Material Science and Technology Division

Propulsion Materials Program
Quarterly Progress Report for
January through March 2008

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Agreement 16307: Modeling/Testing of Environmental Effects on PE Devices

A. A. Wereszczak, T. P. Kirkland, W. L. Daloz, and M. Lance
Oak Ridge National Laboratory

Objective/Scope

Understand the complex relationship between environment (temperature, humidity, and vibration) and the performance and reliability of the material constituents within automotive power electronic (PE) devices. There is significant interest in developing more advanced PE devices and systems for transportation applications (e.g., hybrid electric vehicles, plug-in hybrids) that are capable of sustained operation to 200°C. Advances in packaging materials and technology can achieve this but only after their service limitations are better understood via modeling and testing.

Technical Highlights

Two primary efforts continued during the present report period. They were the mechanical and electrical evaluation of candidate or alternative ceramics for use in a direct copper bonded (DCB) substrate, and the collaboration with the NTRC group of R. Wiles, C. Ayers, and K. Lowe in the development of a direct-cooled PE device.

Evaluation of Alternative Ceramic Substrates

Several electronic ceramic materials are undergoing equibiaxial (ring-on-ring) flexure in air, and while submersed in 50% water - 50% ethylene glycol or 100% water environments. A 96% alumina, a 99.6% alumina, an aluminum nitride, a silicon nitride, a boron nitride, and a polycrystalline silicon carbide are under evaluation. Beryllium oxide was initially considered; however, engineering controls needed for its characterization were deemed too extensive to justify its inclusion in the test matrix. Tests in the two non-air environments are being performed to get a sense of any strength degradation or longer-term chemical incompatibility for consideration of the direct-cooled PE device portion of this project.

A developmental, high-resistivity (> 10^8 Ω•cm) polycrystalline silicon carbide is under consideration for electrical insulation candidacy in this project. Many of its properties make it attractive for use in DBCs. Polycrystalline silicon carbide has a high thermal conductivity (> 125 W/mK), a coefficient of thermal expansion (~ 3-4 ppm/°C) that is close to that of silicon and matches that of silicon carbide semiconductor chips, is perhaps the most economically produced and inexpensive non-oxide ceramics, is relatively strong and very thermal shock resistant, is non-toxic, and is chemically stable with moisture. Like its single-crystal-form, polycrystalline SiC typically responds semi-conductively. However, Saint-Gobain (formerly Carborundum, Niagara Falls, NY) developed a high-resistivity version approximately 20 years ago, and samples of that material are under evaluation in this study. Its resistivity (designated as “SiC ER e11”), measured with an impedance spectrometer, is equivalent to that of common-substrate ceramics alumina and aluminum nitride as shown Figs. 1-2. Breakdown voltage of this

high-resistivity polycrystalline SiC is expected to be high (> 20 kV/mm) but that will be measured during the third quarter to confirm that.

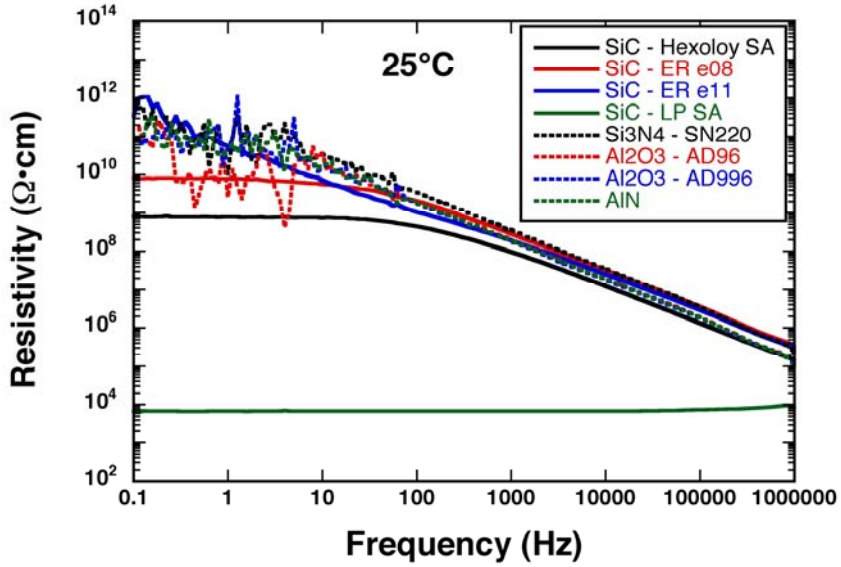


Figure 1. Electrical resistivity as a function of frequency at 25°C. The developmental, high-resistivity polycrystalline SiC ER e11 grade's resistivity is equivalent to that of alumina, aluminum nitride, and silicon nitride.

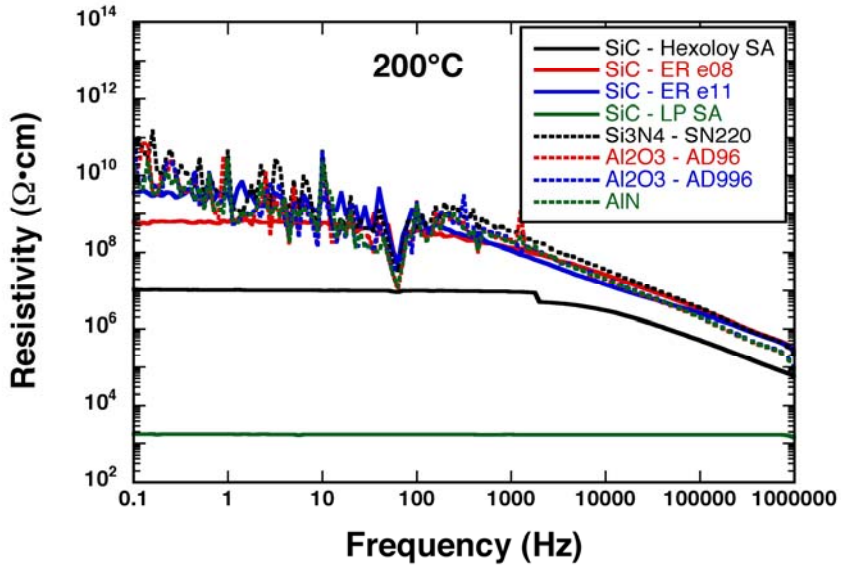


Figure 2. Electrical resistivity as a function of frequency at 200°C. Equivalence of electrical resistivity of SiC ER e11 with Al_2O_3, AlN, and Si_3N_4 was sustained.

Direct-Cooled PE Device

A collaborative effort continued with ORNL-NTRC's Randy Wiles, Curt Ayers, and Kirk Lowe to provide ceramic material selection advice and finite element analysis support to a new direct-cooled PE device concept. Candidate ceramic materials have been surveyed along with prospective manufacturers. The concept was recently submitted for a provisional patent.

Status of FY 2008 Milestones

Establish controlled environmental test facility that can controllably subject PE devices to concurrent temperature, humidity, and vibration conditions. [Sep08]. *On schedule.*

Communications/Visits/Travel

Pertaining to the substrate-related efforts, numerous discussions were held with Kyocera's Adam Schubrin and Saint-Gobain's John Bevilacqua. Regarding the PE-direct-cooling efforts, numerous discussions and visits occurred with NTRC's Randy Wiles, Curt Ayers, and Kirk Lowe, and discussions occurred with Springboard CIM's Gene Krug, Saint-Gobain's John Bevilacqua, Ceradyne's Biljana Mikijelj, and Kyocera's Shin Shinozuka and Sammy Matsuda.

Problems Encountered

None.

Publications/Presentations/Awards

None.

References

None.

Agreement 9237: Carbon Foam for Cooling Power Electronics

N. C. Gallego,[a] Cristian Contescu,[a] B. E. Thompson[b]
[a]Oak Ridge National Laboratory
[b]ThermalCentric, Inc

Objective

Develop and demonstrate an optimized heat exchanger/heat sink design that best utilizes the heat transfer properties of graphite foam to significantly reduce the size and weight of the thermal management system

Highlights

- The design of the cooling system optimized for automotive applications to be built in collaboration with ThermalCentric personnel is in advance state. Significant progress has been made towards accomplishing our milestone.

Progress

After demonstrating the benefits of high-thermal conductivity graphite foam with a proof-of-concept thermal siphon, we will be designing a prototype to be used with an actual automotive power inverter that will be tested at NTRC. The new design will incorporate data from the most recent conductive graphite foam materials developed by Koppers (manufacturer of foam). Significant progress has been made towards completing this year's milestone.

The tests to determine oxidation resistance of graphite foams continued. Three foam materials with different density and pore structures were supplied by Koppers for this test. They are being tested according to the ASTM standard method that is being developed by ORNL for characterization of air oxidation of graphite and other carbon materials. The tests are conducted at 10 L/min air flow in a vertical tube furnace adapted for thermogravimetric measurements. Four test temperatures were selected (575, 600, 650, and 700°C) and the rate of graphite weight loss caused by oxidation is measured. The test helps differentiate between the three foam materials in terms of their oxidation resistance, and provides quantitative information such as activation energy for oxidation reaction and threshold oxidation temperature of each material. These data define practical operation temperatures of thermal management systems based on graphite foam and exposed to aggressive oxidizing environments.

Milestones

Design and optimize a boiling cooler for field testing using more open foams that save energy and have been developed in collaborations with Koppers and ThermalCentric International Corporation. **(09/08)**

Agreement 16305: Materials By Design: Solder Joint Analysis

G. Muralidharan, Andrew Kircher, and Burak Ozpineci
Oak Ridge National Laboratory

Objective/Scope

Advanced hybrid and electric propulsion systems are required to achieve the desired performance and life targets set for future automobiles. As specified in the OVT objectives, a target lifetime of 10-15 years has been projected for hybrid and electric propulsion systems meant for operation in harsh automotive environments. Power electronic components and systems are integral components of advanced automotive hybrid and electric propulsion systems. The trend in automotive power electronics is for using higher operating temperatures which has a detrimental effect on the stability of materials used in such systems. The objective of this task is to evaluate the effects of the higher temperatures on critical metallic materials that are used in power electronic devices and systems and to use the Materials-by-Design approach to identify appropriate combinations of materials that would decrease inopportune failures and maximum lifetime and reliability.

Based on the trend for using higher temperatures in power electronic components, there is a significant need to study failures of electronic packages induced by metallurgical changes of solder joints used as die attaches, and in wire bonds exposed to high temperatures (up to 200°C in contrast to the current 125-150°C exposure) anticipated in such applications. These failures can be induced in solder joints and other components by combination of temperatures, stresses, and current. Coarsening of solder joint microstructure along with the formation of intermetallic compounds takes place during high temperature exposure. Wire bonds are also known to be a key location of failures for packages meant for high temperature use. An understanding of the failures in solder joints and wire bonds will empower us to develop a computation-oriented method for the design of materials for packaging applications.

The approach used in this work would be to study failures in simple package designs so that the emphasis is on materials rather than package design thus avoiding complexities of package design issues that may overshadow materials issues. Packages will be subject to extremes of operational stress levels/temperature levels to the study the origin of failures. Steady-state exposure at high temperatures and cyclic exposures (thermal fatigue) all affect microstructure of the materials, their properties, and hence the failure of joints. X-ray radiography along with acoustic and infrared imaging (as is necessary) will be used to characterize voids present in the solder joints. Knowledge from the failures would enable the selection/development of more appropriate materials that would ensure required lifetimes of 10 to 15 years expected of modules in EVs and Hybrid systems.

Technical Highlights

In this quarter, progress has been made in developing key capabilities for reliability testing of packages. A test chamber EC11A capable of exposing packages to temperatures up to 315°C for long times and to thermal cycling between 315°C

and -184°C has been obtained from Sun Electronics and has been successfully installed (Figure 1).

Several commercially available packages of a 600V diode module (Part # QRC 0640T30) have been obtained from PowerEx for initial evaluation of reliability testing methodologies. As-received forward and reverse electrical characteristics of these diodes are being measured using the setup shown in Figure 2. Figures 3(a) and 3 (b) show an example of the forward and reverse characteristics obtained from one of the diodes. These diode modules will then be subjected to thermal cycling using the Sun EC11A environmental chamber installed in our lab. After a fixed number of cycles, electrical property measurements will be repeated to monitor degradation due to thermal cycling. This work will establish some of the initial methodologies for reliability testing using our newly installed capabilities.

Status of FY 2008 Milestones

Work is on schedule to meet the following milestone:

Evaluate microstructural evolution and causes related to the failure of one most commonly used solder in a selected high temperature package when subjected to stress testing conditions. **(9/08)**

Communications/Visits/Travel

Communications are being carried out with PowerEx about the feasibility of fabrication of simple packages consisting of solder joints with zero void content at their manufacturing facility. Communications with SemiSouth and CREE have been initiated this quarter. Proposals have been submitted to SemiSouth and CREE to purchase some of their active and inactive SiC devices for custom packaging at PowerEx and at ORNL.

Problems Encountered

None

Publications/Presentations/Awards

None

Figure 1. SUN EC11A environmental chamber is available for thermal cycling experiments.

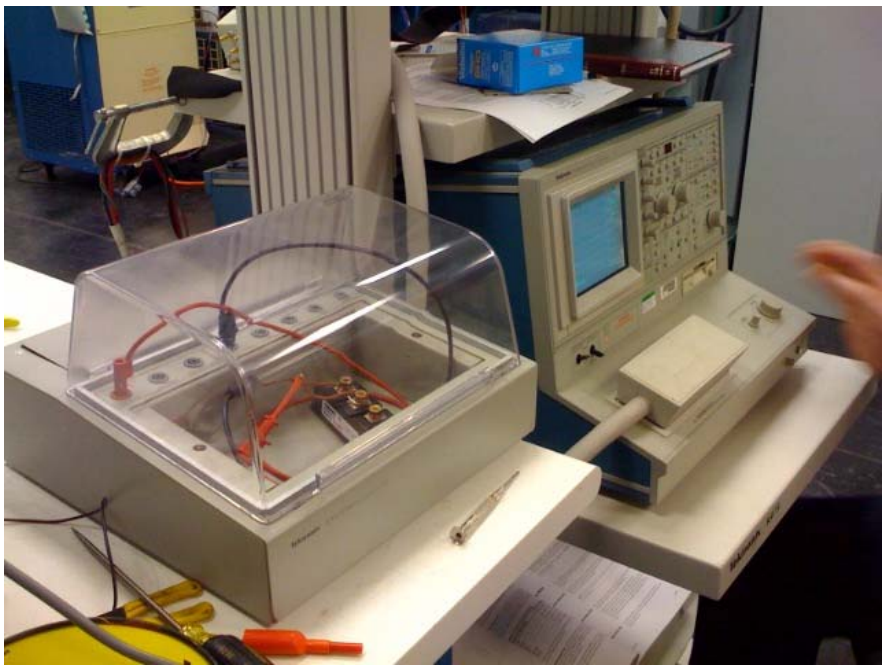
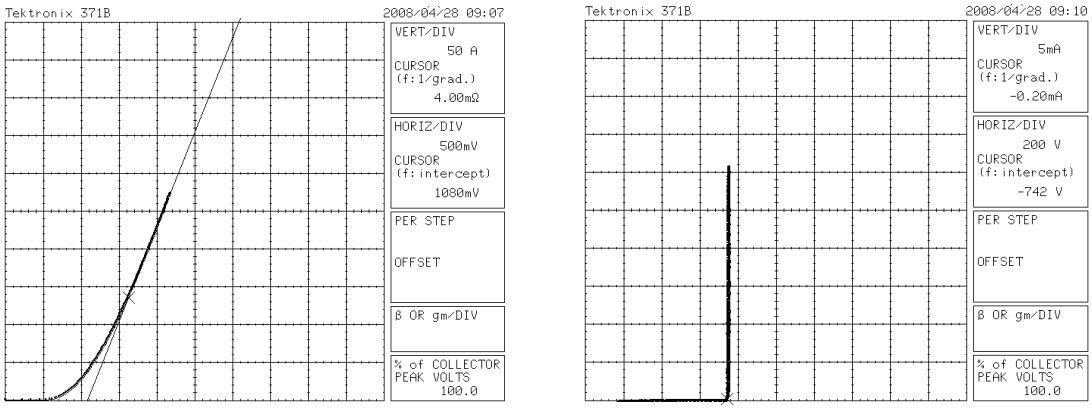


Figure 2. Apparatus used for testing of electrical characteristics of diode module.



(a) **(b)**

Figure 3. Typical electrical properties obtained from the tested diodes; (a) forward characteristics, and (b) reverse characteristics. Effect of temperature cycling on these characteristics will be evaluated.

