ARGONNE NATIONAL LABORATORY
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Energy Technology Division

Research Summary • 2004

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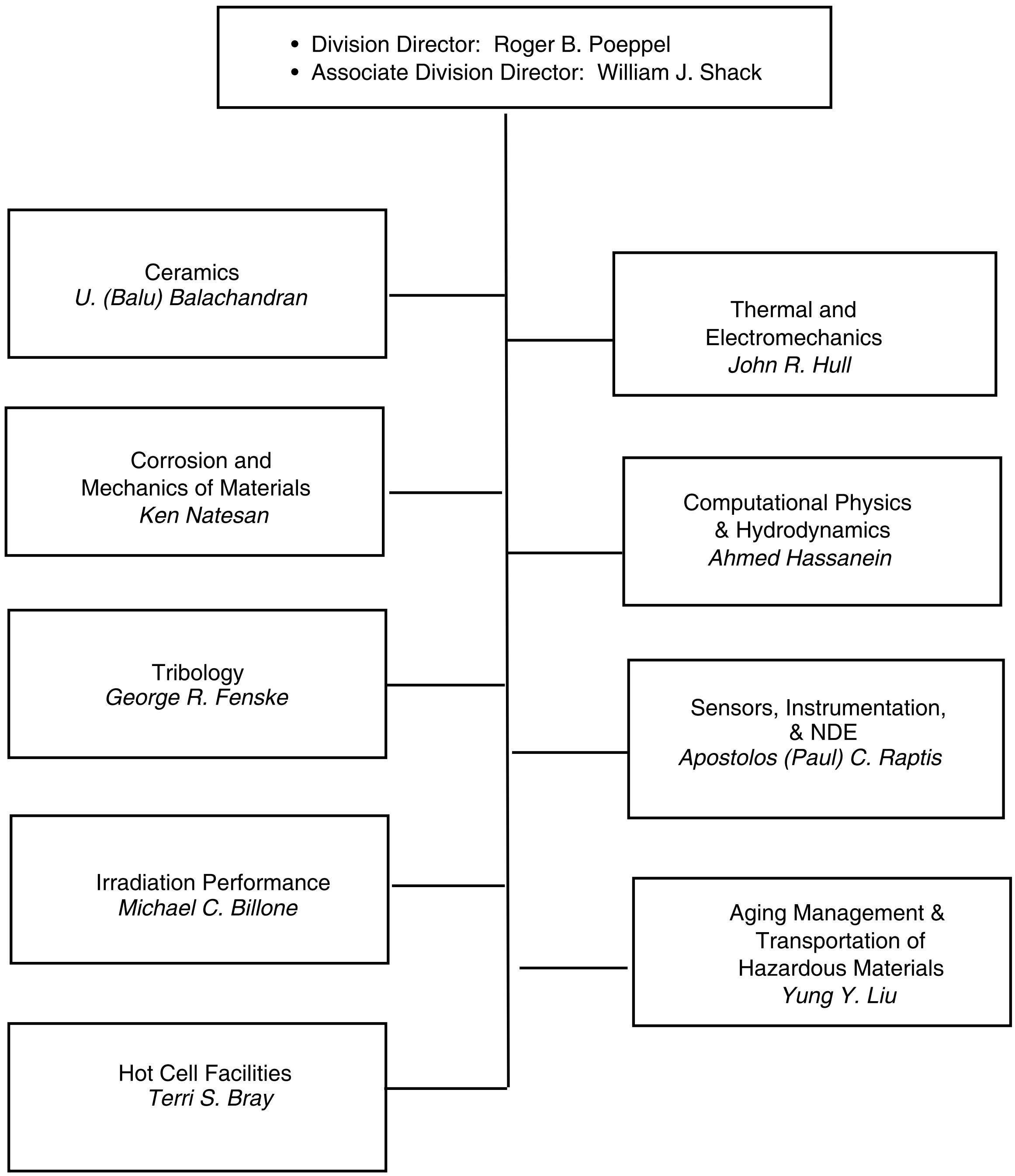
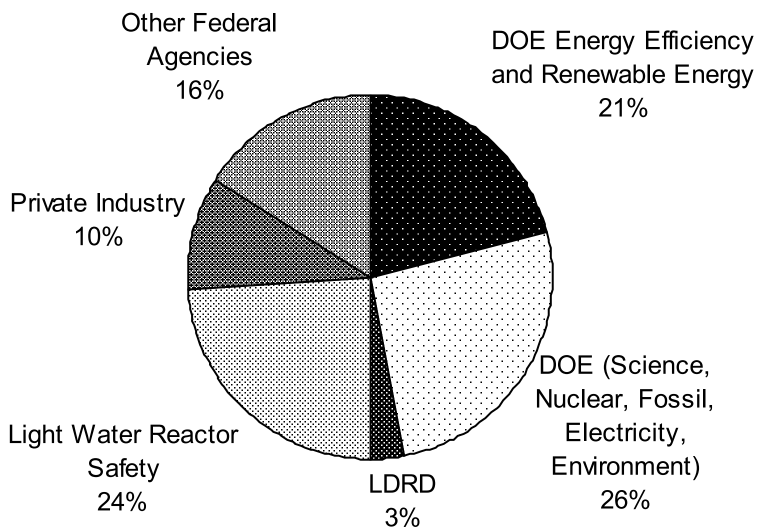


Overview of the Energy Technology Division

The Energy Technology (ET) Division provides materials and engineering technology support to a wide range of programs important to the U.S. Department of Energy (DOE). The Division's capabilities are generally applied to technical issues associated with energy systems, biomedical engineering, transportation, and homeland security. Research related to the operational safety of commercial light water nuclear reactors (LWRs) for the U.S. Nuclear Regulatory Commission (NRC) remains another significant area of interest for the Division. The pie chart below summarizes the ET sources of funding for FY 2004.



Funding Sources for FY 2004

As shown on the preceding page, the ET Division is organized into nine sections. The Division reports administratively to the Associate Laboratory Director (ALD) for Energy and Environmental Science and Technology (EEST). While most of our programs are under the purview of the EEST ALD, we also have programs funded under other ALDs. Some of our research in high-temperature superconductivity, for example, is funded through the Physical Research Program ALD. We also continue to work on nuclear-energy-related programs under the ALD for Engineering Research.

The ET Division's staff are active in national and international professional and scientific societies. They participate in joint programs, working groups, and national and international collaborations. They regularly attend meetings, present papers, organize conferences, and edit conference proceedings and journals. Some teach in local colleges and universities. Staff regularly receive awards and honors in recognition of their various achievements. In the last year, for example, an ET researcher was co-recipient of a prestigious R&D100 Award for invention of nanostructured carbide derived carbon, a thin coating for sliding and rotating equipment applications. Industrial partners are interested in using the coating to seal water pumps in automotive engines to prevent dry-run failure and extend the engine's lifetime. The development of this coating could save billions of dollars and reduce energy consumption. A separate report will be issued documenting recent honors and awards along with publications and presentations.

Recent scientific and engineering achievements by ET staff include the following:

- The HEIGHTS package is a multipurpose computer package developed at ANL to study the effects of particle beams and different radiation interaction with matter. It is finding application in many different fields, including fusion reactor design and development of extreme ultraviolet lithography for manufacture of the next-generation computer chip.

- "Nanofluids"—nanoparticles suspended in a conventional fluid—invented by an ANL research team can improve heat transfer for coolants by as much as 40%.

- An innovative medical treatment involving rapid cooling of the entire brain using an ice slurry is showing great promise for producing cell-protective hypothermia during cardiac arrest.

- Electromagnetic waves generated at millimeter-wave and terahertz frequencies are being exploited for a variety of sensing and detection scenarios applicable to homeland security.

- Staff have been involved in the safety review of applications for license renewal of six operating reactors and have assisted NRC in reducing the time needed for this renewal.

- The goal of producing a high-temperature superconductor with transport critical current density over 1 MA/cm^2 was reached with Y-Ba-Cu-O coated substrates fabricated by the inclined substrate deposition method.

- Ceramic membranes developed at ET appear to efficiently extract hydrogen fuel from gas mixtures at high temperature and high pressure.

- Insights have been gained into the physical mechanism behind metal dusting, a catastrophic corrosion phenomenon that is widespread in several chemical and petrochemical processes.

- Insights have also been gained into the physical mechanism behind material scuffing, which could lead to prevention of catastrophic failure in boundary layer lubrication.

- Our near frictionless carbon coating reduced the friction coefficient of steel surfaces under dry sliding by more than a factor of 100-1000, depending on the test environment. A superhard nanocomposite coating was more effective in lubricated contact, reducing both friction and wear by more than 3-10 times.

- Several tests have been completed on the behavior of high-burnup fuel under conditions relevant to a loss-of-coolant accident in light water reactors. These are the first such tests ever done.

The remainder of this overview highlights major ET research areas on a section-by-section basis.

Computational Physics and Hydrodynamics

The Division continues its long history of research into advanced methods of simulation and modeling of complex systems through the work of the Computational Physics and Hydrodynamics Section. This Section is involved in computational research and modeling for diverse research areas, such as magnetic fusion, inertial fusion, nuclear physics, high-energy physics, and computational physics for medical applications. Many of these activities are based on the development and refinement of the comprehensive multidimensional HEIGHTS (High Energy Interaction with General Heterogeneous Target Systems) computer simulation package. The HEIGHTS package is a multipurpose computer package used to study various effects of particle beams and different radiation interaction with matter. It combines the foremost numerical solution methods, including finite-element, Lagrangian, Eulerian, particle-in-cell, Monte Carlo, and ray tracing techniques. As one specific example, the HEIGHTS package is being used to analyze Be-Li targets as well as free Li jet-to-beam energy deposition for a future high-power nuclear physics fragmentation facility called the Rare Isotope Accelerator. A modified HEIGHTS software package is also being applied to the study of extreme ultraviolet lithography (EUV), a new technique that could be used in dense plasma discharge devices for manufacturing the next generation of computer chips.

The PRIME (particle/radiation interaction with matter experiments) facility, currently being constructed in this Section, will allow state-of-the-art experiments in the area of intense particle/radiation interactions with materials. These include interactions among plasma, matter (solid, liquid, and gas), and modulated energy beams. Studies will focus on particle-matter interactions as they pertain to applications in homeland security, defense (laser attenuation and backscattering from missile plumes), advanced EUV lithography, accelerator high-power target, inertial and magnetic fusion, and space. The strategic plan for PRIME has three main experiments: a laser experiment to help in design of advanced materials for the above applications, a plasma gun experiment to study the effect of intense plasma radiation for a variety of materials (high-Z metals, liquid metals, insulators, alloys), and a charged-particle experiment to study fundamental reactions of advanced materials exposed to an intense beam (100 eV to greater than 10 keV). The PRIME experiments are also designed to benchmark a suite of modeling tools, including HEIGHTS.

The Reduced-Enrichment Research and Test Reactor program at ANL seeks to develop low-enrichment uranium (<20% ^{235}U enrichment) fuels to replace the high-enrichment uranium fuels commonly used in research and test reactors around the world. In support of this program, the Section has modeled irradiation-induced recrystallization in a variety of nuclear fuel types, fission gas-bubble behavior in amorphous uranium silicide, and the effect of irradiation-induced gas-atom re-solution on grain-boundary bubble growth in uranium-alloy fuels.

Thermal and Electromechanics

The Division has a long history of research and development on heat transfer and fluid flow systems for advanced energy systems. While much of this work grew out of nuclear reactor development programs, current emphasis has shifted to the chemical process and transportation industries. The programs of the Thermal and Electromechanics Section provide a good example of this transition. That Section has developed a strong program related to the behavior of compact heat exchange devices and has constructed an array of small general-purpose test facilities to study boiling, condensation, and flow visualization in near-commercial components of advanced energy systems. The current Section activities include design and testing of a unique dryer concept for the paper industry, the study of nanofluids and other novel coolants for automotive thermal management, development of energy-storage devices and fault-current limiters, and the application of phase-change systems such as pumped ice slurries in district cooling.

Over the last 4 years the Section has also developed special slurries and delivery methods for medical cooling applications where inducing cell protective hypothermia is beneficial. The ice slurry is attractive for these applications because of its high energy content. In a new collaboration with the University of Chicago Medical School, we are developing innovative medical treatments involving rapid cooling of the entire brain using an ice slurry to produce cell-protective hypothermia during cardiac arrest, use of a miniature cooling probe to control localized brain swelling/cell death resulting from head trauma or stroke, and use of magnetic particles as carriers of therapies for strokes and cancer.

Sensors, Instrumentation, and Nondestructive Evaluation

The Division continues with its strong program on sensor development for a diverse group of DOE and industrial sponsors. The Sensors, Instrumentation, and Nondestructive Evaluation Section has unique strengths in millimeter-wave and terahertz sensing, ultrasonics, and nondestructive evaluation (NDE) systems. The Section is particularly good at developing a wide variety of industry-specific applications of NDE technology and sensors. The NDE work is directed toward methods for evaluation of ceramic materials to be used in oxygen and hydrogen production from coal combustors, valves for transportation applications, and components in advanced gas turbines and fossil energy systems. Also under investigation are NDE technologies for thermal barrier coatings used in hot sections of gas turbines and for the leading edge components of the space shuttle. Sensor development includes an acoustic-based sensor for fuel vapor in the harsh automotive environment and an ion mobility sensor for detecting NO_x in diesel auto exhausts.

Research related to the operational safety of light water reactors for the NRC remains another significant area of interest for the Division. This research is being performed not only in ET's Sensors, Instrumentation, and Nondestructive Evaluation Section, but also in the Thermal and Electromechanics Section and Corrosion and Mechanics of Materials Section. Steam generator tubes account for more than 50% of the primary pressure-boundary surface of pressurized water nuclear reactors and have experienced in-service corrosive and mechanical degradation of various forms since the beginning of commercial operation of pressurized water reactors. ET is presently conducting the Steam Generator Tube Integrity Program under the sponsorship of the NRC to evaluate the integrity of nuclear steam generator tubes as plants age and degradation proceeds. An important activity under this program has been the design and construction of a tube mock-up that incorporates steam generator tubes containing prototypical flaws. This mock-up is being used to evaluate the reliability of current NDE techniques for the detection and characterization of flaws. Major facilities have also been designed and constructed to determine failure pressures and leak rates for tubes containing a variety of flaws. Experimental data from these facilities are being compared to the predictions of analytical models also being developed as a part of this program.

Electromagnetic waves at millimeter-wave and terahertz (THz) frequencies offer great potential for a variety of sensing and detection scenarios. Building upon earlier work on devices used in the detection of chemical warfare agents, the Section now has a substantial program on instruments using low THz frequencies for detecting chemical, biological, radiological, and concealed materials. These results can be used to project the capabilities and limitations of fast emerging THz sensors, as they become mature, for homeland security applications. In addition, the Section has a new program on biosensing for revival of cardiac arrest victims.

Aging Management & Transportation of Hazardous Materials

Although many of the Division's efforts are best described as advanced technology development projects that draw on a specific engineering or scientific discipline, we also have continuing programs that integrate a large number of specialized areas to provide a unique group capability for a DOE sponsor. The Aging Management and Transportation of Hazardous Materials Section is the best example of this ongoing integrated approach to a specific DOE need. Section staff provide direct technical support to DOE in reviewing Safety Analysis Reports for Packaging (SARPs) of radioactive material shipping packages to ensure compliance with Departments of Energy and Transportation and Nuclear Regulatory Commission regulations. This work spans technical fields such as structural and thermal analysis, shielding and criticality, and operations, maintenance, and quality assurance. Working as a team on specific SARP submissions, staff provide DOE with independent technical review and confirmatory analysis needed to certify packages for shipment of a wide range of potentially hazardous nuclear materials. The work ensures worker safety, public health, and environmental protection and also affects DOE programs such as fissile material disposition, site closure, and waste disposal.

This Section is also involved in updating the NRC "Generic Aging Lessons Learned (GALL)" report and the "Standard Review Plan for License Renewal (SRP-LR)" for operating nuclear power plants in the United States. The SRP-LR and the GALL report are providing guidance to NRC staff reviewers in performing safety reviews of license renewal applications in accordance with the license renewal rule. In addition to guidance development for plant license renewal, Section staff are also involved in the review of license renewal applications for Calvert Cliffs, Arkansas Unit-1, Peach Bottom, St. Lucie, V. C. Summer, Dresden and Quad Cities, Joseph M. Farley, and Arkansas Unit-2. Half of these plants have already received license extensions for 20 years.

Ceramics

Superconductor development remains a large individual program in the Division. The program focuses almost exclusively on the development of second-generation superconductors, in which films of Y-Ba-Cu-O (YBCO) are deposited on textured metallic substrates. The goal of this program is to develop ceramic superconductors for applications in generation, storage, transmission, and distribution of electrical energy. The general target is to produce in collaboration with industrial partners long lengths (>100 m) of conductor capable of carrying $>1 \times 10^6$ A/cm^2 at temperatures approaching that of liquid nitrogen. This work is being done in collaboration with American Superconductor Corp. and SuperPower, a subsidiary of Intermagnetics General Corp.

The Ceramics Section is also developing dense ceramic membranes for separating hydrogen from gas mixtures and for producing hydrogen from water. Because of concerns over global climate change due to carbon dioxide emissions, hydrogen is considered the future fuel of choice for both the electric power and transportation industries. Cooperative agreements have been established with industrial partners to develop the ceramic membrane technology for commercial applications.

Hybrid vehicles require a reduction in the size and weight of power electronic modules. To meet these needs, the Ceramics Section is developing high-dielectric-constant thin-film ceramic capacitors. In a collaborative effort among steel and refractory producers, universities, and national laboratories, the Ceramics Section is also developing refractory materials with improved performance and service life for use in electric arc furnaces. In collaboration with industry and other national laboratories, research is conducted in developing environmental barrier coatings for advanced turbine blades.

The novel room-temperature-setting chemically bonded ceramic known as “Ceramicrete” has been developed in the Division for stabilization of a wide range of DOE waste streams (such as contaminated ashes, salt cakes, and sludges). Ceramicrete also holds promise for treating waste streams generated by the utility, chemical, and defense industries. Several mixed wastes from DOE facilities such as the Savannah River Site, Fernald, Rocky Flats, Argonne East and West, and Idaho National Engineering and Environmental Laboratory have been successfully stabilized with Ceramicrete. The process has been scaled up to stabilize actual wastes; collaborations with private industry are ongoing to demonstrate the stabilization of DOE waste streams. Ceramicrete is also under development for oil-well borehole sealants.

Corrosion and Mechanics of Materials

The Corrosion and Mechanics of Materials Section addresses issues related to corrosion and the effects of various environments on the mechanical behavior of materials used in several types of energy systems. The key corrosion programs related to light water reactors include determination of crack growth rates and low-cycle fatigue properties of irradiated and unirradiated nuclear reactor materials, the corrosion behavior of pressure vessel steels and austenitic steel welds in aqueous environments containing high concentrations of boric acid, and the crevice corrosion behavior of steam generator materials. During the last two years, the Section has been involved in the generation of kinetic data for oxidation of Zr-based nuclear reactor cladding alloys in steam and air environments and in the development of oxidation rate correlations for use in reactor safety analysis codes. During the last year, the Section has initiated a new program to examine the effect of hydrocarbon impurities in helium coolant on the scaling and mechanical properties of structural materials for advanced reactors. The Section is also involved in the development of design rules for fusion reactor applications and for advanced helium-cooled gas reactors that are planned for power generation and hydrogen production. In the non-nuclear area, the Section is conducting experiments in two areas: (1) corrosion of metallic and ceramic materials in complex gas environments and in the presence of deposits relevant to advanced fossil power applications and (2) metal dusting phenomenon, a catastrophic degradation process that is widespread in several chemical and petrochemical processes.

Tribology

The Tribology Section conducts research on advanced tribological systems (e.g., surface engineered materials, lubricants, fuels, and fuel/lubricant additives) for use in aggressive environments. A major portion of this activity focuses on the development and evaluation of high-performance coatings that can be applied to a wide range of materials. Also being investigated are how fuel and lubricant additives interact with surfaces under boundary-layer-lubrication regimes. The coatings are primarily intended to protect engine-component surfaces that undergo sliding and rolling contact in advanced transportation systems, including those powered by diesel and gasoline engines, as well as by advanced energy conversion systems.

In general, the Section's activities encompass the development of advanced surface modification and material processing technologies, as well as evaluation of tribological properties. In the area of coatings that reduce friction, the Section has ongoing projects on development of near-frictionless carbon (NFC) coatings, superhard nanocomposite coatings that show potential for applications where formulated lubricants are employed, and electroless wet-chemical coatings used to fabricate small diesel injector orifices. Related projects include development of processes to join advanced materials using superplastic deformation and advanced glasses for X-ray imaging.

In the area of tribological evaluations, the Section has projects on laser glazing techniques to reduce parasitic friction losses between wheels and rails (railroad transportation), and laser engineered treatment of surfaces (microdimples) to improve friction behavior of surfaces during hydrodynamic lubrication. Also being evaluated are parasitic energy losses in heavy-duty diesel engines to determine the impact of low friction surfaces and low-viscosity lubricants on fuel economy, durability of advanced materials (NFC, low-friction polymers, etc.) for air compressor applications in fuel cell systems, and erosion properties of materials exposed to nanofluids. Further, the Section has major projects to characterize coating properties and tribological mechanisms, including characterization of boundary-layer lubrication mechanisms and the structural, thermal, and electrical properties of advanced coatings.

Irradiation Performance

The activities in the Irradiation Performance Section are aimed at determining and assessing the accident behavior and normal-operation behavior throughout the life cycle of nuclear reactor fuel materials—from their in-reactor performance through their likely behavior during ultimate interment in a repository.

One such activity is an NRC-sponsored program to investigate the behavior of high-burnup fuel under conditions relevant to a loss-of-coolant accident (LOCA) in light water reactors. The LOCA-integral tests involve ramping (at 5°C/s) the temperature of pressurized, fuel-cladding segments in a flowing-steam environment through ballooning and burst (at ≈750°C) to 1204°C, holding for various times to generate oxidation levels consistent with NRC criteria (17% equivalent cladding reacted), slow cooling (at 3°C/s) to ≈800°C, and rapid cooling through water quenching. Behavior of the cladding during, and following, the water quench determines whether the current NRC criteria for LOCA events are conservative for high-burnup fuel rods. Three tests with high-burnup BWR fuel segments have been completed to date. ANL is the only laboratory to have conducted these tests with high-burnup fuel samples. Similar tests are now being performed with pressurized nonirradiated Zircaloy and advanced-alloy cladding materials. The test results for nonirradiated Zircaloy segments provide baseline data for comparison to the results for high-burnup fuel segments and for nonirradiated advanced-alloy cladding segments.

Hot Cell Facilities

The mission of the Hot Cell Facilities Section is to provide research facilities to ET organizations for radiological materials examination and testing. To fulfill this mission, the Section operates four facilities: the Alpha-Gamma Hot Cell Facility, which includes a well-equipped Electron-Beam Instrument Laboratory; the Irradiated Materials Laboratory (IML); the Room DL-114 Glovebox Facility; and the K-2 Hot Cell Facility in Building 200 (Chemistry Division). Characterization and testing of irradiated materials are carried out in the Alpha-Gamma Hot Cell Facility and the Irradiated Materials Laboratory. Recently, we have refurbished the DL-114 Glovebox Facility to carry out hydrogen, nitrogen, and oxygen measurements for Irradiation Performance Section programs. We also took over and restarted a portion of the Building 200 M-Wing Hot Cell Facility to allow tests to be conducted for simultaneous gathering of multiple mechanical properties.

Computational Physics and Hydrodynamics

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The several research disciplines and modeling activities within the Computational Physics and Hydrodynamics Section include combined expertise in heat transfer, thermal hydraulics, atomic and plasma physics, magneto and shock hydrodynamics, radiation transport, physics of material erosion and destruction, particle diffusion and mass transport, and computational fluid dynamics. One major activity is the study and simulation of materials behavior under intense power deposition for various national and international programs that are investigating magnetic fusion, inertial fusion, nuclear physics, high-energy physics, and space, medical, and industrial applications. In the reduced enrichment research test reactor (RERTR) program, the aim is to develop high-density, low-enriched uranium alloy fuels. A near-term goal of the RERTR modeling task is to provide an analytical interpretation of swelling in these materials as a function of irradiation condition and fuel composition. In computational fluid mechanics, the emphasis is on development and implementation of mathematical and phenomenological models of single- and two-phase fluids applied to a variety of advanced applications.

Modeling High-Power Interactions with Target Materials

Much of this activity is based on development of the comprehensive multipurpose HEIGHTS (High Energy Interaction with General Heterogeneous Target Systems) software package to study in detail the various effects of particle beams and radiation interaction with matter. This renowned package is used to model plasma-material interaction in powerful laboratory devices, as well as in tokamak fusion machines in several countries such as Japan, Russia, and the United States. Recent work includes the following:

- In magnetic fusion, we are modeling the effects of plasma/material interactions during normal and abnormal fusion reactor operations. One important problem is modeling the effect of loss of plasma confinement on reactor first-wall and divertor materials. Detailed physics of plasma/solid-liquid/vapor interactions in a strong and oblique magnetic field have been

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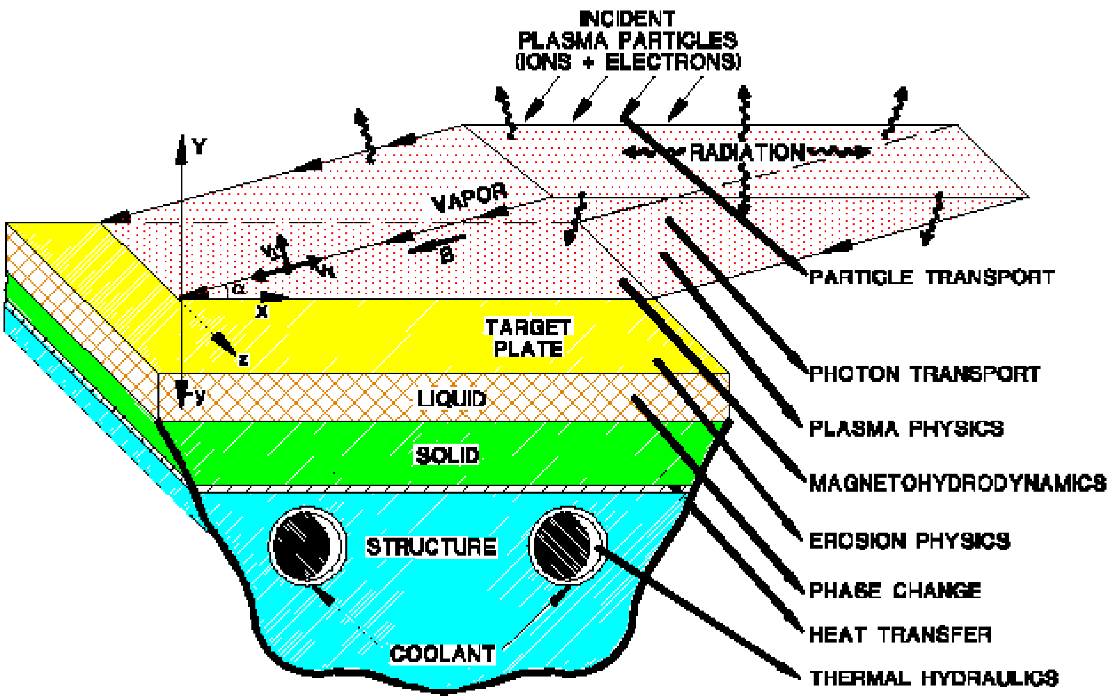
developed in the HEIGHTS package in a comprehensive self-consistent manner, as schematically illustrated in the figure below. Such detailed treatment of the magnetohydrodynamics and photon radiation transport in the vapor-cloud region, for example, is essential for determining the lifetime of plasma-facing components due to plasma instabilities.



Required integrated modeling areas for comprehensive evaluation of damage from loss of plasma confinement

- In the inertial fusion program, we are modeling the effects of pellet/target implosion and the resulting debris on the dynamic response of the reactor chamber walls between microexplosions.

- In the nuclear physics program, our analysis is aiding in design of a viable target system and the study of beam-on-target interaction for the Rare Isotope Accelerator (RIA) presently in the design stage. We are using the three-dimensional (3-D) HEIGHTS package to calculate the thermal response of different target systems cooled by liquid metals as the particle beam penetrates the composite target system. This effort is described in more detail next.

- In the high-energy physics program, we are modeling the target response of the international muon collider and the neutrino factory projects. This requires studying the penetration of free, high-velocity (10-20 m/s), liquid-metal jets in a strong magnetic field of 20 T. We then study the shock hydrodynamic effects due to proton beam bombardment for the production of pions that decay to muons.

- Another recent application of the HEIGHTS package is the study, for medical applications, of the effects of electric shock and injuries resulting from electrical arc explosions.

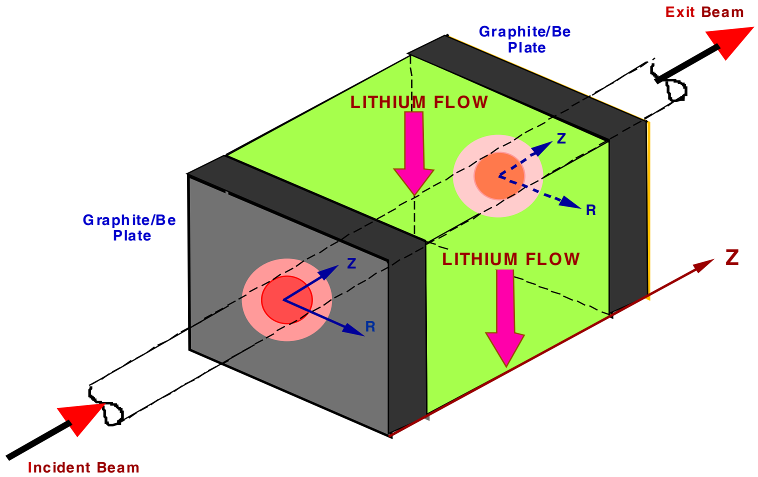
- HEIGHTS can also be used to simulate and understand the processes through which granulated metal nanostructures can be fabricated based on laser ablation under the influence of a pulsed laser beam. Liquid metal droplets of submicrometer size are first splashed out from the melted target surface and then, following charging in a laser-induced plasma, break up to form a nearly monodispersed flux of charged nanometer-sized droplets. This flux is forced to the substrate by an electric field, and the deposited structure is self-assembled in a densely packed amorphous layer due to Coulomb interactions This work is in collaboration with experimentalists at Ioffe Institute in St. Petersburg, Russia.

In summary, HEIGHTS is a comprehensive software package that can run on computers ranging from parallel processors to Cray supercomputers to engineering workstations. HEIGHTS combines the foremost numerical solution methods, including finite-element, Lagrangian, Eulerian, particle-in-cell, Monte Carlo, and ray tracing techniques. Depending on the problem's complexity, run time ranges from one hour to several months.

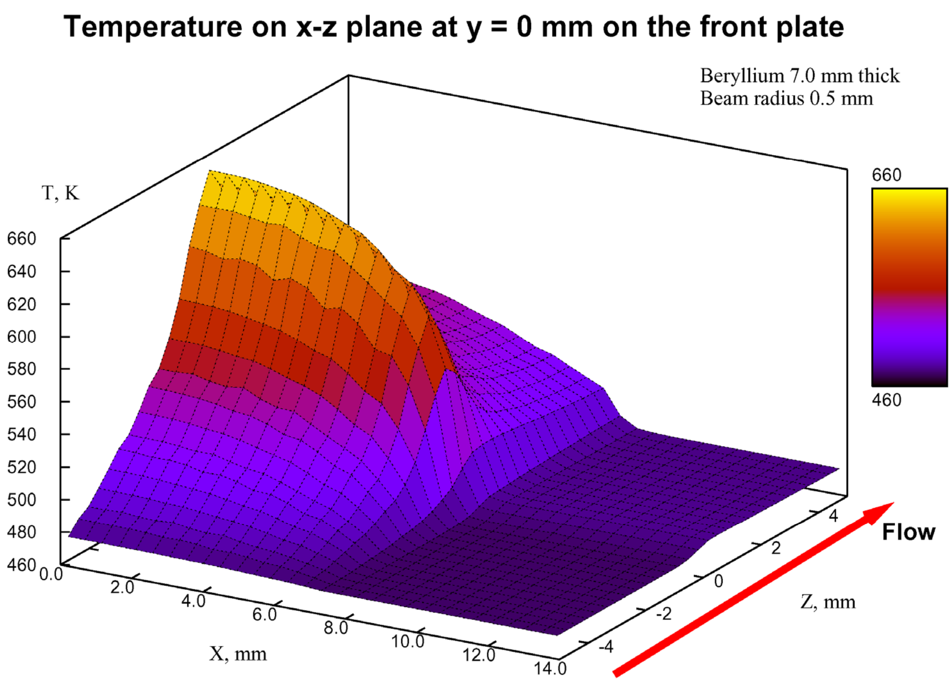
Modeling for the Rare Isotope Accelerator

The HEIGHTS package was used to analyze double-window Be-Li targets as well as free Li jet-to-beam energy deposition for a future high-power nuclear physics fragmentation facility called the Rare Isotope Accelerator (RIA). An adjustable-thickness Li/Be hybrid target is being developed for use at the National Superconducting Cyclotron Laboratory. The lithium serves as a part of the target as well as the coolant. Up to 1 kW of beam power is dissipated in the target and is carried away by the recirculating liquid lithium loop. It is designed for high power beams in the mass range from oxygen to calcium. Tapered beryllium windows combined with a uniform-thickness lithium channel gives an overall target thickness ranging from 0.7 to 3 g/cm^2, which is adjusted by moving the target vertically. HEIGHTS calculations of the temperature profiles in the entrance and exit regions of the target have been carried out (examples given in following figures). These calculations were performed for a ^{48}Ca beam at the thin end of the target (1-mm beryllium windows and 5-mm lithium thickness) and for an ^{16}O beam at the thick end (7-mm beryllium windows and 5-mm lithium). The results show that the temperature increases at the target entrance and exit are reasonable.

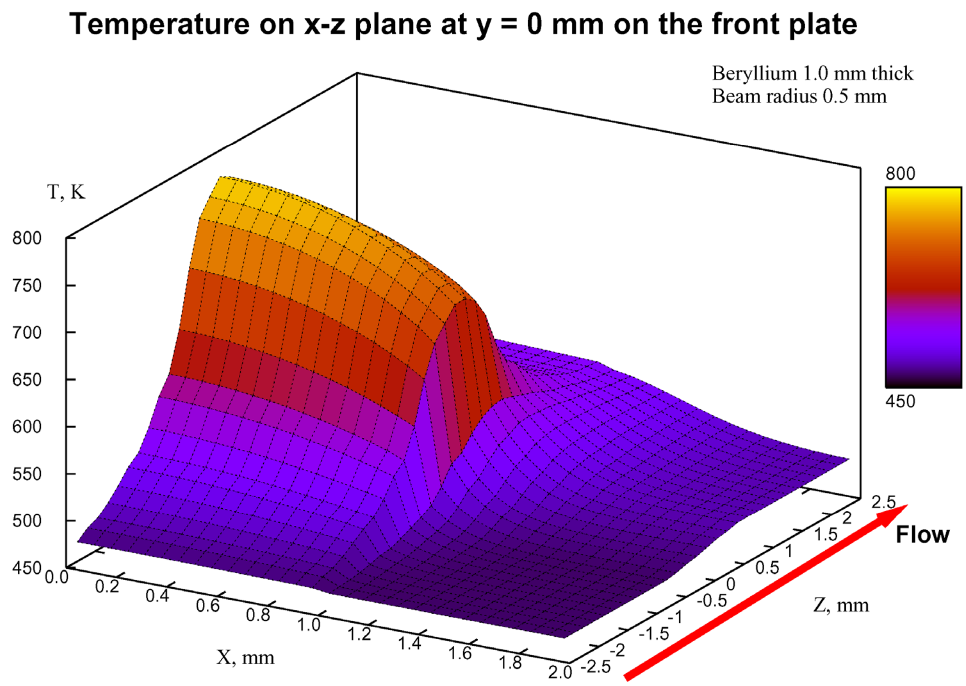
To cope with the resulting high power densities for the future high-power nuclear physics fragmentation facility, windowless liquid lithium targets are being developed for consideration in RIA. In addition, calculations were made for the nozzle design to produce free surface flow. From these calculations we concluded that future nozzles for the RIA target should be designed with a special shape that ensures smooth transition from the initial rectangular inlet to the rectangular outlet. Additional smoothing of corners at the nozzle exit proved to help avoid instant disturbances that exist immediately after the outlet from the nozzle.



Double window-target design for Rare Isotope Accelerator



Three-dimensional thermal calculation of the temperature distribution in the beryllium window and flowing lithium for the case of 200 MeV/u ^{16}O beam at intensity of 1 particle microampere. The peak temperature is at the outside surface of the beryllium and is 660 K.



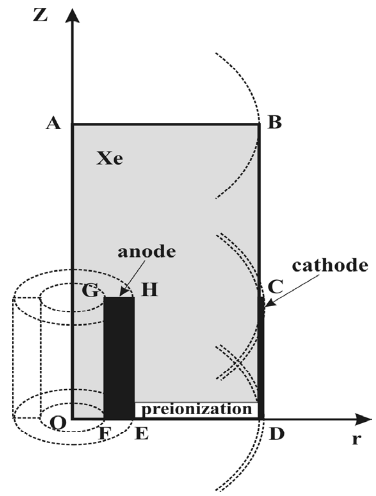
Three-dimensional thermal calculation of the temperature distribution in the beryllium window and flowing lithium for the case of 160 MeV/u ^{48}Ca beam at intensity of 0.5 particle microampere. The peak temperature is at the outside surface of the beryllium and is 800 K.

Development of Extreme Ultraviolet (EUV) Lithography

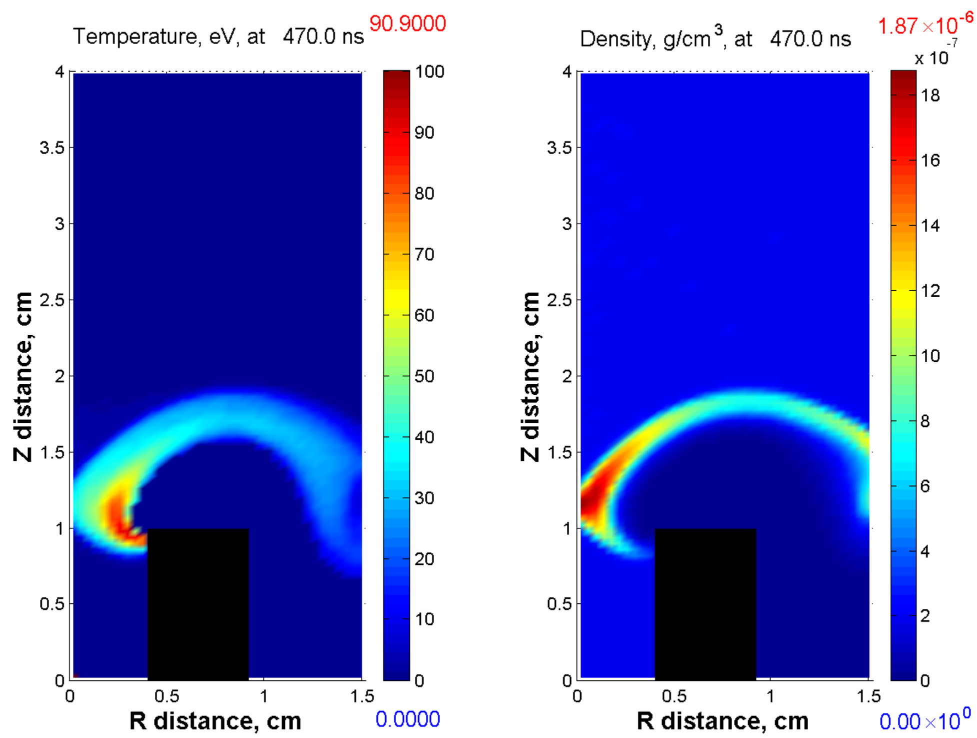
Modeling and Simulation of Discharge Produced Plasma

Discharge produced plasma (DPP) devices have been proposed as a light source for EUV lithography, a technique that would facilitate fabrication of next-generation semiconductors. A key challenge for DPP is achieving sufficient brightness to support the throughput requirements of exposure tools for high-volume manufacturing lithography. To simulate the environment of the EUV source and optimize the output of the source, an integrated model is being developed to describe the hydrodynamic and optical processes that occur in DPP devices. The model includes both plasma evolution and magnetohydrodynamic (MHD) processes as well as detailed photon radiation transport. The model uses the total variation diminishing scheme in the Lax-Friedrich formulation for the description of magnetic compression and diffusion in a cylindrical geometry. Several models are being developed for opacity calculations: a collisional radiation equilibrium model, a self-consistent field model with Auger processes, and a nonstationary kinetic model. Radiation transport for both continuum and lines with detailed spectral profiles are taken into account. The developed models are integrated into the HEIGHTS-EUV computer simulation package. Preliminary results of a numerical simulation of xenon gas hydrodynamics and EUV radiation output have been obtained for various plasma conditions.

Initial simulation of MHD and optical processes that occur in DPP devices of standard Mather-type electrode construction is underway. Such a device is schematically shown below. The electrodes are represented as thick vertical lines and are of equal height. The device is filled by xenon gas under an initial pressure in the range of several tens of millitorr at room temperature, corresponding to an initial density of the gas in the range of 10^{14}-10^{15} cm^{-3}. It is assumed that a preionization step that heats the gas to a temperature of ≈1 eV occurs near the bottom of the device. Given next is a schematic of the DPP device followed by graphs derived from HEIGHTS-EUV calculations for temperature and density with the xenon plasma.



Schematic view of DPP device



Two-dimensional spatial profiles for transient plasma temperature and density simulated by HEIGHTS-EUV code for xenon plasma in dense plasma focus source geometry

Development of Plasma-Facing Materials

Material selection and lifetime issues for EUV lithography tools are of critical importance to the success of future microelectronic devices. Our group works on developing and understanding material design and applications of plasma-facing electrodes, insulators, condenser collector mirrors, and wall materials for EUV sources. Ideal candidate materials at the EUV source should be able to withstand high thermal shock from the short-pulsed plasma; withstand high thermal loads without structural failure; reduce debris generation during discharge; and be machined accurately. Condenser optics requires surfaces that are resistant to impurities (oxygen, carbon) and erosion while maintaining high EUV light reflectivity.

The study of damage, structural changes, and property alterations of the materials exposed to intensive ion and thermal pulses is very important for developing candidate plasma-facing materials for EUV sources and predicting the materials' behavior in different modes of source exploitation. The problem of modeling the effect of powerful plasma pulses on material surfaces is particularly interesting. As with fusion reactors, evaluations of candidate materials are aided by simulation facilities for plasma-material interaction. Facilities operating with intensive plasma beams, electron accelerators, and laser beams generally present the possibility to implement such models at the experimental level.

Currently, our group collaborates with scientists at Troitsk Institute for Innovation and Fusion Research (TRINITI) in Troitsk, Russia. Experiments are being carried out at plasma gun facilities in well-diagnosed and controlled conditions. The plasma gun is applied as a source of pulsed energetic Xe plasma capable of generating Xe plasma streams with a velocity 4×10^6 to 4×10^7 cm/s and duration of the plasma pulse of 10-40 μs. A velocity for the xenon plasma stream velocity of $4–10 \times 10^6$ cm/s is sufficient to obtain plasma temperatures of 40-50 eV, i.e., typical for pinch EUV devices. The formation plasma cloud makes possible the study of erosion and surface damage induced by particles and radiation of Xe plasma at these temperatures. We are actively working on surface analysis of a variety of sample materials and complement this work with intense ion-beam experiments in the new PRIME facility established in our group (see below).

Facility for Particle/Radiation Interaction with Matter Experiments (PRIME)

The PRIME facility, currently being constructed in our Section, will allow state-of-the-art experiments in the area of intense particle/radiation interactions with material. These include interactions among plasma, matter (solid, liquid, and gas), and modulated energy beams: electromagnetic radiation, charged particle beams (electrons, ions, etc.), and other particle sources (clusters, molecules, etc.). Studies will focus on particle-matter interactions (PMIs) as they pertain to applications in homeland security, defense (laser attenuation and backscattering from missile plumes), advanced EUV lithography, accelerator high-power target design, inertial and magnetic fusion applications, and space applications (e.g., debris/satellite interactions, ion thruster nozzle design for space propulsion). The strategic plan for PRIME has three main experiments: a high-intensity laser experiment, a high-intensity plasma gun experiment, and a high-intensity charged-particle experiment. All three experiments are summarized next.

Laser-Matter Interactions

The laser/matter interaction experiment in the PRIME facility will focus on design of advanced materials in areas related to homeland security and defense, advanced weaponry development, EUV lithography development, nanoscience of self-assembled structures, semiconductor and advanced optical interconnects, and industrial laser applications. For example, we will study self-assembled nanostructure synthesis with high-intensity laser systems for application in future military micro-vehicle systems. Directed energy and lethality research in advanced weapons design will also be addressed by capabilities in PRIME complemented by computational modeling.

Plasma-Material Interactions

Plasma-matter interaction experiments will focus on intense plasma radiation for a variety of materials, including high-Z metals, liquid metals, insulators, and alloys. Studies involving plasma instabilities and their effect on surface and bulk properties of materials will be the focus of these experiments.

