Material Science and Technology Division

Propulsion Materials Program
Quarterly Progress Report for
October through December 2007

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

Andrew Wereszczak
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

Three primary efforts initiated during this reporting period. They consisted of thermomechanical stress analysis of a general insulated gate bipolar transistor (IGBT) using finite element analysis (FEA), the mechanical evaluation of candidate or alternative ceramics for use in a direct copper bonded (DCB) substrate, and the collaboration with the NTRC group of R. Wiles, C. Ayers, and K. Lowe in the development of a direct-cooled PE device.

FEA

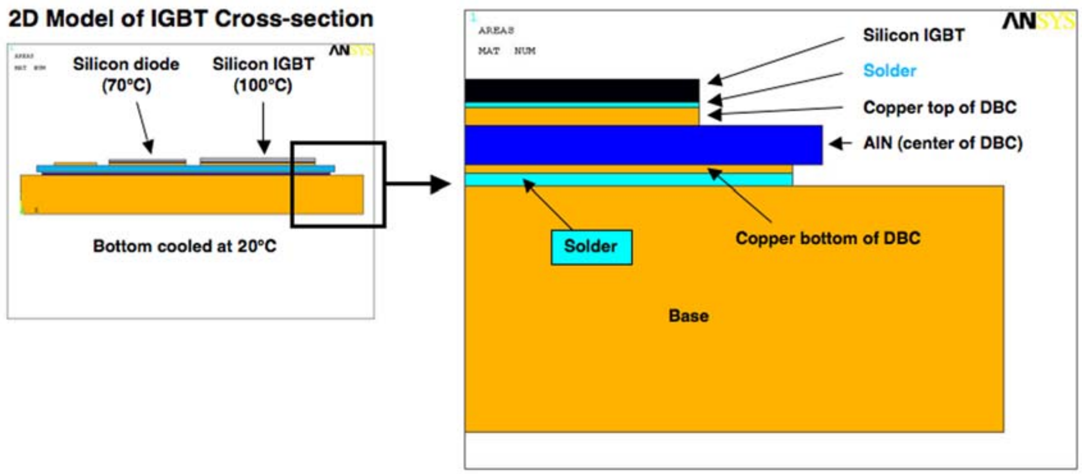
Several finite element analyses were conducted to assist ORNL's Ted Besmann and H.-T. Lin, but perhaps the most important one involved the examination of the competing roles of temperature gradients and yielding solder and copper on the overall thermomechanical stress states in the constituents in an IGBT (Figs. 1-6). Initially, the solder and copper were modeled as linear elastic and concern existed over how that non-representativeness would affect the stress state in the silicon (diode & IGBT itself) and in the ceramic substrate within the DBC. It was found that allowing the solder and copper to yield had a minor role in decreasing the magnitude of the first principal tensile stresses in the silicon and ceramic. This means that the temperature gradients through them dominate the thermommechanical stress development in the silicon and ceramic.

Mechanical Evaluation of Ceramic Substrates

Aluminum oxide (alumina or Al_2O_3) and aluminum nitride (AlN) are two common electronic ceramic substrate materials used in power electronic devices. Alumina is inexpensive but its thermal conductivity is relatively low so it is often not associated with maximized thermal management. Additionally, alumina's coefficient of thermal expansion (CTE) is relatively high making it more prone to fracture from thermal shocking. AlN is attractive because it has a high thermal conductivity and its CTE is relatively low; however, it is expensive and there appears to be a decreasing list of available manufacturers of it. Silicon nitride is a candidate substrate material that has a desirable CTE and has the prospects of being very strong so portion of this project's effort is devoted to the mechanical evaluation of it and its comparison against the commonly used alumina and aluminum nitride. Substrates were acquired during the present reporting period and are now being sectioned for strength testing.

Direct-Cooled PE Device

A collaborative effort is underway with NTRC's Randy Wiles, Curt Ayers, and Kirk Lowe to provide ceramic material selection advice and finite element analysis support to a new direct-cooled PE device concept. Candidate ceramic materials were surveyed for them along with prospective manufacturers. The concept was recently submitted for invention disclosure.



Material / Property	E (GPa)	ν	CTE (ppm/°C)	TC (W/mK)	S_{yld} (MPa)
Silicon	130	0.28	4.1	150	∞ (Elastic)
Copper	135	0.34	17	400	∞ and 138 (Plastic)
AlN ceramic	300	0.24	4.5	150	∞
Solder	12.5	0.36	26	15	∞ and 22

Figure 1. Finite element model of an IGBT and considered properties.

