Material Science and Technology Division

Propulsion Materials Program
Quarterly Progress Report for
January through March 2009

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

A. A. Wereszczak and H. -T. Lin
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

Fractography of the Si and SiC strength test specimens is proving difficult. Because these specimens (chips) were single crystals, almost all specimens twinned during mechanical loading (3-pt, 4-pt, and anticlastic bendings), and their patterns hinder the identification of the failure location. The goal is to censor the Weibull strength data with the fractographical results.

Permanent magnet materials (NdFeB-based) from motors from a Toyota Camry, Lexus, and Prius were provided by ORNL/NTRC's T. Burress for materials characterization. The coefficient of thermal expansions of the three magnetic materials was equivalent. Specimens for elastic modulus and Poisson's ratio measurements have been prepared and await testing. Additionally, microstructural examinations are underway from polished mounts.

A machinable glass ceramic was provided by NTRC's M. Chinthavali for materials evaluation. Coefficient of thermal expansion, elastic properties, and electrical resistance will be measured. Specimens for all those tests are presently being prepared.

Status of FY 2009 Milestones

Compare cooling efficiencies in a hybrid inverter IGBT that contains contemporary and alternative ceramic DBC substrates. (09/09) *On schedule.*

Communications/Visits/Travel

Several communications occurred with Powerex's Duane Prusia. Wereszczak has planned to visit Powerex (Youngwood, PA) and Prusia and colleagues in June to discuss Wereszczak's Si and SiC semiconductor strength testing and potential interactions.

Problems Encountered
None.

Publications/Presentations/Awards
Presentation: O. M. Jadaan, A. A. Wereszczak, and T. P. Kirkland, "Strength of Si and SiC Semiconductor Chips," 33rd International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 23, 2009.

An abstract entitled "Probabilistic Thermomechanical Reliability of Electronic Ceramic Substrates and Semiconductor Chips," by A. A. Wereszczak, T. P. Kirkland, and O. M. Jadaan was submitted to the 5th IEEE Vehicle Power and Propulsion Conference, September 7-10, 2009, Dearborn, MI.

Patent Application: "Direct Cooled Power Electronics Substrate," R. H. Wiles, A. A. Wereszczak, C. W. Ayers, and K. T. Lowe, # 64019, February, 2009.

ORNL/TM-2008/185 Report: "Evaluation of the 2008 Lexus LS 600H Hybrid Synergy Drive System," T. A. Burress, C. L. Coomer, S. L. Campbell, A. A. Wereszczak, J. P. Cunningham, L. D. Marlino, L. E. Seiber, and H. -T. Lin, January, 2009.

References
None.

Agreement 16305: Materials by Design – Solder Joints of High Performance Power Electronics

G. Muralidharan, Andrew Kercher, 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 OFCVT 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^{o}C in contrast to the current 125-150^{o}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 the previous quarter, in collaboration with Powerex Inc., progress has been made in preparing the first four solder joints for thermal cycling testing and high temperature exposure. 2.5 mm x 2.5 mm silicon dies were mounted on a metallized AlN DBC substrate with the metallization consisting of a medium phosphorus (6-12%) Nickel layer followed by a thin Au layer on the surface. 80Au/20Sn was the solder used for attaching the silicon die to the substrate. To understand the initial void content in the solder joint, high resolution x-ray radiography was carried out on all the specimens. This quarter, Au-Sn solder joints were subject to thermal cycling; one set of thermal cycles were carried out between temperatures of -65^{o}C and 200^{o}C with a dwell of 5 minutes at each temperature. This would simulate the use of such joints at a temperature of 200^{o}C and shutdowns from that temperature. Figure 1 shows a typical thermal cycling profile used for the experiments.

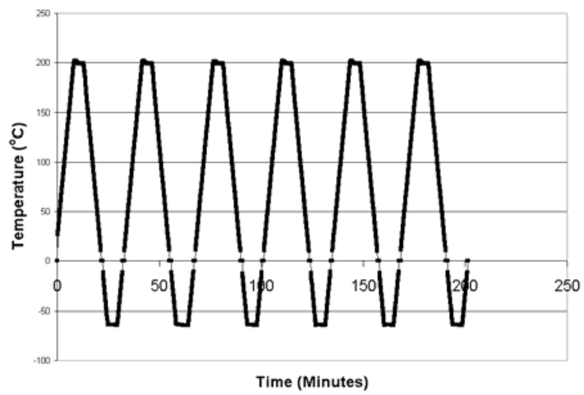


Figure 1. Typical temperature profile used for thermal cycling between -65^{o}C and 200^{o}C.

As a result of this thermal cycling between -65^{o}C and 200^{o}C, the direct bonded copper layer was observed to debond from the AlN substrate after less than 100 cycles. The extent of delamination ranged from complete delamination to partial delamination at the corners and edges as shown in figure 2.

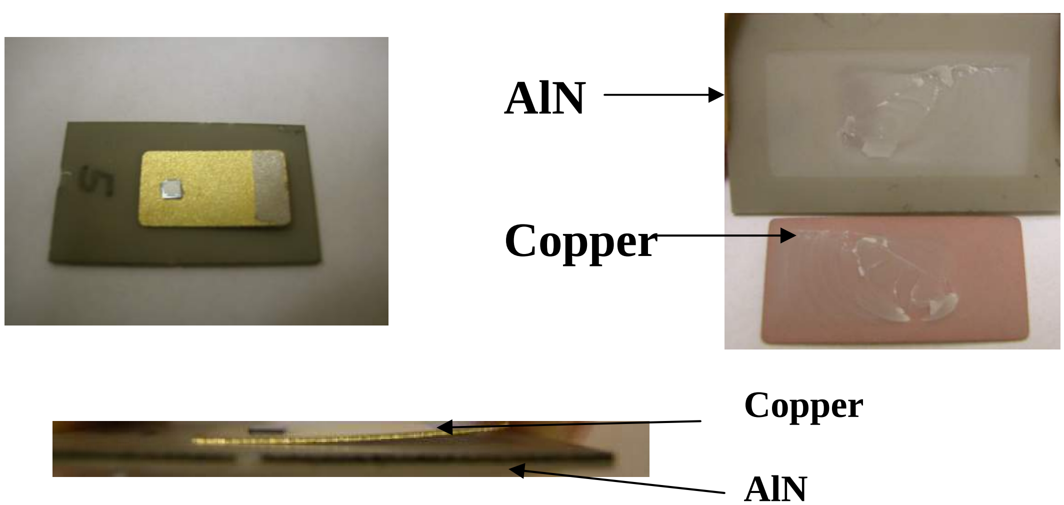


Figure 2. Delamination of the copper layer from the AlN layer was observed in the DBC substrate as a result of thermal cycling between 200^{o}C and -65^{o}C.

To avoid further problems with the delamination and to focus the study on the effect of thermal cycling on the solder joint, the interface between the copper layer and the AlN was protected with a layer of silicone and further temperature cycling was performed between 200°C and 5°C. Figure 3 shows the x-ray radiograph obtained from a joint that was cycled between these two temperatures. Note the presence of significant cracking within the Au-Sn solder and the presence of cracking induced in the die due to thermal cycling. Au-Sn solder with a high melting point retains a significant amount of strength at these temperatures and thus causes cracking of the silicon die.

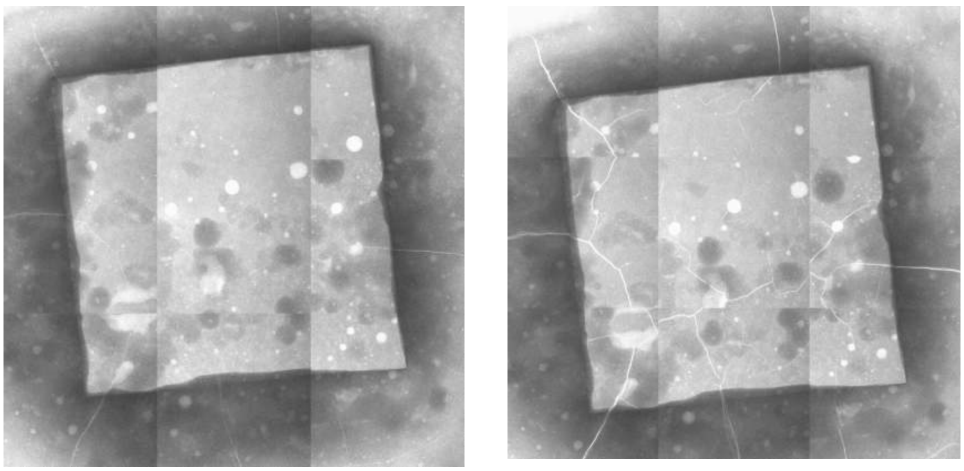


Figure 3. Cracking of the solder joint and the die was observed in Au-Sn joints subject to thermal cycling between 200°C and 5°C. Note that voiding is similar in the two conditions.

This work has shown that use of Au-Sn joints may not be the appropriate candidate for service in these applications even at these higher temperatures. Further work is needed with SiC dies to see if these problems are also observed with SiC dies. At the present time, work has been concluded on Au-Sn solders made with silicon dies and alternate metallization will not be pursued.

On-going work now is focused on an alternate solder: Sn-Ag and the thermal cycling of Ag-Sn solder joints. Results will be reported in the following quarter.

<u>Status of FY 2009 Milestones</u>

Work is on schedule to meet the following milestone.

Complete thermal cycling testing on solder joints prepared with Au-Sn solder and two different substrate metallizations (9/09)

Communications/Visits/Travel
Frequent communications are being carried out with PowerEx to evaluate methodologies and to evaluate progress in understanding the behavior of solder joints.

Problems Encountered

Publications/Presentations/Awards
None

References

(a) (b)

Figure 1 (a). Image of the die attached assembly showing the die and the substrate. (b) High resolution x-ray image of a typical processed solder joint. The size of the chip is 2.5 mm x 2.5 mm.

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 project will develop the laboratory methodology to evaluate the degradation of power electronics materials by evaporative liquids.

Technical Highlights

A laboratory test system that allows for high current flow and shaping of the wave form was designed and built in quarter three of FY08 and was operated for approximately 383.65 hours. This operating time equates to about 690,570 cycles. It was shut down during the first quarter for post-mortem evaluation of the circuit boards that are being tested. One board was removed, and there were no observable environmental effects on the wires or the board after the first period of testing (Figure 1).

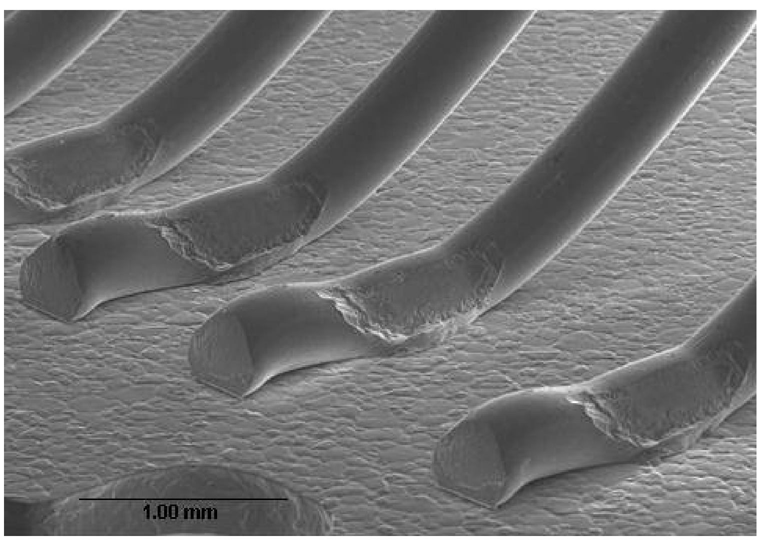


Figure 1. Scanning Electron Micrograph of Board Removed After 690,570 Test Cycles. There Were No Observable Environmental Effects On Wires or Board

The board was replaced by a new board and the test system was prepared for resumption of operation. A thermocouple was epoxied within a groove cut into the back layer of one of the boards in the vicinity of the wires on the front side to allow for a determination of the temperature swing being experienced by the wires during the test cycle. The system was restarted using a new 2 second on and 4 second off cycle. Note the previous conditions consisted of a square wave of one second on and one second off driving 10 amperes through 0.4 mm (400 microns) diameter aluminum wire. Figure 2 shows the oscilloscope trace of a test at 180 amps through the series circuit. This equates to 30 amps through each 15 mil wire, which should produce a reasonable stress. The actual temperature being recorded is not representative of the true temperature being experienced by the aluminum wires because of the insulation provided by the board between the wires and the thermocouple, and the cooling effect from evaporative cooling. However, the observed 3°C differential between the highest and lowest temperatures during the cycle (purple trace in Figure 2), which is smaller than that actually being experienced by the wires, is indicative of the stress being placed on the wires. Work continues on the cycle timing and the current being pushed through the circuits to develop a waveform profile that will allow for failure mechanisms to be expressed. This expression of failure is highly desired so that the limits of performance of the electronic board can be defined and the severity of testing necessary for rapid determination of performance can be ascertained.

