance has a frequency dependence that can be related to the roughness of the interface. These calculations showed that the ac response problem could be formulated in terms of equivalent circuits constructed from the geometrical properties of two fractals called Cantor Bar and Cantor Block.

Several of surface sensitive spectroscopies were used to study the structure and absorption properties of atomically clean NiAl alloys. It was shown that a rippled-layer reconstruction was present in the two outermost layers of the (110) surface, and within the outermost layer Al atoms were displaced outward, and Ni atoms inward with respect to the truncated bulk. Oxygen was found to chemisorb dissociatively on all three surfaces but with lower sticking probabilities compared to pure metals.

The performance of fusion devices is known to be strongly dependent on the condition of the surfaces facing the plasma. Surface impurities enter the plasma where they lower reactivity and radiate power. Procedures were described to produce clean surfaces that employ hydrogen glow-discharge plasmas with controlled additions of methane or other gases. Diamond-like carbon films were produced that result in improved plasmas and promote hydrogen recycling.

High-Temperature Alloys

The critical importance of the distribution and location of alloying elements was demonstrated in a series of talks on high-temperature alloy design. Small additions of boron are well known to promote ductility in Ni_3Al, but only in material containing less than the stoichiometric amount of aluminum. A hydrogen charging technique was described that allows exposure of grain boundaries for analysis by Auger spectroscopy. Boron was shown to be strongly segregated to the grain boundaries, but the concentration varied significantly from boundary to boundary and decreased with increasing aluminum content. Annealing studies demonstrated that the phenomenon was a result of equilibrium segregation. Imaging atom probe studies showed the variable extent of grain boundary segregation of boron (Figure 1) and also revealed boron segregation to anti-phase domain boundaries. Positron annihilation studies in collaboration with Argonne National Laboratory showed a trapping state in alloys containing 25 and 26% aluminum but not with 24%. The suggestion was offered that constitutional vacancies exist in the higher aluminum alloys that interact with boron atoms and thereby reduce the amount of grain boundary segregation. Alloys containing greater than 25% aluminum were shown to exhibit a slight tetragonal character that was reduced by boron additions.

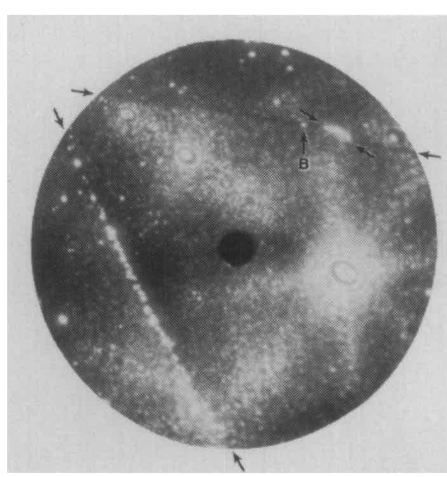

Figure 1. Field-ion micrograph of a pair of grain boundaries in rapidly solidified Ni-24.0 at.% Al-0.24 at.% B. The boron along the boundaries was not uniform and the presence of a thin boron containing phase approximately 1 nm thick was observed. B indicates the position of a single isolate boron atom.

Nickel aluminide can be strengthened appreciably by additions of several of the transition elements. Atom probe and zone-axis electron channeling were used to determine the site occupancy of several elements. Hafnium was shown to have a strong preference for aluminum sites, cobalt a strong preference for nickel sites, and iron a weak preference for aluminum sites.

The elevated temperature ductility of Ni_3Al was found to be reduced by oxygen in the test atmosphere. The effect is a dynamic one that involves the application of stress in the presence of oxygen. Small additions of chromium were shown to reduce the extent of the embrittlement.

Theoretical studies of the bonding properties of transition metal clusters containing interstitial atoms were described. The approach using density functional theory produced accurate total energy and vector force field calculations. Boron was shown to enhance the maximum sustainable stress in nickel and sulfur to reduce it.

Results of several collaborative efforts with industry to produce large quantities of alloys based on Ni_3Al using commercial techniques were presented. The superplastic properties of the alloys allow isothermal forging. Hot rolling of sheet has not been demonstrated, but a twin-roller casting technique produced acceptable sheet material that could be finished by cold rolling.