Experiments will be conducted with a high-intensity plasma gun device (HIPGD) similar in concept to the MK-200CUSP plasma gun at TRINITI. The HIPGD will inject a plasma stream into a cylindrical chamber (length ~ 50 cm, diameter ~ 30 cm) filled with a longitudinal magnetic field of a few teslas. Plasma parameters will include energy densities of 1 to 1.5 kJ/cm^2, pulse duration of about 10 to 15 ms, impact pressure of 100 atm, directed ion energy of 1 to 2 keV, ion and electron temperatures of 1-2 keV, and spot diameter of about 5 cm. General research on high-intensity plasma-material interactions will include the following:

- Dense plasma focus operation to study debris mitigation techniques in EUV lithography applications.

- Plasma-material modification and enhancement of metal properties. A growing research area in Europe and elsewhere is the creation of supermetals by shock treatment of surfaces exposed to pulsed plasma sources.

- Vapor shielding studies of intense plasmas interacting with a variety of materials (C, W, Mo, Cu, Li, and Be).

- Off-normal-event (edge-localized modes, disruptions) studies on candidate plasma-facing components for magnetic fusion applications.

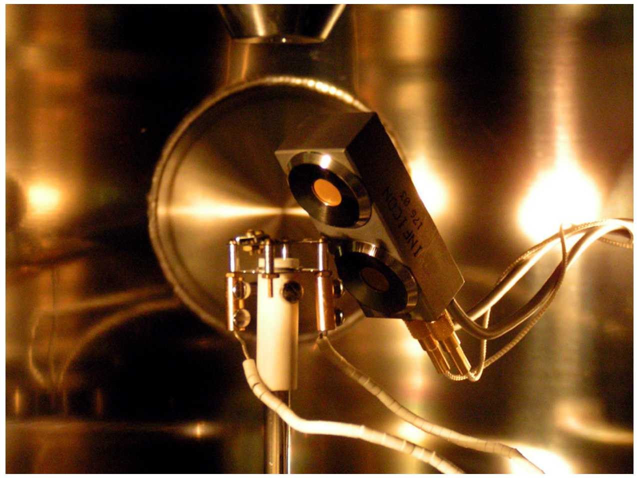
- Intense plasma interactions with ion-thruster cathode/anode materials (W, carbon composites, and Mo).

- Directed energy research for lethality maximization in advanced weapon systems.

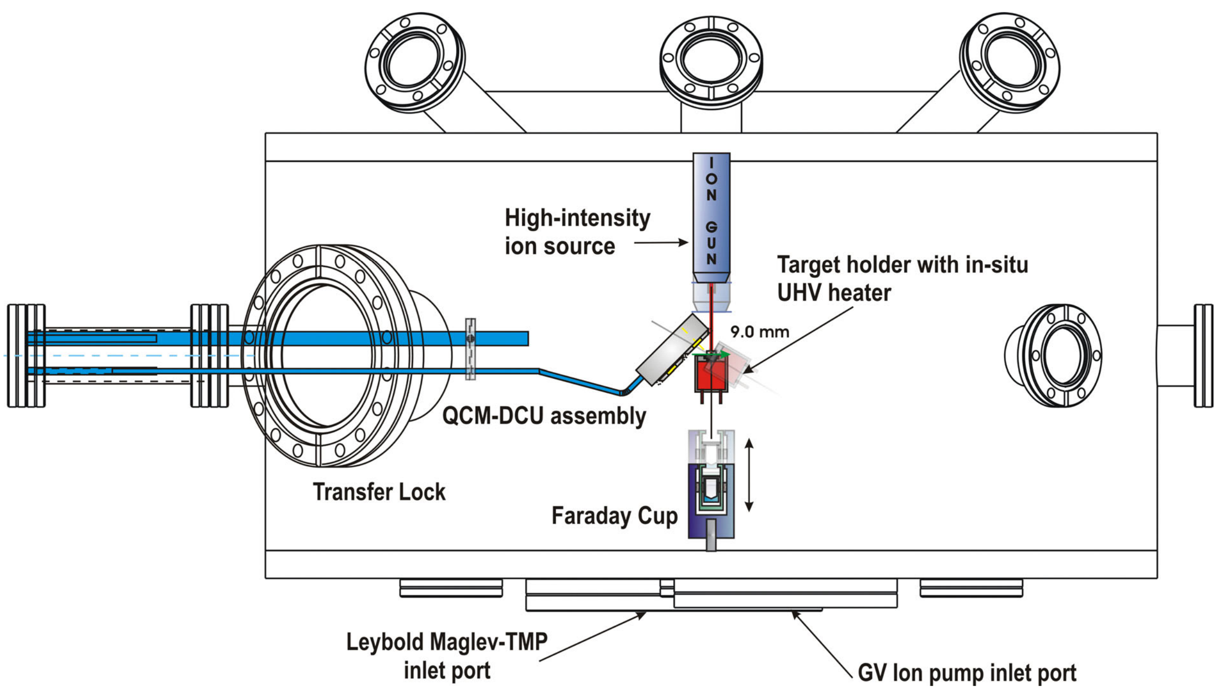
Interaction of Materials with Charged Particles and Components Testing (IMPACT)

IMPACT will make use of moderate- to high-intensity ion and electron monoenergetic beam sources at energies ranging from 100 eV up to greater than 10 keV. The focus of IMPACT research is to study fundamental interactions from an intense beam and a variety of materials relevant to the PRIME research thrusts described above. Surface diagnostics will include low-energy ion scattering spectroscopy, optical emission spectroscopy, ultrafast laser spectroscopy, and quartz crystal microbalance (QCM) technology. In addition, irradiated samples will be characterized ex-situ at surface analysis facilities, including the Center for Microanalysis of Materials (CMM) at the University of Illinois, Champaign-Urbana. The proposed IMPACT research will include:

- Plasma processing (e.g., ion-beam deposition, material modifications under intense ion irradiation).
- Multiply-charged particle bombardment of materials and potential sputtering.
- Lifetime of plasma-facing components of future sun probes.
- Charged-particle interactions with matter (liquid or solid) related to erosion, target modification, backscattering for research in EUV lithography, and semiconductor processing, as well as nanoscience, bioscience, inertial and magnetic fusion, elementary particle research, and space applications.
- Surface processes relevant to industrial and basic research applications, including erosion, reflection, sputtered-particle distributions, surface kinetics, and thermodynamics.
- Bubble formation in liquid metals under intense charged-particle fluxes using low-energy ion scattering spectroscopy and QCM techniques. These studies will be complemented with molecular dynamics research being conducted in the ET Division.
- Energy and angular sputtering and reflection distributions with ultrafast laser spectroscopy and laser-induced fluorescence.
- Behavior of multiply-charged particles on liquid metals.



The quartz crystal microbalance – dual crystal unit (QCM-DCU) diagnostic system in IMPACT. This technique is capable of measuring real-time erosion mechanisms from single and multi-component surfaces.



Design of IMPACT. Capable of measuring erosion (sputtering, desorption, evaporation) under a variety of conditions regarding temperature, angle-of-incidence, incident particle energies, and flux.

Collaborations

PRIME will promote collaborative efforts with ANL research groups. For example, work related to the synthesis of self-assembled nanostructures pertinent to areas in Defense and Homeland Security can open new avenues of collaboration between the ET Division and the new Center for Nanoscale Materials (CNM) at Argonne. The CNM will support a number of collaborative opportunities in the area of synthesis and characterization of nanostructures.

Work pertaining to the characterization and analysis of surfaces studied in PRIME is being proposed at the Electron Microscopy Laboratory and the Center for Microanalysis of Materials at the University of Illinois at Urbana-Champaign. In addition, proposals on surface and near-surface analysis will be prepared at the Advanced Photon Source and the Intense Pulsed Neutron Source at Argonne.

External collaboration is currently being pursued with the University of Wisconsin at Madison, University of California at San Diego, Stanford University, Northwestern University, University of Chicago, and Virginia Tech University. Other collaborations will include the Lawrence Livermore National Laboratory and Jet Propulsion Laboratory. Industrial partners being sought include Intel Corp., XTREME Technologies GmbH, International SEMATECH, Hewlett-Packard, Northrop-Grumman, and Lockheed Martin. Partnerships with small businesses will also be pursued, including Allen Enterprises and NPL Associates Inc.

Educational and Diversity Programs

In addition to service to the scientific and industrial communities, PRIME serves as a cornerstone for academic development. Investment in PRIME has opened and will continue to open new doors for many young students from the high school up to graduate level to foster and enrich their education. Already five undergraduate engineering students from the University of Illinois, Urbana-Champaign, have contributed to the success of PRIME and, in turn, obtained valuable research experience contributing to their engineering education. Collaboration with regional and national universities will provide a source of talented young students that will benefit from their research experience in PRIME. In addition, ties with diversity programs such as the University of Illinois' Society of Hispanic Professional Engineers and Women-in-Engineering student chapters will also serve as one of many avenues to bring young, talented college students to work with state-of-the-art equipment and experiments in the PRIME facility.

Fundamental Atomistic Simulations by Molecular Dynamics and Monte Carlo Methods

"Atomistic simulation" means that during the simulation, all the positions and the momenta of all the atoms, molecules, or ions (or particles) comprising the physical, chemical, or biological system, or at least the most important part of the total system, are calculated and stored in a computer. These calculations are done by either solving the Hamiltonian equations, as in various molecular dynamics (MD) methods, or by using stochastic sampling techniques, as in Monte Carlo (MC) methods. Quite often, these two atomistic approaches are used simultaneously in order to imitate different physical processes taking place at the same time.

After the positions and momenta are obtained, the various observable variables could be derived by averaging over time or over the ensemble.

Some of the MD and MC simulation results that have revealed a new effect or have a remarkable industrial application are discussed in more detail below.

Multiscale Hybrid Molecular Dynamics Model (HyDyn)

In MD simulations, the atomic equations of motion of all interacting particles are solved numerically. Appropriate initial and boundary conditions are supplied. Because of limited computing resources, there is always a problem of choosing a correct size for the model system. For simulation of energetic and heavy (e.g., clusters) ion impacts on a solid surface, all cluster atoms and a "reasonably large" number of target atoms are treated in detail, as "mobile," while the remaining target atoms are represented by either a fixed potential field or by periodic boundary conditions, which means that they are immobile.

In establishing the reasonable number of mobile atoms, one finds that too few atoms may show unphysical effects but that increasing their number has a steep price in computation time and required memory, as both grow rapidly with increasing degrees of freedom in the model. The usual procedure is to estimate a necessary number of the target atoms, often influenced by the available computing power, and to account for the rest of the system by proper boundaries, which would allow the flow of energy deposited by the impact to the bulk of the solid. One of the often-used techniques, based on stochastic Langevin dynamics, employs two or three atomic layers surrounding a central volume treated by MD. These layers of damped atoms represent a "thermal bath," which simulates heat transfer to the bulk of the target. This technique seems to be reasonable in simulation of low-energy processes, such as film deposition.

Heavy-ion energetic impacts on a target consisting of light particles create violent collisions between atoms in the central volume, where equivalent temperature and pressure may reach 10^5 K and 10^6 bars, respectively. For modeling such events, the boundary can be made "flexible" by allowing its expansion to keep, for example, the average pressure constant for a given modulus of elasticity. This technique is not completely satisfactory, as it requires knowledge of materials characteristics over a wide temperature range. The problem of the boundary conditions can be also examined by considering shock waves created by the energetic cluster impact. Unphysical reflections of the shock waves from the system boundary may show up in MD results, distorting the picture of the investigated process.

In our multiscale hybrid MD model (HyDyn), a shock wave theory is used to establish a reasonable size of the collision zone, for which an atomistic MD method is employed. The rest of the system is separated into a buffer zone where MD follows the atomic motion, and the obtained variables are averaged and used as a boundary condition for the remainder of the system, which is treated as a continuum medium and is studied by finite difference methods. Such a hybrid model greatly facilitates and easily solves various problems in areas related to energetic ion collisions with solid targets.

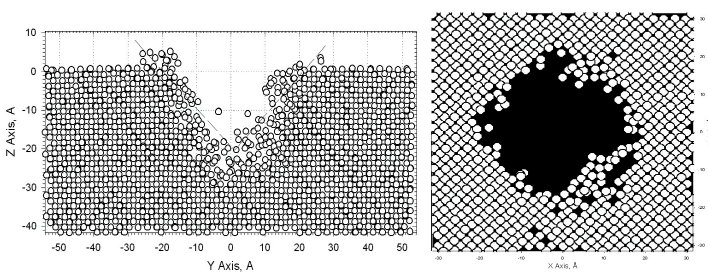
"Lateral Sputtering" Effect

A "lateral sputtering" effect was predicted by our MD simulation for interaction of energetic ions with targets. This effect consists in sputtering of target atoms into directions much closer to a target surface irradiated with cluster ions consisting of many hundreds or thousands of inert gas atoms, with total kinetic energy of at least a few tens of kilovolts. Such angular sputtering geometry is significantly unlike what could be produced by a single-ion collision accelerated to the same energy and bombardment of the same surface because the latter produces a cosine-like angular distribution of sputtered atoms.

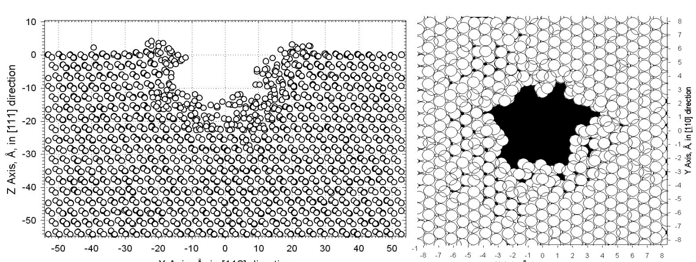
The lateral sputtering effect has been verified experimentally, and it was also shown to be a driving force for another remarkable phenomenon—the surface smoothing effect caused by accelerated cluster ion impacts on atomically rough surfaces. The latter effect has widely been used in the semiconductor and recording media industry.

Nanoscale Craters on Silicon Surfaces

As MD gives the exact position of all the atoms of the irradiated target, it has been a long time challenge to reveal the atomic structure of craters formed on a surface by energetic ion impacts. Our HyDyn code is perfectly suitable for solving this problem. The figures below show side and top views of a simulated crater formed by a heavy Ar cluster ion impact on a Si (001) surface. This picture shows a nearly triangular faceting of the crater, which is due to a higher energy of the Si (111) plane.



(a) Side view and (b) top view of the crater formed by heavy ion impact on Si (001) surface



(a) Side view and (b) top view of the crater formed by heavy cluster ion impact on Si (111) surface

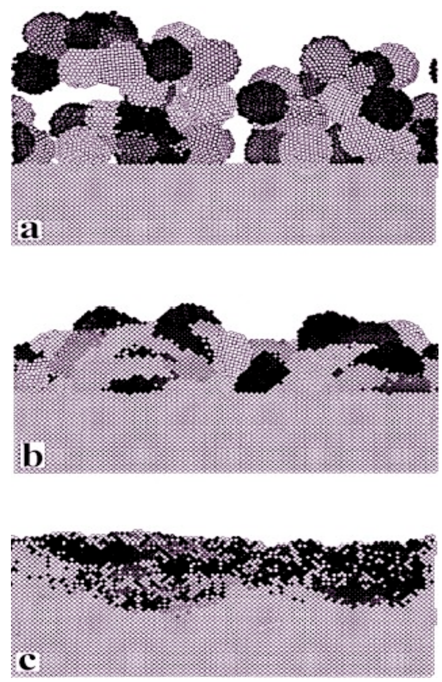
The top view of the crater shows nearly four-fold symmetry with facets formed by four (111) planes crossing the (001) surface. To draw the top views, only those atomic positions were taken that lie below the previous unirradiated surface.

The Si (111) surface shows faceting features quite different from those of the (001) surface. The side view has a round crater and a starfish-looking top view, which is quite surprising. This shape has never been previously observed in simulation or in experiment. The effect is unlike that observed with light or slow ion irradiations and is clearly related to the different dynamics of simultaneous multiple collisions of a heavy projectile with a solid target. This results in transfer of kinetic energy to a large number of surface atoms, which leads to their nonlinear displacement, local melting, amorphization, and enhanced sputtering.

Thin Film Formation

Energetic metal clusters could be produced in a rapid expansion and then ionized and accelerated toward the surfaces to form thin films with extraordinary optical properties, strong adhesion, and high density. Our MD model has been used to predict properties of such films. Depending on the needs, energetic cluster ion impacts can modify initially rough surfaces and produce excellent smooth surfaces or be used in manufacturing of thin films with high adhesion, high density, and high reflectivity of X-rays.

The figures show the results of our MD simulation of 50 cluster impacts, each containing 1043 Mo atoms, deposited with various kinetic energies: (a) 0.1 eV, (b) 1 eV, and (c) 10 eV kinetic energy per atom.

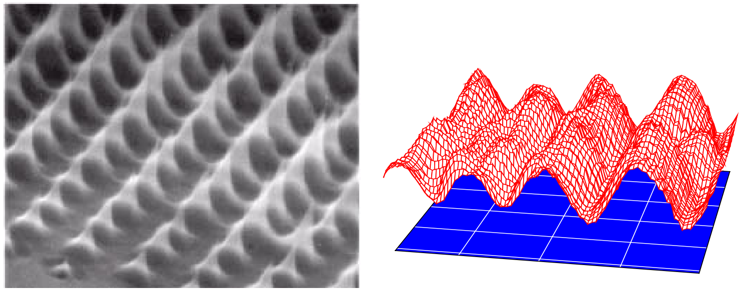


Molecular dynamics simulation of Mo thin film formation by depositing fifty large clusters, each containing about 1000 Mo atoms

Monte Carlo Simulation of Nanostructure Formation on Surface

Nonlinear instability processes in the atmosphere, as well as on liquid and/or solid surfaces, often create ripple structures. This type of instability is seen in cloud formations. When two streams are in parallel motion, but there is a velocity difference between them, a shear layer forms. The shear layer is generally unstable, in that a small perturbation, once formed, will continue to grow.

Nanostructured semiconductor materials developed in recent years, such as nanoscale silicon, porous silicon, and quantum wire/quantum dot structures of III-V compounds, are of great interest to the scientific community and semiconductor industry. These tiny structures possess new optoelectronic properties and have the potential to make significant impacts on light-emitting devices and sensors in optoelectronic technology (see figure below, left). Our Monte Carlo computer simulation of such structures helps reveal the possible outcome of surface nanostructures that can be formed on a Si surface irradiated with energetic heavy ions (see figure below, right).



Chemical deposited structures on a semiconductor surface (left) and Monte Carlo simulation of nanostructure formation on an ion-irradiated surface (right)

Atomistic Simulation of Shallow Junction Formation in Silicon

Shallow junction formation in silicon chips is a hot topic in the semiconductor industry. Reduction of power consumption of integrated circuits and an increase of the device performance would drastically reduce the sizes of circuits and, therefore, would necessitate a similar reduction for the depth of the *p-n* junctions. However, the experimental preparation of "shallow junctions" encounters the space charge problem that exists for traditional accelerator-based ion implanters. One way to bypass the space charge limitation is to prepare and to use large clusters of the implanted elements, with a high mass-to-charge ratio.

Molecular dynamics and Monte Carlo methods have been widely used to reveal a detailed picture of the defect and displacement accumulations and have assisted in understanding the complex processes occurring during ion implantation and the following thermal annealing processes.

Models of Highly-Charged Ion Interactions with Solid Surfaces

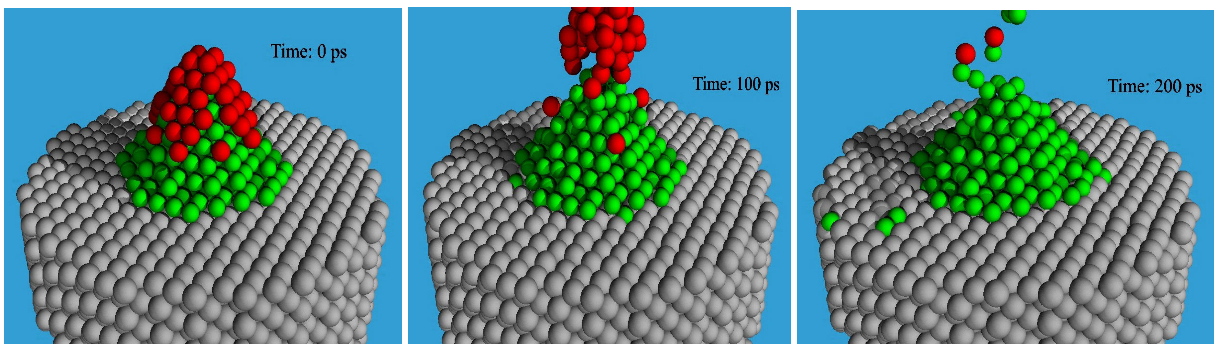
Xe^{q+} where $q \gg 1$ is a highly-charged ion (HCI) in which many electrons are stripped off the Xe atom by energetic plasma processes. Such ions could have a very high potential energy, sometimes much higher than their kinetic energies. If the HCI collides with a conductive or insulating surface, it resonantly attracts electrons and is partially or fully neutralized at the immediate surface vicinity and creates a so-called "hollow atom" (HA) in which captured electrons occupy the distant Rydberg states, hydrogen-like orbitals with large quantum numbers. After HA embeds into the surface, it starts stripping and losing the electrons again. Such processes initiate X-ray and Auger electron emission.

The available experimental results of HCI sputtering of insulating and metal surfaces are rather limited; therefore, MD modeling of the HCI impacts on metals and surface damage is highly desirable. This is a challenging task, as it involves embedding electronic transfer processes into a classical MD code, with an accuracy that could explain experimental results.

Our MD studies of HCI interaction with targets were mainly aimed at obtaining the details of the neutralization processes, HA formation, and the sputtering yield of Si surfaces exposed to Xe^{44+} ions.

Atomistic Models of RF Vacuum Breakdown

As part of a study of RF vacuum breakdown in linacs, an MD model of a Cu (100) surface containing a nano-scale tip has been developed. The bell-shape tip was placed on the top of a Cu surface that was simply cut out of a face-centered-cubic Cu lattice. The Cu atoms interact via a many-body embedded-atom method with a potential derived from a second-momentum approximation of the tight-binding scheme. A cylindrical surface model, containing ~ 10^4-10^5 atoms in the central MD zone, has been adopted while the continuum mechanics calculations have been extended to many times larger volume. A new physical effect—large cluster field evaporation—has been calculated for the first time and could be used for mitigation of the RF vacuum breakdown in linacs. The figures below show the field evaporation process over a time scale of 200 ps predicted in our MD study.



Model simulation of Cu (100) surface with nanoscale tip. (a) Initial position of the Cu tip on a Cu surface that was used for simulation at different temperatures and various electric fields. Red color shows those atoms on the upper part of the tip that were charged with +e charge, and green color depicts the rest of the tip, which was not charged. Gray-colored atoms belong to the surface of Cu (100) and have no electric charge. (b) Snapshot of a Cu tip after 100 ps. (c) The final position of the tip, after 200 ps.

Modeling of Fuel Irradiation Behavior for the RERTR Program

The RERTR program is aimed at development of high-density, low-enriched-uranium (LEU) alloy fuels to replace fuels with high-enriched uranium. An experimental fuel matrix was developed, and the results from the initial irradiations in the Advanced Test Reactor (ATR) are being assessed. The modeling subtask is fully integrated with this experimental program. A near-term goal of the modeling task is to provide an analytical interpretation of swelling in these materials as a function of irradiation condition and fuel composition. The modeling task is aimed at developing mechanistic models describing specific phenomena (e.g., irradiation-induced recrystallization), as well as the development of a fuel performance code (DART) for in-reactor simulations of a full-scale fuel plate (or tube or rod).

Theory of Irradiation-Induced Recrystallization

Irradiation-induced recrystallization appears to be a general phenomenon in that it is observed to occur in a variety of nuclear fuel types, e.g., U-xMo, UO_2, and U_3O_8. We have developed a theory that results in an expression for the fission density at which irradiation-induced recrystallization is initiated. The initiation of recrystallization is to be distinguished from the subsequent progression and eventual consumption of the original fuel grain.

The theory is based on the evolution of a cellular dislocation network upon which impurity atoms and fission gas bubbles nucleate and grow. The model assumes that most fission gas bubbles contain precipitates in accordance with experimental observation. The bubble-size distribution is calculated as a function of fission rate and temperature. Bubble coarsening occurs because of radiation-induced coalescence of bubbles without bubble motion. Precipitates that are greater than a critical size effectively pin triple-point nodes of the resulting subgrain network, thus eliminating them as potential recrystallization nuclei. Recrystallization is induced when the density of viable recrystallization nuclei equals the equilibrium number of nuclei calculated based on thermodynamics. The basic entities out of which these nuclei are composed are interstitial loops. The resulting expression for the fission density at which recrystallization is predicted to initiate is athermal and weakly dependent on fission rate. The calculated dislocation density, fission gas bubble size distribution, and fission density at which recrystallization first appears follow the trends of the measured quantities.

Fission Gas-Bubble Behavior in Amorphous Uranium Silicide

The aluminum dispersion fuel developed at ANL, U_3O_8, is used in many research and test reactors around the world. This fuel is amorphous under irradiation. In addition, at least one of the components of the reaction product formed as a result of interaction between the new candidate fuel U-10Mo and Al is also thought to be amorphous. A model for the behavior of fission gas in irradiated amorphous materials has been developed. The model proposes that gas bubble nucleation occurs within shear bands initiated around free volume regions. Small gas-atom clusters that form within these regions are susceptible to dissolution by forces generated by the plastic flow of material around the cluster. The bubble coarsening process depends on the materials viscosity and on irradiation-induced re-solution. The bubble distribution eventually reaches a point where larger bubbles from the tail of the evolving lognormal size distribution begin to contact the more numerous nanometer-sized bubbles from the peak region. This condition defines the knee in the swelling curve. The fission density at which the knee occurs is a function of fission rate.

Subsequent to the formation of the knee the above process repeats, but now the evolution of the nanometer-size bubble distribution is overlaid on the pre-existing larger bubble population. Both bubble distributions coarsen due to the accumulation of fission gas as the irradiation proceeds. Eventually, a secondary knee point is achieved, and a second population of bubbles in the tenths of a micron size range is generated. Thus, as the population of larger bubbles formed at the primary knee has coarsened, a bimodal population of bubbles is observed subsequent to the secondary knee point. The validity of an evolving lognormal bubble-size distribution in an irradiated amorphous material that coarsens by bubbles growing into each other is supported by the observation of nanometer-sized helium bubbles that form, grow, and coalesce during low-temperature helium implantation in an amorphous alloy. Calculations for the behavior of the knee, swelling, and the fraction of gas in bubbles in irradiated U_3Si_2 intermetallic compounds follow the trends of the measured quantities.

Effect of Irradiation-Induced Gas-Atom Re-solution on Grain-Boundary Bubble Growth

The rim region of high-burnup fuels as well as the recrystallized regions of the new candidate uranium-alloy fuels (e.g., U-10Mo) is characterized by an exponential growth of intergranular porosity. In particular, the understanding of the dynamics of irradiation-induced recrystallization and subsequent gas-bubble swelling requires a quantitative assessment of the nucleation and growth of grain-boundary bubbles. Calculations of bubble growth on the grain boundaries of irradiated nuclear fuels at relatively low temperatures were performed under the assumption that these bubbles are not appreciably affected by irradiation-induced gas-atom re-solution. In contrast, matrix bubbles are strongly affected by this bubble shrinkage mechanism and are generally two to three orders or more of magnitude smaller than the grain-boundary bubbles. A variational method has been derived to calculate diffusion from a spherical fuel grain. The junction position of two trial functions is set equal to the bubble gas-atom knockout distance. The effect of grain size, gas-atom re-solution rate and diffusivity, gas-atom knockout distance, and grain-boundary bubble density on the growth of intergranular bubbles has been studied, and the conditions under which intergranular bubble growth occurs have been elucidated.

Thermomechanical Analysis of Dispersed and Monolithic Fuel

A collaboration agreement between ANL/DOE and CNEA Argentina in the area of LEU advanced fuels has been in place since October 1997. An annex concerning DART code optimization has been operative since February 1999.

During this past year, the thermal FASTDART version was assessed to be an adequate tool for modeling the behavior of LEU U-Mo dispersed fuels under irradiation against RERTR irradiation data. The FASTDART thermal subroutine is able to calculate, at each time step, the maximum temperature point along the z-longitudinal axis, and several temperature values across the meat, from the cladding-meat interface to the meat centerline. Calculated temperatures at each time step are taken into account to derive swelling predictions, reaction layer depths, and volume phase fractions by coupling temperatures to the DART calculus kernel. Reasonable agreement with RERTR irradiation data was found, indicating an adequate DART temperature calculation.

The development of a 3-D thermomechanical version of the code (DART-TM) for modeling the irradiation behavior of LEU U-Mo monolithic fuel was initiated in the past year. The DART-TM thermomechanical code is based upon a pre-existing finite element elastic code, named TermElaS, and on FASTDART, which provides temperature- and irradiation-effect modeling subroutines. Using a given power history, coolant regime data, and fuel plate dimensions, DART-TM calculates at each time step the fission product swelling, the temperature distribution on the nodes of each layer (oxide, cladding, U-Al reaction product and fuel), and the effect of temperature and swelling on stresses and strains. The capability of plotting calculated thermal and stress distributions is also under development.

Modeling of Blood Flow

Formation of atherosclerotic lesions is the leading cause of cardiovascular disease. The complex pulsatile 3-D flow patterns at vascular bifurcations and regions of high curvatures produce aberrant spatial and temporal wall stresses and distributions of blood-borne particulates in localized regions. These regions have high propensity for atherosclerotic lesion formation. Although atherosclerosis is generally considered to be a systemic disease, actual lesion formation is inherently local, being dependent on pathologic interactions of vascular walls with blood and particulate elements, such as monocytes and platelets, circulating in a pulsatile hemodynamic field.

The objective of this two-year project is to build an analytical toolkit that simulates atherosclerotic lesion formation and progression. This toolkit will consist of models for multiphase, 3-D, and pulsatile hemodynamic flows in branched arteries with noncompliant walls, shear-induced deformation of blood-borne particulates, and hemodynamic conditions of cell adhesion to the injured endothelium. The medical benefits resulting from this project will be:

- detailed mapping of localized and temporal hemodynamic parameters, including 3-D shear stress, shear rates, tensile forces, concentrations of different particulates (red blood cells, monocytes, and platelets), and local displacement of vascular walls;

- relative significance of high shear stress in atherosclerotic lesion formation; and

- interactions of blood-borne particulates with the vascular walls and subsequent adhesion to affected endothelium cells.

These benefits will help biomedical engineers and surgeons better manage these important parameters to produce successful treatments and evaluate risk factors.

Thermal and Electromechanics

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Visiting: S.P. Jang[1]

The Thermal and Electromechanics (TEM) Section conducts research and development on new applications in thermal sciences, magnetics, electromagnetics, electrodynamics, superconductivity, and their support technologies. The work, both experimental and analytical, includes (a) developing new and/or improved correlations, prediction methods, and experimental techniques for the design and evaluation of energy-efficient and environmentally acceptable components and processes; and (b) developing and testing components and devices.

The TEM Section receives funding from several diverse sponsors, with the primary source being the U.S. Department of Energy (DOE). Many projects involve collaboration with industry and have informal or formal agreements, such as cooperative R&D agreement (CRADA) relationships. Section members are thus frequently involved with industrial scientists and engineers in these collaborative programs. The Section collaborates with the ET Ceramics Section and with the Materials Science Division in the superconductivity program. Section staff also provide support to the Steam Generator Tube Integrity Program, sponsored by the Nuclear Regulatory Commission (NRC).

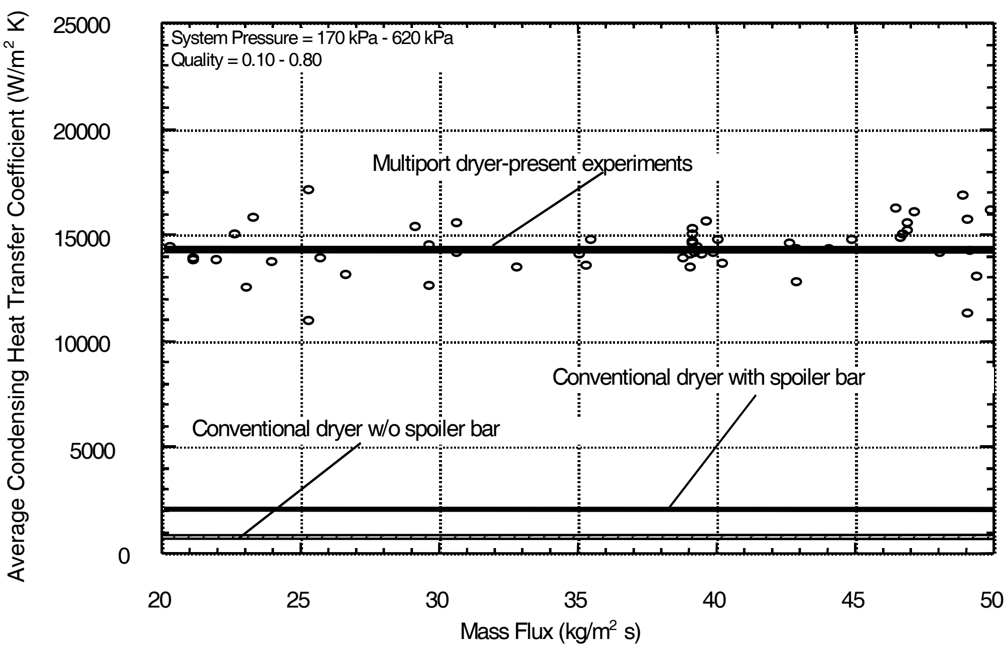
Multiport Cylinder Dryer

The multiport cylinder dryer, ANL's high-performance, small-channel, heat exchanger technology for pulp and paper drying, offers a radically new approach to increasing paper-drying rates. The key feature of the new dryer design derives from the observation that the thick layer of condensate formed around the inner circumference of conventional dryers represents a major resistance to heat flow, thus severely limiting drying capacity. The basic concept of a multiport cylinder dryer uses the flow of steam through "ports," or longitudinally oriented flow passages, close to the cylinder dryer surface. In contrast to conventional cylinder dryers, the "rim of condensate" will be minimized in the multiport cylinder dryer, and the dominant heat transfer mechanism will be forced convection, which is more effective than conduction. Furthermore, the use of multiports in new cylinder dryer designs will increase the surface area, with the result that drying rates will be significantly higher.

The Multiport Dryer Project is funded by DOE's Office of Industrial Technologies to support the American Forest & Paper Association's Agenda 2020. The primary objective of the project is to develop and demonstrate a multiport drying technology that will provide the users of steam-heated cylinder dryers with increased drying rates at competitive retrofit costs.

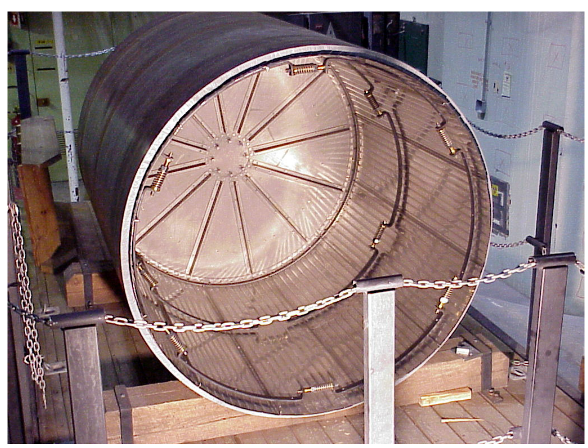
[1] Korea Advanced Institute of Science & Technology.

Results of our proof-of-concept tests are very impressive in that the condensing heat transfer coefficient in a multiport channel is significantly greater than that in a conventional dryer, as shown in the figure below, and the dryer surface temperature profile is nearly uniform. Therefore, ANL's new multiport dryer technology seems to be the best approach for reaching the pulp and paper industry's goal of doubling current evaporation rates. In fact, ANL's multiport dryer team, together with the two industrial partners (Johnson Corp. and Eastern Paper), is at the frontier of drying technology R&D.



Comparison of heat transfer performance of multiport dryers with conventional cylinder dryers. The condensing heat transfer coefficient in the multiport dryer is about seven times greater than that in a conventional dryer with spoiler bars, and about 20 times greater compared than that in a conventional dryer without spoiler bars.

The prototype design for the multiport dryer consists of small components that can be placed inside a dryer through a manhole, and assembled inside. The longest components are 1.5 m, to accommodate typical dryer access space at the manhole in a paper production plant. The design of the multiport dryer insert passed stress analysis at upset system conditions. Multiport prototype dryer inserts have since been fabricated and installed in the Johnson Corp. half dryer. This step confirmed the ability to install modifications through manhole access. The final assembly of the multiport dryer insert in the half dryer is shown in the photograph below.



Fully assembled multiport dryer insert in Johnson Corp. half dryer (approximately 2-m length)

Future work includes development of design correlations, design and fabrication of a prototype multiport cylinder dryer, testing of a prototype multiport cylinder dryer in a full-scale dryer operated at the Johnson Corp. R&D facility for comparison with spoiler bars, and evaluation of the full-scale test results with Eastern Paper and Johnson. With the Eastern and Johnson firms as industrial partners, the transfer of the technology to industry will be facilitated. Successful commercialization of the technology will help DOE and ANL accomplish their missions because the increased productivity will translate into significant improvements in capital effectiveness and financial performance of the country's most capital-intensive industry.

Thermal Management in Heavy Vehicles

Thermal management in heavy vehicles directly or indirectly affects engine performance, fuel economy, safety and reliability, engine/component life, driver comfort, materials selection, emissions, maintenance, and aerodynamics. It follows that thermal management is critical to the design of large (class 6-8) trucks, especially in optimizing for energy efficiency and emissions reduction. With the trend toward more powerful engines (up to 600 hp), more air conditioning, more stringent emissions requirements, and additional auxiliary equipment, the heat rejection requirements of large trucks can be expected to grow substantially (an estimated 40-60%) in the near future. In addition, engine performance requirements are expected to increase, along with a demand for longer component life, reduced maintenance, and improved driver comfort and safety. The challenge will be to design higher-performing thermal management systems that occupy less space, are lightweight, and have reduced fluid inventory.

The Section is engaged in a study of thermal management for heavy vehicles funded by the DOE Office of Transportation Technologies, and Office of Heavy Vehicle Technologies (OHVT). The work follows a roadmap developed after a Section-organized DOE workshop on truck thermal management in October 1999. The approach is to improve the efficiency of heavy vehicles from a thermal management viewpoint by investigating use of phase-change heat transfer, nanofluid coolants, and evaporative cooling to enhance air-side heat rejection, and by operating the coolant at higher temperatures. Work for OHVT also includes a collaboration with Tufts University to investigate the feasibility of regenerative shock absorbers to recover energy.

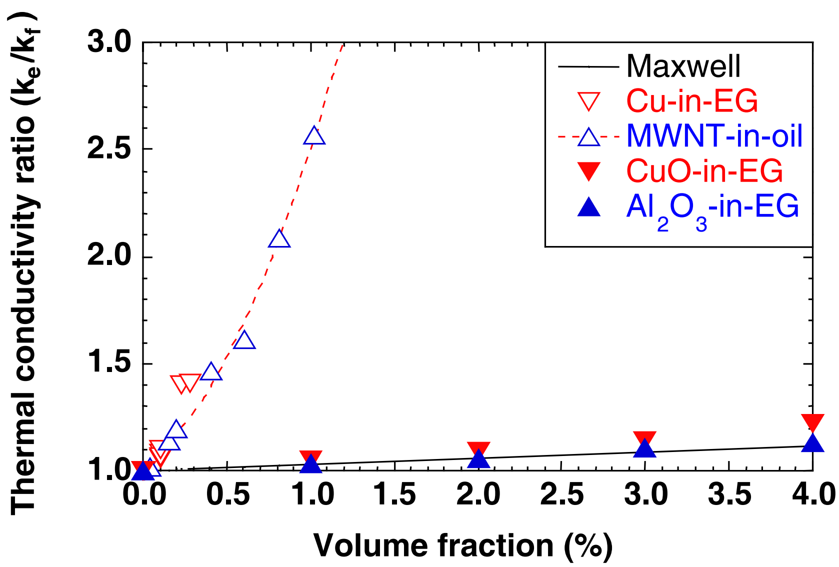
Nanofluids

A new class of heat transfer fluid, called "nanofluids," has been discovered by the Section. Nanofluids are engineered by dispersing nanometer-size solid particles in traditional heat transfer fluids to increase thermal conductivity and heat transfer performance. Experiments conducted by the Section have found that the improvement in heat-transfer properties of several nanofluids is significantly greater than that predicted by existing theory. This represents a fundamental discovery in basic heat transfer.

Nanofluids can be used to improve thermal management systems in many applications, including heavy vehicles. Also, thermal management is becoming one of the key enabling technologies leading to mass production of fuel-cell, electric, and hybrid vehicles, which must operate at temperatures significantly lower than conventional internal combustion engines. Therefore, there is a strong need to develop advanced heat transfer fluids with significantly higher thermal conductivities and improved heat transfer than are presently available and to transfer this technology to the automotive industry.

This work received initial DOE support from the Office of Heavy Vehicle Technologies. More recently, it has also received support from the DOE Office of Basic Sciences. As part of the effort to develop nanofluids, ANL has established a CRADA with Valvoline, Inc.

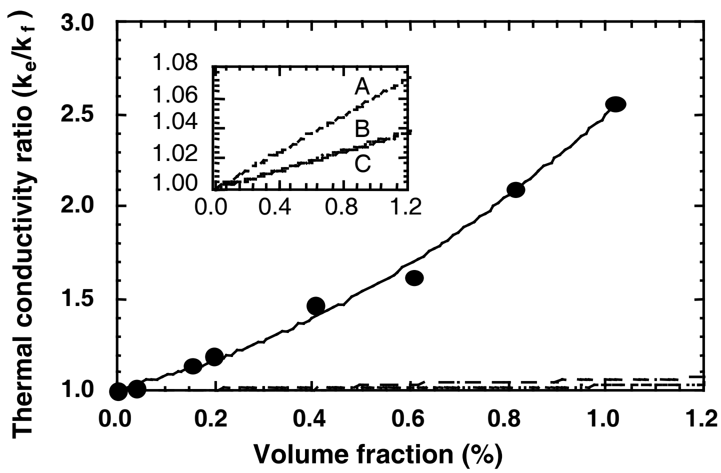
Efforts within the TEM Section have focused on measuring and characterizing the thermal and flow properties of nanofluids as a function of particle material, size, and loading. Earlier research with metallic nanofluids containing <10-nm-diameter Cu nanoparticles dispersed into ethylene glycol have demonstrated that at very low volume fractions of nanoparticles, thermal conductivity can be substantially enhanced over that of the base fluid and of oxide nanofluids containing CuO or Al_2O_3 nanoparticles of average diameter 35 nm, as shown in the figure. This is an unexpected result because established theory predicts no effect of either particle diameter or particle conductivity on nanofluid conductivity.



Thermal conductivity enhancement of copper, copper oxide, and alumina particles in ethylene glycol (EG). Also show are the enhancement measured for multiwalled nanotubes (MWNT) in oil and predicted by Maxwell's theory.

More recently, nanofluids containing carbon nanotubes were produced. Experimental results have demonstrated that nanotubes yield by far the highest thermal conductivity enhancement ever achieved in a liquid: a 150% increase in conductivity of oil at ~1 vol.% for 25-nm nanotubes versus only 40% at 0.3 vol.% for 10-nm copper nanoparticles in ethylene glycol. Interestingly, the thermal conductivity enhancement with the nanotubes is an order of magnitude higher than predicted by existing theories. Furthermore, the measured thermal conductivity is nonlinear with nanotube volume fraction, while all theoretical predictions clearly show a linear relationship (inset of next figure).

Many exciting experimental results have been reported worldwide since the pioneering theoretical work of the TEM Section established this field almost a decade ago. The key features of nanofluids discovered so far include thermal conductivities far above those of traditional solid/liquid suspensions, a nonlinear relationship between thermal conductivity and concentration in the case of nanofluids containing carbon nanotubes, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux. Each of these features is highly desirable for thermal systems and together make nanofluids strong candidates for the next generation of liquid-based coolants. These discoveries also clearly show the fundamental limits of conventional heat conduction models for solid/liquid suspensions. The necessity of developing new physics/models has been recognized by our team. Several mechanisms that could be responsible for thermal transport in nanofluids have been proposed: (1) the motion of the nanoparticles, (2) molecular-level layering of the liquid at the liquid/particle interface, (3) ballistic heat transport in nanoparticles, and (4) the effects of clustering of nanoparticles.



Measured (solid circles) and predicted (dotted lines) thermal conductivity enhancement for nanotube-in-oil nanofluids. Because all calculated values are almost identical at the low volume fractions, some of the calculated values are reproduced on an expanded scale in the inset, where line A = Hamilton-Crosser correlation, line B = Bonnecaze & Brady correlation, and line C = Maxwell theory.

A new project, initiated in July 2000 with the support of the DOE Office of Science and Office of Basic Energy Sciences, is focused on discovering the key parameters that are missing from existing theories and understanding the fundamental mechanisms of thermal-conductivity enhancement of nanofluids. We have begun exploring the theoretical basis for the anomalously increased thermal conductivity of nanofluids. The structure of nanoparticles in nanofluids is being explored experimentally at Argonne's Advanced Photon Source. In related efforts, Texas A&M University is studying the mobility-enhanced energy transport of nanoparticles, while Rensselaer Polytechnic Institute is undertaking molecular-dynamics simulations of the nanostructure and mobility. From the gathered data, a new model of energy transport in nanofluids, which takes into account the nanoparticle size, structure, and mobility effects on the thermal properties of nanofluids, will be developed at Argonne. This interdisciplinary, collaborative project will explore new frontiers in thermal physics research for the design and engineering of next-generation coolants. Nanofluid research could lead to a major breakthrough in solid/liquid composites for numerous engineering applications, such as coolant for automobiles and supercomputers. Better ability to manage thermal properties translates into greater energy efficiency, smaller and lighter thermal systems, lower operating costs, and a cleaner environment.