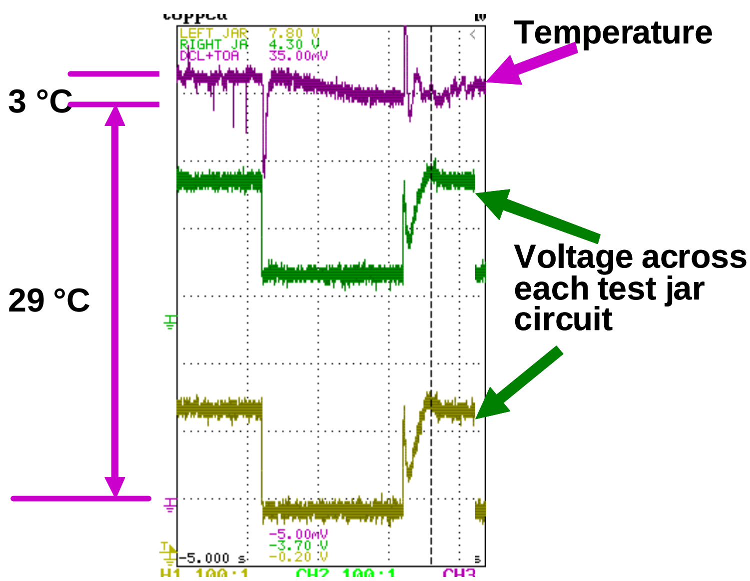


Figure 2. Oscilloscope Trace of a 180 amp Test Through the Series Circuit. This is Equivalent to 30 amps Through Each 15 mil Wire.

Status of FY 2009 Milestones

Validate the proposed methodology for examining the interaction of the electrical components with evaporative coolant. **(09/09)** On track.

Communications/Visits/Travel

None to report.

Problems Encountered

None to report.

Publications/Presentations/Awards
None to report.

References
None to report.

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

Govindarajan Muralidharan and Rick Battiste
Oak Ridge National Laboratory

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 the development of a database of mechanical properties as a function of alloy composition and microstructure (which is a function of processing and heat-treatment). One of the issues relevant to this work has been the relationship between data collected using a rotating beam fatigue system and data obtained using fully reversed fatigue tests.

To enable this comparison, and as requested by our industrial partner, during the previous quarter, fatigue data was obtained for currently used valve alloys at various stresses at a temperature of 760^{o}C. The fully reversed fatigue data obtained from IN751 at 760^{o}C was compared with the rotating beam data available in the literature as shown in Figure 1. Note that roughly an order of magnitude difference is observed between the literature data and data collected using fully reversed fatigue tests at ORNL at this temperature.

In addition, ORNL has recently acquired a rotating beam fatigue test system. Figure 2 shows an image of the rotating beam system that is fully operational. Initial data has been obtained on IN751 at 870^{o}C and is shown in Figure 3. Further tests are in progress.

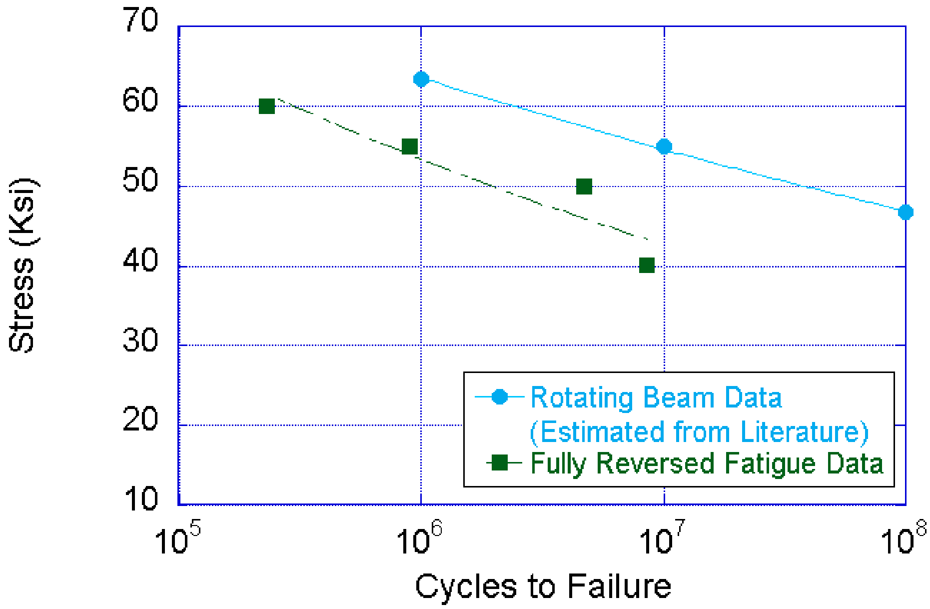


Figure 1. Comparison between fatigue life obtained using fully reversed fatigue tests and literature data on rotating beam fatigue life for a temperature of 760^{o}C. Literature data was obtained from US Patent #6,372,181, M. G. Fahrmann, and Gaylord D. Smith, INCO Alloys.

Figure 2. Rotating beam fatigue system installed at ORNL.

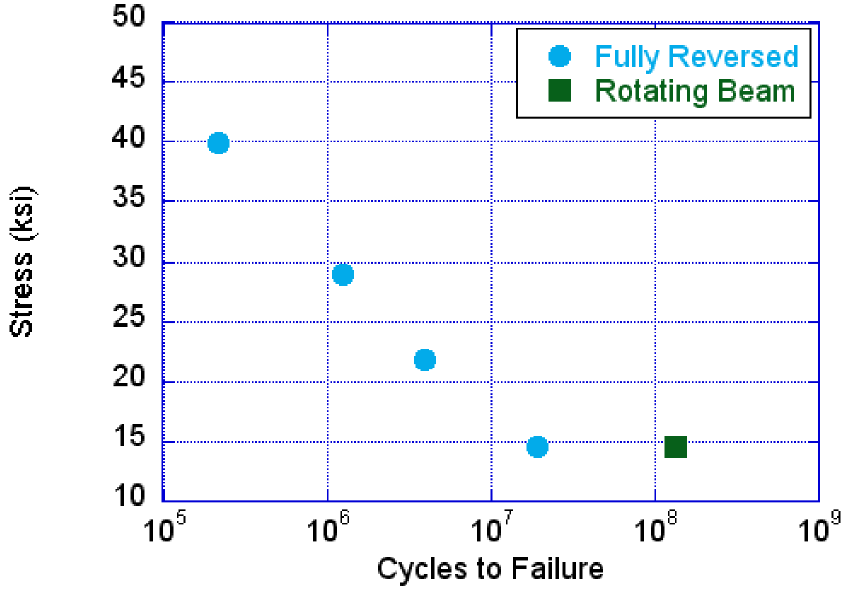


Figure 3. Comparison between fatigue life obtained using fully reversed fatigue tests, and results from rotating beam tests at ORNL for IN751 at a temperature of 870^{o}C.

In addition, computational calculations are being used to identify a preliminary list of alloys for casting of small heats and property measurements

Milestones

Evaluate fatigue properties of the most promising alternate alloys available and select best alloy for component fabrication/testing. **(9/09)**

Agreement 16303: Materials for High Pressure Fuel Injection Systems

Peter J. Blau, Camden R. Hubbard, and Amit Shyam
Oak Ridge National Laboratory

Michael J. Pollard and Jeff A. Jensen
Caterpillar Corporation

Objective/Scope

The objective of this Cooperative Research and Development Agreement (CRADA) between UT-Battelle, LLC and Caterpillar Corporation is to advance the state of the art in the characterization, selection, and use of metallic alloys for high-pressure diesel engine fuel injector nozzles.

During recent decades, fuel efficient, low-emissions diesel engine designs for heavy trucks have relied upon increasing fuel injection pressures to optimize combustion characteristics. Precise fuel metering is required. This key functional requirement has raised concerns over the ability of spray holes to be machined to sufficiently close tolerances to provide desired spray patterns and for the materials to withstand millions of high-pressure pulses without succumbing to fatigue damage. To achieve the purposes of this CRADA, a three-year effort is planned. The data and analyses obtained in the course of this work are expected to provide vital information for designers of high-performance fuel systems for advanced, energy-efficient diesel engines.

The effort began in the summer of 2008 with the development of a working plan involving three avenues of approach: (1) characterization of current fuel injector hole geometry and alloy metallurgy, (2) residual stress analysis of the nozzle tips in the location of the spray holes, and (3) the development and use of fatigue test methodology and analysis to address the special requirements of the next generation of high-pressure fuel injectors.

Technical Highlights

Nozzle hole characterization. Studies of the interiors of spray holes continued on fuel injectors supplied to ORNL by Caterpillar Corporation. These were measured and photographed at varying magnifications and angles as an aid in both metallographic studies and residual stress studies using x-ray and neutron diffraction methods. In additional to the optical metallographic techniques described in the previous report, two new 3-dimensional profiling methods were used: a Hitachi quadrapole back-scattered electron (BSE) detector system, and a Wyko optical interferometric imaging system. Examples of the images from these two instruments are shown in Figures 1 and 2. R. Parten of ORNL developed a specialized grinding method to expose the interior bores of the spray holes for examination. Surface roughness parameters can also be obtained using both of these techniques. Such information is important from two standpoints: first, understanding fuel flow through the spray holes, and second, characterizing potential locations where fatigue cracks could nucleate.

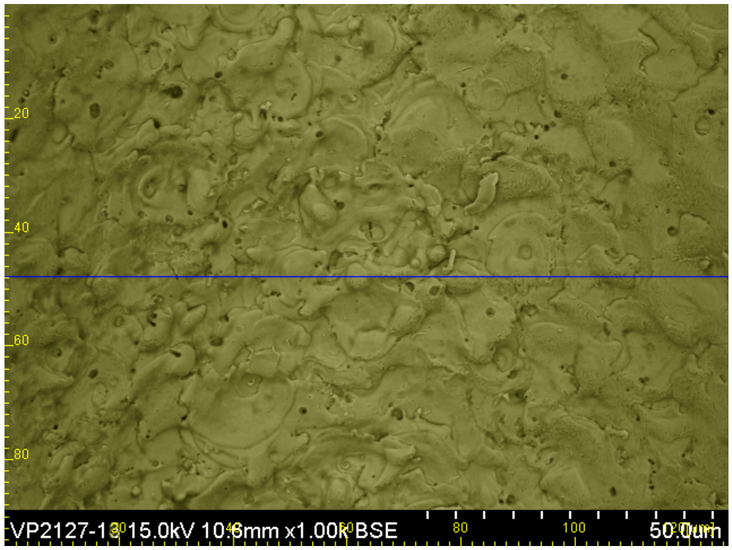


Figure 1. Reconstructed 3-D image of a fuel injector hole bore wall using a cluster of four BSE detectors. Using special software, the image can be tilted and rotated to measure surface features.

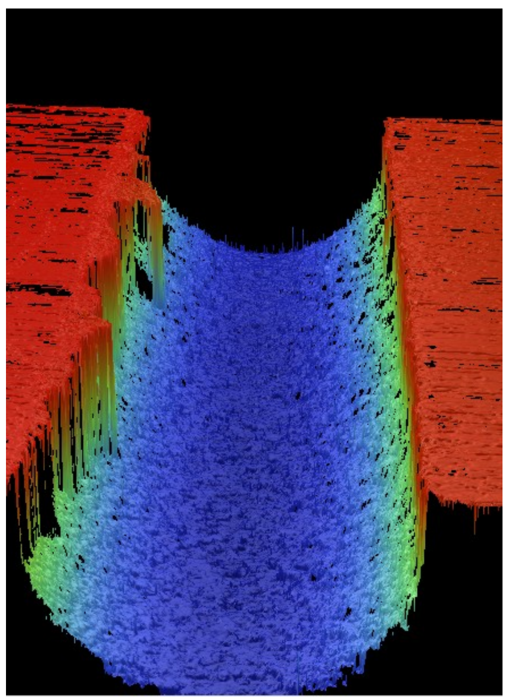


Figure 2. A 3-D reconstruction of the interior bore of an as-finished fuel injector spray hole obtained using vertically-integrated optical interference images on the Wyko instrument.

Residual stress studies continue. Residual stress in a fatigue-critical area of a component part can affect the nucleation and propagation of life-limiting cracks. The shape and size of the fuel injector tips presented significant challenges for residual stress analysis. C. Hubbard traveled to several facilities to investigate the feasibility to obtaining useful residual stress data on nozzle specimens provided for this study. A summary of these preliminary studies is given in Table 1.

Table 1. Summary of X-ray and Neutron Techniques Investigated To-Date

Technique	Facility	Sample Examined	Comments/findings
Laboratory XRD	ORNL-PTS goniometer	Prior bending fatigue test rods	Compressive axial surface stresses resulting from carburizing heat treatment
Synchrotron XRD (low energy x-ray)	NSLS* – X14A beam line	Injector nozzles	Compressive stresses at surface Beam size limited to 1x2 mm
Synchrotron XRD (high energy x-ray)	APS**, ALS**, Stanford	Injector nozzles	Goals are depth mapping gauge volume below 0.3x0.3x0.3 mm (To be scheduled)
Neutron diffraction	HFIR****- NRSF2 beam line	Injector nozzles	Measured d-spacing through barrel wall. Gauge volume limited to 0.5x0.5x5 mm. Unable to determine stress free d-zero needed to calculate strains. Possible gauge volume not small enough.

* National Synchrotron Light Source, ** Advanced Photon Source, *** Advanced Light Source, **** High-Flux Isotope Reactor, National Residual Stress Facility number 2.

