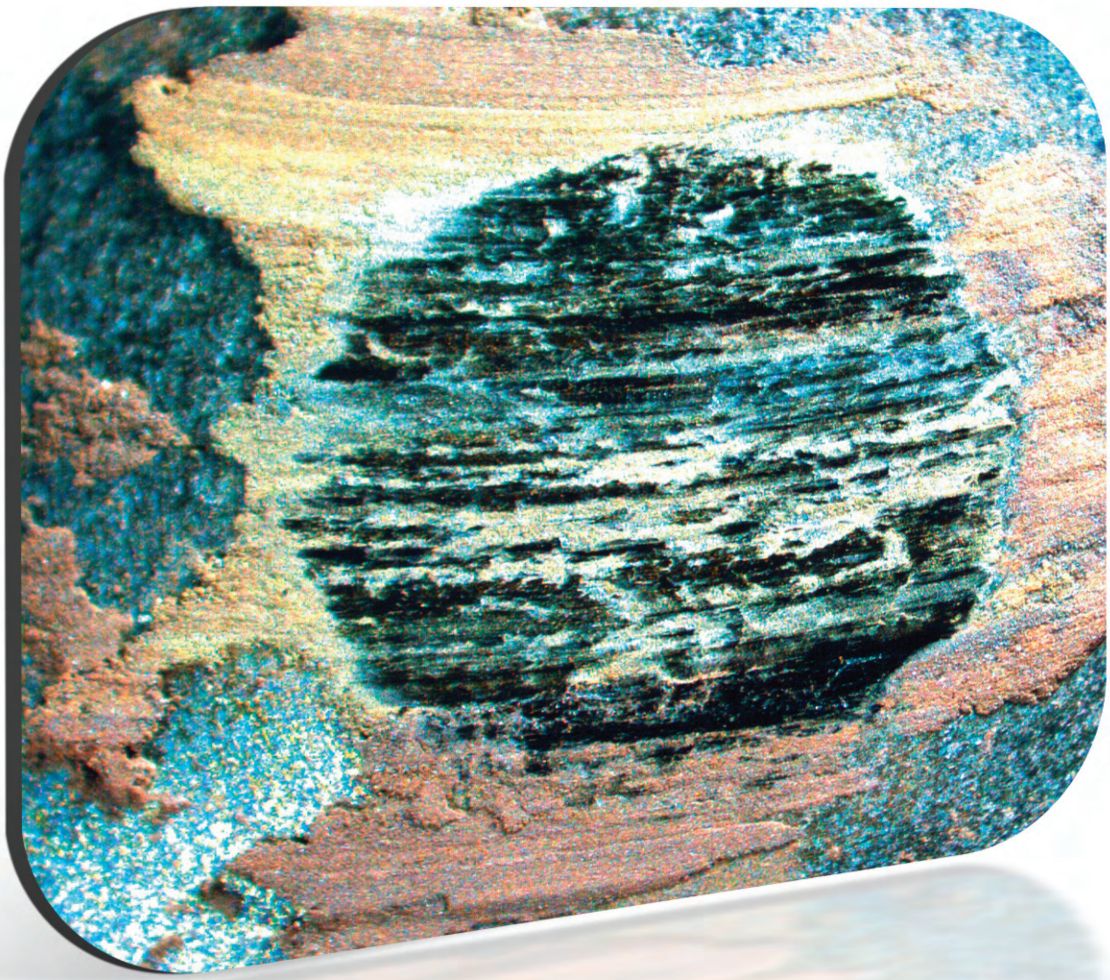
Oak Ridge National Laboratory

High Temperature Materials Laboratory User Program



20th Annual Report

October 1, 2006 – September 30, 2007

High Temperature Materials Laboratory User Program

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by Edgar Lara-Curzio
and
the staff of the High Temperature Materials Laboratory User Program

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Director's Message

Dr. Edgar Lara-Curzio, Director of the HTML.

This year, which marks the 20th anniversary of the High Temperature Materials Laboratory (HTML) and the HTML User Program, I was honored to be named Director of the HTML following Arvid Pasto's retirement after 13 years of leading the HTML. I am looking forward to working with the world-class staff at the HTML, our sponsor at DOE, and key partners in industry and universities to chart a bright future for the HTML and the HTML User Program for the next 20 years.

When the HTML was founded in 1987, it was established as a research facility to address high-temperature materials problems that limit the efficiency and reliability of advanced energy conversion systems, in particular automotive gas turbines and low-heat-rejection heavy-duty diesel engines. Although these two prime movers have since been removed from the research portfolio of the Department of Energy (DOE), the HTML continues to play an important role in addressing one of the top priorities of DOE: to reduce or eliminate the nation's dependence on foreign oil. The HTML is doing that by supporting industry, universities and other federal laboratories in their efforts to achieve greater energy efficiency through technologies such as lightweighting materials to reduce the weight of vehicles, thermoelectric materials to recover waste heat from internal combustion engines, and improved catalysts for exhaust aftertreatment and hydrogen production. Also, to better support the mission of the Vehicle Technologies Program, which sponsors the HTML, this year the HTML discontinued its support for user projects focused on machining of materials.

During FY2007, the HTML User Program hosted 113 individual user visits from 47 different organizations. Approximately three-fourths of the users came to the HTML for the first time. The HTML User Program also received 86 new proposals: 36 from industry, 45 from universities, 4 from other national laboratories, and 1 from another federal agency. Of those 86 proposals, 16 were from new organizations, 14 of which were from industry.

The volume of user activity was particularly high in the 4th quarter of FY2007, when we recorded 55 individual user visits on 35 different projects. Those included 12 user visits as part of 7 different projects at the HTML's Neutron Residual Stress Facility at ORNL's High Flux Isotope Reactor (HFIR). The HFIR was restarted on May 16, 2007 after being shut down for more than a year while a new cold source was installed. The cold source increases the available neutron flux in the 4 to 12 Å range, making HFIR the highest flux reactor-based source of neutrons in the United States.

In FY2007, in collaboration with DOE's Energy Efficiency and Renewable Energy's Hydrogen program, two programs in DOE's Office of Electricity Delivery and Energy Reliability (Superconductivity and Distributed Generation), and DOE's Office of Science SHaRE Program, the HTML acquired a new field emission TEM/STEM instrument (Hitachi HF-3300), which replaces the venerable HF-2000 TEM, one of the most in-demand instruments in the history of the HTML. More information about the capabilities of this unique instrument can be found on page 53. Memoranda of agreement were also established with the SHaRE Program and ORNL's

Center for Nanophase Materials Science to consolidate ORNL's nanoindentation facilities and to share access among the three programs to several instruments and the cost of maintaining them.

Other new capabilities added to the HTML User program during FY2007 include a Calotest™, which is a micro-abrasion, ball-cratering instrument for rapid and accurate measurement of the thickness of tribological films and coatings, as well as a new LaserPit system from ULVAC to measure in-plane thermal diffusivity of thin sheet specimens and thin films. This is especially useful for measurements of thermal conductivity of super lattice thin films, which is an important area of thermoelectric materials. Additional details are in the "New and Updated HTML Capabilities" section that starts on page 49.

This year the HTML's JEOL 2200FS-AC aberration-corrected electron microscope passed its final tests prior to instrument acceptance, with a demonstration of its ability to correlate chemical species identification with structure at the single atomic column level, using electron energy-loss spectroscopy. Further information is on page 51.

Today, as when the HTML was established 20 years ago, the HTML continues to play a pivotal role in enabling the development of materials and technologies that are critical to addressing the energy challenges facing the Nation.

I invite you to review highlights of user projects carried out during FY2007 at the HTML, beginning on page 9. The first three sections summarize HTML user projects in the areas of catalysis, automotive lightweighting materials, and thermoelectrics. These are followed by selected summaries of other user projects.

The HTML Facility

The High Temperature Materials Laboratory (HTML) is a Department of Energy (DOE) user facility dedicated to solving materials problems that limit the efficiency and reliability of systems for power generation and energy conversation, storage, distribution and use. Sponsored by the Vehicle Technologies Program in the Office of Energy Efficiency and Renewable Energy (EERE), the HTML is located at the Oak Ridge National Laboratory (ORNL) in a 37,511-ft^2 building containing six user centers – clusters of specialized equipment available to researchers from industry, universities, and federal laboratories. The HTML also manages a neutron beamline facility at the High Flux Isotope Reactor (HFIR) at ORNL and a synchrotron radiation beamline at Brookhaven National Laboratory's National Synchrotron Light Source (NSLS).

Opened in 1987, the HTML was established in response to the oil embargoes of the 1970s and charged with the mission of working directly with U.S. industry, academia, and government laboratories to develop advanced high-temperature materials such as structural ceramics for energy-efficient engines. Since then, the HTML's scope of work has expanded to include other types of materials with applications to transportation and energy-related systems.

The Program

The HTML User Program has two major objectives:

- Provide researchers with access to a highly skilled staff and to sophisticated, often one-of-a-kind instruments for materials characterization;
- Assist in educating and training materials researchers.

Instruments at the six user centers have extensive capabilities for characterizing the microstructure, microchemistry, and physical and mechanical properties of materials over a wide range of temperatures. Specific capabilities include:

- Diffraction (X-ray and neutron)
- Friction and wear testing, inspection
- Mechanical characterization
- Microstructural analysis down to the atomic level
- Residual stress measurements
- Thermography and thermophysical properties determination

Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, which typically cover no more than 30 days of work during a two-year period. Users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature no more than six months after research is concluded. Papers and presentations must be prepared jointly by users and HTML staff.

For proprietary research, the user owns the research data and all costs at the HTML are paid by the user based on DOE guidelines for ORNL costs.

The User Centers

Diffraction User Center

The DUC provides a unique combination of specialized facilities and a staff of technical experts for determining the structure of materials, using x-ray, synchrotron radiation, and neutron diffraction techniques. A special emphasis is *in situ* characterization of materials under non-ambient conditions (temperature, pressure, and atmosphere).

Equipment

- X-ray Diffraction (high, low, room temperature)
  - Scintag PADX HT-XRD and Scintag XDS2000 LT-XRD
  - Philips X'Pert Pro MPD multi-purpose XRD
  - PANalytical X'Pert Pro MPD XRD
- Neutron* Diffraction at the High Flux Isotope Reactor (HFIR)
  - Room Temperature - 1600°C
- Synchrotron High-Flux Beam Line (at NSLS)
  - RT Capillary Mount, Buehler and Capillary Furnaces

* Primary Funding for the operation of HFIR and NSLS is provided by DOE's Office of Science

Staff

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Jianming Bai

Roberta A. Peascoe-Meisner

Claudia J. Rawn

Geneva N. Worley, Administrative Secretary

Materials Analysis User Center

The MAUC's world-class facilities and staff experts provide characterization of the structure and chemistry of advanced materials, with a special emphasis on relating microstructure to materials performance. The MAUC is comprised of a suite of labs that contain the latest-generation electron microscopes and surface analysis instruments. Research specialties include characterization of nanophase materials such as catalysts, carbon nanotubes and nanoparticulates; structural and functional materials; electron holography (e.g., for dopant profiling in semiconductors); and characterization of multilayer surface films.

Equipment

Field emission transmission electron microscopy (FE-TEM) and aberration-corrected scanning transmission electron microscopy (STEM) instruments allow imaging and chemical microanalysis to the atomic level. Surface analysis is provided by a field emission scanning Auger Nanoprobe, while the electron microprobe allows quantitative chemical analysis of bulk microstructures at the sub-micron level. An environmental SEM characterizes surface morphology and chemistry. The most modern specimen preparation techniques are available, utilizing instruments such as a focused-ion-beam miller with micro-sampling capability, a cryo-ultramicrotome, and assorted devices for slicing, grinding, and polishing.

- Hitachi HF-3300 cold FE-STEM/TEM
- Hitachi FB-2000 FIB Micro Mill
- Hitachi S3400 Environmental SEM
- JEOL 2200FS-AC Aberration-corrected FE-TEM
- JEOL 8200 Electron Microprobe
- K-Alpha X-ray Photoelectron Spectrometer
- Phi 680 FE – Scanning Auger Nanoprobe

MAUC Staff

Larry Allard, User Center Leader

Dorothy Coffey
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Harry Meyer
Karren L. More
Larry Walker

Mechanical Characterization and Analysis User Center

The MCAUC focuses on the mechanical characterization of functional and structural materials. Its staff of technical experts performs mechanical testing and analysis and develops test methods, design codes, and supplemental analytical techniques. MCAUC manages a large collection of mechanical test frames with uniaxial and multiaxial capabilities to conduct tests in tension, compression, flexure, torsion, shear, and internal pressurization in controlled environments over a wide range of strain rates and temperatures using standard or customized specimens. Facilities also include equipment for micromechanical testing and instrumented indentation.

Equipment

- Biaxial Test System (Torsion/Tension-Compression)
- Dilor XY800 Raman Microprobe
- Dynamic Mechanical Analyzer
- Electromechanical and Servohydraulic Test Systems
- Hardness Tester
- High-rate mechanical testing
- Nano and Micromechanical Test Systems
- Resonant Ultrasound Spectrometer
- Test machine for automotive crashworthiness (TMAC)
- Thermal Shock Facility
- Thermomechanical Analyzer

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Christopher Owen Stevens
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Residual Stress User Center

The RSUC's world-class facilities and staff of technical experts emphasize characterization of both surface and through-thickness stresses with state-of-the-art X-ray, synchrotron, and neutron diffraction facilities. Residual stresses affect such important properties as fatigue life, strength, onset of yielding, and resistance to microcracking. X-ray and neutron diffraction methods are available in the RSUC to measure macro- and micro-residual stresses in polycrystalline and single crystal materials ranging from small specimens (thin films) to large industrial components.

RSUC Equipment

- Neutron* Diffraction Residual Stress Mapping Facility (NRSF2)
  Large Specimen XYZ Stage, Small Specimen KAPPA, 2-Circle Orienter

RSUC Equipment (continued)

- Neutron* Powder Diffraction (High Temperature Furnace/Microstresses)
  - Room temperature – 1600°C Vacuum Furnace
- Synchrotron High-Flux X-ray Beam Line
- XRD X'Pert pro with Anton Paar Hot Stage
- XRD Polycrystal-Texture-Stress Goniometer, with rotating anode and standard X-ray tube
- XRD TEC Large Specimen Goniometer

* Primary Funding for the operation of HFIR and NSLS is provided by DOE's Office of Science

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Thermography and Thermophysical Properties User Center

The TTPUC analyzes thermophysical properties such as thermal conductivity, diffusivity, and expansion, specific heat, Seebeck coefficient. It also characterizes thermal stability, high-temperature reactions and compatibility, and high temperature oxidation and corrosion properties. Materials studied at the TTPUC include metals, ceramics, superalloys, glasses, sand, paper, thermal barrier coatings, carbon materials, carbon composites, ceramic composites, metal matrix composites, and thick and thin films. In addition, high-performance infrared (IR) cameras are used in various thermography applications, including mapping temperatures and properties, monitoring processes, and nondestructively evaluating materials and structures. The thermography capability is portable and may be used for offsite user projects.

Equipment

- Differential Scanning Calorimeter – DSC
- Dilatometer
  - Bilayer, Dual Push Rod (1500°C), High Temperature (2400°C)
  - High Speed Quenching, Deformation, or Cryogenic Cooling;
- Electrical Resistivity and High Temperature Seebeck Coefficient/Electrical Resistivity
- Hyperspectral Imaging
- Thermal Analysis
  - Simultaneous DTA/TG, High Mass TGA
- Thermal Conductivity
  - 3-Omega System, Lock in IR Camera
- Thermal Constants Hot Disk System
- Thermal Diffusivity
  - LaserPit in-plane, Laser Flash, Xenon Flash
- Thermography – IR Camera
- Thermosonic NDE
- Total Hemispherical Emittance

TTPUC Staff

Ralph B. Dinwiddie, User Center Leader
Wallace D. Porter
Hsin Wang
Geneva N. Worley, Administrative Secretary

Tribology Research User Center

The TRUC characterizes material properties and performance of load-bearing, engineering surfaces and the materials that separate them. TRUC facilities and staff are a resource for solving problems associated with the use of advanced materials and coatings for the friction, wear, and lubrication of component parts in engines and other energy-conversion systems. In 2007, the new TRUC was formed to redefine the scopes of the two user centers that preceded it: the Machining, Inspection, and Tribology User Center (MITUC) and the Friction, Wear, and Machinabililty User Center (FWMUC).

Equipment

More than fifteen kinds of friction and wear testing configurations are available, including a high-speed sub-scale disc brake apparatus and a high-temperature repetitive impact test system designed to study the durability of diesel engine exhaust valves at temperatures to 850°C. Supporting instruments include a mini-viscometer, microindention hardness tester, optical and measuring microscopes with image analysis, and a micro-abrasion system to measure coating thickness.

- Compact Grindability Test System
- Continuous Loop Abrasion Test
- Durometer – Elastomer Hardness Tester
- EMD Legend Coordinate Measuring Machine
- High-Temperature Oscillatory Scuffing Tester
- Image Analyzer
- KSI-2000 Scanning Acoustic Microscope
- Laser Surface Profile Measuring System (noncontact)
- Mahr Formtester
- Microindentation Hardness Tester, room and high temperature
- Multi-mode Rolling/Sliding Friction & Wear
- Nikon Optical Comparator
- Pin-On-Disk, room and high temperature
- Reciprocating friction/wear, low- and high-load
- Repetitive Impact Testing System
- Scratch Test, portable and instrumented (Revetest)
- Stylus Surface Profile Measuring System
- Subscale Disk Brake Material Tester

Staff

Peter J. Blau, User Center Leader
Randy Parten
Jun Qu

User Projects on Catalysis

Key barriers to achieving emissions reduction targets for heavy truck diesel engines include incomplete development of aftertreatment technologies and the premature degradation of emission control devices due to operation under high-temperature and high flow-rate conditions.

Researchers at the High Temperature Materials Laboratory (HTML) are collaborating with industry, universities and national laboratory users to characterize catalytic materials used in aftertreatment devices in order to improve the fundamental understanding of the thermodynamics and kinetics of nucleation, growth, and sintering. Following are highlights from six HTML user projects in this area.

1) As part of an HTML User Project with the Pacific Northwest National Laboratory (PNNL), researcher Chuck Peden visited the HTML to characterize barium on alumina and platinum on alumina catalysts, as part of PNNL's development of materials for improved trapping of nitrogen oxides in diesel exhaust streams. Peden and the HTML's Larry Allard used the HTML's JEOL 2200FS aberration-corrected electron microscope (ACEM) to characterize the distribution of barium species on the alumina structure. These results were correlated to PNNL's studies of the catalysts using high resolution solid state NMR, which suggested that BaO nucleated at penta-coordinated Al^{3+} sites on the gamma-alumina surface. Correlating these results with studies of other catalytically active species on alumina could open up the possibility of dramatically improving control of dispersion of catalytically active phases.

