Advances in Ceramics through Government-Supported Research

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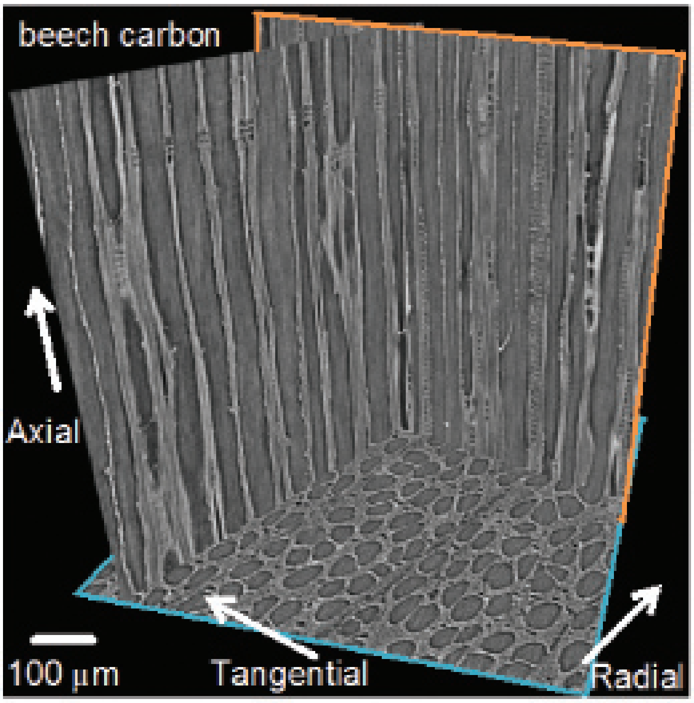


(Credit: S. Stock and T.E. Wilkes)

X-ray microtomograph of pyrolyzed carbon used to produce biomorphic SiC. Image taken at Beamline 2BM of the Advanced Photon Source at Argonne National Laboratory.

Since the 1970s, United States federal program managers involved in structural ceramics research and development have met annually as an interagency committee. In 2007, the name of this committee was changed to the Interagency Coordinating Committee on Ceramics Research and Development† to reflect the much broader nature of the research effort on ceramics throughout the government. Members of this committee represent numerous federal agencies and departments, including the Department of Defense (including all of the major services and the Defense Advanced Research Projects Agency), the Department of Energy, the National Aeronautics and Space Administration, the National Science Foundation and the National Institute of Standards and Technology.‡

The primary function of this committee is to create a forum for communication and coordination among managers of federally-funded R&D programs in ceramics. The ICCCRD provides a mechanism for maximizing the effectiveness and resource sharing of government-supported research, helps prevent redundancy and supplies a forum for discussion of the U.S.'s global position. Unclassified work on ceramics has addressed the use of monolithic, composite and thin-film materials in various appli-

†Formerly known as the Interagency Coordinating Committee on Structural Ceramics (ICCSC).
‡It is open to all federal agencies with an interest. Please contact Steve Freiman: steve.freiman@comcast.net for more information.

cations areas such as transportation, space, defense, health, energy, electronics and construction and building materials. These applications represent large potential markets, introduce new approaches to energy harvesting and conservation, enable space exploration and underpin national defense. This article highlights recent program accomplishment and directions in some of the federally funded research programs in ceramic materials.

Highlights of federally funded research

The most recent ICCCRD meeting was held at NIST in April 2008. Each agency gave an overview of its program with an emphasis on recent changes, priorities and highlights. In addition to the primary topics discussed in succeeding sections, other interesting research was highlighted as well.

For example, the Naval Surface Warfare Center is conducting work on developing high-temperature, high-toughness and oxidation-resistant cermets in the systems: ZrB_2; ZrN; HfN with W, Mo; W_2B with W; and AlN with W, Mo, and Ta.

The NASA Ames Research Center is involved in a program to develop ablative materials for the new Orion lunar module's thermal-protection system. This work involves many of the other NASA centers as well. A material of particular interest is a phenolic-impregnated carbon ablator, termed PICA. NASA Ames is also developing new variants of PICA and other ablators with the goal of providing a suite of thermal protection materials for future NASA missions.