*Fatigue testing methodology***.**   A. Shyam has identified a dual-pronged approach for characterizing the effects of small holes on the fatigue life and crack growth mechanisms of fuel injector alloys. The first prong of the approach is an axial-fatigue test on smooth specimens, with and without holes. The second is a fracture mechanics characterization of cracks initiating and propagating from artificial defects machined on axial and bending specimens. A similar approach was previously applied to the study of the effects of small (~ 100   m diameter) notches on fatigue crack propagation in several engineering alloys [1]. Plans for the upcoming work will be to introduce diesel fuel into the environment and conduct residual stress analysis to more thoroughly understand the implications of the fatigue test results. Additional plans for the fatigue testing matrix will be discussed in June, during an upcoming visit to several Caterpillar facilities in Illinois.

Reference

[1] A. Shyam, J. E. Allison, C. J. Szczepanski, T. M. Pollock and J. W. Jones (2007) “Small fatigue crack growth in metallic materials: A model and its application to engineering alloys,” *Acta Materialia*, 55 (19), pp. 6606-6616.

Future Plans

1) ORNL will visit both the Caterpillar Tech Center in Mossville, IL, and the Fuel Systems facility in Pontiac, IL, to further discuss characterization issues and establish fatigue testing parameters for the upcoming series of baseline tests.

2) Continue exploration of residual stress measurement methods that are suitable for the tips of fuel injectors.

3) Begin baseline axial fatigue tests of fuel injector materials.

4) Continue metallurgical study and spray hole bore characterization by a combination of examination techniques.

Travel

None

Status of FY 2009 Milestone

1) Design and develop a method to conduct fatigue tests on small holes. **(6/2009)** – in process

Publications and Presentations

None this period.

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 an ORNL CRADA project with Caterpillar NFE-07-00995 and DOE OVT Agreement 16304, that began last year, 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. The CRADA will be extended for 12 more months due to success during the 2nd year of the project. Requests for more detailed information on this project should be directed to Caterpillar, Inc.

Highlights

Caterpillar, Inc.

This quarter, Caterpillar completed short-term testing of new, modified J3 seat inserts, to measure and verify improvements in the initial wear resistance. Testing will be extended and expanded on the several new Caterpillar "Buettner-Rig" seat/valve wear-test facilities, to validate the reductions in seat wear. This quarter, Caterpillar continued effort to obtain new test valves of several new advanced Ni-base superalloys. The valve supplier has acquiring the new superalloys and will be making prototype valves components for Caterpillar to test, as well as mechanical properties specimens for testing and evaluation at ORNL.

ORNL

ORNL completed the in-depth microcharacterization studies of wear-tested valves and seats, and completed evaluation of a rig-tested valve of standard Pyromet 31V for 360h at 740^{o}C, for comparison with previous data from similar valve testing at 850^{o}C. Data from these studies of the standard Ni-based superalloy valve have provided the "root-cause" analysis that then enabled selection of new commercial Ni-based superalloys that mitigate the high-temperature degradation and wear found on the seating-surface. The Caterpillar valve supplier is procuring the new Ni-based superalloys.

Technical Progress, 2nd Quarter, FY2009

Background

This is an ongoing ORNL CRADA project with Caterpillar NFE-07-00995 and DOE, OVT Agreement 16304, that began last year, and will last for about 2.5 years. This CRADA project is focused on addressing the wear and failure modes found for 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. The CRADA is scheduled for completion at the end of 2009, but the CRADA is now in the process of being extended for 12 more months due to technical progress and success. Requests for more detailed information on this project should be directed to Caterpillar, Inc.

Approach

Caterpillar has provided and analyzed the baseline wear and mechanical behavior characteristics of engine-exposed valves and seats, and provided similarly exposed components from simulation-rig testing at Caterpillar. ORNL is providing more in-depth characterization and microcharacterization of those valves and seats. Such data has provided the understanding of the underlying degradation mechanism, which then provides the basis for selecting and testing valve and seat alloys with upgraded performance and temperature capability. Caterpillar and ORNL are working 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.

Caterpillar and their major seat-insert supplier previously both performed the initial evaluations of modified processing to J3 seat inserts that showed initial resistance to several different modes of wear found earlier. Last quarter, Caterpillar completed the improvement and expansion of their wear-testing capabilities, based on the "Buettner Rig" design, and began testing and evaluation of seats with modified processing to mitigate lower temperature wear. The initial short-term rig tests confirmed wear-resistance of the modified seat inserts, and expanded testing, including longer times, is scheduled to validate the component benefits.

Previously, Caterpillar initiated a project with one of its valve suppliers to obtain several new heats of advanced Ni-based superalloys for upgraded exhaust valves. These new alloys should have improved performance and higher temperature capability relative to the standard Pyromet 31V alloy. This quarter, the valve supplier obtained these new Ni-based superalloys, and the team is finalizing discussions for the mechanical testing and characterization of specimens made from valve precursor rod-stock at ORNL, and prototype new exhaust valves made from the same rod-stock for Caterpillar to test and evaluate in the wear-test rigs.

Technical Progress – ORNL

ORNL completed in-depth microcharacterization studies of wear-tested valves and seats, including evaluation of a valve rig-tested for 360 h at 740^{o}C, to compare with previous data from similar valve testing at 850^{o}C. These studies include comparison of high-wear and non-wear on the same rig-tested valves, as well as valve-alloys specimens aged at the same temperatures at ORNL. This data clearly established the degradation mechanisms at the surface and sub-surface valve regions. This "root-cause" analysis was also foundational to selecting new Ni-based superalloys that should be capable of better performance at higher temperatures and resist such degradation.

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 as well as one of their exhaust valve suppliers.

Status of Milestones

Perform the initial microanalysis of modified valves and/or seats after simulation-rig testing to evaluate wear-reduction (due Dec. 2008, delayed until June 2009) – Status – Delayed, but still in progress, due to delays and down-time of "Buettner-Rig" facilities at Caterpillar.

Publications/Presentations/Awards

None

Agreement 13329: Design Optimization of Piezoceramic Multilayer Actuators for Heavy Duty Diesel Engine Fuel Injectors

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

D. W. Memering, J. Carmona-Valdes, and R. Stafford
Cummins Inc.

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 improve fuel economy. Though piezoelectric function is the obvious primary function of lead zirconate titanate (PZT) ceramic stacks for fuel injectors, their mechanical reliability can be a performance and life limiter because PZT is 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

1. Piezoceramic Characterization

Study of mechanical properties of the commercial material, PSI-5A4E (Piezo Systems, Inc., Cambridge, MA) using ball-on-ring testing under much higher electric fields, +/- 3.6 kV/mm, was continued during this reporting period. An additional 24 specimens were prepared and studied with 12 tested under each electric field level. These specimens were 10 mm x 10 mm x 0.267 mm, and their surface and poling conditions were same as described in reference [1]. Mechanical results showed that increasing the electric field level to 3.6 kV/mm in both positive and negative directions resulted in additional increase in the mechanical strength of poled PZT. The obtained characteristic strength was around 182 MPa that was ~ 7% higher than that obtained under +/- 2.4 kV/mm (169 -171 MPa). Apparently, the increased electric field led to more domains aligned along the crack plane, consistent with the observed trend of increased mechanical strength. This is due to the fact that the toughening of PZT ceramics was driven by domain switching and thus the increased amount of switchable domains led to a much more energy dissipation and much higher fracture toughness.

Characterization of the mechanical properties of a new piezoelectric material has also been initiated in this reporting period. The tested material is considered one of the potential candidates to be used in the fuel injection system of heavy-duty diesel engine. Specimens were obtained through disassembling a piezo stack (designated as type A) with a recommended chemical solution. Type A piezo stack was supplied by Cummins Inc. as shown in Fig. 1, and the one that had lead wires cut out was used in the current study. Individual PZT plates had an irregular plane shape; namely, a circle with two flat sides. Its nominal diameter was 12.5 mm, flat-to-flat distance 12.6 mm, and thickness 0.562 mm. A 2 mm diameter steel-ball was used in loading, and 10 mm diameter polymer-ring in supporting. A 10 lb load-cell was used in monitoring the load process. The ball-on-ring testing was performed in a displacement-controlled mode with a rate of 0.01 mm/s, and was fully controlled via a LabView program. This rate was selected to have a load-to-failure of about 10 seconds. Test data were processed with the method reported in reference [1] and results are given in Fig. 2 as a Weibull plot on the left and 95% confidence ring on the right. Preliminary test results showed that this material exhibited a characteristic strength of 71 MPa and a Weibull modulus of 5.8. Study of fractography on these fractured specimens is in progress and results will be updated in the next quarterly report. In addition, more tests have been planned for PZT plates to obtain a more representative statistic database.

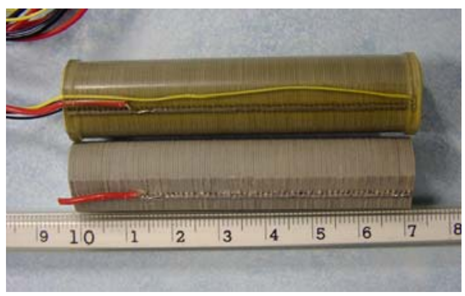
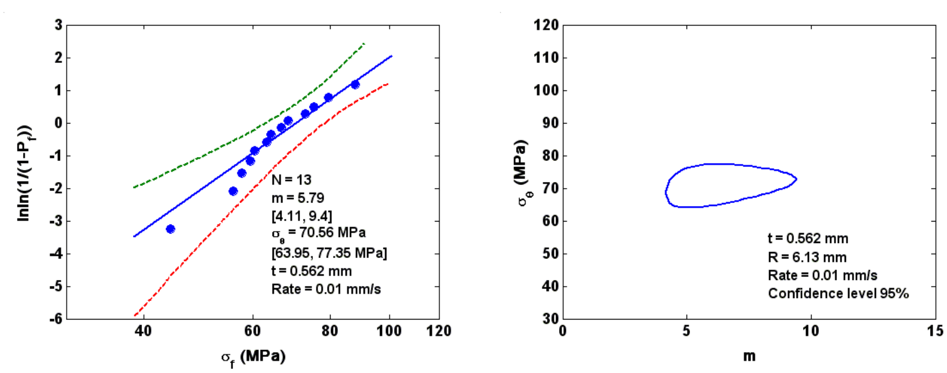


Fig. 1. An image of two piezo stacks supplied by Cummins Inc. and designated as type A; the stack with lead wires cut out (the bottom one without polymer casing) was disassembled by a recommended chemical solution.

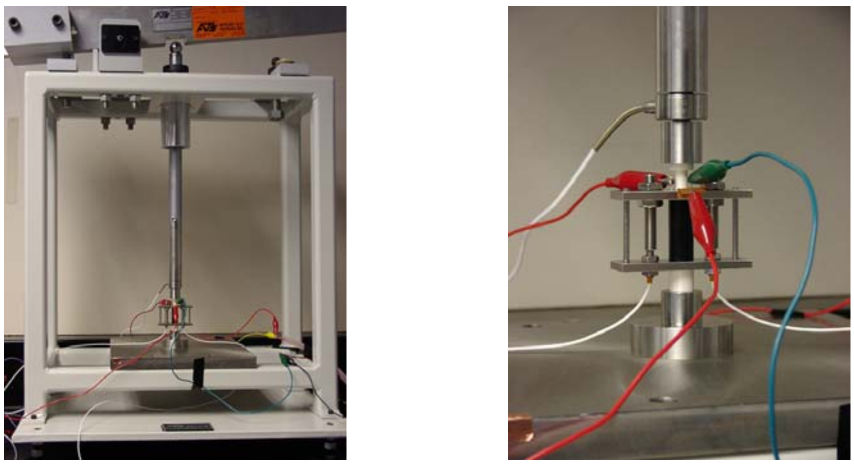


(a) (b)

Fig. 2. Weibull plot (a) and confidence ratio rings (95% confidence level) (b) of flexural strength for the PZT plates extracted from a type A stack.

2. Piezoceramic Multilayer Actuator Characterization

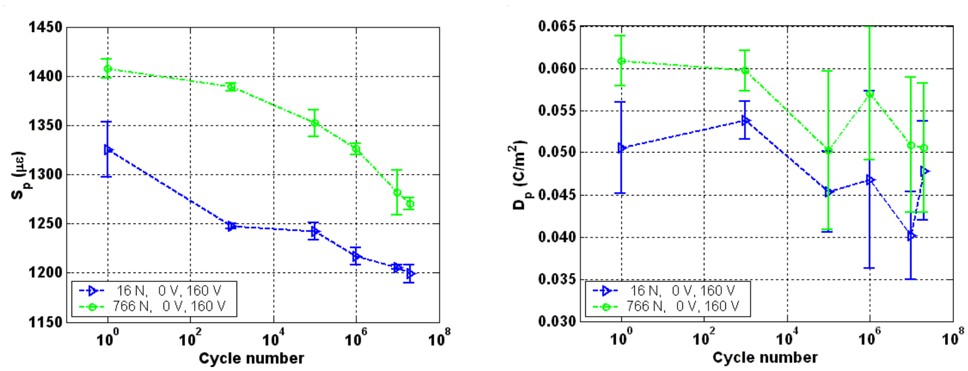
Fatigue testing and characterization on a new piezo stack have also been initiated in this quarter. This type of piezo stacks is under consideration of being used in the fuel injection system of diesel engine. Tested piezo stacks were purchased from a supplier and designated as type B in this study. Type B piezo stacks had an overall size of 6.5mm x 6.5mm x 30mm, a capacitance of 2.9 μF, and were encapsulated with two electrode pins standout. Therefore, the accelerated fatigue test facility had to be modified to accommodate the new dimensional requirement. Some components for the test system have been re-designed and fabricated in this quarter. The assembled setup and enlarged piezo stack section are shown on the left and right sides of Fig. 3.