Agreement 16306: Materials Compatibility of Power Electronics

B. L. Armstrong, D. F. Wilson, C. W. Ayers, and S. J. Pawel
Oak Ridge National Laboratory

Objective/Scope

The use of evaporative cooling for power electronics has grown significantly in recent years as power levels and related performance criteria have increased. As service temperature and pressure requirements are expanded, there is concern among the Original Equipment Manufacturers (OEMs) that the reliability of electrical devices will decrease due to degradation of the electronic materials that come in contact with the liquid refrigerants. Potential forms of degradation are expected to include corrosion of thin metallic conductors as well as physical/chemical deterioration of thin polymer materials and/or the interface properties at the junction between dissimilar materials in the assembled components. Initially, this new project will develop the laboratory methodology to evaluate the degradation of power electronics materials by evaporative liquids.

Technical Highlights

An initial methodology to examine the interaction of the electrical components with the fluids used in evaporative direct cooling systems has been laid out. Candidate power electronic components and coolants are being acquired to begin testing this methodology and the effect direct contact with cooling fluids will have on specific power electronic components. A presentation was given by D. Stinton at the program review in March in Maryland.

Status of FY 2008 Milestones

Develop the methodology to examine the interaction of the electrical components with the fluids used in the evaporative cooling systems. **(09/08)** On track.

Communications/Visits/Travel

A presentation was given by D. Stinton at the program review in March in Maryland.

Problems Encountered

None to report.

Publications/Presentations/Awards

A presentation was given by D. Stinton at the program review in March in Maryland.

References

None to report.

Agreement 11752: Advanced Materials Development through Computational Design for HCCI Engine Applications

Vinod K. Sikka, Govindarajan Muralidharan, Rick Battiste, and Bruce G. Bunting
Oak Ridge National Laboratory

Objectives/Scope

To identify and catalog the materials operating conditions in the HCCI engines and utilize computational design concepts to develop advanced materials for such applications.

Highlights

Technical Progress

Materials-by-Design of Advanced Materials:
In this quarter, work was continued on Ni-based alloys for valve applications. As reported earlier, using thermodynamic modeling, microstructure evaluation, and mechanical property evaluation, high temperature fatigue was identified as a property of critical interest in Ni-based alloy valve materials for the next generation automotive engines. An important part of the on-going work is to develop a database of mechanical properties as a function of alloy composition and microstructure (which is a function of processing and heat-treatment). In this quarter, work has continued on developing this mechanical property database and in particular developing data on the alloy currently used for automotive valves. IN 751 was supplied by Carpenter Technologies in the annealed condition and a two-step aging treatment was used to heat treat the alloys as shown in Table 1. Another IN 751 was obtained from a different source but with a slightly different composition and subjected to a different heat-treatment process more suitable for lower temperature performance.

Figure 1 shows the number of cycles to failure for IN 751 during fatigue testing at 1600°F, subject to the heat-treatments shown in Table 1. Note that at higher stresses the alloy heat-treated using the second heat-treatment process (IN751-2) performs better (greater cycles to failure) whereas at lower stresses, the alloy heat-treated using treatment 1 performs better (IN751-1). In order to understand the origin of these differences, calculations were performed to understand the amounts of γ' present in these two alloys. Figure 2 shows the results of these calculations. Note that IN751-2 has a larger γ' content at 870°C reflected in the higher cycles to failure at the higher stresses. However, at lower stresses and longer exposures at 870°C when coarsening takes place and the γ' particle size increases, this small difference in γ' contents does not seem to play the dominant role. Based upon this work we conclude that both the amount of γ' and its size have to be optimized for best fatigue properties. Furthermore, it emphasizes the importance of heat-treatment. It should be noted that heat-treatments suited for lower temperature use may not always be the best choice for higher temperature use. In addition, a simpler heat-treatment schedule may reduce cost of the final component.

Table 1: Heat treatment conditions used for IN 751

Alloy	Condition Designation	Aging treatment
IN 751-1	IN751-carp	1600°F/4 hrs/ Air cool 1350°F/4 hrs/ Air cool
IN 751-2	IN751-2	Heat-treatment for optimized lower temperature performance

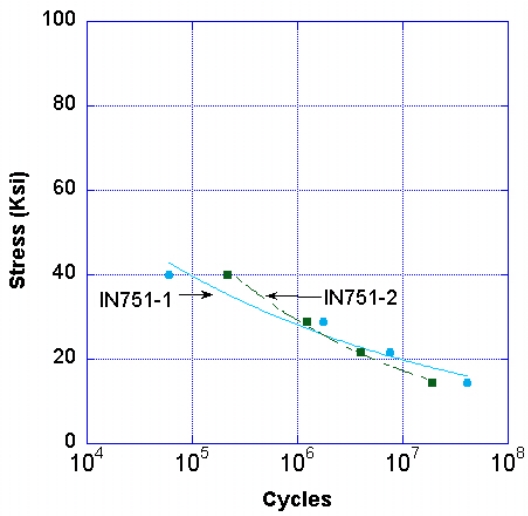
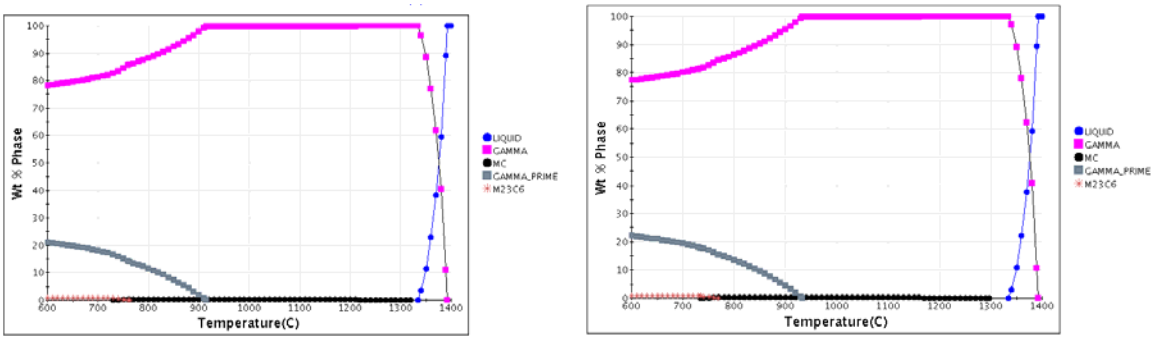


Figure 1. Cycles to failure as a function of stress in Ksi at 1600°F for IN751-1, and IN 751-2. Note that at higher stresses, IN751-2 shows a longer lifetime but at lower stresses, the performance of IN751-1 is either comparable to or better than that of IN751-2. Lines are drawn to aid the eye in comparing the two sets of results.



(a) (b)

Figure 2. Calculations show that IN751-1 (a) has a lower γ' content at 870°C (5.4 wt. %) when compared to IN751-2 (b) (7.7 wt. %).

Milestones

Develop material with the potential to have appropriate performance for valve application through computational modeling and experimental validation. **(9/08) (On-track)**

Agreement 8697: Electrochemical NO_x Sensor for Monitoring Diesel Emissions

Leta Y. Woo, and Robert S. Glass
Lawrence Livermore National Laboratory

Objective/Scope

The main goal is the development of technology for measuring NO_x in diesel exhaust using low-cost, high-sensitivity on-board sensors. Solid-state electrochemical sensors are robust and an ideal platform for exploring NO_x sensing strategies that build upon designs previously demonstrated for the detection of hydrocarbon emissions in automobile exhaust. Characterization of materials and design will be used to optimize the sensor for operation in environments comparable to the exhaust stream of the CIDI engine.

Technical Highlights

Previously, an impedance-based NO_x sensing technique was presented, and criteria for materials and configurations suitable for impedancemetric NO_x sensing were developed. Using the developed criteria, sensor prototypes show reasonable stability (~500 hours) at the operating temperature (650°C), sensor speeds less than 10 sec., sensitivity down to 5 ppm NO_x, and minimal cross-sensitivity to water at the operating temperature of 650°C. Subsequent prototypes have been tested that have a more manufacturable design by incorporating an alumina substrate. Remaining issues include cross-sensitivity to oxygen, temperature sensitivity, and long-term stability (> 500 hours) as well as continuing to improve the sensor platform to be more suitable for commercialization. Current progress has focused on characterizing a recent prototype based on the Au/YSZ system and improving the testing protocol and design of engine dynamometer experiments at Ford testing facilities. Significant improvements were made based on lessons learned from previous attempts. One improvement was the inclusion of a commercially available NO_x sensor downstream of the LLNL prototype to be used for comparison. Preliminary evaluation of the data indicates that the most recent LLNL prototype shows promising performance when compared with the significantly more expensive commercially available NO_x sensor. Other improvements include monitoring temperature fluctuations and better controlling emissions by understanding how to alter engine parameters. Additional evaluation of data is being conducted to determine the performance of the LLNL prototype. Further testing will focus on developing improved prototypes for additional comprehensive laboratory and dynamometer testing.

Status of FY 2008 Milestones

The 1st quarter 2008 milestones have been achieved, including dynamometer testing and progress towards further developing criteria for appropriate materials and configurations. The 2nd quarter milestones that have been achieved include initial evaluation of conducting perovskite oxides, which will continue into the third quarter, and also laboratory investigation of cross-sensitivity to interfering gases, which will be used to evaluate data from engine dynamometer testing. Also, an oral presentation was

made at the 32nd International Conference and Exposition on Advanced Ceramics and Composites.

Communications/Visits/Travel

- Bi-weekly teleconferences with Ford collaborators have continued in order to coordinate efforts in developing a deployable and commercializable NO_x sensor technology.

- Leta Woo attended the 32nd International Conference & Exposition on Advanced Ceramics and Composites, Jan. 27 – Feb. 1, 2008, in Daytona Beach, FL.

- Leta Woo traveled to Dearborn, MI (Feb. 28 & 29) to conduct engine dynamometer testing of LLNL prototype sensors at the Ford facilities.

Publications/Presentations/Awards

- The following manuscript has been published:

  E.P. Murray, R.F. Novak, D.J. Kubinski, R.E. Soltis, J.H. Visser, L.Y. Woo, L.P. Martin, and R.S. Glass, "Investigating the stability and accuracy of the phase response for NO_X sensing 5% Mg-modified $LaCrO_3$ electrodes," *ECS Transactions* 6(20):43-62, 2007.

- An oral presentation entitled "Sensing Mechanism of Impedancemetric NO_x Gas Sensors Based on Porous YSZ/Dense Electrode Interfaces" was presented at the 32nd International Conference & Exposition on Advanced Ceramics and Composites, Jan. 27 – Feb. 1, 2008, in Daytona Beach, FL.

Agreement 9440: Fabrication of Micro-orifices for Diesel Fuel Injectors

George Fenske
Argonne National Laboratory

Objective/Scope

- Reduce soot by improving fuel dispersion using smaller injector orifices
- Develop and evaluate methods for depositing adherent coatings on the inside diameter of fuel injector orifices in order to narrow them down.
    - Size goal: Final orifice diameter of 50 μm
    - Durability goal: Coating must remain adherent after repeated thermal cycling, must be resistant to sustained temperatures >300°C, and must be able to resist repeated impact loads in the needle seat area.
    - Reproducibility goal: Post-treatment orifice diameter variation must be no greater than that of the pre-treatment orifice diameter
- Evaluate the effect of coating on spray pattern.
- Test the effect of coating on deposit formation.
- Transfer developed technology to DOE industrial partners.

Technical Highlights

- Received series of experimental Bosch nozzles from the US EPA NVFEL lab in Ann Arbor and initiated detailed metallurgical study of Bosch and other industrial nozzles to determine chemical and heat treatment history.
- Re-establish coating contract with industrial coater.

Status of FY 2008 Milestones

- Milestones on-schedule

Communications/Visits/Travel

- Teleconference/discussions with USEPA on nozzle chemistry and heat treatment

Problems Encountered

- Failure to obtain nozzle alloy composition and heat treatment history is requiring detailed analysis of candidate nozzles to ascertain composition and microstructure of nozzles for future experiments. [Nozzle alloy and heat treatment is highly proprietary information]

Publications/Presentations/Awards

- ***Fabrication of Small Diesel Fuel Injector Orifices***, George Fenske, DOE VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW, February 25th, 2008

Agreement 11754: Hydrogen Materials Compatibility

Chuck Henager, Jr., Stan Pitman, Joe Ryan, James Holbery
Pacific Northwest National Laboratory

Objectives

- Measure the friction and wear characteristics of injector materials in hydrogen environments, including *in-situ* and *ex-situ* materials characterization.
- Develop accelerated test methods and durability procedures for materials/coatings used on hydrogen injectors.
- Measure the performance of piezoelectric actuators and actuator materials in hydrogen environments.
- Assist in the design of the direct fuel injector for Westport-Ford through materials modeling, analysis, and selection.

Technical Highlights

- **Needle-Nozzle Materials Compatibility Testing.** Hydrogen test device is fully operational; first *in-situ* data set complete. Ex-situ testing is 50% complete; several needle-nozzle tests continue. ILA provided to ORNL-Peter Blau for sliding-impact work to be conducted at ORNL in FY08. *Contact: J. Holbery, 509-375-3686, james.holbery@pnl.gov.*
- **Friction-Wear:** DLC characterization using Raman spectroscopy has been conducted at PNNL. Tribology measurements have been correlated with Penn State to verify *in-situ* apparatus. *Contact: J. Ryan, 509-376-1098, joseph.ryan@pnl.gov.*
- **Coating Test Development:** Prepared M2 and J-10 alloy samples were sent to Morgan Ceramics, Ion Bond, and Argonne National Lab for DLC coating. We have received Morgan and Ion Bond samples; they appear to be of very good quality, we await ANL samples. PNNL nanolaminate coating development continues; PNNL has produced approximately 50% and production continues on remaining laminates. We have begun tribology testing and hydrogen exposure in March on our first coated materials. *Contact: J. Holbery, 509-375-3686, james.holbery@pnl.gov.*
- **Piezo Material Development.** Samples have been requested from Physic Instrument (Germany) to begin single disk testing. This work will be addressed upon the arrival of a post-doc researcher. *Contact: C. H. Henager, Jr., 509-376-1442, chuck.henager@pnl.gov.*

Status of FY 2008 Milestones

1. Complete 100% hydrogen *in-situ* sliding wear tests to quantify injector friction coefficient and resulting material embrittlement with the goal of understanding and predicting the fundamental material degradation / aging mechanisms in hydrogen service environment.

Status: Wear tests are underway on base materials; coatings are currently being manufactured and will follow in the second half of the year.

2. Complete 100% hydrogen *in-situ* piezo actuation tests of commercial PZT formulations, extending on the initial test plan completed in FY07.
Status: PNNL is negotiating with Westport and Physic Instrument for additional PZT materials.

3. Model the diffusion of hydrogen into engine component materials via atomistic models complemented with experimental neutron backscattering data generated on component materials.
Status: This effort is currently behind schedule; pending arrival of post-doc.

4. Complete *in-situ* and *ex-situ* sliding-impact testing of needle-seat combination to understand the failure mechanism on injector seat materials.
Status: Samples are being manufactured, ex-situ testing in process (50% complete), and in-situ testing has just begun.

Communications/Visits/Travel

- Jim Holbery spoke at the H-ICE meeting at Sandia-Livermore to present work on Feb. 11, 2008.
- Jim Holbery presented at the DOE Merit Review meeting on February 25, 2008.
- Jim Holbery visited ORNL to discuss sliding impact testing with Peter Blau on March 6.

Problems Encountered

- There is a need for a Post-Doc researcher on the project. We have identified a candidate, extended an invitation to visit Laboratory in April. Expect hire in June when his post-doc is complete in June.

Publications/Presentations/Awards

- "Hydrogen Direct Injection Technology - Challenges and Opportunities", A. Welch, D. Mumford, S. Munshi, J. Holbery, B. Boyer, presented at NHA Meeting, March 2008.

Agreement 16304: Materials for Advanced Engine Valve Train

P.J. Maziasz, and N. D. Evans,
Oak Ridge National Laboratory

N. Phillips
Caterpillar, Inc.

Objective/Scope

This is a new ORNL CRADA project with Caterpillar NFE-07-00995 and DOE OVT Agreement 16304 that began last quarter and lasts for about 2.5 years. This CRADA project is focused on addressing the wear and failure modes of current on-highway heavy-duty diesel exhaust valves and seats, and then evaluating changes in valve-seat design and advanced alloys which enable higher temperature capability, as well as better performance and durability. Requests for more detailed information on this project should be directed to Caterpillar, Inc.