Analytical electron microscopy was applied to studies of impurity segregation to grain boundaries and to individual dislocations in stainless steel. The presence of segregation was shown to be dependent on the Burgers vector of the dislocation (Figure 2).

The austenitic stainless steels are generally placed in service in metastable conditions and consequently exhibit precipitation reactions during long time exposure at elevated temperatures. Extensive experi-

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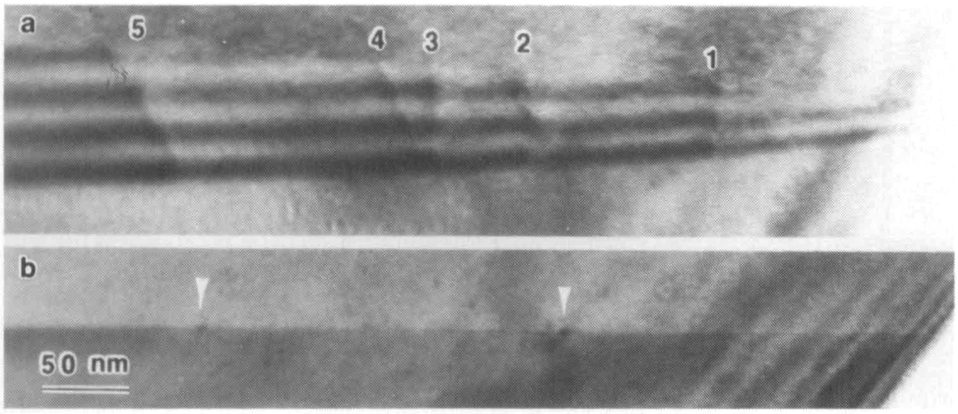

Figure 2. Transmission electron micrograph of an antimony-containing stainless steel, aged for 99 days at 500°C. (a) Interfacial dislocations in a coherent twin boundary. Diffraction contrast analysis indicates dislocations 2 and 5 have different type Burgers vectors than dislocations 1, 3, and 4. X-ray microanalysis shows that dislocations 2 and 5 are enriched in antimony (>2.5 fold) and nickel, whereas dislocations 1, 3, and 4 exhibit the same composition as twin boundary and matrix. (b) Same boundary viewed edge-on. Dark contrast at dislocations 2 and 5 (arrowed), whereas no contrast at dislocations 1, 3, and 4. May be atomic number or Z-contrast effect from antimony.

ence from radiation effects programs, where the reactions are enhanced and modified by irradiation, has led to an understanding of phase stability in these alloys. This understanding is being applied to the design of alloys tailored to resist the formation of undesirable, massive intermetallic phases and to promote fine scale precipitation of carbides and phosphides that can act as strengthening agents. These alloys have creep properties better than existing steels.

Neutron Scattering

Several talks on results from neutron scattering experiments served to illustrate the breadth of the neutron scattering program. Real-time investigations of the kinetics of the order-disorder transition in Ni_3Mn showed that the growth of the ordered zones progresses in several stages each described by a different time constant. Both small-angle and wide-angle neutron scattering studies of polymers were described. The core-shell model for polymer latexes, for which the first monomer polymerizes as a spherical core, the second polymerizes on this surface, etc., was confirmed for the polymerization of polystyrene and polymethylmethacrylate. Small-angle scattering investigations of colloidal suspensions that exhibit non-Newtonian behavior utilized hydrodynamic shear fields or applied magnetic fields to align the colloidal particles, thereby permitting a quantitative analysis of particle size and symmetry. Neutron scattering measurements of the excitation spectra of the itinerant electron materials iron and nickel were compared with the most recent band theory calculations. Because the magnetic excitation spectra for iron and nickel extend to high energies, these measurements were made at the hot source triple-axis spectrometer at Grenoble, France.