Efficient Cooling in Engines with Nucleate Boiling

Currently, cooling systems in heavy vehicles are designed to use a 50/50 mixture of ethylene glycol and water in the liquid state. The heat sink is ambient air, and most of the heat is transferred in the radiator. The amount of heat rejected in the radiator is limited by current radiator designs that are essentially optimal. In addition, precision cooling with the 50/50 liquid mixture is limited by geometry and liquid properties. One method to increase heat transfer rates for both radiator and precision cooling applications is to design the cooling systems to operate with a boiling fluid under certain conditions and/or in certain areas of the engine.

Heat transfer rates in nucleate-boiling cooling systems can be increased by an order of magnitude compared with conventional, single-phase, forced-convective cooling systems. However, successful design and application of nucleate-boiling cooling systems for engine applications require that the critical heat flux and flow instability not be reached. The objectives of this project are to (a) investigate the potential of two-phase flow in engine cooling applications; (b) experimentally investigate the characteristics of coolant boiling, critical heat flux, and flow instability under conditions of horizontal flow, small channel, and low mass flux; and (c) develop predictive methods for boiling heat transfer, critical heat flux, and flow instability under engine application conditions.

This project is funded by the DOE Office of Heavy Vehicle Technologies and Office of Advanced Automotive Technologies. A Two-Phase Nucleate-Boiling Test Apparatus has been designed and fabricated at ANL, in collaboration with the University of Illinois at Chicago, to study boiling heat transfer, critical heat flux, and flow instability of flowing water, ethylene glycol, and aqueous mixtures of ethylene glycol under heavy-vehicle-engine conditions. Preliminary experiments were performed with water and 50/50 ethylene glycol/water mixture at a system pressure about 200 kPa, mass fluxes of 50-200 kg/m^2s, and inlet temperatures from ambient to 80°C. The experiments show a very high heat transfer rate with both fluids, which is promising for engine cooling applications. A general correlation for heat transfer coefficient has been developed based on data from water, 50/50 ethylene glycol/water mixture, and refrigerants (from previous projects). We found that the boiling heat transfer of 50/50 ethylene glycol/water mixture is mainly limited by flow instability rather than critical heat fluxes, which are usually the limits for water boiling heat transfer. Preliminary tests show that stable, long-term, two-phase boiling flow is possible for the 50/50 ethylene glycol/water mixture as long as the mass quality (vapor mass/total mass) is less than approximately <0.2.

The test apparatus has recently been reconfigured to allow measurement of the component fraction of both the liquid and gas phases by means of a refractometer and a residual gas analyzer. It is difficult for vehicles to maintain the coolant concentration at exact 50/50.

Therefore, we are investigating boiling heat transfer of ethylene glycol/water mixtures at concentrations other than 50/50. Experiments are in progress using mixtures 10% off the ideal concentration, i.e., 40/60 and 60/40 ethylene glycol/water mixtures. The tests will provide essential information for the design of the nucleate-boiling cooling system. Future work will also include experimental investigation with higher-boiling-point fluids, such as pure propylene glycol and coolants under development by manufacturers.

Two-Phase Nucleate-Boiling Test Apparatus without thermal insulation

Small-Channel Evaporator

Only a few studies in the literature report on two-phase fluid flow and heat transfer in compact heat exchangers. Nevertheless, extensive applications exist in the process industries, where phase-change heat transfer allows more compact heat exchanger designs with better performance than those used for single-phase operation. To further the application of compact heat exchangers in the process industries, there is a need to understand the fundamental issues of two-phase flow and heat transfer in small channels representative of compact heat-exchanger flow passages.

Two-phase-flow pressure drop was measured as part of flow-boiling heat transfer studies funded by the DOE Office of Energy Efficiency and Renewable Energy and the Office of Science. Testing was performed with three refrigerants (R-134a, R-12, and R-113) at six different pressures ranging from 138 to 856 kPa, and in two sizes of round tubes (2.46 and 2.92 mm inside diameters) and in one rectangular channel (4.06 × 1.7 mm). We have developed a new correlation for frictional pressure drop for two-phase flow in small channels, taking into account the effects of surface tension and channel size; this correlation is applicable for smooth tubes with hydraulic diameters of ≈3 mm for the three refrigerants tested. The correlation was tested against the experimental data for the three refrigerants; the error was ±20%.

Underhood Thermal Analyses for Off-road Vehicles

In off-highway machines, the separate engine compartment suppresses noise to meet regulations and spectator requirements. The enclosed engine compartment results in higher underhood temperatures, higher cooling heat loads, and increased charge air temperatures. Since higher temperatures can reduce component durability and life, analysis of underhood thermal conditions is important for identification of thermal hot spots and assurance of adequate air cooling. The product development cycle of design-analysis-simulation-test involves numerous iterations to come up with an acceptable design. Thus, rapid and accurate simulation techniques are desirable.

The objective of this study was to develop a 1-D thermal-fluid network model using commercial software (FLOWMASTER). This 1-D model serves as a tool to predict/analyze the interactions of engine structure with air, coolant, and oil loops for machine thermal performance. Accurately modeling the engine thermal system requires both experimental and computational fluid dynamics (CFD) data, with boundary conditions obtained from well-controlled laboratory experiments. About 96% of the fuel energy was accounted for during the tests; 3-D CFD simulations were utilized in determining air flow fields and engine-surface heat fluxes. With the thermal interactions modeled successfully, underhood-temperature predictions agreed within 10% of measurements for different inlet locations and air flow rates.

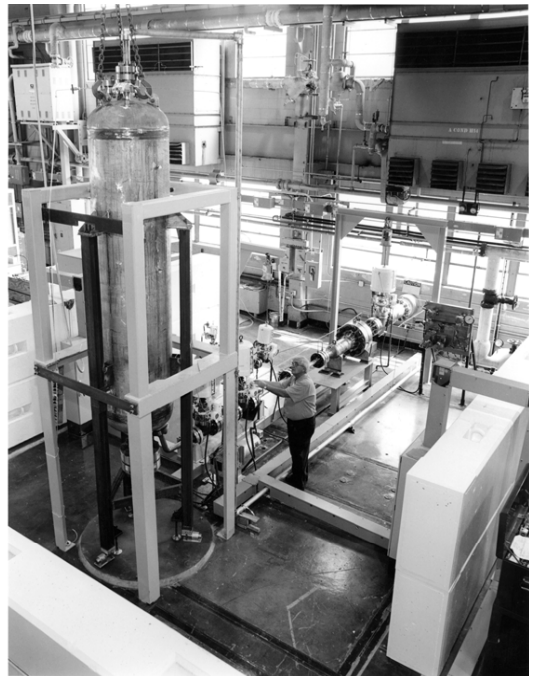
Nuclear Steam Generator Tube Integrity

The ET Division is conducting, for the NRC, a program on the integrity of nuclear steam generator (SG) tubes. A Section staff engineer is participating in the program as lead engineer for the design, fabrication, and operation of two new, large-scale facilities for generating unique data supporting an improved understanding of leakage flows and rupture characteristics in stress-corrosion-cracked (SCC) SG tubes.

The overall objective of this program is to provide the experimental data and predictive correlations and models needed to permit the NRC to independently evaluate the integrity of SG tubes as plants age and degradation proceeds, new forms of degradation appear, and new defect-specific management schemes are implemented. Operation of these facilities has generated insight into the complex behavior of flawed SG tubes.

The facilities include a High-Temperature Pressure and Leak-Rate Blowdown Facility (temperatures up to 343°C, pressures of up to 21 MPa, and pressurized-water flow rates up to 1520 L/min) for conducting tube failure and leak-rate tests under simulated prototype SG operating conditions. The Room-Temperature High-Pressure Facility (pressures up to 52 MPa and flow rates up to 48.4 L/min) is capable of testing at pressures associated with mandated overpressure safety margins.

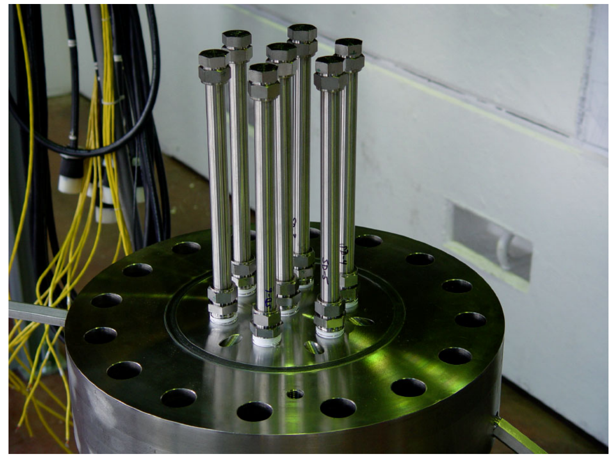
A Model Boiler Facility has been built for the NRC to simulate SCC under prototypic SG thermal-hydraulic and chemistry conditions for the tube/support-plate crevice geometry. The goal is to use this facility to gain a better understanding of the interplay among the tube material, thermal-hydraulic, geometry, and water chemistry conditions that have caused SGs to experience cracking and leaking for more than 20 years. Modeling/analysis has established that the facility will produce prototypic crevice conditions by simultaneously matching both crevice heat flux and temperature.



ANL's steam generator tube pressure and leak-rate blowdown test facility

The model boiler pressure vessel consists of a lower primary reflux boiler chamber, where steam is generated, and a secondary upper chamber, where boiling occurs on the outside of seven SG tubes (0.3-m length), each having a crevice simulator. The reflux boiler chamber is driven by a 40-kW electrical heater that is sized to achieve prototypical heat fluxes across the tubes. The primary side is maintained at desired saturation temperature/pressure by a controller set point on the 40 kW heater, which operates on a bulk-water temperature thermocouple. The secondary side is maintained at the desired temperature/pressure by controlling heat rejection to the ambient air from a finned fan-cooled steam condenser pipe, which uses closed-loop control between a secondary bulk-water temperature thermocouple and a variable frequency/speed drive fan controller. The condenser is a schedule-160, Alloy 800 pipe (4-cm dia, 4-m length) with stainless steel fins brazed to the outside surface, which is divided into three subsections, each having its own motor/fan. The condenser is designed to maintain control of the secondary-side temperature. Primary-side deionized water having a low level of noncondensables is used to maximize the effectiveness of the condensation film heat transfer occurring inside the tubes. The secondary water simulates secondary-side water chemistries of interest (as revealed by autoclave studies on crack initiation and the literature) in

Argonne Model Boiler Facility built for studying stress corrosion cracking of SG tubes pressurized water reactors. Secondary-water chemistry is conditioned and monitored by a continuous bleed/feed system to ensure water chemistry stability and facilitate ease of operation.



Seven capped SG tubes mounted in the top of primary chamber prior to installing the secondary chamber by bolting it to the top flange of the primary chamber.

Ice Slurries for District Cooling

ANL, under U.S. DOE funding, pioneered the development and fostering of ice slurries for district cooling. The cooling capability of an ice slurry pumped to a load can be up to five times greater than that associated with chilled water delivered at the same mass flow rate. This high cooling capacity also allows slurry transmission piping and storage tank sizes to be reduced significantly over that required with conventional, chilled-water cooling systems. Today, both domestic and foreign interests are considering the adoption of this technology for cooling large loads.

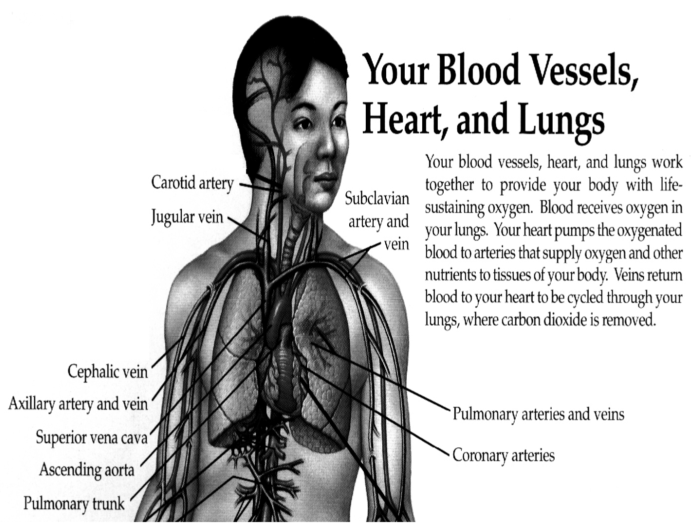
The storage of ice particulate slurry in tanks, however, is complicated because under certain not well understood conditions, the ice crystals will progressively grow together, or agglomerate, making pumping of the slurry from the tank very difficult. It is desirable to store the slurry at the highest packing density possible in order to most effectively utilize the available tank size. Therefore, even if the ice does not agglomerate in the tank, it must be carefully diluted to a packing density that is compatible with pumping it through a pipe delivery network. No reliable means has been developed for tank-slurry extraction or ice-loading control. The ANL Ice Slurry Test Facility is being used in experimental studies on the factors influencing ice crystal agglomeration in ice slurry storage tanks. These studies are also developing methods for minimizing agglomeration and for improving the efficiency and controllability of tank extraction of slurry for distribution to cooling loads.

Ice Slurry Cooling to Induce Protective Heart and Brain Hypothermia

The Section has pioneered the use of ice slurries in a unique biomedical application. Currently, survival from out-of-hospital cardiac arrest is poor, since cells in the brain and heart begin to die within minutes. Similar difficulties also pertain to stroke patients. Many believe the ability of cells to survive ischemia could be significantly enhanced by rapid cooling of the heart and brain, i.e., by resuscitative hypothermia. Despite the potential benefits, few studies have addressed the heat transfer difficulties associated with attempting resuscitative hypothermia without bypass procedures. The Section is collaborating with the University of Chicago Medical School's Department of Emergency Medicine to investigate the use of ice slurries in this process. Initial results indicate that rapid induction of protective hypothermia is feasible in the out-of-hospital environment without the use of complex time-consuming bypass external heat exchangers by using in-body biological heat exchangers cooled with ice particle slurry.

Ice particle slurries can have up to 10 times the cooling capacity of single-phase coolants such as chilled saline. Recent ANL modeling and analysis of brain and heart cooling has shown that external cooling alone cannot achieve the desired fast rate of cooling and suggest that ice slurry cooling of the target areas would be very effective. Furthermore, recent laboratory experiments in ANL's Ice Slurry Research Facility have demonstrated that ice particle phase-change slurries can be engineered with chemicals that are compatible with human tissue and have the desired fluidity. The medical use of slurries for cooling has its technical foundations in ANL's development of ice slurry cooling for buildings. The medical use of slurry is unique and involves many new engineering considerations, including entirely new types of slurry constituents and new methods of production and delivery.

ANL's Ice Slurry Research has developed slurries that are compatible with human tissue and have the needed fluidity to be administered through small-diameter tubing and hypodermic needles. Swine tests using ANL-engineered slurry at the University of Chicago produced heart and brain cooling rates 20 times greater than conventional methods. ANL and the University of Chicago filed three patent applications on making and using slurry for rapidly cooling the heart and brain. Negotiations over intellectual property licensing rights are underway with a private company. We have recently received a five-year grant from the National Institutes of Health to continue development of this technology.



The carotid artery, jugular vein, and lungs are used as in-body ice slurry heat exchangers to achieve rapid targeted cooling of the heart and brain

Brain Cooling Probe for Treatment and Diagnosis

Argonne, in collaboration with the Department of Neurology and Neurosurgery at the University of Chicago, is developing a cooling probe that can be used to induce localized cooling of surrounding tissue in the brain or other organs. This cooling would reduce local cell death, reduce tissue swelling, and measure tissue health.

The probe can cool live tissue 4 to 5°C in a targeted region, measure thermal conductivity of tissue, and diagnose the health of surrounding tissue by changes in cooling characteristics. In work to date, an alpha version of the probe has been designed and built by Argonne, the probe has been used in exploratory animal tests at the University of Chicago, and a patent application has been filed.

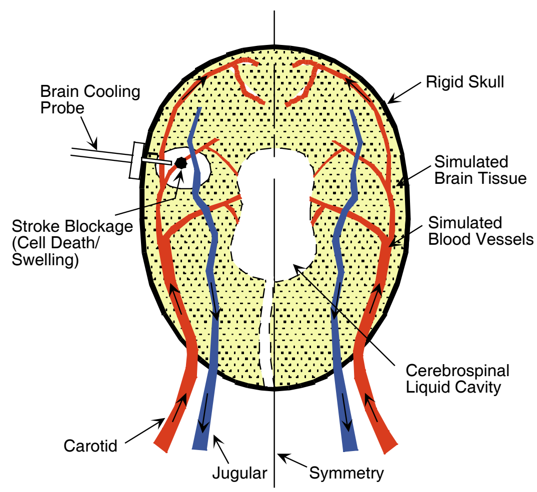
Phantom Head Model to Study Brain Swelling and Cooling

The objective of this project is to develop a phantom head experimental/computational model that simulates brain and skull structural interactions, as well as brain blood flow and heat transfer. Recent accomplishments include the following:

- Developed a design for a phantom head model that uses a glass/silicone replication of the main vasculature of the brain that carries a blood simulant, employs a mixture of open and closed cell foam having the structural and thermal properties of brain tissue to fill voids, and is housed within a rigid skull structure.

- Used medical imaging scans to specify the complex head geometry in computational grids.

- Used computer codes for analysis of brain tissue cooling, magnetic particle guidance in blood vessels, and brain swelling simulations. In particular, the Commix fluid/thermal transport code has been used to model heat transfer between brain probe and brain tissue, and the finite element code ABACUS has been used to predict brain swelling and thermal response.



Phantom head experimental model

In work in progress, a region of brain swelling is being simulated by inflating a small bladder and modeling the shifting of brain matter and resulting stresses due to skull confinement with the ABACUS code. Also, the cooling probe developed by Argonne and the University of Chicago will be inserted in the simulated brain, and the cooling fronts will be measured and then modeled by computer analysis.

Magnetic Nanoparticles for Drug or Radiation Delivery

Argonne and the University of Chicago are collaborating to develop what could be a very versatile drug delivery system. It is based on the idea that small magnetic particles can be engineered to carry therapeutic chemicals or radiation for tumor control. Because they are magnetic, the particles can be guided by an external magnetic field and can be forced to move with or against the flow of blood in veins or arteries or held in a fixed position once they have been conveyed to a target organ, and possibly retrieved when treatment has ended.

The experimental activities are being conducted in parallel with the development of computational models supporting future clinical use of magnetic particles. For the latter, we are using computerized tomography or magnetic resonance scans to generate a computational grid representing some tumor-related problem, generating block elements for a computational fluid dynamics code from clinical data, and modeling, as a moving wall, trapped particle pile growth at the target as a function of time.

Flywheel Energy Storage

Past work in the Section explored the use of high-temperature superconductors (HTSs) in magnetic bearing applications, and various techniques were developed to produce an HTS bearing with extremely low rotational loss. We have demonstrated such a bearing with a rotational drag more than two orders of magnitude lower than that of a conventional magnetic bearing and several orders of magnitude lower than that of mechanical bearings. With this bearing, an energy-efficient flywheel could be constructed with a bearing loss of <2%/day (including parasitic power to cool the HTS). Such a flywheel has potential for use in diurnal utility energy storage or as a replacement for batteries in an electric vehicle. Several patents on this bearing/flywheel concept have been granted and several more are in process. The HTS bearing work benefited from collaboration with Commonwealth Research Corp. The Section is collaborating with Boeing to develop a flywheel energy-storage device.

Fault-Current Limiter

The Section has worked with S & C Electric (a leading U.S. manufacturer of high-voltage switching and protection devices for electric power industry) to jointly carry out a feasibility study on a passive superconducting fault-current-limiter (FCL) concept known as the superconductor shielded core reactor (SSCR). In this study, S & C identified three specific applications and provided electrical specification for the FCL. ANL has designed and constructed a scaled model (480 V/60 A) of an SSCR that uses a melt-cast processed superconductor tube of Bi(Pb)-Sr-Ca-Cu-O (BSCCO). While this BSCCO tube appears to be working, there is evidence that the newly emerging melt-textured bulk Y-Ba-Cu-O (YBCO) may have superior properties (such as critical current density and mechanical strength). Furthermore, we expect that in the near future, relatively large melt-textured YBCO rings can be manufactured at relatively low cost (comparable to that of melt-cast processed BSCCO tube).

Permanent Magnet Fabrication

Another Section project, funded by DOE’s Office of Advanced Automotive Technologies, is improving the production process for low-cost, high-energy-product permanent magnets. Emphasis is being placed on reducing the weight of vehicles. Electric motors are in use in many vehicle systems and offer a significant opportunity for weight reduction. If traction motors are used for electric drive, the opportunity for weight reduction will be even greater. One of the most promising ways to reduce weight in an electric motor is by increasing the energy product of the permanent magnets used in the motors. A higher energy product in the permanent magnet will not only reduce the weight of the permanent magnet, but will also reduce by a similar fraction the weight in the balance of the motor in obtaining the same torque. Energy products in permanent magnets are currently limited by manufacturing processes and are far below the theoretical potential. A further barrier to a more widespread use of these permanent magnets in vehicles is their cost of production. The same process that we have proposed for increasing the energy product is also likely to significantly decrease the manufacturing cost.

The remanent magnetic field is one of the factors in the energy product of a permanent magnet and can be increased by improving the alignment of the magnetic domains before the permanent magnet is sintered. One method to accomplish this is with higher magnetic fields during the pressing process. These magnetic fields are limited in present manufacturing processes by the cooling and structural requirements of pulsed electromagnets. To obtain higher magnetic fields, the use of superconducting magnets will be required. The use of a superconducting magnet will eliminate the joule-heating costs in the pressing operation, but the cost of electricity (probably several cents per kilogram) is a very small fraction of the total cost in manufacturing a permanent magnet. Much greater savings would result from a better uniformity of orientation in the final product. When the particles are aligned in the magnetic field, they tend to follow the magnetic field lines. These lines are distorted by the self-demagnetizing factor of the magnetized particles, i.e., the magnetic field lines generated by the piece being fabricated. With an external magnetizing field of 3-4 T, a self-demagnetizing field of even 1 T is a significant distortion. If a magnetizing field of 8 T or higher were used, this self-demagnetizing field becomes a smaller fraction of the total, and the block being magnetized becomes more uniform. In terms of the manufacturing process, the yield of high-energy-product pieces from a magnetized block would increase significantly, and thus the cost of the manufactured permanent magnet should significantly decrease.

Permanent-magnet manufacturers do not presently use superconducting magnets because they do not cycle quickly. A reciprocating feed will allow the use of superconducting magnets that need not cycle at a production rate equal to that of the present system using electromagnets. We have constructed a large-bore 8-T magnet and associated powder press. We have already pressed NdFeB powder that after sintering has a higher energy product than that obtainable by manufacturers with conventional techniques. We are working with a major U.S. manufacturer of NdFeB permanent magnets to optimize the production process with their powders. Our next major task is to make near-net-shape permanent magnets, which will further reduce the cost of manufacturing. We will also carry out an economic analysis of the superconducting manufacturing system and compare it with the conventional industrial system.

Sensors, Instrumentation, and Nondestructive Evaluation

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The Sensors, Instrumentation, and Nondestructive Evaluation (SI&NDE) Section conducts research and development related to instruments and NDE techniques for characterization of materials and determination of system parameters related to different energy systems (including fossil, transportation, and nuclear). The Section also develops sensors and technologies for non-energy-producing applications such as homeland security and biomedical engineering.

Energy System Applications

The many projects summarized below give a clear indication of the breadth of our SI&NDE work on diverse energy system applications. These projects are mainly funded by three Department of Energy (DOE) offices: Fossil Energy, Transportation Technologies, and Power Technology.

DOE Office of Fossil Energy

NDE for Structural and Functional Materials

This work is part of the overall materials technology development within the area of Fossil Energy Advanced Research and Technology Development. The focus is on development of NDE methods for structural and functional ceramic materials used in fossil energy systems.

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[10] Kansas State University.
[11] Northern Illinois University-DeKalb.

During the past two years we have been working on NDE technology for high-temperature membranes that would allow oxygen and hydrogen production from coal combustion. These separation membranes must be of high uniformity and structural integrity and must have tight seals at joints. As production of these membranes comes closer to reality, NDE methods are necessary to assure uniformity and product reliability. This work is being conducted in cooperation with Los Alamos National Laboratory and Ceramatec Inc. The NDE efforts have been directed toward assessing three-dimensional (3D) X-ray computed tomography using the microimaging station at the ANL Advanced Photon Source (APS). In cooperation with the University of Chicago, sections of various H_2 separation membranes have been studied. The primary emphasis was on the joints necessary to make the H_2 and O_2 separation membranes feasible. The results from the APS microimaging station clearly show that this method has the spatial resolution necessary for these types of analyses.

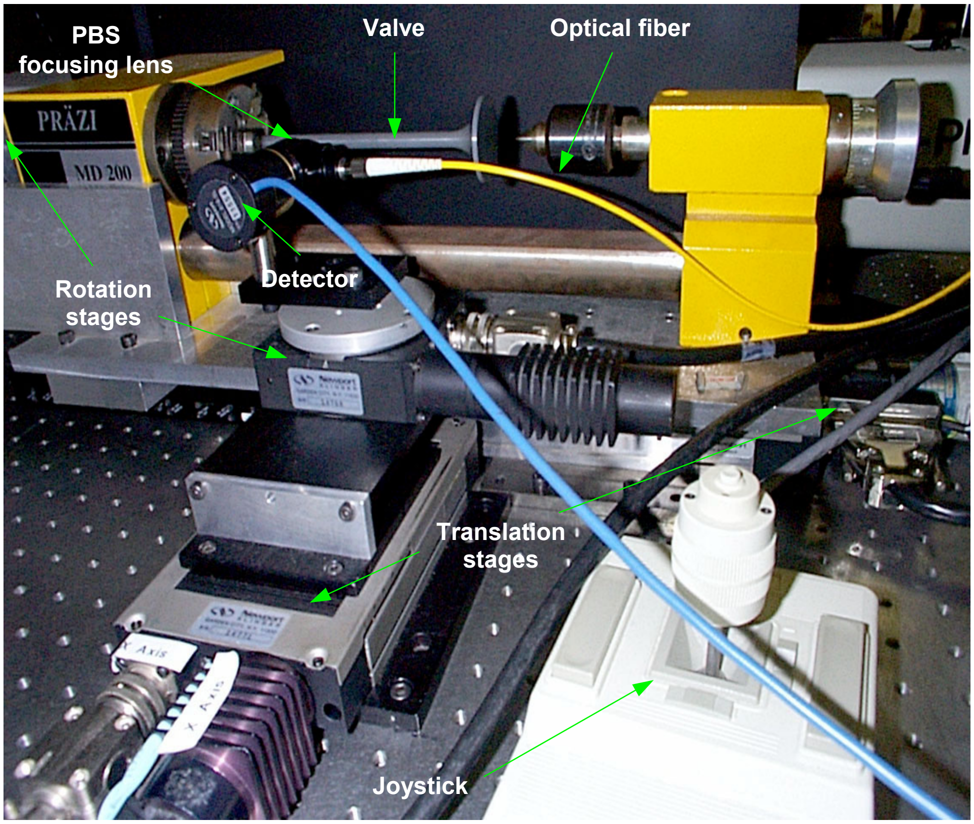
NDE for Oxide-Based Ceramic Composites

The work in this effort is directed toward developing NDE technology for oxide-based ceramic matrix composites for use in advanced fossil energy systems. Such materials offer lower costs and potentially longer life. However, oxides are known to be susceptible to thermal shock and creep. Thus, high-temperature thermal protection systems have been developed. The detection of potential problems such as delaminations and materials degradation thus becomes important. This work is being done in cooperation with Siemens-Westinghouse Power Systems and Composite Optics Corp. Special NDE technologies being developed include time-dependent heating for thermal imaging, air-coupled ultrasonics, and regional X-ray computed tomography.

DOE Office of Transportation Technologies

NDE for Ceramic Valves for Diesel Engines

As part of the Heavy Vehicle Propulsion System Materials Program, DOE Office of FreedomCAR and Vehicle Technologies, NDE technologies are being developed for inspection/evaluation of ceramic valves. This program is a cooperative program with the Caterpillar Technical Center. In this program, silicon-nitride ceramic valves are being machined and evaluated under rig/engine test conditions by Caterpillar. The ANL effort is to develop NDE technologies that will detect and quantify processing- and operation-induced surface/subsurface damage in the ceramic valves. Laser scattering is the primary NDE method. A fast, automated laser-scatter NDE system (photograph below) was developed to scan entire valves. This system has two rotation and two translation stages to align and focus the laser beam on the valve surface during the scan, and the resulting two-dimensional scattering image is used to identify the location, size, and relative severity of subsurface defects/damage. Laser-scattering images were obtained for several bench-tested silicon-nitride valves. The NDE results established the detection sensitivity for two types of defect/damage: (1) surface contact damage and (2) subsurface porosity and pre-spallation due to valve processing.

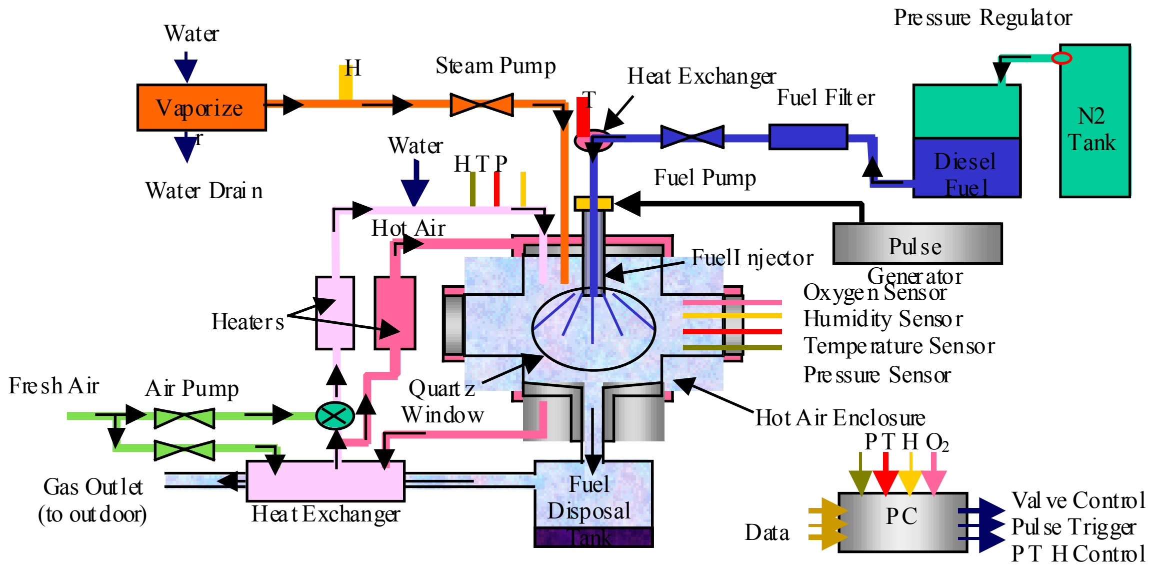


Photograph of automated laser-scattering system for scanning full ceramic valves

Diesel Fuel Reformer

This new program is a joint effort between ET and the Chemical Engineering Division. The objective is to develop a device that will convert diesel fuel into hydrogen-rich gas on board a heavy-duty vehicle in a small fuel processor. The technical approach consists mainly of (1) evaluation of various engineering issues that need to be addressed with regard to diesel fuel reforming and (2) development of a fuel/exhaust-gas mixing device that will optimize diesel-fuel reforming. The main engineering issues are how to avoid pre-ignition and coke formation and how to achieve catalyst stability.

In FY 2003, we completed the test facility design and started construction. The facility, shown in the schematic diagram below, consists of a fuel-injection assembly, simulated exhaust-gas-generating system, and fuel-exhaust-gas mixing apparatus. The proposed sensors and instrumentation for process measurement and control have been identified. We have also established a collaboration with International Truck and Engine Corp., which will provide ANL with diesel-fuel injectors and a fuel-injection controlling system. Fuel/exhaust-gas mixing tests will be conducted in FY 2004 to optimize the design of the mixing device. Numerical simulation will also be performed.



Schematic diagram of the diesel-fuel/air/steam mixing test facility

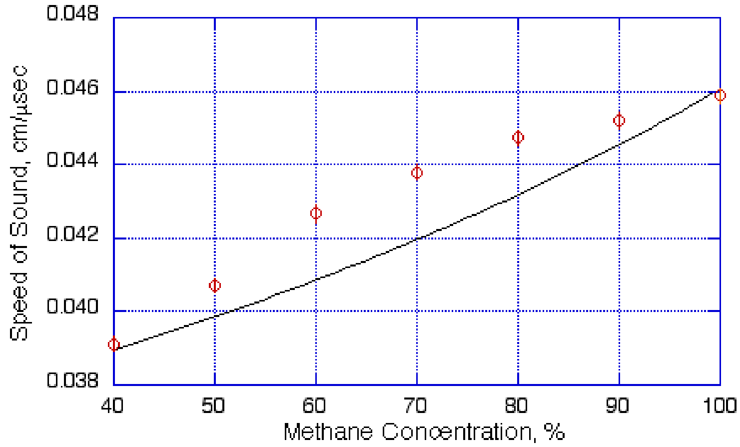
Acoustic Fuel Vapor Sensor

This program, completed in FY 2002, was a joint effort among ANL, Ford Motor Co., and Northwestern University. The objective of the ANL effort was to develop a low-cost, fast-response, acoustic-based fuel-vapor sensor that could be used in the harsh automotive environment to measure or monitor the fuel-vapor mass flow rate and to detect variations in fuel-vapor composition.

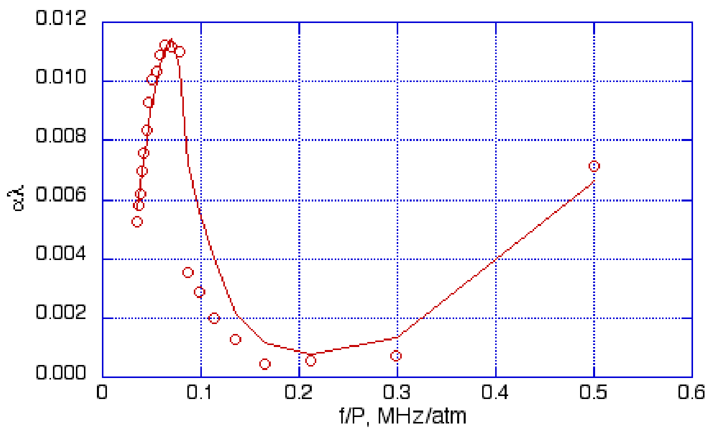
We initially focused on evaluating the use of the (1) speed of sound (SOS) to estimate the fuel gas composition and (2) acoustic relaxation spectra to characterize the fuel-gas composition. A laboratory prototype of the sensor was built and tested with methane gas. The basic design consists of two 0.5 MHz transducers operating in a pitch-catch mode. Gated sine waves of a fixed frequency (0.5 MHz or its harmonics) are propagated in a narrow flow channel, and their reflections are analyzed for variations in amplitude and time of flight, from which attenuation and speed of sound are measured. The prototype uses a high-pressure vessel to house the transducers and the flow cavity. To obtain the acoustic relaxation spectra, we vary the gas pressure because the attenuation in a gas depends on the ratio of acoustic frequency over the gas pressure.

The figure below shows the SOS in methane/nitrogen mixtures. The solid line represents the calculated values based on an isentropic model. Although the measured SOS values (circles) are higher than the calculated curve, we concluded that the SOS can be used to predict the methane concentration in nitrogen gas. This conclusion is justified as long as the carrier gas mixture has a fixed composition so that the mixture of methane and carrier gas can be considered as a binary gas.

Acoustic relaxation spectra of methane and methane/nitrogen mixtures were predicted by a theoretical model developed by Northwestern. We confirmed the model prediction qualitatively. The next figure shows the dimensionless attenuation (attenuation times wavelength, αλ) versus the frequency/pressure ratio (f/P) for 50% methane in nitrogen. The solid line represents the best-fit curve to the data. Clearly, a relaxation peak exists around f/P = 0.07 MHz/atm under ambient conditions, which is somewhat lower than the model prediction (>0.1 MHz).



Speed of sound in methane/nitrogen mixtures
(solid line calculated using isentropic model)



Dimensionless attenuation versus frequency/pressure
in 50% methane in nitrogen

DOE Office of Power Technology

NDE for Ceramics in Microturbines

The concept of distributed energy systems using small gas turbines (< 500 kW_e) is being aggressively pursued by DOE. To obtain the desired efficiency target of >45%, these microturbines need reliable ceramic components in the combustor section. We are testing monolithic ceramic components for the radial flow rotors (mainly silicon nitride) and oxide ceramic composites for the combustor. An issue with the silicon nitride rotors is oxidation. As with nonoxide composites, an environmental barrier coating (EBC) is being developed to protect the rotors. Initial EBCs were made of tantalum oxide. Of concern with these coatings are spallation and erosive wear. We are developing NDE technology for assurance of low-cost, high-yield production of monolithic rotors, prediction of spallation of the EBCs, and characterization of the oxide composites. The NDE technologies under development include fast, high-spatial-resolution X-ray computed tomography for analyzing radial flow rotors, laser back scatter for determining the condition of the EBC coatings, and thermal imaging and air-coupled ultrasonic methods for determining the condition of the oxide composites.

NDE for Ceramics in Stationary Gas Turbines

As part of the DOE Office of Power Technology's Program on Advanced Materials, ANL is a subcontractor to Solar Turbines, Inc., which is developing and evaluating composite ceramics for application to stationary gas turbines. The ANL effort is directed toward development of NDE methods for the ceramic materials being developed and tested for the Centaur H and Mercury gas turbine engines under development for stationary generation of electric power.

The evaluated ceramics include monolithic materials for turbine blades and nozzles and ceramic matrix composite (CMC) materials for combustor liners and transition ducts. The monolithic materials are Si_3N_4, and the CMC materials are both nonoxide (SiC/SiC) and oxide (Al_2O_3/Al_2O_3). The ANL effort includes development of NDE methods to determine the thermal properties (thermal diffusivity) of the CMC materials and obtain full-field mapping of thermal properties, to detect delaminations of the CMC materials, and to detect surface cracks and subsurface cracks in the monolithic materials. We will also attempt to correlate the NDE data with predicted component performance.

Most recent work has focused on composite ceramics. The NDE method based on measurement of thermal diffusivity is now being used to accept/reject ceramic components for use in gas turbines. Full-sized liners (0.3 and 0.8 m in diameter and 0.2 m long) have been successfully analyzed with the thermal imaging method. Tests have been conducted before service and after over 14,000 h of engine test time.

In the thermal imaging efforts, we have acquired a very-high-speed thermal imaging camera and developed the capability for one-sided data acquisition for complex-shaped components. In addition, a new air-coupled ultrasonic system has been set up, and data have been correlated with the infrared image data. The air-coupled ultrasonic system operates at

400 kHz and has a fast scan speed (>10 cm/s). We have added the capability to handle large cylinders, 0.3 and 0.8 m in diameter, so that full-scale turbine engine components can now be examined. Results to date show excellent correlation to the thermal image data. Therefore, we can replace the previous X-ray computed tomography scan method for corroboration of data. However, X-ray computed tomography data are still obtained to establish through-wall information.

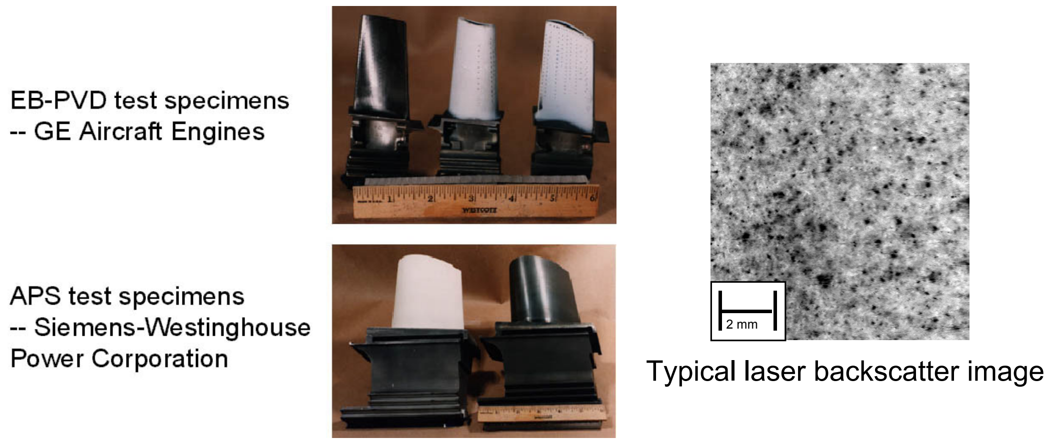
NDE to Detect Machining Damage in Monolithic Ceramics

As part of the DOE Heavy Vehicle Technology Materials Program, ceramic valves are being developed in a cooperative program with Caterpillar Technical Center. The program involves study of NDE methods to detect and quantify machining-induced damage on valves. The objective of this project is to develop NDE technology and methods that will determine the extent of machining-induced damage in monolithic ceramic materials, primarily Si_3N_4. In this work, the Caterpillar Technical Center is producing ceramic specimens under varying machining conditions, including wheel speed, grit type and size, grit-to-wheel bond materials, material removal rate, and downward force. The NDE method under development uses low-power lasers and special optical components in both the input and detector train. Data acquisition is totally automated. The detector train further consists of two specially fabricated optical detectors to provide data from two numerical apertures. Polarization of the reflected light is also accounted for in the detector train. The output from the two detectors is either summed or divided, and each resulting output is used to form an “image” by a raster scan motion of the part under study. The resulting “image,” a speckle pattern of gray levels, is then manipulated by digital image processing. Specifically, the image is viewed as a two-dimensional array of values from which statistical data are derived. In this case a standard deviation and a mean value are determined for each image. Dividing the standard deviation by the mean, we determine a coefficient of variation for each image, which represents some physical area on the specimen. Then, by plotting the coefficient of variation as a function of machining conditions, we obtain an extremely well-behaved correlation; Caterpillar is planning extensive further developments.

NDE for Thermal Barrier Coatings

Thermal barrier coatings (TBCs), usually made of yttria-stabilized zirconia (YSZ), are under development to protect the high-alloy, often single-crystal, materials used in the hot sections of gas turbines. These coating systems are being viewed in new turbine designs as so-called prime reliant. That is, the coating system itself is mandatory for turbine system operation at design conditions. The operating conditions in the turbine engine include thermal excursions, foreign objects passing through the gas path and causing damage, and corrosion conditions. Because of these severe conditions, there is a need for NDE technology that can allow turbine system manufacturers and users to assess the condition of as-coated components as well as to ascertain the condition of the coating during operation. Argonne is developing an NDE technique using elastic optical scattering, wherein the optical translucency of the YSZ is used. That is, a low-power laser is incident on the coating and the light, after penetrating the YSZ, reflects off the TBC/bond coat interface. The scattering of the reflected light is characterized by polarizing filters and special detectors.

This work is being conducted in conjunction with the University of Pittsburgh, University of Connecticut, Praxair Surface Technologies, Solar Turbines, GE Power Systems, Pratt & Whitney, and Siemens-Westinghouse. International collaborators include DHR, the German Aerospace Institute in Cologne, Germany. The figure below shows typical turbine blades and resulting laser scatter data suggesting a delamination. Of primary importance is the ability to predict when the TBC is going to spall.



Gas turbine blades with thermal barrier coatings and laser backscatter image

The NDE work also focused on development of an acousto-ultrasonic method for determination of damage in hot gas filters as a function of axial position along their length. Both monolithic and oxide composite materials were studied. The work has been conducted with the University of Tampere (Finland), Schumacher Corp. (Germany), Southern Research Institute, Southern Company Services, and Oak Ridge National Laboratory. The work demonstrated that data from this NDE method can be directly correlated to the remaining strength of the hot gas filter material. The ANL acousto-ultrasound method was automated and used to characterize a full-length (1.5 m) filter in under 5 minutes.

Advanced Sensors for Advanced Natural-Gas Reciprocating Engines

This program, completed in FY 2003, was supported by the DOE Office of Power Technology under the Advanced Reciprocating Engine Systems (ARES) project. The objective was to develop advanced sensors and control systems for real-time combustion monitoring of advanced natural-gas reciprocating engines. The proposed development includes sensors to measure NO_X emissions and natural-gas composition and a feedback control system. Such sensors are needed to optimize engine combustion and reduce NO_X emissions. Optimization can generally be achieved by adjusting the natural-gas/air ratio to control NO_X emissions.

The targeted real-time NO_X emission sensor must give a fast response and demonstrate high sensitivity to NO_X emissions in the range of 1-100 ppm. The sensor must be able to function under an ARES engine exhaust environment that is typically at high temperature and contains more than 10% moisture. Conventional solid-state electrochemical sensors generally have slow response time and a narrow working temperature range. Our approach was to develop a practical

NO_x sensor based upon ion-mobility spectrometry (IMS). The status of the IMS sensor is outlined below:

- A nonradioactive spark-discharge ionization source that replaces the conventional ^{63}Ni β source was successfully developed and demonstrated.

- A laboratory prototype was built and tested. Negative NO_2 ions were the primary ions detected in the two carrier gas streams tested, dry nitrogen and simulated exhaust gas.