Highlights

Caterpillar, Inc.

Caterpillar completed testing and characterization on an initial set of exhaust valves and their matching seats previously, and then provided fresh exhaust valves and seats to match with those wear-tested in the lab-test rig to ORNL for further analyses. This quarter, Caterpillar facilitated and lead direct interactions with their commercial seat insert supplier, to address specific wear situations.

ORNL

ORNL completed the first phase of microcharacterization of the first set of testing valves supplied by Caterpillar, including more detailed XEDS elemental mapping of complex oxide scales and subsurface structure of the valve surface that wears against the seat. Caterpillar sent additional valves and fresh seats this quarter for aging and microanalysis to complement the first data set.

Technical Progress, 2nd Quarter, FY2008

Background

This is a new ORNL CRADA project with Caterpillar NFE-07-00995 and DOE OVT Agreement 16304 that began last quarter, and will last for about 2.5 years. This CRADA project is focused on addressing the wear and failure modes of current on-highway heavy-duty diesel exhaust valves and seats, and then on evaluating changes in valve-seat design and/or advanced alloys that enable higher temperature capability, as well as better performance and durability. The need for such upgraded valve-seat alloys is driven by the demands to meet new emissions and fuel economy goals which continue to push diesel exhaust component temperature higher. Requests for more detailed information on this project should be directed to Caterpillar, Inc.

Approach

Caterpillar will provide and analyze the baseline wear and mechanical behavior characteristics of engine-exposed valves and seats, and similar exposure of those components to laboratory simulation-rig testing at Caterpillar. ORNL will provide more in-depth characterization and microcharacterization of those valves and seats. Data will provide the basis for selecting and testing valve and seat alloys with upgraded performance. Caterpillar and ORNL will work with Caterpillar's various component or materials suppliers so that potential solutions are commercially viable, and so that prototype components are readily available for Caterpillar's test rig or diesel engine evaluation.

Technical Progress – Caterpillar, Inc.

The CRADA began last quarter. Caterpillar completed their initial testing and characterization on an initial set of exhaust valves and their matching seats in the "Buettner Rig" for engine simulation wear testing with controlled testing conditions (i.e., iso-thermal) at the Caterpillar Technical Center. Caterpillar has also obtained similar valves and seats with long-term wear from various diesel engines, and characterized those to provide a baseline for correlation with the rig-tested components. Caterpillar then provided fresh exhaust valves and seats to match with those wear-tested in the lab-test rig or from engine-service to ORNL for further microstructural and mechanical characterization and analyses. Caterpillar provided additional fresh valve and seat components this quarter, for ORNL to age or expose these materials in air, to provide baseline non-wear surfaces to compare with the valve and seats surfaces experiencing significant wear during testing. Caterpillar also facilitated new dialogue and data exchange between the participants of this project and their major seat-insert supplier.

Technical Progress – ORNL

ORNL completed the initial microcharacterization evaluation of the various fresh and engine-exposed or test-rig worn valve components supplied by Caterpillar last quarter, and began similar microanalysis of the seat-insert components this quarter. ORNL aged pieces of fresh valve and seat components in air to provide non-wear control specimens to show surface oxidation and sub-surface aging microstructures, for direct comparison to the various heavily-worn component surfaces. This effort will continue next quarter.

Communications/Visits/Travel

Detailed team communications between ORNL and Caterpillar occur regularly in multi-party conference calls. Caterpillar has extended team discussions to include their commercial seat-insert supplier.

Status of Milestones (ORNL for DOE)

New CRADA project that started this quarter.

Publications/Presentations/Awards

None – new CRADA project in FY2008.

Agreement 13329: Mechanical Reliability of Piezo-Stack Actuators

H.-T. Lin, A. A. Wereszczak, and H. Wang
Oak Ridge National Laboratory

Objective/Scope

Enable confident utilization of piezo stack actuator in fuel injectors for heavy vehicle diesel engines. The use of such actuators in diesel fuel injectors has the potential to reduce injector response time, provide greater precision and control of the fuel injection event, and lessen energy consumption. Though piezoelectric function is the obvious primary function of lead zirconium titanate (PZT) ceramic stacks for fuel injectors, their mechanical reliability can be a performance and life limiter because PZT is both brittle, lacks high strength, and is susceptible to fatigue. However, that brittleness, relatively low strength, and fatigue susceptibility can be overcome with the use of appropriate probabilistic design methods.

Technical Highlights

This project combines in-situ micromechanical testing, microstructural-scale finite element analysis, probabilistic design sensitivity, structural ceramic probabilistic life prediction methods, and innovative accelerated test methods to systematically characterize and optimally design PZT piezoelectric stack actuators that will enable maximized performance and lifetime in diesel fuel injectors.

The development and adaptation of accelerated test methods continued and software was installed that will enable controlled increases in applied voltage amplitudes as a function of time. It is being used with our existing actuator test facility.

Designs for a “piezo dilatometer” were completed and its parts are undergoing fabrication. It will be used to measure expansion of piezoceramics as a function of applied voltage and also enable the study of changes in that expansion under high voltages.

Additional fatigue tests involving a lead zirconate titanate (PZT) multilayer actuator with a plate-through electrode configuration continued under an electric field (1.7 times that of a coercive field of PZT material) and a concurrent mechanical preload (30 MPa). For the first test, a total of one billion cycles were carried out on the actuator; at 50 Hz (taking approximately 8 months to accumulate that many cycles). Variations in charge density and mechanical strain under a high electric field and constant mechanical loads were observed. The dc and the first harmonic (at 10 Hz) dielectric and piezoelectric coefficients were subsequently characterized by using fast Fourier transformation. The intent behind the present (shorter-term) tests is to better understand transient changes in piezoactuation response that occurred in the 1B cycle test.

Final steps were completed for the formation of a three-year CRADA with Cummins. Its start is anticipated at the beginning of the Q4 FY08.

Status of FY 2008 Milestones
Measure and compare reliability of competing commercially available piezoactuators under consideration for use in diesel fuel injectors. [09/08] *On schedule.*

Communications/Visits/Travel
Lin and Wereszczak had a conference call with staff of Cummins Inc. (Columbus, IN) on 12 Feb 08 to discuss piezoactuator issues.

Problems Encountered
None.

Publications/Presentations/Awards
A manuscript submitted to the *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* entitled "Effects of Electric Field and Biaxial Flexure on the Failure of Poled Lead Zirconate Titanate," H. Wang and A. Wereszczak, December 2007, is under review.

A manuscript entitled "Fatigue Response of a PZT Multilayer Actuator under High-Field Electric Cycling with Mechanical Preload" by H. Wang, A. A. Wereszczak, and HT Lin, was submitted to the *Journal of Applied Physics* and is under review.

References
None.

Agreement 13332: Friction and Wear Reduction in Diesel Engine Valve Trains

Peter Blau
Oak Ridge National Laboratory

Objective/Scope

The objective of this effort is to enable the selection and use of improved materials, surface treatments, and lubricating strategies for value train components in energy-efficient diesel engines. Depending on engine design and operating conditions, between 5 and 20% of the friction losses in an internal combustion engine are attributable to the rubbing between valve train components. Moreover, wear and consequent leaks around valve seats can reduce cylinder pressure and engine efficiency while leading to increased emissions and material wastage. This effort focuses on understanding the complex wear processes in diesel engine exhaust valves and seats, and applies that knowledge to help engine designers in selecting materials and surface treatments for increased reliability and reduced engine emissions.

FY 2007 witnessed the completion of a high-temperature repetitive impact (HTRI) testing system that is capable of testing the surface durability of candidate exhaust valve materials at engine temperatures. In FY 2008, a three-pronged approach was initiated to investigate the role of wear plus oxidation on the durability of valve material surfaces and apply that understanding to practical engine materials selection. The three prongs are: (1) conducting studies of the effects of surface damage on the growth and repair of oxide scales on contact surfaces exposed to exhaust temperatures, (2) investigating the wear characteristics of selected Fe-, Ni-, and Co-base alloys in the HTRI apparatus built in FY 2007, and (3) developing a multi-component, materials-based model for valve recession that contains the effects of mechanical damage, oxide formation, and adhesive transfer. Information is being shared on a continuing basis with a U.S. diesel engine manufacturer who has also supplied production-grade valves for study.

Technical Highlights

Experiments on the Healing of Oxide Scales after Abrasion. The materials used in engine exhaust valves and their mating valve seats must operate in an abusive environment. They are exposed to a combination of high ambient temperatures, oxidation by hot gases, and mechanical contact that eventually produces surface deformation and wear. The hotter a valve gets, the faster the surface reacts with the surrounding environment and the faster an engine runs, the higher the frequency of impacts that the valve sealing surfaces must withstand. Metallurgical changes also occur within the valve and seat alloys, and alloying elements diffuse more quickly as temperature rises. In order to model the valve wear process and begin to estimate service life, one must understand the conjoint role of oxidation plus wear. During this quarter, a series of experiments was begun to investigate whether the oxide that forms on mechanically damaged surfaces of high-temperature alloys, like those used in valves, differs in composition and properties from an oxide that forms on the surface without the effects of prior mechanical damage.

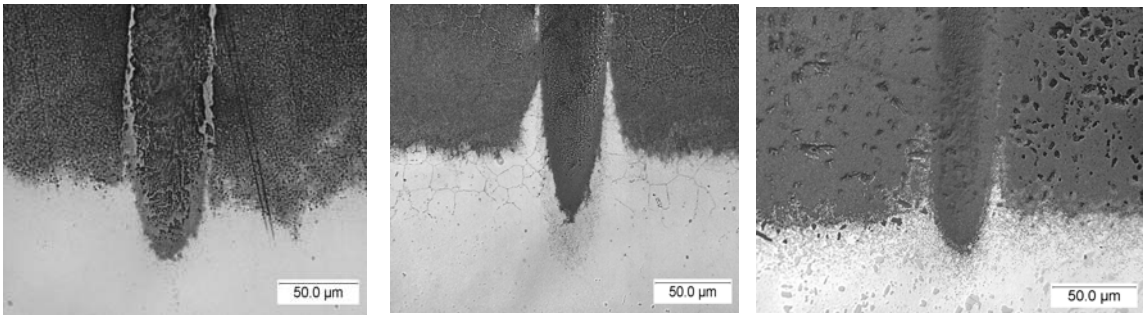
To study the effects of composition on the rehealing of oxide scale damage a series of tests of Fe, Ni, and Co-based alloys was undertaken. The commercial designations and nominal compositions of the three alloys are given in Table 1. Custom 465 is a martensitic Fe-base, age-hardenable alloy designed for corrosion resistance, Pyromet 80A is Ni-based, oxidation resistant alloy with creep-resisting properties, and Stellite 6B is a Co-based, superalloy used for corrosion- and wear-resistance.

Table 1. Composition (wt. %) and Vickers Microindentation Hardness of Specimen Materials

Element	Stellite 6B*	Pyromet 80A**	Custom 465**
Fe	2.65	0.75	bal. (~74.)
Ni	2.48	bal. (~ 74.)	10.75 – 11.25
Co	bal. (~ 58)	1.00	-
Cr	29.8	20.00	11.00 – 12.50
Mn	1.46	0.35	0.25 (max.)
Mo	0.06	-	0.75 – 1.25
Si	0.55	0.35	0.25 (max.)
Ti	-	2.35	1.50 – 1.80
Cu	-	0.05	-
Al	-	1.25	-
W	3.78	-	-
C	1.02	0.06	0.02 (max.)
S	< 0.01	0.007	0.010 (max.)
P	< 0.01	-	0.015 (max.)

* ASM Handbook, Desk Edition, 2nd ed. (1998)
** Carpenter Technology Corp., data.

After polishing, test coupons of the three alloys were oxidized for two hours at 850°C, a surface temperature typical of some diesel engine exhaust valves. Then scratches were made on their scale-covered surfaces and they were hardness-tested. Subsequently, they were replaced into the furnace for another four hours to investigate whether the oxide composition on the damaged areas was different than that adjacent to the damage, on the surfaces that had been exposed to air for six hours. A special metallographic technique, called taper-polishing, was used to reveal the structure of the scratching damage as well as the adjacent oxide scales. Images of scratches on the three alloys are shown in Figures 1(a), (b), and (c). During the next period, surface chemical analyses of these scratches and the surrounding oxides will be performed to study the effects of surface damage and scale removal on re-oxidation.



(a) Custom 465 (b) Pyromet 80A (c) Stellite 6B

Figure 1. Taper-polished cross-sections of scratches that were made on oxide scales and then subjected to further oxidation at 850°C. (*Note*: Due to the 5-degree tilt of the taper polish, the dimensions of features the vertical direction are effectively enlarged by a factor of 10X.)

Future Plans

1) Perform surface compositional analyses of oxidized Fe-, Ni-, and Co-based alloys that were subjected to damage and then re-oxidized, then prepare a journal article to complete Milestone (1) listed below.

2) Continue high-temperature repetitive impact tests.

Travel

None

Status of Milestones

1) Complete experiments on the effects of surface damage on oxide formation and prepare a paper for journal submission. **(03/08,** delayed until **6/08** pending compositional analysis**)**

2) Submit a final report that summarizes wear studies on candidate valve materials and presents a model for valve seat recession. **(09/08)**

Publications and Presentations

None

Agreement 9089: NDE of Diesel Engine Components

J. G. Sun and N. Phillips*
Argonne National Laboratory

***Caterpillar, Inc.**
Technical Center

Objective/Scope

Emission reduction in diesel engines designated to burn fuels from several sources has lead to the need to assess ceramic valves to reduce corrosion and emission. The objective of this work is to evaluate several nondestructive evaluation (NDE) methods to detect defect/damage in structural ceramic valves for diesel engines. One primary NDE method to be addressed is elastic optical scattering. The end target is to demonstrate that NDE data can be correlated to material damage as well as used to predict material microstructural and mechanical properties. There are two tasks to be carried out: (1) Characterize subsurface defects and machining damage in flexure-bar specimens of NT551 and SN235 silicon nitrides (Si_3N_4) to be used as valve materials. Laser-scattering studies will be conducted at various wavelengths using a He-Ne laser and a tunable-wavelength solid-state laser to optimize detection sensitivity. NDE studies will be coupled with examination of surface/subsurface microstructure and fracture surface to determine defect/damage depth and fracture origin. NDE data will also be correlated with mechanical properties. (2) Assess and evaluate surface and subsurface damage in Si_3N_4 and TiAl valves to be tested in a bench rig and in an engine. All valves will be examined at ANL prior to test, during periodic scheduled shut downs, and at the end of the planned test runs.

Technical Highlights

Work during this period (January-March 2008) focused on development of data processing software to improve the quality and accuracy of acquired laser-scatter valve images and on NDE evaluation of a set of Si_3N_4 specimens machined by laser-assisted machining.

1. Laser-Scatter NDE Evaluation of Engine-Tested Valves

The ANL-developed laser-backscatter valve-scan system has been successfully utilized for high-speed inspection of the entire surface/subsurface of a Si_3N_4 or TiAl engine valve. To achieve high-speed operation, the data acquisition rate is synchronized with the motion of the valve surface that is at a constant-speed rotation. However, while the data acquisition rate is maintained accurately by a data-acquisition board, the speed of the valve rotation typically varies depending on the friction condition within the lathe support (bearing) that couples the rotation-stage shaft to the valve chuck (see Fig. 1). Friction is a function of many parameters, including load, room temperature, speed, out-of-use duration, etc. and is difficult to control. As a result, the number of total pixels acquired for each valve revolution may not exactly match the length of the surface circumference. This causes the final laser-scatter image to be skewed, as seen

in Fig. 2a. In this case, the skew is from top-left to bottom-right, which corresponds to a reduced speed of the rotation stage (due to higher friction in the lathe support bearing). The skew does not affect characterization of the size and shape of the detected subsurface flaws, but may alter the relative positions of the flaws on the valve surface.