2) In the area of bimetallic catalysts, University of Texas-Austin professor Miguel Jose Yacaman is working with HTML researcher Larry Allard to characterize model bi-metallic catalysts on the order of 2-5nm in size with controlled compositions ranging from pure Au to pure Pd. These materials

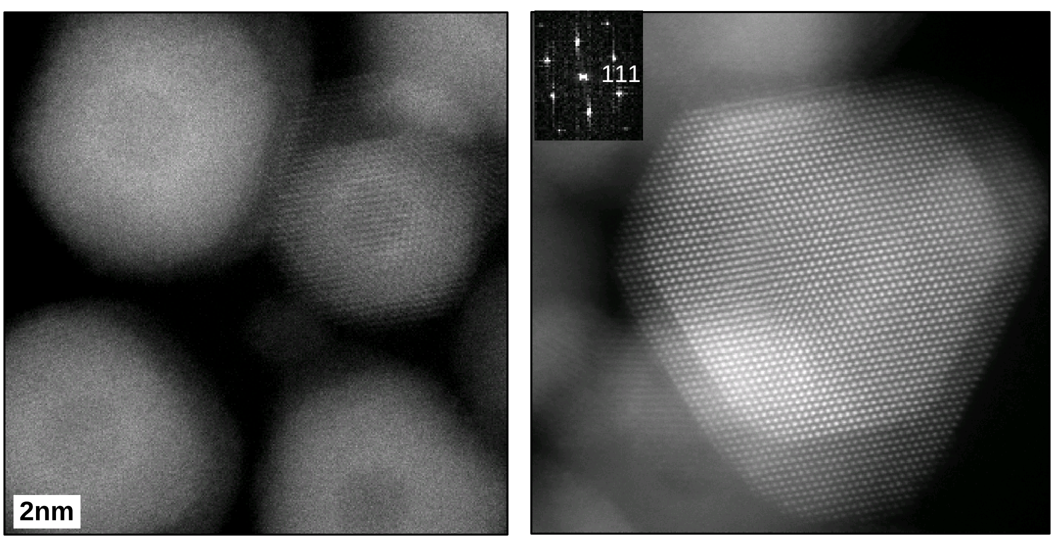


Fig. 1. Left: High-angle annular dark-field image of Au-Pd nanoparticles, showing dark core and two shells. Composition consistent with Pd core, Au-rich first shell and Pd-rich outer shell. **Right:** High-resolution image of one of the particles perfectly oriented in <110> zone axis direction (cube face diagonal), showing details of compositional changes at the atomic level.

are of interest because they have the potential of replacing more expensive precious metals used in aftertreatment systems. Using the HTML's ACEM it was possible to obtain details of surface structure and defects of the particles as well as their chemical composition. A 'core-shell' structure was seen in virtually 100% of the particles (Fig. 1, previous page) indicating that the core is likely nearly pure Pd, and the clearly resolved first and second shells are Au-rich and Pd-rich, respectively. At high resolution columns of atoms are clearly resolved. This is perhaps the best image of such a nanoparticle ever taken, made possible by the excellent imaging capabilities of the HTML's ACEM.

3) As part of another University of Texas-Austin HTML User project, Professor Paulo Ferreira and HTML researcher Larry Allard studied the atomic structure of bimetallic catalysts comprising Pt-Co compounds on carbon, using high-resolution annular dark-field imaging in the ACEM. This study seeks to understand the nature of core-shell structures observed in these particles, which range from 1-20 nm in size. Specifically, small particles appear to have a core-shell structure, with a disordered zone at the periphery of the particle (Fig. 2, left). As particles grow with heat

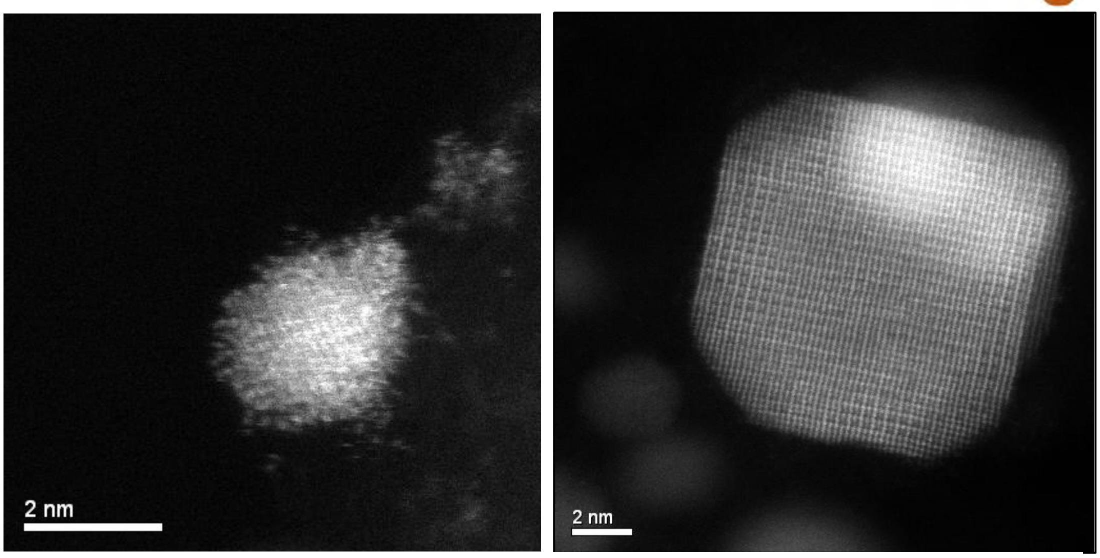


Fig. 2. While fine Pt-Co particles have a disordered outer shell (left), as they grow, an ordered Pt_3Co structure develops.

treatment, for example, an ordered Pt_3Co structure appears to develop (Fig. 2, right). These catalysts are of particular interest for fuel cell applications, as the addition of Co makes them more economical than pure Pt, and higher catalytic activity is an additional advantage.

4) Prof. Moira Ridley of Texas Tech University is collaborating with HTML researcher Larry Allard to study the structure of 4nm and 20nm TiO_2 (anatase) particles. The objective of her HTML user project was the characterization of the particles morphology and crystallography using the HTML's ACEM. This microscope's capability to image nanoparticle structure at the atomic level in the high-angle annular dark-field mode was ideal for this study.

5) Dr. Steven Bradley of UOP and HTML researcher Larry Allard are conducting a fundamental study of metal cluster arrangements on oxide supports, with a focus on the kinetics of the development of bimetallic catalyst clusters with various reaction treatments. Dr. Bradley is collaborating also in the development of an *in situ* heating and gas reaction capability for the HTML ACEM, as it is an obvious extension of the observations of the behavior of atoms and clusters under the influence of energetic electron beam conditions. Preliminary studies of as-prepared samples of platinum and tin on theta-alumina showed that the heavy metal species are distributed at the single atom to few-atom clusters over the alumina surface. The exceptional resolution of the ACEM in the annular dark-field mode is enabling images like the one in Fig. 3 to be obtained, leading to a basic understanding of the influence of support structure and reaction treatments on the development of catalyst microstructures.

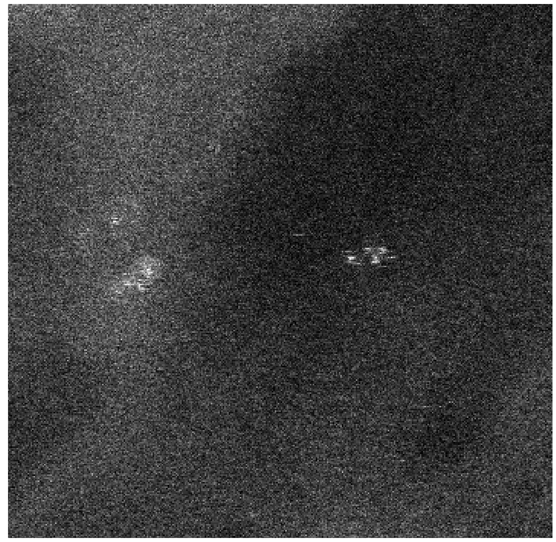


Fig. 3. Platinum and tin atoms dispersed on theta-alumina. Contrast of individual atoms may be related to their atomic number.

UOP
A Honeywell Company

6) The HTML's Dr. Larry Allard has initiated work with Prof. Abhaya Datye of the University of New Mexico, who is analyzing a bi-metallic catalyst system used in steam reforming of methanol. Reforming fuels for hydrogen production is an important component of DOE's sponsored research into converting renewable feedstocks into hydrogen to power fuel cells. A second aspect of the research is selective oxidation of the CO, which is a poison for fuel cells. The structure of Pd-Zn alloy particles supported on alumina is being characterized, with a particular interest in the tendency to form a surface alloy of Zn after low temperature reduction.

The University of New Mexico

User Projects on Automotive Lightweighting Materials

DOE's Automotive Lightweighting Materials activity is focused on structural materials (lightweight metals, polymer composites) for body and chassis applications that can significantly reduce the weight of passenger vehicles without compromising vehicle lifecycle cost, performance, safety or recyclability. To best take advantage of the properties of polymer composite and lightweight metals in structural components, a significant shift must be made in component design philosophy. Additionally, the differences in properties of materials under consideration require the development of enabling technologies to predict the response of materials after long-term loading, under exposure to different environments, and in crash events.

The High Temperature Materials Laboratory is collaborating with users from industry and universities to address these problems. For example, Quickstep™ Technologies users visited the HTML to determine the effect of fiber and matrix type on the crushing resistance of fiber-reinforced composite tubes for automotive structural applications. Quickstep™ Technologies was established in 2001 to commercialize an out-of-autoclave process to manufacture advanced composite materials. Quickstep™ Technologies engineers Aaron Brighton, Dale Brosius and Ben Ludtka along with ORNL staff members Don Erdman and Mike Starbuck determined the effect of impact speed on the crushing resistance of composite tubes manufactured according to the Quickstep™ process (Fig. 4). A total of 72 crush tests were carried out on ORNL's unique Testing Machine for Automotive Crashworthiness (TMAC) using a range of speeds between 0.25 and 4 m/s. The two material systems investigated included: a quick cure resin prepreg with T700 fiber and a glass fiber-reinforced polypropylene matrix composite. Tube specimens measured approximately 240 mm long with a 60 mm inner diameter and contained four layers of material layered in a "Swiss roll" configuration. It was found that the specific energy absorption (SEA) values were greater than 55 kJ/kg for carbon/epoxy composites and greater than 35 kJ/kg for glass/polypropylene composites. When compared with typical steel and aluminum SEA values of 15 kJ/kg and 30 kJ/kg respectively, the benefits of using composite materials in crash structures is apparent.

Fig. 4. Quickstep™ engineers Aaron Brighton and Dale Brosius retrieving a composite tube after a crush test using ORNL's TMAC.

The development of models to predict the response of materials in crash events requires accurate description of the effect of strain rate on their mechanical behavior. As part of a joint user project with Ford and General Motors, Dr. Hui-Ping Wang of the General Motors R&D Center and John Lasecki from the Ford Research and Innovation Center (Fig. 5, next page) carried out exploratory tests to determine the rate-dependence of the mechanical response of graphite-fiber reinforced epoxy matrix composites with three different fiber orientations (25, 45, and 60 degrees). Working with ORNL staff members Don Erdman and Mike Starbuck, tests were performed at several rates between 1 m/sec and 18 m/s using unique high-rate testing capabilities in the Mechanical

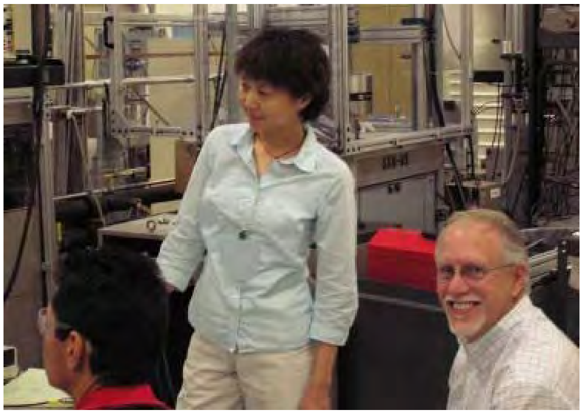
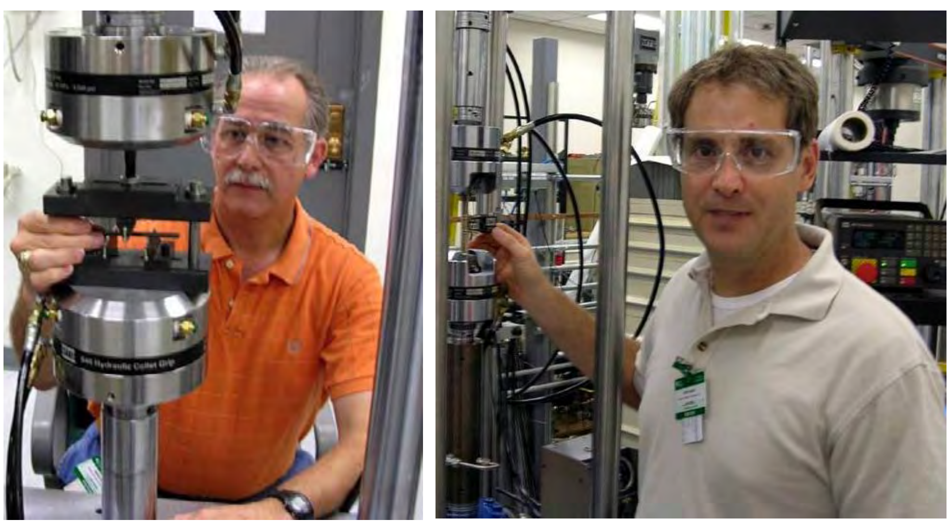


Fig 5. Hui Ping (GM), John Lasecki (Ford, right) and Mike Starbuck (ORNL) preparing a high-rate tensile test of a graphite fiber-reinforced epoxy composite.

Characterization and Analysis User Center at the HTML. Preliminary results obtained from this investigation revealed discernable rate sensitivity for the response of these materials, which will have to be characterized and subsequently incorporated in predictive models.

One of the goals of DOE's Automotive Lightweighting Materials Program is to enable commercially available glass- and carbon fiber-reinforced composite materials with lifecycle costs equivalent to conventional steel. Materials Innovation Technologies LLC (MIT LLC) is a small business established in 2005 to develop innovative manufacturing methods and commercialization of various technologies, including composite materials for transportation applications. As part of a DOE Small Business Innovative Research (SBIR) Phase-II project, MIT LLC is developing the Three-Dimensional Engineered Preform (3-DEP) process as a cost-effective alternative for manufacturing carbon, glass, and natural fiber reinforced polymer composites for automotive



Materials Innovation TECHNOLOGIES

Fig. 6. MIT's Mark Janney (left) and David Haack conduct tensile and flexural tests on composites manufactured with 3-DEP process.

lightweighting applications. MIT LLC engineers David Haack and Mark Janney (Fig. 6) visited the HTML to work with ORNL researchers Rick Battiste and Edgar Lara-Curzio to characterize the static (stiffness, strength) and dynamic (impact resistance) properties of composite materials processed according to the 3-DEP process. Materials of interest included composites with various fiber architectures reinforced with carbon, glass and natural fibers. Initial results revealed that the properties of composites manufactured by the 3-DEP process are comparable to those of composites manufactured according to established manufacturing procedures. The availability of low-cost composite materials will facilitate their widespread use in transportation applications and enable improved fuel efficiency.

Magnesium-based alloys have long been of interest to the transportation industry because of their high strength-to-weight ratio and potential for lightweighting of trucks and automobiles. One of the primary barriers to the wide-scale introduction of magnesium-based alloys has been unfavorable cost with respect to competing alloys such as aluminum. Researchers at Toyota Technical Center, USA are developing processing techniques utilizing high magnetic fields, which could result in improved mechanical properties and lowered heat-treating costs. As part of an HTML User project, Dr. Justin Clark from Toyota (Fig. 7) and the HTML's Wally Porter studied the precipitation kinetics of the AZ80 magnesium alloy. Knowledge of the kinetics of precipitation (e.g., aging, or precipitation hardening) is critical to optimize the mechanical properties of alloys. Solution annealed specimens of AZ80 were tested at a series of isothermal aging temperatures utilizing HTML's quenching dilatometer. These results were used to provide a baseline model for subsequent work using magnetic fields, which could induce faster precipitation kinetics and lead to shorter times at heat treat temperatures, resulting in energy savings and lowered cost.

Fig. 7. Dr. Justin Clark, Toyota Technical Center.

Another challenge for automotive lightweighting materials is to reduce vehicle weight while concurrently maintaining safety and recyclability. Professor Holly Stretz and her research group at Tennessee Technological University are developing nanocomposite materials formed from polymers and organoclays, which could be used for recyclable body panels in automobiles. These materials exhibit enhanced properties at very low filler level, such as increased thermal stability and good flame retardancy. Using the HTML's high temperature x-ray diffractometer Professor Stretz and HTML staff members Andrew Payzant and Robbie Meisner studied changes in these organoclay/polymer nanocomposites during heating in an N_2 environment. The results of these investigations will support the formulation of kinetic models for predicting part failure and the manufacturing and recyclability of lightweight composites for automobile components.

Although carbon fibers are primarily used as reinforcements for composites in structural applications, carbon fibers are also being considered for catalyst support in fuel cells. In this case, analyzing the microstructure of the fibers is important for understanding their functionality. HTML staff member Jane Howe collaborated with a team of researchers at Applied Sciences Inc. (ASI) in characterizing the microstructure of carbon nanofibers. This work was performed remotely using the HTML's Hitachi HF2000 TEM and an Internet link, while the ASI team was in a conference room in their Cedarville, Ohio facility (to accommodate the company president's confinement to a wheel chair). This study revealed that the carbon nanofibers possessed an optimal microstructure for this application, which consists of turbostratic carbon on the surface and a nested conic arrangement of graphene planes in the core (Fig. 8).

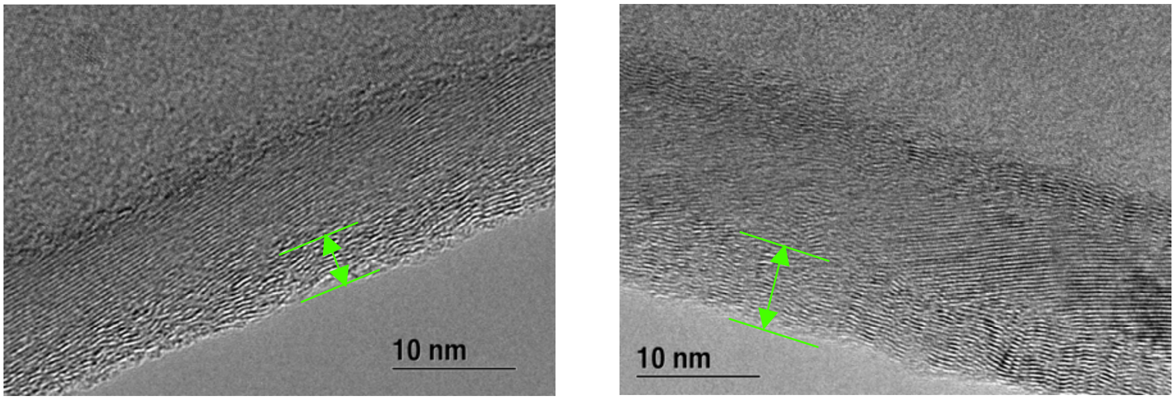


Fig. 8. Carbon nanofiber with turbostratic carbon outer layer highlighted by the arrows. CNF at left has a thinner turbostratic layer, which is a more favorable structure than CNF at right for catalysis applications

User Projects on Thermoelectric Materials

Effective use of waste heat from internal combustion engines significantly increases vehicle fuel economy. Only about 30-35 percent of the fuel's energy currently is used for vehicle propulsion. Approximately 35-40 percent is lost in the exhaust gases and another 30-35 percent is lost to the coolant. Recovery of energy from engine exhaust and/or engine cooling system represents a potential for 10 percent or more improvement in overall engine efficiency.

The temperature differences between the ambient air and the radiator, lubricating oil sump, exhaust gas, exhaust gas recirculation loop, turbocharger compressed air discharge (engine intake air), and brakes present opportunities for direct conversion of heat to electricity, known as the Seebeck effect (an electric current is generated when a temperature differential is applied across a thermoelectric material).

Michigan State University Professors Eldon Case and Tim Hogan and their students Fei Ren (Fig. 9) and Jennifer Ni are participating in an HTML User Program project to characterize the thermal and mechanical properties of hot-pressed lead-antimony-silver-tellurium (LAST) and lead-antimony-silver-tellurium-tin (LAST-T) thermoelectric materials, which are promising because they have a figure of merit, ZT, of about 1.7 at 700 K. In their research with HTML staff member Hsin Wang, they determined the effect of temperature on the thermal conductivity, thermopower (Seebeck coefficient), and electrical resistivity of both p-type and n-type LAST-m materials. To date this material has the best properties reported for bulk thermoelectrics.

In collaboration with HTML researchers Rosa Trejo, Amit Shyam and Edgar Lara-Curzio, the

Fig. 9. MSU graduate student Fei Ren using the RUS to determine the elastic properties of thermoelectric materials.