- Negative-ion current intensity was correlated with both NO_2 and NO_x concentrations up to 200 ppm with high sensitivity and linear dependence.

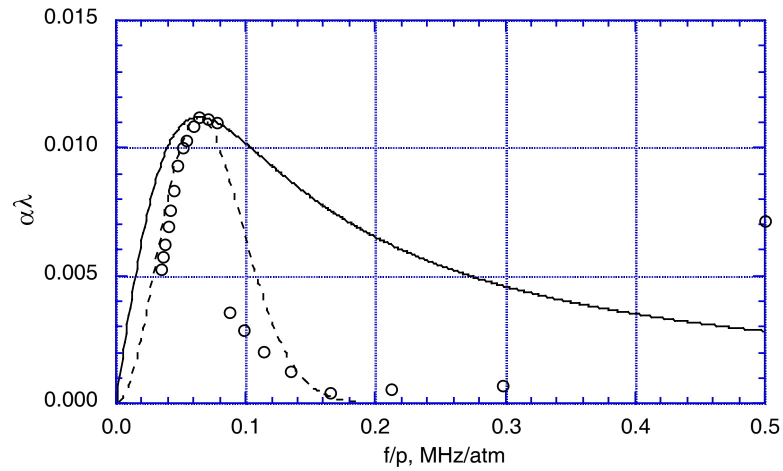
- The present IMS sensor can produce a measurement in less than ten seconds, depending on the speed of the data acquisition system.

The second sensor being developed concerns the natural-gas composition. The approach taken is based on the acoustic properties of the gas mixtures, namely, the speed of sound and sound attenuation. A typical fuel gas composition of a natural-gas reciprocating engine consists of 82-96% methane, 2-7% ethane, 0.4-1.1% propane, and up to 0.6% higher hydrocarbons. Semiconductor sensors generally cannot fulfill the requirements because of slow response time, limited detection range, and cross sensitivity. The advantages of an acoustic sensor are fast response, robustness, and low cost; the drawbacks are poor sensitivity and applicability primarily to binary gas mixtures. We, therefore, focused on measurements of additional acoustic parameters such as acoustic attenuation for natural-gas identification.

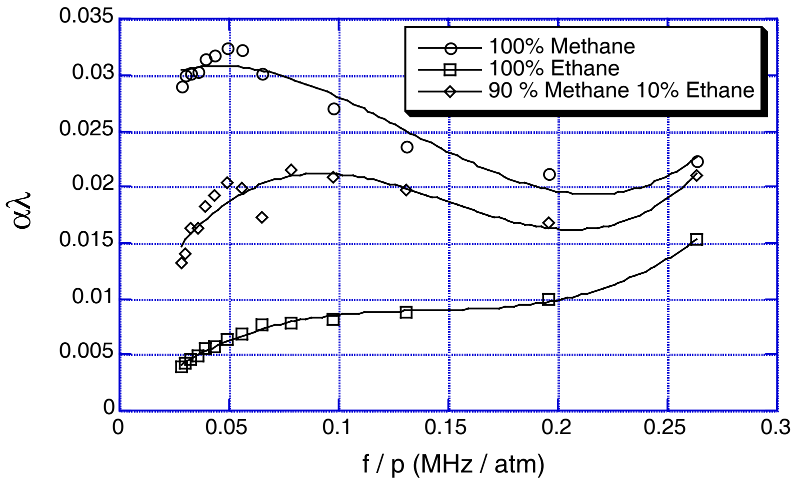
Our attenuation measurements cover an *f/p* range from 0.05 to 0.5 MHz/atm. In this range, an acoustic relaxation peak was observed for methane. The figure below shows the dimensionless attenuation as a function of *f/p* in a 1:1 mixture of nitrogen/methane. A relaxation peak at $f/p \approx 0.06$ MHz/atm is detected. The solid curve shows the theoretically predicted decay of the relaxation process. To better fit the data, we derived an empirical expression, which is plotted as the dashed line in the figure:

$$\mu_R = A\mu_{\max}\left[\frac{f/p}{(f/p)_{\max}}\right]^2 \exp\left\{-\left[\frac{f/p}{(f/p)_{\max}}\right]^2\right\}$$

where μ_{max} is the peak maximum, and A is a constant. The next figure shows the acoustic attenuation for pure methane, pure ethane, and a methane/ethane (0.9:0.1) mixture. The pure methane showed a relaxation peak at $f/p \approx 0.05$ MHz/atm, shifted to a slightly lower *f/p* as compared to the (1:1) methane/nitrogen mixture. The peak was shifted to higher values of *f/p* when ethane was introduced. The relaxation peak for pure ethane was not resolved very well. The data also show that the attenuation in an ethane/methane mixture falls between the attenuation in methane and ethane, but it may not provide a direct quantitative measure of the gas composition.



Attenuation per wavelength vs. frequency over pressure in 1:1 methane/nitrogen mixture



Attenuation per wavelength vs. frequency over pressure in methane, ethane, and methane/ethane mixture

The status of the acoustic sensor is summarized as follows:

- The sensor can detect changes in binary-gas composition by measuring changes in the speed of sound.
- An acoustic relaxation peak was detected for methane gas and its mixtures.
- By combining the sound speed and attenuation measurements, one can determine the composition of a natural gas that contains multiple components.

However, further development is needed to determine the sensitivity and reproducibility. At present, we believe the sensor can determine the percent of ethane or nitrogen in methane, but the percent of propane in methane may be difficult to determine.

NDE for Continuous Fiber Ceramic Matrix Composites

Work on continuous fiber ceramic matrix composites (CFCCs) was transferred from the DOE Office of Industrial Technologies to the Office of Power Technologies in FY 2002. This work is directed toward development of NDE methods that yield information on ceramic process development/reliability, damage level from either oxidation or impact, and effectiveness of repairs. Development efforts were focused on thermal imaging, air-coupled ultrasonics, and water-coupled ultrasonics and were highly interactive with various industrial suppliers: Honeywell Advanced Composites (now GE Power Systems/Composites), Textron, McDermott Industries, B. F. Goodrich, and Composite Optics. In the case of Honeywell Advanced Composites, several specimens were prepared for the study of thermal imaging and air-coupled ultrasonics relative to processing variables in the polymer impregnation process. Successful correlations with mechanical properties were established. For example, sensitivity to damage levels in SiC/SiC 2-D laminated CFCC material, induced by instrumented pendulum impactors, was studied by thermal imaging and air-coupled ultrasonic analysis; correlations were excellent.

Work for Others

Defense Advanced Research Projects Agency (DARPA)

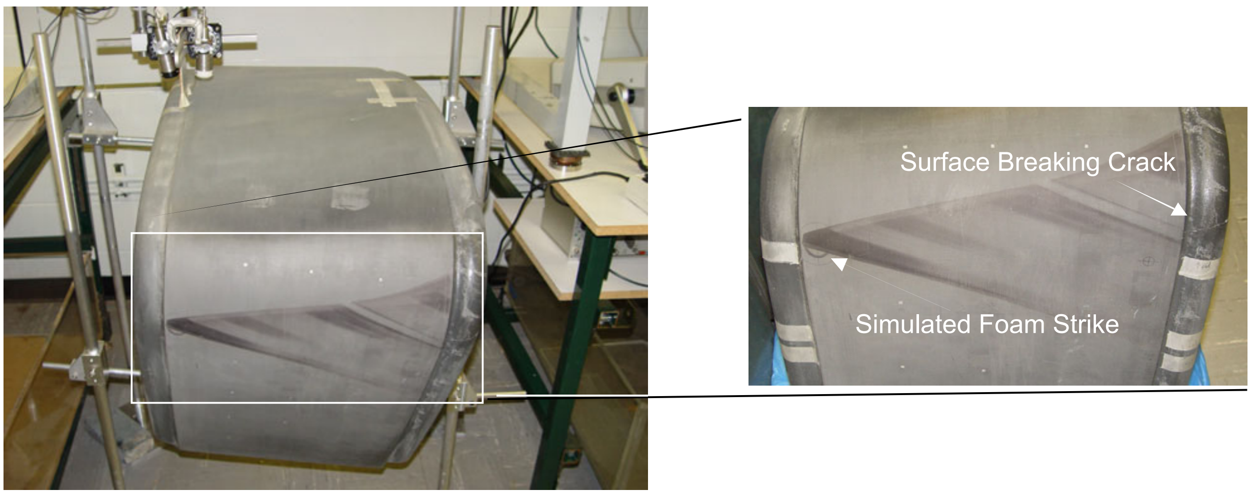
As part of a DARPA-sponsored effort to develop a hypersonic ram jet engine, special carbon-carbon composite materials are being fabricated for this engine. Argonne's specialized NDE capabilities, primarily X-ray computed tomography, were singled out for this effort. Argonne has been pioneering development efforts to use large-area X-ray detectors with industrial X-ray heads in a computed tomographic imaging mode. The large-area detectors, which can have 2000 by 2000 pixel arrays with 2-bytes per pixel, generate huge data sets. Many data sets are over 1-2 gigabytes in size. Handling these large data sets has demanded extensive computing capability. A new Beowolf cluster was assembled for this purpose. Data reconstruction times for the large data sets has gone from 48 hours to less than 45 minutes with this new computer arrangement.

Air Force

The Air Force work was directed towards developing NDE methodology coupled with proper materials models such that the remaining useful life of the ceramic matrix composites can be estimated. In this work, we studied guided plate waves using 150 kHz frequency transducers. A special test fixture allowed one transducer to be used to excite the plate wave, while two transducers served as detectors. The attenuation and acoustic wave speeds were used for the flexural mode. The material behavior model found to be of value was the shear-lag model. Use of this model, together with the guided plate wave analysis, proved an excellent predictor of life for SiC/SiC materials. Both monotonic loads and cyclic loads with tension-tension fatigue were studied.

National Aeronautics and Space Administration (NASA)

As a part of the investigation into the space shuttle Columbia accident, Argonne's NDE efforts were recognized by NASA as vital. The Columbia Accident Investigation Board demanded that before the shuttle would fly again, appropriate NDE technology be in place to assure reliability of the reinforced carbon-carbon (RCC) materials that make up the leading edge of the shuttle wing. Argonne investigated several types of NDE technology in this effort: thermal imaging, noncontact ultrasonics, eddy current probing, and X-ray computed tomogaphy. The figure below shows a photograph of one of the NASA shuttle leading edge components under study. Further details on the eddy current technology being developed for NDE are given later in this section.



Photograph of one of the leading edge components under study by NDE

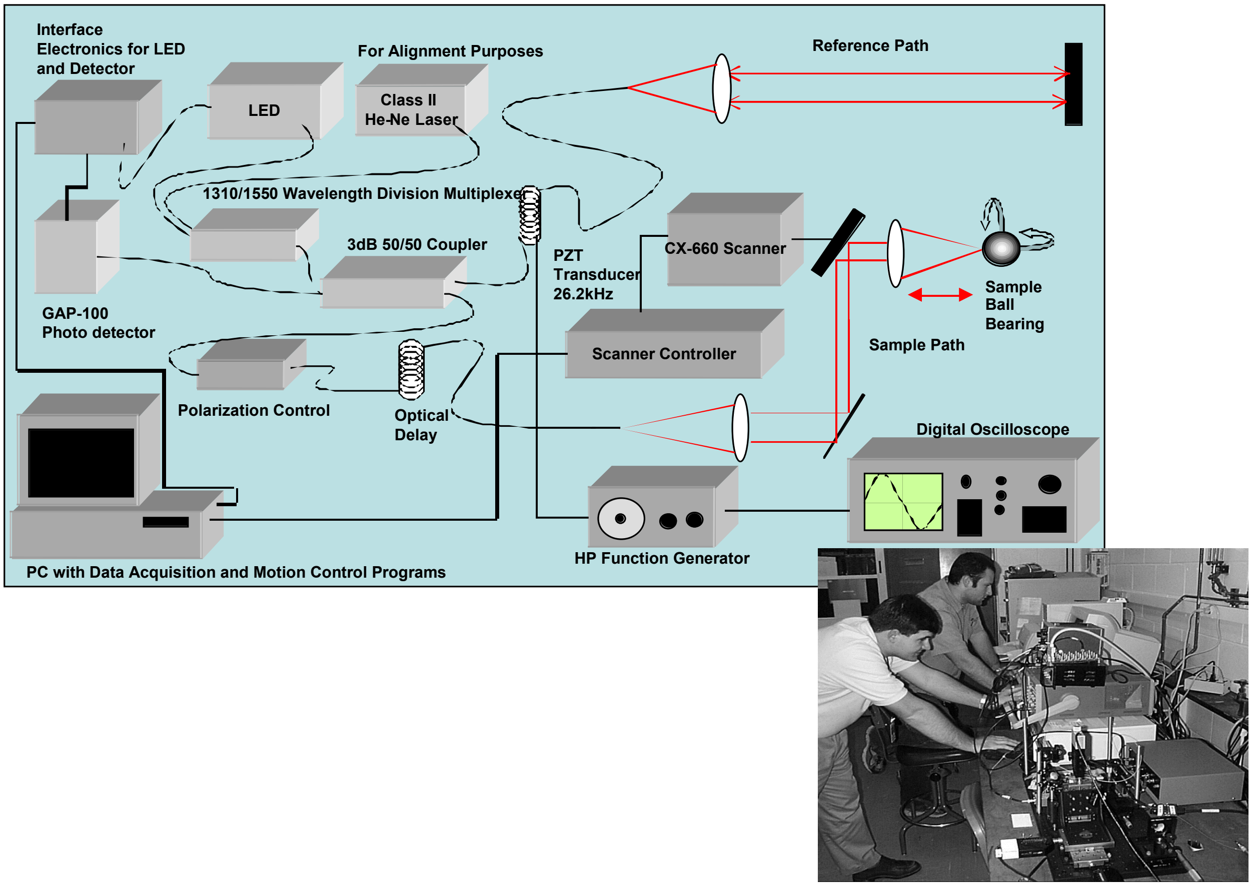
Industrial Firms

We are developing various NDE technologies for the following industrial efforts:

1. Thermal imaging and eddy current technology as part of Siemens-Westinghouse effort to develop solid oxide tubular fuel cells.

2. X-ray computed tomography, air-coupled ultrasonics, and one-sided thermal imaging of oxide-oxide ceramic composites as part of the Siemens-Westinghouse effort to develop advanced low-emission gas turbines.

3. An optical coherence tomography system for examining dense silicon nitride ceramic bearing balls as part of an effort funded by Saint-Gobain Industrial Ceramics and Plastics.



Block diagram for optical coherence tomography system

Safety-Related Applications

Work in this area concerns the safe and reliable operation of nuclear power plants and NASA's space shuttle. Existing challenges to characterize and size various forms of complex cracking in steam generator tubes from nuclear plants could be minimized by selecting appropriate eddy-current probes and analyzing the generated data by specially developed computer algorithms. The improved reliability in in-service inspection will lead to more efficient generation of electricity, helping to maintain nuclear plant capacity by reducing the chance of an unscheduled shutdown caused by improper assessment of complex cracks. In addition, results will help eliminate needless plugging of steam generator tubes by improved understanding of inspection results and their importance. We are also developing eddy current technology for detection of flaws in the leading edge structural subsystem of the NASA space shuttle.

DOE Office of Nuclear Energy, Science, and Technology

The objective of this Nuclear Energy Plant Optimization Project is to improve the analysis of eddy current data for axial and circumferential stress corrosion cracks in steam generator tubes. The high-resolution eddy current probe that was selected for this study is the RG3/4, which is a surface-riding transmit/receive (T/R) probe developed by RDTech. Inherently low lift-off noise and an absolute type response are the primary characteristics that make this directional probe a viable candidate for flaw sizing. Inspection data were acquired with RG3/4 using the steam generator mock-up at Argonne.

By combining the effort to increase signal-to-noise ratios for the X-Probe array (the RG3/4 is a rotating element of the X-Probe array), along with enhanced flaw imaging and sizing algorithms from a program sponsored by the Nuclear Regulatory Commission (NRC) (discussed next), a powerful capability is being developed for characterizing and sizing cracks in the tube sheets of steam generators. The RG3/4 data will be processed by computer algorithms developed at Argonne to produce NDE profiles.

Evaluation of the eddy current probe will continue using field-degraded tubes removed from the steam generator of the McGuire Reactor under NRC sponsorship and data provided by the Electric Power Research Institute (EPRI) from their qualification program for the RG3/4. Eddy current data from radioactive field samples are being collected for this evaluation using the NDE glovebox at Argonne.

Conventional denoizing techniques such as wavelet transformations require some a priori knowledge about the nature of the degradation. This information is not always available from eddy current data, which can limit the use of such techniques for automated data analysis. Blind source separation (BSS) techniques, on the other hand, seem to be ideal for noise with strong spatial variability, which often appears in conjunction with eddy current signals. Such signal processing methods allow extraction of additional information from already available eddy current data. Conventional independent component analysis techniques assume a linear mixing of signal and noise. However, this may not always be the case for eddy-current inspection results in the presence of deposits and support structures. We are investigating novel nonlinear BSS methods, which provide a more powerful and general methodology in dealing with eddy current sources of noise.

Nuclear Regulatory Commission

International Steam Generator Tube Integrity Program

Key objectives of the International Steam Generator Tube Integrity Program (ISG-TIP) at ANL is to evaluate advanced NDE and signal analysis techniques for reliable in-service inspection (ISI) of original and repaired steam generator tubes and to assess improved correlations between eddy current results and flaw morphology, leak rates, and failure pressure. Degradation-specific management requires detailed knowledge about the specific nature and severity of flaws. Improved techniques (eddy current and others) are needed for more reliable inspection and interpretation of flaws. The reliability and accuracy of the techniques need to be quantified so that plugging criteria and the consequences of degraded tubes remaining in service after inspections can be evaluated. Further, the robustness of the voltage and other eddy-current parameters and techniques needs to be evaluated with respect to their range of applicability.

Round-Robin Exercise

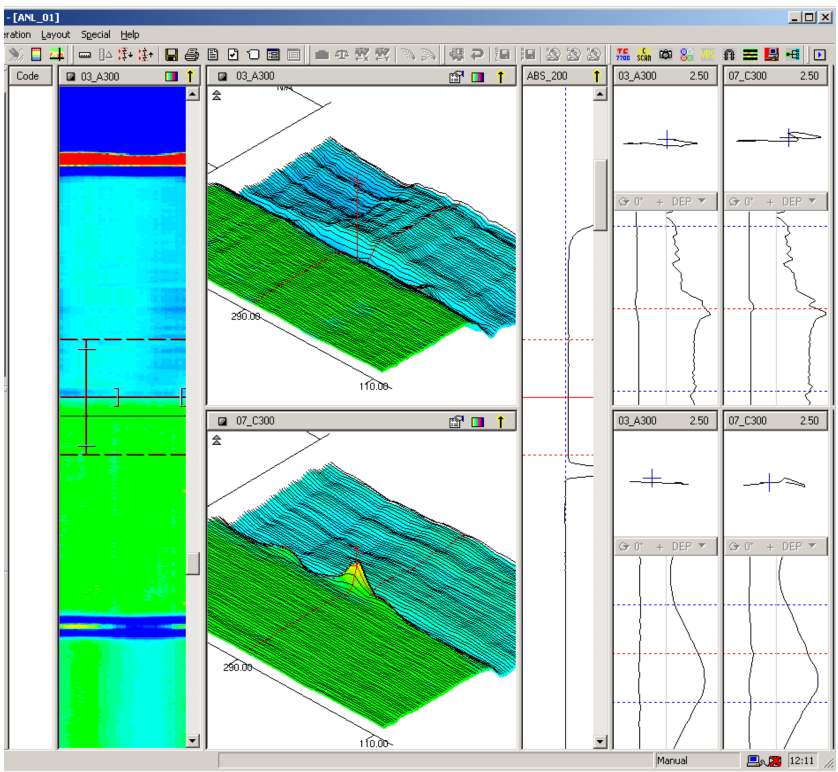
A major outcome of nuclear reactor regulatory activity over the past 10 years has been the development and implementation of two key concepts, condition monitoring and operational assessment. Condition monitoring is an assessment of the current state of the steam generator (SG) relative to the performance criteria for structural integrity. Operational assessment involves an attempt to assess the state of the generator relative to the structural-integrity performance criteria at the end of the next inspection cycle. Predictions of the operational assessment from the previous cycle can be compared with the condition monitoring to verify the adequacy of the methods and data used to perform the operational assessment.

A key factor in establishing the reliability of operational assessment and condition monitoring is the NDE techniques used to determine the flaw distribution in terms of detection and characterization of flaws and the capability to assess their impacts on the structural and leakage integrity of SG tubes. An NDE round-robin exercise has been used to independently assess SG inspection reliability. This exercise employed the steam generator mock-up at ANL. The purpose was to assess the current state of ISI reliability for SG tubing, determine the probability of detection as a function of flaw size or severity, and assess the capability for flaw sizing.

Eleven teams participated in analyzing bobbin and rotating probe data from the mock-up that were collected by qualified industry personnel. The mock-up tube bundle contains hundreds of cracks and simulations of artifacts such as corrosion deposits, support structures, and tube geometry variations that, in general, make the detection and characterization of cracks more difficult. An expert NDE Task Group from ISI vendors, utilities, EPRI, ANL, and the NRC has reviewed the eddy current signals from laboratory-grown cracks used in the mock-up to ensure that they provide a realistic simulation of those obtained in the field. The number of tubes inspected and the number of teams participating in the round-robin are expected to provide better probability-of-detection data and characterization accuracy than are currently available from industry performance demonstration programs.

The mock-up tube bundle consists of 400 Alloy 600 tubes made up of nine test sections, each 0.3 m (1 ft) long. The test sections are arranged in nine levels, each having 400 tube sections. The lowest level simulates the tube sheet, while three other levels simulate tube support plate intersections. The remaining five levels are free-span regions. Bobbin coil data were collected on all 3600 tube sections of the mock-up by using magnetically biased ("mag-biased") probes. A mag-biased, rotating, three-coil probe was used to collect data from all 400 tube-sheet and special-interest test sections. Eddy current data were collected by a qualified industry team and stored on optical disks. The round-robin teams later analyzed the data with an ANL proctor present to monitor the analysis process. The intent was to make the analysis as close a simulation of an actual inspection as possible. The procedures and training sets were developed in cooperation with the NDE Task Group so that the inspection protocols and training would mimic those in current practice.

The reference state for each flaw in the mock-up, i.e., crack geometry and size, was established by calculations using a multiparameter algorithm developed at ANL for analyzing eddy current data (see next figure). Results were analyzed for all eleven round-robin teams, including the team-to-team variation in the probability of detection, along with the population average. The detection results for the 11 teams were used to develop probability-of-detection curves as a function of maximum depth and the parameter m_p, a stress multiplier that relates the stress in the ligament ahead of the crack to the stress in an unflawed tube under the same loading. Because m_p incorporates the effect of both crack depth and length, it better characterizes the effect of a flaw on the structural and leakage integrity of a tube than do traditional indicators, such as maximum depth. The probability-of-detection curves were represented as linear logistic curves, and the curve parameters were determined by the method of maximum likelihood. The statistical uncertainties inherent in sampling from distributions and the uncertainties due to errors in the estimates of maximum depth and m_p were determined. In addition, the 95% one-sided confidence limits, which include errors in maximum depth estimates, were determined along with the probability-of-detection curves.



Array-probe eddy current map of a crack in a roll transition of a tube simulating the tube sheet level of a steam generator. The image shows the eddy current signal amplitude as a function of position. The lower image but not the top shows that the crack is circumferential in orientation.

Eddy current noise varies from plant to plant and can interfere with the quality of the data used to assess the integrity of the steam generator tubing. How much EC noise can be tolerated before data quality is affected and detection capability degraded is a key current issue and part of the Argonne ISG-TIP effort. Possible actions for low signal to noise of data include changing technique, determining if flaws can be detected in the presence of noise, and adjusting probability of detection and sizing uncertainty. The current effort has shown that noise levels that may not significantly affect detection can have a profound effect on sizing results.

Computer-Aided Data Analysis

In conventional eddy-current data analysis of SG tubing, human analysts are trained to differentiate flaw-induced signals from artifacts by analysis of the behavior of signals, typically extracted from their impedance plane trajectory and signal amplitude, through application of a series of rules. Manual analysis of multiple-frequency eddy-current data is a tedious and challenging process. No qualified technique, manual or automated, currently exists that could provide reliable estimation of flaw size over a wide range of SG tubing damage. Conventional data analysis methods become rather subjective when dealing with complex forms of degradation such as stress corrosion cracking. Signal distortion by interference from internal/external artifacts in the vicinity of a flaw further complicates discrimination of flaw signals from noise. Analogous to the manual analysis of eddy-current inspection data, computer-aided data analysis algorithms can be developed based on analysis of characteristic behavior of eddy current signals as a function of frequency. Because all available information can be examined rather than a selected subset in the case of a manual analysis, such algorithms allow more effective identification of subtle forms of degradation. Computer-based algorithms that imitate some form of human decision-making process are generally labeled as “expert systems.”

Multiparameter algorithms for the computer-aided analysis of eddy-current NDE data have been developed and implemented in a PC-based software called MATLAB, a high-level scripting language that provides an efficient environment for data manipulation and computation, together with convenient graphical user interfaces and graphical displays of the results. The effectiveness of these multiparameter algorithms has been evaluated in studies on electrodischarge-machined notches, laboratory-grown flaws, and in-service flaws. The ANL expert system for the sizing and imaging of flaws from pancake-coil data is currently being further improved. The algorithms are being modified for use with other eddy current probes, and the resulting flaw-sizing accuracy and ligament-sizing capability is being evaluated and compared with those for the existing algorithm using the pancake-coil probe. Advanced signal processing and filtering techniques are being further evaluated for use with eddy current data from bobbin coils and other rotating probes to improve flaw detection and sizing for ISI of steam generator tubes. In response to inquiries by the industry partners, efforts are also being made to further develop the analysis methods implemented at ANL for field application.

Barrier Integrity Research Program

The objective of this program is to reevaluate the basis for all existing leakage requirements and establish a technical basis for improved leakage requirements in nuclear power plants. The work being performed includes (1) a review of leakage operating experience and current leakage requirements, (2) evaluation of barrier integrity monitoring systems, (3) evaluation of leak rate studies, and (4) development of problem cases for leakage calculations. This program supports the implementation of the NRC Assessment of Barrier Integrity Action Plan and will provide a technical basis for improved requirements needed to maintain the integrity of the reactor coolant pressure boundary.

In one of the tasks, the sensitivity, reliability, response time, accuracy, and feasibility for leak detection systems (e.g., sump monitors, gas and particulate monitors) are being established and compared with technologies that can meet new requirements that may be necessary to detect the types of leakage that occurred recently in a nuclear-plant pressure vessel head. Leak detection may be improved by use of moisture sensitive tape, acoustic monitoring and advanced radioactive particulate, and gas detectors. The advantages and disadvantages of systems commercially available but not currently used in the U.S. are being determined. Two such systems are the FLUS humidity sensor and ALUS acoustic sensing, both from Seimens. While the FLUS system monitors the increase in local humidity caused by a leak, the ALUS system listens to changes in sound levels picked up by piezoelectric sensors attached to wave guides. The sensitivity depends on the background noise, which varies widely in a plant. Another system is called ARMS, which draws air through a filter to concentrate the particulates that are detected by a radiation monitor. A few ARM systems have been installed in the U.S.

For leak rate studies, we have developed correlations between crack size, crack tip opening displacement, and leak rate. The emphasis is on leak rates associated with stress corrosion cracking. The results are expected to show that the leak rates associated with through-wall cracks can be very low. The first set of computations was carried out for stainless steel piping with intergranular cracking in boiling water reactors and leak rates ranging from 0.1 to 100 gal/min. The output is length of circumferential through-wall cracks. The results obtained for crack lengths at various leak rates are compared against the critical crack length for the specified value of the bending moment. This work is being carried out as a collaboration with Engineering Mechanics Corp.

A barrier integrity database is being developed. The database contains three types of information: LWR leak events, leak detection systems, and crack monitoring systems. Sources being used to provide input to the database include Licensee Event Reports and NRC reports covering prior work. Literature searches are also being carried out to identify other relevant publications.

National Aeronautics and Space Administration (NASA)

Advanced NDE of reinforced carbon-carbon (RCC) components of the leading edge structural subsystem (LESS) in the space shuttle are required to ensure early detection of anomalies and to help facilitate repair procedures of this critical subsystem. To meet this objective, a team of industry, national laboratories, and NASA centers was assembled. Argonne was selected as one of the sites to assess advanced eddy-current technology for the inspection of RCC composites. Argonne’s role under this program, coordinated by NASA Langley Research Center (LaRC), was to both analytically and experimentally assess the capability of modern multifrequency eddy-current (MFEC) technology for the detection of discrete flaws at different depths within the RCC layer. Evaluation of the MFEC technology encompassed numerical electromagnetic modeling, probe design and system interface, and data collection and analysis.

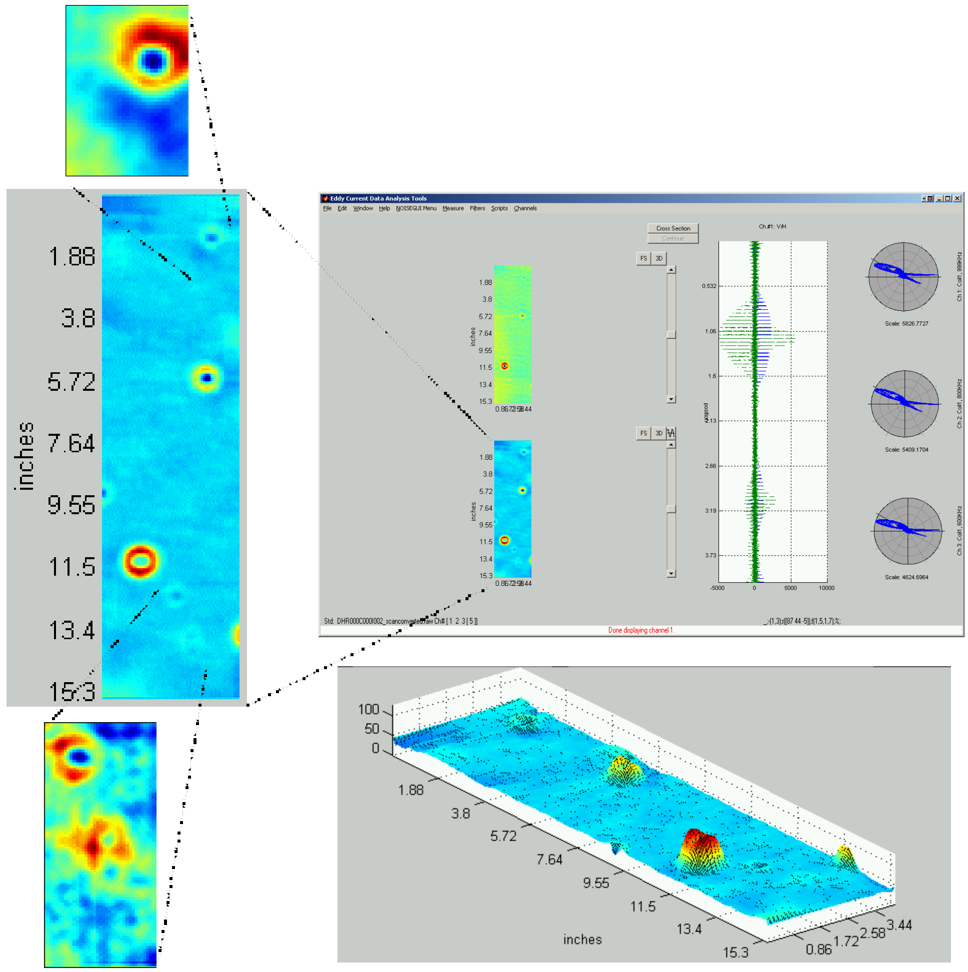
Three-dimensional finite-element modeling was performed to simulate the eddy-current probe response to flaws of interest in low-conductivity RCC structures. Numerical simulations focused initially on calculation of the probe impedance variation at several excitation frequencies and for a range of flaw sizes in layered media simulating the LESS. Theoretical results were initially verified through comparison with experimental data. These limited investigations clearly demonstrated the usefulness of numerical electromagnetic techniques for modeling the interaction of induced fields with complex media. Reliable models can be an effective tool for optimizing various eddy-current test parameters of interest and, in turn, reducing costly sample preparation and testing.

The NDE facility at ANL was used to examine various RCC samples with the MFEC inspection system. Test pieces mostly contained manufactured flaws of various sizes. Data were collected by two transmit/receive probes having different size coils. Inspections were performed in both contact (surface-riding) and noncontact manner. Results of the experimental investigations demonstrated the capability of the technique to detect flaw sizes of interest at the reaction layer, as well as those located deeper within the test piece.

Efforts also focused on data visualization, signal processing, and data analysis methods to help improve the detection of localized flaws in RCC composites. A series of MATLAB scripts has been integrated through a single graphical user interface to allow off-line manipulation of MFEC inspection data. The analysis tool contains a series of frequency and spatial domain filters that can be sequentially applied to the data. Data can be displayed in various formats, which help to better visualize potential eddy-current indications. Feasibility studies suggest that significant improvement in signal-to-noise ratio can be achieved by applying the appropriate filtering schemes.

Following the completion of the feasibility studies, a review committee recommended further development of the MFEC technique for in-situ inspection of LESS. Argonne will collaborate with the LaRC in support of various efforts under this program.

Pictures showing different view angles of the curved RCC test piece with artificial subsurface flaws used for blind tests. Sample size: ≈ 0.46 × 0.46 m.



Eddy-current inspection data on ≈ 0.1 × 0.4 m section of RCC test piece.
Several subsurface flaws are clearly detectable from the processed C-scan data.

Homeland Security Applications

Electromagnetic waves at millimeter-wave and terahertz frequencies (THz) offer promising sensing applications for homeland security. Frequencies from 0.1 to 10 THz are considered THz radiation. For gas-phase molecules, the rotational signatures peak at THz frequencies, with three to four orders of magnitude improvement in sensitivity than possible at microwave frequencies. At low pressures (~1 mtorr), the selectivity of detection is nearly 100% (zero false positives). With such high sensitivity and selectivity, THz systems can be used to monitor public facilities and high-occupancy buildings for toxic industrial chemicals, chemical agents, and trace explosives in a continuous and autonomous manner. These systems can also be used for wide-area monitoring of toxic chemicals in open air, although they lose some selectivity in this case due to broadening of spectral lines with pressure. Because of better penetration in materials than optics, they can also be used for detection and imaging of weapons concealed under clothing. Furthermore, the wavelengths in the THz range appear to resonate with biological macromolecular structures and DNA strands in a unique manner. These systems, because of their inherently fast response, can be used as “detect to protect” sensors for early detection and warning of bioaerosols such as spores, bacteria, viruses, and pathogens. Described below is the work we have done and are doing on THz (millimeter-wave) devices for diverse applications.

Chemical Sensing

Funded by DOE's National Nuclear Security Administration (DOE-NNSA), the purpose of this work is to investigate the use of fingerprint-type molecular rotational signatures in the mm-wave spectrum to sense airborne chemicals. The mm-wave sensor, operating in the frequency range of 225-315 GHz, can work under all weather conditions and in smoky and dusty environments. The chemical plume to be detected is situated between the transmitter/detector and the reflector. Millimeter-wave absorption spectra of chemicals in the plume are determined by measuring the swept-frequency radar return signals with and without the plume in the beam path. The problem of pressure broadening, which hampered open-path spectroscopy in the past, has been mitigated in this work by designing a fast sweeping source over a broad frequency range. The heart of the system is a backward-wave oscillator (BWO) tube that can be tuned over 220-350 GHz. Using the BWO tube, we built a mm-wave radar system and field-tested it at the DOE Nevada Test Site at a standoff distance of 60 m. The mm-wave system detected chemical plumes very well; detection sensitivity for polar molecules such as methyl chloride was down to 12 ppm for a 4-m two-way pathlength.

Gas Leak Detection

Funded by DOE's Office of Fossil Energy, National Energy Technology Laboratory, we have developed a microwave radar for remote and fast imaging of gas leaks for protection of natural gas pipeline infrastructure. The underlying principle is the change in radar reflection, refraction, and scattering properties of leak plumes with respect to the surrounding air. The problem of radar detection of gas leaks from a point source is akin to meteorological targets in weather prediction — both deal with gas-phase media and the volume scattering from dielectric property changes. The source of radar returns in meteorological radars is the change of reflectivity, refraction, and scattering caused by storms, rain, cloud, atmospheric turbulence, and wind movement. Even in the absence of contrasting dielectric materials such as water and ice droplets in the atmosphere, the radars can detect clear-air turbulence and wind shear due to wave scattering caused by index-of-refraction inhomogeneities.

In collaboration with AOZT Finn-Trade Co. (St. Petersburg, Russia), we performed a theoretical and experimental investigation to show the feasibility of the radar technique. The gas dynamics of the leak jet were modeled first to determine the plume geometry and the variation of gas concentration in air with distance from the leak source. From the turbulence-induced static and dynamic changes of the index of refraction, the radar backscatter cross section of the plume was determined next. To verify the model predictions and to determine the detection sensitivity of gas leaks, a commercial X-band radar system was interfaced with a computer to enable data collection and specialized signal and image processing. Two gas-plume tests were conducted, one with a cold nitrogen plume at 60 m from a liquid nitrogen dewar for initial testing, and the other with a propane leak from a 50-L cylinder at 720 m from the radar. Because of condensation, the cold nitrogen plume was easily detected, even for small leaks. The propane leak test was more realistic in that it simulated the spread and dynamics of a methane leak as well as its radar cross section closely. The radar signals obtained between two distance channels corresponding to the plume and background atmosphere showed a clear change in signal level for the propane plume. The radar cross section of the propane plume, calculated from the radar return, agreed well with the model results. The results thus indicate the technical feasibility of the radar technique for remote and fast inspection of gas pipelines for leaks.

Radiation Detection

Funded by the DOE's Initiatives for Proliferation Prevention Program, we have worked with the AOZT Finn-Trade Co., which pioneered the use of microwave (MW) pulsed radars for detecting radioactive plumes. The main source of radar return is the index-of-refraction inhomogeneities of the air space caused by the ionization of air molecules and the additional effects that the ions and radioactive particles produce in air to enhance the radar reflectivity and scattering. For example, aerosol particles can be attracted to the ions by electromagnetic induction. In addition, these charged particles serve as nuclei for condensation of water vapor, which offers a large radar cross section. The technique was demonstrated by using a 3.2-cm MW radar mounted on the top of a van at a distance of 9 km from a nuclear power plant. The radar imaged the weak radioactive cloud emanating from the ventilation stacks of the nuclear power plant during normal operation. The typical release level was 25-50 Ci in a 24-h period. The radar images of the nuclear power plant showed a clear difference between the times when the plant was operating and when it was idling.

Trace Explosives Detection

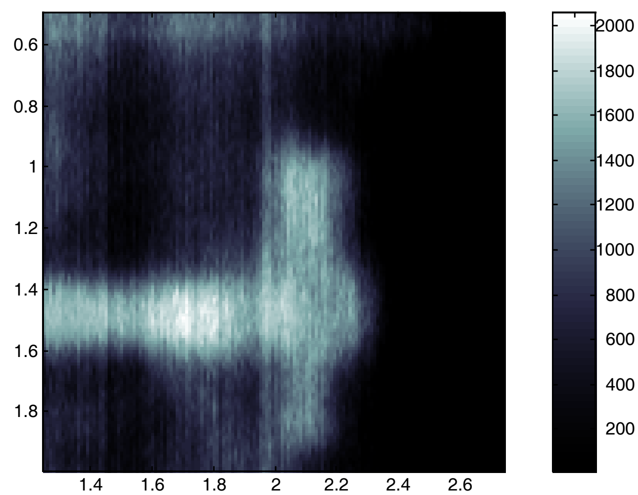
Funded by DOD's Technical Support Working Group, a team consisting of Sarnoff Corp., Argonne National Laboratory, Sandia National Laboratories, and Dartmouth College is developing a portal design and detection scheme for fast screening of people for trace explosives. The objective is to demonstrate the feasibility of THz spectrometry for monitoring of trace explosives. In particular, we will identify the rotational spectral signatures of common explosive molecules and their absorption strengths. We will also determine the selectivity of these spectral lines with respect to confounding molecules in the background air. The outcome of this task will provide the basis for design and fabrication of the Sarnoff's Smith-Purcell THz absorption spectrometer.

Because the vapor pressures of explosive molecules are very low, we have built a heat cell for studying their THz signatures. Using a BWO-based spectrometer, we will test the signatures of explosive molecules in the frequency range of 100 to 300 GHz, where their rotational spectral lines are expected to peak from *ab initio* calculations.

Concealed Weapons Detection

Funded by DOE-NNSA, we investigated the potential of passive mm-wave imaging for detection of concealed devices. Radiometry in the millimeter wavelengths has been used for remote sensing of the earth and atmosphere. Earth resources such as vegetation, soil moisture, and snow cover, as well as weather patterns and military targets, have been imaged with this technology. Unlike visible or infrared (IR) techniques, mm-wave radiometer has the advantage of all-weather capability. Because the thermal contrasts of objects are different in the mm and IR bands, mm-wave radiometer can complement IR imaging systems.

In this work, we developed and tested a focal-plane imaging radiometer at 160 GHz. The figure below shows a scanned image of a hammer placed on the floor of the laboratory at a distance of 36 inches from the lens plane. The metallic head and wooden handle of the hammer are clearly visible. The image contrast is mainly due to differences in emissivity of the materials. Because mm-waves can penetrate clothing and plastic materials, a focal-plane imaging array camera holds the potential for detection of concealed devices under clothing, buried roadside bombs, and land mines.



Passive millimeter-wave image of a hammer

Biological Detection

We have investigated the potential of real-time dielectric sensing for detection and classification of biological species. Though many methods of measuring the dielectric properties of materials exist in the literature, they lack specificity in identifying materials. Therefore, few chemical or biological sensors based on such dielectric measurements exist at this time. We have developed a new method that provides a degree of selectivity based on the extent to which the complex dielectric constant of a material affects the signal pattern of a resonator. Using a TE_{10} microwave cavity, we have demonstrated proof of principle by testing four powder samples: acetaminophen (powdered Tylenol caplet), isobutylphenyl propionic acid (powdered Ibuprofen caplet), bovine albumin (protein), and herring sperm DNA. The cavity showed distinct and repeatable response patterns for the four biomolecules, thus showing promise for the use of the dielectric method to identify biological macromolecules.

The method is applicable at any excitation frequency from radio-frequency to terahertz range; however, if the excitation frequency is selected to correspond to one of the resonance (relaxation-type or spectroscopic) frequencies of the material under investigation, the degree of selectivity and the sensitivity of detection can be improved significantly. The resonance-enhanced dielectric method holds the potential for a fast first screening of chemical or biological agents in the form of gas, powder, or aerosol.

Synchrotron Radiation-Based Terahertz Source

In collaboration with ANL's Advanced Photon Source and Energy Systems Division, we are developing a coherent high-power pulsed THz source based on ballistic electron bunch compression. The building blocks of a synchrotron-based THz source include an electron source that can produce short pulses of relativistic electrons, a dipole or an undulator magnet that is coupled to the electron source to produce coherent long-wavelength radiation, and photon transport optics and detectors for collecting and characterizing the radiation. In FY 2003, all the building blocks were commissioned and were tested individually. The electron source has been fully commissioned in terms of input RF power conditioning at 2856 MHz. The first electron-beam-based measurements demonstrated that the gun is behaving as the theory predicted. The complete system will be tested for THz radiation, followed by chemical and biological materials testing.

Superconductor-Based Terahertz Source

Collaborating with the Materials Science Division, we are developing a high-temperature superconductor-based miniature THz source. The purpose is to demonstrate a compact, tunable, solid-state terahertz source of sub-millimeter electromagnetic waves using strongly-driven Josephson vortices in layered, high-temperature superconductors, like $Bi_2Sr_2CaCu_2O_8$ (BSCCO). Although theoretical efforts have predicted large power output, two primary technical challenges must be overcome: (1) the large mismatch of impedance (light velocity or index of refraction) between BSCCO and free space, and (2) heating.

Biomedical Applications

In collaboration from the Emergency Resuscitation Research Center of the University of Chicago, we are developing a novel biosensor for an important medical application—revival of sudden cardiac arrest victims. Oxidants such as reactive oxygen species and reactive nitrogen species play critical roles in cell signaling and cell injury during pathologic conditions such as ischemia/reperfusion. Specifically, two of the most diffusible oxidants, hydrogen peroxide and nitric oxide, play important roles in ischemia/reperfusion injury. The objective of our work is to develop a highly sensitive real-time sensor for noninvasively measuring these species in human-exhaled breath as biomarkers of cell injury.

Because the concentration levels of H_2O_2 and NO in exhaled breath are expected to be in the parts per billion range, we selected for further development a sensitive infrared technique based on tunable diode laser absorption. We designed and built a tunable diode laser at an infrared wavelength range of 1260-1290 cm^{-1}, where the H_2O_2 peak appears in the absorption spectra and where interfering species like H_2O and CO_2 have minimal interference. Serial dilutions of H_2O_2 in water were prepared from 0.01 to 0.0001 wt.%. Extreme care was taken to minimize sample contamination, deposits on cell wall, or decomposition by dust or contaminants. The vapor from the headspace of a tube with test solution was pumped into the cell to a pressure of 3 torr. Measurement results showed decreasing detection peaks for 0.01 to 0.0001 wt.% samples. The lowest concentration level (0.0001 wt.%) detected corresponds to 30 ppb in the vapor phase. Further improvement by an order of magnitude is possible by integrating the signal longer than the 1-ms time constant employed. Having reached our sensitivity goal, the University of Chicago is anxious to use the device to validate the hypothesis of noninvasive oxidant stress measurements via breath analysis.