The NASA Glenn Research Center is working on multifunctional ceramic materials combining, for example, basic mechanical or load-bearing properties with electrical power generation. In one such application, thermoelectric materials are integrated into insulated hot walls of engine exhaust structures to harvest waste heat by conversion to electrical energy. Thermoelectric material processing approaches are being pursued that create nanostructural features that effectively scatter phonons (lowering thermal conductivity) – without sacrificing electron transport – while simultaneously enhancing mechanical properties (strength, toughness and creep deformation). The resulting structures have the potential to improve efficiency and safety by reducing volume, weight, cost and power consumption. The structures can also reduce system complexity in locations where the power can be used for wireless-based sensors and actuators.

NASA Glenn is also investigating high-temperature piezoelectrics for turbine engine applications, particularly for active combustion control for fuel modulation to mitigate thermoacoustic instabilities. The idea is to gain better gas flow control to improve mixing characteristics using pulsed air injections to reduce nitrogen oxide emissions and improve efficiency. Piezoelectric actuators can be used as synthetic jets for active flow control to mitigate the boundary layer separation on the blade surface, reduce tip losses and control noise. Applied to turbomachinery, shunted and unshunted piezoelectrics can reduce blade vibration that, in turn, reduce the stress, increase safety margins and extend materials life.

Two main challenges in producing high-temperature piezoelectrics are (a) to increase Curie temperature (T_C) without an increase in loss tangent, and (b) to demonstrate high piezoelectric activity. $BiScO_3$–$PbTiO_3$ – (BS–PT) -based systems exhibited high T_C (>400°C) and large piezoelectric coefficients (>400 pC/N) near the morphotropic phase boundary.

To improve BS–PT ceramics, investigators have taken two approaches. The first is microstructure engineering: Excess Bi_2O_3 proves to be a successful liquid-phase-forming additive to improve the BS–PT piezoceramics for high-temperature applications because of increased resistivity and enhanced piezoelectric activity.

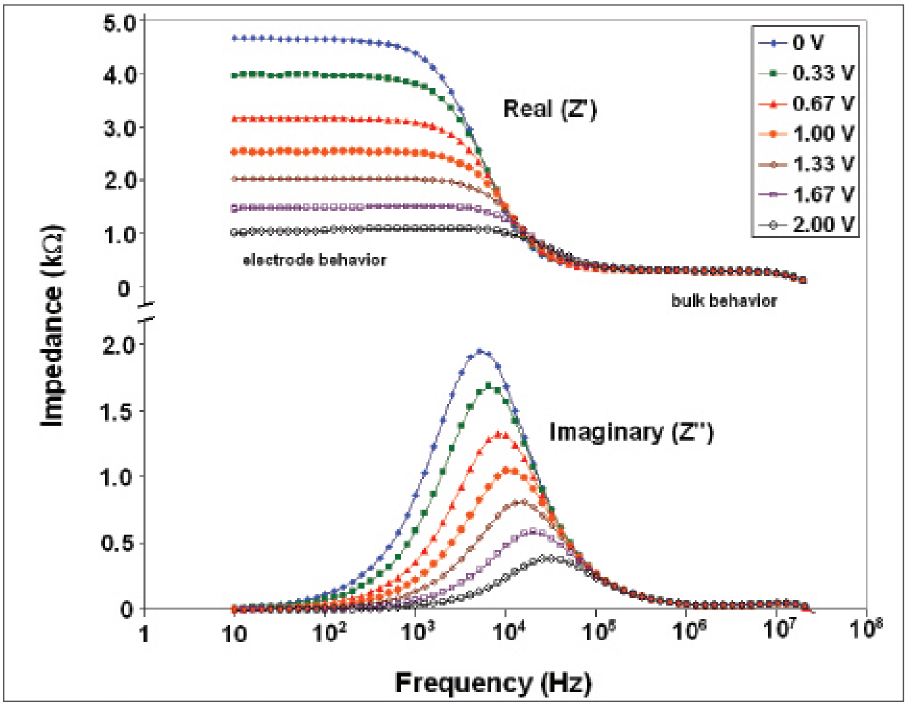
The second approach is compositional engineering: Donor doping using Zr and Mn improves high-field properties such as coercive-field and maximum-field induced strain. In addition, despite a decrease in electromechanical activity, the operating temperature improves by approximately 100°C when compared with state-of-the-art PZT type 2 ceramics.

The following sections focus on three of the primary topics discussed during that meeting: advanced ceramic-matrix composites, lightweight armor, and computation and modeling applied to ceramic materials. There is a fair amount of overlap between the third topic and the first two, as computational approaches have become more integral to research and development efforts.