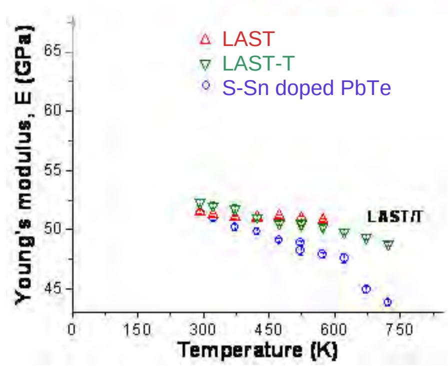


Fig. 10. Temperature dependence of Young's modulus as determined by high temperature RUS for S-Sn doped PbTe and newly developed materials LAST and LAST-T.

MSU team used the HTML's Resonant Ultrasound Spectrometer (RUS) to determine the elastic constants of these materials, which were found to decrease with temperature. Specifically, they found that the decrease is greater for the Sn doped PbTe than for the LAST and LAST-T materials (Fig. 10). These studies will provide the necessary information to analyze the distribution of stresses in thermoelectric converters and thus enable improved design of reliable waste heat recovery devices, since high efficiency thermoelectric devices must survive vibrations encountered in vehicle applications.

As part of another HTML User Project, Kansas State University Professor James Edgar and graduate student Li Du (Fig. 11) worked with ORNL researcher Michael Lance to determine the growth stresses in aluminum nitride crystals in order to understand the sources of those stresses and to improve their reliability. Aluminum nitride is an attractive material because of its potential use in power electronics and thermoelectric converters. Using the HTML's Raman microprobe, they tracked the Raman peak for AlN at 656 cm^{-1} to measure stress. Figure 12 (left) displays a stress map obtained from a region on the sample where two AlN grains were growing into one another (Fig. 12, right). The Raman peak shifts to lower frequency at the interface, which suggests a tensile stress in the grain that has its c-axis hitting the side of the right-most grain. The model used by the Kansas State University researchers suggests that a tensile stress should form at that location during crystal growth. Thus, facilities at the HTML have helped to confirm a model and accelerate the understanding of the process to grow these crystal materials.

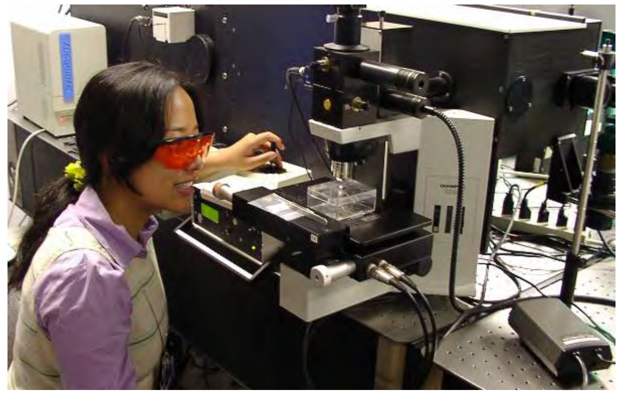


Fig. 11. Li Du collects data using the HTML's Raman microscope.

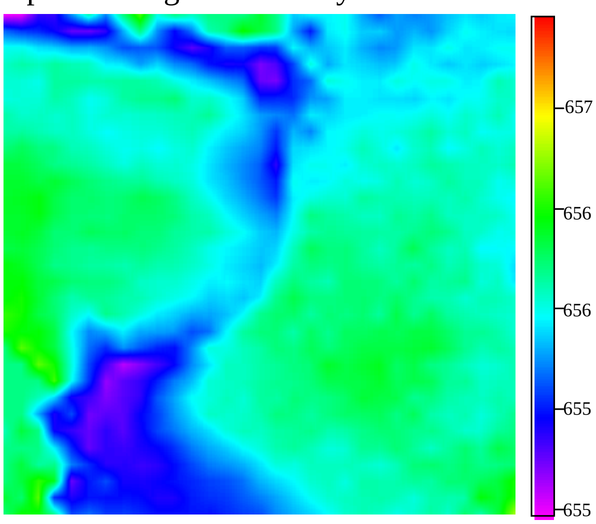


Fig. 12. A 30 by 30 μm stress map (left) was obtained from a region on the sample where two AlN grains were connected (above). At the interface, the AlN Raman peak shifts to lower frequency (blue color), suggesting a tensile stress.

contact: Andrew Payzant, Leader, payzanta@ornl.gov, 865/574-6538

Georgia Tech chemists study CO_2 absorption/desorption in lithium silicate

Research problem: Use in-situ high-temperature XRD to characterize the absorption/desorption of CO_2 in lithium silicate

Implications: Improved understanding of the kinetics of the phase transformation could lead to a potential technique for CO_2 absorption and sequestration

Description of Work: Professor Angus Wilkinson and under-graduate student Ignacio Becerra-Licha utilized HTML's high temperature x-ray diffraction capabilities to characterize the reversible absorption of carbon dioxide in lithium silicate. Samples of Li_4SiO_4 were heated to above 500°C, and exposed to CO_2, which rapidly converted the starting compound to a mixture of Li_2CO_2 and Li_2SiO_4. Switching to an inert gas (nitrogen) reversed the reaction at high temperatures, although the carbonate could be retained if the sample was cooled to ambient temperatures in the presence of CO_2 (Fig. 13). Such materials may prove useful in fuel reforming or for removal of CO_2 from exhaust streams. Using the XRK900 reaction chamber on the PANalytical X"pert Pro diffractometer, high-quality data were sequentially collected in 15-minute intervals to evaluate the reaction kinetics as the temperature and atmosphere were varied. In this first phase of the HTML proposal, only dry gases were utilized, but the effects of water vapor on the mechanism of CO_2 uptake will be the focus of a second visit.

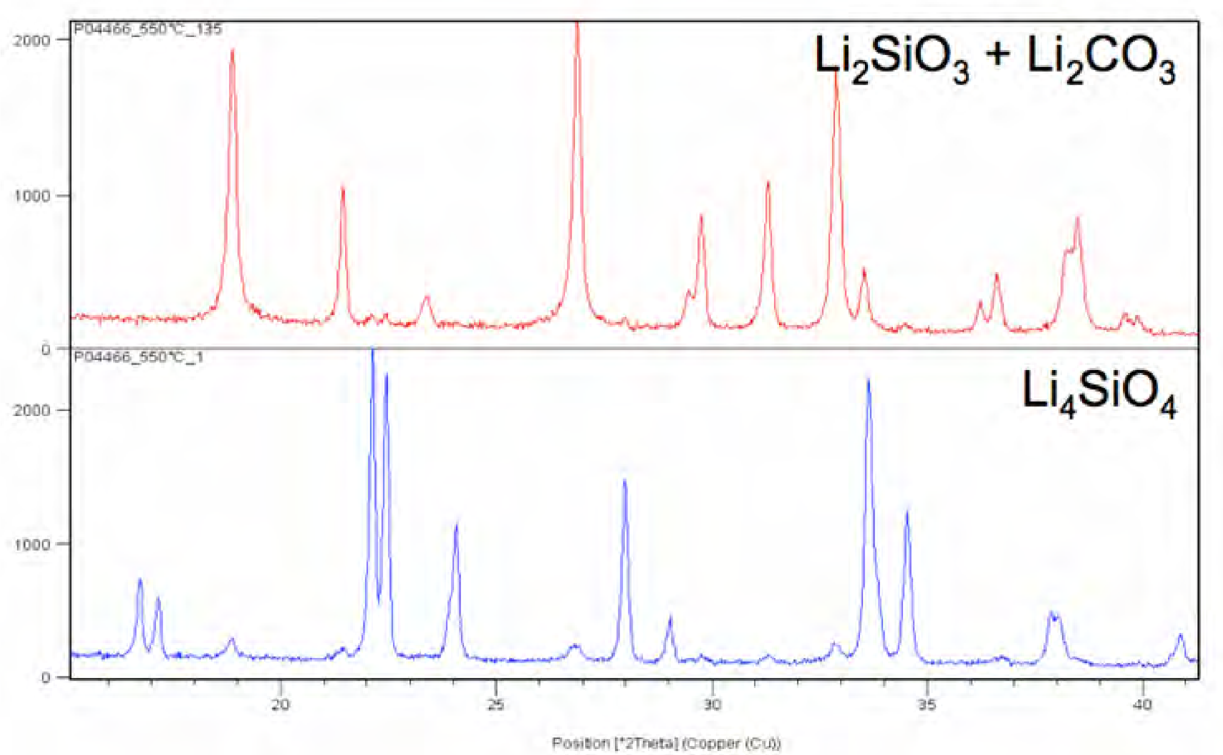


Fig. 13. Lower XRD scan at 550°C in N_2, upper XRD scan made on same sample after switching to CO_2 atmosphere. The absorption/desorption reaction is completely reversible at high temperatures.

Virginia Tech uses high temperature XRD to study phase relations at metal-ceramic interfaces

Research problem: Use in-situ high-temperature XRD for quatitative phase analysis of metal–ceramic interfaces at high temperature

Implications: Improved metal-ceramic interfaces for functional and structural components

Description of Work: A more detailed understanding of phases forming at metal-ceramic interfaces has the potential to improve high-temperature processes for materials with potential applications in transportation industries. Based on prior thermodynamic predictions, Vairaj Payyapilly from Virginia Tech and HTML's Claudia Rawn used *in situ* x-ray diffraction to study phase evolution in metal/ceramic interfaces, to corroborate the predicted phase assemblages that would occur under the same conditions. The design of the sample was a simple diffusion couple with the two phases in contact, and preliminary experiments of Al coatings on Al_2O_3 and TiO_2 substrates did not reveal the intermediate phases predicted. Future experiments are being considered where the Al coating will be sandwiched between substrate materials.

HTML assists Caterpillar, Inc.

Research problem: proprietary materials corrosion analysis

Implications: eliminate corrosion source in heavy equipment engines

Description of Work: Caterpillar utilized the HTML's x-ray diffraction, x-ray fluorescence, and electron microprobe expertise to resolve outstanding questions relating to a proprietary materials corrosion issue. HTML staff Andrew Payzant, Larry Walker, and Roberta Peascoe worked with Caterpillar's Dr. John Truhan to solve the problem. The combination of characterization techniques enabled a detailed description of the chemistry and structure of the corrosion product, which was used by Caterpillar to determine and eliminate the source of the corrosion.

XRD study of the impact of isovalent doping on GaN films for semiconductors

Research problem: to reduce the specific contact resistance of semiconductor/metal junctions

Implications: the development of more efficient white light-emitting diodes (LEDs)

Description of Work: Prof. Louis Guido from the Virginia Tech Materials Science and Engineering Department and Claudia Rawn of the HTML used x-ray diffraction to characterize GaN films that had been co-doped with arsenic (As). Characterization of the GaN films' physical properties showed that co-doping with As significantly improved the electronic properties and that the electron and hole transport properties were roughly equivalent to some of the best materials reported to date. Preliminary experiments on one sample at the HTML were undertaken to understand the epitaxial relationships and to correlate the structure features such as grain size and twist and tilt of the film to the substrate with the As content. Additional experiments will be conducted at HTML's synchrotron beamline X14A to complete the matrix of variables such as film thickness and As content and how they correlate with structural features.

Caterpillar characterizes diesel engine deposits

Research problem: Determine the structure and chemistry of diesel engine piston deposits to identify highly abrasive phases

Implications: Mitigation of engine deposits, improved engine life andenergy conservation through longer lasting engine parts

Description of Work: Depending on their chemistry and structure, the deposits that build up on diesel engine pistons and cylinders may adversely affect the wear, and hence, performance and lifetime of the engine. The composition, structure, and distribution of these deposits in diesel engines is not well-known. Caterpillar's Dr. John Truhan utilized HTML's expertise in x-ray diffraction, x-ray fluorescence, and electron microprobe to examine the structure and chemistry of diesel engine piston deposits at various locations from three cylinders of a field-return engine. Care was taken by the User to segregate deposits from various locations such as the crown, lands and ring grooves. Knowing the composition, structure, and distribution of these deposits allowed Caterpillar to consider methods to prevent formation of certain deposits, and to mitigate their effects and improve engine life. HTML staff Andrew Payzant, Larry Walker, and Roberta Peascoe worked with Dr. Truhan to identify the compounds formed in these engines. Of particular interest was that highly abrasive alumina particles, which had been tentatively identified in a preliminary study done elsewhere, were shown not to be present.

Palladium alloys for hydrogen separation studied at HTML

Research problem: A need for more detailed understanding of the implications of the processing steps used to form thin palladium alloys foils on porous metal supports

Implications: Reliable high-volume production of pure hydrogen gas is essential to the proposed "hydrogen economy."

Description of Work: Dr. Paul Thoen of the Colorado School of Mines and DUC leader Andrew Payzant collected high temperature XRD data on palladium foils electroplated with different thicknesses of gold, in order to observe "in situ" with x-rays the alloying process used by CSM to reach the desired microstructure. The HTML XRD facilities include unique capabilities to study these materials at high temperature under gas environments from oxidizing through inert to reducing. The gold layer was found to alloy with the palladium to form a thin gold-palladium alloy coating on an unalloyed palladium interior, with the composition and thickness of the gold-palladium alloy dependent on the starting thickness and annealing temperature (Fig. 14, next page). These foils are utilized in a joint hydrogen separations project between CSM, Pall Corporation, and Chevron-Texaco, funded in part by the USDOE.

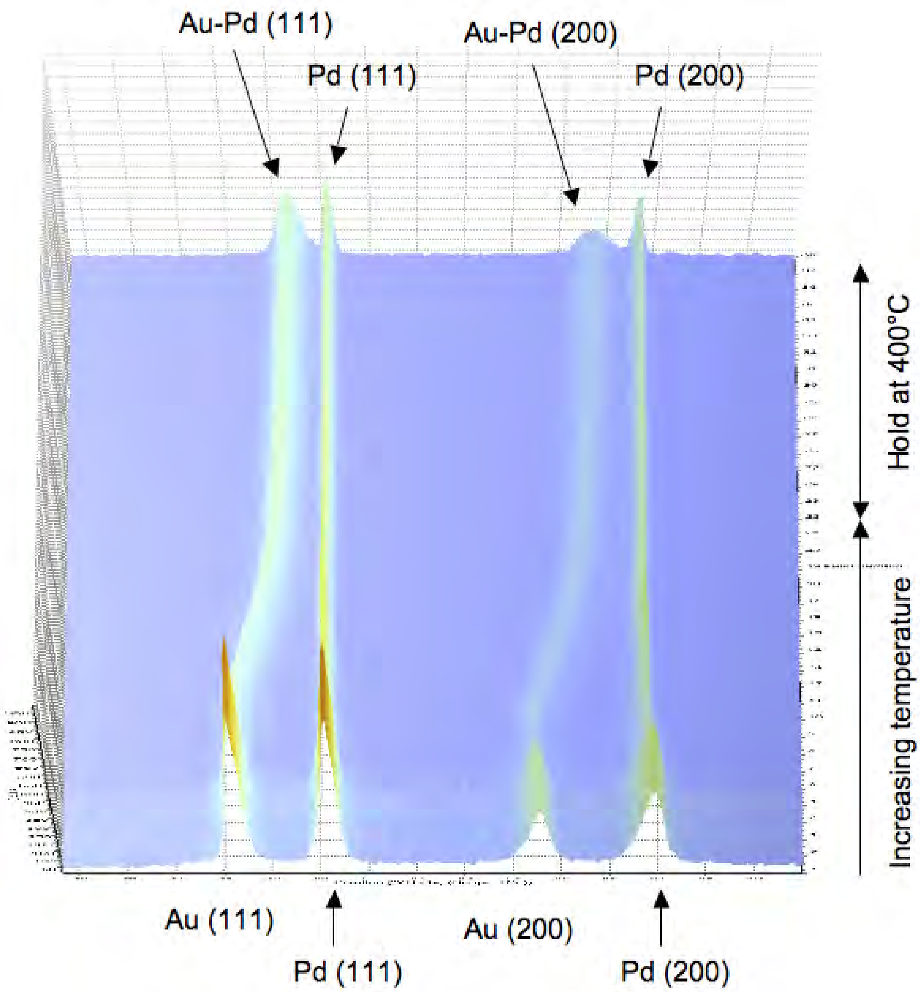


Fig. 14. High Temperature XRD scans on Palladium foil coated with Gold. Shifts in gold coating (Au) peak positions indicate alloying with palladium (Pd), whereas substrate peaks do not shift.

Tennessee Tech and HTML study formation of deletrious phases in concrete

Research problem: Identification of ettringite phases in late age concrete as a proof-of-concept study

Implications: Formation of ettringite crystals in concrete is a significant concrete durability problem.

Description of Work: Dr. Benjamin Mohr from Tennessee Tech University used the HTML's *in-situ* diffraction capabilities to identify the formation of late age ettringite phases in concrete. The formation of crystalline ettringite is known to cause stress in concrete and lead to cracking. It is anticipated that a basic research study could be developed using x-ray diffraction as a primary means to study the formation and evolution of ettringite in aged samples. Such a study could lead to methods to mitigate the formation or allow for expansion and thereby result in a significant improvement in the infrastructure of the United States through prolonging the service life and sustainability of our concrete infrastructure. In the first phase of this study, Dr. Mohr and DUC staff Robbie Peascoe and Andrew Payzant performed quantitative phase analyses of several fresh and aged concrete samples using the XRD facilities at the HTML. For illustration,

Fig. 15 compares fresh (black) and aged for 150 days at 80°C (green) concrete to pure ettringite (red). The ettringite peaks are clearly resolved in the aged sample, but are not present in the fresh sample.

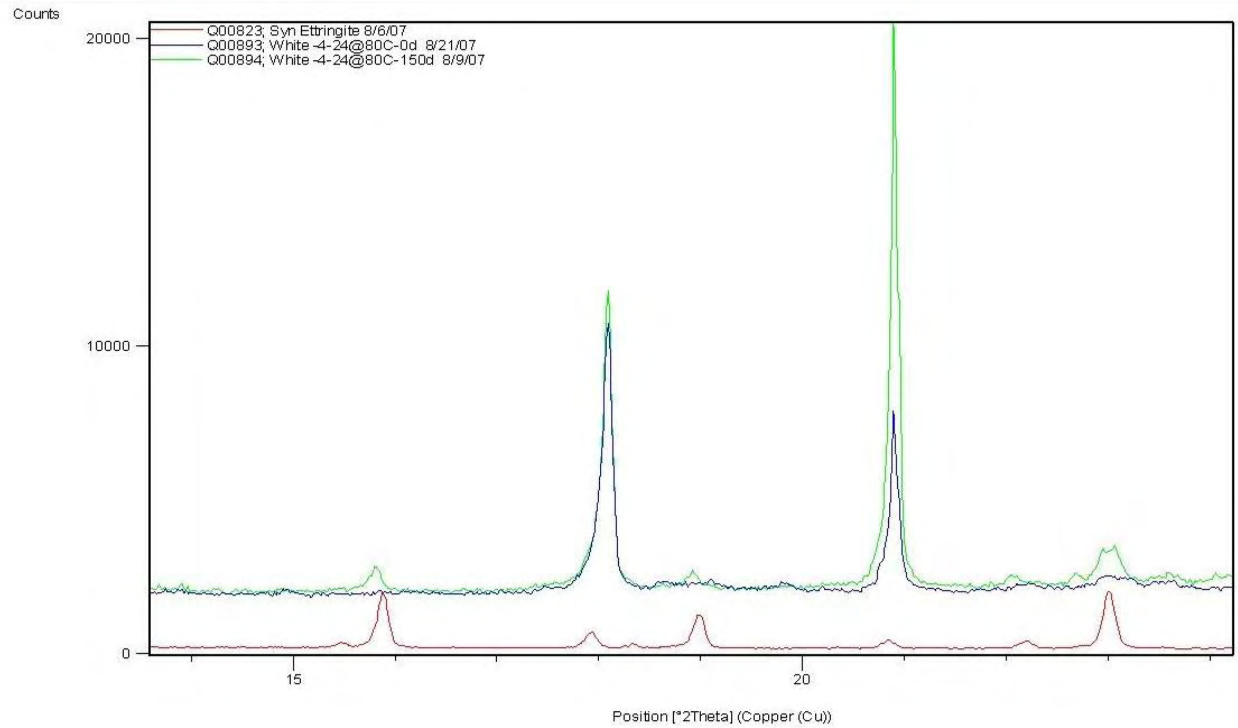


Fig. 15. Portion of diffraction patterns of fresh concrete (black), aged concrete (green) and pure ettringite (red) imaged on the PANalytical X'Pert Pro MPD diffractometer with Cu k-alpha radiation.