Aging Management and Transportation of Hazardous Materials

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For the Nuclear Regulatory Commission (NRC), the Aging Management and Transportation of Hazardous Materials (AM-THM) Section provides direct technical support on developing and updating guidance for the review of license renewal applications for operating nuclear power plants. The Section also provides technical assistance to NRC on the review of license renewal applications for several nuclear power plants, the review of current licensing actions, and other regulatory improvement activities.

For the Department of Energy (DOE), the Section provides direct technical support by reviewing Safety Analysis Reports for Packaging (SARPs), which concern compliance of radioactive material shipping packages with DOE Orders and with NRC and Department of Transportation (DOT) regulations. In addition, the Section provides technical assistance to DOE on generic waste management and transportation issues, guide and handbook development, and training courses on quality assurance, and the application of the American Society of Mechanical Engineers (ASME) Code to radioactive materials packaging.

Review of License Renewal Applications and Technical Assistance

There are 103 operating nuclear power plants in the United States. These plants (98 GWe capacity) provide approximately one-fifth of the nation's electricity without contributing to regional air pollution or global emissions of greenhouse gas. Operation of these plants annually avoids emission of over 150 million metric tons carbon, about five million tons of sulfur dioxide, and 2.4 million tons of nitrogen oxides. More than half of these plants will reach the end of their initial 40-year licensing periods by 2020 and most of the remaining ones by 2030. A 20-year renewed license term would partially mitigate the need to build more base-load power plants (see figure below) and greatly reduce carbon emissions.

Today the U.S. utilities find license renewal of their nuclear plants economically attractive for several reasons, including a significantly increased average capacity factor, reduced operating cost, and improved NRC regulatory process. In 1990, the average capacity factor for the U.S. nuclear power plants was about 70%, which resulted in 577 billion kilowatt-hours (kWh) of electricity production. The average capacity factor increased to almost 90%, or

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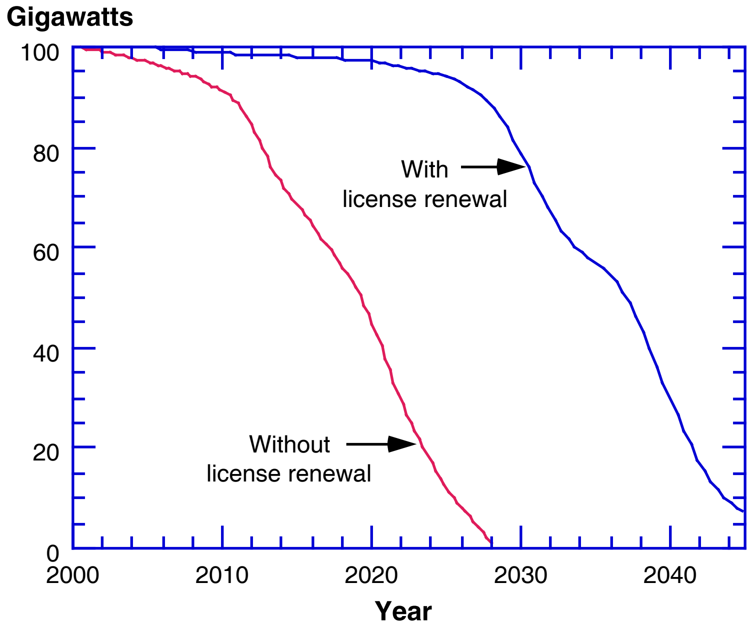


U.S. nuclear power generation with and without additional 20-year license renewal

754 billion kWh, by the end of 2000, and to 91.5%, or 778 billion kWh, in 2002. This increase in electricity output is equivalent to adding 23 new 1000-MWe power plants to the nation's electricity grid. These performance records have translated into lower electricity production costs and improved economic performance for nuclear power plants, which provides the needed incentive to seek license renewal.

In December 1991, the NRC published a rule in Title 10, Code of Federal Regulations, Part 54 (10 CFR Part 54) that provided the regulatory basis for nuclear power plant owners to seek license renewal for operating nuclear power plants. This rule required an applicant to identify "aging mechanisms unique to license renewal" that could affect the safety performance of plant components and structures. In 1995, the NRC revised the rule to emphasize management of aging effects on plant components and structures. Under the revised rule, the estimated cost to prepare an application was reduced from $40 million, based on the original 1991 rule, to between $10 and $15 million with an NRC review schedule of less than 30 months. In March 2000, the NRC approved the renewal of operating licenses for the Calvert Cliff nuclear plants for an additional 20 years. Two months later, the NRC approved the renewal of the operating licenses for the Oconee plants. The NRC completed review of each license renewal application (LRA) in less than 24 months, thus demonstrating that the regulatory process for reviewing license renewal applications is reasonably stable and predictable.

Since the early 1990s ET and the AM-THM Section staff have worked with NRC on projects documenting the industry and the NRC positions on various aging effects and mechanisms for the passive, long-lived components in light water reactors (LWRs) and developing guidelines for reviewing the license renewal applications. Many of these positions are based, in part, on the NRC-sponsored research at ET in areas such as thermal aging embrittlement of cast austenitic stainless steel, environmentally assisted cracking, and steam-generator tube integrity.

Since 1998 the AM-THM staff, along with staff from Brookhaven National Laboratory, have worked with NRC in developing two guidance documents for implementation of the license renewal rule with input from interested stakeholders: "Generic Aging Lessons Learned (GALL)" report, NUREG-1801, and "Standard Review Plan for Review of License Renewal Applications for Nuclear Power Plants (SRP-LR)," NUREG-1800, both published in July 2001. The GALL report documents the basis for determining when existing aging management programs are adequate and when those programs should be augmented for license renewal. Altogether, 45 existing aging management programs were generically evaluated for mechanical, structural, and electrical components in LWRs. These generic aging management programs include, for example, ASME Section XI in-service inspection, reactor water chemistry, boiling water reactor (BWR) vessel internals, nickel-alloy nozzle penetrations, steam-generator tube integrity, flow-accelerated corrosion, bolting integrity, fire protection, structure monitoring, and electrical cables and connections. The GALL report is referenced in the SRP-LR as the basis for identifying those programs that warrant particular attention during NRC's review of a license renewal application.

Section staff have been involved in the safety review of six license renewal applications following the guidance of GALL and SRP-LR. The six plants are St. Lucie, Peach Bottom, V. C. Summer, Dresden and Quad Cities, Joseph M. Farley, and Arkansas Nuclear One-Unit 2. The staff performed safety evaluation of aging management reviews for reactor coolant systems and auxiliary systems, as well as related aging management programs and time-limited aging analyses. The review process included evaluation of the relevant portions of the application, issuance of requests for additional information, evaluation of the applicant's responses to these requests, preparation of the draft safety evaluation report, and support for the NRC staff in the Advisory Committee Reactor Safeguards meetings.

The Section staff are also involved in documenting the lessons learned during the review of license renewal applications. These lessons will be incorporated into the future revisions of GALL and SRP-LR. This effort includes review of industry-prepared topical reports that are approved by the NRC staff and referenced in the license renewal applications.

The GALL and SRP-LR reports have provided improved guidance for preparation of the license renewal applications and uniform and efficient review of applications by the NRC staff. The review schedule has been reduced to about 22 months if there is no public hearing (30 months with public hearing). We anticipate that the review process will become even more effective and efficient as the guidance documents are further revised to incorporate the lessons learned during the review of the license renewal applications. The section staff will continue to be involved in revising these guidance documents and reviewing the future applications using the improved review process.

As of January 2004, the NRC has reviewed and approved 10 applications for 23 reactors (approximately 21 GWe capacity). Nine applications for 17 reactors are currently being reviewed. An additional 18 applications for more than 24 reactors will be submitted to NRC through 2007. Eventually, it appears that the utilities will be submitting license renewal applications for nearly all nuclear power plants in the U.S. Keeping the 103 nuclear power plants running in the U.S. for an additional 20 years beyond their original 40-year design lives can have a tremendous socioeconomic impact and environmental benefit to the country.

The ET and AM-THM Section staff are also involved in reviewing several reports related to internal components of BWR irradiated stainless steel vessels. Section staff are reviewing three such reports related to underwater weld repair of irradiated BWR internals. The main safety concern associated with this weld repair is helium-induced cracking and degradation of mechanical properties that take place during welding. Once approved by the NRC staff, these reports will provide cost-effective tools for managing irradiation-assisted stress corrosion cracking in BWR vessel internals.

SARP Review and Technical Assistance

The SARP Review Group provides DOE with an independent review and evaluation of the information contained in a SARP that describes the packaging used to transport radioactive materials. The review is conducted to apprise DOE of the ability of the packaging to meet all DOE orders and federal regulations for safe transport. The process ensures that a consistent and independent review is performed, while maintaining the authority granted to DOE by the DOT for the packaging evaluation and certification.

The SARP Review Group operates independently of other Section programs and comprises a staff encompassing the disciplines and experience necessary to perform in-depth review and confirmatory evaluation of the entire range of information provided in a SARP, which is a voluminous document consisting of nine chapters: General Information and Drawings, Structural, Thermal, Containment, Shielding, Criticality, Operating Procedures, Acceptance Tests and Maintenance Program, and Quality Assurance. Together these chapters in the SARP should provide technical evidence demonstrating that the radioactive-material package meets all applicable safety standards and regulations. The primary goal of the review is to verify and ensure that the packaging will perform as intended under both the normal conditions expected in transport and the hypothetical accident conditions. These transport conditions are detailed in the regulations contained in Title 10 of the Code of Federal Regulations, Part 71. The regulations contain specific environmental and mechanical loading conditions that the package must be able to accommodate during transport. Because of the hazardous nature of the package contents, the regulations are necessarily severe. Consequently, each element of the review is essential and requires, more than other programs, an integrated team effort from the SARP Review Group.

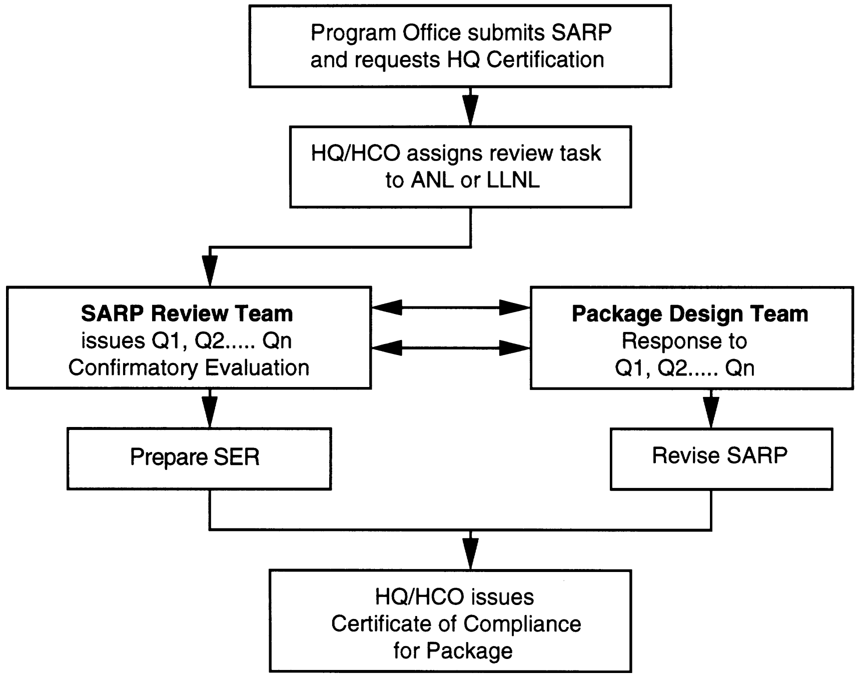
Over the years the Group has reviewed many SARPs for various radioactive material contents, including low-enrichment uranium ingots, source capsules, highly enriched uranium metals and oxides, plutonium metals and oxides, and actinides. The packages of these SARPs are sponsored by various DOE Offices, and their certifications invariably lie on the critical paths of major DOE programs in environmental remediation, site cleanup and closure, and fissile material disposition. On the low-enrichment uranium ingots, for example, the Section's work has enabled more than 400 shipments of 3,277 MTU (metric tons uranium) to Portsmouth, Kentucky. Of the more than 20 different payload types required by the Fernald site in Ohio, 17 have been received as a direct result of the technical review support provided by the Section. This work has earned DOE recognition and kept the project on schedule to complete the disposition of the nuclear product material at the Fernald and Hanford sites.

Technical Assistance Activities

As mentioned earlier, the AM-THM Section staff in the SARP Review Group provide technical assistance to DOE in several areas, including guide and handbook development, training, and other technical support as required by DOE. Section staff have been involved in the review of (a) the NRC Standard Review Plan for Transportation for Radioactive Materials (NUREG-1609), (b) the DOE Criteria for Safe Storage of Plutonium Metals and Oxides (DOE/STD-3013), (c) the DOE Order 460.1B on Packaging and Transportation Safety, (d) the DOE Packaging Review Guide, Rev. 2, (e) the IAEA Regulations for the Safe Transport of Radioactive Materials, ST-1, and (f) various Federal Notices of Rule Making activities on transportation of radioactive materials by DOT and NRC. Section staff has also been involved in the preparation of the DOE Radioactive Materials Packaging Handbook (ORNL/M-5003) and Reengineering EM's Package Certification Program (DOE/EM-0383).

The goal of reengineering DOE's Package Certification Program is to enhance process efficiency in order to meet an expected increase in workload in future package certification. Because SARP review is the major activity supporting package certification, Section staff were deeply involved in the reengineering of the certification process, which is shown in the simplified flow chart below. The process begins when a DOE program office submits a SARP and requests DOE-HQ certification of the package. Depending on workload, the HQ Certifying Official (HCO) assigns the SARP review task to either ANL or Lawrence Livermore National Laboratory (LLNL). Once the technical review of a SARP starts, it becomes an iterative process of questions and responses between the SARP review and package design teams until all issues are resolved, and the reviewers have verified, through independent confirmatory evaluation, that the SARP has indeed demonstrated package compliance to all applicable safety regulations. The outcome of the SARP review is documented in a Safety Evaluation Report (SER) that provides the basis for issuing a Certificate of Compliance for the package. The SER is part of the approval record for the package and is accessible to the public (it is posted at www.rampac.com).

Despite the best efforts by the SARP review teams to streamline the review, package certification ultimately depends on the design team that must prepare and/or revise a SARP that demonstrates package compliance to all applicable safety regulations. During the certification reengineering workshop, more than 40 ideas for process improvement were generated and ranked according to three criteria: (a) relative ease of implementation, (b) crucial or most important, and (c) most cost-effective. "Provide training for package designers and new SARP applicants" was ranked top of the crucial or most important idea for process improvement, whereas "Update the package review guide more often or send out new issues list more frequently" was a close second. These recommendations have echoed the importance and need for the training courses described below.



Simplified flow chart for the DOE package certification process

Training Courses

Since the early 1990s, Section staff in the SARP Review Group have developed two training courses for DOE: (a) Application of the ASME Code to Radioactive Material Transportation Packaging and (b) Quality Assurance to Radioactive Material Packaging. Section staff developed these courses based on the review experience of more than 39 SARPs, which show that the majority of the review questions are in the structural chapter (≈26% of 2,785 questions total in the period 1986-2001); the general information, containment, operating procedures, and quality assurance chapters each received ≈10% or more of the questions. The statistics of the Section's SARP review thus clearly indicate where training should be conducted.

The ASME Code Course

Section staff presented the first ASME Code course in March 1994 in Germantown, MD, to a select group of DOE and NRC personnel. The purpose of that course was to gauge its effectiveness and obtain feedback from knowledgeable regulators. Since then, the course has been thoroughly updated to the latest codes and federal regulations. As presently constituted, the 2-day ASME Code course consists of 20 lectures taught by four Section staff, an LLNL SARP review staff, and one outside expert who is either from NRC or an independent consultant.

Both NRC and DOE recommend Section III of the ASME Code for radioactive materials transportation packagings because it is the only available authoritative guidance for the design, fabrication, examination, and testing of nuclear power plant components. However, designers and fabricators of transportation packagings are usually not too familiar with similar activities covered in the ASME Codes for nuclear power plants. Thus, the overall objective of the course is to show the participants how to design, fabricate, examine, and test a transportation packaging so that it meets all governing federal regulations and applicable ASME Code requirements. The course includes lectures on specific topics such as materials of construction, design and stress analysis, bolting design and analysis, brittle fracture considerations, fabrication, examination, and testing.

Design and construction of a transportation packaging to the requirements of the ASME Code is only one step in a process that results in the certification of a package for shipping radioactive materials. Demonstration of package compliance to all applicable safety regulations can be done by analysis (using the ASME Code procedures) or by physical testing. Even though qualification by testing usually does not require detailed stress analysis of the structural components of the package, the materials of construction must be rigorously pedigreed following the ASME Code or equivalent materials specifications. Thus, qualification by testing must be supported by a comprehensive quality assurance plan to provide materials traceability, documentation of construction methods, and documented evaluation of test results. The ASME Code course discusses physical testing as the other acceptable method of qualification and demonstrates how the applicable ASME Code rules are applied for these cases.

The Quality Assurance Course

Since 1987, Section staff have presented the QA training course 29 times to more than 650 participants. (The most recent session was at ANL in November 2000.) Over the years, the course has evolved with time and changes in codes and regulations such as DOE Order 460.1A and the ASME/NQA-1. However, the course has always emphasized the development of a quality assurance (QA) plan for a package and a QA chapter in a SARP based on a graded approach according to the importance to safety. The main objective of the course is to teach techniques for the development of a QA plan at the onset of a project, which aids in the establishment of effective QA requirements in the QA chapter on all aspects of a packaging design, fabrication, testing, maintenance, repair, operation, document control, verification, etc. Other issues discussed in the course also include compliance-based versus performance-based QA programs, grandfathering, and the role of QA in the life cycle of radioactive material packagings.

The ASME Code and the QA courses supplement each other in many ways. Meeting the ASME Code requirements depends on having a thorough QA program for the package. As an example, when an older packaging was designed and constructed under a robust QA program, the materials used in the packaging construction, even though they may not be specified by the ASME Code, should have a pedigree that is often sufficient to satisfy Code rules to be acceptable and provide the required safety margins.

Other Activities

Section staff have been involved in other activities for the development of new programs. The activities include (a) development of a methodology to enhance electrical power grid security and reliability, (b) gathering of data for storage and transportation of spent nuclear fuel, and (c) studies of heat transfer in nanofluid. The latter two are discussed in other sections of this report.

Section staff received limited funding for the grid security and reliability work in 2002. For this activity, we tested software (TELOS) that analyzes patterns in electricity use to learn how to predict demand and avoid blackouts. This test involved correlating the electric power consumption and weather information at ANL over a year's time, predicting future power consumption on the basis of that analysis, and comparing the predictions with actual use. Good agreement was found. Ultimately, a smart electric grid could be developed in which information about where electric demand originated would be used to forecast future demand and automatically fix potential problems. Such a self-healing computerized system could greatly improve the reliability and security of large, national power grids. The work generated increased interest following the August 2003 blackout in the United States and Canada.

Ceramics

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The Ceramics Section investigates the synthesis, fabrication, and characterization of ceramic materials to optimize their properties for practical engineering applications. In most cases, the applications are intended to facilitate the generation, transmission, storage, distribution, and conservation of energy. For example, the goal of the superconductor program is to develop ceramic superconductors for more efficient generation, transmission, storage, and distribution of electrical energy.

Ceramic membranes are being developed to separate hydrogen from product gases in a coal gasification plant and to produce hydrogen through the dissociation of water. The cementitious properties of phosphate–based materials are used to stabilize radioactive and chemical wastes. These phosphate-based materials have found other applications, for example, in the waste recycling and biomedical fields. In the structural ceramics/composites program, more reliable and less-expensive structural ceramics, composites, and thermal and environmental barrier coatings are being developed and evaluated for use in advanced high-efficiency gas turbines and other applications. Hybrid vehicles require a reduction in the size and weight of power electronic modules; to meet these needs, thin-film ceramic capacitors with high dielectric constants are being developed.

Since the previous review in 2001, several changes have occurred in the Section's staff. Six new postdoctoral fellows and one permanent staff member were added to work on various programs. Eight of our Laboratory Graduate Participants received graduate degrees and took positions in industry, national laboratories, or academia. Two staff members joined other sections in the ET Division, one staff member transferred to the Ceramics Section from another Section, one post-doc became a Term Appointee, and one Lab-Grad student was hired as a post-doc after receiving his Ph.D. from the University of Florida.

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[1] Special Term Appointee.

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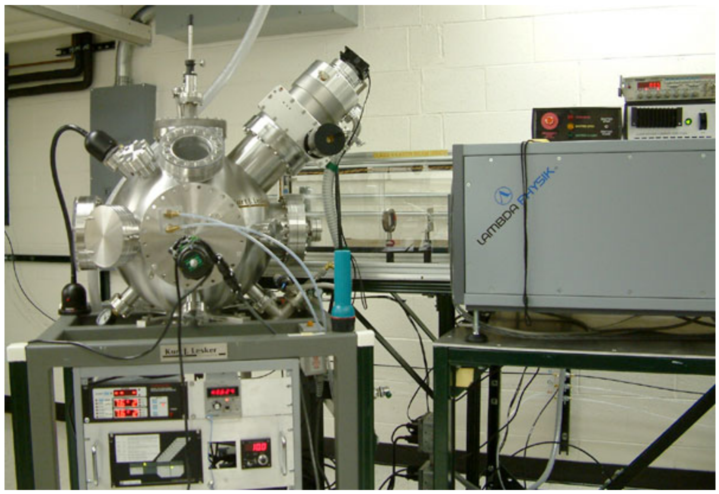
Our facilities have been upgraded by expansion of our laboratory space and several purchases. Two new pulsed laser deposition (PLD) systems and an inclined substrate deposition (ISD) system were designed and installed for superconductor fabrication. A scanning probe microscope and X-ray diffraction unit were purchased for superconductor characterization. Another PLD system was installed to carry out transparent metal oxide research. A third gas chromatograph and two additional permeation reactors were assembled and put into use for research on ceramic membranes. New components were purchased for the extrusion of thin-walled membrane tubes. A high-pressure consistometer has been obtained to simulate oil-well conditions for the phosphate-bonded ceramic research.



New PLD system with 248 nm laser operating at up to 100 Hz, 600 mJ/pulse, with laser beam rastering for deposition of buffer and superconductor layers

Superconductor Development

Superconductor development remains a major program in the Ceramics Section. The goal of this program is to develop ceramic superconductors for applications in the generation, storage, transmission, and distribution of electrical energy. The DOE program target is to produce, in collaboration with industrial partners, long lengths (≈500 m) of conductor capable of carrying 10^6 A/cm^2 at temperatures > 35 K. Program focus is on the two systems that appear to be the most promising as practical engineering materials: Y-Ba-Cu-O (YBCO) and Bi(Pb)-Sr-Ca-Cu-O (BSCCO). However, to maintain its position in the forefront of high-critical-temperature (T_c) superconductor research, the program also investigates promising new materials as they are developed.

To be used in electric power applications, superconductors must have high critical current density (J_c), and equally important, they must be available in long lengths. Powder-in-tube (PIT) processing of BSCCO materials remains the most promising method for fabricating long superconductors with high J_c. In PIT processing, the precursor powder is sealed in a silver tube, then mechanically worked and heat treated to form a thin tape of silver (or silver alloy)-sheathed superconductor.

The Section collaborates with American Superconductor Corp. (AMSC), the world leader in PIT processing of BSCCO superconductors. In the work with AMSC, the focus is on phase formation, reaction kinetics, and optimization of the microstructure and properties of tapes. As part of this collaboration, effects of stoichiometry and heat-treatment conditions on phase-evolution kinetics are studied. Our agreement with AMSC involves interactions with the University of Wisconsin and Los Alamos National Laboratory. Our findings are incorporated into AMSC's tape manufacturing scheme, and AMSC reported a world-record J_c of 70 kA/cm^2 in a short rolled tape. The long-length (>200-m) tapes carry a critical current of ≈150 A at 77 K. From such a conductor, coils for a 5 MW motor have been constructed.

To characterize the superconducting properties of long-length conductors, a test facility was assembled. This facility allows us to pass >2000 A of current through 1-m-long bulk superconductor rods and tubes. The performance of superconductors in an applied background magnetic field (an important parameter for practical application) is also determined in our test facility.

Because BSCCO exhibits poor flux pinning (i.e., less resistance to the motion of magnetic flux), applications of this superconductor have been limited to those areas where operations are conducted at 35 K in a magnetic field of 1 T, or at 65 K in a field of ≈0.1 T. Because YBCO behaves better than BSCCO in the presence of a magnetic field, efforts are now underway to use it for conductor development. Fabrication of well-aligned YBCO by the PIT technique is very difficult, so an alternative approach for depositing YBCO on a textured surface was developed; this is usually referred to as the "coated-conductor" method. Close control of substrate/buffer layer(s) texture is required for production of useful coated conductors. We are developing a technique to fabricate YBCO coated conductors. We have recently fabricated YBCO coated conductors with J_c = 1.2 MA/cm^2 at 77 K.

The Section collaborates with AMSC, SuperPower, Inc. (SP), and Universal Energy Systems, Inc. (UES), in developing coated conductors. In the work with AMSC, the focus is on ISD development and electrical, mechanical, and microstructural characterization of coated conductors. The collaboration with SP is directed at issues associated with PLD and metal-organic chemical vapor deposition. Substrates prepared by ISD are also provided to SP. Work with UES focuses on development of the PLD technique to deposit YBCO on ISD substrates prepared at UES and characterization of the buffer and superconductor layers.

In the ISD approach, a flexible metallic substrate is held at an angle to the direction of the plume of the species to be deposited, and texturing is obtained without the assistance of an ion gun. We have evaporated MgO by e-beam and obtained biaxially textured MgO layers on Hastelloy substrates. The ISD deposition rate is more than one order of magnitude higher than in ion-beam assisted deposition, a leading alternative approach. After depositing the appropriate buffer layers, YBCO was deposited on ISD samples. In collaboration with UES, we have fabricated several 1-m-long ISD-MgO tapes. ANL's Advanced Photon Source is used to characterize the coated conductors.

For improved reliability and performance prediction, an evaluation of residual stresses/strains and strain tolerance of coated conductors is critically needed. To this end, residual stress evolution in multilayered YBCO-coated conductors is being modeled and predicted by finite element analysis. The predicted results have been verified by experimental measurement of residual stresses by optical interferometry. The residual stresses are correlated with the measured bend strain tolerance of the coated conductors in an effort to optimize processing.

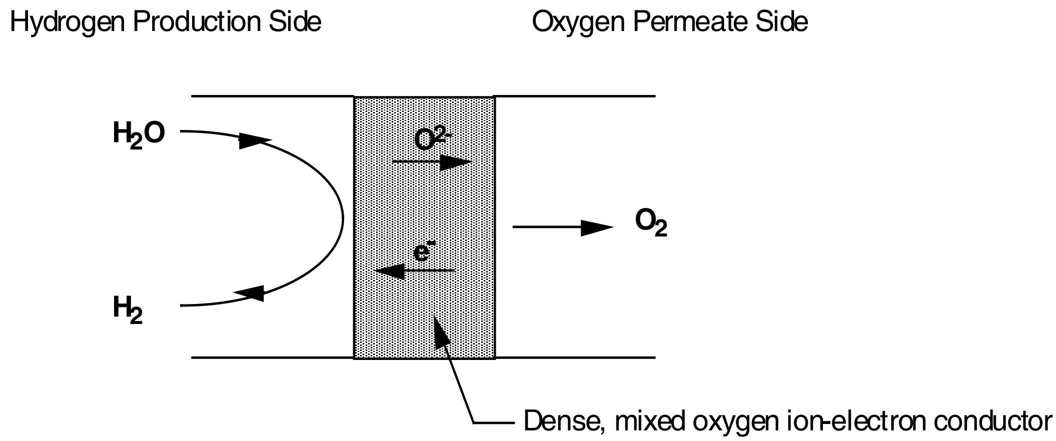
Many of the envisioned applications of high-temperature superconductors require greater resistance to the motion of magnetic flux, i.e., improved flux pinning. To improve flux pinning, nanophase oxides such as TiO_2, ZrO_2, and Al_2O_3 were added to $YBa_2Cu_3O_x$, $Bi_2Sr_2CaCu_2O_x$, and $TlBa_2Ca_2Cu_3O_x$. These additions resulted in formation of nanometer-scale compounds such as $BaTiO_3$ and $BaAl_2O_4$ and increased pinning by factors of 2 to 10 at temperatures below 50 K. In another approach, sol–gel methods were used to directly form intragranular nanophase inclusions during the synthesis reaction.

Ceramic Membrane Development

The Ceramics Section is developing dense ceramic membranes for separating hydrogen from gas mixtures as part of the effort by the DOE Office of Fossil Energy (FE) to maximize the use of vast domestic fossil resources and ensure a fuel-diverse energy sector while responding to global environmental concerns. The development of cost-effective membrane-based reactor and separation technologies is of considerable interest for applications in advanced coal-based power and fuel technologies. Because concerns over global climate change are driving nations to reduce CO_2 emissions, hydrogen is considered the fuel of choice for both electric power and transportation industries.

Hydrogen is presently recovered using cryogenics, pressure swing adsorption (PSA), and membrane systems, each of which has limitations: cryogenics is generally used only in large-scale facilities with liquid hydrocarbon recovery, because of its high capital cost; and PSA typically recovers less hydrogen from the feed stream and is limited to modest temperatures. Currently used membrane systems are susceptible to chemical damage from H_2S and aromatics and have limited temperature tolerance. Dense ceramic-based membranes are simple and efficient alternatives to the existing methods for hydrogen recovery.

The goal of this project is to develop a dense ceramic-based membrane for separating hydrogen from gas mixtures at commercially significant fluxes under industrially relevant operating conditions. Of particular interest is the separation of hydrogen from product streams that are generated during coal gasification, methane partial oxidation, and water-gas shift reactions. Potential ancillary uses of the membrane include dehydrogenation and olefin production, as well as hydrogen recovery in petroleum refineries and ammonia synthesis plants, the largest current users of deliberately produced hydrogen. Because the membrane will separate hydrogen without using electrodes or an external power supply (i.e., its operation will be nongalvanic), it requires materials that exhibit suitable electronic and protonic conductivities as well as high hydrogen diffusivity and solubility. Good mechanical properties are also necessary to withstand operating stresses. In addition, the materials must be fabricated into thin, dense membranes to maximize the hydrogen flux and maintain high hydrogen selectivity.



Hydrogen production through water splitting using dense ceramic membrane

Materials development for the hydrogen-separation membrane follows a three-pronged approach. In one approach, we investigate monolithic, mixed proton/electron conductors (e.g., perovskites doped on both A- and B-sites). For maximum hydrogen transport, the protonic and electronic conductivities should be nearly equivalent. This effort focused initially on $BaCe_{0.8}Y_{0.2}O_{3-x}$ (BCY); however, its low electronic conductivity does not support a high nongalvanic hydrogen flux, and it is not stable in atmospheres with high concentrations of CO_2. To identify a more stable oxide whose protonic and electronic conductivities are better matched, we utilize principles of solid-state defect chemistry to choose appropriate dopants and adjust the doping levels.

In the second approach, we develop cermet membranes using mixed proton/electron conductors intimately mixed with a metallic component. In cermets made with mixed proton/electron conductors, the metal enhances the hydrogen permeability of the ceramic phase by increasing the electronic conductivity. Depending on the hydrogen permeability, the metal may provide an additional transport path for the hydrogen. Alternatively, the cermet membrane may be made with a mixed oxygen ion/electron conductor, which can produce hydrogen by removing oxygen that is produced by thermally dissociating water.

In the third approach, we develop composites that contain a metal with high hydrogen permeability, a so-called hydrogen transport metal, dispersed in a suitable matrix material, which could be either a ceramic or a metal. In these composites, hydrogen is transported almost exclusively through the hydrogen transport metal, and the matrix serves primarily as a structural support.

The highest hydrogen flux achieved to date, >20 cm^3 (STP)-min^{-1}-cm^{-2}, was obtained with an ≈0.05-mm-thick membrane at 900°C using 100% H_2 as the feed gas. Another membrane produced hydrogen through water splitting at a rate >9 cm^3 (STP)-min^{-1}-cm^{-2}. Methods for fabricating these materials into thin, dense membranes are being developed, and the chemical and mechanical stabilities of the membranes are being studied to estimate their expected lifetime. Specifically, mechanical properties evaluation is performed as a function of processing variables, and the results are correlated with fractographic evaluations of critical flaws to optimize process parameters. The stability of ANL membranes in H_2S-containing atmospheres is being tested in H_2/He mixtures containing 51-2922 ppm H_2S and in syngas (61.3% H_2, 8.2% CH_4, 11.5% CO, 9.0% CO_2) containing 100 ppm H_2S (with 10% He for measuring leakage). Based on relatively short-term (≤250 h) exposures, the stability limit appears to be in the range 400-900 ppm H_2S in H_2/He mixtures. Longer-term evaluations are underway. Scoping-level evaluations will be performed to identify potential applications of ceramic-based hydrogen separation membranes. Areas that will be evaluated include overall market scale, typical site operating scale, process integration opportunities and issues, and alternative-source economics. The Section is working with Eltron Research, Inc., and ITN Energy Systems, Inc., in the area of hydrogen transport membranes.

Waste Stabilization

The Ceramics Section has demonstrated a process for stabilizing hazardous, radioactive, and mixed wastes by using novel phosphate ceramics that set at room temperature. Chemically bonded ceramics based on magnesium, magnesium/potassium, iron, and zirconium phosphates can stabilize a wide range of DOE waste streams, such as contaminated ash, salt cakes, and sludge, and thus they hold promise for treating waste streams generated by the utility, chemical, and defense industries. The process stabilizes problem wastes such as secondary waste streams arising from thermal treatment processes (such as vitrification and plasma arc treatment) and other chemical processes used for destroying organics. The process also can be used to stabilize wastes containing volatile species and pyrophorics, which cannot be treated by thermal stabilization.

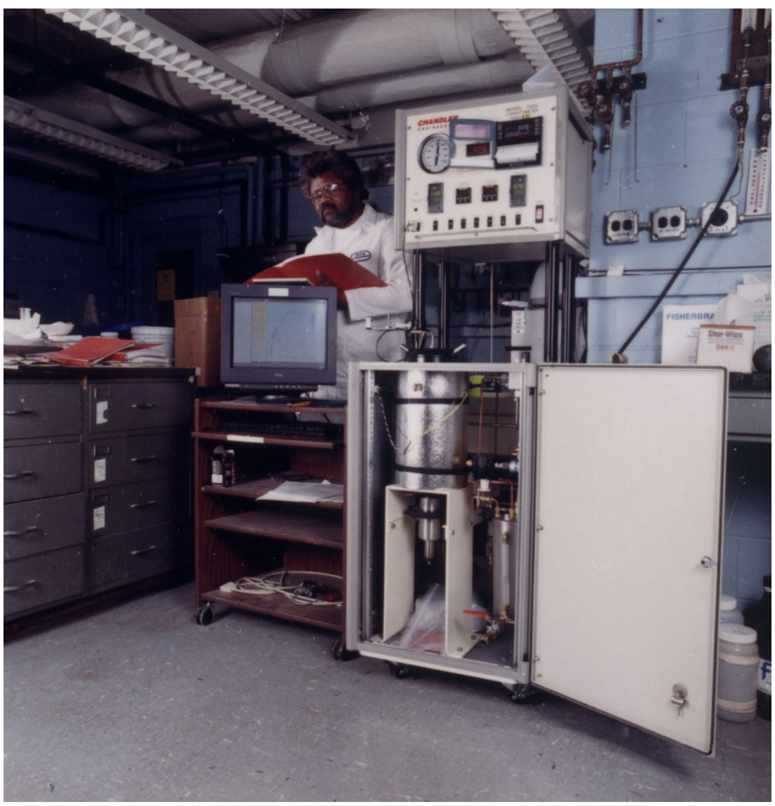
Stabilization of these materials involves both chemical solidification and physical encapsulation of wastes, resulting in superior waste forms. Optimization of the phase compositions, microstructures, and mechanical and physical properties has led to the development of dense and durable waste forms. Because of the high waste loading and low-temperature operation, chemically bonded phosphates are a low-cost alternative to other stabilization technologies. As part of treatability studies, several mixed wastes from DOE facilities such as Savannah River Site, Fernald, Rocky Flats, Argonne East and West, and Idaho National Engineering and Environmental Laboratory have been successfully stabilized in phosphate ceramics. The process has been scaled up to stabilize actual wastes; collaborations with private industry are ongoing to demonstrate the stabilization of DOE waste streams.

Chemically bonded phosphate ceramics have been shown to bind various high-volume innocuous wastes such as plastics, cellulose fibers, ash, and lumber. With our phosphate ceramics technology, these wastes can be made into inexpensive value-added construction products. The waste materials are mixed in powder or shredded form with the phosphate binder and fabricated into a variety of forms such as blowable or pumpable insulation, particle boards, and bricks. Because the phosphate binder is inorganic, the resulting products are nonflammable. Relevant properties of all resulting materials have been evaluated to establish their applicability for storage or use as lightweight, fire-resistant, environmentally benign construction materials for energy conservation.

The phosphate-bonded ceramic-based sealants have been developed to meet the cementing needs related to exploration and completion of oil and gas wells (see next figure). Collaborative projects are ongoing to demonstrate the technology at pilot and field scales in actual oil fields. The phosphate-bonded ceramic technology has also found potential application as a root canal cement, and we have started working with Tulsa Dental Products to modify the ceramic composition to make it biocompatible.

Structural Ceramics and Composites

The Ceramics Section has been involved in a DOE-funded program on thermal barrier coatings (TBCs) and environmental barrier coatings (EBCs). This work is in support of DOE's Advanced Turbine System (ATS) Program, which is aimed at developing a new generation of land-based gas turbine systems that provide cost-effective utility and industrial power generation at low cost, improved efficiency, and increased service life, and that meet environmental requirements. Generally, our effort has been directed toward providing critical information on processing, microstructure, residual stresses, mechanical/thermomechanical properties, damage evolution, and failure modes/mechanisms in order to develop improved TBCs and EBCs for ATS applications. Current effort is focused on the performance evaluation of EBCs. To this end, we have assessed and extended the application indentation technique for measurement of the elastic modulus of thin EBCs. This technique is very quick and cost-effective and provides reliable data.



High-pressure consistometer to simulate oil-well conditions for phosphate-bonded ceramic research

The reliable measurement of the elastic modulus of thin EBC layers has facilitated numerical and analytical modeling of residual stresses and damage evaluation in EBC systems. The residual stresses are correlated with measured mechanical properties for improved processing and life-time prediction modeling of EBCs. We found that the observed anisotropy in mechanical behavior at the EBC/substrate interface results from the anisotropy in residual stresses at the interface due to thermal expansion mismatch between the EBC and substrate. As a part of the performance evaluation, thermal fatigue tests of EBCs and TBCs are performed in a bottom-loading furnace, and damage evolution during mechanical fatigue loading is monitored using a mechanical test facility attached with a high-power microscope. Results indicate that TBC failure occurs from the coalescence and growth of microcracks that are preferentially initiated at the TBC/substrate interface, as opposed to the growth of a single crack.

In another DOE-funded program, a novel test methodology using miniature disk specimens is being assessed for mechanical evaluation and reliability prediction of turbine components with and without EBCs. The reduced size of the test specimens is expected to facilitate measurements from different sections of a complex-shaped turbine component that have varying thermal and stress histories in actual turbine environments.

Capacitor Development

The Ceramics Section is developing advanced capacitor technologies to support DOE's program on vehicle electrification. Advanced power electronic modules, the heart of the electrical propulsion system, require low-cost, high-energy-density capacitors with reduced weight and size. Such capacitors can be realized by fabrication of microelectronic-scale $(Pb,La)(Zr,Ti)O_3$ (PLZT) thin-film (<0.5 μm) capacitors. PLZT, a ferroelectric material, possesses superior dielectric properties such as high dielectric constants, high breakdown fields, and low dielectric losses.

Our efforts are centered on fabricating PLZT thin films by chemical solution deposition, developing a fundamental understanding of processing effects on dielectric properties, and arriving at robust processing strategies for anticipated devices. This program is a collaborative effort with ANL's Materials Science Division.

We have developed techniques to fabricate ferroelectric thin films on base-metal foils. Integration of base-metal electrodes provides a significant cost advantage over current noble metal electrodes used in conventional multilayer ceramic capacitors. Our film-on-foil dielectric sheets can be used to fabricate discrete capacitors, or laminated directly into the printed wire board as imbedded passive devices.

Appropriate growth conditions were determined for deposition of PLZT thin films on Ni foils. The effects of film composition, growth conditions, and thermal processing were investigated and correlated with electrical properties. We have also developed buffer layers to inhibit the effects of a parasitic interfacial layer and thereby yield film-on-foil elements with excellent dielectric properties. Dielectric constants of 1400, a capacitance density of 1.8 $\mu F/cm^2$, dielectric losses as low as 0.03, with breakdown fields of 1.6 MV/cm have been obtained.

Concurrent with this effort we are also developing novel electrode designs which result in a graceful controlled loss of capacitance should a failure occur.

Argonne works closely with the Center for Dielectric Studies at Pennsylvania State University. We have also developed strong working relationships with microelectronic equipment companies developing ferroelectric thin film technologies, capacitor companies, and the automotive end–users.

Corrosion and Mechanics of Materials

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Programs of the Corrosion and Mechanics of Materials Section address specific concerns related to corrosion and the effects of various environments on the mechanical behavior of materials used in several types of energy systems. The research is sponsored by various branches of the U.S. Department of Energy (DOE) that include the Office of Fusion Science, the Office of Fossil Energy, and the Office of Industrial Technologies. In addition, the U.S. Nuclear Regulatory Commission (NRC) supports light water reactor (LWR) research, which includes studies of effects of reactor environments on low-cycle fatigue and crack propagation in reactor structural alloys, irradiation-induced susceptibility to stress corrosion cracking, cladding criteria for high-burnup fuel, air oxidation kinetics for Zr-based alloys, and effects of impurities in helium on scaling and mechanical properties. Highlighted below is our research into aging degradation of light water reactors, corrosion in advanced combustion power systems, design criteria for materials subject to neutron embrittlement in fusion reactors, and metal dusting in various industrial processes.

Light Water Reactors

To continue safe operation of current LWRs, the aging degradation of the reactor structures must be adequately understood and managed. Potential aging mechanisms include fatigue and environmentally assisted cracking of piping and pressure vessels, and irradiation-assisted stress corrosion cracking (IASCC) of reactor internals. Nonsensitized austenitic stainless

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[1] Special Term Appointee.

[2] Part Time.

[3] Serves two sections.

[4] Bradley University.

[5] Korea Atomic Research Institute.

[6] National Institute of Fusion Science, Japan.

[7] Nuclear Regulatory Commission.

[8] University of Texas at El Paso.

[9] Lafayette College.

[10] Waubonsee Community College.

[11] Schenectady County Community College.

[12] Harvey Community College.

[13] Marmara Research Center, Turkey.

[14] U. of Illinois at Chicago.

steels (SSs) become susceptible to intergranular failure after accumulation of a sufficient neutron fluence. Such cracking has occurred in control-blade sheaths and handles and in instrument dry tubes of boiling water reactors (BWRs). Intergranular cracking has also occurred in more safety-significant structural core components in BWRs, such as the top guide, shroud, and core plate. However, the relative contributions of neutron fluence, material composition, heat-treatment condition (sensitization), and fabrication variables (welding method and residual weld and fit-up stresses) to crack initiation and growth are not clear. The current LWR research is focused on (a) fatigue of pressure vessel and piping steels, (b) crack growth in austenitic SSs, (c) IASCC of austenitic SSs, and (d) environmentally assisted cracking in high-nickel alloys.

Fatigue Testing of Carbon Steels and Low–Alloy Steels

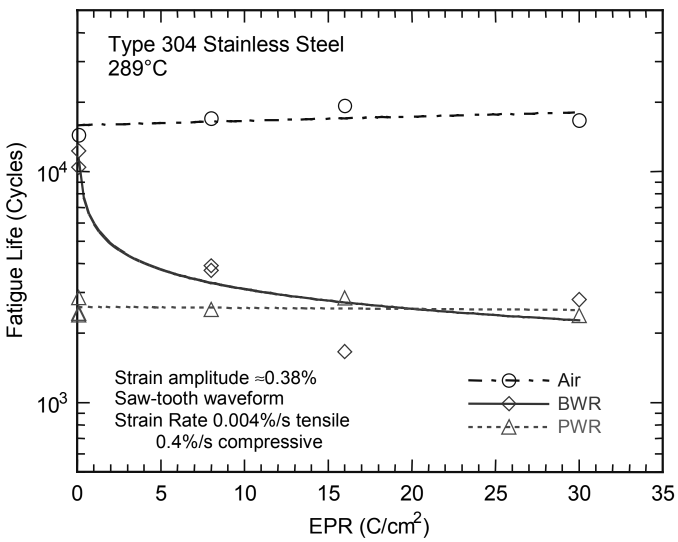
Carbon and low-alloy steels and austenitic stainless steels are used extensively in LWR steam supply systems as piping and pressure vessel materials. The environmentally related increase of fatigue crack growth rates in pressure vessel and piping steels in high-temperature water is well known. LWR coolant environments can also significantly affect the fatigue lives of these steels. Under certain conditions of loading and environment, the fatigue lives of these steels can be a factor of 70 lower in coolant environments than in air. Fatigue tests are being conducted in air and simulated LWR environments to obtain data under conditions where information is lacking in the existing fatigue data base. Additional studies have been undertaken to determine crack initiation and crack growth characteristics, and to better understand the actual mechanism of degradation. The results indicate that the decrease in fatigue life of pressure vessel and piping steels is caused primarily by the effect of the environment during the early stages of fatigue damage, i.e., growth of cracks that are <200 μm deep (Stage I crack growth). The mechanisms for the enhancement of the growth rates are slip dissolution/oxidation in carbon and low-alloy steels and hydrogen-induced cracking in austenitic stainless steels.