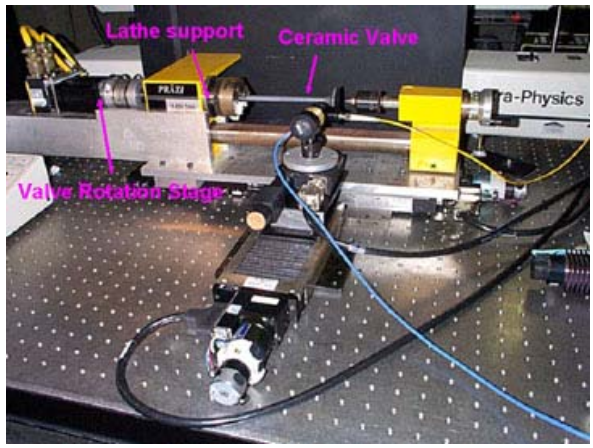
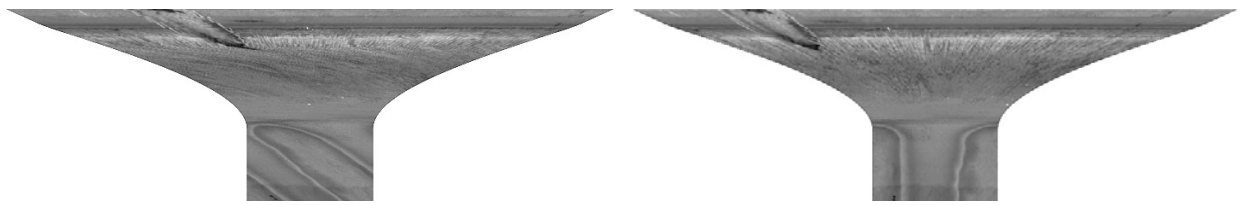


Fig. 1. Laser-scatter valve scan system.

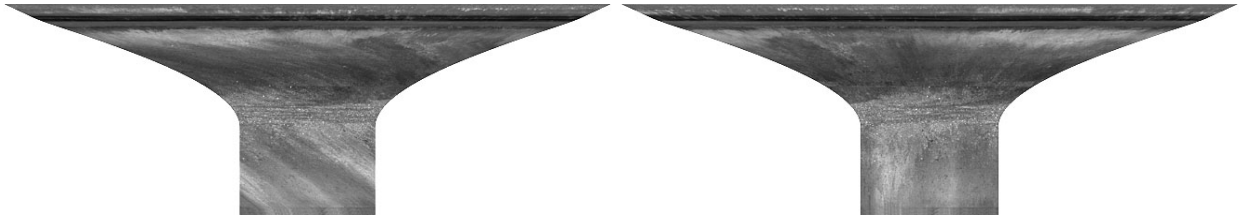


(a) (b)

Fig. 2. Laser-scatter scan images of intake valve I#12 at end of engine test: (a) before correction, (b) after skew correction.

Effort during this period was directed to resolve this problem so the dimensions and positions of surface/subsurface flaws can be accurately determined from the NDE images. One way to achieve this is to implement a skew correction scheme in the image processing codes that derive the final laser-scatter image from the raw scan data. Because each scan for a valve revolution starts from a random beginning point, the alignment of consecutive scan lines is obtained by a cross-correlation matching operation. The following skew-correction scheme was then designed into this operation to optimize the matching. If the scanned length is shorter than the valve circumference, dummy pixels are added to fill the remaining length. The added dummy pixels will not affect the image quality and data accuracy because they are located in random positions in the final image (due to the random start of each scan line) and the width of each scan line is typically <10 µm. On the other hand, excess pixels may be removed from the acquired data if the scan-line length is longer than the valve circumference. This skew-correction scheme has been implemented in the cross-correlation image processing code which was used to reprocess the laser-scatter images for all Si_3N_4 valves after the end of the engine test. Figure 2b shows the reprocessed image of valve I#12. Compared with the un-corrected image in Fig. 2a, the corrected image

in Fig. 2b shows a perfect alignment of scan lines along the axial direction over the entire valve-head surface. Another example is shown in Fig. 3, the laser-scatter image for valve E#1 at before and after the correction. In general, dummy pixels accounting to ~1% of the total number of pixels were appended to each scan line for these images.



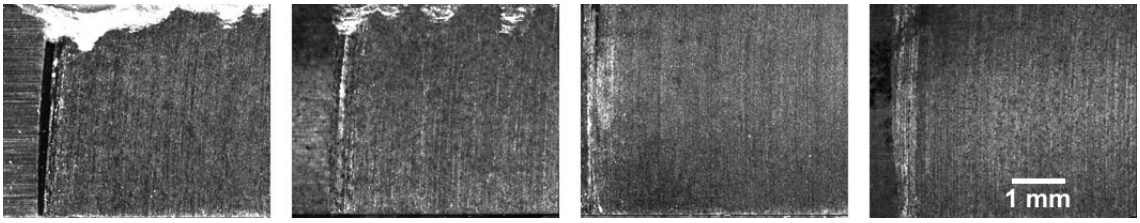
(a) (b)

Fig. 3. Laser-scatter scan images of exhaust valve E#1 at end of engine test: (a) before correction, (b) after skew correction.

2. Laser-Scatter Evaluation of Si_3N_4 Surfaces Machined by Laser Assisted Milling

Laser assisted machining (LAM) of structural ceramics has attracted considerable amount of research to further understand the complex process and to demonstrate LAM's viability as an economical industrial machining process for ceramics. It has been shown that laser heating induces plastic behavior for ceramics, which facilitates the generation of longer chips, decreased cutting force, and reduced surface/subsurface damage as compared to grinding. As a result, LAM may produce stronger machined ceramic parts with significant cost reduction.

Dr. S.T. Lei of Kansas State University is investigating laser assisted milling for silicon nitrides to address its technical and economical benefits under a NSF sponsored grant. He has requested ANL to perform laser-scatter NDE evaluation for machining induced subsurface damages in a set of 13 laser-assisted-milled (LAMilled) specimens (MOR bars of 4mm wide and 50mm long). These specimens were machined within the typical ranges of several machining parameters, including laser-heating temperature, depth of cut, feed rate, and cutting speed. Figure 4 shows laser-scatter images of 4 LAMilled specimens machined with different laser-heating temperatures. It is evident that exit edge shipping (on top edge of the images) significantly reduced at higher temperatures. However, the level of subsurface damage appears to be the weakest (i.e., less high-scatter-intensity lines) at the temperature of 1349°C. The depth and severity of subsurface damage could be assessed more accurately using 3D confocal microscopy or optical coherence tomography systems at ANL.

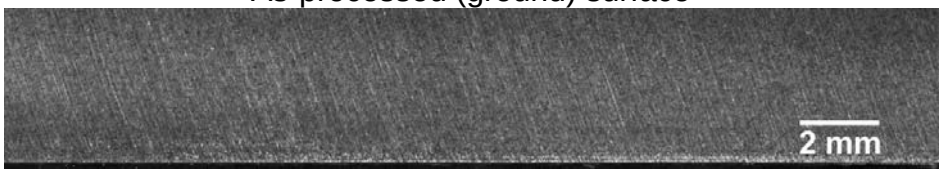


T = 838°C 1172°C 1349°C 1595°C

Fig. 4. Laser-scatter images of LAMilled Si_3N_4 surfaces with various heating temperatures.

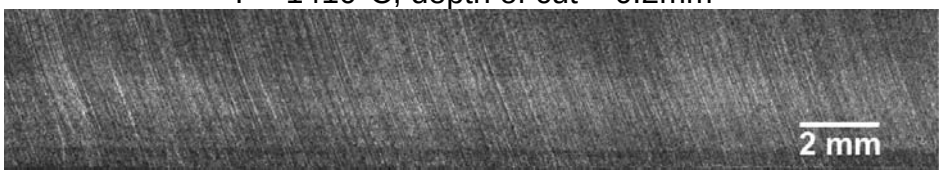
Figure 5 shows laser-scatter images of an as-processed (ground) surface and 3 LAMilled surfaces with different cutting depths. It is apparent that the LAMilled surfaces exhibit a different subsurface damage pattern than that in the ground surface: there is a generally higher level of laser-scatter intensity and less distinct machining-damage lines in the LAMilled surfaces. In general, deeper cut resulted in more severe subsurface damage, shown as high-scatter-intensity lines in the images.

As-processed (ground) surface



T = 1605°C, depth of cut = 0.05mm

T = 1410°C, depth of cut = 0.2mm



T = 1433°C, depth of cut = 0.4mm

Fig. 5. Laser-scatter images of as-processed and LAMilled Si_3N_4 surfaces machined with various depth of cut conditions.

Status of Milestones

Current ANL milestones are on schedule.

Communications/Visits/Travel

Dr. S. T. Lei of Kansas State University visited ANL on Dec. 14, 2007 to discuss collaborative work on NDE evaluation of LAM Si_3N_4 surfaces for cost-effective machining studies.

J. G. Sun presented a paper entitled "Optical Methods for Nondestructive Evaluation of Subsurface Flaws in Silicon Nitride Ceramics" at the 32nd International Conference & Exposition on Advanced Ceramics and Composites held in Jan. 27-Feb. 1, 2008 in Daytona Beach, FL.

J. G. Sun visited Caterpillar, Inc. on Feb. 7, 2008 to discuss project progress and direction.

J. G. Sun participated the DOE Vehicle Technologies Annual Merit Review Meeting held in Feb. 25-28, 2008 in Bethesda, MD.

Problems Encountered

None this period.

Publications

J. G. Sun, J. M. Zhang, M. J. Andrews, J. S. Trethewey, N. S. L. Phillips, and J. A. Jensen, "Evaluation of Silicon-Nitride Ceramic Valves," Int. J. Appl. Ceram. Technol., Vol. 5, pp. 164-180, 2008.

Agreement 15050: Materials-enabled High Performance Diesel Engines

M. D. Kass, T. J. Theiss, and H. T. Lin
Oak Ridge National Laboratory

Objective/Scope

This project is focused on improving the performance, emissions and efficiency of heavy-duty diesel engines through the application of materials enabled technologies. The range of material systems is comprehensive and includes 1) improved structural materials to accommodate higher cylinder pressures and temperatures, 2) improved durability and corrosion resistance, 3) low inertial components to improve transient response, 4) improved emissions aftertreatment performance, and 5) waste heat recovery systems.

Highlights

ORNL received $900K of internal funding to construct an additional heavy duty engine-dynamometer test cell. The supporting infrastructure is being procured along with the instrumentation. ORNL and Caterpillar have discussed potential areas of interest and a timeline is being devised for baseline experimentation.

Technical Progress, 2nd Quarter, FY2008

Background

ORNL and Caterpillar are engaged in discussions to establish a CRADA in 2008 focusing on materials-enabled advancements to heavy duty diesel engines. Caterpillar has provided ORNL with a 2005 C-15 ACERT engine and two 600 hp DC motoring dynamometers to support this activity. Materials scientists at Caterpillar are working with their engine/combustion research staff to develop a pathway to combine materials expertise with engine research and development needs. A research team at ORNL comprising engine/combustion staff with materials scientists has held several discussions with Caterpillar staff to address issues and potential concerns. To help move this effort forward the Fuels, Engines, and Emissions group received $900K of internal support to setup an engine test cell, dedicated to this effort, in a vacant room located at the NTRC building. Building modifications and equipment procurement has been initiated. The test cell is scheduled to be available for use in June 2008.

Approach

This unique activity will incorporate the materials research and engine/combustion expertise at Oak Ridge National Laboratory to investigate potential materials enabling technologies for heavy-duty diesel engines. Caterpillar has provided a C-15 ACERT engine for this effort and has also contributed two dynamometers. Caterpillar will provide technical support and oversight. Caterpillar engineers will also define the operating parameters to be studied. The specifics and details of the CRADA are currently being negotiated. Caterpillar and ORNL will work with Caterpillar's various component or materials suppliers so that potential solutions are commercially viable.

Communications/Visits/Travel

A team of ORNL researchers met with staff from the Caterpillar Engines Research group led by Dave Milam. The CRADA was discussed in the context of incorporating the Engine Research group into the CRADA with the Materials Technology group. Dave Milam agreed to partner on this effort and will be contributing to the in-kind contribution through technical support and hardware necessary to establish a research engine at ORNL.

Status of Milestones (ORNL for DOE)

New CRADA project being negotiated.

Publications/Presentations/Awards

Mike Kass gave a presentation entitled “Materials-enabled High Efficiency Diesel Engines” at the DOE Annual Merit Review.

Agreement 9130: Development of Materials Analysis Tools for Studying SCR Catalysts

Thomas Watkins, Larry Allard, Michael Lance, Harry Meyer and Larry Walker
Oak Ridge National Laboratory

Krishna Kamasamudram, Cheryl Klepser and Alex Yezerets
Cummins Inc.

Objective

The objective of this effort is to produce a quantitative understanding of the interdependence between structure and performance to develop options for an exhaust after treatment system with improved final product performance in order to meet the US Environmental Protection Agency emissions requirements for 2010 and beyond.

Technical Progress

Plans were made to hydrothermally age a commercial Fe-zeolite powder between 500-900°C for different times (between 1-100 hours) at a space velocity of 40000 lit/lit/h. The atmosphere will be 10% H_2O, 18% O_2 and 72% N_2. Catalyst aging will be followed by in situ X-ray diffraction (XRD) characterization. The in situ or ex-situ aged powder catalysts will be further analyzed with transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman Spectroscopy and infrared spectroscopy (IR). The potential to do or obtain nuclear magnetic resonance (NMR) measurements to study the de-alumination of the hydrothermally aged zeolite powder is being investigated.

Meeting

Alex Yezerets gave a presentation titled “Catalyst Characterization, CRADA No. ORNL-02-0659 with Cummins Inc.” at the FY 2008 DOE Vehicle Technologies Program Annual Merit Review held at the Bethesda North Marriott Hotel and Conference Center on Monday February 25, 2008.

Agreement 10461: Durability and Reliability of Ceramic Substrates for Diesel Particulate Filters

Amit Shyam, Thomas R. Watkins and Edgar Lara-Curzio
Oak Ridge National Laboratory

Objectives/Scope

To develop/implement test methods to characterize the physical and mechanical properties of ceramic diesel particulate filters (DPFs), and to implement a probabilistic-based analysis to quantify their durability and reliability.

Highlights

- The mechanical and thermal shock characteristics of a field tested diesel particulate filter (135,000 miles) were characterized and compared to a virgin filter.
- Implications of the spatial variation in properties on the reliability of DPFs are identified.

Technical Progress

The mechanical reliability of engineering systems is determined by the intersection of the operating stress distribution with the mechanical strength distribution of the component material. DPFs fabricated from porous cordierite have a complex microstructure with microcracks that can heal themselves during high temperature operation and reopen during subsequent cooling. This microstructural phenomenon makes the mechanical properties of the DPF a dynamic property which can change as a result of the operating service history. It is therefore, of interest to characterize the mechanical and thermal shock characteristics of filters that have been returned from field service in order to refine the lifetime prediction procedure for DPFs. The results from such characterization are reported.

A high mileage filter was removed from service during a routine upfit of test hardware and obtained for analysis. The filter was fully functional and showed no evidence of abuse or loss of filtration efficiency. The high mileage filter was characterized by Cummins via time-of-flight ultrasound techniques (pulse echo mode). The filter was sectioned in half and one half sent to Oak Ridge National Laboratory. The ultrasound test results on the ORNL section are shown in Figure 1. The circled numbers, ”apparent length”, in Figure 1 indicate the time a sound pulse took to go through various regions of the filter converted to apparent length of the filter in inches. The difference in the apparent lengths in Figure 1 indicates the change of the relative properties of the core and the outer regions of the filter. Specimens for mechanical and thermal expansion evaluation were evaluated from the two different regions of the filter with the highest and the lowest time of travel. These regions are labeled C13 and C19 in Figure 1. The relative co-ordinates of the specimens prepared for thermal expansion and mechanical property evaluation were carefully documented within the filter.

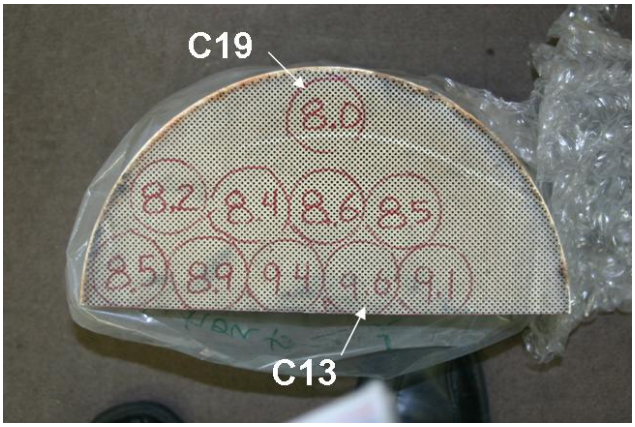


Figure 1. The half-cross section of a high mileage DPF. The numbers indicate the apparent length in inches by the amount of time sound waves took to travel longitudinally though a specific region of the filter.