(a) (b)

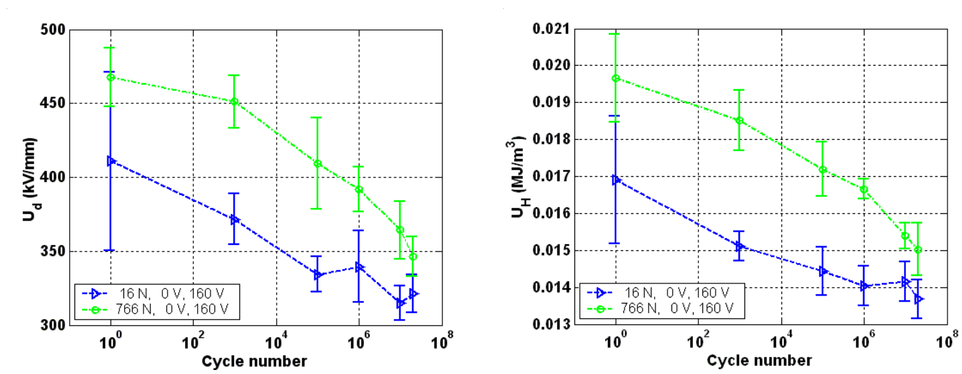
Fig. 3. Modified piezo fatigue test facility (a) and enlarged piezo section (b) where a type B piezo stack is under testing.

Extensive prefatigue tests have been conducted with a variety of combined mechanical and electric loading conditions; namely, unipolar electric waveform with constant mechanical preloads. Dielectric breakdown was observed for four of type B stacks and obtained breakdown voltages ranged from 320 V to 480 V. As a result, the fatigue testing on type B stacks began with an electric loading condition of 50 Hz, 0/160V sine wave with a 766 N mechanical preload. The fatigue evaluation was based on the measurements with 2 Hz, 0/160 V sine wave with two mechanical preload levels, 16/766 N. The measurements were conducted according to the procedures given in reference [2]. Variations of mechanical strain and charge density are given in Fig. 4, and those of piezoelectric and dielectric hysteresis in Fig. 5. In general, both the mechanical strain and charge density reduced approximately 10% at 2 x 10^7 cycles; and the piezoelectric and dielectric hystereses decreased about 25% at the same time. The cyclic fatigue for this load condition was designed to reach 1 x 10^8 cycles, and related data will be reported in the future.



(a) (b)

Fig. 4. Variations of mechanical strain (a) and charge density (b) of type B piezo stack during the electric cycling with a mechanical preload.



(a) (b)

Fig. 5. Variations of piezoelectric (a) and dielectric (b) hysteresis of the same piezo stack as shown in Fig.4 during the electric cycling with a mechanical preload.

References

1. Wang, H. and Wereszczak, A. A., Effects of electric field and biaxial flexure on the failure of poled lead zirconate titanate, *IEEE Trans. Ultrasonic, Ferroelectrics, and Frequency Control*, 55 (12), 2008, 2559-2570.
2. Wang, H., Wereszczak, A. A., and Lin, H.-T., Fatigue response of a PZT multilayer actuator under high-field electric cycling with mechanical preload, *J. Appl. Phys.*, 105 (1), 2009, 014112.

Status of FY 2009 Milestones

Measure and compare piezoelectric and mechanical reliabilities of tape-cast and pressed PZT piezoceramics. **(09/09) on schedule**

Communications/Visits/Travel

Conference calls on CRADA update with Cummins Inc. were held on March 4 and April 2, 2009, respectively.

Publications/Presentations/Awards

1. Wang, H., Lin, H.-T., Cooper, T. A., and Wereszczak, A. A., Mechanical strain and piezoelectric properties of PZT stacks related to semi-bipolar electric cycling fatigue, presented at *33rd Int. Conf. on Adv. Ceramics and Composites*, Jan. 18-23, 2009, Daytona Beach, FL, and accepted to the Proceedings.
2. Wang, H., Wereszczak, A. A., and Lin, H.-T., Fatigue response of a PZT multilayer actuator under high-field electric cycling with mechanical preload, *J. Appl. Phys.*, 105 (1), 2009, 014112.
3. Wang, H. and Wereszczak, A. A., Effects of electric field and biaxial flexure on the failure of poled lead zirconate titanate, *IEEE Trans. Ultrasonic, Ferroelectrics, and Frequency Control*, 55 (12), 2008, 2559-2570.

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, leaks around valve seats from wear or deposit build-up can reduce cylinder pressure and engine efficiency while also leading to increased emissions. This effort focuses on understanding the complex wear-oxidation processes that occur in the interface between diesel engine exhaust valves and seats. The knowledge gained is expected to help engine designers to select improved 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 to test the surface durability of candidate exhaust valve materials at diesel engine temperatures. In FY 2008, the conjoint role of wear plus oxidation was investigated in more detail, establishing that oxidation products that form on mechanically-damaged surfaces differ from those on statically oxidized surfaces. Selected Fe-, Ni-, and Co-base alloys were used as model materials and resulted in two journal publications and a conference presentation. A high-temperature, repeated impact (HTRI) apparatus was designed in FY 2007 and completed in FY 2008. The development of that apparatus presented significant engineering challenges, but when it was improved, it enabled important experimental work to be conducted on corrosion-assisted wear effects at the high temperatures typical of exhaust valve operation. The development of a model for exhaust valve wear will complete this project.

Technical Highlights

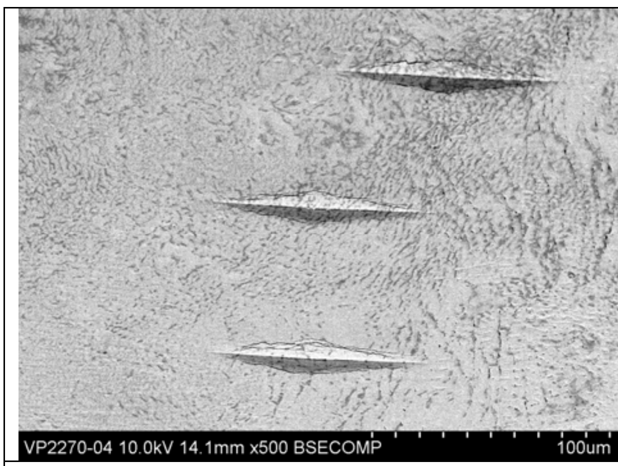
Looking toward the completion of this project in September 2009, with the development of a wear model for diesel exhaust valves, the results of several tasks undertaken during the past two FY have been organized into a body of reported work. That work, in addition to the examination of exhaust valves removed from actual diesel engines, will support the development of physically-realistic wear model. Two publications based on the findings of this project have been accepted for archival journals, and another three are nearing completion (see ‘Publications and Presentations’). A final publication will describe the wear model.

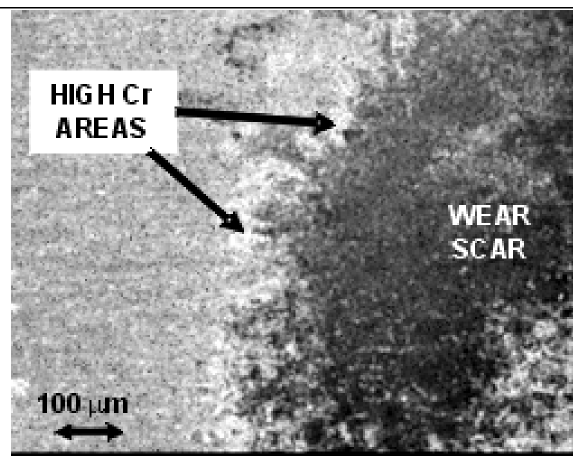
International Conference on Tribo-Corrosion. During this reporting period, the ORNL principal investigator had the opportunity to attend and present an invited talk the Second International Symposium on Tribo-Corrosion in Wiener Neustadt, Austria. This symposium was one of a series of topical meetings organized and sponsored by the Tribo Corrosion Information Network, a confederation of researchers headquartered at the University of Strathclyde in Scotland. The goal of that organization is as follows:

"The TrICorr Network was established to link researchers and engineers in Higher Education and Industrial and Research Technology Organisations to further the understanding of tribo-corrosion mechanisms of materials."

The symposium was held at a jointly government and industry supported institute called the Austrian Center for Competence in Tribology (AC2T). It boasts a staff of 75 who are devoted to tribology research, and there is a prospect to double that staff within the next year or two. Details of the symposium content and the AC2T are available in an ORNL Foreign Trip Report.

Repetitive Impact Tests. Results from recent high-temperature, repetitive-impact tests on the HTRI apparatus described in previous reports, indicated how a mechanically-mixed layer of oxide and metal ('tribolayer') forms when metals impact and slip under high-temperature, oxidizing conditions. Figure 1(a) shows three Knoop microindentation hardness impressions on a tribolayer that formed on a Ni-based alloy following 20,000 impacts from a Co-based alloy counterface at 800°C in air. Figure 1(b) shows a kα X-ray map of Cr that has been mechanically redistributed by repetitive impacts. The original Cr_2O_3 has been pushed to the margins of the wear scar, and the central impact zone has become Cr-poor. Note also that the chromium oxide that formed outside of the wear scar is higher in Cr content (brighter) than the material within the scar.





(a) Tribolayer formed on a Ni block after 20,000 repetitive impacts by Co alloy. (Backscattered electron image)	(b) Redistribution of Cr resulting from repetitive impact plus slip on the wear scar (X-ray map)

Figure 1(a). Features of a mechanically mixed tribolayer, and (b) elemental redistribution of Cr on areas repetitively impacted at 800°C in air.

In addition to completing the final repetitive impact experiments, a set of used valves and valve seats is being obtained. These will be examined, and their contact surface features measured, in order to provide further information for the development of a physically-realistic exhaust valve wear model.

Future Plans
1) Complete high-temperature, repetitive impact tests on the candidate alloys and study the microstructures produced by combined impact, slip, and oxidation.

2) Examine worn diesel valves to support the development of an exhaust valve wear model.

3) Begin preparation of the wear model to complete Milestone 2.

Travel
P. Blau attended and presented an invited paper entitled: "Elevated-Temperature Tribology of Metallic Materials" at the 2nd International Symposium on Tribo Corrosion in Wiener Neustadt, Austria (March 14-15). The meeting was attended by 92 persons from 13 countries. It was held at the Austrian Center for Competence in Tribology, a modern facility with a staff of 75 specialists in tribology. A foreign trip report is available upon request.

Status of FY 2009 Milestones
1) Prepare and submit a journal article that describes the new high-temperature test method for diesel exhaust valve materials. **(03/09 – completed)**

2) Prepare and a final report or journal article that summarizes the role of wear with oxidation in controlling the durability of diesel engine exhaust valve materials. **(09/09)**

Publications and Presentations

Accepted and/or published:
1) P. J. Blau and T. M. Brummett, "High-Temperature Oxide Regrowth on Mechanically-Damaged Surfaces," *Tribology Letters*, Vol. 32 (3), pp. 153-157

2) P. J. Blau, T. M. Brummett, and B.A. Pint, "Effects of prior surface damage on high-temperature oxidation of Fe-, Ni-, and Co-based alloys," accepted for the 2009 International Conference on Wear of Materials, Las Vegas, Nevada, April 19-22; and for publication in the journal *Wear*.

3) P. J. Blau, Trip Report, 2nd International Symposium on TriboCorrosion ("TriboCorrosion '09"), March 17-18, 2009, Oak Ridge National Laboratory, Oak Ridge, TN.

Submitted:
4) P. J. Blau, "Elevated-Temperature Tribology of Metallic Materials," submitted to *Tribology International*

5) P. J. Blau, "Development of a High-Temperature Repetitive-Impact Apparatus for Exhaust Valve Material Testing," submitted to the International Joint Tribology Conference, ASME/STLE, Memphis, TN, October 19-21, 2009.

Agreement 17894: NDE Development for ACERT Engine Components

J. G. Sun
Argonne National Laboratory

J. A. Jensen
Caterpillar, Inc.
Technical Center

Objective/Scope

Applications of advanced materials in diesel engines may enhance combustion and reduce parasitic and thermal losses, thereby improving engine efficiency. Engine components developed from advanced materials, however, require rigorous assessment to assure their reliability and durability in more stringent operating conditions. The objective of this work is to develop and assess various nondestructive evaluation (NDE) methods for characterization of advanced engine components in a Caterpillar heavy-duty ACERT experimental engine at ORNL. NDE technologies established at ANL, including optical scanning, infrared thermal imaging, ultrasonics, and x-ray CT, will be further developed for detection of volumetric, planar, and other types of flaws that may limit the performance of these components. NDE development will be focused on achieving higher spatial resolution and detection sensitivity. Current efforts are directed in applications of optical methods for valvetrain components, X-ray and ultrasonic for joinings, and thermal imaging for thermal barrier coatings (TBC).

Technical Highlights

Work during this period (January-March 2009) focused on investigating synchrotron x-ray CT and on developing multilayer thermal modeling method for TBC characterization.