For carbon and low-alloy steels, the magnitude of the environmental effects on fatigue life increases as the level of dissolved oxygen (DO) in water is increased. In contrast, the fatigue lives of austenitic SSs are decreased significantly in low-DO water (<0.01 ppm DO). Also, the effect of environment is not influenced by the composition or heat treatment condition of the steel; the effect increases with decreasing strain rate and increasing temperature.

The effect of heat treatment can be quantified in terms of electrochemical potentiodynamic reactivation (EPR). The degree of sensitization of stainless steels is assessed by a potentiodynamic sweep over a range of potentials from passive to active and measures the amount of charge associated with the corrosion of chromium-depleted regions surrounding chromium carbide-precipitated particles. An EPR value less than 1.0 designates an unsensitized microstructure, while greater than 4 corresponds to a fully sensitized microstructure.

In high-DO water, the fatigue lives of austenitic SSs are influenced by the composition and heat treatment of the steel. As shown in the figure, fatigue life is lower for sensitized Type 304 steel in BWR water; the decrease in life appears to increase as the degree of sensitization is increased. Furthermore, the fracture mode is different in water. In air, irrespective of the degree of sensitization, the fracture mode for crack initiation and crack propagation is transgranular, most likely along crystallographic planes, leaving behind relatively smooth facets.

In the high-DO water, the initial crack appeared intergranular for sensitized material, implying a weakening of the grain boundaries. By contrast, in low-DO environments, cracks initiate and propagate in a transgranular mode irrespective of the degree of sensitization.



The effect of material heat treatment on the fatigue life of Type 304 stainless steel in air, BWR, and PWR environments (left) and fracture surface morphology in high-dissolved oxygen environment (right)

Environmentally Assisted Cracking of Ni-Base Alloys

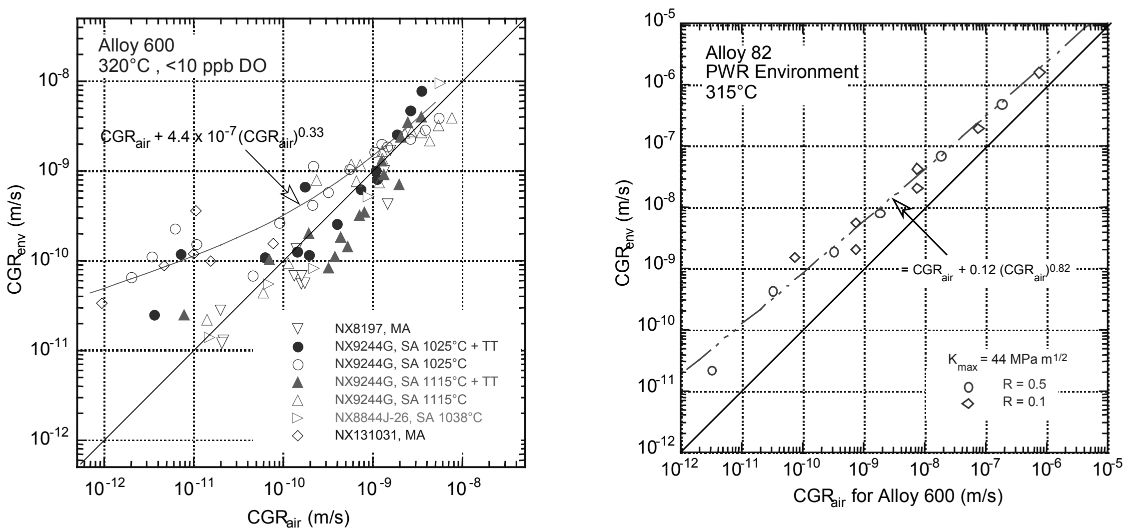
The Ni-base alloys used as LWR construction material have experienced stress corrosion cracking (SCC). In the fall of 1991, for example, a leak was discovered in the penetration to the pressure vessel head at the Bugey 3 plant in France. Metallurgical evaluations indicated that the leak was caused by primary-water SCC. The main crack had initiated in Alloy 600 base metal and propagated into the Alloy 182 weld metal. Subsequent inspections of penetrations in the control rod drive mechanisms of domestic and foreign PWRs identified a small number (<5% of the penetrations inspected) with axial cracks. None of the cracks was through-wall, and until recently, no more leaks occurred in pressure-vessel head penetrations. From the summer of 2000, SCC has occurred in penetrations of control rod drive mechanisms for several PWRs in the U.S., as well as in outlet nozzle-to-pipe dissimilar weld metals. More recently, cracks have been found in bottom-mounted instrumentation nozzles.

Long-term operating experience indicates that although wrought Ni-base Alloy 600 is susceptible to SCC, until recently, the weld metal (Alloys 82 and 182) used with Alloy 600 had not shown environmentally assisted cracking. However, laboratory tests indicate that in PWR coolant environments, the SCC susceptibility of Alloy 182 may be greater than that of Alloy 600, and the SCC susceptibility of Alloy 82 may be comparable to that of Alloy 600. This apparent inconsistency between field and laboratory experience is an issue that needs further investigation. An ANL program is underway to evaluate the resistance of Ni-base alloys and their welds to environmentally assisted cracking in simulated LWR coolant environments. Information has been obtained on the effect of temperature, load ratio, and stress intensity on environmentally assisted cracking of these alloys in simulated LWR environments.

To obtain a qualitative understanding of the degree of enhancement and the range of conditions over which significant environmental enhancement is observed, it is helpful to plot the observed crack growth rates (CGRs) against those expected in air under the same mechanical loading conditions, i.e., the same stress intensity range, cyclic stress ratio, and rise time. The next figure shows corrosion fatigue results for various heats of Alloy 600 and 82 weld metal tested in a simulated PWR environment. There is significant environmental enhancement of the CGR for Ni-base alloys at both low- and high-DO levels. The next figure (left side) shows that, for Alloy 600 at CGRs greater than $\approx 10^{-9}$ m/s, the mechanical driving forces dominate; at lower CGRs, the environmental contributions dominate. These same observations do not appear to be valid for Alloy 82 in a PWR environment (next figure, right side).

Irradiation–Induced Stress Corrosion Cracking of Austenitic Stainless Steels

In recent years, failures of reactor internal components have been observed after the components have reached neutron fluence levels $> 5 \times 10^{20}$ n•cm^{-2} (E > 1 MeV). The general pattern of the observed failures indicates that as nuclear plants age and fluence increases, various apparently nonsensitized austenitic stainless steels become susceptible to intergranular failure. Some components (e.g., BWR core shroud, control-blade handle and sheath) have cracked under low applied stresses. Although some failed components can be replaced, structural components such as the BWR top guide, shroud, or core plate would be very difficult or impractical to replace. Understanding IASCC is thus necessary to determine operating and inspection requirements for reactors that have reached threshold fluence levels.



Corrosion fatigue data for Alloy 600 and Alloy 82 in low-dissolved-oxygen (<10 ppb) water

The primary effects of irradiation on the reactor internals, which are usually fabricated from Type 304, 316, or 348 SSs, include alteration of microchemistry, microstructure, and mechanical properties. Irradiation produces defects and defect clusters in grain matrices and alters the dislocation network, dislocation loop, and dislocation channel structures, leading to radiation-induced hardening. Irradiation also leads to changes in the stability of second-phase precipitates and the local chemistry near grain boundaries, precipitates, and defect clusters.

Grain-boundary microchemistries that differ significantly from the bulk composition can be produced not only by radiation-induced segregation but also by thermally driven equilibrium and nonequilibrium segregation of alloying and impurity elements. Neutron irradiation also alters the water chemistry. Although irradiation-induced grain-boundary depletion of Cr has been considered for many years to be the primary metallurgical process that causes IASCC, numerous IASCC characteristics cannot be explained well by Cr-depletion theory.

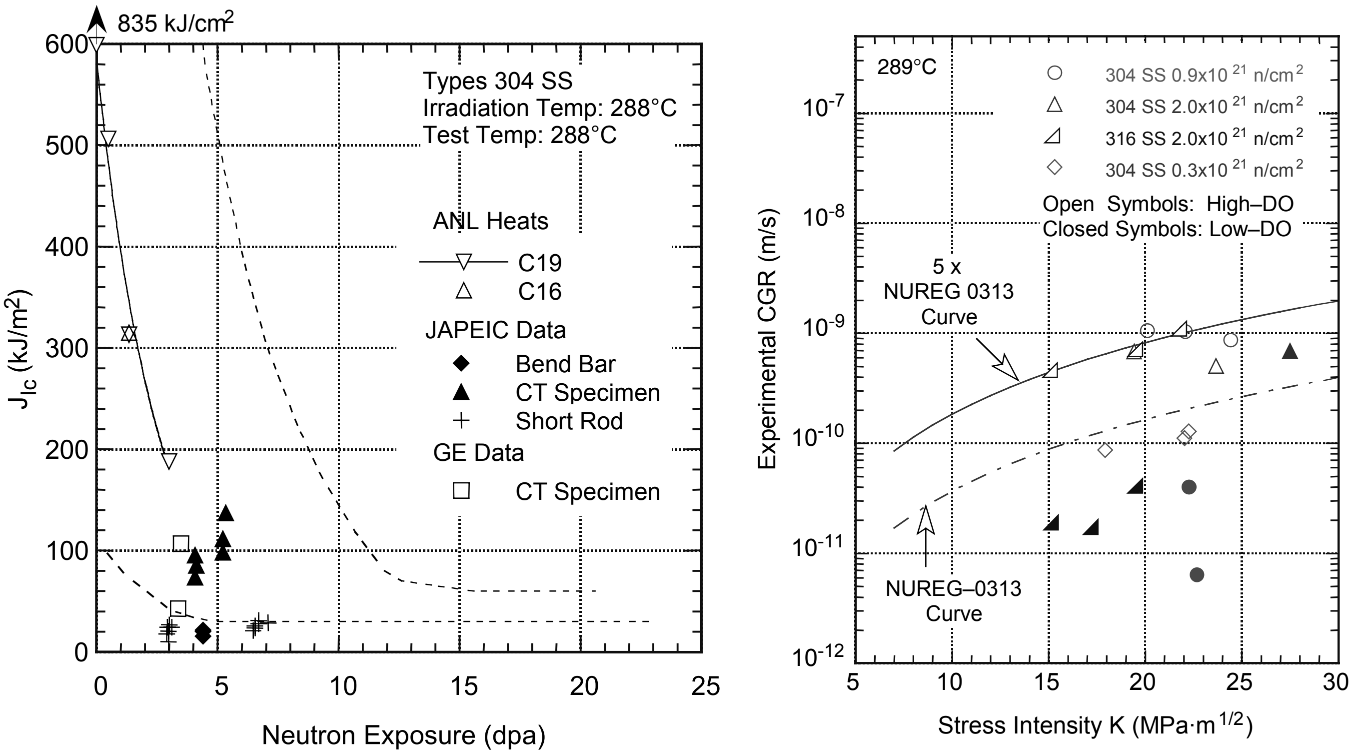
Our work in this area includes (a) determination of crack growth rate, fracture toughness, and susceptibility to IASCC of irradiated stainless steels in BWR-like water; (b) stress corrosion testing, tensile testing, and microstructural analysis of decommissioned EBR-II (Experimental Breeder Reactor-II) components irradiated to very high dose; (c) microstructural characterization and failure analyses of BWR core shroud welds and simulated mockup welds fabricated by a shielded-metal-arc procedure; and (d) test design and specimen irradiation in a PWR-relevant irradiation experiment in the BOR-60 reactor in Russia, in cooperation with the International Group on Cooperative IASCC Research. Highlights of these efforts are summarized below.

Crack Growth Rates and Fracture Toughness of Austenitic Stainless Steels in BWRs

Austenitic SSs are used extensively as structural alloys in the internal components of reactor pressure vessels because of their superior fracture toughness. However, exposure to high levels of neutron irradiation for extended periods leads to significant reduction in the fracture resistance of these steels. Experimental data have been obtained on fracture toughness, corrosion fatigue, and SCC of austenitic SSs that were irradiated to fluence levels of ≈0.3, 0.9, and 2.0×10^{21} n/cm^2 (E > 1 MeV) (≈0.45, 1.35, and 3.0 dpa) at ≈288°C. The irradiations were carried out in a helium environment in the Halden heavy water boiling reactor. Fracture toughness tests were conducted in air, and CGR tests in normal water chemistry (NWC) and low-DO BWR environments at 288°C.

Neutron irradiation at 288°C decreased the fracture toughness of all steels tested. The figure below (left) gives the fracture toughness curves for Type 304 SS derived from tests at ANL, the Japan Power Engineering and Inspection Corp. (JAPEIC), and General Electric (GE). The data from commercial heats (JAPEIC and GE) generally fall within the scatter band (dashed lines in figure) for the data obtained at higher temperatures. For Type 304 SS irradiated to 0.3, 0.9, and 2.0×10^{21} n/cm^2, the fracture toughness values decrease as follows: 507, 313, and 188 kJ/m^2, respectively. The fracture toughness curves for irradiated Types 304 and 316 SS are comparable.

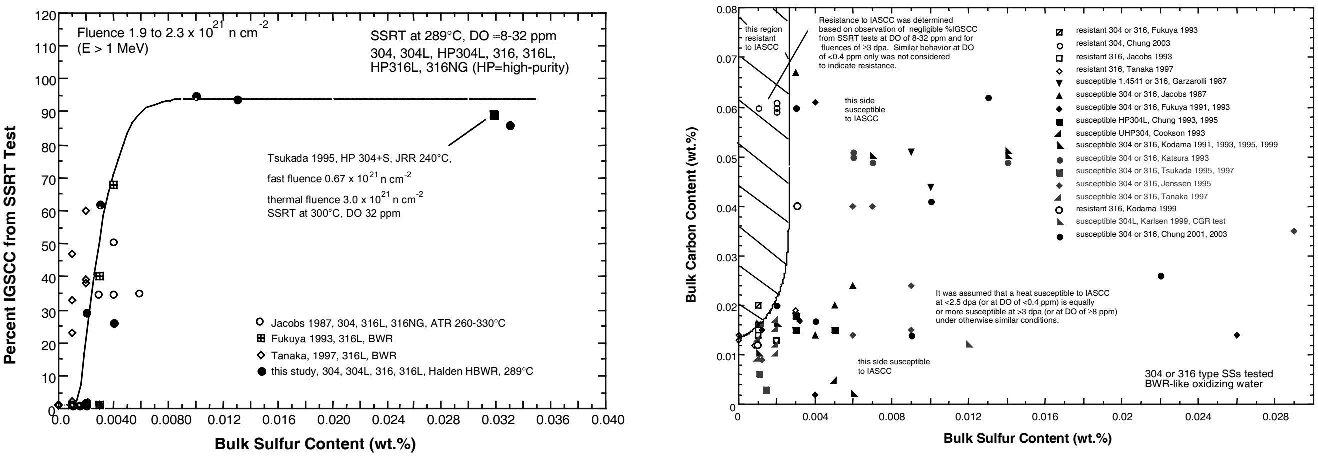
The tests for the steels irradiated to either 0.9 or 2.0×10^{21} n/cm^2 indicate significant enhancement of CGRs in the NWC BWR environment (next figure, right). The CGRs under SCC conditions are a factor of ≈5 higher than the disposition curve proposed in the NRC report NUREG–0313 for sensitized austenitic SSs. In low-DO BWR environments, the CGRs of the irradiated steels decreased by an order of magnitude. The beneficial effect of decreased DO was not observed for Type 304 SS irradiated to 2×10^{21} n/cm^2. Type 304 SS irradiated to 0.3×10^{21} n/cm^2 (0.45 dpa) showed very little environmental enhancement of CGRs in the NWC BWR environment. The CGRs for Type 304 irradiated to 0.3×10^{21} n/cm^2 under SCC conditions are below the disposition curve for sensitized SSs in low-DO water (8 ppm), as given in NUREG–0313.



Fracture toughness (J_{Ic}) of austenitic stainless steels as a function of neutron exposure at 288°C (left) and SCC growth data for irradiated austenitic SSs in high-purity water at 289°C (right)

IASCC of Austenitic Stainless Steels in BWRs

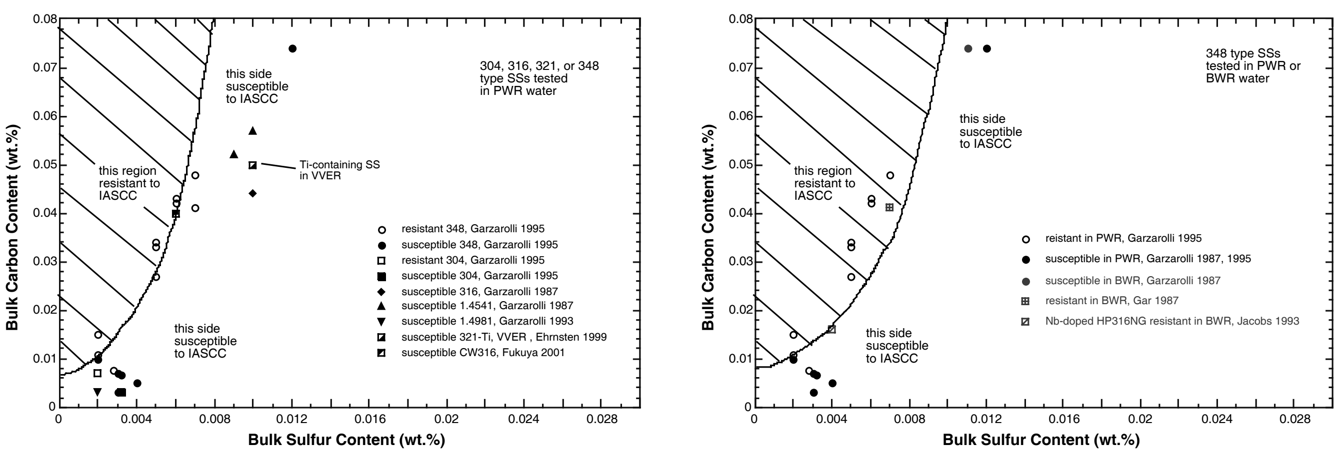
Slow-strain-rate tensile (SSRT) tests in simulated BWR water were conducted on model austenitic SSs that were irradiated at 289°C in helium to ≈0.3×10^{21} n•cm^{-2} (≈0.4 dpa) and ≈2.0×10^{21} n•cm^{-2} (≈3 dpa) (E>1 MeV) in the Halden reactor. Fractographic analysis by scanning electron microscopy was conducted to determine susceptibility to IASCC as manifested by the degree of intergranular fracture surface morphology. Susceptibility to IASCC increased drastically as the damage level increased from ≈0.4 to ≈3 dpa. Bulk S content provided the best and the only good correlation with susceptibility to IASCC at >2 dpa. Type 304 and 316 SSs containing S ≤0.002 wt.% were resistant, whereas at S concentrations >0.003 wt.%, susceptibility increased drastically. This finding indicates that the deleterious effect of S is dominant at high fluence, and that an S-related critical phenomenon occurs. Sulfur content of ≤0.002 wt.% does not necessarily render low-carbon steel (Types 304L, 316L) or high-purity-grade steels resistant to IASCC, indicating a beneficial effect of C. Our two-dimensional map of bulk C and S concentrations shows the range in which Type 304, 304L, 316, and 316L SSs are resistant or susceptible to IASCC. This map is consistent with all data obtained for neutron-irradiated steels tested in BWR-like oxidizing water. Grain-boundary segregation of S was determined by Auger electron spectroscopy for BWR neutron absorber tubes fabricated from two Type 304 SS heats.



Effects of S on susceptibility to intergranular SCC of Type 304 and 316 SSs (C content ≈0.060 wt.%) irradiated to 3 dpa (left) and range of bulk S and C contents that renders a 304- or 316-Type steel susceptible or resistant to IASCC in BWR-like oxidizing water (right)

IASCC of Austenitic Stainless Steels in PWR Environment

Similar to the effort to evaluate the compositional characteristics of SS heats resistant to IASCC under BWR conditions, steels reported to be resistant to IASCC under PWR conditions were analyzed. Most of the data reported for PWR conditions were for Type 348 SSs. The two-dimensional maps of bulk S and C concentration (see below) show the range in which Type 304, 316, and 348 SSs have been reported to be resistant to IASCC under PWR conditions. Compared with BWR oxidizing condition, good resistance to IASCC under PWR conditions is observed for a wider range of S concentration.



Range of bulk S and C contents that renders austenitic steels susceptible or resistant to IASCC in PWR condition (left) and similar range applicable to Nb-stabilized steels for BWR and PWR conditions (right)

Susceptibility to intergranular fracture in 23°C air was determined for ≈3-dpa steels with and without exposure to the SSRT conditions in 289°C water. Similar bending tests were also performed on hydrogen-charged BWR components in 23°C vacuum. Both types of bend fracture exhibited similar characteristics dominated by hydrogen-induced irradiation-assisted cracking

(IAC). Steels that showed high susceptibility to IASCC in 289°C water exhibited low susceptibility to hydrogen-induced IAC in 23°C air or vacuum, and vice versa. A heat that contains an unusually high content of S (0.022 wt.%) and an unusually low content of Mn (0.36 wt.%) failed as a result of virtually complete intergranular corrosion in 23°C air. This failure, not influenced by hydrogen, could not be explained on the basis of hydrogen-induced IAC but can be explained by a grain-boundary process in which Ni and S segregation plays an important role.

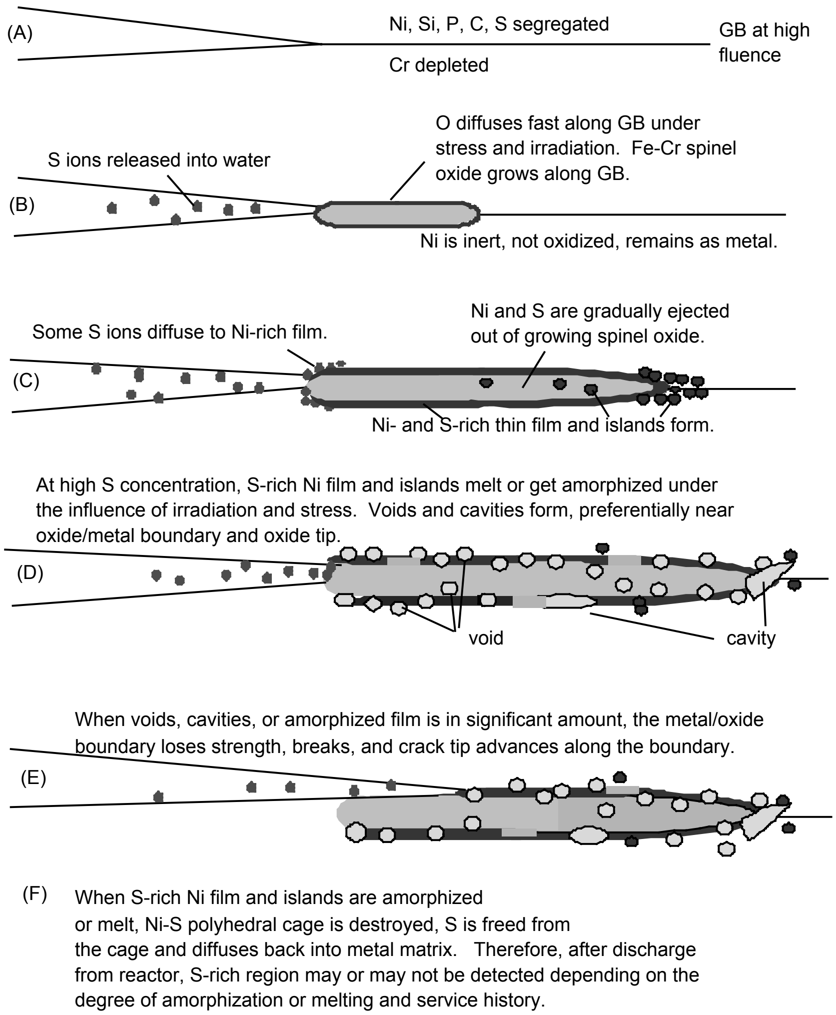
A large number of cold-worked and solution-annealed heats of Type 348, 316, and 304 SSs were irradiated to ≈5 and ≈10 dpa at 323°C in the BOR-60 reactor; irradiation to ≈40 dpa is in progress. The lower-dpa specimens are being transported from Russia for tensile and SCC testing in PWR water.

Initial Model of IASCC of Austenitic Stainless Steels

An initial model of IASCC was developed in consideration of several key observations in this study and elsewhere. The model is based on the following observations: (a) dominant effect of S, (b) evidence of grain-boundary (GB) segregation of S in unirradiated steel and in irradiated core internal components, (c) properties of the Ni-S binary that contains S-segregated grain boundaries, and (d) crack-tip microstructure and microchemistry of irradiated steels. The key aspects of the model are illustrated in the next figure.

Steam Generator Tube Integrity Program

Steam generator tubes, which account for more than 50% of the primary pressure boundary surface of PWRs, have experienced in-service corrosive and mechanical degradation of various forms since the beginning of PWR commercial operation in the late 1950s. Various forms of degradation have resulted in the plugging of well over 100,000 tubes to date around the world. In addition, 68 steam generators in 22 U.S. plants had been replaced by the end of 1998 at a cost of about $100 to $200 million each, and more replacements are underway or planned. Environmentally induced degradation through intergranular SCC and intergranular attack is the most serious degradation process at present. This degradation commonly occurs in crevice regions at tube support plate and tube sheet locations or under sludge piles, although intergranular SCC has also been observed in the free span of the tubes. Because of its variable and often complex morphology, this cracking can be difficult to detect and size by conventional inspection techniques, and the failure pressure and leak-rate behaviors of degraded tubes are not readily predictable.



Model of irradiation-assisted SSC in austenitic stainless steels

One of the objectives of this ET program is to evaluate and experimentally validate models to predict potential degradation modes and provide guidance for operational assessments. Model development requires better understanding of crevice conditions and SCC initiation, evolution, and growth. The models will be validated by comparing the predictions from field experience with respect to SCC of Alloy 600 steam generator tubes. The methodology benchmarked by Alloy 600 field experience will then be used to predict the behavior in the field of Alloy 690 steam generator tubes based on the laboratory data for Alloy 600 and 690 and the field experience for Alloy 690.

The models for predicting ligament rupture, unstable burst, and leak rate of flawed Alloy 600 tubes developed in the program have been incorporated into CANTIA, an integrity assessment code for steam generator tubes that was originally developed by Dominion Engineering for the Canadian Nuclear Safety Commission. Several other modifications were also made in ANL/CANTIA, which can model either axial or circumferential cracks, but not both simultaneously. An integrated mechanistically based model has also been developed (under a subcontract with Dr. Roger W. Staehle) to predict the secondary-side SCC failure of steam generator tubes under normal operating conditions. This effort is continuing with development of a quantitative model that is physically based on the prediction of secondary-side SCC initiation for the different submodes of SCC in given environments.

An autoclave facility for corrosion and stress corrosion initiation tests has been constructed. The facility consists of two independent recirculating loops. Each loop has an 8-L (2.1 gal) Hastelloy C276 autoclave vessel, high pressure pump, furnace, feed water system, effluent treatment system, pressure and temperature control units, electrochemical test system, and safety-related components. The vessels are rated for a design pressure of 14.5 MPa (2100 psi) at 350°C (662°F). In this new facility, SCC initiation tests are planned on reverse U-bend and tubular specimens fabricated from multiple heats of Alloy 600MA, Alloy 600TT, and Alloy 690TT. Tubular specimens are to be statically loaded with periodic cycling at stress levels of 75%, 100%, and 150% of yield strength. Crack growth rate experiments are also planned on tubular fracture mechanics specimens under various stress intensities. The results from the autoclave tests will be utilized in model boiler experiments, and in the development of predictive models.

Mechanisms of Pb-induced SCC are also being studied. A variety of microscopic analysis techniques are being used to elucidate how Pb affects the protective films on the steam generator tubes, and to identify the particular valence states and compounds that do form. Preliminary tests were performed to investigate the effects of Pb on the electrochemical behavior of Alloy 600 in aqueous solutions. The results indicate that Pb ions would influence passivity of the Alloy 600 surface. Measurements of anodic polarization and potentiostatic electrochemical impedance spectroscopy were performed with deaerated solutions of pH 4.5 at 25 and 90°C, with or without addition of Pb (as 300 ppm Pb^{2+}). The results indicated that lead was incorporated into the Alloy 600 specimen surface and enhanced electronic conductance. Incorporation of lead on the surface was examined for specimens tested at different electrochemical potentials (ECP). The specimens tested at cathodic potentials to the Pb/Pb^{2+} equilibrium showed Pb on the surface, while those tested at anodic potentials did not. The Pb/Pb^{2+} equilibrium ECP was calculated to be –0.210 and –0.259 V (vs. standard hydrogen electrode) at 25 and 90°C, respectively. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were obtained on an Alloy 600 specimen surface that was treated potentiostatically in the above aqueous solutions. The AES data showed that depth concentration profiles of the major alloy elements (Ni, Cr, and Fe) are consistent with the bulk chemical analysis, except in the near surface region of 10-20 nm depth. Lead is observed up to 23 at.% in the surface layer of 20 nm for a specimen that was polarized at –0.27 V in the Pb-containing solution. XPS will provide information on oxidation states of the elements at the specimen surface within an effective depth of 3 nm. Additional AES and XPS will be performed on specimens treated under different electrochemical conditions. Further electrochemical tests, AES, and XPS will be applied to specimens produced at higher temperature and pressure in the autoclaves.

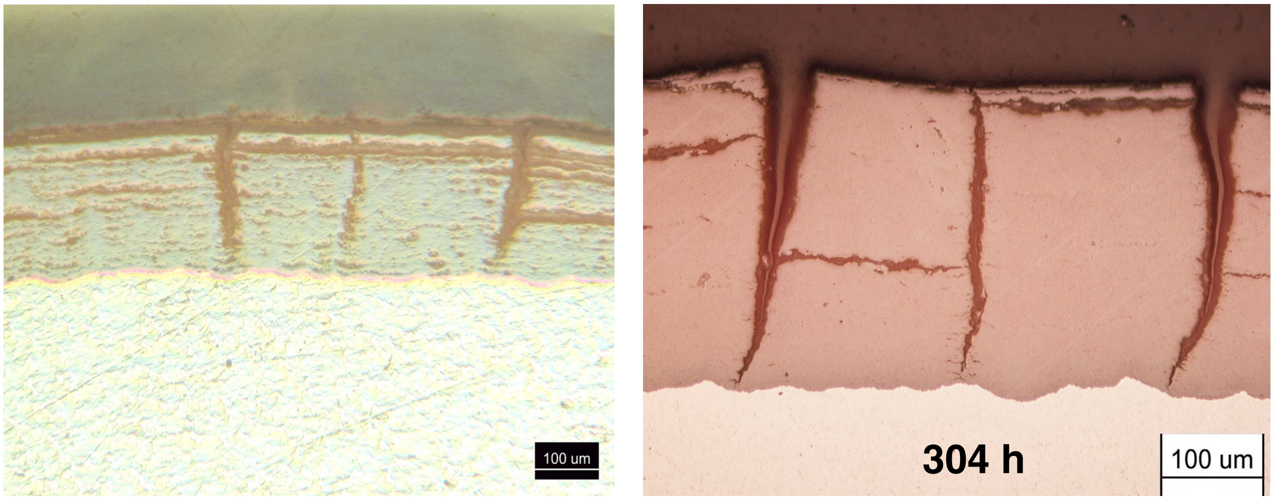
Steam generator tubes from McGuire Unit 1 and tube/tube sheet crevices were examined by destructive analysis. Intergranular cracks and attacks were observed at the secondary side, at the roll transition zone underneath crud deposits. To estimate the crevice chemistry that was present under operating conditions of the McGuire steam generator, we performed chemical and microstructural analyses for the deposits within the tube-to-tube sheet crevices in sections removed from the McGuire plant. A wide variety of elements were present in the crud deposits, including Fe, Ni, Cr, Al, Si, Mg, Cu, Ti, Mn, Ca, K, and S. The copper was present in the deposit as metallic copper. The presence of metallic Cu indicates that the electrochemical potential was below the Cu/Cu oxide equilibrium. The steam generator unit had operated initially with Ni-Cu moisture separator reheaters. It was not possible to identify whether lead was present. Additional microscopy is continuing to check for very local lead deposits at the crack and metal-metal oxide interfaces.

Air Oxidation Kinetics for Zr-based Alloys

An experimental program was conducted to generate data on the air oxidation kinetics of unirradiated Zircaloy-4 and Zirlo cladding with an oxide layer that is representative of the current inventory of spent fuel discharged after a medium or high level of fuel burnup. Several experiments were conducted in which ring specimens were exposed in a steam environment at several temperatures and for various time periods. Based on a detailed analysis of weight change and oxide thickness from these tests, a steam exposure time of 140 h and temperature of 550°C were selected to simulate the oxide layer (≈25-30 μm in thickness) on the cladding in a spent fuel pool.

The steam-preoxidized specimens were subsequently oxidized in air at temperatures in the range of 300-900°C. Oxidation tests in air emphasized temperatures in the range of 300-600°C, which is representative of cladding heatup in the event of a partial or full draining of spent fuel pool coolant. The maximum air oxidation times ranged between 300 h at 600°C and ≈1000 h at 300°C. Weight change and oxide thickness measurements were made on the specimens exposed at various times to establish the kinetics of the scaling process as a function of temperature. Bare capsules of Zr-based alloys were also exposed in air for comparison of the oxidation behavior of the cladding with and without steam-preoxidation.

Results showed that the initial oxide scale developed in steam was adherent and crack free in both alloys but tended to crack when exposed in air at 600°C. The thickness of the oxide developed during air exposure increased significantly with time, and the transverse cracks persisted over the entire thickness of the scale, as shown below in the microphotographs. The growth rate for oxide at 500°C in air was much less, and the scales exhibited virtually no cracks, even after an exposure time of 400 h at 500°C. The oxidation rates in air for steam-preoxidized specimens were minimal to negligible at 400 and 300°C after exposure times of 600 and ≈1000 h, respectively. The data showed that in the pre-breakaway region, oxygen ingress into Zirlo occurs at a higher rate than in Zircaloy-4. In the post breakaway region, the rates for Zirlo are somewhat lower than for Zircaloy-4 at ≤500°C; however, at ≥600°C, the rates for Zirlo are higher than for Zircaloy-4.

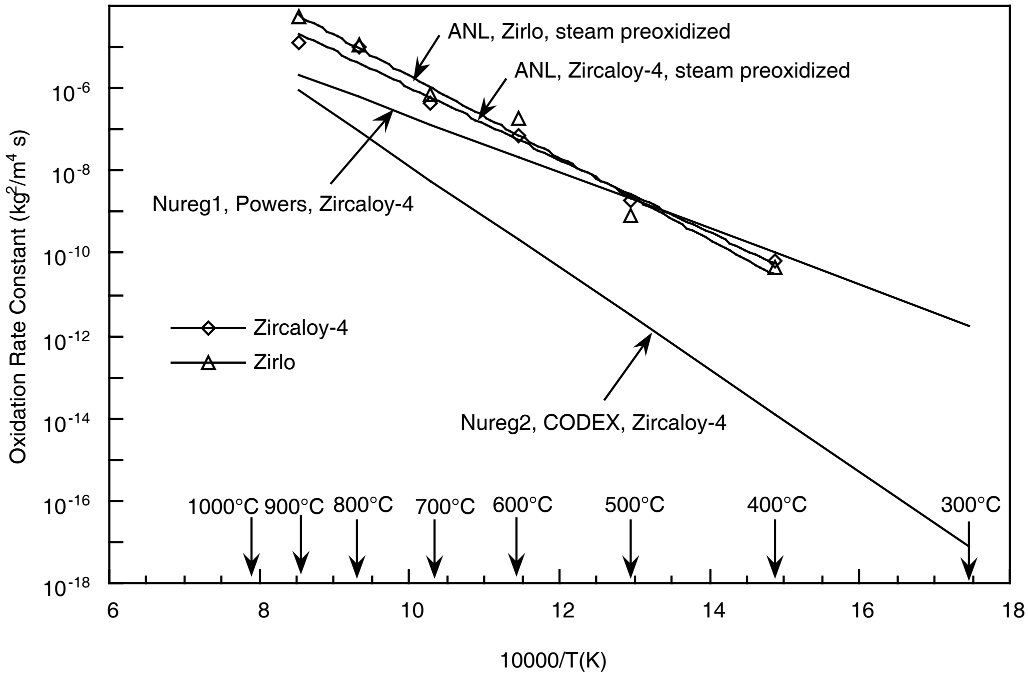


Scanning electron photomicrographs of cross sections of steam-preoxidized Zircaloy-4 (left) and Zirlo (right), after oxidation in air for ≈300 h at 600°C

Weight change and oxide thickness, determined in the present program, were used to develop correlations to depict the air oxidation behavior of the alloys as a function of time and temperature. The results (see figure below) showed that the correlation developed for Zircaloy-4 from the oxidation data generated in the current project is in fair agreement with that based on previously published correlations (Nureg1 and Powers). However, the predictions based on Nureg2 and CODEX correlations for Zircaloy-4 are several orders of magnitude lower than those based on current work, especially at lower temperatures.

Fossil Energy

Conceptual designs of advanced coal-fired combustion systems require furnaces and heat transfer surfaces that operate at much higher temperatures than those in current coal-fired power plants. The combination of elevated temperatures and hostile combustion environments necessitates the development and application of ceramic materials in these designs. However, downstream of the combustion zone, a transition from ceramic to metallic materials will be required, and the metallic components will experience much more elevated temperatures than those in current combustion systems. Furthermore, they will be subjected to combustion environments in which the deposit and gas chemistries could be different from those in current boiler systems. Studies of the high-temperature corrosion of metallic and ceramic materials are being conducted in simulated coal-gasification atmospheres and coal-combustion environments typical of conventional pulverized coal-fired boilers, fluidized-bed systems, and low-NO_x boilers and Advanced Fossil Power Systems. This effort is directed at establishing mechanisms of corrosion, predicting the onset of breakaway corrosion, and evaluating the role of stress and deformation in corrosion processes.



Comparison of the temperature dependence of the oxidation rate constant (in post-breakaway region) for air oxidation of steam-preoxidized Zircaloy-4 and Zirlo derived from this project with those for Zircaloy-4, based on previous correlations

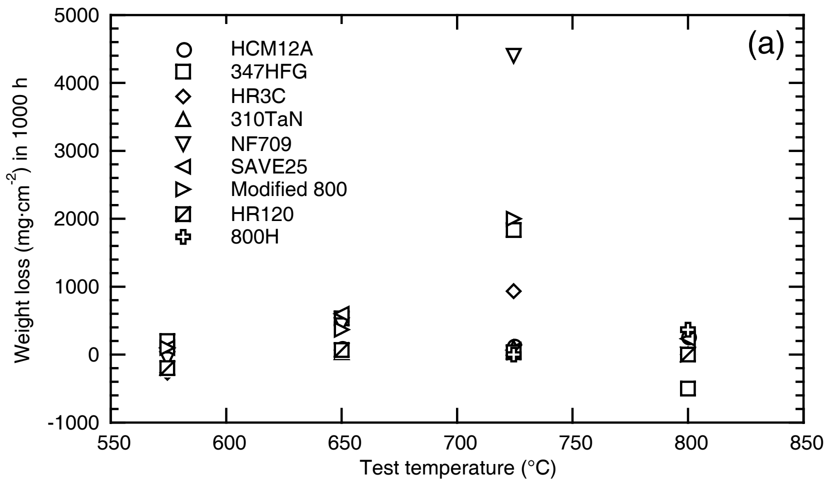
Sulfidation and chloridation resistance of structural alloys (namely, model Fe-Cr, Fe-Cr-Ni, and Fe-Cr-Al alloys; Fe-Al intermetallics with controlled additions of several refractory metals and rare earth elements; and commercial high-Cr alloys) is being evaluated by thermogravimetric tests, and postexposure microstructure of corrosion scales is being characterized by several electron/optical microscopy techniques. Alloy additions are made by bulk alloying and as overlay or diffusion coatings. Another major thrust of the program is to evaluate the effects of corrosive environments on the tensile and creep properties of metallic alloys and fracture toughness properties of monolithic and ceramic/ceramic composite materials. Further collaborative programs, supported by DOE's Fossil Energy and its Materials Division of Basic Energy Sciences, are in progress to examine fundamental aspects of scaling in structural materials exposed to oxidizing environments and to develop ultrahigh-strength Mo-Si intermetallic alloys and $MoSi_2$-Si_3N_4 composite materials.

Our recent work has focused on the corrosion behavior of alloys in advanced coal-fired combustion systems. In advanced boiler systems, the presence of slag constituents, sulfur, alkali, and chlorine determine the thermodynamic activity of various deposit constituents. An important difference between the conventional boiler system and the advanced system is in the chemical and physical characteristics of the ash layers that can be deposited on the heat transfer surfaces. Such deposits can lead to corrosion of waterwall boiler tubes, steam superheaters, and air tubes during service in coal-fired systems. Fire-side metal wastage in conventional coal-fired boilers can occur via gas-phase oxidation or deposit-induced liquid-phase corrosion. The former can be minimized by using materials that are oxidation resistant at service temperatures of interest. On the other hand, deposit-induced corrosion of materials is an accelerated type of attack influenced by the vaporization and condensation of small amounts of impurities such as sodium, potassium, sulfur, chlorine, and vanadium, or their compounds, that are present in the coal feedstock. In advanced combustion systems, because the metals in the superheater regions will be at a much higher steam temperature, the alkali sulfate and coal ash will be the predominant deposit. Several factors (including sulfur, alkali, chlorine in coal feedstock; excess air level during the combustion process; and metal temperature) determine the extent of corrosion of superheater materials in coal-fired boilers.

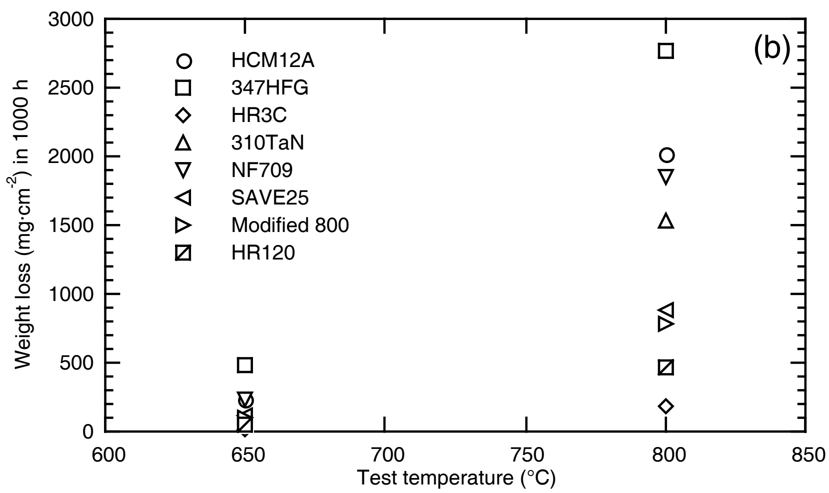
The objective of the present work is to evaluate the corrosion performance of state-of-the-art candidate materials in coal ash, alkali sulfate, and alkali chloride environments at temperatures in the range of 575-800°C. The experimental program is aimed at developing an understanding of corrosion mechanisms as a function of alloy composition and deposit chemistry, and at quantitatively determining the scaling and internal penetration of the alloys.

The figure below (a) shows the weight change data for nine alloys tested in mixtures of coal ash and alkali at temperatures between 575 and 800°C for 1000 h. The results indicate that the weight loss rates increase with temperature up to 725°C and decrease to low values at 800°C. In fact, several of the alloys showed either negligible weight loss and/or gained weight after exposure at 800°C. The corrosion rates followed a bell-shaped curve with peaks near 725°C for all the alloys used in this study. The data in this figure should only be used qualitatively, because the weight loss rates could have been affected by the removal of scales during removal of the coal ash deposit from the specimen surface, even though every effort was made to remove only the ash deposits by brushing. Generally, the scales adhered more to some alloys than others, and caution should be exercised in using this information for corrosion allowance for components.

The following figure (b) shows the weight loss rates for eight alloys at 650 and 800°C, obtained when exposed in a deposit mixture that contained 5 wt.% NaCl. Based on the weight loss data, the presence of NaCl in the deposit has little effect on the corrosion rate at 650°C. Most of the alloys used in this study exhibited similar weight loss rates after exposure in deposits with and without NaCl. On the other hand, at 800°C, several alloys exhibited accelerated corrosion in the presence of deposit that contained NaCl, when compared with the rates observed for the same alloys in the absence of NaCl. Currently, the study is continuing to establish the performance envelopes for advanced alloys for use in DOE's Vision 21 coal-fired system.