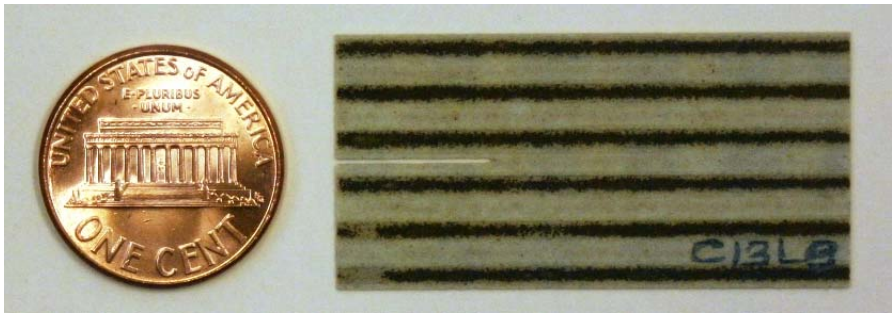


Figure 2. A double-torsion specimen prepared from a high mileage filter. The alternate dark lines are due to soot loading on the inlet channels of the filter.

The coefficient of thermal expansion (CTE in 20-1000°C), fracture toughness and elastic modulus of specimens from the high mileage filter were characterized. Figure 2 is an image of a double-torsion specimen prepared from a high mileage filter. The values of the properties for specimens from the C13 region (core – highest time of flight) and the C19 region (circumference – lowest time of flight) are reported and compared to a similar virgin filter substrate material in Table 1. A single test was performed for elastic measurements by resonant ultrasound spectroscopy (RUS) and thermal expansion along directions that are parallel and perpendicular to the extrusion direction. Five tests were conducted for fracture toughness measurements by the double-torsion methodology and the average and standard deviation of the values are reported. The density values of the 0.275 $\pm$ 0.005 mm thick double torsion specimens before notching are also reported in Table 1. Since the density of the substrate is also related to the soot loading, the corresponding porosity is not reported. Procedures for the above mentioned characterization techniques have been reported in FY07.

Table 1. The comparative thermal expansion, elastic modulus and fracture toughness of a virgin DPF and specimens from two regions of a high mileage DPF.

Material	**Parallel CTE** (ppm/K)	**Perpendicular CTE** (ppm/K)	**Average CTE** (ppm/K)	**Elastic Modulus** (GPa)	**Fracture Toughness** (MPa√m)	**Density** (g/cc)
Virgin (not coated)	0.21	0.63	0.42	11.91±0.15	0.32±0.04	1.19±0.02
C13 coated	0.71	1.23	0.97	10.74±0.29	0.35±0.03	1.19±0.03
C19 coated	0.36	1.09	0.73	12.84±0.37	0.40±0.02	1.23±0.02

The elastic properties of the specimens from the high mileage filter are of interest for determining the thermal shock characteristics of the filter. It is to be noted that the elastic modulus of the material in the core region (C13) is about 20 % lower than the elastic modulus of the outer region (C19). This is consistent with a 20 % higher time of flight for the core region as shown in Figure 1. It is therefore, concluded that the microstructure of the core region changes as a result of the filter service environment with respect to the cooler outer region. The elastic modulus of the virgin filter substrate material which did not have a catalytic coating applied is in between the values for the core and outer regions of the filter. As shown in Table 1, the fracture toughness of the core region and the outer region of the filter are higher compared to the virgin material by 10 % and 20 %, respectively which may be related to the catalytic coating. In conclusion, as a result of the elevated temperature filter operating environment, the mechanical properties of the outer region of the filter (cooler section of the filter) do not show the same properties as the core region.

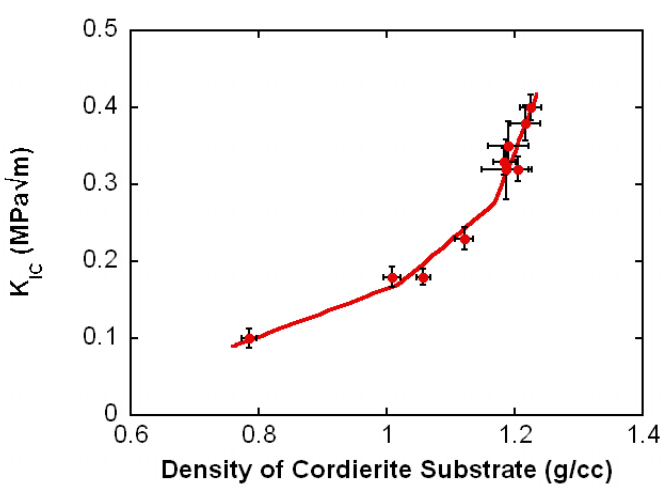


Figure 3. The fracture toughness of ten different cordierite substrates as a function of density of the substrate.

The changes in the spatial (and maybe temporal) characteristics of a DPF can be utilized to refine the lifetime prediction calculations. While the filter operating environment leads to slight changes in the mechanical characteristics, the overall trend is that of the fracture toughness being a function of the density of the substrate. This is demonstrated in Figure 3 where the fracture toughness of ten cordierite substrates with different levels of density is compared. The fracture toughness values increase with increasing density of the substrate. The variation of fracture toughness with density is consistent with results reported in FY07.

Publications

A. Shyam, E. Lara-Curzio, T.R. Watkins and R. J. Parten, "Mechanical characterization of diesel particulate filter (DPF) substrates" (accepted and in press - Journal of the American Ceramic Society).

Meetings

Bimonthly meetings with Cummins personnel were held during the reporting period.

Alex Yezerets gave a presentation titled "Durability of Diesel Engine Particulate Filters, CRADA No. ORNL-04-0692 with Cummins Inc." at the FY 2008 DOE Vehicle Technologies Program Annual Merit Review held at the Bethesda North Marriott Hotel and Conference Center on Monday, February 25, 2008.

Agreement 10635: Catalysis By First Principles - Can Theoretical Modeling And Experiments Play A Complimentary Role In Catalysis?

C. Narula, M. Moses, L. Allard
Oak Ridge National Laboratory

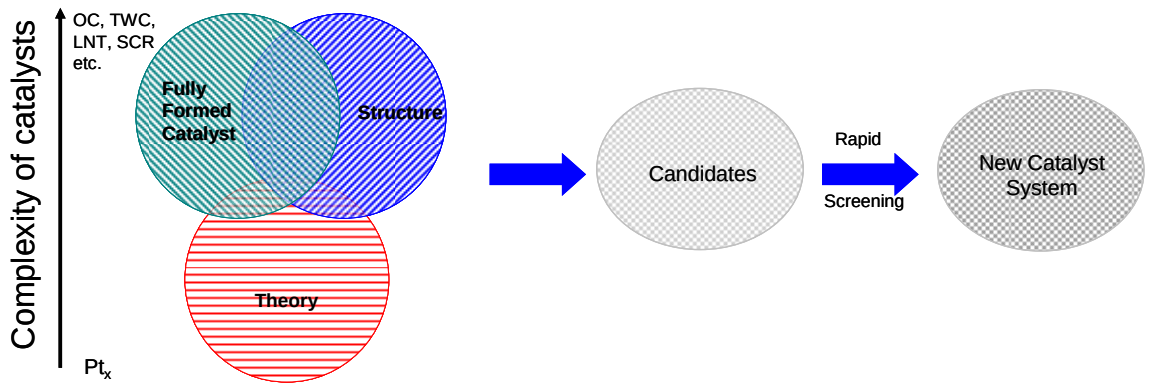
Objective/Scope

This research focuses on an integrated approach between computational modeling and experimental development, design and testing of new catalyst materials, that we believe will rapidly identify the key physiochemical parameters necessary for improving the catalytic efficiency of these materials. The results will have direct impact on the optimal design, performance, and durability of supported catalysts employed in emission treatment e.g. lean NO_x catalyst, three-way catalysts, oxidation catalysts, and lean NO_x traps etc.

The typical solid catalyst consists of nano-particles on porous supports. The development of new catalytic materials is still dominated by trial and error methods, even though the experimental and theoretical bases for their characterization have improved dramatically in recent years. Although it has been successful, the empirical development of catalytic materials is time consuming and expensive and brings no guarantees of success. Part of the difficulty is that most catalytic materials are highly non-uniform and complex, and most characterization methods provide only average structural data. Now, with improved capabilities for synthesis of nearly uniform catalysts, which offer the prospects of high selectivity as well as susceptibility to incisive characterization combined with state-of-the science characterization methods, including those that allow imaging of individual catalytic sites, we have compelling opportunity to markedly accelerate the advancement of the science and technology of catalysis.

Computational approaches, on the other hand, have been limited to examining processes and phenomena using models that had been much simplified in comparison to real materials. This limitation was mainly a consequence of limitations in computer hardware and in the development of sophisticated algorithms that are computationally efficient. In particular, experimental catalysis has not benefited from the recent advances in high performance computing that enables more realistic simulations (empirical and first-principles) of large ensemble atoms including the local environment of a catalyst site in heterogeneous catalysis. These types of simulations, when combined with incisive microscopic and spectroscopic characterization of catalysts, can lead to a much deeper understanding of the reaction chemistry that is difficult to decipher from experimental work alone.

Thus, a protocol to systematically find the optimum catalyst can be developed that combines the power of theory and experiment for atomistic design of catalytically active sites and can translate the fundamental insights gained directly to a complete catalyst system that can be technically deployed.



Although it is beyond doubt computationally challenging, the study of surface, nanometer-sized, metal clusters may be accomplished by merging state-of-the-art, density-functional-based, electronic-structure techniques and molecular-dynamic techniques. These techniques provide accurate energetics, force, and electronic information. Theoretical work must be based on electronic-structure methods, as opposed to more empirical-based techniques, so as to provide realistic energetics and direct electronic information.

A computationally complex system, in principle, will be a model of a simple catalyst that can be synthesized and evaluated in the laboratory. It is important to point out that such a system for experimentalist will be an idealized simple model catalyst system that will probably model a “real-world” catalyst. Thus it is conceivable that “computationally complex but experimentally simple” systems can be examined by both theoretical models and experimental work to forecast improvements in catalyst systems.

Our Goals are as follows:

- Our theoretical goal is to carry out the calculation and simulation of realistic Pt nanoparticle systems (i.e., those equivalent to experiment), in particular by addressing the issues of complex cluster geometries on local bonding effects that determine reactivity. As such, we expect in combination with experiment to identify relevant clusters, and to determine the electronic properties of these clusters.
- Our experimental goal is to synthesize metal carbonyl clusters, decarbonylated metal clusters, sub-nanometer metal particles, and metallic particles (~5 nm) on alumina (commercial high surface area, sol-gel processed, and mesoporous molecular sieve), characterize them employing modern techniques including Aberration Corrected Electron Microscope (ACEM), and evaluate their CO, NO_x, and HC oxidation activity.
- This approach will allow us to identify the catalyst sites that are responsible for CO, NO_x, and HC oxidation. We will then address support-cluster interaction and design of new durable catalysts systems that can withstand the prolonged operations.

Technical Highlights

Our results on experimental studies of Platinum-Alumina Systems and their nanostructural changes under NO-oxidation conditions are summarized in the following paragraphs. We have initiated our study of nanostructural changes in this catalyst system during hydrocarbon oxidation also.

Experimental Studies

NO Oxidation: We have exposed 1nm 2%Pt/γ-Al_2O_3 catalyst, prepared by the traditional impregnation method from $H_2PtCl_6 \bullet xH_2O$, to NO oxidation conditions to study the microstructural effects. Our fresh material contained monodispersed Pt particles ranging from 0.6 to 1.7 nm in diameter with an average size of 0.9 nm, see Figure 1.

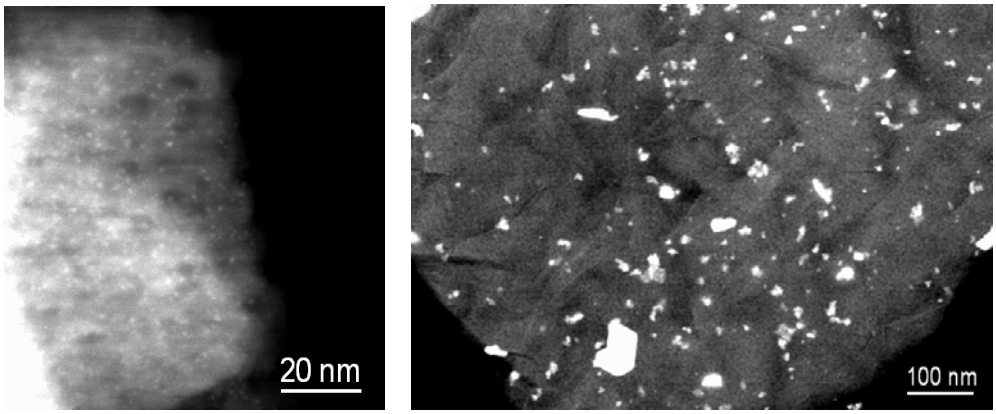


Figure 1. DF-STEM images of 2%Pt/γ-Al_2O_3 fresh (left) and after 2 cycles of NO oxidation to 650°C (White spots represent Pt).

The catalysts NO oxidation activity was evaluated at a space velocity of 50,000 h^{-1} by monitoring the concentration of NO and NO_2 every 50°C from 100-650°C, see Figure 2. NO oxidation is equilibrium limited by the reverse NO_2 reduction at higher temperatures, eq. 1. The sample was evaluated up to 650°C to confirm the temperature at which NO_2

$$NO + \tfrac{1}{2} O_2 \rightleftharpoons NO_2 \qquad \text{Eq. 1}$$

reduction becomes more favored. In the first cycle, NO oxidation initiated at ~250°C and increased through 400°C after which the reverse reduction reaction dominated, and the NO_2 production plummeted. However, during the 2nd NO oxidation cycle, oxidation occurred from 150° to 400°C before reversing. Microstructural changes were studied after the 2nd cycle in order to correlate them to the increase in the NO oxidation activity window seen in the second cycle.

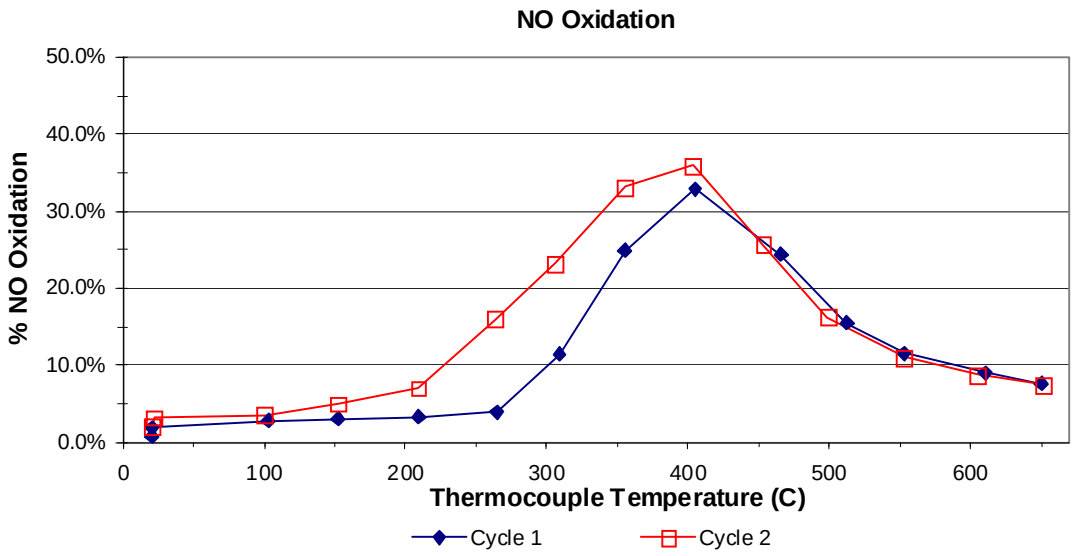


Figure 2. Percentage of NO_2 production as a function of time over a 1 nm 2%Pt/γ-Al_2O_3 catalyst for 2 cycles.

After cycling the 1nm Pt catalyst to 650°C under NO oxidation conditions (10%O_2/ 500ppm NO/ N_2 balance) twice, the particles had sintered to an average size of 10.4nm ranging from 2.8 to 48.9nm, see figure 1. Figure 3 shows the particles size distribution comparison to the starting material (fresh 1nm Pt) which highlights the significant sintering the accord. Also shown for comparison is the distribution of 2%Pt/γ-Al_2O_3 that had been annealed to 650°C/5h (fresh 12 nm Pt). The tested samples distribution is similar to that of the fresh 12nm Pt but shift 2nm lower suggesting the growth pattern observed is temperature related and not an effect of NO oxidation conditions The reverse NO_2 reduction process as a function of temperature were identical for both cycles, starting at 450°C and progressing comparable to 650°C, suggesting that the reverse reaction is not size limited but temperature limited.