Ceramic-matrix composites

Improved ceramic matrix composites continue to be a topic of major interest for engine and rocket nozzle applications because of their less catastrophic mode of failure. Particularly exciting are NASA's efforts at the Glenn, Langley, and Dryden laboratories, and the Air Force Research Laboratory, focused on SiC-matrix materials reinforced with SiC fibers. These materials are used in advanced hot-section turbine engine components to take advantage of their higher temperature capability. Performance limits are being pushed by incorporation of the most refractory SiC fibers combined with advanced fiber-reinforcement architectures. One goal is to understand high-temperature creep behavior that is likely a factor limiting operating conditions.

Other research is looking at possible material-degradation mechanisms in the operating atmospheres and environmental-barrier coatings to combat degradation. Assuring a safe operating timeframe for these advanced materials is a prerequisite for their insertion into critical components. The development of life-prediction models is being carried out by the AFRL. The lab is also evaluating carbon-reinforced SiC composites with an eye on applications in fighter aircraft engine exhaust systems. AFRL has also directed efforts toward C/SiC and SiC/SiC composites for rocket nozzle applications, including actively cooled constructions. Testing, accomplished in a rocket-combustor rig at NASA Glenn, has been successful so far.



Effect of DC bias on the frequency-dependent real and imaginary impedances of an Al_2O_3 composite containing 20 vol% SiC(w). Increasing the bias depresses the parts of the curves that are associated with the contacts

Many NASA labs are also conducting research on ceramic-matrix composites for aeronautic and space applications. Applications include developing methods of repairing damage to C/SiC composites used in the space shuttle orbiter, nondestructive evaluation of SiC/SiC and C/SiC composites, oxidation and creep studies, and development of ultra-high-temperature ceramic systems.

The latter includes work on diboride–carbide systems for hypersonic applications. That effort involves a collaboration among the Air Force, Navy and others in the ceramics community. Much of the work at NASA Ames (funded by NASA's Fundamental Aeronautics Program) focuses on exploring and controlling the properties of UHTCs through processing and compositional changes.

One project supported by NSF (award No. 0710630) focuses on using natural templates to form ceramic composites. This work is directed by Katherine Faber at Northwestern University and is carried out in cooperation with researchers in Spain and Russia. Biomorphic SiC is produced by the controlled pyrolysis of wood. This leaves a carbon scaffold for infiltration by liquid silicon1; the silicon then reacts with carbon to form SiC. Researchers then can further infiltrate the resulting bio-SiC scaffold to make ceramic-metal composites.[2]

The resulting microstructures are complex, honeycomb-like structures. X-ray microtomography (performed at Argonne National Lab at the Advanced Photon Source) provides a glimpse of the three-dimensional structure of the carbon, SiC or composite. The shape, size and arrangement of the channels (from the wood's vessels and cells) play an important role in the infiltration by molten materials and, ultimately, in the mechanical and thermomechanical properties of these materials.

In another NSF-supported project (award No. 0604211), Rosario Gerhardt of the Georgia Institute of Technology is examining the effect of metals on the Schottky barrier response of electrical contacts in SiC-whisker–Al_2O_3composites (fabricated by Advanced Composite Materials in Greer, SC)[3]. The addition of SiC whiskers to Al_2O_3 creates a composite with sharply reduced brittleness and greatly enhanced electrical conductivity compared to conventional ceramics.

However, when metallic electrodes are attached for electrical applications, the total conductance of such a composite is often severely limited by bottlenecks to the current flow. Investigations have shown that these restrictions occur at the interfaces between the electrodes and the whiskers on the composite surface, and increase the total resistance by approximately 100 times, or more.

This resistance makes studying transport through the bulk of the composite difficult because most of the measured signal comes from the contacts. However, when investigators use impedance spectroscopy to separate out this blocking contribution to the resistance, with an appropriate choice of electrode material, the blocking is less than 10 percent. By combining this information with current-mode atomic force microscopy, investigators can show that interface Schottky barriers between the electrode metal and the whiskers on the composite surface caused the blocking. This blocking behavior is vividly revealed by the bias dependences of impedance spectra taken from bulk samples and I-AFM scans of the surface.[1] This improved understanding of the contact issues should facilitate further investigation of transport in various insulator-conductor composites over a range of length scales.

Although most government work currently focuses on non-oxide CMC, AFRL maintains efforts for oxide CMC that builds upon prior DOE and NIST programs. Emphasis is on combustor liner applications using advanced-oxide CMC concepts. Demonstrations are pending for land-based and aerospace power turbines.