1. Synchrotron X-Ray CT for Metallic Parts

X-ray computed tomography (CT) was investigated for potential NDE inspection of joints. ANL has developed high-energy (420 kV) and high-resolution x-ray systems for inspection of large ceramic components with great success. For large metallic components, however, industrial x-ray sources usually don't have sufficient intensity (flux) to produce high-quality images with good signal-to-noise ratio. In collaboration with a beamline scientist, effort in this period was directed to investigate a prototype x-ray CT system using the synchrotron x-ray source at ANL's Advanced Photon Source (APS), which is a DOE user facility. The synchrotron x-ray source has a peak energy of >250keV with sufficient flux. A preliminary test was conducted for a turbine blade made of a nickel-based superalloy, which is a difficult material to penetrate by X-rays. Figure 1 shows a typical constructed cross-sectional CT slice of the blade. The image pixel size was at ~60µm (pixel size of ~10µm is possible). The constructed slice has some beam hardening effect, represented by variation in component grayscale, due to the energy distribution of the X-ray source. However, volumetric features with sizes in 100µm and smaller may be identified. For crack detection, micro CT imaging with synchrotron source was demonstrated capable to detect cracks with gap opening smaller than one tenth of the imaging pixel size. Therefore, it is expected that synchrotron CT imaging is suitable for NDE inspection of joints/welds in diesel engine components.

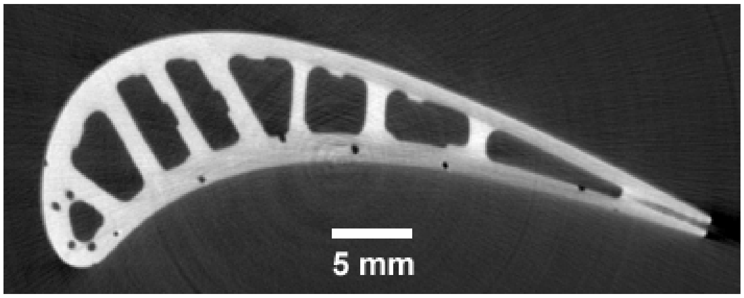


Fig. 1. Typical synchrotron CT slice of a superalloy turbine blade.

2. Thermal Imaging for Thermal Barrier Coatings

Effort during this period was focused on developing a multilayer thermal modeling method based on pulsed thermal imaging for quantitative measurement of TBC thermal properties (conductivity and heat capacity). In this method, a TBC is modeled by a multilayer material system and the 1D heat-transfer equation describing the pulsed thermal-imaging process is solved by numerical simulation. The numerical solutions (of surface temperature decay) are then fitted with the experimental data at each pixel by least-square minimization to determine unknown parameters in the multilayer material system. Multiple parameters in one or several layers can be determined simultaneously.

The multilayer modeling method was used to determine TBC thermal properties, conductivity and heat capacity, with known TBC thickness. The experimental sample is an as-processed TBC specimen with a surface area of 25.4 mm in diameter (sample curtsey of Dr. A. Feuerstein, Praxair Surface Technologies, Inc.). The top ceramic coating is 0.127 mm thick, and the nickel-based superalloy substrate has a thickness of 3.1 mm. The TBC surface was coated by a black paint for the thermal imaging test. The predicted TBC conductivity and heat capacity distributions are shown in Fig. 2. It is seen that the predicted thermal conductivity and heat capacity images are uniform. Some minor variations of the predicted properties are visible in the images, which are mostly due to the nonuniformity of the black paint and small flaws on surface. The predicted average TBC conductivity is 1.65 W/m-K, which is consistent with the typical value of such TBCs (1.71 W/m-K). The predicted average TBC heat capacity is 3.3 J/cm^3-K, which is higher than typical TBCs. The reason for a higher predicted heat capacity is probably due to the black paint applied on TBC surface. Nevertheless, these results indicate that the multilayer modeling method can be used to predict TBC parameters.

To verify the prediction accuracy, Fig. 3 compares the experimentally measured data and the corresponding predicted theoretical data for a typical pixel within the image. Although the data fit was carried out for the temperature (Fig. 3a), the fitting was also very accurate for the temperature derivative, Fig. 3b. The slight discrepancies of the temperature derivative data between the measured and predicted in early time period ($t < 0.01$s) was likely due to the surface roughness and effects related to the black paint, and in the later period (t > 0.1s) to the lower surface temperature (< 1°C) that corresponds to a lower signal to noise ratio.

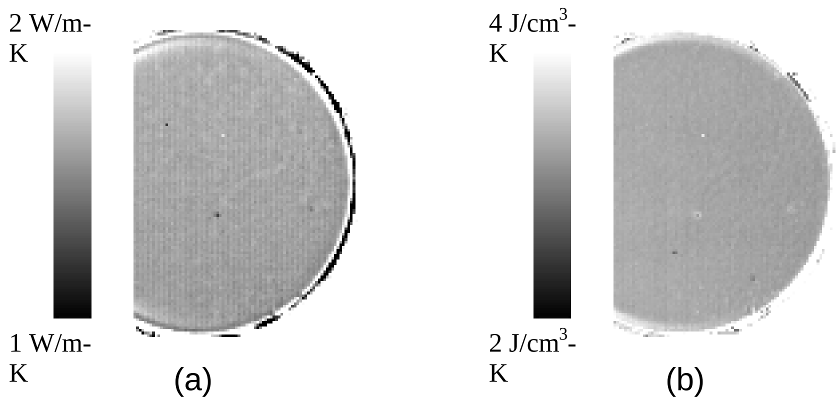


Fig. 2. Predicted TBC (a) conductivity and (b) heat capacity images of a TBC specimen.

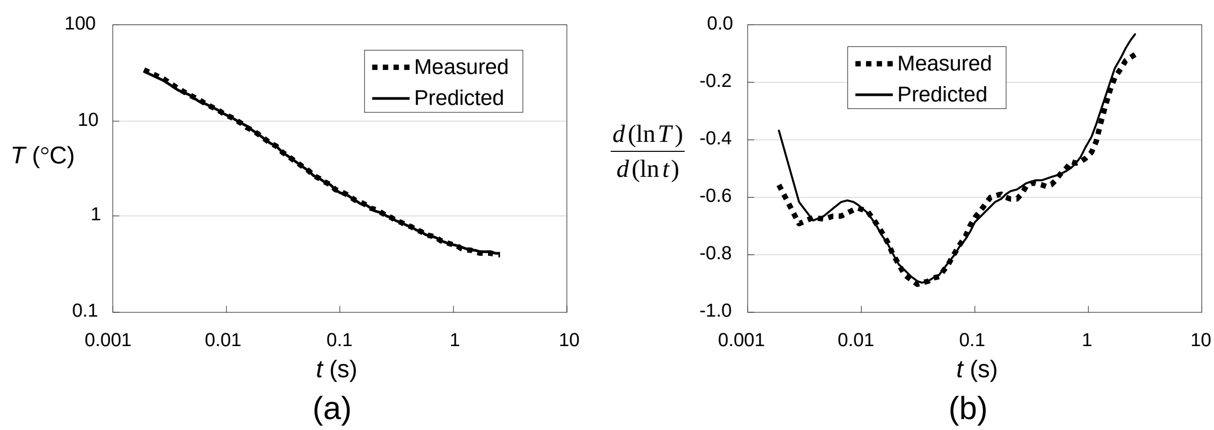


Fig. 3. Comparison of measured and predicted surface (a) temperature and (b) temperature-derivative data for a typical pixel in the Fig. 2 images.

3. Optical Imaging for Thermal Barrier Coatings

In addition to thermal imaging, optical methods were also attempted for NDE inspection of TBCs. These include the laser backscatter and optical coherence tomography (OCT). Optical methods may detect coating cracks/delaminations and, with OCT, determine crack depth. However, they are limited by optical penetration depth, so are normally used for thin TBCs. These optical methods will be investigated for NDE of coated diesel engine components.

Status of Milestones
Current ANL milestones are on schedule.

Communications/Visits/Travel
J. G. Sun attended and presented two papers at the 33rd International Conference on Advanced Ceramics and Composites held Jan. 18-23, 2009, in Daytona Beach, FL.

J.G. Sun plans to attend the 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting being held May 18-22, 2009, in Arlington, Virginia.

Problems Encountered
None this period.

Publications
J.G. Sun, E.R. Koehl, S. Steckenrider, C. Vieillard, and T. Bayer, "Nondestructive Inspection of Ceramic Bearing Balls Using Phased Array Ultrasonics," paper presented at the American Ceramic Society's 33rd International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, FL, January 18-23, 2009.

J.G. Sun, "Measurement of Thermal Barrier Coating Conductivity by Thermal Imaging Method," paper presented at the American Ceramic Society's 33rd International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, FL, January 18-23, 2009.

Agreement 15050: Materials-Enabled High Efficiency Engines

Michael Kass, N. Domingo, Robert M. Wagner, and D. Edwards
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.

Progress This Quarter (January – March 2009)

- Completed instrumentation of the engine, coolant, intake and exhaust systems. Numerous thermocouples and pressure transducers were placed at selected locations to accurately measure the availability of the thermal energy released during combustion.
- The throttle assembly components were received and wired up with the engine ECU. The engine was operated at several speed and load settings. An initial shakedown indicated that the engine and dynamometer are operating properly.
- Preliminary discussions are being held to identify components for evaluation. A thermal barrier material has been selected and is being considered for engine experiments.

Publications/Presentations/Awards

No publications or presentations to report during this quarterly period.

Agreement 10635: Catalysis by First Principles - Can Theoretical Modeling and Experiments Play a Complimentary Role in Catalysis?

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

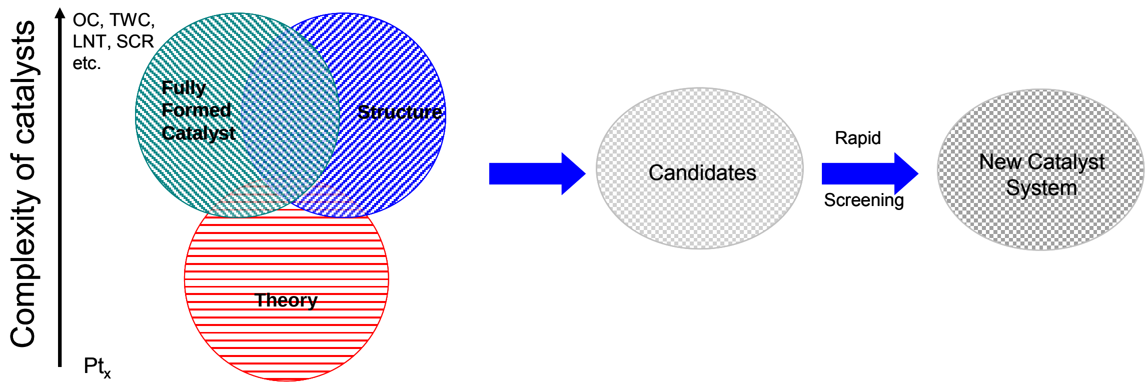
Objective/Scope

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.

We have focused on the oxidation catalyst to develop and demonstrate catalyst by design protocol as a prelude to developing catalyst by design protocols for complex emission treatment catalysts; e.g., TWCs, NO_x traps, and HC-SCR catalysts. Our goals are as follows:

- Our theoretical goal is to carry out the calculation and simulation of realistic supported 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 CO-oxidation conditions are summarized in the following paragraphs. The results show how sample to sample variation can affect results. The effect of switching from gamma to theta alumina as a support material for the Pt particles is also illustrated.

Our early theoretical studies on gas phase unsupported clusters have been useful in developing the "catalyst by design" protocol. However, the results of theoretical studies on gas phase clusters can not be compared with experimental studies because the gas-phase cluster of 10 atoms exhibits chemistry almost approaching that of bulk metal particles. In view of this, we have initiated theoretical studies of supported clusters and their interaction with CO, NO_x, and HC. We also summarize our theoretical studies.

Theoretical Studies

We have selected θ-alumina supported Pt clusters for theoretical studies because these clusters can be synthesized and the experimental results can be compared with theoretical results. While this is also true for γ-alumina and α-alumina supported clusters, there are limitations of these supports. The structure γ-alumina remains to be conclusively determined preventing its theoretical examination. α-Alumina, on the other hand, has practically not surface area and does not make a good support for catalyst. θ-Alumina can be easily synthesized, exhibits a surface area of ~100 m^2/g, and has a well-defined structure.