Materials Analysis User Center (MAUC)

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UT investigates surface of electrochemically polarized Zr-based bulk metallic glasses

Research problem: To understand the corrosion behavior of bulk metallic glasses

Implications: development of corrosion-resistant materials

Description of Work: Dr. Harry Meyer worked with University of Tennessee Prof. Peter Liaw and his student Brandice Green in a study of Zr-based bulk metallic glasses (BMGs). These materials have received attention due to their high glass-forming ability and attractive physical properties, such as high strength, low Young's modulus, and high fatigue endurance limits. These alloys are being investigated for coatings and biomedical applications. The prospective applications, especially biomedical related, have underscored the importance of the aqueous corrosion behavior of these materials.

The anodic-polarization behavior of $Zr_{50}Cu_{40-X}Al_{10}Pd_X$ (x = 0 and 7 atomic %) BMGs was investigated in a 0.6 M NaCl electrolyte. Initial anodic polarization of both alloys led to a region where small increases in the applied potential induced significant increases in the current densities. Continued polarization of both BMGs resulted in a diffusion controlled regime. However, the limiting diffusion current density of $Zr_{50}Cu_{33}Al_{10}Pd_7$ was higher than that of $Zr_{50}Cu_{40}Al_{10}$. Scanning Auger microanalysis was used to investigate the oxide formed during polarization and to analyze the chemistry within corrosion pits. The pits formed on both BMGs were enriched with Cu and Cl (Fig. 16 below). Corrosion pits on $Zr_{50}Cu_{33}Al_{10}Pd_7$ were additionally enriched with Pd. A corrosion mechanism relating to the formation of CuCl and Cu_2O was proposed based on both polarization and microanalysis results.

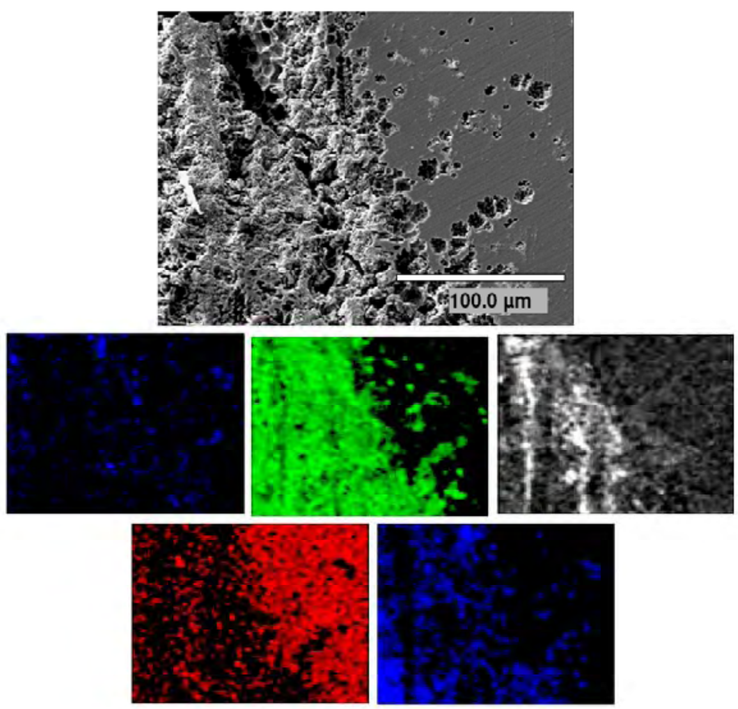

Fig. 16. Scanning electron image of a heavily corroded portion of the polarized $Zr_{50}Cu_{40}Al_{10}$ sample. (row 2, L to R) Auger elemental maps of C, O, and Cu; (row 3, L to R) Zr and Cl.

HTML helps Vesta Ceramics compete for SBIR

Research problem: investigate tunable energy release in nanocomposite thermites

Implications: small business development in field of automotive energetic materials

Description of Work: Vesta Ceramics, a small business in California, started working with the HTML in early 2007 on a user project involving nanocomposite superthermites. Vesta has been developing them with tunable energy release using high-surface area, mesoporous silicon powders. Porous Si particles are produced from metallurgical grade Si with a surface area of up to 150 m^2/g; then small nanometer-size clusters of metal oxides such as Fe_2O_3 are deposited within the pores of porous Si particles using sol-gel synthesis. The intimate mixture of the oxidizer particles and Si is expected to result in a thermite reaction with improved energetic properties such as ignition sensitivity and energy released. MAUC researchers Jane Howe and Larry Walker helped Vesta's Terry Tiegs characterize the thermites using three types of electron microscopy in just a month of turn-around time. A STEM (scanning transmission electron microscopy) image is shown in Fig. 17. The characterization study assisted Vesta in optimizing its process parameters, and Vesta used part of the results gained at HTML in their Phase II SBIR proposal. The company is so impressed with the quality work provided at HTML that they will set up a funded project with ORNL if the Phase II SBIR is funded.

Fig. 17. A z-contrast STEM image shows iron oxide (brighter area) deposited on porous Si (darker objects).

Investigation of friction layer on C/C/SiC aircraft brake materials

Research problem: Microstructure characterization of the friction layer on brake pads after friction tests

Implications: Because frictional behavior of brake materials is closely related to friction layer formation, a better understanding of the friction layer microstructure in advanced C/C and C/C/SiC friction materials leads to improved brake systems.

Description of Work: Ph.D. candidate Soydan Ozcan of Southern Illinois University is researching the mechanisms of adsorption/desorption of moisture in carbon-carbon composites and the effect of contaminants on the different types of energy dissipating friction processes of carbon-carbon composite brake materials. Using the focused ion beam (FIB) technique, cross-sectional samples of the thin friction layers were prepared by HTML staff member Dorothy Coffey. Transmission electron microscopy (TEM) was used to study the nanostructure of the friction layer, as shown in Fig. 18 below. The electron diffraction patterns and lattice images reveal the variation of crystallinity in the carbon composite. Mr. Ozcan will present the results obtained at the HTML at the American Ceramic Society's Daytona Beach 2008 conference.

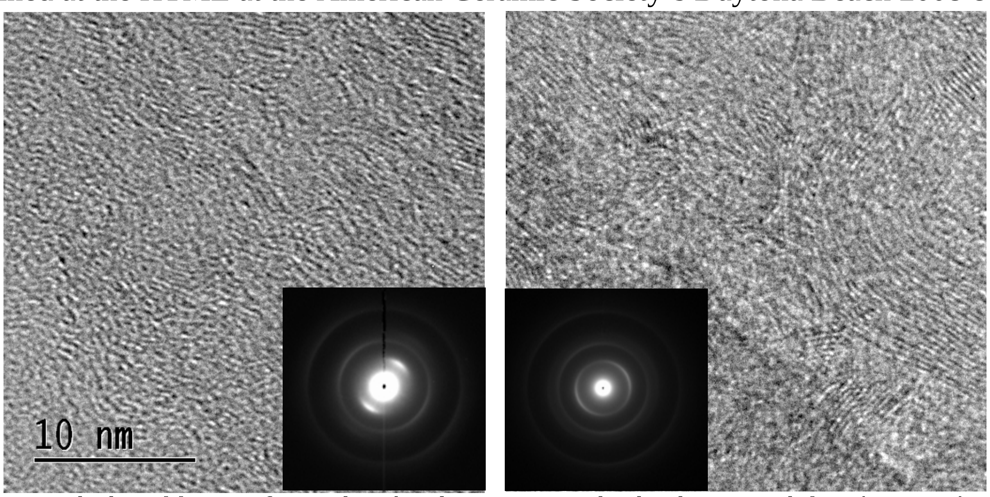

Fig. 18. Frictional layer of a carbon/carbon composite brake material. Micrograph at left with electron diffraction pattern insert of the carbon fiber; and at right, TEM image and diffraction pattern of the carbon matrix. The matrix has a higher degree of crystallinity than the fiber.

Capstone Turbine assesses the effects of landfill gas on hot section components of a C30 MicroTurbine™

Research Problem: Determine the effect of operating a microturbine on landfill gas containing ~150 ppm H_2S

Implications: Improve microturbine operating life by reducing premature failure of hot section components and/or component fouling due to siloxane deposits and other contaminants

Description of Work: Capstone Turbine has installed hundreds of C30 MicroTurbines at landfills to operate on landfill gas. To assess the effects of landfill gas on the hot section components of the microturbine, a C30 engine with ~24,000 hours of operation at a landfill was decommissioned, torn down, and the hot section components sectioned for analysis at the HTML. Capstone's Wendy Matthews used the electron microprobe (JEOL 8200 EPMA) and scanning electron microscope (Hitachi S-3400 Environmental SEM) expertise available at the HTML to examine samples taken from the combustor, fuel injectors, turbine nozzle, turbine wheel, and recuperator. While the landfill gas at this particular site had low H_2S content (~150 ppm), the gas did contain a number of other contaminants. Analysis of the hot section components revealed minimal deposits and no evidence of accelerated corrosion. Dr. Karren More and Larry Walker of the HTML staff worked with Ms. Matthews to identify the deposits found on the hot section components. The discovery of a thin silicon oxide deposit (Fig. 19) on all of the hot section components was of particular interest, as was the minimal oxidation damage to the 347SS recuperator core after ~24,000 hours of service.

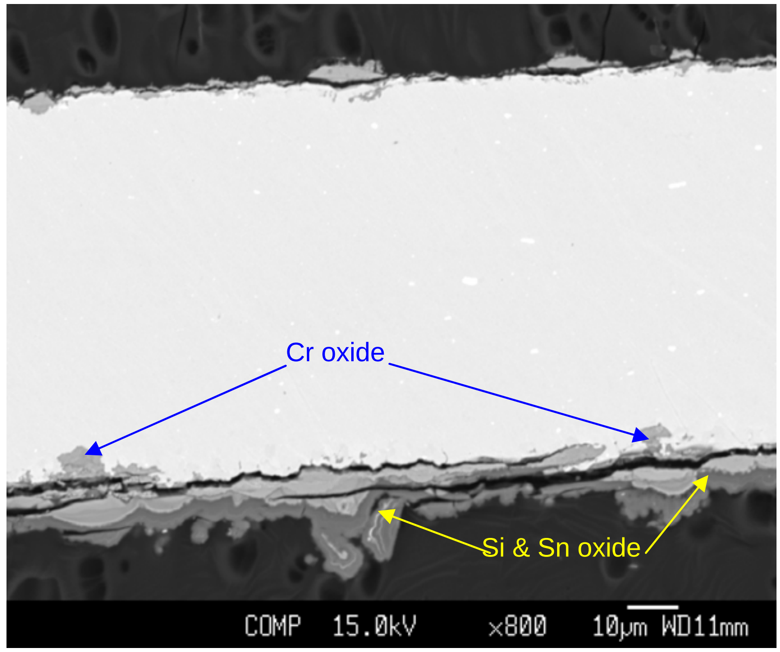

Fig. 19. Scanning electron micrograph of cross-section of a recuperator air cell.

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Measurement of elastic and piezoelectric constants of langatate (LGT) with resonant ultrasound spectroscopy (RUS)

Research problem: determination of elastic and piezoelectric constants of LGT

Implications: development of sensors for more fuel-efficient engines

Description of Work: Current Acoustic Wave (AW) devices for applications in sensing and frequency control typically use quartz. New piezoelectric crystals, including the LGX family (langatate, langasite, and langanite) have many attractive characteristics for AW devices, including higher piezoelectric coupling and density than quartz and the capability to operate at temperatures in excess of 1000°C, well above a phase transition experienced by quartz at 570°C. However, LGX crystals are still in an early developmental stage and accurate measurements of their material properties at high temperatures are needed. As part of an HTML User Project, Prof. Mauricio Pereira da Cunha and graduate student Peter Davulis of the University of Maine (Fig. 20), along with MCAUC researchers Amit Shyam and Edgar Lara-Curzio, determined the elastic and piezoelectric constants of LGT crystal up to 1200°C. These crystals have trigonal symmetry, and the stiffness matrix of the material is described by six independent elastic constants. The low symmetry of the material required development of new software codes for analysis, and finite element modeling was performed to verify the results of the analysis. The elastic stiffness and the piezoelectric matrix were established at room temperature. An unusual result was the activation of enhanced energy loss mechanisms at temperatures between 450-650°C as shown in Fig. 21. Current work focuses on understanding the intermediate temperature peak-broadening phenomenon and establishing the temperature dependence of the six elastic constants. The availability of LGX-based devices could result in sensors for more fuel-efficient engines.

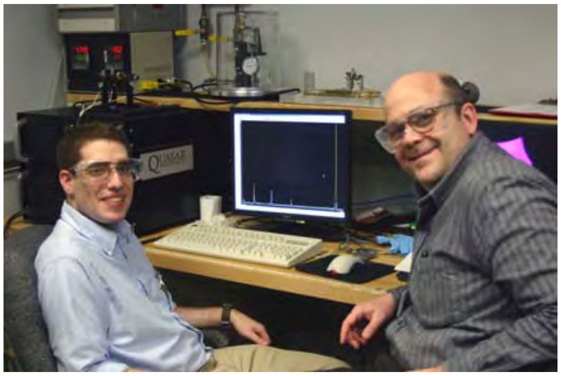


Fig. 20. Davulis (left) and da Cunha at HTML's high temperature RUS equipment.

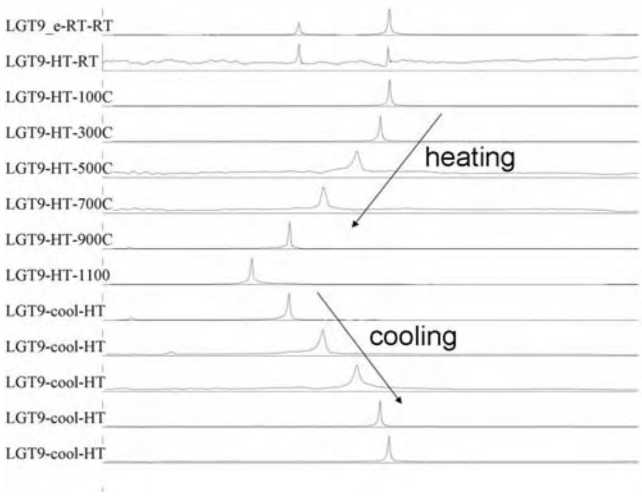


Fig. 21. Temperature dependence of a resonant mode at nearly 130 kHz. The resonant frequency of this mode decreases with increasing temperature, and there is enhanced material damping in the intermediate temperature range.

Florida State investigates mechanical properties in 316LN alloys for superconductors

Research problem: Mechanical characterization of M316LN stainless steel alloy used as conduit in superconducting magnet applications

Implications: Development of reliable electrical superconductors

Description of Work: The characterization work at the Florida State A&M University campus on conduit materials used in super-conducting magnet applications is part of a collaboration between the FAMU-FSU College of Engineering and the Magnet Science and Technology Department of the National High Magnetic Field Laboratory. Professor Peter Kalu and his research team at Florida State University (FSU) are investigating the possibility of using M316LN as a conduit material for superconducting magnet applications and have received HTML approval for two phases of characterization work. Under one proposal, FSU graduate student Steven Downey (Fig. 22) visited the HTML to work with MCAUC researchers Rosa Trejo, Laura Riester and Edgar Lara-Curzio to study both the effect of heat treatments on the hardness of grains, grain boundaries and twin boundaries and also the relation of these results to the microstructure of the material, in particular the presence of grain boundary precipitates. Steven used the HTML's Hysitron nanoindenter to determine the hardness of the material and to image the indents (Fig. 23).

Fig. 22. FSU graduate student Steve Downey using the Hysitron nanoindenter to measure the hardness and elastic properties of M316LN.

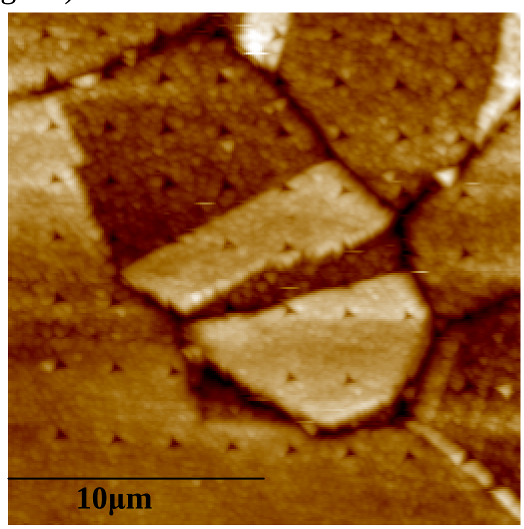


Fig. 23. Nanoindentations in "Piezo image" of an M316LN sample aged for 100 hours.

On another user project, FAMU researchers Dr. Peter Kalu and Steven Downey worked with HTML research staff member Dr. Harry Meyer to identify changes in chemical composition at the grain boundaries (GB) of M316LN caused by the heat treatment and resultant precipitate formation. These changes were characterized using scanning Auger microanalysis on the Phi 680 Scanning Auger Nanoprobe (SAN). Images A and B in Fig. 24 (next page) show the un-annealed material: gray-scale image is the secondary electron micrograph (SEM) and colored image is an Auger elemental map for Fe (green) and Cr (red). No distinct Cr-rich regions appear in the Auger map. Images C and D display the same data for the annealed M316LN. Yellow circles indicate selected examples of Cr-rich particulates. Further particulate analysis revealed that nitrogen was also present and indicated that chrome nitride was most likely formed at the grain boundaries. Continued work on *in-situ* fractured samples is underway to learn more about what is present at the GB. The results of these on-going investigations will help determine the effect of time and temperature on microstructural changes in M316LN as well as the feasibility of using it as a conduit material for superconducting magnet applications.

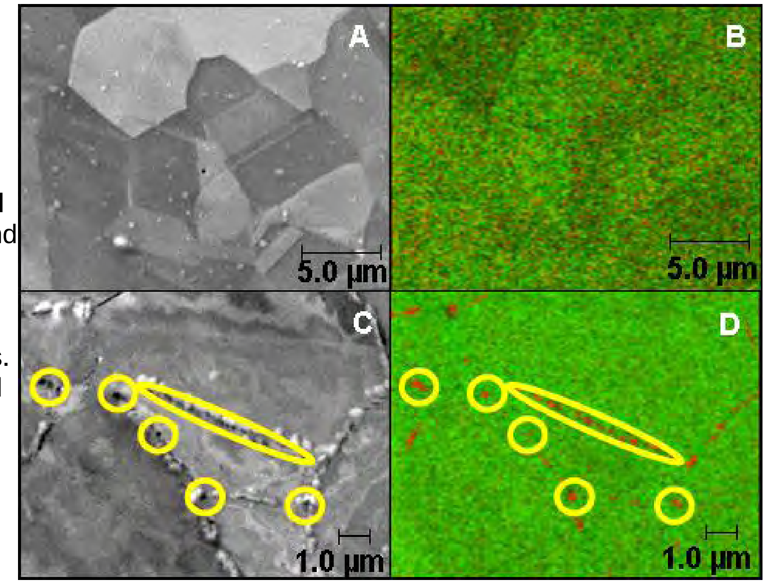


Fig. 24. SEM and Auger elemental maps for un-annealed (A and B) and annealed (C and D) M316LN stainless steel. The annealed sample clearly shows Cr-rich particulates at the grain boundaries. Further analysis also demonstrated that these particles were N-rich.

Georgia Tech dissertation work focused on solid oxide fuel cells

Research problem: Characterization of mica compressive seals for solid oxide fuel cells

Implications: Reliable compressive seals could enable the development of durable and reliable SOFCs.

Description of Work: Solid oxide fuel cells (SOFCs) are energy conversion devices that produce electricity directly from a gaseous fuel by the electrochemical combination of the fuel with an oxidant. SOFCs have high fuel-to-electricity conversion efficiency and very low environmental emissions. While planar SOFCs offer higher power density relative to tubular designs, they require high-temperature gas seals. Researchers at the Georgia Institute of Technology are characterizing mica materials that could be used as compressive seals for SOFCs. Graduate student Christopher Green visited the HTML to work with MCAUC researchers Rosa Trejo and Edgar Lara-Curzio to characterize the leak rate of compressive seals as a function of seal material composition, temperature, compressive stress applied, seal surface roughness, and interfacial conformity (Fig. 25). Chris and his advisor, Prof. Jeffrey Streator, are also developing micro and macromechanical models to identify the role of these parameters on the performance of compressive seals. This on-going investigation will provide valuable information to enable the development of reliable seals for SOFCs.