Lightweight ceramic armor

With the greater military presence in Afghanistan and Iraq, there is an increased need for opaque and transparent lightweight armor ceramics. Investigators at the Army Research

Laboratory in Aberdeen Proving Ground, Md., are giving emphasis to vehicular and personal protection. High-hardness and low-density materials are of interest including B_4C, SiC, AlON, $MgAl_2O_4$, glass and TiB_2.

At the NSF, one project led by Manish Chhowalla and Adrian Mann at Rutgers University in cooperation with ceramic armor manufacturers focuses on B_4C. The aim of the proposed research is to thoroughly understand the structure of B_4C and then modify it to improve performance at high-velocity impacts.

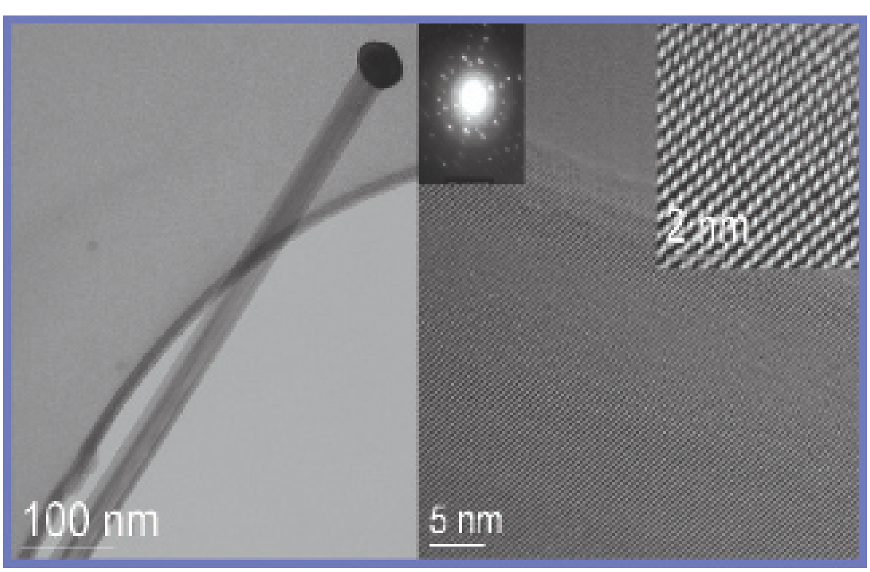
The basis for this work comes from ab initio calculations that indicated B_4C has numerous coexisting polytypes due to similar lattice parameters and stability energies. One of these polytypes has a very low impact resistance and serves as the weak link in B_4C that leads to its premature failure at high impact velocities.[4] Calculations have recently revealed that it is possible to eliminate this polytype by the addition of silicon.[5]

These researchers have developed a technique to synthesize metastable silicon-containing B_4C powders consisting of nanowires.[6] To determine whether the alloyed sample has improved physical properties, they are working on producing a larger volume for testing. Because ballistic tests are expensive and time consuming to perform on a large number of samples, they have developed a simple method that uses electric fields to detect shock-induced failure.[7] An electric field is applied between two electrodes and any changes in phase are detected in situ by Raman spectroscopy. This technique allows real time monitoring of shock-induced phase changes on a large number of samples and test cycles.

The work at ARL is particularly concerned with developing models describing an impact event. One of the difficulties in developing improved armor ceramics is finding a laboratory test procedure that will correctly predict the response of structural ceramics to high-stress, high-rate impact environments.

For example, robust multiscale, physics-based models are needed to reliably simulate their mechanical response to high-rate impact environments. It is well known that variations in material characteristics (phases, microstructure and defects) can significantly affect the quasi-static, mechanical behavior of structural ceramics. There are, however, many significant differences between the high-rate and quasi-static stress environments, including stressed volume, over-stressed condition, stress waves propagation and rate, kinetic effects, mixed spatially-varying macro-stress states, activation of new micro-mechanical mechanisms and possible phase transformations.