Weight loss data for alloys after exposure in mixtures of synthetic coal ash and alkali sulfates at 575 to 800°C



Weight loss data for alloys after exposure in mixtures of synthetic coal ash, alkali sulfates, and NaCl at 650 to 800°C

Fusion Energy

Since 1995, ANL has had primary responsibility for the development of new design rules regarding various components in a fusion reactor, particularly those subject to irradiation embrittlement. During 1998, ANL issued the final draft of the structural design criteria for in-vessel components in the International Thermonuclear Reactor (ITER). Following completion of the engineering of ITER, we have been involved in extending the design rules to high-temperature applications for advanced blanket designs currently under study in the U.S.

Design criteria input has also been supplied to the U.S. Advanced Research Innovation and Evaluation Study (ARIES) regarding rules for fusion reactor materials such as copper alloys, which embrittle significantly at relatively low neutron damage levels. Materials data input for the

ARIES spherical tokamak has been provided for copper alloys, aluminum alloys, low-activation ferritic steels, silicon carbide, and tungsten.

Stress analysis and design criteria require a well-developed data base for the candidate structural materials. The Advanced Materials Section of DOE's Office of Fusion Energy Sciences is actively supporting mechanical property research into reduced activation ferritic/martensitic steels, V alloys, and monolithic and composite SiC. We have the lead role in the U.S. as interface between the design communities and the materials community. This involves assessing the data bases and presenting them in a usable, relevant form to U.S. design teams. In addition, an active role is played in the assessment of the vanadium-alloy data base needs and the planning and post-test analysis of additional experimental work performed at ANL in the areas of tensile, impact, and creep properties.

Recently, the U.S. rejoined the international ITER program, which has been developing a detailed design of an experimental thermonuclear reactor that will eventually be built. The U.S. is currently gearing up to design the test blanket module, which will be installed inside the reactor chamber and will be used to test various designs of tritium breeding blanket. We are actively participating in the structural analysis and design of the test module.

Metal Dusting

Metal dusting is a catastrophic corrosion phenomenon that leads to the disintegration of structural metals and alloys into dust composed of fine particles of the metal/alloy and carbon. This phenomenon has been observed in the chemical and petrochemical industries, in reformer and direct-reduction plants, in processes that generate syngas, and in other processes where hydrocarbons or other high-carbon-activity atmospheres are present. Failures have been reported in ammonia plants as reduced energy requirements result in a lower steam/H_2 ratio while CO/CO_2 ratios have tended to increase. Even though metal dusting is widely prevalent, the general approach to minimize the problem in industry is to avoid the temperature/process conditions that are conducive for the attack, usually at a penalty in production, efficiency, and cost. Also, fixes such as sulfur poisoning of surface sites and preoxidation of alloy to stabilize chromia on high-Cr alloys are applied case-by-case, primarily based on experience with performance of materials in such environments. DOE’s Office of Industrial Technologies is supporting a three-year project in cooperation with several industrial partners to address the metal dusting problem from a fundamental scientific base using laboratory research in simulated process environments and subsequently field testing materials in actual process environments with participation from the U.S. chemical industries.

An extensive program has been in progress at ANL to establish the mechanisms for metal dusting degradation in metallic materials exposed to carbon-bearing gaseous environments, to identify the key parameters that influence the onset of metal dusting and propagation of degradation, to establish the metal wastage under a variety of exposure conditions, to characterize the morphology of degradation by a wide variety of analytical techniques, and to assess the effect of alloy chemistry in the role and the extent of metal dusting. Several conclusions can be drawn from the study to date.

There are two major issues of importance in metal dusting. First is formation of carbon and subsequent deposition of carbon on metallic materials. Second is the initiation of metal dusting in the alloy and subsequent propagation of the degradation. The first is influenced by carbon activity (a_C) in the gas mixture and the availability of the catalytic surface for carbon-producing reactions to proceed. There may be a threshold in a_C (>>1) for carbon deposition. Metal dusting of the alloy in the reformer environments is determined by a competition between the oxide scale development and access of the virgin metal surface to the carbon deposit.

A new metal dusting mechanism was proposed in this study. Mechanisms for degradation of both Fe- and Ni-base alloys are related to the catalytic crystallization of carbon that deposits from the gaseous environment. The only difference is that iron carbide acts as a catalyst in Fe-base alloys, whereas nickel metal instead of nickel carbide acts as a catalyst in Ni-base alloys. To achieve good crystallinity, carbon dissolves, diffuses through, and precipitates at defects of iron carbide or nickel metal. The accumulation of carbon leads to separation of carbide or nickel grains into nano-size particles. The growth of carbon nano-filaments is the successive step in metal dusting. The free energy difference between poorly and well crystalline carbon is the driving force for both metal dusting and the growth of carbon nano-filaments. We believe that the proposed mechanism can better explain the experimental observations made on Fe- and Ni-base alloys subjected to metal dusting degradation.

The local nature of dusting (initiated by pits on the alloy surface) on structural alloys shows that defects in the oxide scales play a large role in initiation. Oxide scaling may not occur if a_C is >>1 and/or if the H_2O content in the environment is very low. Laboratory experiments have clearly indicated the effect of gas chemistry (in particular, H_2O content) in the scaling, carbon deposition, and dusting initiation. It is evident that the environment in reformers is high enough in oxygen partial pressure that a Cr-rich alloy can develop a chromia scale (given enough exposure time) before carbon deposition. The presence of an oxide scale may not prevent metal dusting but can delay its initiation, thereby slowing the overall attack.

Raman spectra show the existence of spinel, Cr_2O_3, and disordered chromium oxide in the scale grown on high-chromium Fe-base alloys. All three phases act, to different degrees, as protective layers to prevent alloys from metal dusting corrosion. The spinel phase is not as stable as Cr_2O_3. It could be reduced by the deposited carbon, and metal dusting corrosion would initiate from the reduced defects.

The composition of the oxide scale is important in metal dusting corrosion. Cr_2O_3 is a better phase than spinel to resist metal dusting since spinel can be reduced. If alloys can generate more Cr_2O_3 and less spinel on the surface, their abilities to resist metal dusting will increase. Therefore, alloys with more Cr and less Fe content perform well in carburizing atmospheres. The composition of the oxide scale also changes with exposure time: spinel content increases and chromium oxide content decreases. For that reason, alloys are easily attacked by metal dusting after long time exposure since spinel content increases.

Metal dusting degradation involves two steps, namely, the incubation period and the propagation. The incubation period is determined by the carbon activity in the gas phase, alloy chemistry, system pressure, and probably the exposure temperature. For the same exposure conditions, the incubation period for the onset of metal dusting is significantly greater for the Ni-base alloys when compared with that for Fe-base alloys.

At present, the continuing work will focus on developing materials, coatings, and claddings that are resistant to metal dusting attack under high carbon environments at elevated temperatures and pressures.

Tribology

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The Tribology Section conducts research on advanced tribological systems (e.g., surface engineered materials, lubricants, fuels, and fuel/lubricant additives) for use in aggressive environments. A major portion of this activity focuses on the development and evaluation of high-performance coatings that can be applied to a wide range of materials. Also being investigated are how fuel and lubricant additives interact with surfaces under boundary-layer-lubrication regimes. The coatings are primarily intended to protect engine-component surfaces that undergo sliding and rolling contact in advanced transportation systems, including those powered by diesel and gasoline engines, as well as by advanced energy conversion systems being developed under the sponsorship of DOE's Office of FreedomCAR and Vehicle Technologies (FCVT); Office of Hydrogen, Fuel Cells, and Infrastructure Technologies; and U.S. industry. The overall goal of the Tribology Section is to promote industrial competitiveness by developing new tribological technologies and by solving problems associated with friction, wear, and lubrication. The Section has established and maintained close contact with

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transportation-related industries to determine their critical tribological needs and to facilitate the transfer of technologies developed at ANL.

The Section provides technical oversight for approximately $11 million in FCVT programs. These programs include computational fluid dynamics of tractor-trailers, friction and wear of engine components and brake materials, and thermal management through use of nanofluids, evaporative cooling, and nucleated boiling. Technical oversight is also provided on major FCVT programs related to “the more electric truck,” lightweight auxiliary power units, ceramic rotors and disks for disk brakes in heavy vehicles, hybrid mining equipment, locomotives, and class 3-6 trucks.

The Section’s activities include the development of advanced surface modification and material processing technologies, and evaluation of tribological properties. In the area of coatings that reduce friction, the Section has ongoing projects with DOE on development of near-frictionless carbon (NFC) coatings, superhard nanocomposite coatings that show potential for applications where formulated lubricants are employed, and electroless wet-chemical coatings used to fabricate small diesel injector orifices. Related projects include development of processes to join advanced materials using superplastic deformation and advanced glasses for X-ray imaging.

In the field of tribological evaluations, the Section has projects on laser glazing techniques to reduce parasitic friction losses between wheels and rails (railroad transportation), and laser engineered treatment of surfaces (microdimples) to improve friction behavior of surfaces during hydrodynamic lubrication regimes. Also being evaluated are parasitic energy losses in heavy-duty diesel engines to determine the impact of low friction surfaces and low-viscosity lubricants on fuel economy, durability of advanced materials (NFC, low-friction polymers, etc.) for air compressor applications in fuel cell systems, and erosion properties of materials exposed to nanofluids. Further, the Section has major projects to characterize coating properties and tribological mechanisms, including characterization of boundary layer lubrication mechanisms, and the structural, thermal, and electrical properties of advanced coatings (e.g., NFC).

Efforts are also in place to commercialize technologies developed in the Tribology Section. These include numerous efforts to deposit NFC coatings on prototype components for specific applications, and efforts to commercialize boric-acid based lubricants for metal-forming applications. To a lesser degree, we also are involved with projects to evaluate/assess the tribological properties of NFC, ultrananocrystalline diamond coatings for micro-electromechanical devices, and seal applications.

The following sections describe in greater detail the Tribology Section’s research strengths and the programs that support activities in these areas. The major strength of the Section lies in its ability to not only develop processes to form novel coatings that are lubricious and wear-resistant, but more important, to perform detailed evaluation of the tribological properties of materials and coatings under a wide range of conditions that simulate those found in various energy-intensive sectors. This combined expertise in surface modification and tribological characterization is unique and allows us to more effectively develop advanced surface modification treatments tailored to specific applications. Another strength is our Section's ability to characterize microstructural and surface chemistry evolution of materials and coatings exposed to tribological environments.

Coating Process Development

Projects in this area are aimed at exploring the factors that control the tribological properties of surfaces given surface-modifying treatments such as ion-beam-assisted deposition (IBAD), ion beam deposition, microwave and plasma-assisted chemical vapor deposition, and plasma-sputter deposition. The major emphasis is on developing low-friction, highly wear-resistant surfaces that can endure extreme tribological conditions due to high loads, speeds, and temperatures. We have developed a variety of low-friction, wear-resistant coatings and deposited them on metals, ceramics, and polymers intended for utilization in components for low-heat-rejection diesels and other high-temperature advanced engines and engine power trains. Specific examples include the development and testing of diamondlike carbon coatings (DLCs) on polymers and ceramic parts under conditions of high loads, speeds, and temperatures; development of smooth, nanocrystalline diamond films on ceramics for machining and sliding wear applications; development of naturally occurring lubricious-oxide layers on superalloys for gas turbine applications at temperatures to 1000ºC; development of wear-resistant boride layers on steels and other alloys. We are continuing efforts on the development of DLC films (which we now call NFC) that exhibit extremely low friction coefficients (<0.001) under dry sliding conditions. Response from industry on the NFC coatings continues, and we currently have collaborations with CemeCon to commercialize the process. More recently, we have initiated efforts to develop superhard nanocomposite coatings in collaboration with the Istanbul Technical University. These coatings have chemical and mechanical properties that make them extremely attractive for engine applications.

Our coating processing research focuses on two broad deposition techniques: development of low-friction and low-wear surfaces by a variety of surface-modification methods, including physical-vapor-deposition (PVD) techniques, and development of ultrahard, low-friction diamond, diamondlike, and other similar coatings by plasma-assisted chemical vapor deposition (PACVD).

Chemical Vapor Deposition Coatings

Over the past 36 months, the Section's coating development effort has focused primarily on the use of PACVD to deposit NFC coatings. The Section has two facilities for deposition of these coatings: a PACVD unit and a microwave PACVD unit. The microwave PACVD system was procured for the study and development of polycrystalline diamond films. While the microwave plasma deposition source allows production of diamond, NFC, and similar ultrahard coatings on ceramics and other high-temperature materials, the main thrust of the R&D on this system is production of smooth, adherent crystalline diamond films that serve as lubricious, wear-resistant coatings without causing severe wear of mating components.

The plasma-sputtering system was designed as a PVD system, but is now being used in a PACVD mode using an RF-etch capability. This system consists of a 0.6-m-diameter vacuum vessel set up for diode (RF-diode, RF-magnetron, or DC-magnetron) sputter deposition from three target locations. This system is being utilized because, in general, PACVD can be scaled up much more readily to handle large quantities of parts than can IBAD or microwave-assisted CVD, where the technology is not as mature. Recent R&D efforts on this system have shown that very high-quality NFC films can be achieved, and that the tribological properties can be effectively tuned and optimized for particular conditions by controlling the gas chemistry.

Physical Vapor Deposition Coatings

When the Tribology Section was established almost 20 years ago, its primary focus was on generic long-term research on advanced surface modification processes to improve the friction and wear performance of materials used in energy-intensive sectors such as transportation. The coating research originally focused on PVD processes with major emphasis on IBAD. This facility consists of a large, ultrahigh-vacuum chamber with two individually controlled electron-beam evaporation sources and simultaneous or sequential ion sources that produce ions with energies from a few eV up to 1500 eV. Materials that can be evaporated include Ag, Al, B, Ba, Ca, Cr, Cu, Fe, Mg, Mo, Nb, Ni, Pt, Sn, Ti, and Zn, either singly or in combination. Various types of specimen holders enable rotational motion, ensuring uniformity in the coating. Parts as large as engine pistons can be coated. In addition, the Section has a three-target sputtering apparatus for the deposition of multilayer coatings comprising Si, Au, B, C, Al, Ti, Cr, Fe, Ni, Cu, Mo, Ag, W, Pt, or Al_2O_3. An ultrahigh-vacuum apparatus for depositing fullerene compounds as tribological coatings has been built, as has an apparatus for exposing test specimens to fuels and solvents.

Tribological Testing and Surface Characterization

The Tribology Section has developed specialized benchtop systems to evaluate and characterize the friction and wear properties of materials and components under a range of operating conditions. These facilities include seven unidirectional pin-on-disk tribometers and three reciprocating pin-on-flat tribometers. The Section is also procuring/designing four additional tribometers to evaluate NFC coatings. The unidirectional pin-on-disk tribometers can operate at up to 1000°C in environments ranging from lab air to inert (e.g., dry nitrogen and argon) to liquid (e.g., water, oil, diesel fuel, and gasoline) lubrication at rotational speeds up to 4000 rpm. The reciprocating pin-on-flat tribometers operate at frequencies ranging from 1-2 Hz up to 500-1000 Hz and at temperatures ranging from room temperature to 900°C in environments including air, inert gases, and liquids (oils, gasoline, diesel fuel, and pressurized gases).

Additional facilities to characterize the mechanical properties of surfaces include a low-load microhardness tester, device for coating adhesion measurements, surface profilometers, optical and scanning electron microscope, and more recently, a high-temperature extensometer to monitor thermal bowing in laminated materials arising from differences in thermal expansion properties.

Together, these rigs and characterization capabilities are used to evaluate the friction and wear properties of materials and components under a wide range of conditions that simulate tribological conditions in advanced systems. The characterization capabilities are used extensively to evaluate and identify the physical mechanisms that contribute to friction and wear of materials and components and thereby develop strategies to improve the tribological performance.

Boundary Lubrication Mechanism

Most critical components in diesel engines and transportation vehicle subsystems are oil lubricated. Satisfactory performance of these components and systems is achieved through a combination of materials, surface finish, and lubricant oil formulations, which are often selected by an Edisonian trial-and-error approach. To progress from the empirical trial-and-error approach to predicting lubricated-component performance, we believe a better understanding is required of the basic mechanisms regarding the events that occur on lubricated surfaces. Consequently, the primary objective of the present project is to address some of the fundamental mechanisms of boundary lubrication and failure processes of lubricated surfaces. The technical approach taken in this study differs from the usual one of posttest characterization of lubricated surfaces and, rather, will develop in-situ characterization techniques for lubricated interfaces that will use the X-ray beam at the Advanced Photon Source (APS) located at ANL. Using a combination of X-ray fluorescence, reflectivity, and diffraction techniques, we will study, in real time, the interaction between oil lubricants and their additives and the surfaces they lubricate. Such study will provide the basic mechanisms of boundary lubrication. In addition to surface chemical changes, material aspects of various tribological failure mechanisms will be studied.

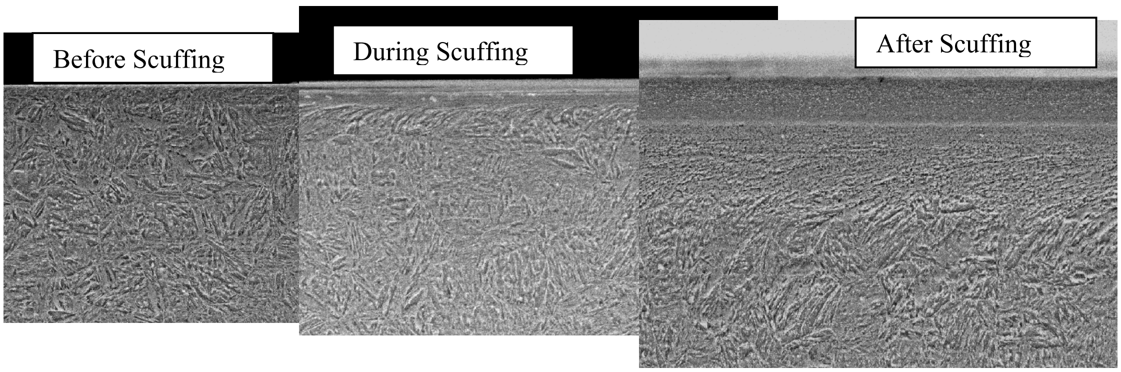
Effort during the past year focused on two parallel tasks: study of the scuffing mechanism and development of methods for X-ray characterization of boundary films.

Scuffing Mechanism

Scuffing, defined as a sudden catastrophic failure of a lubricated surface, is poorly understood and a major source of reliability problems in engine components. It is usually accompanied by a sudden rapid rise in friction coefficient, noise and vibration, and contact temperature, as well as loss of surface integrity. Microstructural changes that occur during scuffing of hardened 4340 steel were studied by analyzing samples before, during, and after scuffing.

In a time span of an order of a microsecond, significant microstructural changes were observed to accompany scuffing. The original microstructure of tempered martensite was transformed into a layer of very fine-grained, severely deformed material. The next figure shows SEM photomicrographs of the near surface layer before, during, and after scuffing. X-ray analysis also showed that the surface layer after scuffing contained ≈60% retained austenite, indicating that the contact temperature after scuffing exceeded the austenitizing temperature of 4340 steel.

Drawing upon these microstructural changes and other phenomenological observations of the scuffing process, we have proposed an initiation mechanism based on adiabatic shear instability. When surfaces are brought in contact, high contact stresses at asperities will lead to localized plastic deformation, which will lead to work hardening of the deformed area as dislocation density increases. With increasing contact severity, more work hardening will occur. As more plastic deformation of the surface layer occurs, some of the plastic work is converted into heat, causing thermal softening. Scuffing is then initiated when the rate of thermal softening exceeds the rate of work hardening. At such a point, rapid deformation will occur in a very short time; hence, the process is adiabatic. The large amount of heat generated will rapidly increase temperature, which will further accelerate plastic deformation and eventually lead to catastrophic failure.



Scanning electron micrographs before, during, and after scuffing of 4340 steel

Based on this scuffing mechanism, it is the possible to connect propensity of a material to scuffing with some material properties. Numerous criteria have been set for the initiation of adiabatic shear instability. Perhaps the simplest one is the critical strain (γ_c) at which the rate of work hardening is equal to the rate of thermal softening. Thus, scuffing will be initiated at a local point on a sliding surface when the shear strain at that point exceeds the critical strain, given as

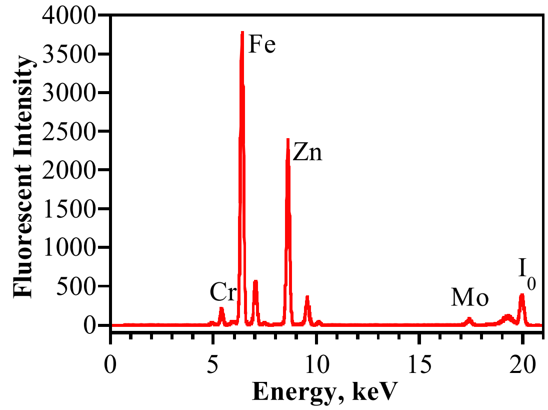
$$\gamma_c = \frac{n\rho C}{0.9\frac{\partial\tau}{\partial T}}$$

where n is the work hardening index, ρ is the density, C is the heat capacity, τ is the shear strength, and T is the temperature.

Preliminary validation of this model of scuffing initiation was conducted with hardened 4340 steel tempered at various temperatures as a means of varying the critical strain for shear instability. A more comprehensive validation is underway with various materials and alloys. With this model, it is possible to estimate susceptibility of various materials to scuffing. The model also provides a means for a material-based solution or strategy to preventing scuffing in lubricated engine components.

X-ray Characterization

In this task, the composition and structure of tribo-chemical films generated from a model anti-wear lubricant additive, zinc diathiophosphate (ZDDP), were characterized by glancing-angle X-ray fluorescence, diffraction, and reflectivity at the APS. A typical fluorescence spectrum of a tribo-chemical film that identified the key elements present in the film is shown.



X-ray fluorescence spectrum of tribo-chemical film formed by ZDDP anti-wear oil additive

Depth profiling of the compositional variation of tribo-chemical films was done by two methods. For laboratory studies, tribo-chemical films are usually generated either by rubbing surfaces together in the presence of the additive-containing lubricant being studied, or thermally, by heating a piece of metal submerged in oil that contains the additive. Although universal agreement has not been reached among researchers, it is generally assumed that the films generated by the two methods are essentially the same. Results of our analysis of depth compositional variation of the films generated by the two methods, however, clearly showed that the structure and composition of the films are not the same.

Although it might be easier to produce boundary films for laboratory study by thermal treatment, the results from such a study may not be applicable to tribological interfaces because the films are not necessarily the same. Films produced by these two methods with other model additives will be characterized in our future effort to assess the generality of the current observation with ZDDP. It is conceivable that the thermally generated and the tribo-contact generated films may be similar for some other additives.

Laser Glazing of Railroad Rails

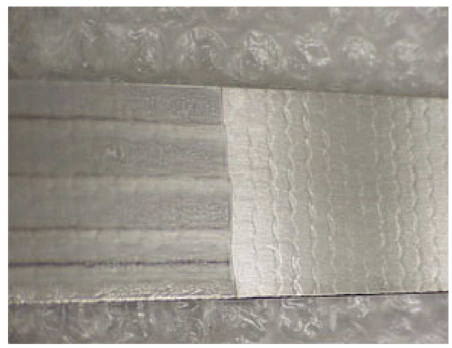
Wheel/rail interactions account for a significant fraction of the energy consumed in rail transport. Past studies have indicated that energy savings could be as high as 24% when friction at the wheel/rail interface is properly managed. The key aspect is control of the friction forces. Our research focuses on the development of a laser glazing technique that imparts a durable, low-friction surface to the gage face of the rails to reduce parasitic frictional losses between the flange and rail gage. The tasks associated with this project involve process development (laser glazing), friction and wear testing of laser-modified surfaces (glazed and shot-peened), microstructural characterization of laser-modified surfaces, and development of a model of surface deformation.

Process Development

The process development effort primarily focused on laser glazing. Parametric studies were performed to optimize the conditions under which a glazed layer forms on 1080 steel. Two approaches were developed: one that involved a single pass of a 1.6-kW pulsed laser over a given area, and one that involved multiple overlapping passes. The Knoop hardness of the glazed regions was two to three times greater than that of the substrate, depending on whether a single-pass (factor of three harder) or multipass (slightly over two harder) process was employed.

A commercial laser glazing process that utilized a high-power diode laser was also investigated. In this case, bars of 1080 steel were processed by a commercial vendor (NuVonyx Inc.) and subsequently tested at ANL. A third laser modification process, laser shot-peening (LSP), was also evaluated. Bars of 1080 steel were processed by LSP Technologies to “peen” near-surface regions. LSP does not involve melting near-surface regions; rather, it utilizes a laser to shock near-surface regions, thereby introducing high compressive stresses and hardness. The accompanying photographs show the surfaces of 1080 steel treated by both methods.

1080 steel glazed with a high-power diode laser



1080 steel laser peened (right side) and glazed and peened (left side)

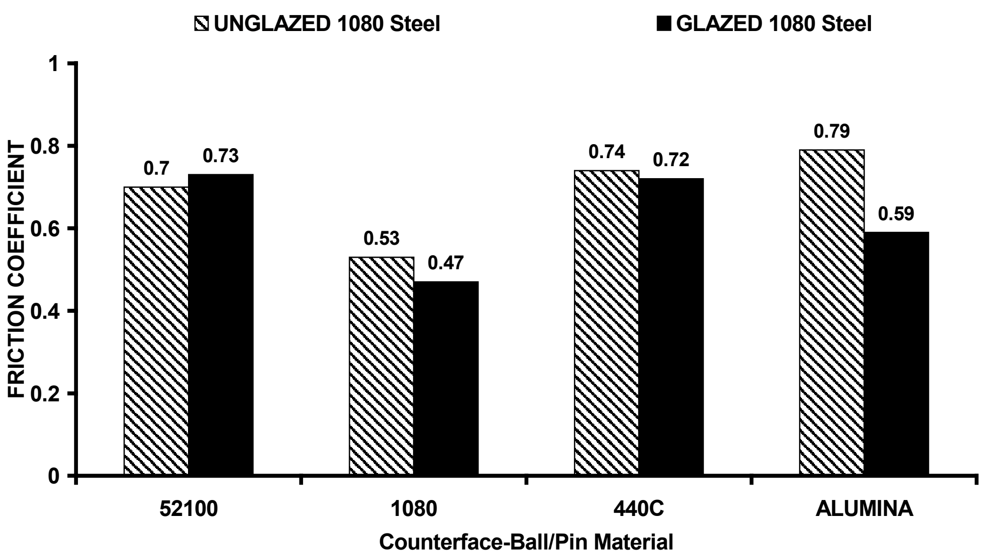
Friction and Wear Tests

Friction and wear tests were performed to evaluate the potential of glazing for reduction of frictional losses between the wheel flange and gage face of the rail. Initial tests were performed at Falex Corp. by using a block-on-ring configuration and low speeds, and at the test facility of the Association of American Railroads (ARR) in Pueblo, CO, by using a full-scale ring/wheel-on-block/rail operated under controlled slip conditions. Detailed tests were performed at ANL on twin-roller, pin-on-disc, and reciprocating pin-on-flat configurations.

The block-on-ring tests at Falex measured the breakaway torque/force (e.g., static friction coefficient) required to initiate rotation (defined as 0.013 rpm) under loads of 100-900 lb (445-4005 N) in 100-lb (445-N) increments. Dynamic block-on-ring tests were not performed because earlier tests showed that debris accumulation produced unreliable comparisons under dry, heavily loaded conditions. The Falex test results showed static friction coefficients of ≈0.35-0.45 for untreated 1080 steel, which dropped to values of 0.2 to 0.4 for differing glazing conditions.

The AAR tests were similar to the Falex tests in that they measured the breakaway friction (friction to start rotation) and the friction during maintained rotation. The AAR tests were performed on a segment of rail that was glazed on the top; the rail top was subjected to pure rolling and, at the end, to rolling/sliding contact. The static friction coefficient of the untreated 1080 rail varied from 0.2 to 0.5, depending on the applied load, whereas the friction coefficient of the glazed regions varied from 0.1 to 0.25. Dynamic friction coefficients for the glazed regions varied from 0.2 to 0.35, depending on load, compared to 0.2 to 0.55 for unglazed regions.

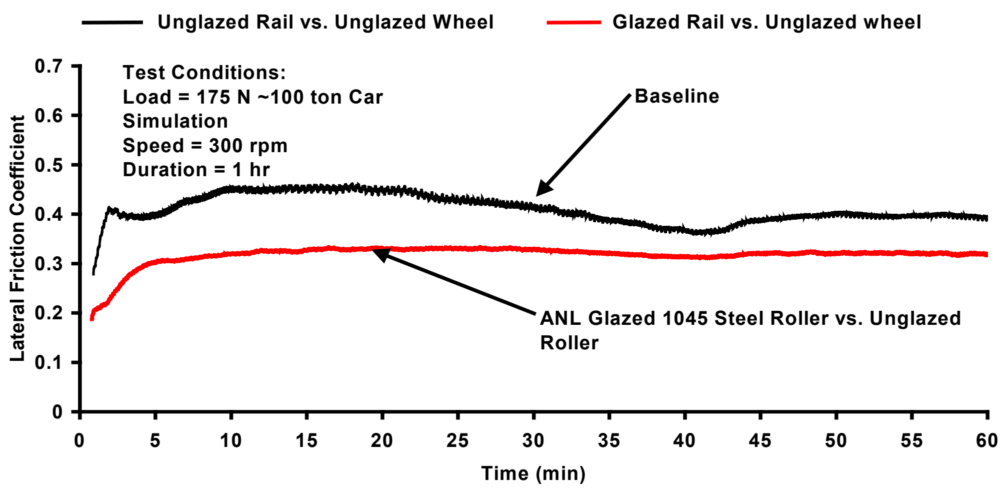
The benchtop tests at ANL were more controlled than the full-scale tests at the AAR facilities. The environment was more repeatable in terms of surface contaminants and more consistent in terms of relative humidity, two factors that significantly affect the frictional response. The pin-on-disc tests used flats of 1080 steel, glazed and unglazed, that rubbed against stationary balls or pins (52100 steel, 1080 steel, 440C steel, or alumina). The tests revealed that the composition of the pin/ball had a significant impact on the friction coefficient (see figure).



Pin-on-disc friction coefficient for glazed and unglazed steel sliding against different pin materials

The general trend was that the glazing reduced the friction coefficient by 3-35%, depending on the material. The greatest reduction was for the alumina ball sliding against the 1080 steel, suggesting that a strong chemical adhesion mechanism may be active with the metallic counterparts.

A twin-roller test configuration was also employed to more closely simulate the rolling contact stresses present at wheel-rail interfaces. The system is configured to measure the lateral friction forces. Tests were performed with a 1045 steel rail and wheel discs that were through-hardened or glazed. The glazing effectively reduced the friction coefficient from roughly 0.4 for the unglazed condition to 0.3 for the glazed rail rotating against an unglazed 1045 steel counterpart (see figure).



Twin roller friction on glazed and unglazed 1045 steel as function of test time

Similar tests were performed on 1045 steel rollers that were treated with a diode laser by a commercial vendor (NuVonyx). The NuVonyx-treated samples also exhibited lower friction than the untreated steel; however, the low-friction behavior did not endure for as long as that of the ANL-treated coupons. This difference is due, in part, to the fact that the NuVonyx laser treatment was not as well optimized as the ANL treatment.

Tests were also performed to evaluate the durability of the glazed region, in particular, to determine if the glazed region would delaminate from the underlying steel. This is a major concern for railroad applications because delamination could be a precursor to the formation of cracks that lead to rail degradation. Long-term (24 to 48 h) twin-roller tests at a high angle-of-attack were performed. A 24-h test simulates the passage of ≈1100 one-hundred car trains (each loaded at 100 tons). In all cases, the glazed region remained intact and showed no evidence of delamination.

Microstructural Characterization

Microstructural characterization of glazed steel coupons was performed to determine if a “white layer” was produced that could account for the reduced friction. Optical and electron microscopy (both scanning and transmission microscopy) were used to characterize the microstructure. Microhardness was also measured in the glazed regions as a function of depth into the substrate.

Characterization by cross-sectional scanning electron microscopy (SEM) of as-glazed 1080 steel coupons indicated a martensitic region (glaze) over the base 1080 steel (pearlitic). High-resolution cross-sectional SEM of multipass laser-glazed 1080 steel that was subjected to rolling-sliding wear at the Transportation Technology Center (Pueblo, CO) confirmed the presence of martensite. The martensite/glazed region consisted of two grain structures: equiaxed and columnar.

The presence of a thin white layer with a different microstructure was not confirmed. A thin layer (2-10 μm thick) was observed, but this was attributed to edge rounding that occurred during sample preparation.

The microhardness measurements for several samples were very consistent from sample to sample, even between samples produced by the ANL process and the NuVonyx process. The 1080 substrate hardness was 300-400 Knoop, increasing to ≈1100 Knoop, then decreasing to 800-900 Knoop near the surface. Samples that were exposed to multipass laser treatments were softened. The near-surface regions maintained a hardness of 800-900 Knoop; however, in regions further from the surface, the hardness decreased to 500-600 Knoop.

Model Development

We are developing a model for deformation in nanocrystalline metals that is consistent with the observed deformation characteristics of such materials. The model is relevant to this project in that, if rapid solidification by laser glazing leads to a nanocrystalline surface layer, that layer will deform in accordance with those observed characteristics. These deformation characteristics support reduced friction and wear.

The model is based on the observation that, like metallic glasses, nanocrystalline metals exhibit very high yield strength, because plastic flow is not facilitated by crystal dislocations in such materials. Also, after yielding, flow in nanocrystalline metals is nonhardening and, therefore, perfectly plastic. Related to this is the observation that flow is restricted to narrow shear bands in these materials. This phenomenon leads to plastic instability and limited bulk ductility in tension, but allows considerable plastic flow in compression. In theory, plastic flow is accomplished by sliding along grain boundaries, which, in as-formed nanocrystalline metals, are in a higher energy state than they are in the same metal with a conventional grain size. Physical properties of the boundary, such as atomic arrangement, excess free volume, and other deformation-related properties, are tied to the grain boundary diffusivity. As in many shear-banding situations, flow must initiate at some local stress concentration or weak boundary. The sliding boundary will induce sliding in neighboring boundaries, not so favorably oriented, by imposing an additional local shear stress on them. Also, a sliding boundary can experience an increase in excess free volume because flow must occur in a nonconservative way by moving atoms past one another without the aid of dislocations. This excess free volume makes the deformed boundary more susceptible to further flow. Therefore, shear not only propagates across the material from one sliding boundary to another, but is restricted to a narrow shear band associated with the deformation-weakened boundaries. The result of this mode of deformation can result in not only nonhardening flow (since there are no dislocations), but also strain softening, albeit at a very high flow stress. Hence, energy losses (friction) from plasticity are limited because of the high yield stress, and, if yield does occur, it does so in a nonhardening manner, which mitigates delamination wear.

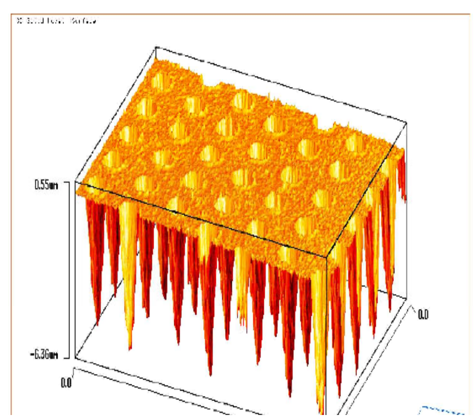
Future tasks will address several major barriers that must be overcome before this glazing technology is adopted by the railroad industry as a method to improve fuel economy. These tasks include demonstration tests at the test facilities of the Canadian National Research Council and the Transportation Technology Center.

Friction and Wear of Laser Textured Surfaces

SurTech Ltd. has developed a laser surface texturing (LST) technology that enhances the overall tribological performance of lubricated sliding and rotating surfaces. This technology involves creation of microdimples (100-µm diameter and about 10-µm depth) having a regular pattern on a given surface applied by a pulsating laser beam. Under hydrodynamic lubrication, and in the conformal contact configuration, the presence of microdimples on the contact surfaces can lower friction coefficients and also may potentially reduce wear. Under oil- or water-lubricated conditions, shallow dimples can serve as reservoirs for oil and water and thus increase the hydrodynamic lubrication efficiency of these surfaces. This low-friction technology has the potential for application in various engine components, such as the interface between the face seal and cylinder liner piston ring.

The main objective of this project is to produce well-controlled dimples on sliding and rotating conformal surfaces and to evaluate their tribological performance under a wide range of conditions that are typically found in engines and rotating equipment. At this initial phase, tribological evaluation will focus primarily on rotating face seals and lubricated engine components. The durability of the dimples and possible optimization of dimple size, depth, and pattern for various lubrication regimes are also being investigated. Furthermore, potential beneficial effects of soft and hard overcoats having super-hard and low-friction properties are being explored.

Argonne efforts have been devoted to evaluating LST for water pump seals and oil lubrication of steel surfaces. Several SiC face seals and rectangular steel samples were laser textured by Surtech Ltd. with microdimples. The dimpled samples were returned to Argonne for characterization and testing.

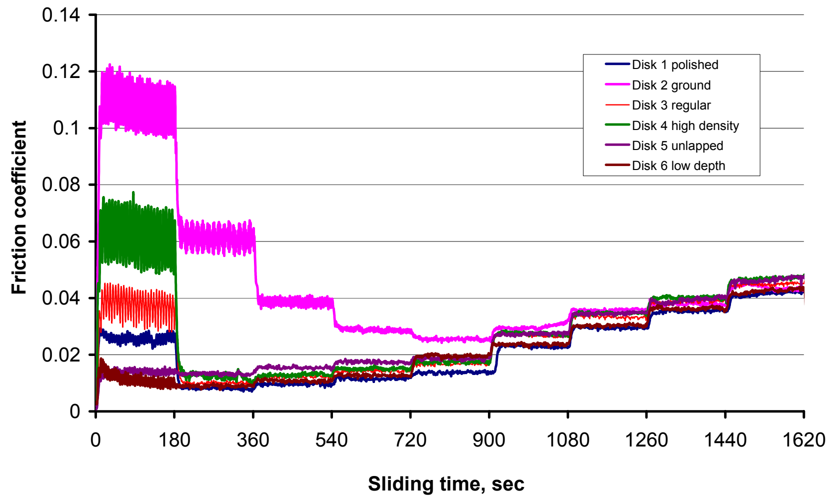


Three-dimensional image of laser-dimpled SiC seal face

The adjacent figure shows a 3D image of a dimpled SiC face seal. As is clear, the dimples are produced in a geometric array, and they are typically 4 to 5 µm deep and about 100 µm in diameter. After wear tests on the dimpled surfaces at face pressures of up to 50 psi (3.4 atm), the dimples remained mostly intact; but at much higher face pressures, some wear marks were observed, especially at or near the center of the wear tracks. The depth of the wear groove was about 1 µm. Also, some of the dimples appeared to have been filled with wear debris particles. Seal test results demonstrated that laser dimpled surfaces reduced frictional torque by 40 to 60%, depending on face pressure and other test conditions.

Oil lubricated tests were conducted in unidirectional sliding using the standard pin-on-disc contact configuration in a commercially available test rig. The variation of friction coefficient with time (and hence, sliding speed) for a typical test is shown in the next figure. The friction behavior in the test with the ground disc shows the classic Streibeck curve, in which the friction coefficient under the boundary lubrication regime is high, with a typical value of about 0.12. As the sliding speed increases, the oil film thickness also increases. After about 180 sec, the ratio between oil film thickness and composite surface roughness moves the contact into the mixed lubrication regime, with a concomitant reduction in friction. At much higher speeds, the oil film thickness is high enough to completely separate the sliding surface, and hydrodynamic lubrication is in effect.

The friction behavior for other dimpled and polished discs also shows the same trend, but with much lower magnitudes at the low sliding speeds. This finding suggests that microdimpling either reduces the magnitude of the boundary regime friction coefficient or shifts the operating condition for boundary lubrication to lower speeds. The operating mechanism requires further study.



Variation of friction coefficient with time (and velocity) in test with discs having different surface treatments

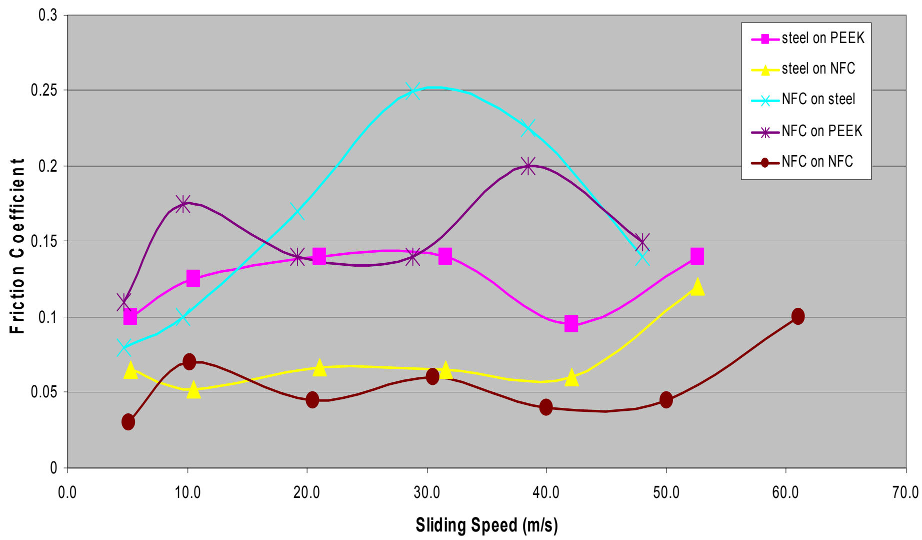
Low-Friction Coatings and Materials for Fuel-Cell Air Compressors

A critical need in fuel cell systems being developed for cars and other vehicles is an efficient, compact, and cost-effective air management system to pressurize the fuel cell systems to about 3 atm. Pressurization of fuel cells will result in higher power density and lower cost. Because no off-the-shelf compressor technologies are available to meet the stringent requirements of fuel cell air management, several compressor and blower systems are currently being developed for DOE by different contractors. The efficiency, reliability, and durability of compressors depend on effective lubrication or friction and wear reduction in critical components such as bearings and seals. Conventional oil or grease lubrication of compressor components is not desirable because such lubricants can contaminate and poison the fuel cell stack. The objective of this project is to develop and evaluate low-friction coatings and/or materials for critical components of air compressor/expanders being developed by various contractors for DOE vehicle-fuel-cell systems. The work this year focused on evaluation of materials and coatings for the Toroidal Intersecting Vane Machine (TIVM) of Mechanology, LCC, as well as the development of a generalized material selection methodology for compressor components.

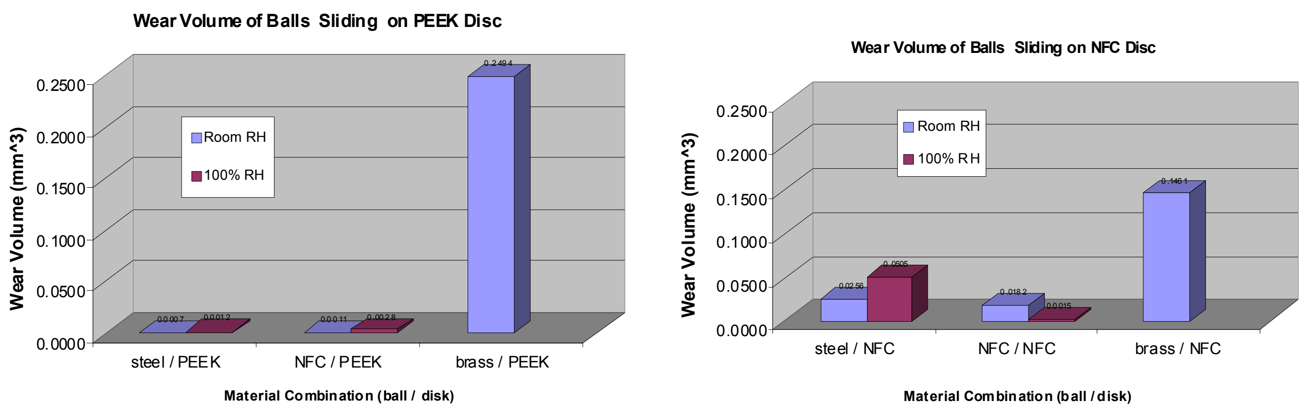
The primary sources of friction in the TIVM are the vane sliding interface, housing compressor seal, and expander bearings. Design analysis shows that an overall system friction coefficient less than 0.3 is required to meet the DOE program target for efficiency. The most critical of these three sources is the vane sliding interface, because of its high sliding speed of 60-75 m/s. Selection of appropriate vane material is critical for successful operation of the TIVM compressor/expander.

A three-ball-on-disc test rig was refurbished to make it more robust. The design changes allow more accurate measurement of friction coefficient as the variation in the normal force is taken into account. The test rig is also now equipped with an environmental coated chamber, allowing the variation of relative humidity.

Friction and wear tests were conducted as a function of sliding speed for candidate vane materials and coatings at ambient-room relative humidity (~30%) and at 100% relative humidity. The figure shows the variation of the friction coefficient with sliding speed for various materials and coatings meeting the friction requirement of 0.3 under ambient-room air. The lowest friction coefficient was obtained when both the disc and the ball surfaces were coated with NFC. The steel-on-PEEK-polymer combination shows friction coefficients less than 0.15 for the speed range evaluated. Under 100% relative humidity, the friction coefficients for all the materials evaluated were lowered. This may be due to hydrodynamic lubrication by the presence of water at the sliding interface. At very high sliding speed, the friction coefficients for all material pairs were approaching the same value. This finding is consistent with the possibility of hydrodynamic lubrication by water. The next figures show the wear on balls of various materials sliding on PEEK- and NFC-coated discs, respectively. Minimal wear was observed on the balls sliding on PEEK, except for brass. The higher hardness of the NFC coatings produced more wear on the balls that slid against it.