We have initiated our work by carrying out a density functional theoretical study of bulk θ-alumina employing Vienna *ab initio* simulation package (VASP). Calculations were performed for generalized gradient approximation (CGA) of Perdew and Wang. The structure was fully relaxed with respect to volume as well as cell-internal and –external coordinates. Extensive test indicated that 600 eV was a sufficient cut-off to achieve highly accurate energy differences. The calculated cell parameters are as follows: a = 11.93; b = 2.94; c = 5.71; β = 103.88; V = 193.15. These data compare very well to experimental values of a = 11.85; b = 2.904; c = 5.622; β = 103.8; V = 187.8. The cell internal positions are as follows:

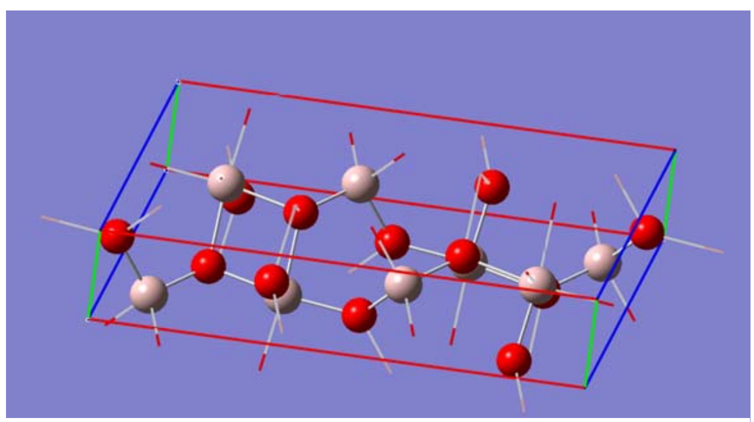
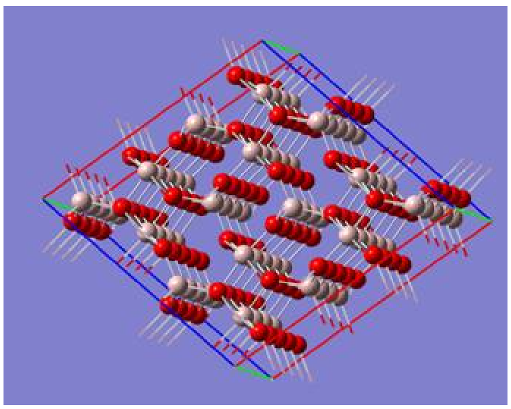


Figure 1: Calculated Structure of θ-Alumina

Calculated: Al*1* (0.909, 0.204), Al*2* (0.658, 0317), O*1* (0.160, 0.109), O*2* (0.495, 0257), O*3* (0.826, 0434)
Experimental: Al*1* (0.917, 0.207), Al*2* (0.660, 0316), O*1* (0.161, 0.098), O*2* (0.495, 0253), O*3* (0.827, 0427)

Thus, VASP has provided very accurate calculation of bulk θ-alumina. In order to carryout metal supported θ-alumina theoretical studies, we optimized [010] charge neutral surface of θ-alumina which is 4 cell deep and 2 cell wide and contains 180 atoms. A vacuum of 15Å was introduced below and above the cell. The calculated cell parameters are as follows: a = 11.838; b = 11.64; c = 11.242; β = 103.79. The structure and the density of states are shown in the following figure:



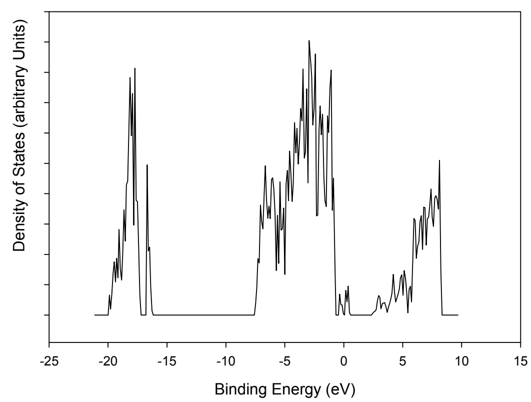
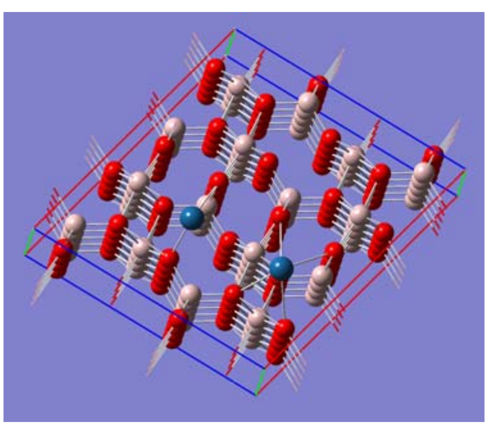


Figure 2: θ-Alumina slab geometry for (010) surface (left) and density of states (right)

We also optimized the single Pt, Pd, Ag, or Au atom adsorbed on the [010] surface of θ-alumina by placing the single atom on two different locations (i) metal atom bonded to two oxygen atoms and (ii) metal bonded to four oxygen atoms.



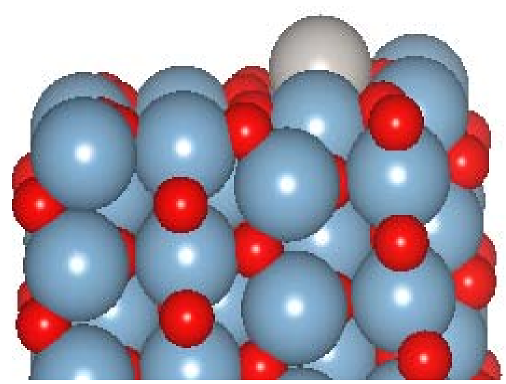


Figure 3: Pt location on 010 surface (left) and optimized geometry (right)

The optimum structure in both cases was divalent metal atom bonded to two surface oxygen atoms (Pt-O bond distances 2.18 and 2.13Å, O-Pt-O 140.55º). The space filling model of a single Pt- atom on [101] θ-alumina is shown in Figure 3. This structure is representative of Pd, Ag, or Au adsorbed on the θ-alumina surface.

The accurate calculations of density of states of Pt, Pd, Ag, and Au single atoms adsorbed on θ-alumina surface are in progress and will be presented in the next quarterly report along with the changes in density of states of θ-alumina surface due to adsorption of metal atom and adsorption energy of metal atoms.

Our next step is to calculate the structure Pt clusters (2 atom and larger) on θ-alumina surface.

Experimental Studies

Since we are using θ-Al_2O_3 as the support material for our theoretical calculations, it is essential to know how 1nm Pt particles are arranged on the θ-Al_2O_3 support experimentally. Initial nanostructural characterization of this catalyst using an Aberration Corrected Electron Microscope in STEM mode was carried out. Figure 4 shows a HAADF image of freshly synthesized 1nm Pt/θ-Al_2O_3 catalyst. This is the same catalyst used in our previously reported oxidation studies. The atomic make-up of the Pt nanoclusters involves on average 10-20 Pt atoms. This is similar to what we see by ACEM-STEM for 1nmPt/γ-Al_2O_3. Further nanostructural characterization is being done to determine on what face of the θ-Al_2O_3 support the nanoclusters are sitting.

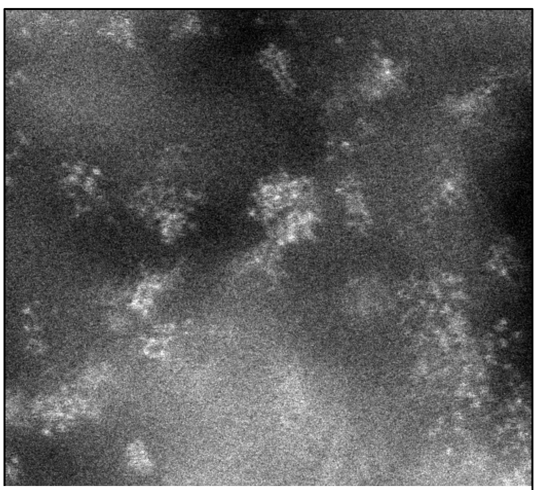


Figure 4. ACEM HAADF-STEM image of 1nm Pt/θ-Al_2O_3.

Triple Oxidation: 1nm 2%Pt/γ-Al_2O_3 catalyst, prepared by the traditional impregnation method from $H_2PtCl_6 \cdot xH_2O$, were exposed to triple oxidation conditions to begin looking at how the Pt clusters behave in more complex systems. The triple oxidation conditions refers to exposing the catalyst to a gas composition of 5%CO, 500ppm NO, 500ppm hydrocarbons (2:1 mix of propene and propane), and 10%O_2. A space velocity of 50,000 h^{-1} was obtained using N_2 as a balance gas to reach the required flow rate of 3L/min. The oxidation of each gas was monitored by analyzers attached to our bench-top exhaust reactor.

The triple oxidation study was studied from inlet gas flow (just before catalyst sample) temperatures of 133.5°C to 465.5°C, see Figure 5. CO oxidation reached 100% conversion quickly at 167°C, and remained completely oxidized throughout the remainder of the test. At this same temperature, the C_3 hydrocarbon mix reached 95% conversion. NO oxidation to NO_2, which is equilibrium limited, reached a maximum conversion of 45.5% at a slightly higher temperature of 251.5°C before the reverse NO_2 reduction reaction became favored. Interestingly, at the same temperature that NO oxidation reached its maximum conversion (251.5°C), a small drop in the hydrocarbon oxidation was observed. Oxidation of the hydrocarbon gases began approaching completion by the next temperature monitored (306.5°C) and reached ~97% by 420.5°C.

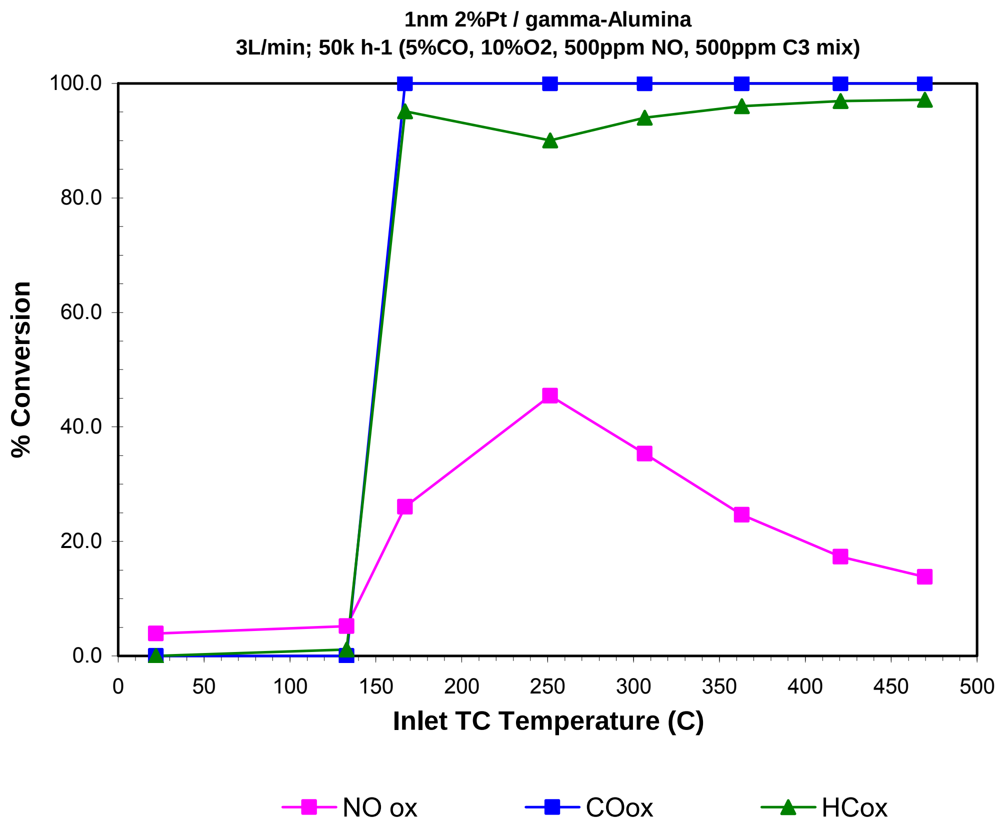


Figure 5. Conversion graph depicting CO, NO and hydrocarbon (HC) oxidation over 1nm Pt/2%Pt/Al_2O_3 catalyst as a function of inlet gas flow temperatures of 133.5°C to 465.5°C.

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

- We will carry out selective catalytic reduction of diesel emissions on catalyst and monitor nanostructural changes in catalyst samples.

- Theoretical calculations will be carried out on the structure of Pt clusters (2 atom and larger) on θ-alumina surface.

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

M. DeBusk presented an invited paper on “Catalyst by design: Combining the power of theory, experiments, and nanostructural characterization for catalyst development” at the American Chemical Society Meeting, March 22-27, Salt Lake City, Utah.

C.K. Narula co-organized a symposium on Catalysis at American Chemical Society Meeting, March 22-27, Salt Lake City, Utah.

SAE international judged our technical paper, SAE-2008-01-0416, as one of the most outstanding papers of 2008 and included it for publication in SAE International Journal of Materials and Manufacturing.

Publications

1. C.K. Narula, “Catalyst by Design – Bridging the Gap between Theory and Experiments at Nanoscale Level,” Encyclopedia of Nanoscience and Nanotechnology, Vol. II, Taylor & Francis, New York, 2008, pp 771-782 (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, SAE Int. J. Mater. Manu., 1(2008) 182-188.
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_xO_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. Moses-DeBusk, M.; Narula, C.K. "Catalyst by design: Combining the power of theory, experiments, and nanostructural characterization for catalyst development," 227th National American Chemical Society Meeting, March 2009 (invited).
2. 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).
3. 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).

4. Blom, D.; Allard, L.; Narula, C.; Moses, M.; "Aberration-Corrected STEM ex-situ Studies of Catalysts" Wednesday, Microscopy and Microanalysis Meeting, 2007, August 5-9, Ft. Lauderdale, Florida. (Invited).
5. 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
6. 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
7. 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
8. 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
9. 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, C.H.J. Peden, J.-H. Kwak and L. Germinario
Oak Ridge National Laboratory

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 Drs. S. A. Bradley of UOP Co., and C. H. F. Peden of PNNL. NOx trap catalyst materials BaO/Al_2O_3 are being studied with Dr. Peden and Dr. Ja Hun Kwak at PNNL.