Ultimate failure is a function of the temporal and spatial interaction of the macrostresses with the ceramic materials at the microstructural and nanostructural scales, including elastic and inelastic deformation, damage nucleation and evolution and resulting failure from the macroscale (top down) or from the nanoscale (bottom up). The macromechanical response, assuming homogeneous, defect-free mechanically isotropic bodies are known, but the spatial micromechanical responses and stochastic variability are not well established. As computing power and speed continues to increase, the ability to simulate the mechanical response at the microstructural and mesostructural level will become much more important. Many existing models and codes are extrapolations from metal behavior and exclude defects, microcracking, ceramic plasticity, ceramic-specific failure mechanisms, high pressure phase transformations, sample homogeneity and sample-to-sample variability. To address these issues, the ARL, with its industry partners, is working to develop validated, robust ceramic models and computer codes.



B_4C nanowires doped with silicon: (a) optical image, and (b) transmission electron microscopy images and diffraction pattern. Credit: M. Chhowalla.

Computation and modeling

The ICCCRD agreed in advance to focus on the role of computation and modeling in materials research, development and use, and heard presentations from various government agencies regarding their individual computation and modeling programs.

AFRL reported on computation and modeling efforts related to CMCs focusing on environmental degradation, deformation and damage evolution mechanics and fiber architecture optimization. Numerical models of the complex interactions of fiber architecture with the matrix also are being developed. Other activities include the modeling of the oxidation kinetics of ultra-high-temperature ceramics and the prediction of deformation twinning in complex oxides.

The Air Force Office of Scientific Research is funding modeling research programs in such diverse areas as computational design of oxidation-resistant coatings for composites.

At NASA Ames, the primary modeling emphasis is on materials for thermal protection. Examples include the structure and mechanics of polymer-based composites, char formation on polymer composites and simulations of ablative composites.

Work at NIST concentrates on the development of models to predict the behavior of scanned probe microscope components, property prediction for gate dielectric materials and the performance of nanoparticles injected into the body as a remedy for specific tumors.

At the meeting, the AFRL's Chris Woodward offered his perspectives on computational modeling and the report[8] of the National Materials Advisory Board study on "Integrated Computational Materials Engineering." The purpose of this study was to investigate the benefits of a computational approach in materials and to establish a roadmap for the development of an ICME infrastructure, including databases and model integration. In the summary to their report, the NRC committee concluded that three things must happen if ICME is to reach its potential to reduce development costs, lower manufacturing costs, improve material and component life and allow for agile response to changing market demands. These are:

- ICME must be embraced as a discipline in the materials science and engineering community, leading to changes in education, research and information sharing.
- Industrial reluctance to accept ICME must be overcome.
- The government must give coordinated support for the initial development of the ICME tools, infrastructure and education.

Summary

The attendees found that the ICCCRD provided a valuable forum for discussion of ongoing ceramics research. One stimulating topic of discussion was the need for access to property data over a broad range of materials. The development of improved process and behavior models depend on the quality of input data. The point was made that while such data needs are widely acknowledged, no single agency or organization has the mission or the resources to provide both editorial support and access methods. A primary topic at next year's meeting will be education in the field of ceramics. ■

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References

[1]B.D. Bertram and R.A. Gerhardt, "Room-Temperature Properties of Electrical Contacts to Alumina Composites Containing Silicon Carbide Whiskers," submitted Nov. 2008.

[2]V.S. Kaul, K.T. Faber, R. Sepulveda Ferrer, A.R. de Arellano López and J. Martinez-Fernández, "Precursor Selection and Its Role on the Mechanical Properties of Porous SiC Derived from Wood," *Mater. Sci. Eng. A*, **428** [1-2] 225-32 (2006).

[3]T.E. Wilkes, J.Y. Pastor, J Llorca and K.T. Faber, "Mechanical Properties of Wood-Derived Silicon Carbide Aluminum Alloy Coposites as a Function of Temperature," *J. Mater. Res.*, 23 [6] 1732-43 (2008).

[4]G. Fanchini, J.W. McCauley and M. Chhowalla, "Behavior of Disorder in Boron Carbide Under Stress," *Phys. Rev. Let.* **97**, 035502 (2006).

[5]G. Fanchini and M. Chhowalla, unpublished results.

[6]V. Gupta, G. Fanchini, S. Miller, J. A. Sharab, J. Bentley and M. Chhowalla, "Effect of Growth Parameters and Si-doping on Boron Carbide Nanostructures;" under review.

[7]G. Fanchini, V. Gupta, A.B. Mann and M. Chhowalla, "In Situ Monitoring of Structural Changes in Boron Carbide Under Electric Fields," *J.of Am. Cer. Soc.* **91**, 2666-69 (2008).

[8]*Integrated Computational Materials Engineering*: The National Academies Press, Washington, DC, 2008.