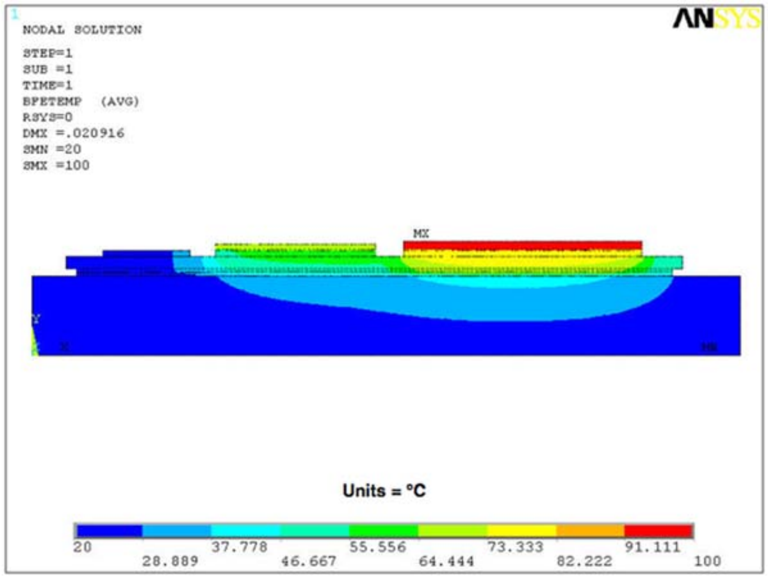


Figure 2. Steady-state temperature profile from a 100°C existing in the IGBT, 70°C in the diode, and 20°C at the bottom.

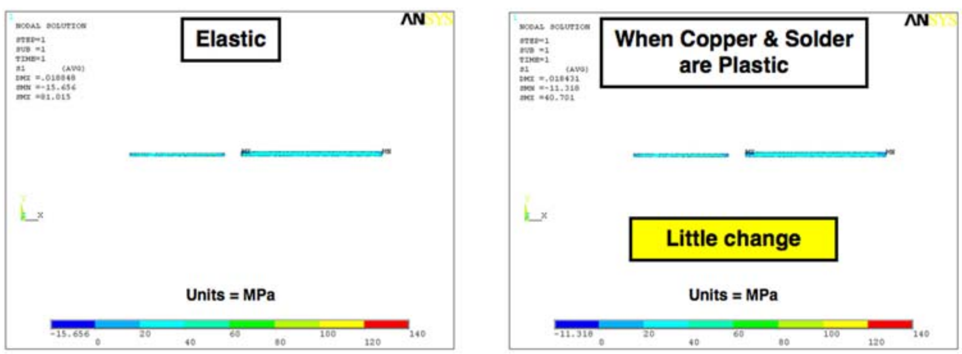


Figure 3. Comparison of the first principal stresses in the silicon diode and IGBT when the solder and copper are considered elastic or allowed to yield. Their yielding did not appreciably change the stresses in the silicon. The temperature gradient (coupled with silicon's CTE) within the silicon has much more of a dominating effect on its stress development.