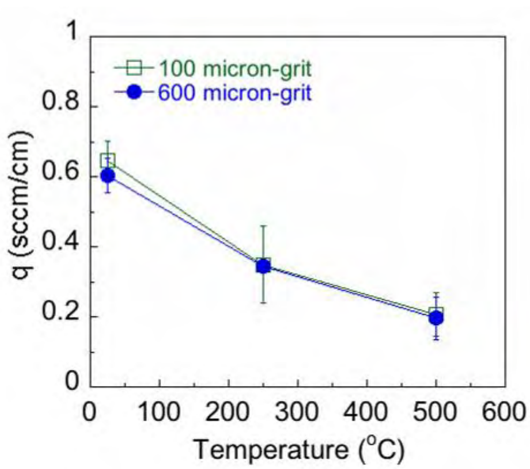


Fig. 25. Leakage rate vs. temperature for mica compressive seals.

Residual Stress User Center (RSUC)

contact: Camden Hubbard, Leader, hubbardcr@ornl.gov, 865/574-4472

Novatek, Inc. measures residual stresses

Research problem: To measure the surface and bulk residual stresses in diamond cutters

Implications: Understanding the current residual stresses can lead to lower-stress profile designs resulting in longer lasting cutters.

Description of Work: Researcher John Fernandez from Novatek, Inc. and the RSUC's Cam Hubbard measured crystalline phases and residual stresses in several polycrystalline diamond-coated W-C/Co cutters used for oil and gas drilling. The durability and longevity of these cutters is important in many applications. For example, failure of the coating on cutters for drilling on an oil rig costs ~$500k/day. X-ray diffraction showed that the diamond coating was a mixture of four or more crystalline phases. Because of the multiphase coating, residual stress studies will proceed at HTML's X14A synchrotron beamline and the neutron residual stress mapping facility (NRSF2).

CAT visits RSUC to study the effect of machining parameters on the residual stress of ceramics for diesel engine exhaust valves

Research problem: Determine the residual stresses in machined Si_3N_4 using x-rays

Implications: Better parts mean lower warranty costs
Greater fuel efficiency by using ceramic valves

Description of Work: A large number of Caterpillar parts require machining to tight tolerances and smooth surface finishes. Many of these components, such as intake and exhaust valves for diesel engines, are used in harsh engine environments, where increases in operating temperatures and pressures are beneficial to efficiency. Materials such as ceramics lend themselves to these operating conditions more easily than metals. For brittle materials such as ceramics, finishing processes play a critical role in determining component life and performance, with significant implications in terms of warranty costs. The purpose of this project is to characterize the residual stresses in a series of machined samples in order to develop cost-effective machining processes for ceramic components, resulting in optimal performance and extended life and reliability. This involves optimizing the stock removal (rough machining) as well as the finish machining operations in order to minimize subsurface damage to the ceramic components. The RSUC is uniquely qualified to perform this work because of the combination of ceramic and x-ray residual stress expertise, specialized equipment, and extensive experience in characterizing the depth profile of stresses in ground ceramics.

Fig. 26. Nate Phillips adjusts sample height on the PTS rotating anode diffractometer.

Nate Phillips (Caterpillar, Fig. 26) visited Thomas Watkins (HTML) to determine the axial residual stresses in a series of machined Kyocera SN235P Si_3N_4 cylindrical samples using a grazing incidence x-ray diffraction technique on the PTS rotating anode x-ray unit. As shown in Fig. 27 below, the finished-machined specimens exhibit larger residual stresses and the highest Weibull modulus (from prior HTML work) relative to the rough ground specimens. The high Wiebull moduli indicate a narrow distribution of flaws within the ceramic. The compressive surface residual stress should make it harder for cracks to propagate. Although not shown, finish machining shears the material more than the rough grinding, creating a more smeared, deformed surface, possibly making the flaws more uniform, which would result in higher Weibull moduli.

Because of the useful results, additional x-ray as well as Raman and nanoindentation work is planned. This work will help Caterpillar produce better, more fuel-efficient and less polluting diesel engines, thus contributing to EERE’s overall mission of developing more energy-efficient and environmentally friendly highway transportation technologies that will enable America to use less petroleum.

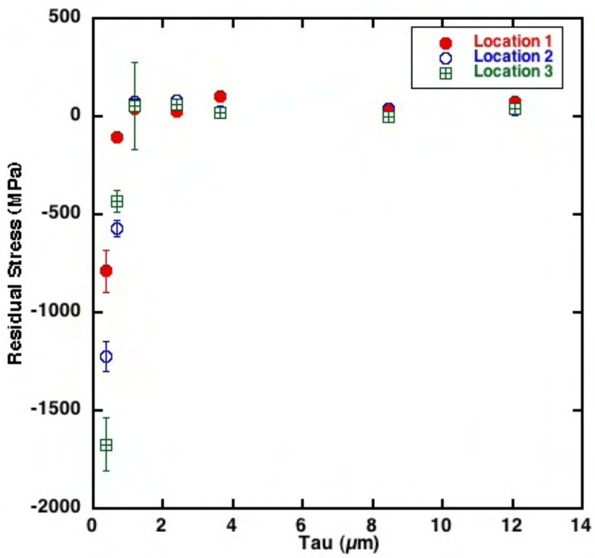


Fig. 27. Axial residual stresses at three locations on a finish-ground sample (wheel speed= 125 m/s; grinding speed 100 mm/min.) as a function of x-ray penetration depth.

John Deere studies residual stress distribution in 1400-lb road grader gears

Research problem: Determine the residual stresses distribution in road grader gears

Implications: Energy conservation through better manufacturing processes that produce higher quality, *long-lasting* parts/equipment

Description of Work: After months of planning, including a site visit to the John Deere Davenport Works manufacturing facility, researchers from John Deere visited the Residual Stress User Center to determine the residual stress distribution within a road grader gear (Fig. 28-a, next page). Residual stresses resulting from welding and heat treating can cause significant problems, both in manufacturing and in the service life of welded and heat treated assemblies. There are no simple, cost-effective methods of measuring residual stresses post processing, particularly around the teeth of a gear. Quantification of such stresses would allow design or manufacturing engineers to more effectively define part geometries as well as welding and heat treatment processing to minimize detrimental effects of residual stresses.

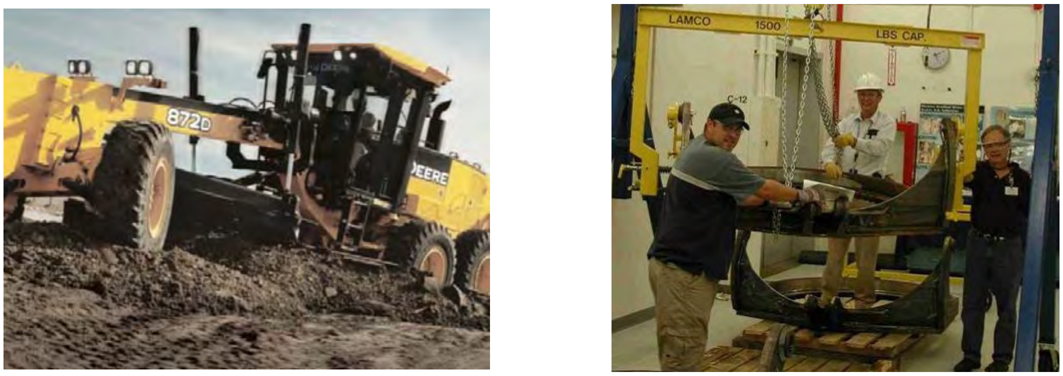


Fig. 28-a). John Deere road grader. The grader gear controls the blade, which moves the earth. **Fig. 28-b).** Using a lift plan, (L to R) Barton Bailey, Camden Hubbard (ORNL) and Tom Mauger (John Deere) lift a gear.

The John Deere team was led by Tom Siegel, Engineering Supervisor at the John Deere Davenport Works, and Tom Mauger, Laboratory Services Supervisor at the John Deere Moline Technology Innovation Center. HTML collaborating researchers were Cam Hubbard, Tom Watkins, and Bart Bailey. This research effort involved the heaviest HTML samples in its 20-year history, with each of the five gears weighing *1400 pounds*. The grader gear was *5 feet* in diameter and was examined with our large specimen x-ray residual stress gantry system (Fig. 28-b). During a one day demonstration of the newest portable x-ray stress analyzer, engineers from the Technology for Energy Corporation (TEC) contributed to the project by performing measurements in regions on the “bottom” side of the gear, which were inaccessible to the ORNL equipment (Fig. 29, left). The results graphed in Fig. 29 (right) indicate the residual stresses are large and vary significantly with location. The engineers at John Deere will now be looking into refinements in the welding and heat treating to reduce this variation. Ultimately, this project will help John Deere produce better, long-lasting parts, which in turn will conserve energy and raw materials, as parts do not have to be replaced as frequently.

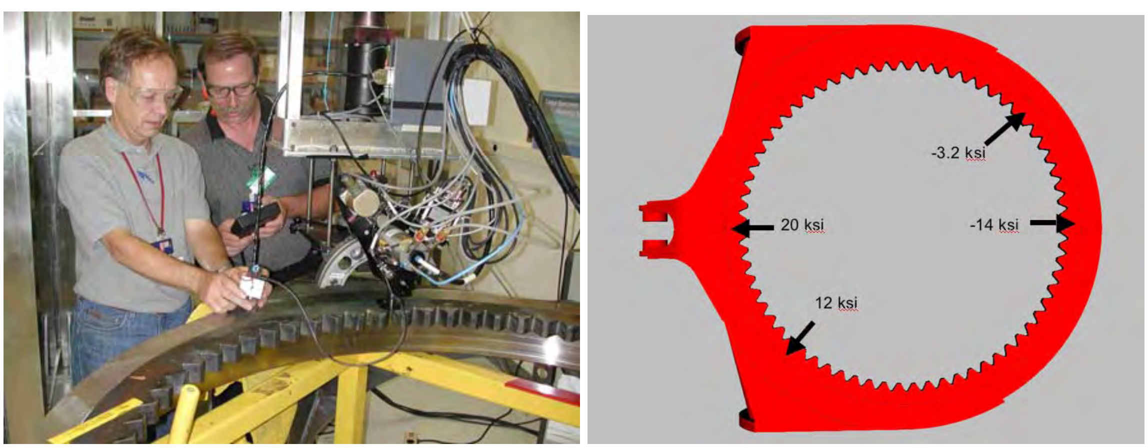


Fig. 29. Tom Mauger (left) and Kent Schumacher (John Deere) adjust the height of ORNL’s large specimen x-ray unit by adjusting its height using a remote control cabled to a Z-motor. The x-ray unit, a TEC 1640, is suspended on a gantry with x, y and z movements available. The yellow cart holds the gear with the “top” side up. Figure at right depicts the residual stress distribution in one of the gears.

Researcher from NCSU studies stresses near socket and butt weld joints

Research problem: To investigate the relationships among residual stresses, strain response and fatigue behavior of weldments

Implications: Understanding these relationships could lead to more durable and reliable weldments and components.

Description of Work: North Carolina State graduate student Pei-Yuan Cheng (Fig. 30, left) and the HTML's Cam Hubbard continued an on-going study of the changes in residual stress in socket and butt-welded joints of 304 stainless steel and ASTM A513/5 carbon steel due to cyclic fatigue. During fatigue tests of these welded specimens, it has been observed that the mean strain (measured with strain gauges) increases or ratchets up with increasing number of fatigue cycles. In an effort to understand this phenomenon, the residual stress distribution on the surface of welded joints was mapped at various stages of fatigue life using the RSUC's TEC large specimen x-ray goniometer (Fig. 30, right). Samples

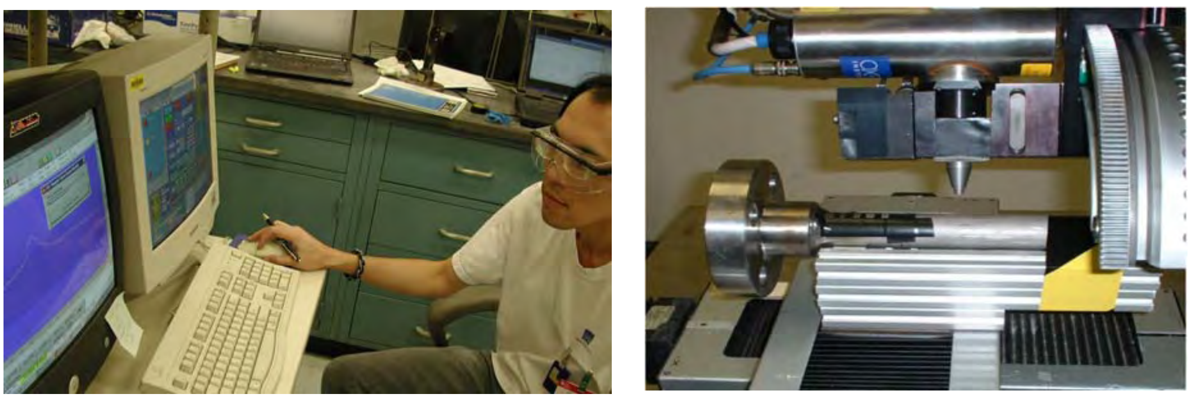


Fig. 30. At left, Pei-Yuan Cheng monitors the data collection process. At right, the 304 stainless steel sample with a socket weld set up for hoop strain measurement.

were electropolished at selected locations along the tube axis, starting at the toe of the weld. The X-ray diffraction axial residual stress measurements showed that a reduction of the initial compressive axial residual stresses occurs within 20 fatigue cycles (Fig. 31). This reduction of the initial compressive axial stresses suggests that, as fatigue cycles accumulate, the probability of circumferential crack initiation should increase with fatigue cycles. Neutron diffraction will be used for through the tube wall thickness stress measurements at the same locations now that the x-ray results of the surface residual stresses have been completed.

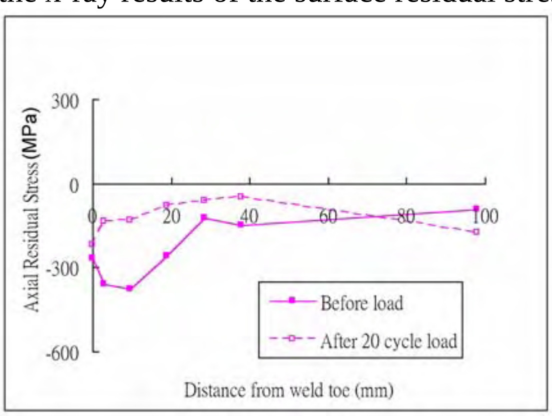


Fig. 31. The surface axial residual stress as a function of distance along the length of the sample before and after fatigue loading.

Texture characterization of lithium niobate films by NC State

Research problem: To understand the relationships between deposition conditions and the microstructure of lithium niobate coatings

Implications: Refined deposition processes could lead to better surface acoustic wave devices.

Description of Work: Surface acoustic wave (SAW) devices, which operate on the basis of the piezoelectric transduction of acoustic waves, are employed as filters, oscillators and transformers. Together, lithium niobate (LN) films on diamond substrates have applications for high frequency SAWs. However, when LN is deposited directly onto diamond, it is polycrystalline with small grain size, which leads to undesirable acoustic wave scattering. Professor Jag Kasichainula (Fig. 32) visited the RSUC and research staff member Tom Watkins as part of his on-going study of buffer layer influence on deposition of diamond films on lithium niobate (LN).

A series of samples was prepared to explore the texture of deposited LN layer. Laser physical vapor deposition of AlN and LN was carried out sequentially on sapphire, silicon and polished diamond films grown on silicon substrates. Because of the thin nature of the films, RSUC's powder-texture-stress goniometer with rotating anode x-ray source was used. LN deposited on an AlN buffer layer on top of sapphire substrates showed epitaxial growth with LN (0002) // AlN (0002)// sapphire (0006). LN deposited on an AlN buffer layer on Si (111) substrate showed highly oriented films with LN (0002). LN deposited on an AlN buffer layer on polished diamond substrate showed a largely polycrystalline, multiphase film with some texture in the LN phase (Fig. 33). The observation of epitaxial growth of LN on AlN buffer layers on (0006) sapphire and (111) Si single crystal substrates indicates that the AlN buffer layer does impart strong texture. Further refinement of the deposition process holds significant promise for substantial improvement of SAW devices.

Fig. 32. Dr. Jag Kasichainula fills the Dewar on the detector on the PTS rotating anode unit with liquid N_2.

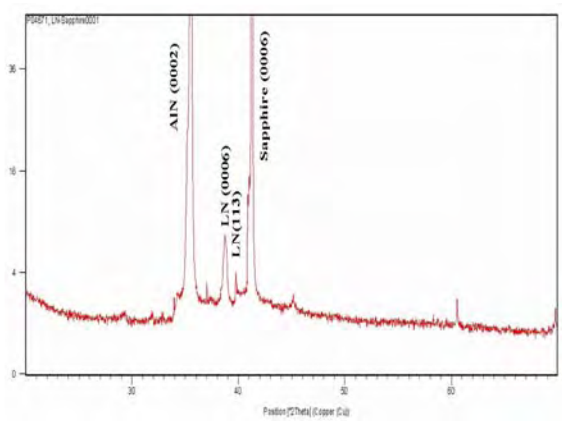


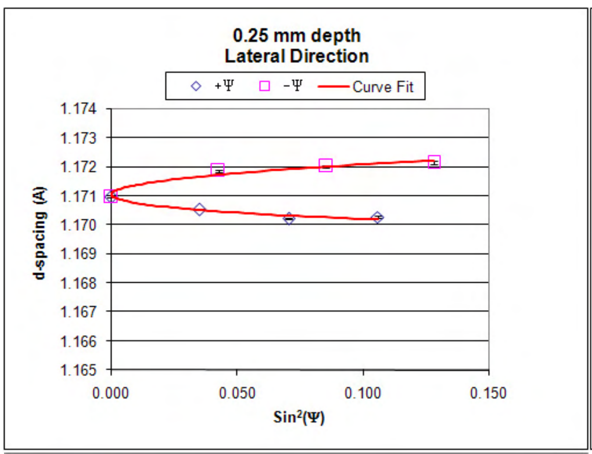
Fig. 33. XRD pattern showing the epitaxial growth of LN (0006) on AlN (0002) buffer layer on a (0006) sapphire substrate.

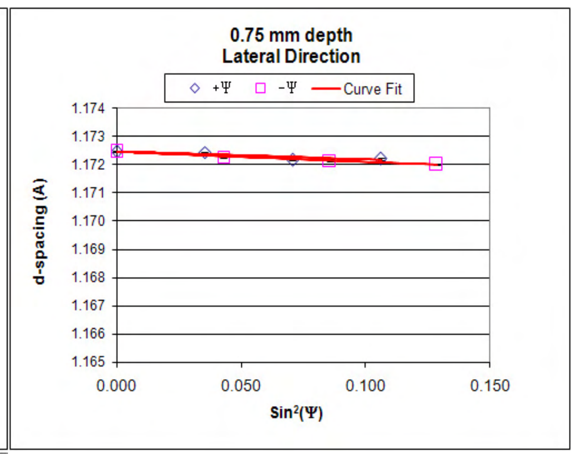
UT-Martin maps carburized gear stresses with neutron residual stress mapping

Research problem: Use non-destructive method to determine the magnitude of residual stresses in carburized gears

Implications: Successful demonstration of non-destructive stress measurements in carburized surfaces to several millimeters in depth opens the door for greater understanding of the stresses due to carburization.