Theoretical studies previously reported for this project have shown that O, CO, NO, CO_2, and NO_2 are more strongly adsorbed Pt nanocluster than bulk Pt. However, the studies indicated that if the Pt nanoclusters were oxidized that then the adsorption was weakened. Our experimental CO oxidation studies displayed greater CO oxidation activity on the smaller nanoclusters than the larger clusters. Suggesting that the nanoclusters were Pt-oxides since the CO_2 formation and desorption is exothermic every step along the reaction path regardless if Pt is a nanocluster or bulk material.

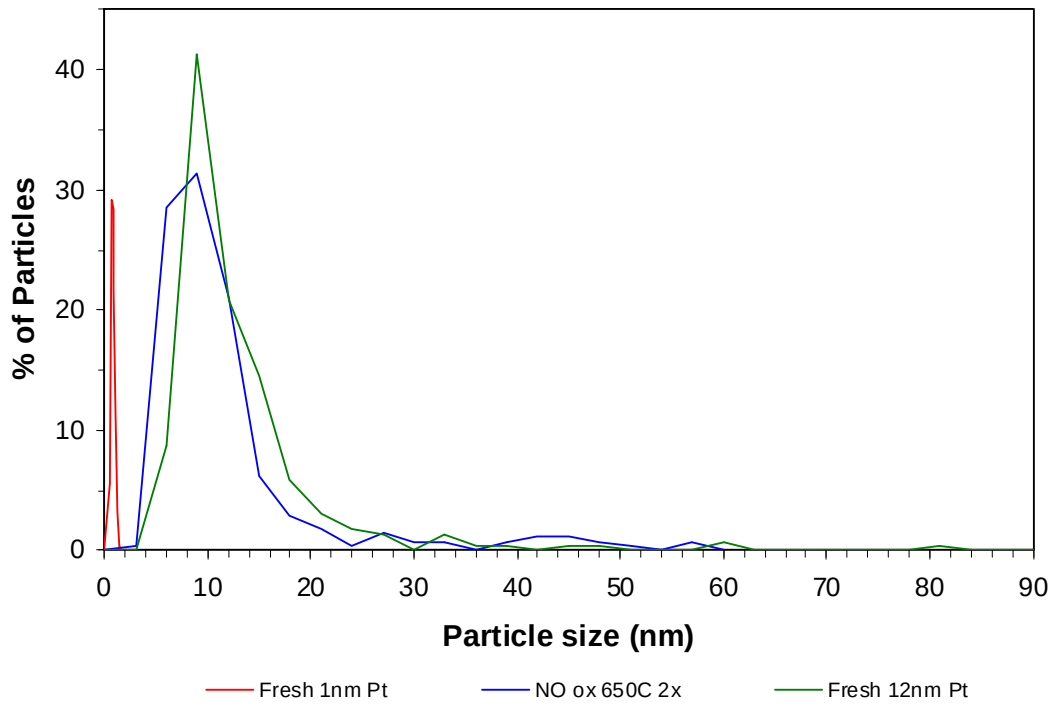


Figure 3. Particle size distribution of fresh 1 nm 2%Pt/γ-Al_2O_3, after 2 cycles of NO oxidation up to 650°C and fresh 12 nm 2%Pt/γ-Al_2O_3 catalyst.

On the other hand, DFT studies show that the NO_2 formation and desorption energies on Pt nanocluster is significantly more endothermic compared to bulk Pt(111). Our experimental results reported here show the Pt nanoclusters being less active for NO oxidation than the larger Pt clusters. This result suggest that for NO oxidation the weaker NO and O adsorption strength on the oxidized Pt is not sufficient to over come the increased endothermic reaction path for smaller Pt nanocluster.

Next Steps: We plan to carry out the following tasks:

- We will carry out NO_x and HC oxidation on catalyst and monitor nanostructural changes in catalyst samples. We will also correlate the results with theoretical studies.

- We will continue to investigate the thermal chemistry of CO and NO oxidation on free Pt and Pt oxide clusters as well as the properties of Pt and Pt oxide clusters supported on metal oxides (include magnesia and alumina). These investigations will help us gain a better understanding of the structural and catalytic properties of the supported Pt clusters and identify the effect of the support on these important properties.

Other Activities

A joint project on lean NO_x treatment is on going with John Deere Co. under work for others arrangement.

Communication/Visitors/Travel

C.K. Narula presented a talk titled "Bridging the Gap between Theory and Experiments – Nano-structural Changes in Supported Catalysts under Operating Conditions" at SAE 2008 World Congress, April 14-17, Detroit, MI.

Publications

1. C.K. Narula, "Catalyst by Design – Bridging the Gap between Theory and Experiments at Nanoscale Level" Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008 (invited).
2. C.K. Narula, L.F. Allard, D.A. Blom, M. Moses-DeBusk, "Bridging the Gap between Theory and Experiments – Nano-structural Changes in Supported Catalysts under Operating Conditions" SAE-2008-01-0416.
3. C.K. Narula, L.F. Allard, D.A. Blom, M.J. Moses, W. Shelton, W. Schneider, Y. Xu, "Catalysis by Design - Theoretical and Experimental Studies of Model Catalysts", SAE-2007-01-1018 (invited).
4. C.K. Narula, M.J. Moses, L.F. Allard, "Analysis of Microstructural Changes in Lean NO_x Trap Material Isolates Parameters Responsible for Activity Deterioration" SAE 2006-01-3420.
5. Y. Xu, W.A. Shelton, and W.F. Schneider, "The thermodynamic equilibrium compositions, structures, and reaction energies of Pt*x*O*y* (*x* = 1-3) clusters predicted from first principles," *Journal of Physical Chemistry B,* 110 (2006) 16591.
6. Y. Xu, W. A. Shelton, and W. F. Schneider, "Effect of particle size on the oxidizability of platinum clusters," *Journal of Physical Chemistry A*, 110 (2006) 5839.
7. C.K. Narula, S. Daw, J. Hoard, T. Hammer, "Materials Issues Related to Catalysts for Treatment of Diesel Exhaust," *Int. J. Amer. Ceram. Tech*., 2 (2005) 452 (invited).

Presentations (last 12 months)

1. Narula, C.K.; Allard, L.F.; Blom, D.A.; Moses-DeBusk, M.; "Bridging the Gap between Theory and Experiments – Nanostructural Changes in Supported Catalysts under Operating Conditions", Society of Automotive Engineers – World Congress, April 2008 (invited).
2. Narula, C.K.; Moses, M.J.; Xu, Y.; Blom, D,A,; Allard, L.F.; Shelton, W.A.; Schneider, W.F.; 'Catalysis by Design – Theoretical and Experimental Studies of Model Catalysts', Nanomaterials for Automotive Applications, Society of Automotive Engineers – international Congress, March 2007 (invited).
3. Blom, D.; Allard, L.; Narula, C.; Moses, M.; "Aberration-Corrected STEM ex-situ Studies of Catalysts" 8/8/07 Wednesday, Microscopy and Microanalysis Meeting, 2007, August 5-9, Ft. Lauderdale, Florida. (Invited).
4. Narula, C.K.; Moses, M.J.; Blom, D,A,; Allard, L.F.; 'Catalysis by Design – Bridging the Gap Between Theory and Experiments– DEER 2007, Detroit, MI

5. Allard, L.F.; Blom. D.A.; Narula, C.K.; Bradley, S.; Catalyst Characterization via Aberration-Corrected STEM Imaging, 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007
6. Blom, D.A.; Moses, M.; Narula, C.K.; Allard, L.F.; Aberration-Corrected STEM Imaging of Ag/Al2O3 Lean NO_x Catalyst, 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007
7. Narula, C.K.; Moses, M.; Blom, D.A.; Allard, L.F.; Nano-structural Changes in Supported Pt Catalysts during CO oxidation, 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007
8. Moses, M.; Narula, C.K., Blom, D.A.; Allard, L.F.; Ex-situ Reactor Enabled Microstructural Monitoring: Elucidating Lean NO_x Trap Deterioration Parameters, 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007

Agreement 9105 - Ultra-High Resolution Electron Microscopy for Characterization of Catalyst Microstructures and De-activation Mechanisms

L. F. Allard, C. K. Narula, P. J. Ferreira, M. J. Yacaman, S. A. Bradley and C. H. F. Peden

Objective/Scope

The objective of the research is to characterize the microstructures of catalyst materials of interest for the treatment of NO_x emissions in diesel and lean-burn gasoline engine exhaust systems. The research heavily utilizes new capabilities and techniques for ultra-high resolution transmission electron microscopy with the HTML's aberration-corrected electron microscope (ACEM). The research is focused on understanding the effects of reaction conditions on the changes in morphology of heavy metal species on "real" catalyst support materials (typically oxides), and the understanding of the structures of model mono-, bi- and multi-metallic catalyst systems of known particle composition. With the former systems, these changes are being studied utilizing samples treated in both steady-state bench reactors and a special *ex-situ* catalyst reactor system especially constructed to allow appropriate control of the reaction. Model samples of nanoparticulates of controlled composition on carbon or oxide supports are also being studied in collaboration with the catalysis group at the University of Texas-Austin (Profs. M. Jose-Yacaman and P. Ferreira). Studies of the behavior of Pt species on oxide substrates are also being conducted with colleagues S. A. Bradley of UOP Co., and C. H. F. Peden of PNNL.

Technical Progress

In-Situ electron microscopy: Work is continuing in understanding and characterizing the performance and behavior of the new Protochips in-situ heater device, using the JEOL 2200FS-AC ACEM. To review briefly, Protochips Inc. provides a novel heater technology, comprising a thin (~100nm) 500nm square conductive ceramic film suspended on a 3mm diameter Si chip. When installed in a special-made specimen rod, electrical leads contact two electrode pads on the Si chip, providing current that heats the film. Because of its low mass, a heating rate of 1 million degrees per second is reached, with similar cooling rates also demonstrated. This unique capability offers a number of potential experimental operating modes. For example, we can image a sample area at (nominally) room temperature, then blank the beam off the sample, heat for a give time and temperature (say to 500°C for 10min), and instantly bring the sample back to RT for a second round of imaging. This minimizes the effects of the electron beam on the heating experiment, so we know with greater confidence the maximum temperature experienced by the sample (e.g. catalyst powder). Alternatively, it is sometimes useful to record scanning images (dark-field and bright-field recorded simultaneously) in a rapid sequence when the temperature is high enough to cause significant morphological changes in the sample over short times. This latter case is illustrated by the tests we conducted using a model catalyst comprising silver (Ag) nanoparticles dispersed on a thin carbon file that had been collected over the surface of a Protochips heater chip. The Ag particles were initially produced by arc discharge, and stabilized with carbon from a hydrocarbon source. They were dispersed in isopropyl

alcohol, and a droplet was deposited on the heater chip. The nanoparticles showed a uniform dispersion over the surface of the thin carbon film previously suspended over the heater membrane.

In order to observe the effects of temperature on the Ag nanoparticles, we ran a heating experiment starting at a nominal temperature of 350°C, and gradually raised the temperature at intervals of 50°C, to a final temperature of 700°C. The melting point of bulk Ag is 961°C. Figure 1a shows a collection of various sized particles, at 350°C and a recorded magnification of 1Mx, using annular dark-field (ADF) imaging. ADF images show bright contrast relative to atomic number; the higher the atomic number, the greater the signal and therefore the brighter the image feature. No significant changes were noted over a period of time when the sample was held at this temperature. Images were recorded magnifications from 10Mx to 500kx, and the sample temperature was not lowered to RT at any point during the experiment. After a number of sets of ADF images were recorded at increasing temperatures, until the image of Fig. 1b (image #62) was recorded at 500°C. A short time later, the image of Fig. 1c (image #70) was recorded, again at 500°C. The temperature was then raised abruptly to 700°C, and rapid changes were noted in the residual Ag particle images. The images of Fig. 2 were recorded in rapid sequence with the temperature held at 700°C. The area was moved slightly to focus on the remaining large particles, since all the smaller particles disappeared (apparently melted and evaporated) at the lower temperatures. Figure 2a is image 80, Fig. 2b is image 86 and Fig 3b is image 94. After image 94 was recorded, the sample was returned to RT, and a further series of images was recorded at various magnifications. At 700°C, the Ag particles appear to melt and diminish in size by evaporation, rather than to coalesce into larger particles as might be expected by classical sintering theory. Noted in the ADF images of the final state was the presence of very small residual 'patches' of bright contrast which did not change further with the temperature held for a longer period at 700°C (see arrows in Fig. 2c). Also noted was a residual 'filmy' region of slightly higher contrast than the background carbon film, which apparently surrounded the Ag particles. The bright field image of Fig. 3 shows the remaining Ag particle at a magnification of 2Mx. The particle is surrounded by an apparent shell of graphite, with 3-4 sheets spaced at a nominal 3.4 Ångströms (the basal plane of graphite) seen. Similar graphite shells were observed surrounding the other large particles. This suggests a reason for the behavior of the Ag particles during heating; the presence of the graphite shells prevented coalescence of the particles, but did not prevent diffusion of Ag through the shells to allow evaporation.

To determine the nature of the residual patches of bright contrast, the sample was moved to the new Hitachi HF-3300 TEM/STEM instrument, which is equipped with an energy dispersive x-ray spectrometer (EDS) for elemental analysis. The location of the hole in the heater membrane in which the initial observations were made was noted (by simply counting the holes relative to a corner of the heater electrode) prior to specimen transfer. Figure 4 shows the whole heater geometry in a BF image from the HF-3300 (which allows much lower magnification images than the ACEM. Figure 5 is a BF image of the particle area seen in Fig. 2c; the bright patch in Fig. 2c is circled in Fig. 4. EDS spectra were recorded adjacent to and on this image feature (areas A and B

respectively), and it was determined that the residual patch contained largely iron. Other similar patches showed the same composition, which suggested that the original Ag particles contained a small concentration of iron that was left when the Ag evaporated. The laboratory at the U. of Texas-Austin that provided the original Ag particles was notified of this unexpected finding; the source has not been identified as of this writing.

This heating experiment was also interesting because it showed that the behavior of ultrafine particles differs significantly from the behavior expected in bulk material. From the literature [1], the upper melting temperature for a sphere can be found from the expression

$$T_M^{upper} = T_0\left(1 - \frac{2\sigma_{SL}}{L_0 r}\right)$$

where L_o is the latent heat of melting, T_o is the melting temperature of the bulk material, σ_{SL} is the solid/liquid interfacial energy per unit area and r is the radius of the nanoparticle. The term $2\sigma_{SL}/r$ is associated with the increase in internal pressure resulting from an increase in the curvature of the particle with decreasing particle size. Because the variables σ_{SL}, L_0 and *r* are all positive quantities, this means that the upper melting temperature of a spherical nanoparticle decreases with decreasing particle size. We are currently processing our experimental data, to see if we can relate our observations of the behavior of Ag and other composition nanoparticles under the environmental conditions (vacuum, electron beam exposure, etc.) of the electron microscope to the theoretical expression given above. Those results will be reported later.

References

[1] P.R. Couchman, W.A. Jesser, Nature, Vol. 269, October 6, p.481, 1977

Status of Milestones

On schedule

Communications/Visits/Travel

L. F. Allard presented a plenary lecture at the Texas Society for Microscopy, entitled “In-Situ Observation of Catalytic Materials at High Temperatures with the Aberration-Corrected Electron Microscope.”

Publications

D. Ferrer, D.A. Blom, L.F. Allard, S. Mejia, E Periz-Tijerina and M.J. Yacaman, “Atomic Structure of Three-Layer Au/Pd Nanoparticles Revealed by Aberration-Corrected Scanning Transmission Electron Microscopy,” *J. Mater. Chem.*, 2008, 18,

2442. (This article was chosen as a “Hot Paper” and highlighted on the JMC web site at: http://www.rsc.org/Publishing/Journals/jm/JMCHot_nanotech.asp
Note: The editors state: “*Journal of Materials Chemistry hot papers featured in this nanotechnology section have been rated as "outstanding" by expert reviewers in the field*.”