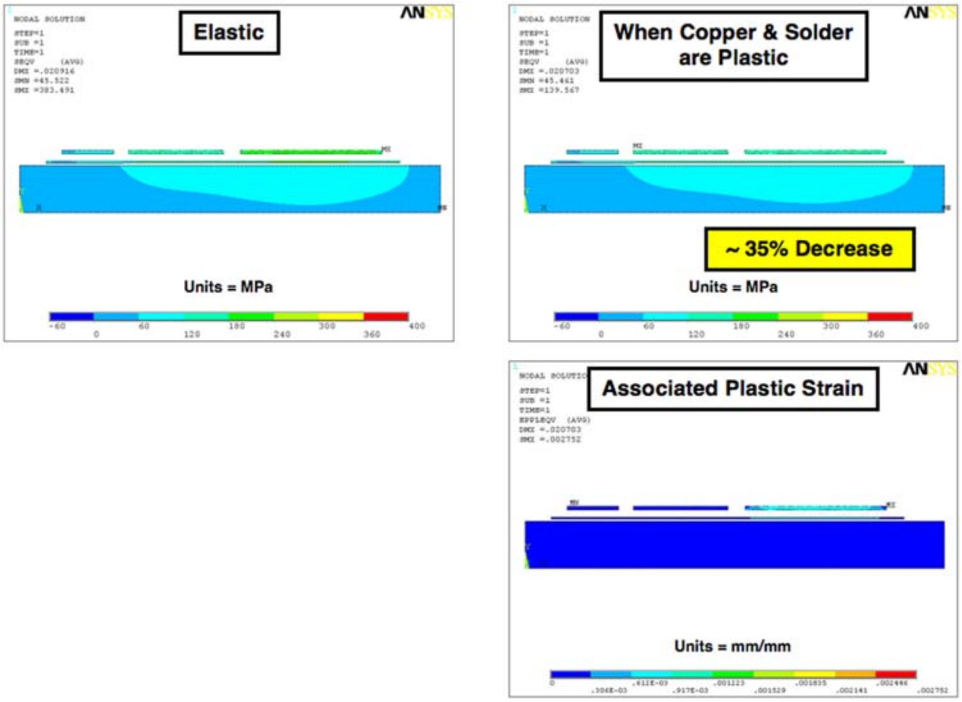


Figure 4. Comparison of the von Mises stresses within the copper constituents when the solder and copper are considered elastic or allowed to yield. As expected, the stress within the copper significantly decreases because of yielding.

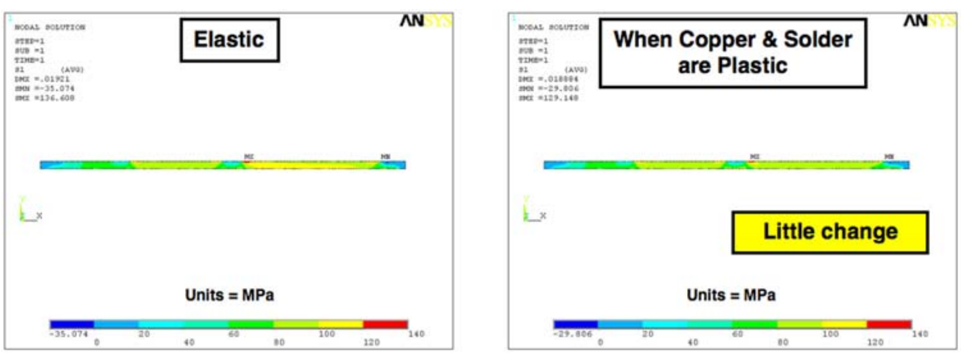


Figure 5. Comparison of the first principal stresses in the ceramic substrate when the solder and copper are considered elastic or allowed to yield. Their yielding did not appreciably change the stresses. The temperature gradient (coupled with the ceramic's CTE) within the ceramic has much more of a dominating effect on its stress development.