Structural and Electronic Ceramics

The extensive research on structural and electronic ceramics, including a description of a new user-oriented laboratory for high-temperature materials research, were highlighted in the closing session of the meeting. The High Temperature Materials Laboratory (HTML) is a large new materials research laboratory scheduled for completion at ORNL by early spring of 1987. Within the HTML, the Metals and Ceramics Division will have four User Centers and three of its present ceramic research groups. The instrumental capabilities of the four User Centers and plans for operation of the Centers to facilitate easy access by users from industry and universities were discussed. The four User Centers include (1) a Materials Analysis Center having extensive microstructural and surface analysis capability, including electron microscopy, Auger, ESCA, and SIMS capability in addition to SEM and electron microprobe instruments; (2) a high-temperature X-ray Diffraction Center having powder diffraction capability in various atmospheres at temperatures up to 2000°C; (3) a Physical Properties Center having capability for measuring enthalpies of phase reactions, thermal expansion, and thermal transport at temperatures to 2000°C; and (4) a Mechanical Properties Center having capability for measuring fracture strength, fatigue, and creep of materials at temperatures to 1600°C. Researchers from outside ORNL are encouraged to consider use of these new facilities in their high-temperature materials research.

Recent results in studies of high toughness ceramic systems were described in a series of papers. Modeling and experimental observations on toughening ceramic oxides via use of metastable zirconia and hafnia phases demonstrated that fracture toughness values as high as 17 MPa$\sqrt{m}$ are achievable using this approach. These ceramics are very resistant to weakening due to surface damage, and analytical models have been developed to explain and predict the toughness based upon thermodynamic arguments. A paper on toughening of alumina and mullite using silicon carbide whiskers described how the mechanical properties depend upon the whisker content and critical processing variables. Fracture toughness values up to 9 MPa$\sqrt{m}$ have been achieved with accompanying strengths to 700 MPa at whisker concentrations of 20 vol.% in alumina. These materials were shown to be highly resistant to thermal shock damage. Electron microscopy and ESCA analyses showed that the surface chemistry of the whiskers is critical to achieving good mechanical properties.

Ceramic matrix composites synthesized

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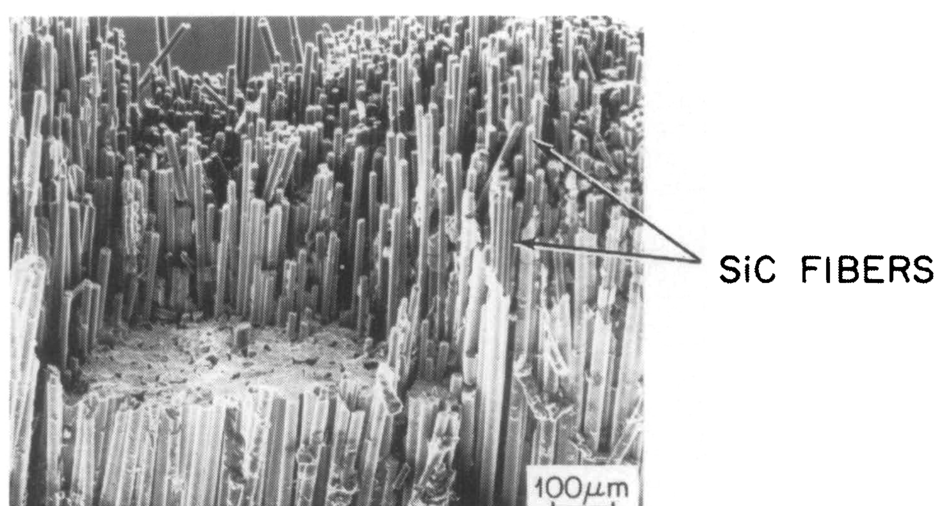

Figure 3. Scanning electron micrograph of a fracture surface in a composite containing silicon carbide fibers in a silicon carbide matrix produced by chemical vapor infiltration. Note the extensive fiber pullout that leads to strain tolerant behavior in this material.