Description of Work: Neutron residual stress mapping usually uses three orthogonal strain measurements along with a measured strain free d-spacing (d-zero) to determine the stresses in the three orthogonal directions. However, as the d-zero or strain free d-spacing changes with depth due to changes in carbon content, conventional methods for neutron stress analysis cannot be successful. Therefore, UT-Martin and ORNL explored an alternate method, similar to the $\sin^2\Psi$ method used in X-ray stress analysis, to first determine the d-zero value and then stresses as a function of depth. Non destructive mapping of stresses in carburized steels has been demonstrated at NRSF2 with a spatial resolution of 0.5 x 0.5 mm wide match stick type gage volume (height depends on sample). The measurements on a carburized gear tooth demonstrated that, when plane stress conditions hold, the $\sin^2\Psi$ method can also be applied for near surface, non- destructive depth profiling of stresses (Fig. 34). Mappings on the face side of a gear tooth to depths of 2 to 3 mm show the expected compressive initial layer followed by a tensile layer at greater depth. In the near surface compressive layer, the data indicate significant shear stresses, possibly due to gear tooth geometry constraints. From the data, the Fe-C d-zero value as a function of depth was determined.





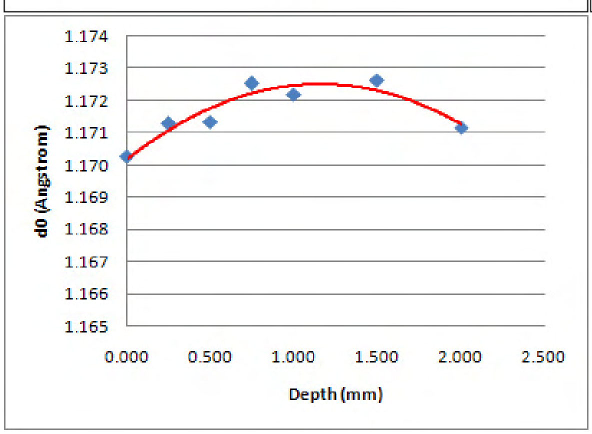


Fig. 34. In graphs at top left and right, the fit to the measured d-spacings as a function of tilt angle Ψ for 0.25 and 0.75 mm depths of gage volume. The splitting of the +Ψ and –Ψ curves at 0.25 mm depth indicates a shear stress exists in the carburized layer near the surface. In graph at lower left, the strain free d-spacing (d-zero) as a function of gage volume depth as derived from the various curve fits to the tilt data.

University of Tennessee-Martin faculty-student team studies loaded gear strains

Research problem: Test neutron diffraction strain mapping as a non-destructive method for measuring the critical bend radius for loaded gears

Implications: Results from these studies can be used to validate models for the maximum load in gear systems and as a consequence improve the power density of vehicle transmissions.

Description of Work: Recent studies at NRSF2 clearly show that loaded gears in particular and *in situ* studies in general can take advantage of non-destructive, through-thickness strain mapping in order to better predict fractures. NRSF2 was used by Faculty and Student Team (FaST) users from the University of Tennessee-Martin to study *in situ* loading of gears via mapping residual strains around the critical bend radius where fracture is most likely to occur under high load. The experiment tested the FEM predictions of the stresses in this vital location for gear life and power density. The Static Load Application Device (Fig. 35), developed by Professor Robert LeMaster of UT-Martin and his students (Fig. 36) in conjunction with Bart Bailey and Camden Hubbard of the HTML, was designed and built for *in situ* neutron strain mapping experiments at NRSF2. A hydraulic press applied a known load to the upper gear, while the lower gear remained fixed. Measurements were made near the location where the teeth of the two gears meshed. The mapping of strains as a function of depth at the critical bend radius location was performed with a beam thickness of just 0.3 mm in the mapping direction and gage volume of 2.7 cubic millimeters. Results on the statically loaded gear pair under applied loads shows the systematic change of the residual compressive strain at the critical bend radius to a tensile strain as the load is increased.

Fig. 35. Static Load Application Device is prepared for use at NRSF2.

Fig. 36. UT-Martin FaST students Bryan Boggs (left) and Jeff Bunn present results at an ORNL summer student poster event.

contact: Ralph Dinwiddie, Leader, dinwiddierb@ornl.gov, 865/574-7599

MIT researcher studies bubble formation in nanofluids

Research problem: Understand the effect of nanoparticles on bubbles/boiling in heat transfer

Implications: The development of fluids for improved thermal management systems

Description of Work: Dr. In Cheol Bang of MIT's nuclear reactor program visited the TTPUC to study heat transfer during bubble formation of fluids used for cooling of fuel rods. A boiling system was designed at MIT and brought to the TTPUC for work with the HTML's Dr. Hsin Wang. The heater was indium tin oxide on a sapphire substrate. The IR camera was focused directly at the bottom of the heater via a 45-degree gold mirror. Both water- and ethanol-based fluids were investigated, as well as the addition of nano-particles to the fluids. The heater temperatures during bubble formation, a critical heat flow condition, as well as fast-moving hot/cold spots due to convection heat flow were observed and recorded (Fig. 37). Understanding the role of nanoparticle addition in the heat transfer characteristics of fluids will lead to better thermal management systems for power generation applications.

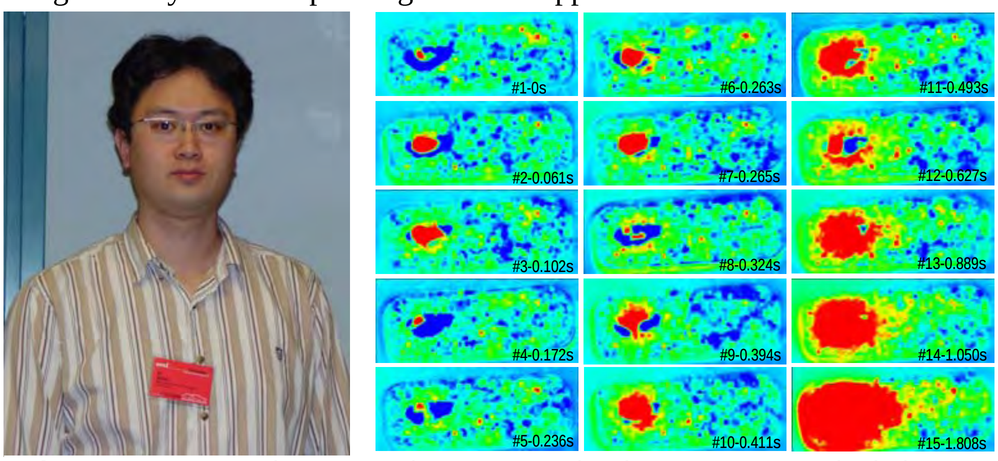


Fig. 37. MIT researcher Dr. In Cheol Bang and IR images of electrode during a boiling experiment.

Mississippi State researcher completes W-Cu alloys study

Research problem: Develop a model to predict thermal conductivity from alloy compositions

Implications: Improved alloys for component cooling in automotive applications.

Description of Work: Dr. Seong-Jin Park (Fig. 38) and Prof. Randall German of Mississippi State's Center for Advanced Vehicular Systems have completed a collaborative study with the TTPUC's Dr. Hsin Wang on Cu-W alloys that began in Fall 2006. Temperature thermal conductivity tests for tungsten-copper alloys were analyzed because these materials exhibit high thermal conductivity and can be used for thermal management in vehicles. Thermal diffusivities from room temperature to 1000°C were obtained for eight different compositions. Tungsten concentrations varied from 65% to 85%, and copper concentrations varied from 35% to 15% correspondingly. The W-Cu alloy thermal conductivity ranged from 200W/mK to 300W/mK at room temperature and decreased about 10%

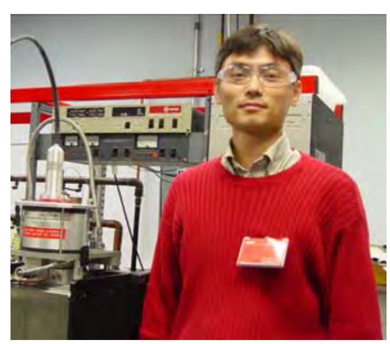


Fig. 38. Dr. Seong Jin Park.

at 500ºC. Assisted by HTML staff members Hsin Wang and Ralph Dinwiddie, the MSU researchers performed the experiments using both the Xenon flash system and the Anter laser flash system in an argon environment. Thermal conductivity of the alloys was found to vary as a function of tungsten content, and the values agreed very well with theoretical predictions. Initial results were presented at the PowderMet2007 Conference, May 13-16, 2007 in Denver, Colorado.

SUNY-SB graduate students measure relationship of microstructure and transport properties in thermal barrier coatings (TBCs)

Research problem: Characterization and analysis of thermal and mechanical properties of thermally sprayed coatings

Implications: Greater understanding of long-term performance and life prediction of thermal barrier coatings (TBCs) for next-generation turbine engines

Description of Work: Graduate students Weiguang Chi (Fig. 39) and Yang Tan (Fig. 40) from the State University of New York, Stony Brook have completed experiments at both the TTPUC (Dr. Hsin Wang) and at the Mechanical Properties User Center (Dr. Amit Shyam). At the TTPUC, they studied the thermal diffusivity/conductivity of plasma sprayed thermal barrier coatings (TBCs) using the Anter FL5000 and Xenon flash diffusivity system, as well as the TTPUC's new LaserPIT system for the first time in an HTML user project. TBCs prepared by three different starting powders and with various thermal histories were characterized from room temperature up to 1200°C. During his visit, Mr. Chi conducted in-plane thermal diffusivity measurements of TBCs as follow-up to extensive experiments at SUNY-SB on the room temperature properties and microstructure (porosity) of 36 different TBC test specimens. In-plane thermal diffusivity results were comparable to those SUNY-SB researchers obtained using their Holometrix room temperature laser flash system. The transport properties, especially the high temperature data, were used to model temperature distribution and heat flow under TBC application conditions. Fig. 41 (next page) displays results from one sample.

Fig. 39. Weiguang Chi.

Fig. 40. Yang Tan.

In related work, Mr. Tan prepared TBC specimens for resonant ultrasound spectroscopy (RUS) to determine the elastic constants of these materials. Measurement of elastic modulus of TBCs is not routinely performed due to the difficulty in preparing samples and accounting for geometric factors. During his visit, RUS data were successfully collected and analyzed, with follow-up analysis at SUNY-SB. The elastic modulus and thermal conductivity data will provide critical information for understanding and modeling the high temperature thermal and mechanical behavior of TBCs.

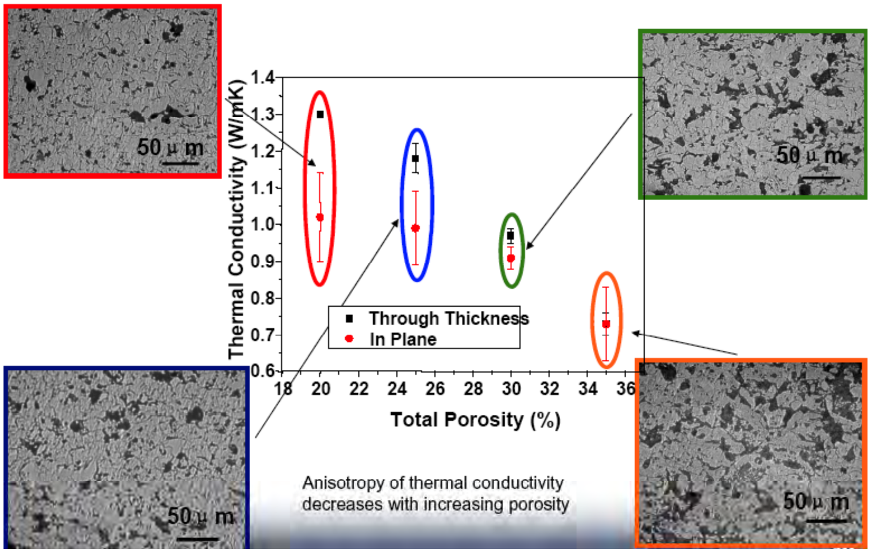


Fig. 41. Microstructure vs. Thermal Conductivity (SUNY-SB)

Thermal transport study of ceramic composites conducted by U of Missouri

Research problem: Characterize high-temperature thermal transport properties of cermets

Implications: Reliable thermal transport properties enable the design and utilization of better thermal shock resistance materials

Description of work: Sean E. Landwehr from University of Missouri-Rolla and Dr. Hsin Wang of the HTML conducted thermal transport properties studies of ZrC and a ZrC-30vol% molybdenum cermet. Because of their high thermal shock resistance and refractoriness, these materials are being considered for thermal protection systems in space applications. The project is supported by both the Naval Surface Warfare Center and the U.S. Army Space and Missile Defense Command. Two sets of samples (12 test specimens) were prepared at UMR and tested using the room temperature Xenon flash system and Anter laser flash system up to 1000°C. Thermal conductivity values obtained from the flash diffusivity measurements were found to be in good agreement with the expected values of the composites. Thermal conductivity of the materials is an important design parameter for these applications.

Purdue researcher investigates low density thermal barrier coatings

Research problem: Characterize thermal and mechanical properties of low density thermally sprayed coatings

Implications: Results are important for improving thermal barrier coatings for both aircraft and land-based turbine engines.

Description of Work: Kent Van Every (Fig. 42, next page), a Purdue University graduate student of Prof. Rodney Trice, worked with Dr. Hsin Wang at the HTML to test thermal transport properties of low- density thermal barrier coatings (TBCs) previously prepared at the Ames Laboratory. Coatings were about 200-300 microns thick and were thinner than the common 400-600 microns thick 8YSZ TBCs. Thermal diffusivity of these coatings was

Fig. 42. Kent Van Every.

determined at room temperature using the Xenon flash system and then measured from 100 to 1200°C in the Anter laser flash system. Thermal diffusivity values were comparable to those for thicker coatings, probably due to the pore morphology. In addition, mechanical properties testing of these coatings are being conducted at Purdue University. For thermal barrier coatings, one of the most important characteristics is lower (and stable) thermal transport properties after prolonged exposure to high temperatures.

Wear comparison test for John Deere – rear axle spool on tracked tractor

Research problem: wear testing of materials for farm tractor rear axle spool and gear ring

Implications: Development of test methods to quantify wear

Description of Work: Mark Beltowksi of John Deere's Product Engineering Center in Waterloo, Iowa, visited the HTML during the last week of February to conduct wear tests on candidate materials for mating parts on a rear axle spool and gear ring on a rubber-tracked farm tractor (Fig. 43). The current nodular cast iron material and two higher-strength nodular cast irons were subjected to both lubricated and non-lubricated tests. The lubricant was a John Deere commercial product recommended for this application. Because the first series of experiments on a pin-on-disk apparatus (Fig. 44) did not provide sufficient wear to obtain an accurate comparison of the materials, Beltkowski and the HTML's Peter Blau decided to use a more robust test, a reciprocating pin-on-flat method that provided more measurable wear in an accelerated manner. Both Brinell hardness tests and Vickers microindentation tests were also conducted to characterize the three disk materials.

Fig. 43. Rubber-tracked farm tractor, model 9520T (photo courtesy of Deere & Company)

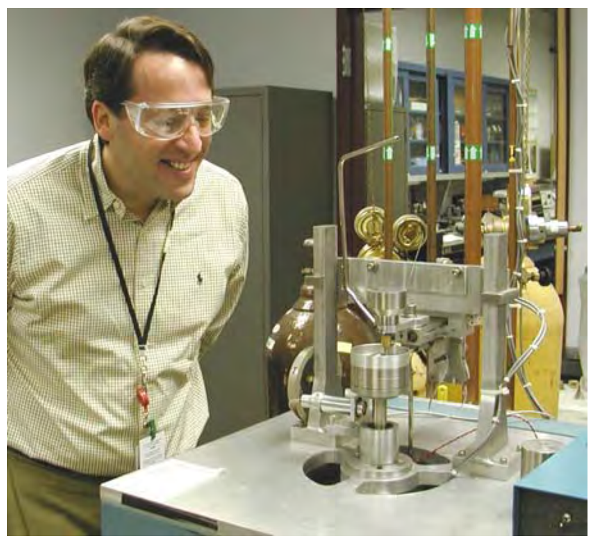


Fig. 44. M. Beltowksi supervises an initial pin-on-disk experiment. Lubricant was applied initially to the surface and not replenished.

Normalized, volumetric wear rates (mm^3/N-m) were calculated using diamond stylus profiles of wear grooves on the flat specimens, and using the diameter of the wear scar on the slider tip. Lubrication with HY-GARD J20C reduced the wear rate by a factor of approximately 10,000 times, but the difference in wear rates due to using harder cast irons was reflected in both lubricated and non-lubricated results. A convenient parameter for wear resistance (WR) is the inverse logarithm of the volumetric wear rate: the higher the value, the more wear resistant the material. Brinell hardness number (HB) is plotted versus WR of the cast iron specimen in the Fig. 45 (next page). The effects of material and hardness are evident in the graph, and a linear relationship exists between WR and HB. Optical microscopy also revealed significant differences in surface damage features between lubricated and non-lubricated tests (Fig. 45, next page). In the latter, higher friction induced additional plastic deformation and fracture, with the production of submicron debris particles. Despite an improvement in wear rate with higher hardness, there was no evidence for differing dominant wear mechanisms between one material and another. It was more a question of degree of damage than a change in wear mechanisms. Results will be published in the journal *Wear*.

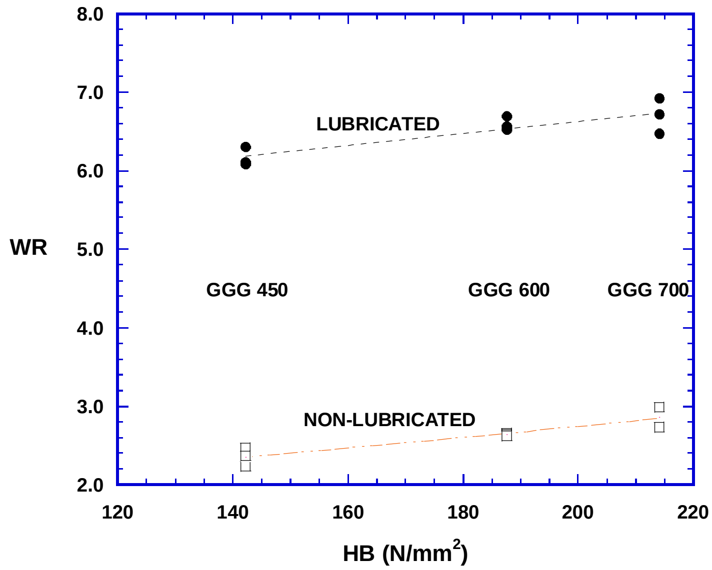


Fig. 45. Effects of material type and the use of a lubricant on the wear resistance of a current cast iron material (GGG450) and two candidate materials (GGG600, GGG700).

Auburn University Studies Friction Reduction Using Engineered Surfaces

Research problem: Verify effect of tailored surfaces on friction reduction

Implications: Microscale surface engineering enhances lubrication of engine parts and improves efficiency

Description of Work: Professor Robert Jackson of Auburn University visited the Tribology Research User Center and collaborated with Jun Qu and Peter Blau to study the effects of biomimetic surface textures on friction and lubrication. By controlling the shapes and sizes of surface features, the hypothesis, supported by Jackson's modeling work, is that lubricated friction can be controlled and reduced. Specimens of polymeric material were prepared at Auburn and tested under reciprocating sliding conditions using the Plint TE-77 machine in the flat-on-flat contact configuration (Fig. 46). Some of the specimens had textured surfaces and others did not. Friction force was monitored at a rate of 500 readings per second and used to calculate friction coefficients at various loads and speeds with water lubrication. In general, the friction force decreased with increasing contact pressure; however, it was determined that the sliding velocity needed

Fig. 46. Prof. Jackson at the Plint TE77 wear testing and reciprocating friction machine used to study biomimetic surfaces. Driving mechanism and specimen fixtures at lower right.

to be higher in order to observe the hydrodynamic effects expected for the biomimetic surfaces. Future experiments are planned in order to test the surfaces at increased speed.

Probing the Structure of Wood with High Frequency Sound Waves

Research problem: Test the feasibility of using a Scanning Acoustic Microscope to measure certain elastic properties of wood fiber-based bio-composites.

Implications: Enable the development of improved natural-fiber-based, bio-composites for producing recyclable automotive parts.