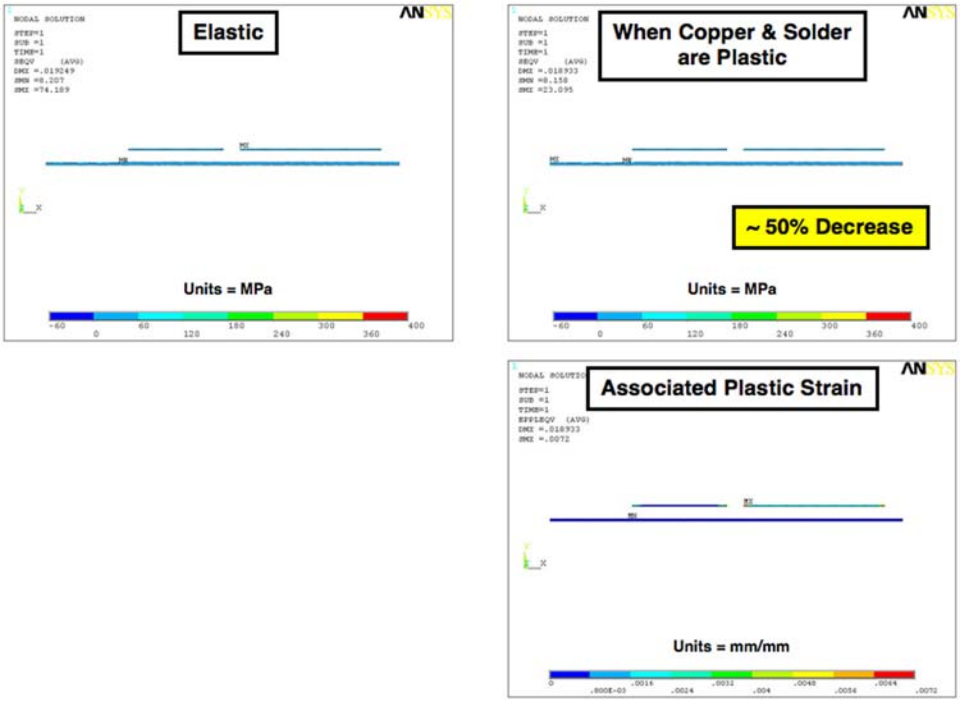


Figure 6. Comparison of the von Mises stresses within the solder constituents when the solder and copper are considered elastic or allowed to yield. As expected, the stress within the solder significantly decreases because of yielding.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

Pertaining to the substrate-related efforts, numerous discussions were held with Kyocera's Adam Schubring, Saint-Gobain's John Bevilacqua, and Ceradyne's Biljana Mikijelj. Regarding the PE-direct-cooling efforts, numerous discussions and visits occurred with NTRC's Randy Wiles, Curt Ayers, and Kirk Lowe, Springboard CIM's Gene Krug, Saint-Gobain's John Bevilacqua, Ceradyne's Biljana Mikijelj, and several companies having capabilities to deposit copper onto ceramics. Wereszczak visited the capacitor manufacturer Kemet on November 7, and that was followed up by January 16 visit from Kemet's Mike Randall and Claes Nender to NTRC. Lastly, regarding FEA efforts, numerous discussions were held with NTRC's Madhu Chinthavali.

Problems Encountered

None.

Publications/Presentations/Awards

None.

References

None.

Agreement 9237: Carbon Foam for Cooling Power Electronics

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

Objective

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

Highlights

- Determination of design parameters for cooling inverter chosen bin mutual agreement between ORNL and ThermalCentric personnel and to be tested at the NTRC have been initiated.

Progress

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

Additionally, tests have been started to characterize the oxidation resistance of graphite foam in air. Koppers supplied us with three types of foams (varying density and pore structure) for this study. We are following the draft procedure outlined by ASTM standard method that has been developed for graphite and machined carbon materials. In this method the oxidation resistance is characterized based on measurements of oxidation rates at various temperatures and evaluation of activation energy and threshold oxidation temperature for a given materials. Results from this study are expected to be used as a guideline to define the practical operating temperatures of thermal management systems based on graphite foam and exposed to harsh oxidizing environments.

Milestones

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

Agreement 16305: Materials by Design: Solder Joint Analysis

G. Muralidharan and Andrew Kircher
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 this quarter, preliminary work has been performed on the initial identification of a solder joint alloy composition, solder joint fabrication, and solder joint characterization. 80 wt. % Au 20 wt. % Sn (Au80Sn20) solder was identified as an initial candidate for evaluation of the effect of high temperatures. This solder is a fairly common high temperature solder with a melting point of 278^{o}C and can be reflowed (solder joint can be formed) without the use of a flux. Since the melting temperature of the solder is much greater than 200^{o}C, it is a solder that can be used in power electronic devices/systems in hybrid and electric vehicles. For the initial trial runs, this solder was obtained in the paste form mixed with a flux. Processing of a composite consisting of two pieces of Directly Bonded Copper Substrates sandwiching a solder joint as shown schematically in Figure 1 was attempted using an infrared furnace available within the processing group at ORNL (see figure 2). The infrared furnace allowed rapid heating to reflow temperatures and subsequent cooling of the solder joint. Cross-sectional optical imaging and scanning electron microscopy of the compound joint after completion of the processing step allowed the examination of the microstructure and integrity of the solder joint. Results of the imaging showed the presence of undesirable voids within the solder joints. Use of Au-Sn performs will be preferred in the future to minimize voiding within the solder joints.

Use of radiography to study solder joint voiding was also verified in this preliminary work. Figure 3 shows a radiograph through a package consisting of a single die attached to a metallic substrate. Seen in the image are the solder joint and wire bonds. Also note the voiding present within the solder joint represented by the lighter colored regions. Future work will exploit the techniques for processing and characterized developed during this quarter.

In the following quarter, further work will be performed in processing the solder joints with Au-Sn performs. Thermal cycling tests will be carried out on the processed solder joints to understand the evolution of microstructure and damage within the solder joints.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

Communications have been carried out with PowerEx about the feasibility of fabrication of simple packages consisting of solder joints with zero void content at their manufacturing facility. Communications have also been carried out with Sun Electronics Inc. on the purchase of a thermal cycling chamber capable of cycling packaged parts between high temperatures and sub-zero temperatures.