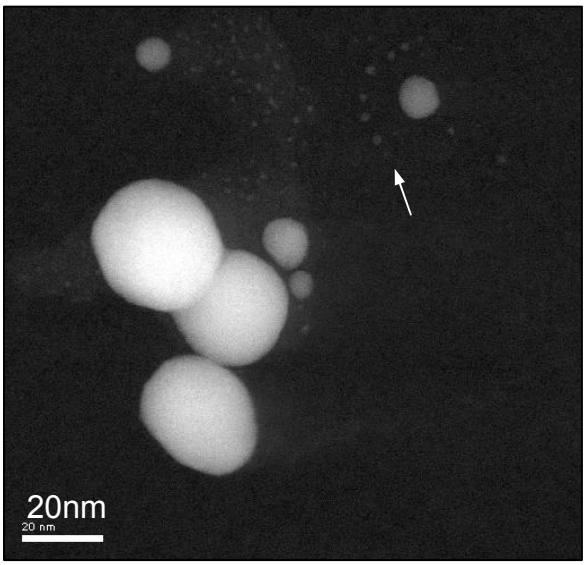


Fig. 1a ADF image showing the initial collection of Ag particles on C film, at 350°C. Note ultrafine particles (arrowed).

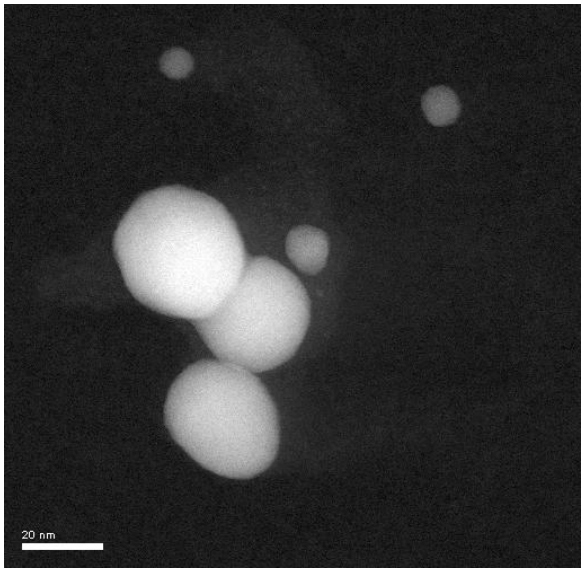


Fig. 1b Same area immediately after reaching 500°C. Ultrafine particles have disappeared, and another small particle has also vanished, with very little apparent changes to the larger particles.

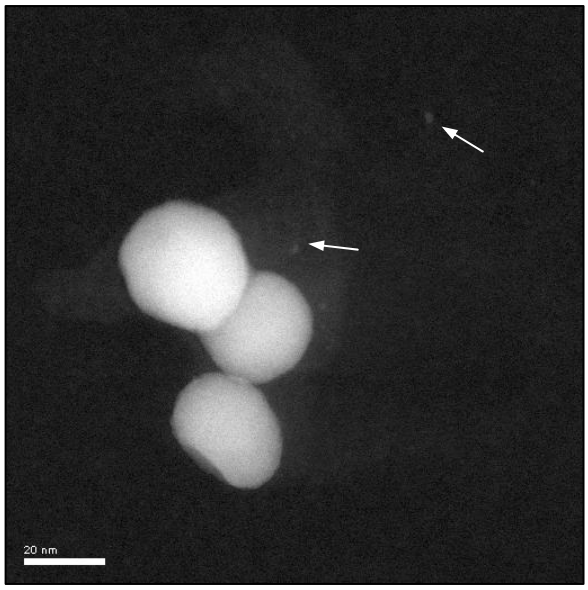


Fig. 1c Same area after a short time at 500°C. Medium-sized particles have vanished, but large particles still show little change. Note tiny residual patches of bright contrast at original locations of particles (e.g., arrows).

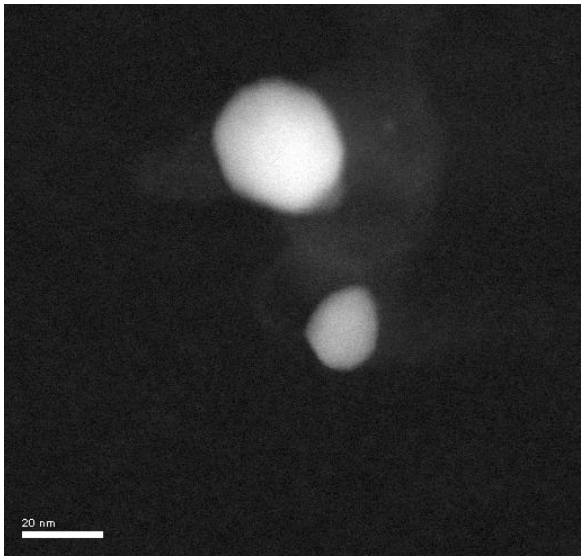


Fig. 2a First image of larger particle grouping after a short time (few minutes) at 700*C. The middle particle has vanished, and the lower particle is largely diminished, with an apparent curved upper edge reminiscent of a molten droplet. The larger upper particle still shows very little change.

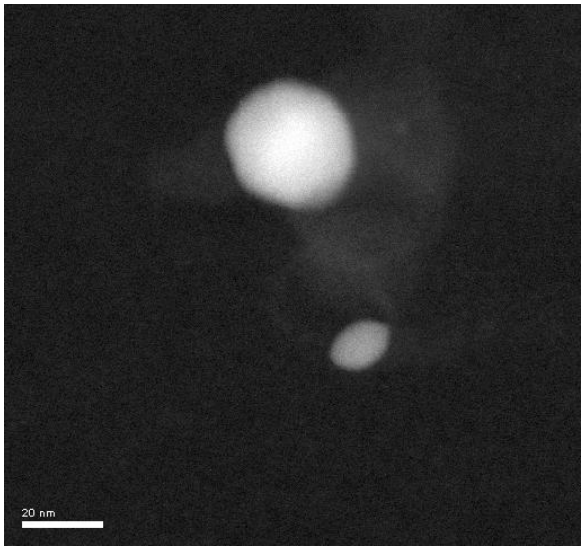


Fig. 2b Image recorded within 2min. of fig. 2a. Lower particle is rapidly diminishing in size, and small changes begin to be seen in the largest particle.

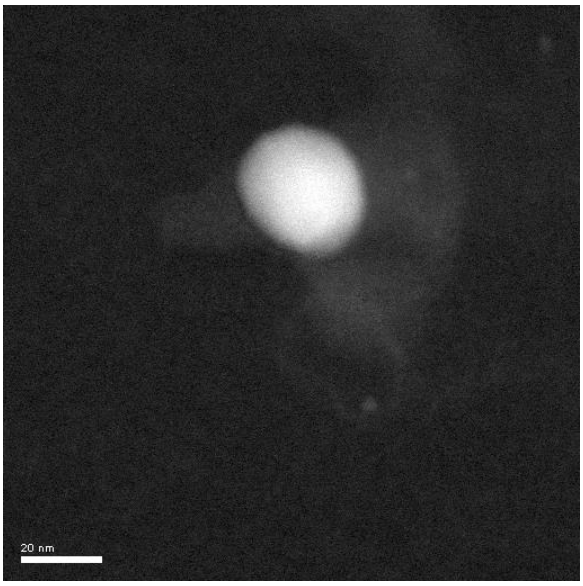


Fig. 2c Image recorded after an additional 2 minutes, showing lower particle vanished, with small residual particle (arrow). The carbon shell

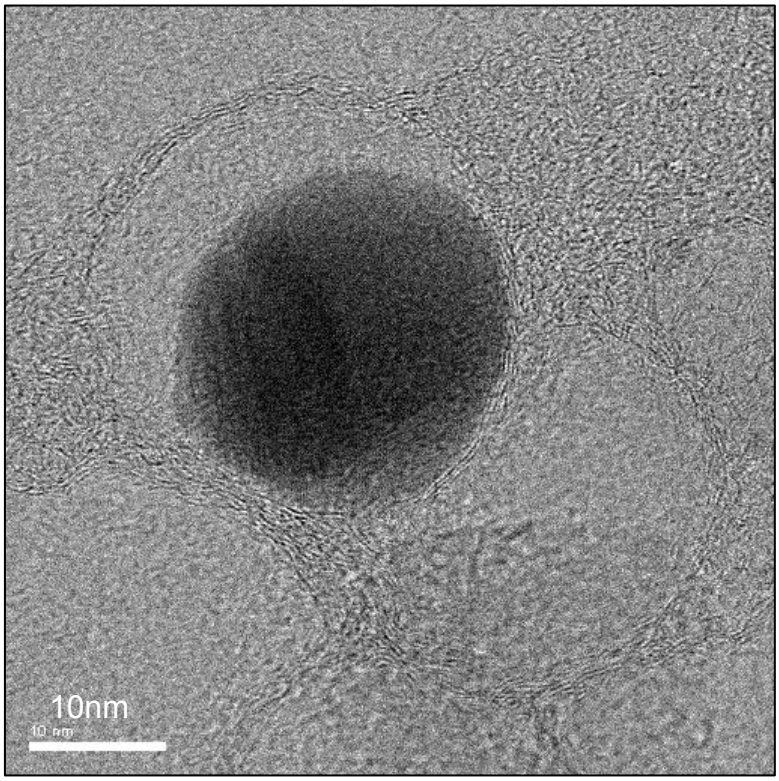


Fig. 3 BF image of largest particle, after sample returned to RT. The graphite “shell” structure of 3+ layers is resolved.

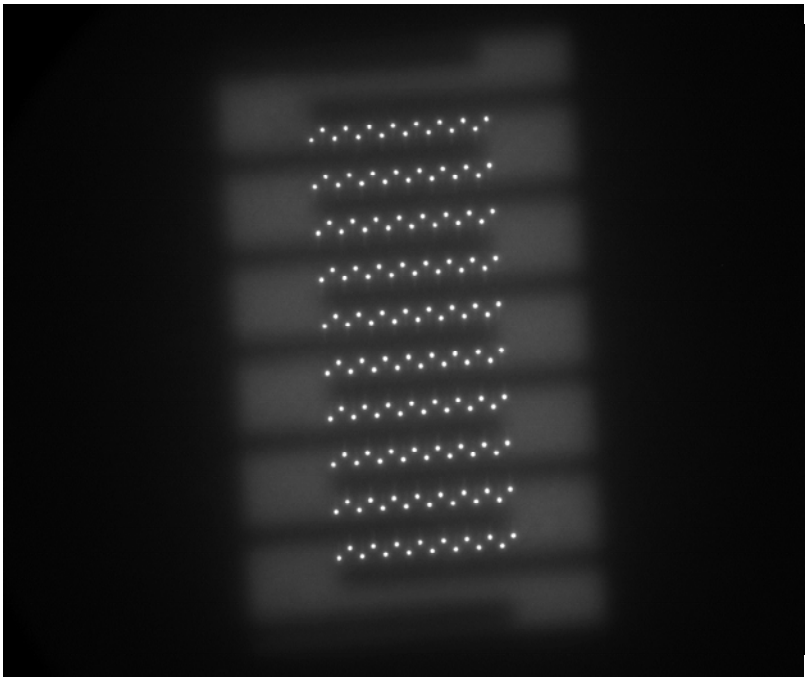


Fig. 4 BF image at very low magnification from the HF-3300 instrument, showing one of the unique heater chip geometries (this is a “finger” device, describing the shape of the electrodes).

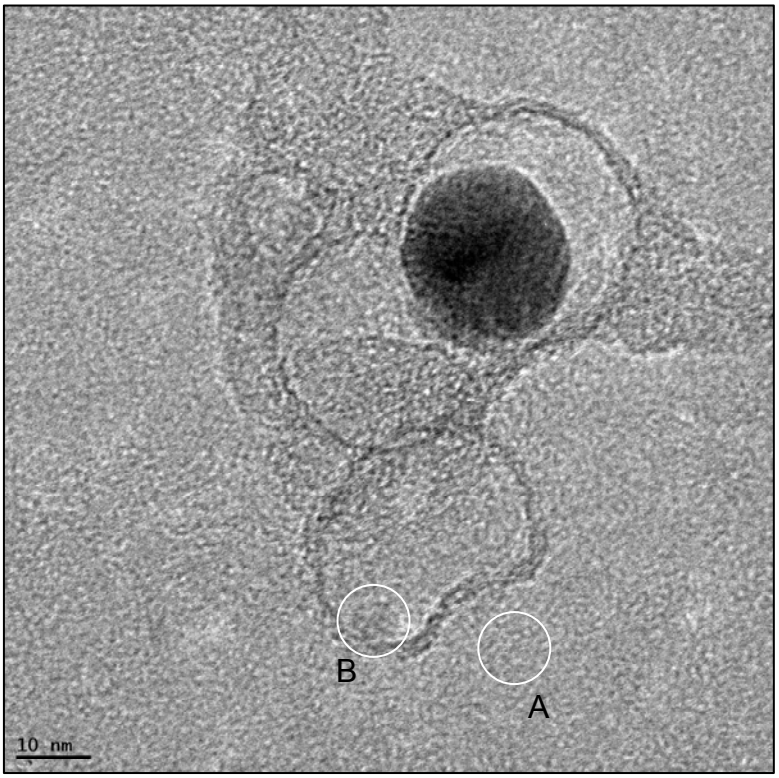


Fig. 5 BF image from HF-3300, acquired during EDS experiment. The spectra shown in Fig. 6 were acquired from areas A and B as shown.

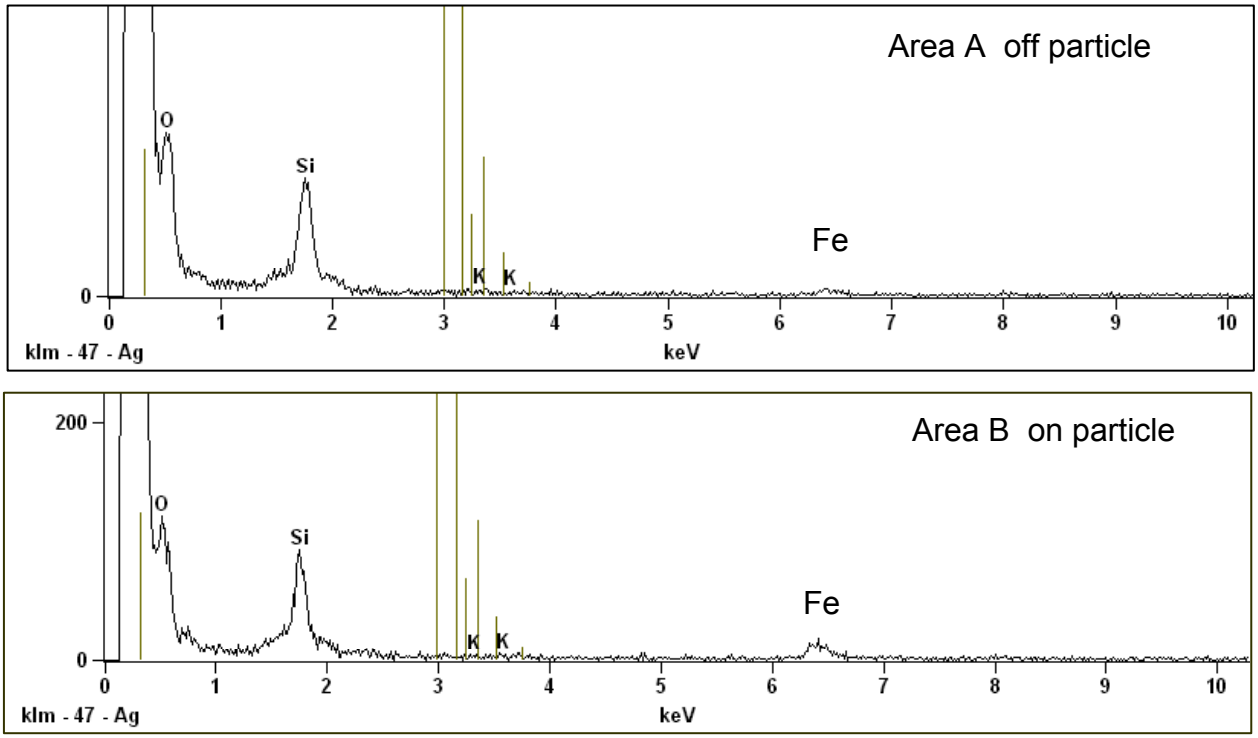


Fig. 6 EDS spectra showing presence of Fe in residual particle left after evaporation of lower Ag particle.

Agreement 9110: Life Prediction for Diesel Engine Components

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N. Philips and J. Jenson
Caterpillar, Inc.