Technical Progress

In-Situ Microscopy Developments

Recent advances in aberration corrected electron microscopy (ACEM) are providing new tools and opportunities for studying chemical processes at gas-solid interfaces at atomic resolutions. In the area of heterogeneous catalysis, STEM-based high-angle annular dark-field imaging (HA-ADF) has provided the potential for direct observation of single heavy atoms and atom clusters. [1]. This approach has been used to study catalytic properties by directly probing structure development as a result of metal particle-substrate interactions, and used to explore the combined effects of temperature, promoters, and organic ligands on the evolution of catalyst structure [2-3]. Associated with this new tool is the potential for artifacts, such as electron beam-induced polymerization of organic components [4], and the influence of the electron beam on heavy atom diffusion and nanostructuring [5]. Experiments were conducted in order to develop sample preparation techniques and imaging protocols that are suitable for achieving sub-Ångström resolutions at ambient temperatures. In-situ heating studies were also conduct using Aduro™ heater devices manufactured using MEMS technology by Protochips Inc. (Raleigh, NC) [6].

Atomic-scale imaging of small molecule-metal cluster interactions *in situ* under catalytic temperatures was recently initiated [7], using the aberration-corrected JEOL 2200FS STEM/TEM instrument, equipped with a CEOS GmbH corrector on the probe-forming lenses, housed in ORNL's Advanced Microscopy Laboratory. After exploring sample

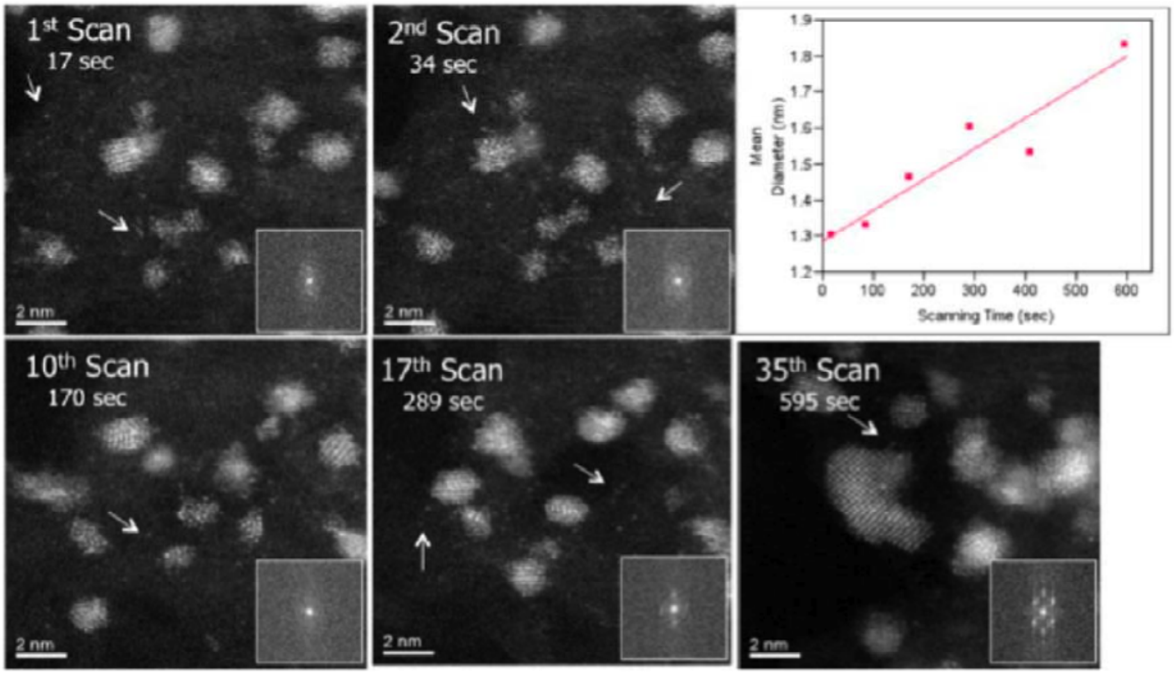


Fig. 1. Electron irradiation effects on diffusion of single atoms (arrows). Amorphous atom clusters (rafts) grow in size and develop crystalline domains after extensive scanning. Plot show mean particle diameters as highly correlated ($R^2 = 0.90$) with electron scanning times.

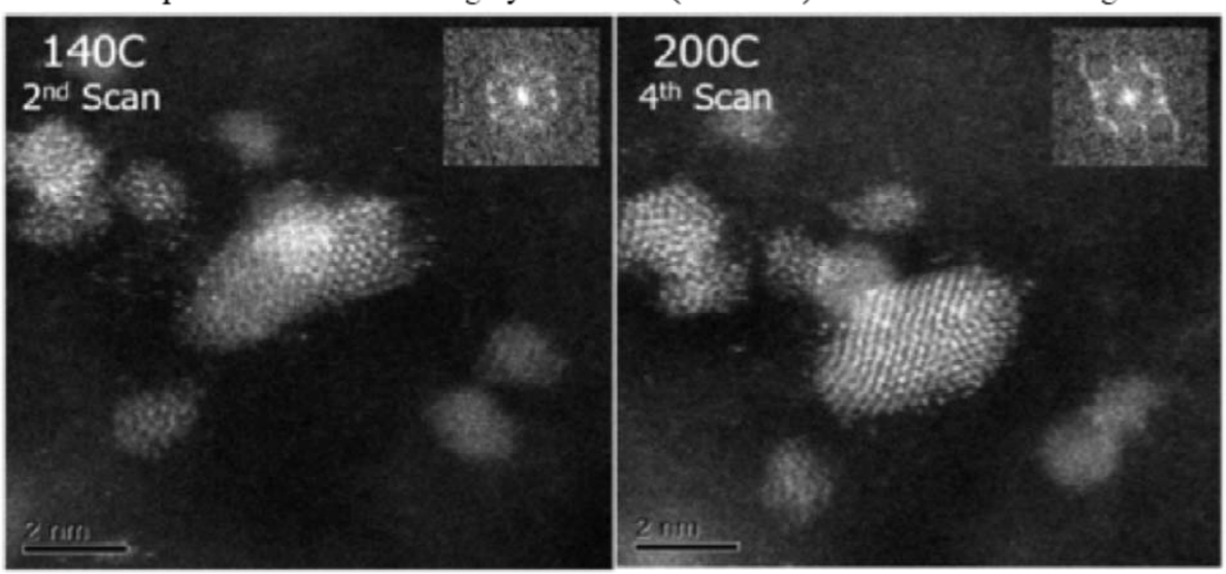


Fig. 2. In-situ heating of Ru/C catalyst preparations, in vacuum, provided evidence for a temperature-induced migration, coalescence and ordering at 200°C, that is independent of electron-beam effects.

preparation protocols suitable for atom-level imaging at ambient temperatures, experiments were conducted to identify and minimize the inadvertent sources of organic contaminants introduced with the sample during preparation. Sigma-Aldrich, 5% ruthenium on carbon was the source of catalyst materials used in this study. Catalysts were deposited from an alcohol suspension onto holey carbon films supported on either Cu grids or Protochips Aduro™ devices. Beam irradiation effects were studied by repeated scanning of suitable areas using the normal high-resolution mode. A partial sequence of images is shown in Fig. 1. Single Ru atoms (arrows) and amorphous atom clusters (rafts) are clearly evident and undergo extensive ordering and crystallization after repeated scanning that is reminiscent of Ostwald ripening. The plot in Fig.1 shows a linear dependence of the mean particle diameter with increasing electron scanning times. A similar linear dependence of crystal growth for short thermal heating times (<30 min.) was also reported in studies on sintering behavior of Pd nanoparticles [8]. In-situ heating experiments (Fig. 2) conducted in the microscope column using the Aduro devices provided evidence for a temperature-induced migration, coalescence and ordering at 200°C, that is independent of electron-beam induced effects.

Progress on the Second-Generation E-Cell Holder: The first prototype environmental cell holder we developed with Protochips Co. was described in the annual report. That holder proved to be unacceptable for use in our ACEM, because it was too thick to be used practically on a routine basis. The design employed an upper thin film window and a lower thin film window, sandwiched around a heater chip on which the catalyst powder sample could be dispersed. This resulted in a design that was 1.7mm thick, which barely fit into the 2mm gap of our objective lens pole piece. The new holder is a “two-window” device, with the upper window being a heater chip that would have the catalyst sample dispersed on the interior side, between the heater membrane and a lower thin film window. Figure 3 shows a comparison of the Gen 1 and Gen 2 E-cell holders for the ACEM in top view (note images show equivalent magnifications). Figure 4 shows the two holders in end view. Figure 5 compares schematically the 3-chip and 2-chip designs.

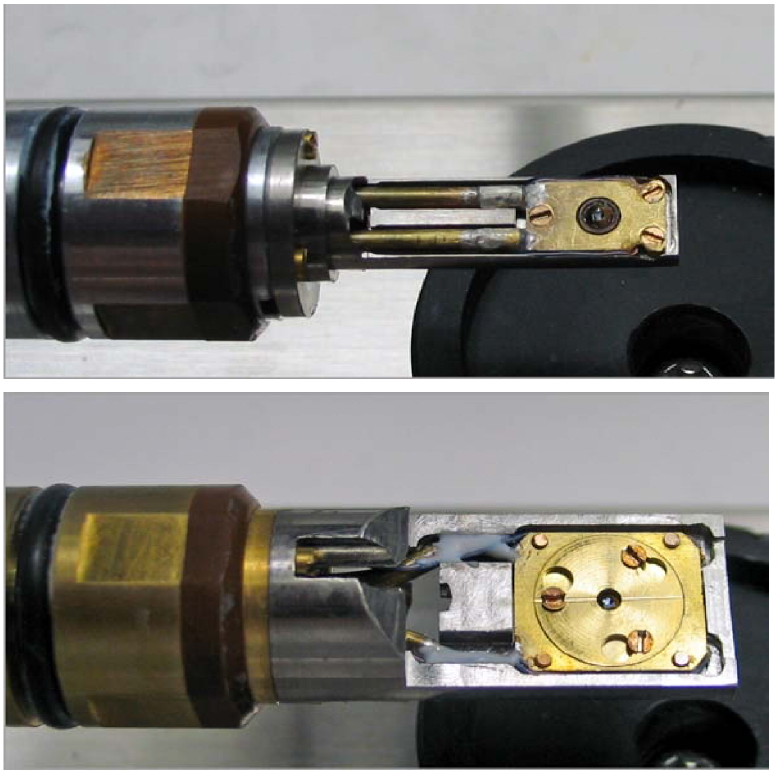


Fig. 3. Comparison of Gen 1 (top) and Gen 2 (bottom) E-cell holders for the JEOL 2200FS ACEM.

Fig. 4. Gen 1 (left) and Gen 2 (right) E-cell holders shown in end view. Cell thicknesses are 1.7mm and 1.38mm, respectively.

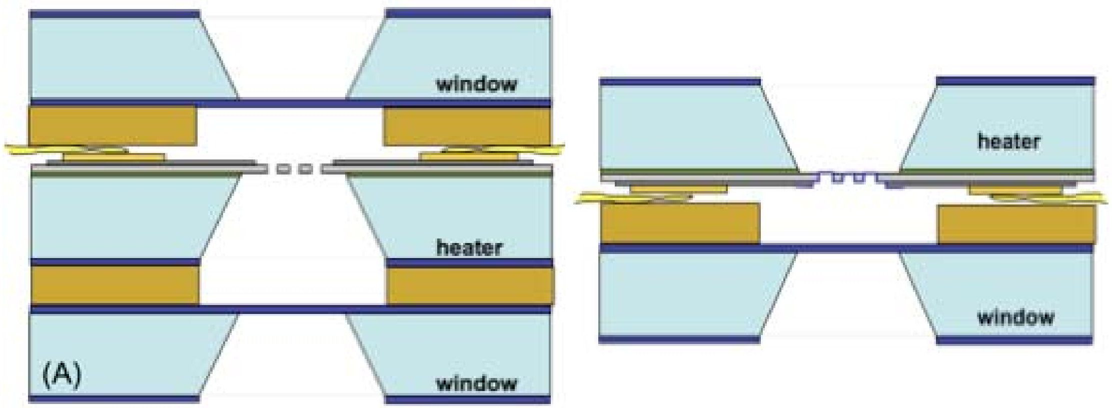


Fig. 5. Schematics of the 3-chip (left) and 2-chip designs for the Gen 1 and Gen 2 E-cells, respectively.

Initial testing of the E-cell has focused on the nature of imaging at the atomic level with the beam passing initially through an amorphous upper window material (50 nm of silicon nitride as a 'worst case.' A test window was installed in the Gen 2 E-cell, and a test specimen of gold on iron oxide catalyst was dispersed on the bottom side of the window. Prior to deposition of the catalyst, the holder was plasma cleaned for 30 min. A sample area was chosen, and the sample was placed under a 'beam shower' in the microscope, for another 30-min period. The plasma cleaning and beam showering treatments are standard procedures to help minimize the buildup of contamination at high magnifications. Initial observations showed that lattice fringes in the iron oxide could be imaged in bright-field mode, but no lattice or atomic columns were seen in HA-ADF imaging mode. This suggests that the 50 nm thickness of the window causes beam spreading to the extent that it degrades the resolution in dark-field mode, but still allows the interference effects operating in bright-field mode to show lattice. Protochips will fabricate new nitride windows with thicknesses down to 20 nm or less to allow further testing.

PNNL NO_x trap research collaboration: we completed microscopy on samples of BaO-Al_2O_3 NO_x trap materials for a study we have worked on with Drs. Ja Hun Kwak and C.H.F. Peden at PNNL. The work was published in the Journal of Catalysis (see below). Another paper was prepared and submitted to Science, and is currently under review.