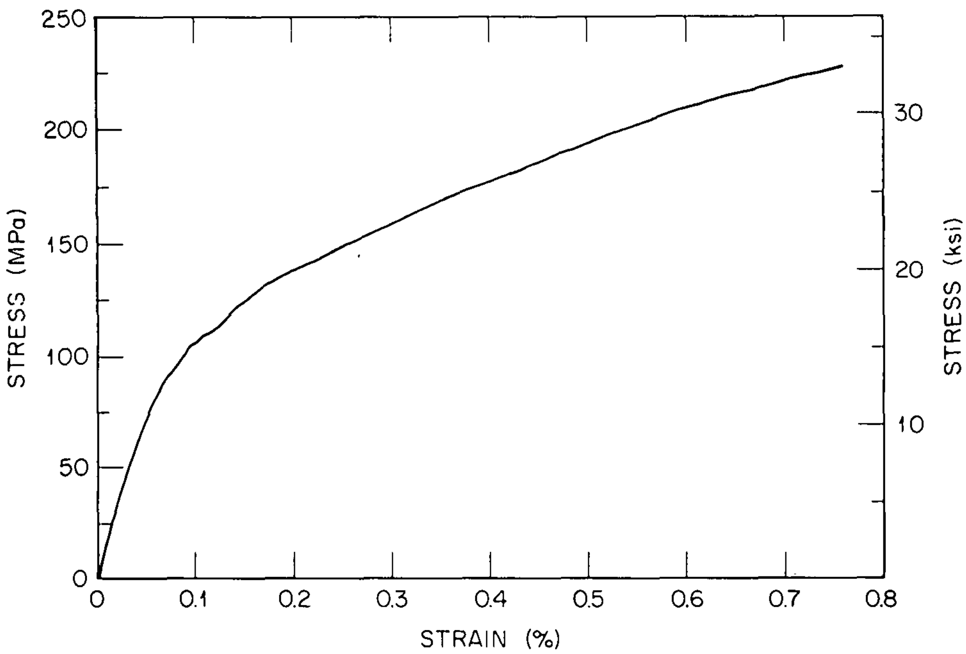

Figure 4. Stress-strain curve for materials shown in Figure 3. Unlike monolithic ceramics, these materials undergo significant amounts of strain before fracture.

using long fibers of silicon carbide and matrices were produced by chemical vapor infiltration of silicon carbide (Figure 3). True tensile strains of up to 0.7% were achieved in these materials before fracture occurs. In these systems, interfacial chemistry and structure were identified as critical to achieving fiber pullout, which is essential to achieving high strain deformation before fracture (Figure 4).

The joining of ceramics to metals has long been a highly empirical enterprise, because of lack of fundamental understanding of the interfacial energy balance and of the factors that influence the ability of the brazing alloy to wet the ceramic material. Recent work showed that the so-called "active" metals such as titanium or zirconium function differently than previously thought, and that these metals segregate preferentially in complex phases at both the metal and ceramic interfaces. By using new ways to distribute these active metals within the interface structure before high-temperature processing, fracture strengths up to 300 MPa and fracture toughness values up to 6 $MPa\sqrt{m}$ were achieved when joining various metals to ceramics such as alumina and partially stabilized zirconia.

Zinc oxide varistors are of great interest for use in high voltage transmission line systems, since they would permit use of these voltage spike protection devices at many places on the transmission line, provide improved spike protection to the system, and could be more economical than presently used protection devices. The microstructure of the zinc oxide ceramic is critical to its use in such applications, since the grain size must be very small and the "active" elements such as bismuth must be distributed very uniformly within the grain boundaries for these devices to be practical. Using the extensive ORNL expertise in sol gel technology, zinc oxide ceramics with uniform grain sizes of about two micrometers were synthesized and are now being evaluated by the electrical utility industry. Modeling of the electron energy bands in these ceramics was used to explain the varistor effect in these ceramics and to learn how to improve the switching properties further. A new dynamic laser light scattering instrument was described that is being used to study quantitatively how monosized particles of oxides can be nucleated and grown under highly controlled chemical conditions. Very uniformly sized spherical particles of silica in the 80 nm range were grown using the hydrolysis of tetraethoxyorthosilane using an alcohol solvent. Uniformly sized oxide particles produced and controlled within this apparatus should allow synthesis of dense ceramics of these oxides at sintering temperatures several hundred degrees lower than is possible using conventional powders.