Objective/Scope

There are four primary goals of this research agreement, which contribute toward successful design and implementation of advanced lightweight material components to achieve high-efficiency engine of 55% of heavy-duty diesel engines by 2012 as set under the 21st CT program: 1) the generation of a mechanical engineering database of candidate advanced lightweight materials before and after exposure to simulated engine environments; 2) the microstructural evolution and accompanied chemical changes during service in these advanced materials; 3) material selection, development, and design of complex-shaped components, and 4) application and verification of probabilistic life prediction methodology for advanced high-efficiency diesel engine components. The methodology implemented would also help to manufacture consistent mechanical reliability and performance of complex shaped components.

Technical Highlights

Detailed characterization of mechanical properties and microstructure of advanced TiAl and silicon nitride valve heads after 555-h NG engine tests were carried out to provide insight into the effect of engine environment on the mechanical reliability and corrosion resistance. The mechanical data and SEM analysis for those NG engine tested valves provide inputs to end user to verify its probabilistic component design and life prediction under the application condition.

Detailed SEM analysis on fractured silicon nitride and TiAl valve heads showed that the strength limit flaw was either the existing internal volume defects, i.e., pores or the deep machining grooves presence on the surface. Observations of microstructure near the subsurface of transition regions also showed that there was little or no environmental attack, indicating superior corrosion resistance to those metallic counterparts currently employed.

Discussions between ORNL and Caterpillar have been initiated to define the lightweight materials and components for the new CRADA entitled “Materials-enabled High-efficiency for Heavy-Duty Diesel Engines.”

Long-term tensile creep tests of commercially available TiAl alloys were continued this reporting period. The test conditions specified are relevant to the temperature and tensile stress profiles imposed on the TiAl turbo wheel under the engine operational conditions obtained via the FEA modeling task carried out by end users. The database generated from these long-term tensile creep studies will then be used for verification of probabilistic component design and life prediction task critical to end users.

Status of FY 2008 Milestones

Complete mechanical and microstructure characterization of TiAl components before and after ACERS diesel engine testing. **(09/08**) – On schedule.

Communications/Visits/Travel

H. T. Lin visited Dr. N. Philips and J. Jenson of Caterpillar to discuss the characterization results of engine tested TiAl and silicon nitride valves and materials research plan for the new CRADA on February 7, 2008.

H. T. Lin attended the 2008 OTT Annual Merit Review, Washington DC, February 24-26, 2008.

Problems Encountered

None

Publications/Presentations/Awards

N. Philips, J. Tretheway, M. Andrews, J. Jenson, H. T. Lin, J. G. Sun, T. Theiss, M. Kass, and N. Domingo, "Advanced Materials for Lightweight Valve Train Components," presented at the 2008 OTT Annual Merit Review, Washington DC, February 24-26, 2008.

References

None

Agreement 14957: Thermoelectrics Modeling

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Oak Ridge National Laboratory

Objective/Scope

Measure needed thermomechanical and thermophysical properties of candidate thermoelectric (TE) materials and then use their data with established probabilistic reliability and design models to optimally design automotive and heavy vehicle TE modules. Thermoelectric materials under candidacy for use in TE modules tend to be brittle, weak, and have a high coefficient of thermal expansion (CTE); therefore, they can be quite susceptible to mechanical failure when subjected to operational thermal gradients. A successfully designed TE module will be the result of the combination of temperature-dependent thermoelastic property and strength distribution data and the use of the method of probabilistic design developed for structural ceramics.

Technical Highlights

Several hundred test specimens of p- and n-type bismuth telluride were purchased (Marlow Industries Inc., Dallas, TX) for thermophysical, thermoelastic, and mechanical characterizations. All specimens were fabricated in either a prismatic or a plate geometry as shown in Fig. 1. This thermoelectric material is mature and its testing will provide a reference database that can be used to compare developmental thermoelectric materials too. The measurements of Young's Modulus, Poisson's ratio, CTE, thermal conductivity, and uniaxial and biaxial flexure strength as a function of temperature have all commenced. The large number of specimens enables the generation of statistically significant strength data. Any anisotropic variation of E, ν, CTE, and strength is under exploration. Fractography of tested strength specimens is underway and failure initiation sites and strength-limiting flaw types are being identified. The uniaxial and biaxial flexure strength test methods will enable us to censor the data according to edge-type and surface-type, and perhaps even volume-type flaws.

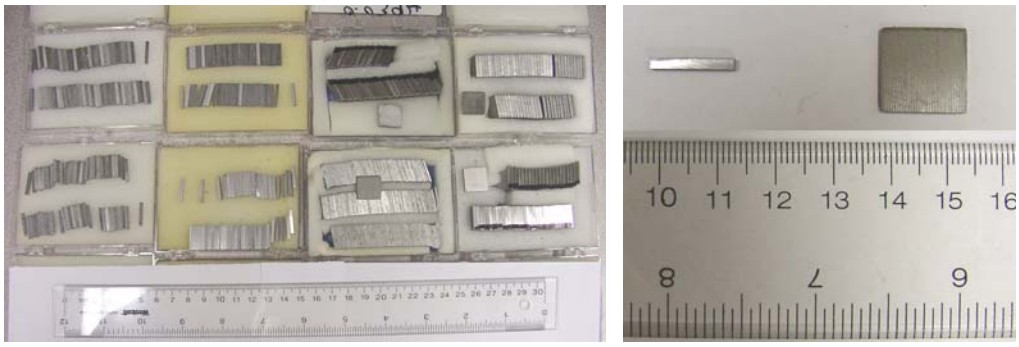

Figure 1. Hundreds of bismuth telluride test specimens (left) enable the study of thermophysical, thermoelastic, and mechanical properties as a function of n- or p-type, orientation, and temperature.

Thermal and electrical transport properties were studied on the Marlow specimens from room temperature to 225ºC. P-type specimens in both orientations were tested using the laser flash technique for thermal diffusivity. Thermal conductivity was calculated using the product of thermal diffusivity, specific heat, and density. Electrical transport properties of both n-type and p-type specimens were obtained in the same temperature range using the ULVAC ZEM-2 system. Electrical resistivity and Seebeck coefficient were measured on the same specimen along the cut direction. Thermal diffusivity was measured on a different specimen perpendicular to the cut direction. Significant anisotropy was observed in both and n-type and p-type materials.

Dilatometry of p- and n-type bismuth telluride was completed. Testing ranged between room temperature and 250°C. Because the thermoelectric properties of this material are known to exhibit transverse anisotropy, test coupons were sectioned in both orientations from both the p- and n-type materials, and this enabled our study of thermal expansion as a function of orientation.

Elastic property (elastic modulus and Poisson's ratio) measurements were completed. The plate-like geometry of the p-type bismuth telluride enabled high temperature measurement with the ultrasound resonance ultrasound spectrometer so that was performed to 250°C in both orientations. N-type specimens were only available in this study with the prismatic geometry so only room temperature measurement of the elastic properties were performed; however, both orientations of n-type bismuth telluride were measured though and compared with that of p-type.

Room temperature equibiaxial (ring-on-ring) was completed with the p-type material in both orientations. The specimen geometry was nominally 15x15x1 mm and a 6.35/12.7 mm ring-diameter-pair was used. Preliminary results are showing that one of the orientations is approximately 50% larger than the other. Fractography is presently underway. Companion testing will be done at an elevated temperature to-be-determined after consultation with Marlow.

Lastly, room temperature uniaxial flexure (three-point-bending) was initiated with both the n- and p-type materials and as a function of orientation using the 2x2x15mm prismatic bar geometry. Companion testing will be done at an elevated temperature to-be-determined after consultation with Marlow.

Status of FY 2008 Milestones

Generate thermomechanical property database on a candidate p- and n-type thermoelectric materials that will be used to model and predict probabilistic reliability of a TE device. **[09/08]** *On schedule.*

Communications/Visits/Travel

Communications occurred with Peter Hiller of Robert Bosch GmbH (Stuttgart, Germany) during the 32nd International Conference on Advanced Ceramic and Composites, Daytona Beach, FL, 27Jan-01Feb, 2008. Hiller had expressed interest in this project's bismuth telluride mechanical property data and our interpretations of it.

Numerous communications were held with staff at Marlow Industries, Dallas, TX. Wereszczak and Wang will visit there 24 April 2008.

Problems Encountered

None.

Publications/Presentations/Awards

O. M. Jadaan and A. A. Wereszczak, "Probabilistic Design Optimization and Reliability Assessment of High Temperature Thermoelectric Devices," presentation give and companion article now in proceedings review, 32nd International Cocoa Beach Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, 26 January - 01 February 2008.

References

None.

Agreement 16308: Themoelectric Materials

David J. Singh
Oak Ridge National Laboratory

Objective/Scope

We will use modern science based materials design strategies to find ways to optimize existing thermoelectric materials and to discover new families of high performance thermoelectrics for waste heat recovery applications. The emphasis will be on the thermoelectric figure of merit at temperatures relevant to waste heat recovery and on other properties important for applications, especially anisotropy and mechanical properties.

Technical Highlights

(1) Oxide thermoelectric materials:
The focus of this work is to identify oxide materials that offer a combination of high thermoelectric performance and applicability to vehicular applications. A key consideration that is special for vehicles is that the materials must be at least potentially inexpensive. This constrains the elements that can be used in the thermoelectric materials. In particular, the high cobalt concentration in thermoelectric Na_xCoO_2 is undesirable. We have therefore been screening other oxides with compositions based on lower cost elements. In particular, we are using bonding topology as a screen since this was identified in our prior work as underlying the narrow bands of Na_xCoO_2 which in turn are one of the main reasons for its desirable thermoelectric properties. We have already identified three potential materials based on this analysis and have performed first principles calculations to better determine the thermoelectric performance. These materials are two spinel titanates, which were discussed in the FY2008Q1 report, and delafossite $YCuO_2$. This latter composition is particularly favorable based on our recent results.

We calculated the band structure and thermopower of $YCuO_2$ as a function of doping and temperature as well as various transport functions related to conductivity. The band structure as obtained with the linearized augmented planewave method [1] and thermopower are shown in Fig. 1. These show that not only is $YCuO_2$ a potentially low cost material, but that it also has a very high thermopower and is much more isotropic than Na_xCoO_2. In fact, the calculated thermopowers as obtained from the electronic structure using Boltzmann transport theory [2] are clearly superior to those of Na_xCoO_2 at temperatures of relevance for vehicular applications. Furthermore, the more isotropic transport properties of $YCuO_2$ relative to Na_xCoO_2 are important because this result implies that inexpensive ceramic, and possibly sol-gel processing could be used for this material, while much more expensive single crystal and textured ceramic processing is thought to be needed for Na_xCoO_2. We are currently studying ways of controlling doping in $YCuO_2$. The electronic structure suggests a number of doping strategies, perhaps the most likely of which is to use excess Cu. In any case, the structure of the valence bands, which are primarily derived from copper states, implies that high conductivity and high power factors are likely. These results have been communicated to C. Narula at ORNL, who is evaluating the material for synthesis via sol-gel and other routes. We are

also continuing to investigations of the spinel titanates for which Boltzmann transport calculations are being done and searching for other potentially useful compositions.

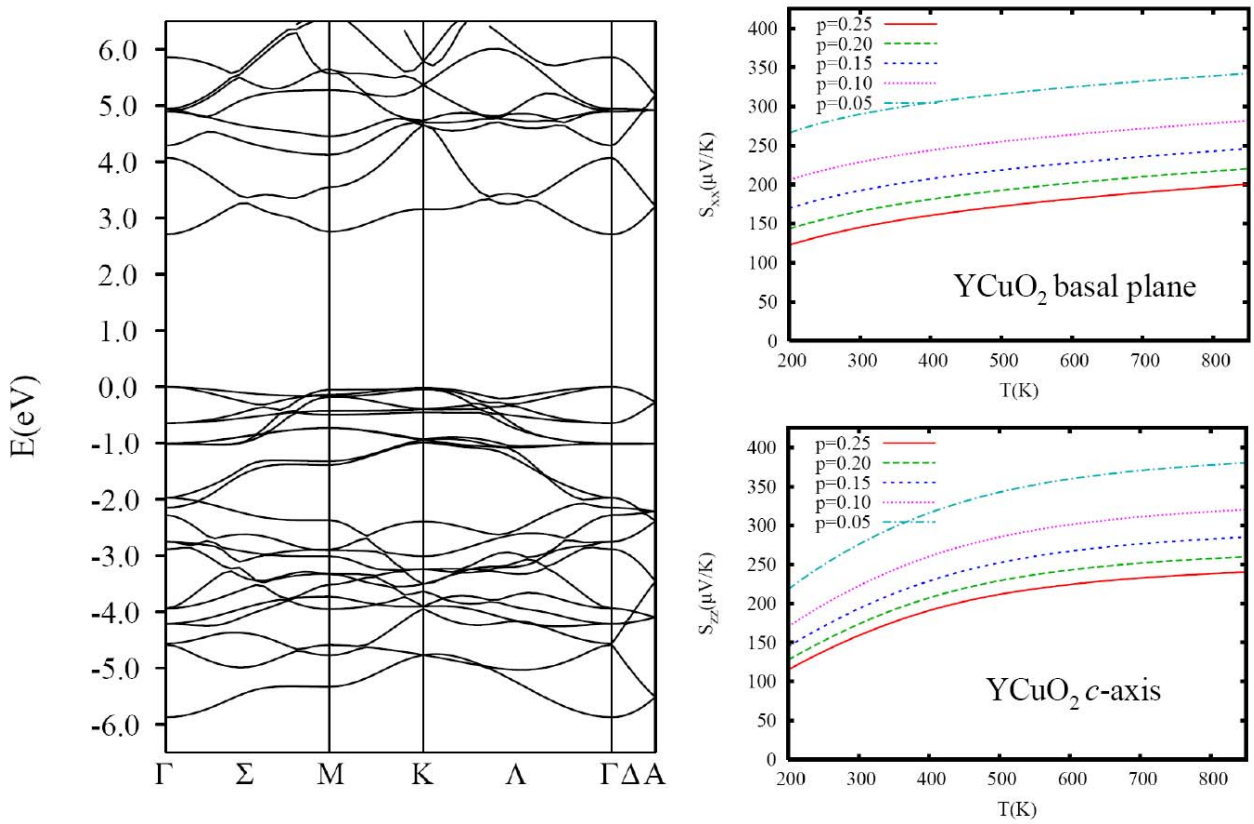

Fig 1: Calculated band structure (left) and thermopower (right) for delafossite structure $YCuO_2$. Note the very high thermopowers found in the temperature range of relevance for vehicle waste heart recovery. Note also that the basal plane and *c*-axis thermopowers are both high.

(2) Non-oxide materials:
As discussed in the FY2008Q1 report, we have been performing first principles electronic structure and Boltzmann transport calculations to evaluate the potential for using La-Te phases for waste heat recovery. While the initial results showed that quite low carrier concentrations would be needed to shift the operating temperature for those materials to the range needed for waste heat applications, we more recently found that the transport functions that govern conductivity indicate that the electron phonon scattering is suppressed at low carrier density. This would lead to an increase in the power factor. These results have been partially communicated to J. Snyder at California Institute of Technology (CalTech), who is performing experimental characterizations of this material. We are planning to discuss these results with the CalTech group during a meeting in late April and will combine experimental data with results of first principles calculations to better assess the potential of this material.

(3) Thermal conductivity:

We are presently testing computer code for first principles dynamical calculations on thermoelectric materials. This will be used in conjunction with Green-Kubo theory to calculate thermal conductivity of bulk and nanostructured thermoelectrics.

Status of FY 2008 Milestones

We are progressing towards our milestone of predicting a new thermoelectric composition. Strategies that will be used are to continue investigation of spinel based titanates, Cu containing delafossites, and rare-earth chalcogenides. Depending on the results we will continue with those materials and/or investigate alternate narrow band oxides containing mixed-valent transition element ions.

Communications/Visits/Travel

1. D.J. Singh: Travel to March American Physical Society Meeting, New Orleans, LA, to chair session on thermoelectric sodium cobaltites and to interact with other thermoelectric researchers. 3/08/2008-3/15/2008.
2. D.J. Singh: Travel to Besthesda, MD for DOE Vehicle Technologies program review. 2/24/2008-2/29/2008.

Problems Encountered

No significant problems encountered this quarter.

Publications/Presentations/Awards

1. D.J. Singh, “Oxide Thermoelectrics”, MRS Symp. Proc. **1044**, U02-05 (2008).

References

1. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method, 2nd Edition*, Spinger, Berlin, 2006.
2. G.K.H. Madsen and D.J. Singh, “BoltzTraP: A code for calculating band-structure dependent quantities”, *Computer Physics Commun.* **175**, 67 (2006).