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[1] M. Isaacson, J. Langmore, N. W. Parker, D. Kopf and M. Utlaut, Ultramicroscopy 1 (1976) 359-376.
[2] E.D. Boyes, P. L. Gai, Ultramicroscopy 67 (1997) 219.
[3] R. Sharma, P. A. Crozier, *Environmental Transmission Electron Microscopy in Nanotechnology*, Microscopy in Nanotechnology, Kluwer Academic, New York, 2005.
[4] M. Isaacson, D Kopf, M. Ohtsuki and M Utlaut, Ultramicroscopy 4 (1979) 97-99.

[5] L.T. Germinario, R. Reed, M.D. Cole, S.D. Rose, J.W. Wiggins, M. Beer, S.E.M. 1 (1978) 69-76.

Status of Milestones

On schedule

Communications/Visits/Travel

L. F. Allard, Invited Seminar, University of South Carolina Interdisciplinary Mathematics Institute series on Imaging in Electron Microscopy. Seminar title: *Imaging the behavior of atoms, clusters and nanoparticles during elevated temperature experiments in an aberration-corrected electron microscope.* March 16-18, 2009

L. F. Allard, Invited Seminar, University of Texas-San Antonio, Dept. of Materials Science and Engineering. Seminar title: Introduction to Aberration-Corrected Electron Microscopy. March 20, 2009

Publications

"Understanding the nature of surface nitrates in BaO/γ -Al_2O_3 NO_x storage materials: A combined experimental and theoretical study," Ja Hun Kwak, Donghai Mei, Cheol-Woo Yi, Do Heui Kim, Charles H.F. Peden, Lawrence F. Allard and János Szanyi, *Journal of Catalysis* **261** (2009) 17–22.

"Co-ordinatively unsaturated $^{Al3+}$ centers as binding sites for active catalyst phases on γ-Al_2O_3," Ja Hun Kwak, Jianzhi Hu, Donghai Mei, Cheol-Woo Yi, Doheui Kim, Charles H.F. Peden, Lawrence F. Allard and Janos Szanyi; submitted to *Science*, under review.

Agreement 17859: Durability of ACERT Engine Components

Hua-Tay Lin, T. Kirkland, and A.A. Wereszczak
Oak Ridge National Laboratory

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

Instrumentations of thermal cycling and thermal shock test facilities have been designed and fabricated (still in process) during this reporting period. The objective this thermal testing is to provide a baseline data and also insight into durability and integrity of thermal barrier coating (TBC) designed and employed on ferritic Fe steel alloys with high SI content. The ferritic Fe steel alloy is the current production material used for the exhaust components in the heavy-duty diesel engines. The application of TBCs would allow end users to significantly reduce the heat rejection and also prevent the oxidation/corrosion degradation process encountered in the current production materials. It thus could avoid the application of the very high-cost stainless steel materials for the exhaust port and manifold components. This is one of the key enabling materials technologies that would allow end users to achieve 55% engine efficiency by 2012 as set under the 21st Century Truck Program.

Three types of TBCs, which provide the thermal and oxidation/corrosion protection, will be evaluated. Two types of coatings will be applied onto the as-cast Fe steel substrates (6.4 mm thick) via air plasma spray process and the other one will be using the ceramic conversion process deposited via the slurry approach. The thermal shock test will be carried out between 760°C (1400°F) and 20°C (68°F) to simulate the temperature cycling condition during the engine operation. Two sizes of substrates (e.g., 25 mm x 25 mm and 50 mm x 50 mm) will be evaluated to understand the effect of surface area on the thermal shock response. In addition, long-term aging of the coated steel coupons at 760°C up to 1000h in air and/or controlled environment will be carried out to evaluate the oxidation resistance and microstructure stability. Detailed optical and SEM analyses would be performed following the thermal testing. NDE analysis will also be carried out before and after the thermal testing by ANL to identify the potential delamination of TBCs. After completion of the screening step the real exhaust components coated with the down-selected TBC will be tested in C15 ACERT engine located at NTRC under the specified test condition. Variables such as temperature, exhaust flow rate, transients, and exhaust chemistry would be closely monitor as well.

Status of FY 2009 Milestones

Complete mechanical database and microstructure characterization of new components designed for ACERS diesel engine. **(09/09**) – On schedule.

Communications/Visits/Travel

Communications and conference calls with Drs. Philip and Jenson at Caterpillar regarding the discussion of test matrix and candidate TBC systems for ACERS engine and components.

Communications with Dr. Kass at NTRC regarding the up-to-date status on the installation of C15 ACERT engine.

Problems Encountered

None.

Publications/Presentations/Awards

None.

References

None

Agreement 14957: High Temperature Thermoelectrics

A. A. Wereszczak and H. Wang
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

Strength Testing

A high temperature fixture was developed during this quarter that will enable flexure strength testing up to at least 500°C. The fixture is self-contained, has built-in provisions for semi-articulated loading (i.e., self-alignment), and made of alumina ceramic. It has an oxygen gettering material reservoir that lessens the oxidation rate of the prismatic bend bars. Lastly, its simple design allows for rapid insertion and extraction of the test specimen, so an attractive testing rate can be achieved.

N- and P-type skutterudites were received from General Motors's J. Salvador and readied for high temperature strength testing. Dilatometry was run on the compositions. It was observed that one of the compositions is susceptible to oxidation. This observation is what drove the effort for the flexure strength fixture to have a gettering feature. Metallographic mounts were prepared for microstructural examinations.

The development of an in-situ, thermal gradient test fixture that allows for concurrent flexure strength testing continued. Temperature measurement approaches using an infrared camera underwent refinement.

Collaboration with Marlow

The new CRADA with Marlow Industries will commence in early Q3. A kick-off meeting is scheduled for April 28, 2009 at Marlow's headquarters in Dallas, TX.

Status of FY 2009 Milestones

Generate thermoelastic and mechanical property database as a function of temperature on at least one candidate HTTE p- and n-type material fabricated by Marlow Industries. *On schedule.*

Communications/Visits/Travel

Wereszczak attended the 33rd International Conference on Advanced Ceramics and Composites, held in Daytona Beach, FL, January 20, 2009, and gave a presentation entitled "Strength of Bismuth Telluride".

Numerous communications occurred between Wereszczak and Marlow's J. Sharp during the present reporting period.

Problems Encountered

None.

Publications/Presentations/Awards

Presentation and proceedings paper: A. A. Wereszczak, T. P. Kirkland, O. M. Jadaan, and H. Wang, "Strength of Bismuth Telluride," in press, *Ceramic Engineering and Science Proceedings*, (2009).

J. R. Salvador, J. Yang, X. Shi, H. Wang, and A. A. Wereszczak, "Transport and Mechanical Property Evaluation of $(AgSbTe_2)_{1-x}(GeTe)_x$ (x=0.8, 0.82, 0.85, 0.87 and 0.90)," In press, *Journal of Solid State Chemistry*, 2009.

J. R. Salvador, J. Yang, X. Shi, H. Wang, A. A. Wereszczak, H. Kong, and C. Uher, "Transport and Mechanical Properties of Yb-Filled Skutterudites," In press, *Philosophical Magazine*, 2009.

2nd Place Award for Best Paper from 32nd International Conference on Advanced Ceramics and Composites: O. M. Jadaan and A. A. Wereszczak, “Probabilistic Design Optimization and Reliability Assessment of High Temperature Thermoelectric Devices,” *Ceramic Engineering and Science Proceedings*, 29, [3], 157-172 (2008).

References

None.

Agreement 16308: Science Based Approach to 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

Vehicular applications of thermoelectric materials will be greatly facilitated by the identification of high performance materials that have low cost and are available in large quantities. One barrier is that many thermoelectric compositions are based on tellurium, which has acceptable cost at present, but a very limited supply, which may imply large price increases in response to demand. In this regard, a high performance non-telluride replacement for PbTe would be very helpful. The PbTe family includes some of the best known thermoelectrics for waste heat recovery, specifically the LAST compositions and Tl-doped PbTe. In prior work under this program, we had identified the soft ferroelectric mode of PbTe as an important ingredient in the high performance of PbTe based materials, since this enables low thermal conductivity. The lighter chalcogenide, PbSe, is not in proximity to ferroelectricity and does not show good thermoelectric performance due in large part to a higher thermal conductivity. However, it is known that nanostructuring can strongly reduce thermal conductivity under certain circumstances, and these seem to be applicable to PbSe. Specifically, the groups of D. Cahill (Illinois) and D. Johnson (Oregon) have shown that ultralow thermal conductivity is obtained in disordered layered WSe_2 and furthermore that a series of undoped intergrowth compounds of WSe_2 and PbSe can be synthesized. We note that tungsten is a lower cost material compared to tellurium, and is available in much larger quantities. The general formula for these compounds is $(WSe_2)_m(PbSe)_n$. The simplest of these structures (m=1, n=1) is shown in the left panel of Fig. 1. These materials have exceedingly low thermal conductivity – lower than PbTe. Based on this, we initiated studies of the electronic and transport properties of these compounds. The goals are to determine whether they will have sufficiently high thermopowers at reasonable doping levels to provide high performance and to determine what layer thicknesses should be used in these nanostructures to achieve a reasonable balance between low thermal conduction, and electrical conductivity.

To date, we have determined the atomic positions for the m=1, n=1 and m=1, n=2 compounds from first principles and used these to calculate electronic structures (see Fig. 1). We also did virtual crystal calculations to investigate doping effects. We find that for hole doping these materials behave electronically like separated PbSe and WSe_2 blocks, with the electronic transport dominated by the PbSe, while for electron doping the behavior is more complex. We also performed preliminary transport calculations based on our first principles electronic structures. We find that high thermopowers can indeed be achieved in these materials at reasonable carrier concentrations. We also were able to estimate electronic mean free paths by combining experimental literature data for PbSe with our calculated electronic structures. While we are still analyzing the data, our preliminary results indicate the optimum performance will be for nanostructures with thicker PbSe layers than have been investigated experimentally to date, i.e. layer thicknesses with *n*~20.

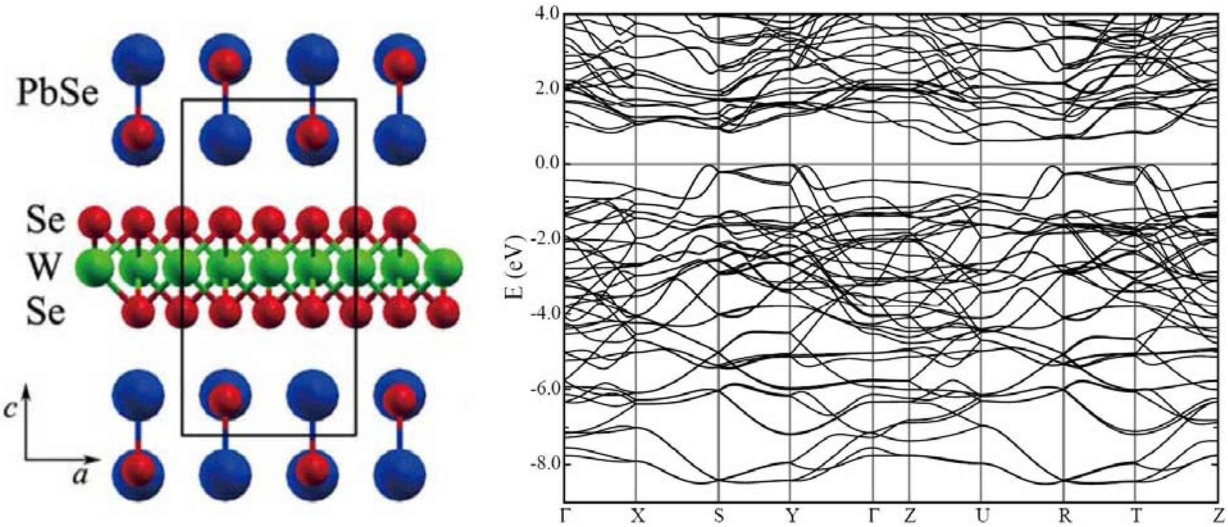

Fig 1. Crystal structure of $(WSe_2)_n(PbSe)_m$: n=1,m=1 (left) and calculated band structure (right).

In addition, we finalized two technical reports this quarter, both of which were published in Physical Review B. One was on La-Te thermoelectrics, showing the connection between performance and band structure, and the other was on $BaMn_2Sb_2$ and $BaMn_2As_2$, which were studied as possible low cost Te-free thermoelectrics.

Status of FY 2009 Milestones

We are progressing towards our milestone of predicting a new thermoelectric composition. Strategies that will be used are to continue investigation of Cu containing delafossites, other narrow band oxide materials, and chalcogenides. We also plan to continue investigation of nano-structured PbSe and related materials. 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

None this quarter.

Problems Encountered

No significant problems encountered this quarter.

Publications/Presentations/Awards

Publications:

1. A.F. May, D.J. Singh and G.J. Snyder, "Influence of band structure on the large thermoelectric performance of lanthanum telluride", Physical Review B **79**, 153101 (2009).
2. J. An, A.S. Sefat, D.J. Singh and M.H. Du, "Electronic structure and magnetism in $BaMn_2As_2$ and $BaMn_2Sb_2$", Physical Review B **79**, 075120 (2009).

References

1. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method, 2nd Edition*, Springer, 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).
3. J. An, A. Subedi and D.J. Singh, "Ab initio phonon dispersions of PbTe," Solid State Communications **148**, 417 (2008).
4. C. Chiritescu, D.G. Cahill, N. Nguyen, D. Johnson, A. Bodapati, P. Keblinski and P. Zschack, "Ultralow thermal conductivity in disordered layered WSe_2 crystals," Science **315**, 351 (2007).