Description of Work: This exploratory project was conducted by Prof. Siqun Wang and graduate student Cheng Xing of the Forest Products Center at the University of Tennessee-Knoxville using the HTML's scanning acoustic microscope (SAcM). In collaboration with the HTML's Dr. Jun Qu, they conducted tests to determine whether a SAcM could measure elastic properties, such as Poisson's ratio, while also imaging microstructural details, indentation damage, and subsurface flaw arrangements in wood fiber-based bio-composites. The work is part of a project supported by the U.S. Department of Agriculture.

Specimens of wood and lyocell fibers were mounted and prepared for study at the University of Tennessee. Then, acoustic images of wood fibers were successfully captured at 400 MHz and 1.0 GHz. As shown in Fig. 47, the microstructure of wood fibers is clearly revealed by the SAcM. Attempts to measure elastic properties were unsuccessful because the wood fibers quickly absorbed water that was used as the coupling fluid to transmit the acoustic signal between the objective lens and the specimen. Due to this problem, the next user visit will focus on two tasks: 1) investigating more water-resistant lyocell fibers, and 2) attempting to image water-saturated wood fibers.

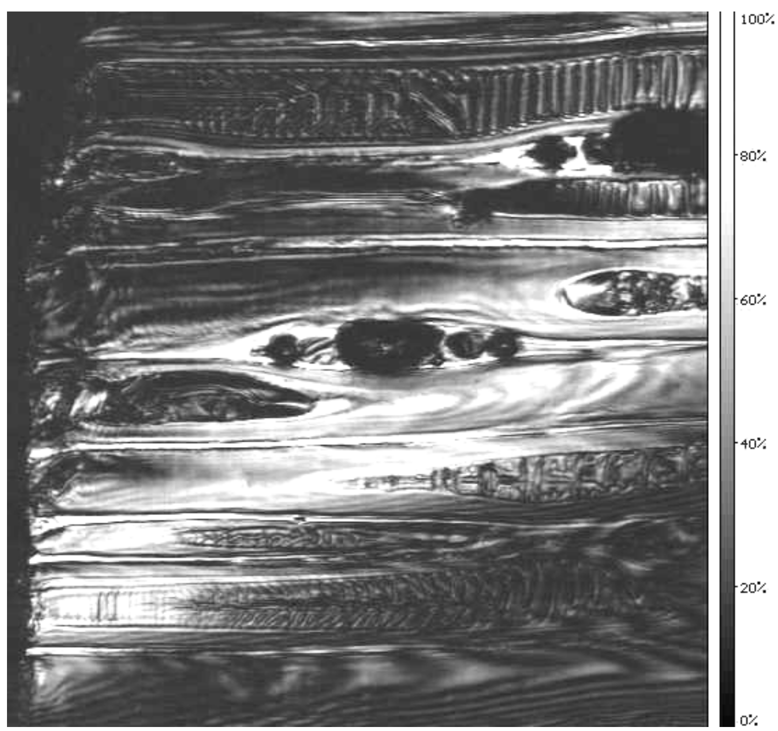


Fig. 47. Acoustic image of wood fibers (field of view 312 x 312 μm, acquired at 1.0 GHz).

New and Upgraded HTML Capabilities

NRSF2 Launches Productive User Program upon HFIR Restart in May 2007

With completion of the High Flux Isotope Reactor (HFIR) cold source installation and successful safety testing completed, the HFIR returned to full power in May 2007 with fuel cycle 408. Successful conclusion of three major tasks (slit system snout fabrication, sample positioning system upgrades, and fabrication of ancillary systems) allowed HTML staff members Camden Hubbard, Bart Bailey, and Ke An to complete a series of tests and calibrations of the Second-Generation Neutron Residual Stress Mapping Facility (NRSF2) (Fig. 48). The 408 cycle was the first time all the components of the new instrument were completed and installed, with a large number of major improvements over the first-generation facility, including:

Fig. 48. The newly commissioned Neutron Residual Stress Mapping Facility (NRSF2) at the HFIR began productive HTML User Program operation in May 2007.

- new monochromator with choice of six different wavelengths and, due to vertical and horizontal focusing, increased flux and sharper peaks;
- large, rigid goniometer and sample positioning system with both accuracy and 1000-pound capacity;
- new slits system and snout assemblies for precise definition of the sampling volume, thus doubling the NRSF2 performance; beam width from 0.3 to 5 mm, and beam height from 0.3 to 20 mm;
- laser tracker and two theodolites that enable precise sample location on the instrument and rapid preparation for data collection;
- seven-detector array and detector shield yielding nearly seven-fold increase in the fraction of the Debye cone collected, which enables NRSF2 to measure faster and/or to use smaller sampling volumes;
- new and enhanced software for real-time analysis that is invaluable for assessing progress of the experiment;
- 5000-pound force uniaxial load frame for *in situ* studies of materials under applied loads;
- other accessories: several furnaces (controlled environments and vacuum), a new Z-elevator for large specimens and the load frame, and a two-circle Eulerian cradle for texture studies.

In addition to user projects highlighted in the Residual Stress User Center section, other scheduled users included Third Wave Systems (stresses in rolled Al plates), Electric Power Research Institute (stress mapping in weld overlay plates to be used as standards), University of Tennessee-Knoxville and ORNL (residual stresses in friction stir-processed welds change with aging), Mississippi State University (LENS rapid prototyped stresses), University of Missouri (ceramic matrix composites), and University of Tennessee (stress mapping in CT sample under load). The RSUC also measured an international residual stress standard made of a ring and plug of aluminum and assessed potential for projects from future users and research sponsors.

Work initiated with Protochips Co. on *in situ* heating capability for ACEM

Research Problem: Development of tools and techniques for the in situ high-temperature characterization of processes relevant to materials for energy

Implications: Availability of tools for the *in situ*, real-time characterization of materials at elevated temperatures will lead to better materials for energy storage, catalysis, and thermoelectric conversion.

Description of Work: An SBIR-funded project has been initiated with Protochips Co. (Raleigh, NC) to develop a novel specimen heating capability for ultra-high-resolution imaging of catalyst samples in the HTML's aberration-corrected electron microscope (ACEM). Protochips produces heater elements composed of thin silicon nitride membranes supported on 3mm diameter silicon chips, which are fabricated using semiconductor manufacturing techniques. The membranes are patterned with holes a few microns in diameter and support typical holey carbon films onto which catalyst powders are dispersed. The elements are retained in a special heater holder fabricated by MAUC consultant Prof. Will Bigelow (University of Michigan, Fig. 49) showing the silicon nitride membrane to be heated to high temperatures very quickly, e.g. 1100°C in 1 millisecond. Because of the very low mass, cooling to low temperature is essentially as rapid. It is expected that this geometry will be ultra-stable, and will allow atomic level imaging when the specimen is at elevated temperatures. This is a new paradigm for heating experiments in the electron microscope, and it has the potential to be extended to allow gas reaction studies as well.

Fig. 49. John Damiano and David Nackashi (seated front) of Protochips Co., work with HTML's Larry Allard, consultant Prof. Will Bigelow, and HTML user Steve Bradley (seated) of UOP, LLC, in the kick-off of the *in situ* heating holder project. New holder tip, with lead wires connected to heater chip, shown inset.

JEOL aberration-corrected electron microscope (ACEM) passes final tests

The HTML's JEOL 2200FS-AC aberration-corrected electron microscope passed its final tests prior to instrument acceptance, with a demonstration of the capability to correlate chemical species identification with structure at the single atomic column level, using electron energy-loss spectroscopy. Dr. Douglas Blom of the HTML staff and Dr. Toshihiro Aoki of JEOL Co. imaged a thin foil control sample of stoichiometric strontium titanate for this test (Fig. 50). The electron beam was oriented looking down an edge of the cubic structure, showing strontium columns isolated from titanium columns, as in the cartoon below. Information about titanium was collected at every point of the image, using an electron energy-loss filter built into the electron optics. This allowed a display of the presence of titanium (far right) by processing the data after the image and energy-loss data were collected (so-called "spectrum imaging"). The results clearly show the ability of the ACEM to image atomic species at the single column level.

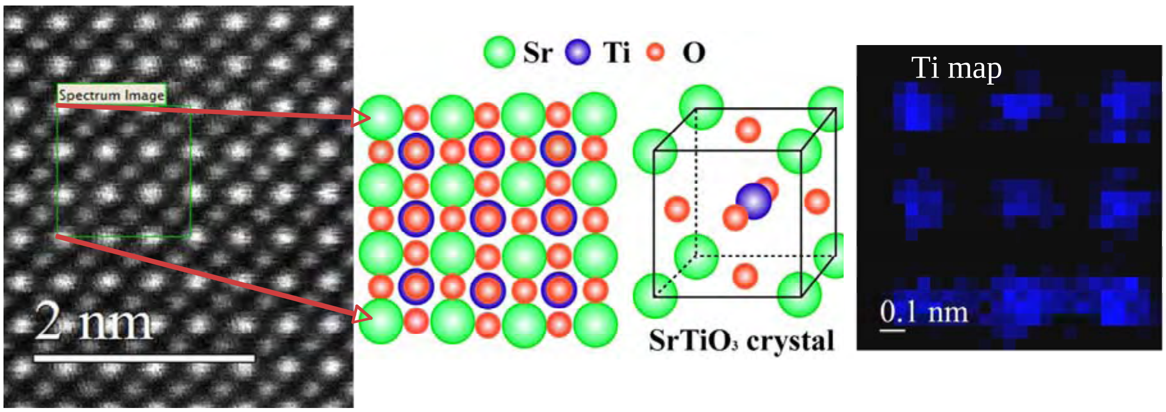


Fig. 50. ACEM image of stoichiometric strontium titanate displaying single-column titanium atoms.

New capability for coating thickness measurement

A new piece of apparatus called a Calotest™ has been added to the TRUC portfolio of characterization instruments (Fig. 51). The micro-abrasion, ball-cratering instrument enables rapid and accurate measurement of the thickness of tribological films and coatings. In addition, the new ball-cratering capability will allow the TRUC to support HTML user projects as well as ORNL in-house research efforts in coating development. The instrument holds both flat and rounded parts and uses timed exposure to a rotating ball and a fine-grained slurry to polish dimples into coated surfaces (Fig. 52). Coating thicknesses from a few hundred nm to several µm can be calculated from the relative diameters of the circles produced by micro-abrasion. Specimens in a variety of shapes are accommodated on the articulating arm, so coating thicknesses on items such as cylindrical drill shafts and fuel

Fig. 51. Ball cratering system with multi-axis specimen holder and control unit.

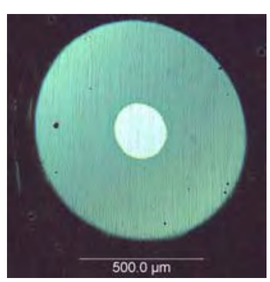


Fig. 52. Image of a polished 'dimple' in a 5.7-µm thick hard coating on a tungsten carbide substrate.

injector plungers can be determined. This additional capability will enable more quantitative correlation between coating properties and wear behavior.

Unique HFIR capability enables *in situ* measurements during thermal-magnetic processing

A major milestone has been achieved in pioneering research at the High Flux Isotope Reactor (HFIR) on the use of thermal-magnetic processing to develop the next generation of structural and functional materials. For the first time ever, *in-situ*, time-resolved measurements of the shift in the equilibrium phase transformation temperatures by the application of a high magnetic field at elevated temperatures have been accomplished using neutron diffraction methods on Fe-C binary alloys. These fundamental science experiments were conducted using the HFIR Wide Angle Neutron Diffractometer (WAND) instrument that essentially enabled all of the diffraction peaks to be monitored simultaneously as the micro-structure evolved under the influence of the external magnetic field. Prior to the installation of this unique capability at the HFIR, the influence of high magnetic fields on phase equilibria had to be inferred from samples no longer under the applied field. These breakthrough results validate the predictions of Local Spin Density Functional calculations and substantiate all prior ORNL R&D efforts in this emerging extreme environment science and technology research area. The Laboratory Directed Research and Development (LDRD) Program of the Oak Ridge National Laboratory sponsored this research. The LDRD team was lead by Gerry Ludtka and included Camden Hubbard. Measurements using HTML's NRSF2 of the change in carbon concentration as a function of magnetic field are planned for the next operating cycle opportunity due to the material's high sensitivity for d-spacing shifts.

New data collection software improves x-ray residual stresses studies

In January 2005, the original equipment manufacturer discontinued all support for our four older diffractometers. In response, a contractor was hired to work with Thomas Watkins and Roy Wallen to design and build a new microprocessor, as well as write LabView^{TM}-based software for data collection. The second version of the microprocessor has been built and the "Diffractometer Control Software" (DCS) now successfully controls the diffractometer and collects data using the following: theta-2theta scans, detector scans, rocking curves, chi scans, phi scans, pole figures by Schulz method, and "Stress Scans" for chi or omega tilts – all via step or continuous mode with constant time or counts. DCS outputs the multiple formats required by users including: ASCII, *.XRDML, *.epf (for pole figures) and GSAS formats. DCS controls the diffractometer motors, senses the collision switches and "markers" used for calibration, opens and closes the shutter, and records signals from the detector. One valuable new feature allows the operator to oscillate or "rock" non-scanning axes in order to improve grain averaging by increasing the opportunity for more grains to diffract.

This feature has already been a significant help to Bryan Barnard, a researcher from the UT Department of Materials Science (Fig. 53, left, next page), who is studying the development of residual stresses in Ni-Cr superalloys due to fatigue and corrosion. Data scatter has been reduced when rocking is employed, allowing for proper stress analysis (Fig. 53, right). Future versions of DCS will control the other diffractometers, with added features such as advanced pole figure and stress data collection techniques, the ability to collect data using a position sensitive detector, and support for temperature control. This software will result in better RSUC characterization and analysis to our users, which in turn helps EERE/OFCVT customers ultimately develop improved automotive materials used to produce more energy-efficient vehicles.

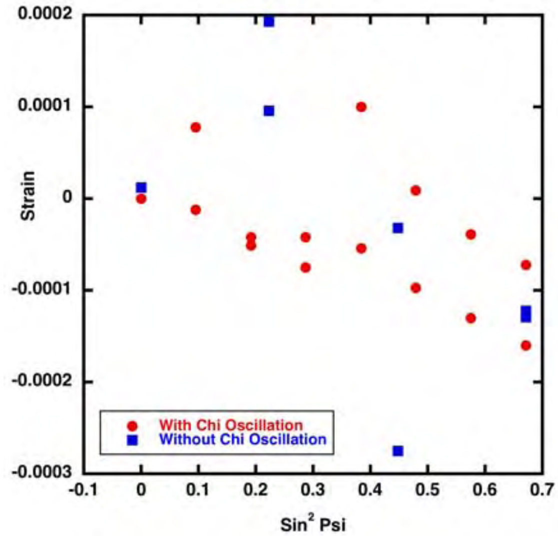


Fig. 53. (Left) Bryan Barnard (University of Tennessee) utilizes the new rocking function to oscillate his sample and increase averaging. (Right) The strain as a function of the $\sin^2\psi$ for Haynes 75 alloy (75 Ni-20 Cr-5Fe) after isothermal oxidization at 800°C for 1000 hours under an applied stress of 6.7 MPa.

Upgraded Field Emission TEM/STEM Delivered from Hitachi

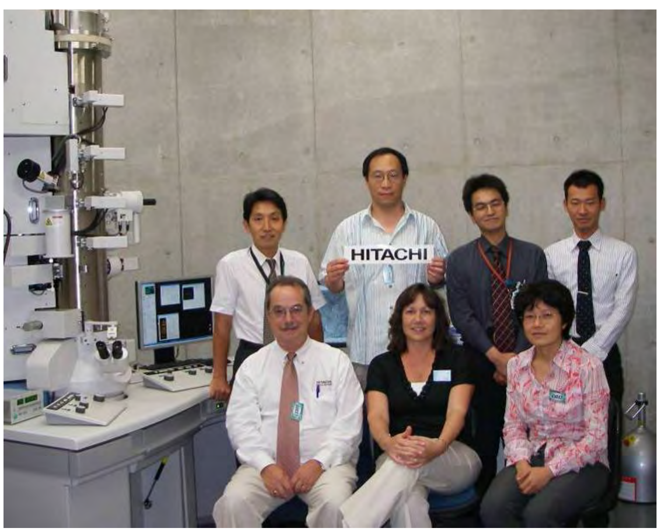


Figure 54. The newly delivered HF-3300 cold field emission TEM/STEM instrument. Douglas Griffith (seated left) hosted HTML's Karren More and Jane Howe at the Hitachi Naka factory for pre-shipment testing.

HTML staff members Jane Howe and Karren More traveled in late August to the Hitachi Naka Factory in Mito, Japan for pre-shipment testing of the newly purchased HF-3300 field emission TEM/STEM instrument (Fig. 54), which replaces the venerable HF-2000 TEM, one of the most in-demand instruments in the Materials Analysis User Center. The new microscope will operate at 300kV (as compared to 200kV for the HF-2000). It will provide higher resolution, an order of magnitude better x-ray analysis capability, two biprisms to allow advanced electron holograpy imaging capabilities, a 4-megapixel CCD camera (rather than the 1-megapixel camera on the HF-2000), and a capability for scanning transmission imaging (not available on the HF-2000). An additional advantage is that the specimen holders will be compatible with our focused ion beam milling instrument. Computer control of all functions, including apertures, will allow facile remote operation of the instrument. Factory testing prior to delivery showed all specifications were met and in many cases were exceeded. Complete installation of the microscope is expected in November 2007.

Expanded surface analysis capability at HTML

The HTML has recently received on consignment a Thermo Fisher Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS), which expands the HTML's surface analysis capabilities. The K-Alpha XPS instrument (Fig. 55) in combination with the existing Phi-680 Scanning Auger Nanoprobe yields enhanced characterization of solid materials surfaces.

Auger analysis uses a probe beam of electrons (5-20 kV) which induces the emission of low energy secondary electrons, backscattered electrons, x-rays, and special secondary electrons called "Auger electrons." Because of their kinetic energy, detectable Auger electrons only are emitted from the top few monolayers of the sample and identify the atoms that are present. Auger analysis is possible even on extremely small length scales, down to about 130 nm, and is primarily limited to conductive materials not sensitive to degradation by energetic electrons.

XPS analysis also provides elemental information. The emitted photoelectrons of XPS are created by shining x-ray photons (for our instrument, x-rays are monochromatic Al k_{α} photons) on the surface of interest. The surface sensitivity of the photoelectrons is derived from their kinetic energy, allowing only those electrons generated within the top few monolayers to escape. Although the spatial resolution of XPS is somewhat lower than that of the Auger nanoprobe (K-Alpha analysis spot size ranges from 30 to 400 microns), there are advantages in using XPS over Auger analysis. XPS data not only provide elemental identity, but they also give chemical bonding information. For example, when metal atoms are present, XPS determines whether they are present as a metal or as an oxide. Likewise, the various carbon chemical bonds can be distinguished using XPS. In addition to metal and semiconductor samples, XPS analysis is possible on any vacuum-compatible material, including polymers, organic films, bio-materials and inorganic insulators.

Fig. 55. Thermo Fisher Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS).

LaserPit system adds new capabilities for thin film thermal conductivity measurements

Fig. 56. ULVAC LaserPit system installed at TTPUC for thin film studies.

The installation of a new LaserPit system from ULVAC (Fig. 56) was completed in late March 2007. The system measures in-plane thermal diffusivity of thin sheet specimens and thin films. Based on the Angstrom method, the new system uses a line laser and 1μm resolution step motor to measure thermal wave (amplitude and phase) propagating along a thin sample. Using a differential method, thin films coated on a glass substrate can be measured. This is especially useful for measurements of thermal conductivity of super lattice thin films (a very important area for thermoelectrics) and provides the HTML with another important tool for characterizing thermal transport properties of advanced materials. This new capability will enhance HTML research that supports key EERE objectives.