Variation of friction coefficient with sliding speed for TIVM vane candidate materials under ambient-room air



Wear volume in various balls sliding against PEEK disc (left) and NFC-coated steel disc (right)

More detailed friction and wear evaluation of candidate materials and coatings for Mechanology TIVM vanes showed that humid air will not have an adverse effect on the friction behavior, at least for a short duration of time. The long-term effect of humidity must be assessed as part of future effort.

Parasitic Engine Losses

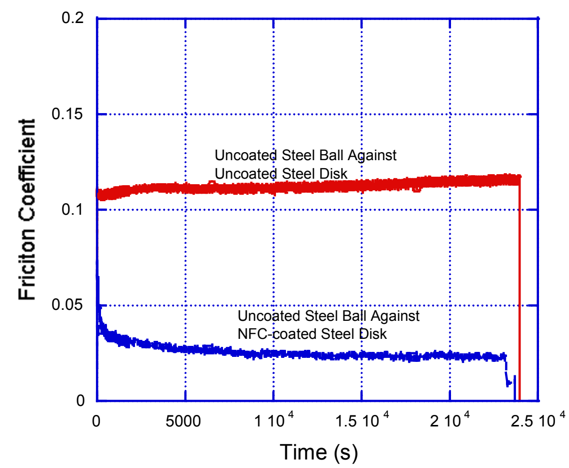
Friction, wear, and lubrication influence energy efficiency, durability, and environmental soundness of all kinds of transportation systems, including diesel engines. Total frictional losses in a typical diesel engine may alone account for more than 10% of the total fuel energy (depending on the engine size, driving condition, etc.). The amount of emissions produced by these engines is related to the fuel economy of that engine. In general, the higher the fuel economy, the lower the emissions. Higher fuel economy and lower emission in future diesel engines may be achieved by the development and widespread use of novel materials, lubricants, and coatings. For example, with increased use of lower viscosity oils (that also contain the least amounts of sulfur and phosphorus-bearing additives) the fuel economy and environmental soundness of future engine systems can be dramatically improved. Furthermore, with the development and increased use of smart surface engineering and coating technologies, even higher fuel economy and better environmental soundness will be feasible.

The main goal of this project is to develop a suite of software packages that can predict the impact of smart surface engineering and coating technologies (e.g., laser dimpling, NFC, and superhard nitride coatings) on reducing parasitic energy losses from diesel engine components. The project also aims to validate the predictions using experimental friction and wear studies at Argonne National Laboratory. Such information will help identify critical engine components that can benefit the most from the use of novel surface technologies, especially when low-viscosity engine oils are used to maximize the fuel economy of these engines by reducing churning and/or hydrodynamic losses. A longer-term objective is to develop a suite of computer codes capable of predicting the lifetime/durability of critical components exposed to low-viscosity lubricants.

Argonne and Ricardo, Inc., are working together to identify engine components that can benefit from low-friction coatings and/or surface treatments. The specific components considered include rings, piston skirt, piston pin bearings, crankshaft main and connecting rod bearings, and cam bearings. Using computer codes, Ricardo also quantified the impact of low-viscosity engine oils on fuel economy. Ricardo also identified conditions that can result in direct metal-to-metal contacts, which in turn can accelerate engine wear and asperity friction.

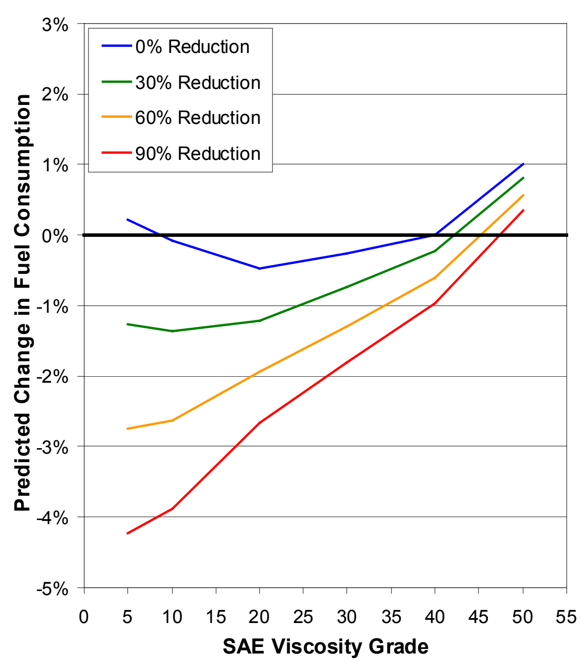
At Argonne, systematic studies were carried out to develop low-friction and high-wear resistant coatings for use in critical engine parts and components. One of the coatings studied extensively was NFC, which can provide friction coefficients of 0.001-0.01 under dry sliding conditions, especially in inert gas environments. Under lubricated sliding conditions, depending on the additive package in an oil and the oil viscosity, this coating was able to reduce friction by more than 40%. The next figure shows its friction performance in a fully formulated synthetic oil. This coating was highly optimized to respond well to the lubricated test environments. The reduction in friction in this case is more than 80%.

In addition to NFC coatings, we have explored the properties and potential usefulness of a series of superhard nano-composite nitride base coatings. The measured hardness of these coatings is more than 50 GPa, and their friction and wear performance (especially under lubricated sliding conditions) is exceptional. They can provide very low friction under even severe boundary-lubricated sliding conditions, as compared to base steel samples. Because of their superhard nature, we could not measure any wear on these coatings, and the pins that slid against the coated surfaces had also suffered minimal wear losses.



Friction coefficients of steel/steel and steel/NFC-coated steel test pairs in a fully formulated engine oil under boundary-lubricated sliding conditions

With further development and optimization, NFC films as well as superhard nanocomposite coatings may indeed prevent wear during sliding under conditions where low-viscosity oils are used. They can also provide low friction to help further increase fuel efficiency. Laser dimpling of selected engine components may also offer additional benefits in terms of reducing friction and thus increasing the fuel economy of engines. Some of these surface treatments and/or coatings will soon be applied on portions or segments of real piston rings and cylinder liners to further substantiate their effectiveness under conditions that closely simulate the actual engines. We also plan on producing these coatings on actual rings, liners, and other engine components and have them tested at Ricardo as well as at various OEMs.



Model predictions of change in fuel consumption vs. SAE lubricant viscosity grades and asperity friction reduction

In the collaborative effort with Ricardo, Inc., preliminary results from the computer simulations showed that hydrodynamic friction decreased with reductions in lubricant viscosity, while wear loads and asperity friction increased. This is mainly due to the reduction of churning losses associated with the shear rheology of high-viscosity oils. However, the decline in hydrodynamic friction is eventually offset by the increase in asperity friction. For each level of asperity friction reduction, there is a lubricant viscosity that provides the minimum overall fuel consumption (see figure). For an SAE 5 grade oil, simulations predict an overall fuel savings of greater than 4%, if a surface treatment is used to reduce boundary friction by 90%. Contact severity and wear loads are substantially increased in such low-viscosity environments, and they would need to be mitigated to avoid increased wear by using superhard coatings.

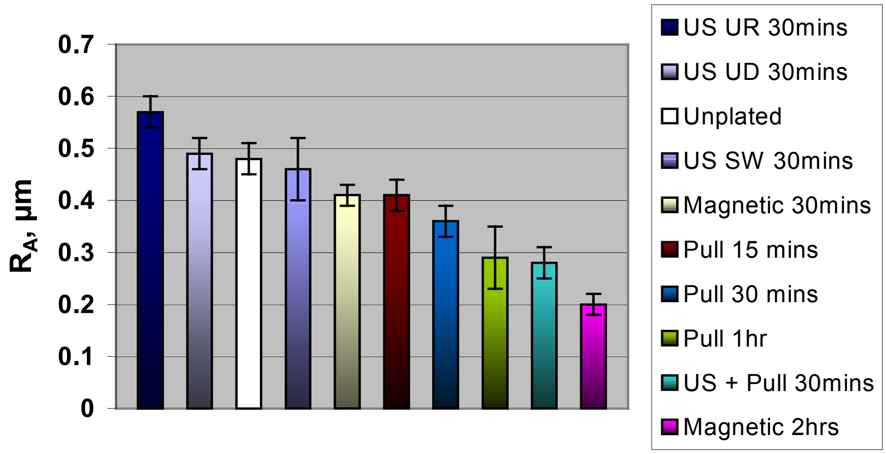
Fabrication of Small Fuel Injector Orifices

Recent work on the control of particulate matter (PM) emissions and improvement of engine combustion efficiency in diesel engines has shown the effectiveness of reduced injector orifice diameter in promoting fuel atomization, leading to more complete combustion and reduction in soot formation. The current industry target is 50-μm diameter, although mean droplet size and soot incandescence both decrease steadily with orifice diameter; thus, any reduction in orifice diameter should result in improved efficiency and reduced PM emissions. Advancements in electrodischarge machining (EDM) technology currently used to fabricate orifices are not expected to achieve the 50 μm target, nor will they alleviate the rough interiors they produce. Current EDM'd orifices must be polished using an abrasive slurry to achieve an acceptable surface finish (0.5 μm R_A with a surface morphology characterized by sharp peaks and valleys). During the fuel injection process, this leads to a highly turbulent layer adjacent to the wall, which reduces the effective fuel delivery area of the orifice. As the orifice diameter is pushed down toward 50 μm, the impact of surface finish is greatly magnified, thus demanding even smoother finishes.

In addition to being a potential route to economical production of 50-μm-diameter fuel injector orifices, electroless nickel (EN) plating offers potential solutions to the above-described problems. It is possible to deposit coatings with different surface chemistries, some of which may reduce the propensity of diesel fuel to form deposits on the injector nozzle. The morphology of plated surfaces appears to be generally smoother, as well.

As a result of interactions with an injector supplier (Siemens), we began to consider surface roughness as a critical parameter. We performed a number of trials using different deposition methods to determine the change in surface roughness with EN plating at various thicknesses and under various deposition conditions. The accompanying figure contains a plot of surface roughness (R_A) values for orifice walls plated under different conditions, compared with the R_A value of an unplated orifice wall. As part of this study, we also established that although ultrasonic agitation of the plating bath increases the deposition rate, it also tends to increase the surface roughness compared to the unplated surface. In general, the longer the plating time, the smoother the plate.

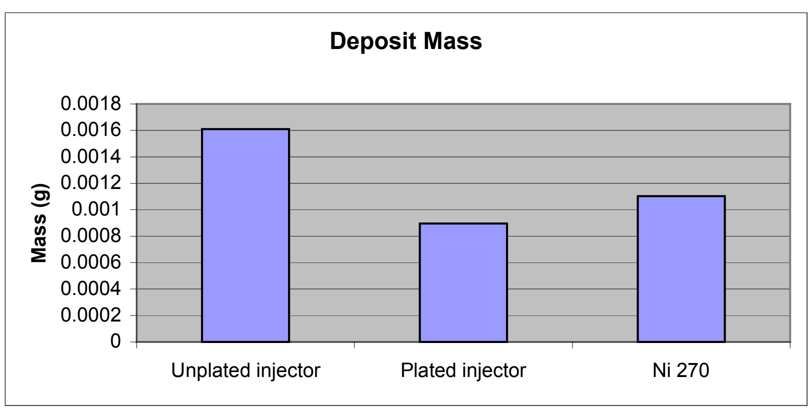
Erosion due to cavitation is expected to be a major problem in fuel injectors as orifice diameter decreases and injection pressure increases. The mechanical properties of EN plating depend upon the amount of phosphorus in the plate, its microstructure, and its thermal history. To determine the effect of plating bath composition on the plate's mechanical properties, we measured the Knoop hardness of the plate as a function of position (and thus bath depletion). The first plate to be deposited was hardest; then, as the bath depleted, the plate hardness decreased. Thus, we should be able to tailor the plating hardness for maximum erosion resistance by maintaining the bath composition at a particular level.



Surface roughness for different deposition conditions

We designed, constructed, and tested a system for forced-circulation plating of multiple injectors. To avoid the previous difficulty with orifice clogging, the bath was filtered before being pumped into a multiple-injector manifold. Initial test results showed that forcing circulation at even modest pressures resulted in marked reduction in deposition rate on the orifice interior. However, the coating on the orifice interior was also quite smooth. Further work is ongoing.

As described above, deposits are expected to be a significant problem for small orifices. Thus, we have begun to characterize the relative vulnerability of EN-plated injectors to deposit formation. Initial tests involved heating plated and unplated injector surfaces to about 240°C, dropping diesel fuel onto them, and measuring the change in mass. We expected the nickel plate to be less susceptible to deposit formation than pure nickel (also tested for comparison) due to the presence of phosphorus in the coating. As shown in the figure, EN plating affords a nearly twofold reduction in deposit mass over the unplated steel. We are planning further tests to characterize the deposits and their adhesion to the metal surface.



Deposit mass on pure nickel, unplated injector segment, and plated injector segment

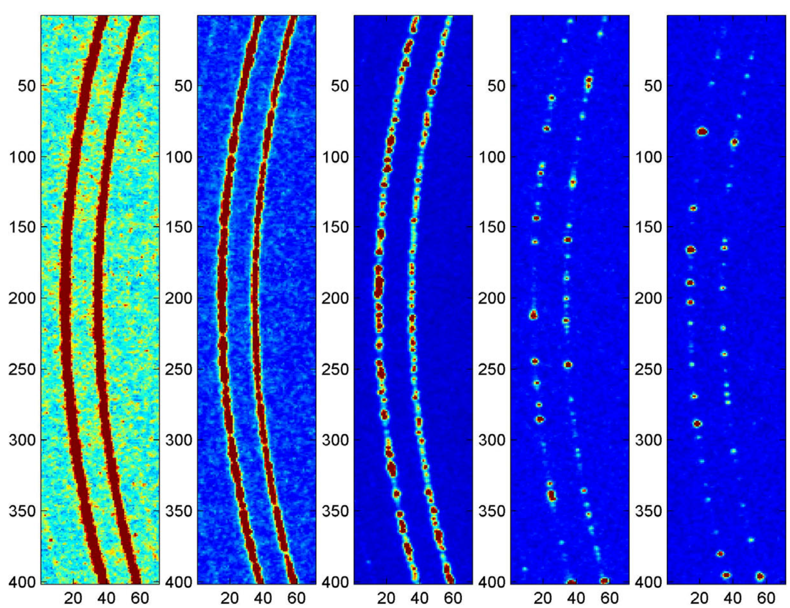
Before the large forced-circulation plating system was completed, we tested another method of forcing bath circulation through the injector. Spinning the injector in the plating bath resulted in a low, constant flow of plating bath through the injector. Using that method, we have successfully reached and surpassed the goal of 50-µm diameter.

Joining of Advanced Materials

The objective of this project is to join advanced materials using plastic flow (ceramics, composites, intermetallics, cermets, etc.) that cannot be readily joined to form strong joints and to understand the science underlying the basis for joining.

Samples of nickel aluminide (Ni_3Al containing boron) have been successfully joined using plastic deformation. Pore-free bonds were achieved at 1100°C (the temperature at which the material becomes superplastic) for fairly rapid strain rates in a 20% hydrogen/argon mixture. Joining at lower strain rates was not successful because, it is believed, oxidation occurred and prevented bonding.

We have claimed that deformation of a fine-grained ceramic is controlled by grain boundary sliding. If cavitation does not occur, the grains must rotate. While sliding can be observed and measured, rotation has not been experimentally accessible. However, using the fine-focused beam of high-intensity X-rays from the APS, grain rotation may be possible to observe. Initially, we examined a 2.1-µm-grain-size alumina/2% zirconia polycrystal to determine if we can detect individual grains. The results are encouraging (see figure). We also have resolved and oriented 50 grains in a 3-µm equiaxed sample of $SrTiO_3$.



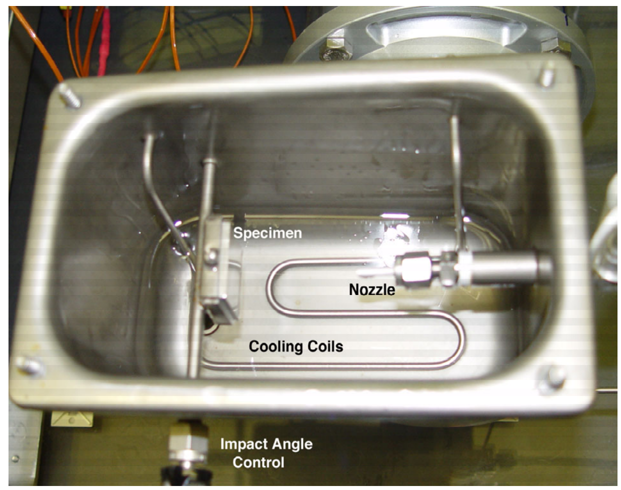
Part of the diffraction pattern from a 2.1-µm-grain-size alumina containing 2% zirconia using 80.7 keV photons for the APS. The beam size decreases and the exposure time increases from left to right.

We have shown that oxidation prevents bonding for low strain rates by performing experiments in pure hydrogen. Oxidation of Ni_3Al by annealing in air was investigated, and the oxidation products were identified by using spectra analysis on the SEM.

The critical flaw size in the bonded ceramic samples fractured in four-point bending was measured, and the residual stress calculated. Agreement with finite-element analysis was good. No samples fractured at the interface, proving the efficiency of joining by plastic deformation.

Erosion of Materials in Nanofluids

Many industrial technologies face the challenge of thermal management. With an ever-increasing thermal load due to trends toward greater power output for engines and exhaust gas recirculation for diesel engines, cooling is a crucial issue in transportation. The conventional approach for increasing cooling rates is use of extended surfaces such as fins and microchannels. However, current designs have already stretched this approach to its limits. Therefore, an urgent need exists for new and innovative approaches to ultrahigh-performance cooling. Nanofluids seem to show enormous potentials as a coolant for radiators, as discussed earlier in the section on "Thermal and Electromechanics" at ET. For the nanofluids to find commercial application, however, it must be shown that liquid erosion of typical radiator materials will be tolerable. Hence, the DOE Office of FreedomCar and Vehicle Technologies funded a new program to investigate this potential problem.



Experimental chamber for erosion tests with nanofluids

For this new program, we have designed and constructed an apparatus that measures the erosion rates of fluids containing various nanoparticles and nanotubes pumped at velocities typical for heavy-vehicle radiators, 1 m/s, up to about 15 m/s. Angle of impacts on a given specimen can be varied up to 90°C. The photograph is a view of the specimen chamber with the cover removed, showing the specimen and the nozzle. Some baseline data have been obtained on fluid velocity as a function of pump speed and specimen weight loss as a function of time. Testing will begin after refinements in the apparatus are completed.

High-Resolution X-ray Detector with Medical Applications

This is a new project funded by the National Institute of Health/National Institute of Biomedical Imaging and Bioengineering. The goal is to develop improved spatial imaging for X-ray detection that will have application in the diagnosis and treatment of numerous diseases. In combination with complementary imaging methods, the proposed innovation has the potential to increase sensitivity to specific types of tissue damage.

The proposed project will produce experimental glass samples at the University of Paderborn in Germany and Monash University in Australia; the samples will be characterized at ANL using differential scanning calorimetry and Raman spectroscopy. The photoluminescence quantum efficiency and spatial resolution of the glasses will be measured at the ANL Advanced Photon Source, and a read-out system will be engineered at Containerless Research Inc. (Evanston, IL).

Current X-ray photon storage materials such as image plates are fundamentally limited in their spatial resolution by scattering in the read-out stage from grain boundaries in the polycrystalline materials that are used. Imaging with a thin and transparent glass sheet as proposed here minimizes this scattering effect; scattering would, therefore, no longer limit the spatial resolution of the material. The whole of medicine would benefit from such a detector. Disease could be diagnosed before symptoms develop using improved contrast and targeting. With increased speed of detection and improved image resolution, patient comfort would be increased and radiation dose decreased.

So far, we have prepared fluorozirconate glass samples that have shown that doping with chlorine gives the maximum photostimulated luminescence (PSL) effect. The glasses contain crystallites. Annealing these samples increases the size of the crystallites, which further enhances the PSL effect, but makes the glasses opaque. We thus need to develop clear glasses for the best resolution.

The crystallites in the glass have a sensitivity that is an order of magnitude greater than the corresponding single crystal. Our current research and planned experiment focus on why this should be so. Along with all the regular characterization we will perform measurements at the ANL Advanced Photon Source to determine the role that the glass matrix plays in the properties of these glasses.

Irradiation Performance

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Secretary: S.M. Hagamann

The activities in the Irradiation Performance Section (IPS) are aimed at determining and assessing the normal-operation and accident behavior of neutron-irradiated materials throughout the life cycle of the materials from their in-reactor performance through their likely behavior during ultimate interment in a repository. This environment includes neutron damage and chemical, metallurgical, and mechanical processes that occur during operation in fission research and power reactors. Subsequent environments include short-term storage in the reactor pool, longer-term storage in He-filled dry casks, and permanent storage in moist air. To accomplish these tasks, the Section utilizes the major facilities operated by the Hot Cell Facilities Section (next chapter).

Light Water Reactor Materials

The Section's activities in the fission reactor area are focused principally on light water reactors (LWRs). The principal ongoing and upcoming activities in this research are described below.

High-Burnup Cladding Performance

The program, "High-Burnup Cladding Performance," is a major long-range research effort in the Section with participation by staff from ET's Corrosion Section. Funding comes from the NRC Office of Nuclear Regulatory Research (NRC-RES). The purposes of this program are to determine the behavior of LWR fuel rods under conditions relevant to loss-of-coolant accidents (LOCA) and to establish a mechanical properties data base for high-burnup (>60 MWd/kg) Zircaloy cladding. These data are needed for the analysis of various transients, including LOCA, reactivity-initiated accidents (RIA), and anticipated transients without scram (ATWS), and are important in licensing-safety analyses and acceptance criteria. The mechanical properties data are also needed for assessment of spent-fuel cladding behavior during transfer, transportation, dry-cask storage, and repository storage. To accomplish these objectives, the project is divided into three major tasks: Fuel Characterization, LOCA-Related Tests, and Mechanical Properties Tests.

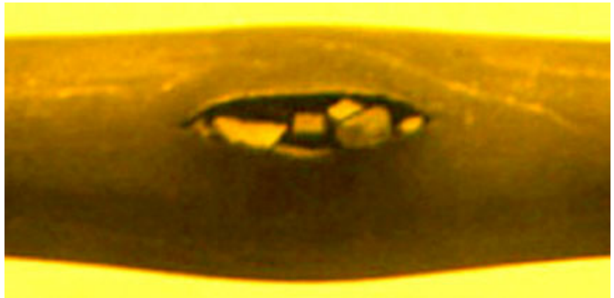
Fuel Selection and Characterization

Under a special agreement between the Electric Power Research Institute (EPRI) and NRC/RES, EPRI has supplied us with segments of seven Zircaloy-2-clad fuel rods from a boiling water reactor (BWR) and twelve Zircaloy-4-clad fuel rods from a pressurized water reactor (PWR). The two types of fuel had undergone high burnup (>60 MWd/kg). Both fuel and cladding are being characterized by the IPS. The high-burnup BWR rod segments were received at ANL in May 2000. The high-burnup PWR fuel rods were received at ANL in May 2001. In addition, three lower-burnup PWR rods (≈36 MWd/kg), which had been stored in dry casks for 15 years, were received at ANL in February 2001. Early in the program, PWR fuel rod segments (≈50 MWd/kg) from the Three Mile Island-1 (TMI-1) Reactor were used to demonstrate our ability to characterize fuel and cladding and to validate the experimental procedures for characterization, as well as to conduct all aspects of the program.

LOCA-Related Tests

This task involves steam-oxidation kinetics studies of traditional-Zircaloy and advanced-alloy (ZIRLO and M5) cladding at high temperatures, LOCA-integral tests, and post-LOCA-quench ductility tests. The oxidation kinetics studies have been completed on nonirradiated and high-burnup Zry-2 at 1000-1200°C. Similar work is in progress for nonirradiated and high-burnup Zry-4. In parallel to this effort to compare the behavior of archival and high-burnup Zircaloy cladding, we are comparing the oxidation kinetics and post-quench ductility of advanced cladding alloys (ZIRLO and M5, as well as the Russian E110 alloy) to the behavior of Zry-2 and Zry-4 tested under the same conditions and analyzed by a common methodology. Samples of these alloys are oxidized at temperatures in the range of 1000-1260°C, slow-cooled to 800°C, and water-quenched prior to subjecting them to ring-compression ductility tests. All tests at 1000°C and 1100°C have been completed. Tests at oxidation temperatures of 1200°C and 1260°C are in progress. ANL is the only lab with permission to test these cladding alloys and to publish the results in the open literature.

The LOCA-integral tests involve ramping (at 5°C/s) the temperature of pressurized, fuel-cladding segments in a flowing-steam environment through ballooning and burst (at ≈750°C) to 1204°C, holding for various times to generate oxidation levels consistent with NRC criteria (17% equivalent cladding reacted), slow cooling (at 3°C/s) to ≈800°C, and rapid cooling through water quenching. Behavior of the cladding during, and following, the water quench determines whether the current NRC criteria for LOCA events are conservative for high-burnup fuel rods. Three tests with high-burnup BWR fuel segments have been completed to date: ramp-to-burst to study ballooning and burst behavior; ramp-to-1204°C, hold in flowing steam for 5 min, and slow cool to study fuel behavior and hydrogen and oxygen pickup; and the full LOCA integral sequence, including quench. ANL is the only lab to have conducted these tests with high-burnup fuel samples. Similar tests are being performed with pressurized nonirradiated Zircaloy and advanced-alloy cladding materials. The test results for nonirradiated Zircaloy segments provide baseline data for comparison to the results for high-burnup fuel segments and for nonirradiated advanced-alloy cladding segments.



(a)

(b)

LOCA integral results for ramp-to-burst tests:
(a) high-burnup BWR Zry-2 and
(b) nonirradiated BWR Zry-2

Mechanical Properties Tests

Tensile tests with high and low strain rates for RIA and LOCA analyses are in progress to determine the mechanical properties of BWR and PWR Zircaloy cladding in both the hoop and axial directions. In addition, biaxial tube burst tests are planned for fuel cladding at a range of internal pressures and heating rates, and biaxial tests are in progress using the plane-strain specimen geometry developed by Penn State University (PSU).

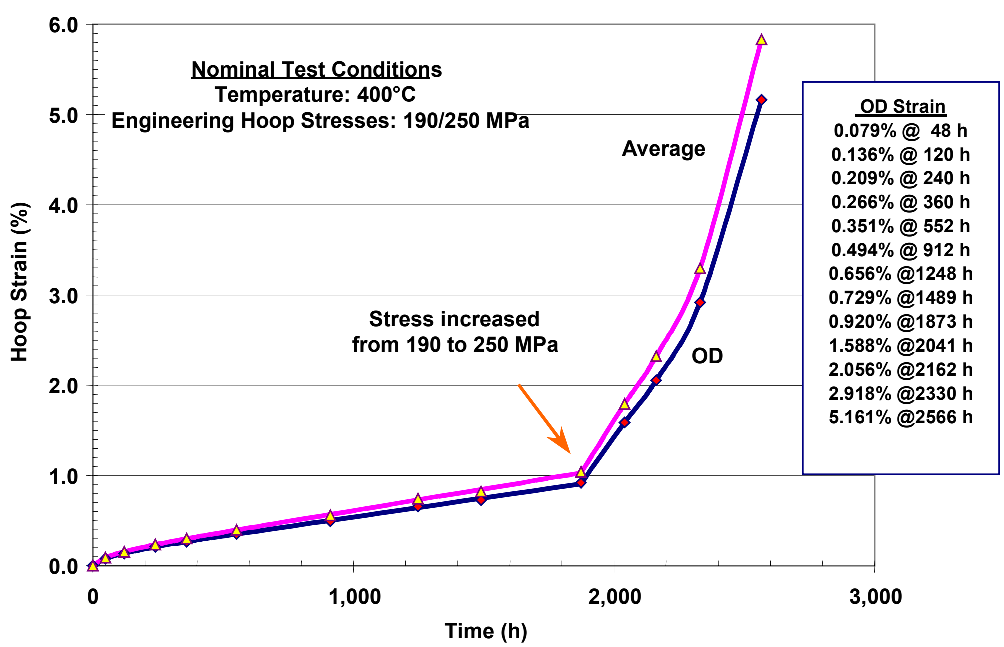
Extensive finite-element analyses have been conducted by the ET Corrosion and Mechanics of Materials Section to determine the optimal specimen for these tests and to interpret the results of the ring hoop-tensile tests. The TMI-1 PWR cladding was used to demonstrate IPS capabilities of performing hoop tensile tests with irradiated cladding ring samples (July 2002). However, the demonstration test, which was performed out-of-cell, proved to deposit too much contamination on the loading grips to continue testing. As a result, a radiological glovebox was constructed to house the testing machine and samples. A smaller glovebox was also built for installation of an automatic microhardness indenter. The changes in spacing of the microhardness indents are used to determine local strains directly following the test. Axial, hoop, and PSU plane-strain tests of high-burnup cladding are in progress.

Dry Cask Storage

The IPS is investigating spent-fuel behavior during dry cask storage. Certain issues remain unresolved for criteria on 20-year dry-cask storage of high-burnup fuel, as well as for the extension of storage times to >20 years for intermediate-burnup fuel. These issues relate to effects of high-burnup degradation – mainly hydrogen pickup and orientation of hydrides – on cladding integrity during transport and 20-year storage, as well as the effects of longer storage times for both intermediate- and high-burnup cladding. Improvements in the mechanical properties data base, particularly for thermal creep, and in modeling are needed to provide a technical basis for dry cask storage and transportation criteria.

For intermediate-burnup fuel rods (≤45 MWd/kg), IPS completed its program in characterizing and testing (axial tensile properties and long-term thermal creep) of PWR cladding (from the Surry Reactor) that has been irradiated to 36 MWd/kg and stored in a helium-filled cask for 15 years. The results of these studies were used by the NRC Spent Fuel Project Office to formulate staff guidance (ISG-11, Rev. 2 and Rev. 3) regarding criteria for vacuum-drying and transfer, transport to interim storage, dry storage, and transport to a permanent repository. In particular, the thermal creep data generated by IPS at 400°C were used to justify the 400°C limit imposed on these operations. Even after 15 years of dry storage the Surry cladding had a creep ductility > 5%. The Surry work was funded jointly by NRC, EPRI and DOE.

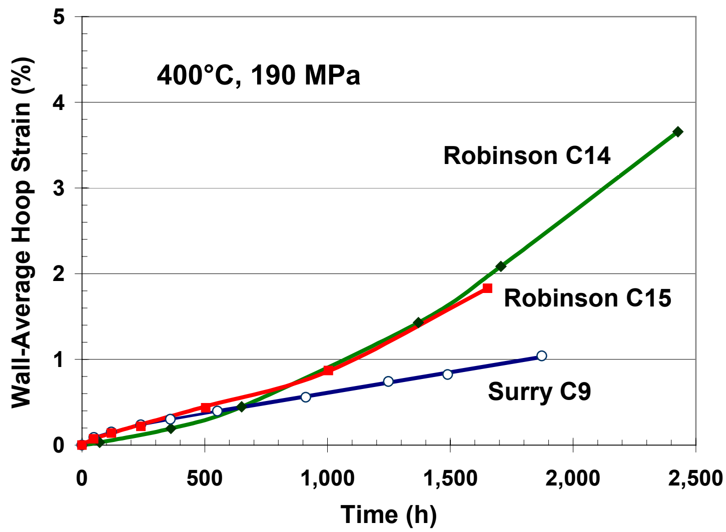
For the high-burnup portion of this work, several H. B. Robinson PWR rods (67 MWd/kg) have been used in the NRC-sponsored program to generate data on fuel isotopic content, fuel and cladding metallography, cladding hydrogen analysis, cladding tensile properties, and cladding creep properties. ANL's Chemical Engineering Division has been conducting the fuel isotopic and burnup analyses for this program. Thermal creep tests were conducted using high-burnup PWR cladding samples with ≈600 wppm hydrogen. These samples have more than twice the hydrogen content and neutron exposure – both considered to decrease creep rate and creep ductility – of the Surry Reactor samples. There were two surprising results from this investigation. First, the Robinson cladding exhibited a higher creep strain rate than the Surry cladding with both materials tested at 400°C and 190 MPa hoop stress.



Thermal creep of Surry cladding at 400°C after 15 years of dry cask storage

The second surprising result came after the last run of Robinson sample C15. It was cooled under full pressure, much the same as two of the Surry samples had been cooled, to study the reorientation of hydrides from the circumferential to radial direction. The presence of radial hydrides can significantly reduce the ductility of the cladding in response to hoop-stress loading. After the sample cooled to ≈200°C at a hoop stress of 190 MPa, it failed rather dramatically, even though Surry samples had survived such cooling under higher internal pressures and stresses. This failure occurred in June 2003 and has resulted in a redirection of the program to investigate the conditions under which hydrides reorient to the radial direction and the consequences of such reorientation on cladding response to tensile and impact loading. Recently DOE, independently of NRC, has funded IPS to study the effects of radial hydrides on high-burnup cladding performance because of concerns regarding cladding response to fuel unloading from dry casks and transportation of the fuel to permanent repositories.

Having the commercial high-burnup fuel at ANL has proven to be a great asset. Through a DOE contract with Sandia National Laboratories to investigate the vulnerability of fuel in dry casks to transportation accidents and sabotage, IPS has been funded to fabricate and test rodlets for Sandia from the high-burnup Robinson PWR fuel segments, as well as from the dry-cask-stored Surry rod segments. This effort was initiated late in FY2003 and will continue through FY2005, with possible expansion in the area of supplying test rodlets from research reactor fuel.



Thermal creep behavior of high-burnup Robinson and low-burnup Surry cladding at 400°C and 190 MPa

Reduced Enrichment Research and Test Reactor Fuel

The Reduced Enrichment Research and Test Reactor (RERTR) program is developing low enrichment uranium (<20% ^{235}U) fuels to replace the high enrichment uranium fuels commonly used in research and test reactors around the world. High-density U_3Si_2, U-6Mo and U-10Mo dispersion fuels in an aluminum matrix have been developed and tested to high burnup. IPS has an important role in the RERTR program: to examine and evaluate the fuel plates after the irradiation. A secondary task is to prepare and ship samples to ANL-West for additional examinations. The IPS effort includes immersion density measurements to determine swelling, metallography, microhardness, and scanning electron microscopy examinations to determine fission-gas-bubble distribution and fuel-matrix interaction. The current IPS efforts are focused on characterizing the U-Mo plates from the RERTR-4 and RERTR-5 experiments with U-235 burnups as high as 82%.

Other Current Activities

The Section is actively working in a number of other research areas. For example, we are continuing the slow-strain-rate tensile testing of irradiated stainless steel under a program with the Japan Nuclear Cycle Development Institute (JNC). In addition, we are doing characterization of metal fuel and mixed-oxide fuel from JNC.

The Section is also continuing its collaboration with the ET Corrosion Section in the NRC's Irradiation-Assisted Stress Corrosion Cracking Program for LWR stainless steel components. Our efforts provide the investigators with the necessary fractographic (SEM) and microchemical (Auger microprobe) data for evaluating stress corrosion cracking.

Future Directions

The strength of the Section continues to be our expertise in characterizing irradiated fuels and cladding materials and in performing tests and interpreting results for irradiated cladding and fuel-cladding samples. The IPS staff includes experts in nuclear and mechanical engineering and in materials science. In addition to our staff being an asset, we have a wide range of spent commercial reactor fuel that can be used in future research programs to address national-need issues. These fuel rods are clad in conventional Zircaloy-2 and Zircaloy-4 tubes. An obvious expansion of our high-burnup program is to continue such work for fuel rods with advanced cladding alloys (M5 and ZIRLO). Through agreements between NRC and Westinghouse Electric Co., we have already begun work on nonirradiated ZIRLO. Through a similar agreement between NRC and Framatome ANP, we have been able to add nonirradiated M5 to our LOCA-relevant research. Independently, we have responded to a request from Framatome to generate mechanical properties data for M5 that are applicable to issues regarding normal reactor performance and dry cask storage.

Hot Cell Facilities

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Salaried Staff and Technicians: D.J. McGann and S.M. Baumann

The Hot Cell Facilities Section provides research facilities to ET (as well as other ANL organizations) for the examination and testing of radiological materials. To that end, the Section manages and operates three facilities in Building 212: the Alpha-Gamma Hot Cell Facility (AGHCF), the Irradiated Materials Laboratory (IML), and the Room DL-114 Glovebox Facility. Characterization and testing of irradiated materials are carried out in the AGHCF and IML. We have refurbished the DL-114 Glovebox Facility to carry out hydrogen, nitrogen, and oxygen measurements for programs within the Irradiation Performance Section. Recently, we took over and restarted a portion of the M-Wing Hot Cell Facility (K-2 Cell) in Building 200 to allow multiple simultaneous tests of mechanical properties for radioactive materials.

Alpha-Gamma Hot Cell Facility

The AGHCF has capabilities for handling and analyzing irradiated nuclear fuel and other radioactive materials. The facility was designed and built to conduct postirradiation examinations of fuels and structural components for reactor development, and that role has expanded over the years to include analysis and testing of components for current reactors. The research has helped in the development of safe and reliable fuel systems for advanced commercial power reactors and research reactors. In addition, research on spent nuclear fuel from the DOE inventory has provided information for the future handling of irradiated materials so that safe methods for their treatment or internment can be identified.

The AGHCF consists of a multiroom, kilocurie hot cell that operates in a high-purity nitrogen atmosphere; an air cell called the Clean Transfer Area; an electron beam laboratory containing a scanning electron microscope, an electron microprobe, and a scanning Auger microprobe; shielded gloveboxes and a contaminated materials laboratory for preparation of lightly radioactive or contaminated materials; a machine shop; and supporting equipment areas.

In the last two years, numerous facility improvements were made possible with ~$1M in funding from the Laboratory, the facility's Associate Laboratory Director, and the ET Division. These improvements include the following:

- Four original shielding windows were replaced in early 2003.
- The facility's 20-year-old local annunciator alarm system, which monitors facility operating parameters, was replaced in 2003.
- New leaded glass was added to most gloveboxes to improve shielding and reduce worker doses; as a result, doses for manipulator repair have been reduced by 50%.

- Two new criticality-safe vacuum cleaners were purchased for use inside of the hot cell.

- Retrospective air sampling systems were purchased for key facility exhaust systems to monitor effluent releases and to ensure HEPA filter integrity. We also purchased various shielding items, including lead aprons, lead-lined gloves, lead blankets, movable lead-blanket hanging racks for localized and temporary shielding, shielded drums for waste collection, and lead walls for localized shielding during manipulator repair operations.

- Two facility-specific databases were upgraded and automated. The first tracks the facility's periodic maintenance and action items and notifies personnel via email when actions regarding technical safety requirements are coming due. The second database tracks the special nuclear materials and other programmatically valuable samples in the facility.

Fire protection improvement projects at ANL funded by DOE also benefited the facility. During 2002 and 2003, the facility's fire detection and alarm system was replaced, and the fire suppression system (sprinklers) was upgraded.

In addition to the physical improvements, several safety basis documents were revised to better address the necessary actions to maintain the facility's safety record. The modifications were in the form of improved procedures and substantial revisions to the Safety Analysis Report. The facility's Maintenance Implementation Plan was also revised during 2003.

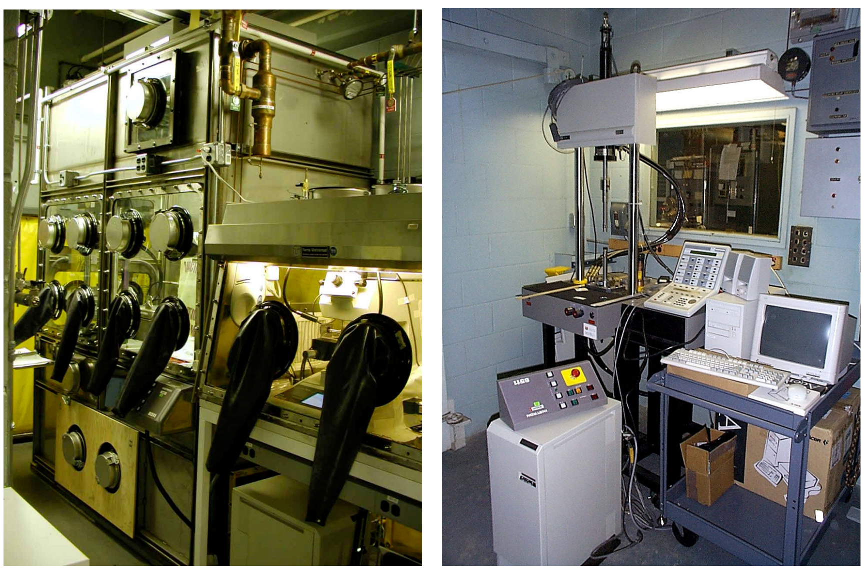
We are planning one major improvement project for 2004. The facility's Associate Laboratory Director has provided the funds necessary to replace 18 of the 20 master-slave manipulators. The Section has worked with the maintenance group for ANL-West hot cells to identify free manipulators that can be modified for use in the AGHCF; this equipment recycling will result in a savings of approximately $1.75M in capital equipment costs. We have hired ANL-West maintenance personnel to perform the modifications and to provide new manipulators, which are expected to begin arriving in early 2004. The manipulator replacement project will result in significant improvements in operational efficiencies and reduction in maintenance costs.

Irradiated Materials Laboratory

The IML has capabilities for handling, testing, and analyzing irradiated materials. The facility was designed and built to conduct postirradiation examinations of structural components for reactor development, and that role has expanded over the years to include testing of components. The research has helped to increase knowledge of irradiated materials behavior and properties for commercial power reactors and research reactors. The facility has also provided information for the development and testing of advanced alloy materials for the DOE fusion program. Testing capabilities include tensile and creep-rupture under vacuum or inert atmosphere up to 800°C, slow-strain-rate tensile testing up to 320°C in a controlled water environment, fracture toughness testing up to 320°C in a controlled water environment, and instrumented Charpy-impact testing (drop-weight system) to -190°C. Sample preparation capabilities include a remotely operated electric discharge machine for cutting precise specimens from irradiated materials.

The IML consists of four air-atmosphere hot cells (centicurie, beta/gamma). The interior of each cell (1.8 m wide by 1.5 m deep by 2.9 m high) is maintained at a negative air pressure. Each cell is equipped with movable doors that allow needed equipment to be easily installed, removed, and reconfigured to support the mission of the cell.

The improvement projects discussed for the AGHCF also benefited the IML. In particular, a new ~$250K glovebox was fabricated and installed; this glovebox will allow programs to safely conduct tensile tests on irradiated cladding materials. The glovebox was outfitted with leaded glass as part of the shielding improvements. Other facility improvements included the installation of additional shielding surrounding the facility and shielded waste containers; these improvements will not only benefit facility occupants but will also reduce the background radiation levels in spaces adjacent to the facility.



New glovebox for Irradiated Materials Laboratory. Left: "benchtop" containment. Right: glovebox containment.

Room DL-114 Glovebox Facility

The DL-114 Glovebox Facility consists of five gloveboxes that are used for a wide variety of experimental work. The facility was refurbished in 2000 for the purpose of installing and operating hydrogen, oxygen, and nitrogen determinators, which are used to study the properties of irradiated cladding materials. The improvements described for the AGHCF also benefited this facility; in particular, lead glass shielding windows were installed on two of the gloveboxes to reduce operator doses by an estimated 50%.

M-Wing K-2 Hot Cell Facility

The M-Wing K-2 Hot Cell Facility in Building 200 was placed into operation in 2002. The facility had been unused for many years, and a small amount of maintenance was required to bring it into operational status. The facility is extremely flexible; it houses four work stations for the installation of experiments requiring significant shielding and minimal contamination control. Equipment can be moved into and out of the facility with relative ease, as the work conducted in the facility is designed to produce little loose contamination. During 2003, tensile tests with irradiated stainless steels were conducted, and creep experiments on high-burnup cladding are planned.

Resource Planning

The Hot Cell Facilities Section (HFS) maintains a minimum staff; this helps assure the most efficient operation. The Section acquires any additional staff needed to operate and maintain the facilities on a case-by-case basis. For example, if an instrumentation and control system needs maintenance, the facility hires a service organization to perform that task. Typically, the cost associated with hiring the service organization is well below the cost of maintaining in-house staff. Another example of efficient management involves the window refurbishment project; this project resulted in limited operations in the AGHCF for approximately 6 months. The nonspecialized window-related tasks in the project (i.e., project management, window assembly, testing, and installation) were contracted to a different ANL-East division with the necessary expertise and spare capacity to complete the work. This “matrixing” effort allowed AGHCF technicians with programmatic specialties to continue programmatic work in other HFS facilities and to complete facility-related specialized tasks on the project in a parallel effort.

Another example of matrixing involved manipulator repair. Beginning in 2002, the facility began hiring ANL-West maintenance personnel to repair AGHCF and other HFS manipulators. The technicians at ANL-West were chosen for this maintenance activity because they specialize in manipulator repair, while the AGHCF technicians at ANL-East complete manipulator repair only as needed. In addition, relying on ANL-West technicians allows the AGHCF technicians to focus on programmatic activities, their specialty. Because of the increased productivity and difference in effort costs, the total cost savings for manipulator repair is ~25%.

Thus far, our resource planning effort has been successful and has had minimal impact on the research programs due to scheduling conflicts and delays. Serious effort will continue to be necessary to ensure that the facilities are sufficiently operational to maintain programmatic progress.