News from HTML User Centers

JEOL ACEM "Sign-Off" Ceremony held at HTML and ACEM passes final tests

During the annual meeting of the HTML's Guidance and Evaluation Panel, final acceptance of the JEOL 2200FS aberration-corrected electron microscope (ACEM) was celebrated at the HTML. Participants included Dr. Michael Kersker, JEOL Director; Dr. James Roberto, ORNL Deputy Director for Science and Technology; Wayne Lin, Program Coordinator DOE-Oak Ridge Operations; Dr. James Eberhardt, Chief Scientist, DOE-OFCVT; and Dr. Arvid Pasto, HTML Director (Fig. 57). HTML staff member Dr. Douglas Blom demonstrated the capability to control the ACEM remotely, by running the microscope (housed in the Advanced Microscopy laboratory adjacent to the HTML) from the lobby, and recording an image showing single atoms of gold in a model nanoparticle specimen. This signing concluded the project begun in September 2000 with the placement of the original order with JEOL USA.

Fig. 57. L-R: Arvid Pasto, James Eberhardt, Mike Kersker, Jim Roberto, Billie Russell, Wayne Lin

Neutrons for Materials Science and Engineering Educational Symposium and the Neutrons for Stress, Texture, and Transformations Workshop

The Educational Symposium held April 18, 2007, and the neutrons workshop held April 19, 2007, were organized by HTML's Camden Hubbard with colleagues from SNS and University of Tennessee (Xun-Li Wang). The events were sponsored by the Oak Ridge Chapter of ASM; ORNL's HTML User Program and the Neutron Sciences Directorate; UT-ANSWER, an NSF International Materials Institute; and UT-ORNL Joint Institute for Neutron Sciences. Attended by over 130 participants, the Educational Symposium was developed to expand awareness of the diverse applications of neutron scattering and of the expanding facilities in North America for students and faculty in materials science and engineering studies. Presentations from university faculty, U.S. government laboratories, and ORNL research staff provided a broad overview of the many applications of neutron scattering to studies of materials. Web site for further details is http://neutrons.ornl.gov/workshops/EdSym2007/.

Over 60 engineers, scientists and students (Fig. 58, next page) participated in the Neutrons for Stress, Texture and Transformations (NTS2) Workshop, which was designed for members of the engineering community interested in using neutrons for a wide range of diffraction applications. Future uses of the new ORNL Engineering Neutron Diffraction facilities that were emphasized included phase and texture mapping; non-destructive stress, *in situ* load, and furnace measurements; and characterization of materials deformation behavior. The connection to

Fig. 58. Attendees at the Neutrons for Stress, Texture and Transformation Workshop held at ORNL's Spallation Neutron Source Iran Thomas Auditorium.

modeling of residual stress generation and deformation processing was also discussed. Speakers from England, Canada, Japan and Germany presented the industrial applications of engineering neutron diffraction developed at their national facilities. Dr. Yan Gao of General Electric and Dr. Weizhou Li of Caterpillar described the needs of U.S. energy and transportation industries. Status updates on both the 2nd Generation Neutron Residual Stress Mapping Facility (NRSF2) at HFIR and also VULCAN at SNS, were presented by Drs. Xun-Li Wang and Camden Hubbard, respectively. Dr. Hank Prask of NIST summarized the needs for neutron diffraction residual stress standards. The workshop closed with a round-table discussion of how the new ORNL facilities could meet the needs of the nation. Web site for further details is http://neutrons.ornl.gov/workshops/NST2/.

Neutron Scattering for Structural Materials Class Held

The Advanced Neutron Scattering Network for Education and Research (ANSWER) organized a week-long intensive course on neutron diffraction (MSE 676: Neutron Scattering for Structural Materials Research) on November 6–10, 2006. Led by the University of Tennessee (UT) and Oak Ridge National Laboratory (ORNL), ANSWER is one of the NSF sponsored International Materials Institutes supported. The neutron class included attendees from universities such as Iowa State, Johns Hopkins, Central Florida, Virginia, and Queen's University in Canada, as well as Los Alamos National Laboratory, UT, and ORNL. The course included a tour of the HTML (High Temperature Materials Laboratory) and SNS (Spallation Neutron Source) at ORNL and a presentation on HTML and RSUC facilities.

Tutorial on "Neutron Scattering for Structural Materials Research"

The neutron scattering tutorial was held at the 2007 TMS Annual Meeting in Orlando, Florida on February 25, 2007. The tutorial was sponsored by the National Science Foundation (NSF), International Materials Institutes (IMI) Program, a partnership of the Advanced Neutron Scattering network for Education and Research (ANSWER) at the University of Tennessee (UT) and Oak Ridge National Laboratory (ORNL). The tutorial aimed at educating academic and industrial researchers about the fundamentals and applications of neutron-scattering studies for structural materials research. Topics covered included fundamentals of neutron scattering for solving industrial problems, neutron scattering sciences and facilities at ORNL and Los Alamos National Laboratory (LANL), and integrating neutron and mechanical behavior studies. The lecturers were Dr. Ian Anderson from the ORNL Spallation Neutron Source; Dr. Camden

Hubbard of the High Temperature Materials Laboratory (HTML) at ORNL; Dr. Dimitry Sediako from Chalk River Laboratory, Canada; Dr. Mark Bourke at LANL; and Prof. Peter Liaw from University of Tennessee. The tutorial attracted attendees from academic institutions such as University of Virginia, University of Central Florida, University of Illinois, University of Western Ontario, University of Alabama, Iowa State University, and University of Tennessee. In addition, during the conference week an exhibition booth was set up to provide information on the neutron materials research activities at various facilities, including the HTML, HFIR (NRSF2) and SNS at ORNL. The exhibition also promoted fellowship opportunities available from the ANSWER program for research collaborations using these facilities.

VULCAN Instrument Development Team (IDT) Meeting

During a November 1-2, 2006 IDT meeting at the Oak Ridge SNS site, the VULCAN design and construction was reviewed. The project has made excellent progress and is on time and within budget. Contributions from the HTML to the VULCAN Engineering Diffraction Instrument include the laser alignment systems and additional detector banks. The construction site for the external building for VULCAN was the tour highlight. The potential for real-time, *in situ* characterization of processes such as friction stir processing, fatigue, casting, and biaxial and uniaxial loading is indicative of future high-impact research to be conducted at VULCAN.

TMS Outstanding Student Paper Award to HTML User Wanchuck (Chuck) Woo

Woo, a Ph.D. candidate in University of Tennessee's Department of Materials Science and Engineering, won the 2nd place award in the TMS (The Minerals, Metals & Materials Society)-sponsored international competition for graduate students in materials research: "2006 TMS Outstanding Student Paper Contest - Graduate Division."

Presented to only two graduate students each year, the award recognizes his outstanding thesis work in the field of physical/mechanical metallurgy and material science as evidenced by the paper, "Residual stress, texture, and natural aging kinetics of a friction-stir processed 6061-T6 aluminum alloy: A neutron diffraction study." The award, including a $750 scholarship, was presented to Woo at the 136th TMS Annual Meeting & Exhibition (February 25-March 1, 2007) in Orlando, FL.

Chuck's dissertation advisors, Drs. Hahn Choo and Peter Liaw (professors at UT); Drs. Z. Feng, X.-L. Wang, C. R. Hubbard, and S. A. David (scientists at ORNL); and Drs. D. W. Brown and B. Clausen (scientists at LANL) participated as advisors on the winning paper. Chuck's research is supported by the NSF's International Materials Institutes (IMI) Program and ORNL's Laboratory Directed Research and Development (LDRD) program.

HTML User Center Leader Camden Hubbard (far right) and former HTML Director Victor Tennery were both recognized at the 2006 Society Awards Ceremony held during the American Ceramic Society 108th Annual Meeting, October 16, 2006, for their extensive contributions to ceramic science and service to the American Ceramic Society (ACerS). Hubbard was inducted as a Fellow of the American Ceramic Society, and Victor Tennery received the Arthur Frederick Greaves-Walker Award.

HTML Director Edgar Lara-Curzio completed his tenure as Chair of the Engineering Ceramics Division of the American Ceramic Society. ACerS President Kathy Faber presented a Presidential Commendation to Dr. Lara-Curzio for "his outstanding contributions as the 2006-07 Engineering Ceramics Division Chair, including his visionary leadership in advancing the International Conference on Advanced Ceramics and Composites to a new level of success."

TTPUC Staff Recognized at International Thermal Conductivity Conference

During the 29th International Thermal Conductivity Conference (ITCC29) and the 17th International Thermal Expansion Symposium (ITES17), held in Birmingham AL from June 24-27, 2007, TTPUC staff received multiple honors from the research community:

- **Ralph B. Dinwiddie** received the Thermal Conductivity Award, the most prestigious award in its field. The award recognized his contribution to the field and many years of dedicated service to the research community.
- **Hsin Wang** was elected Fellow of the ITCC for his technical achievement and contribution to the conference. In addition, he was elected Chairman of the Board of Governors of the ITCC, Inc. His main responsibility is to oversee the organization and operation of the bi-annual International Thermal Conductivity Conference.

Conference Talk Stimulates New User Projects

Dr. Peter Blau, leader of the Tribology Research User Center (TRUC), presented a talk on the measurement and analysis of engine component scuffing at the 13th Diesel Energy-Efficiency and Emissions Research (DEER) Conference in Detroit. Case studies of previous user projects with Detroit Diesel Corporation and Deloro-Stellite Corporation were used as examples of the Tribology Research User Center's expertise in helping diesel engine makers and suppliers select scuffing-resistant materials for emission control system components such as waste-gate bushings for exhaust gas recirculation. The talk generated inquiries from original equipment makers that are expected to result in new TRUC user projects during FY2008.

ASTM Wear Symposium and Standards Development

Measuring the friction and wear characteristics of coatings and surface treatments requires special techniques that may be unsuitable for bulk materials. Therefore, TRUC's Dr. Peter Blau and Dr. Steve Shaffer, Battelle Memorial Institute, Columbus, Ohio, planned and co-chaired the June 21, 2007, ASTM Symposium in Miami Beach, Florida entitled "Wear and Friction Test Methods for Coatings and Surface Treatments." Symposium papers addressed a wide range of applications, ranging from tape recording heads to the hydrogen-fueled internal combustion engine. Materials of interest included nano-composite coatings, diamond-like films, hard coatings, and electroplatings. Shaffer and Blau also co-edited the symposium proceedings, published in the *Journal of ASTM International*.

NEW HTML USER AGREEMENTS EXECUTED DURING FY2007

Executed	Agreement #	User Agreement Partner
12/21/2006	UR-07-602	Vesta Ceramics, San Diego, CA
01/10/2007	UR-07-589	Lockheed Martin Aeronautics Company, Ft. Worth, TX
01/23/2007	UR-07-611	Ceramic Tubular Products, LLC, Lynchburg, VA
01/25/2007	UR-07-601	South Dakota School of Mines and Technology, Rapid City, SD
05/11/2007	UR-07-735	Quickstep Technologies, Brighton, MI
06/05/2007	UR-07-609	U.S. Army Corps of Engineers / Engineer R&D Center, Vicksburg, MS
06/15/2007	UR-07-659	L & L Products, Inc., Romeo, MI
07/31/2007	UR-06-058	Materials Innovation Technologies LLC, Fletcher, NC
07/31/2007	UR-07-773	Radiation Monitoring Devices, Inc., Peoria, IL
10/10/2007	UR-08-812	Mattson Technology, Inc., Fremont, CA

NOTE: Two proprietary user agreements also were executed during FY 2007.

HTML operations for FY2003 – FY2007

(showing user proposals and user agreements)

FY	New proposals				Cumulative proposals			
	Total	**Industrial**	**Academic**	**Other**	***Total***	**Industrial**	**Academic**	**Other**
2003	*72*	27	44	1	*1253*	514	693	46
2004	*87*	28	54	5	*1340*	542	747	51
2005	*110*	56	52	2	*1450*	598	799	53
2006	*84*	38	45	1	*1534*	636	844	54
2007	*86*	36	45	5	*1620*	672	889	59

FY	New agreements – last five years			
	Total	**Industrial**	**Academic**	**Other**
2003	*50*	44	4	2
2004	*53*	47	5	1
2005	*33*	27	6	0
2006	*19*	18	1	0
2007	*12*	10	1	1

User Agreement Totals as of 9/30/2007

Industrial	Academic	Other
277	129	5

Grand Total Agreements: 411

Publications and Presentations Related to HTML User Proposals

Journal Articles (* = user)

Chi, W.*, S. Sampath*, **H. Wang**, "Ambient and high temperature thermal conductivity of thermal sprayed coatings," *J. Therm. Spray Technol.* **15** [4], 773-778 (2006).

Evans, R. D.*, H. P. Nixon, C. V. Darragh*, **J. Y. Howe**, **D. W. Coffey**, "Effects of extreme pressure additive chemistry on rolling element bearing surface durability," *Tribol. Int.* **40**, 1649-1654 (2007).

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Garlea, E.*, **H. Choo**, V. O. Garlea, P. K. Liaw*, **C. R. Hubbard**, "Incoherent neutron scattering measurements of hydrogen-charged zircaloy-4," *Mater. Sci. Forum* **539-543**, 1443-1448 (2007).

Hubbard, C. R., Y. Sun*, **F. Tang**, Y. Lu, **H. Choo**, P. K. Liaw*, "Changes in lattice strain profiles around a fatigue crack through the retardation period after an overloading," *J. Physics B* , **385**, 633-635 (2006).

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Lee, K., **P. J. Blau**, J. J. Truhan*, "Effects of moisture adsorption on laboratory wear measurements of brake friction materials," *Wear* **262,** 925-930 (2007).

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Smith, S.*, S. N. Melkote*, **E. Lara-Curzio**, **T. R. Watkins**, **L. Allard**, **L. Riester**, "Effect of surface integrity of hard turned AISI52100 steel on fatigue performance," *Mater. Sci. Eng. A* **459**, 337-46 (2007).

Stoica, G. M.*, **E. A. Payzant**, J. Wu, J. Liao, J. E. Spruiell*, P. K. Liaw*, "Development of novel polycrystalline ceramic scintillators," *Adv. X-Ray Anal.* **49**, 116-121 (2006).

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Tian, H., P. K. Liaw*, D. E. Fielden, L. Jiang, B. Yang, C. R. Brooks, M. D. Brotherton, **H. Wang**, J. P. Strizak, L. K. Mansur, "Effects of frequency on fatigue behavior of type 316 low-carbon, nitrogen-added stainless steel in air and mercury for the Spallation Neutron Source," *Metal. Mater. Trans. A : Phys. Metall. Mater. Sci.* **37** [1], 163-174 (2006).

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Ni, J. E.*, F. Ren*, E. D. Case*, **R. M. Trejo**, **A. Shyam**, **E. Lara-Curzio**, E. J. Timm, "Effect of thermal fatigue on the mechanical properties of lead-antimony-silver-tellurium (LAST) thermoelectric materials," Materials Science and Technology 2007 Conference, Detroit, MI, Sept. 16-20, 2007.

Pagliaro, P.*, M. B. Prime*, B. Zuccarello, B. Clausen, **T. R. Watkins**, "Validation specimen for contour method extension to multiple residual stress components," ICEM Conference Proceedings, **246**, Alexandroupolis, Greece, July 01-06, 2007.

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Ren, F.*, J. E. Ni*, E. D. Case*, **R. M. Trejo**, **E. Lara-Curzio**, E. J. Timm, "Temperature dependence of elastic moduli of LAST/LAST-T thermoelectric materials," Materials Science and Technology 2007 Conference, Detroit, MI, Sept. 16-20, 2007.

Tan, Y.*, J. P. Longtin, S. Sampath*, **H. Wang**, "Thermal and electrical conductivity modeling and measurements for thermal sprayed coatings," IMECE 2006 Conference, Chicago, IL, Nov. 5-10, 2006

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Presentations (* = user)

Aytruk, E.*, **E. A. Payzant**, "A novel characterization of Pd/Ag alloy - phase nucleation and growth kinetics via in-situ time-resolved high temperature x-ray diffraction analysis" (presented by E. Ayturk), AIChE 2006 Annual Meeting, San Francisco, CA, Nov. 12-17, 2006.

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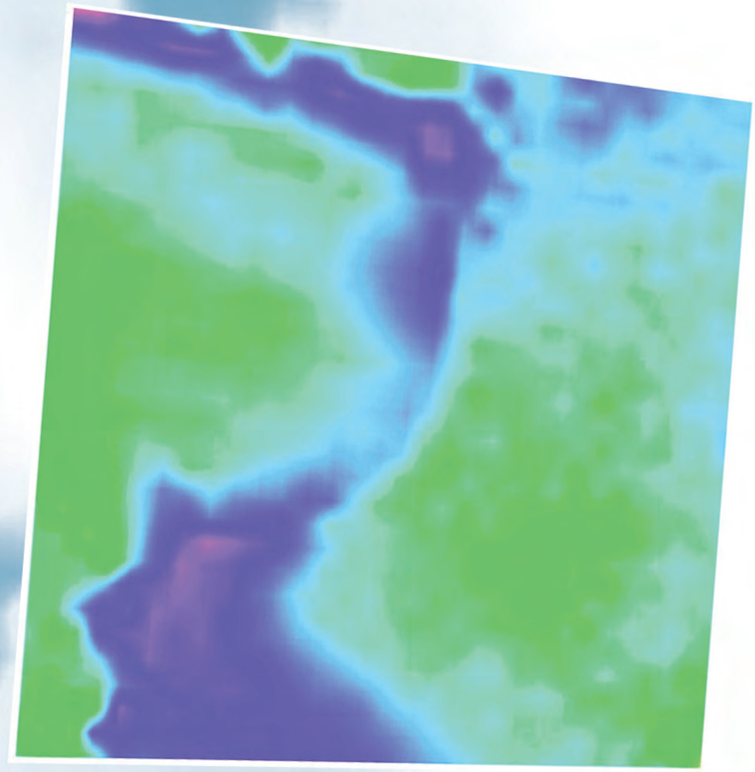
FRONT COVER

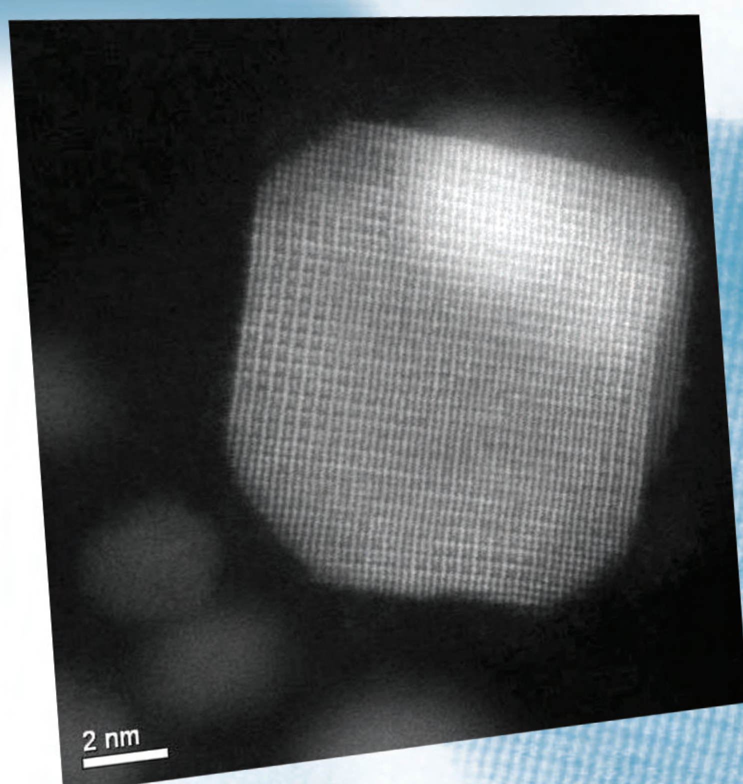
Sliding wear damage on the tip of a hemi-spherical pin of an experimental, titanium-based nanocomposite containing TiC. The worn area shows evidence of transferred adherent material, and the halos surrounding it are agglomerated oxide particles produced during sliding at 450° C against a tool steel counterface.

BACK COVER

(Top) A 30 μm x 30 μm stress map obtained from a region on the sample where two AlN grains were connected. At the interface, the AlN Raman peak shifts to lower frequency (blue color), suggesting a tensile stress that forms during crystal growth.

(Bottom) Core-shell structure of a Pt-Co on carbon catalyst material, using high-resolution annular dark-field imaging in the aberration-corrected electron microscope. The ordered Pt_3Co structure appears to develop as a result of increased temperature.





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