Problems Encountered

Problems were encountered with the processing of solder joints and have resulted in modification of processes.

Publications/Presentations/Awards

None

References

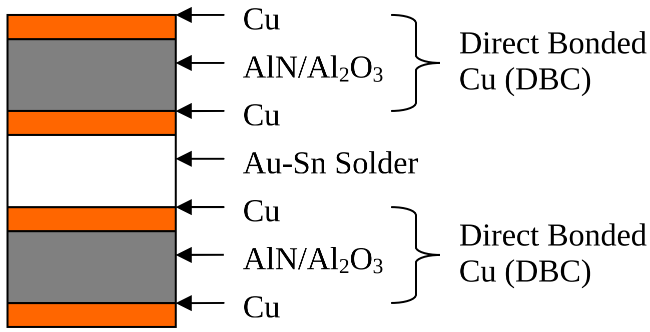


Figure 1. Schematic of the Experimental Joint Consisting of DBC Substrate Bonded To A Second DBC Substrate Using Au-Sn Solder.

Figure 2. Infrared Heating Furnace and Associated Computer Data-Acquisition System Used for Rapid Heating of Solder Joints.

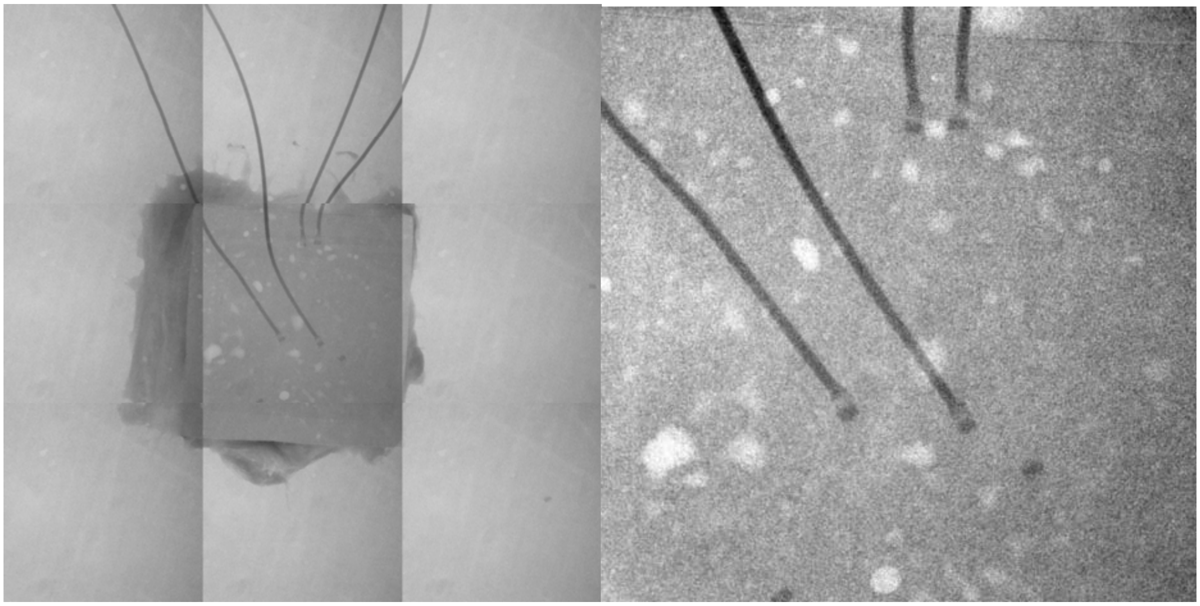


Figure 3. X-ray images of a SiC die attached to a metallic substrate using a solder joint. Also seen are wire bonds made to the SiC die.

Agreement 16306: Materials Compatibility of Power Electronics

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

Objective/Scope

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

Technical Highlights

This is a new start project. A kick-off meeting took place. The meeting participants included B. Armstrong, K. Cooley, A. Wereszczak, M. Govindarajan, and D. Stinton from the propulsion materials program and L. Marlino, M. Olszewski, C. Ayers, R. Wiles, and B. Ozpineci from the power electronics program. Direct cooling was selected as the cooling application to be studied. Candidate power electronic components and coolants for the study were discussed.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

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

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

Objectives/Scope

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

Highlights

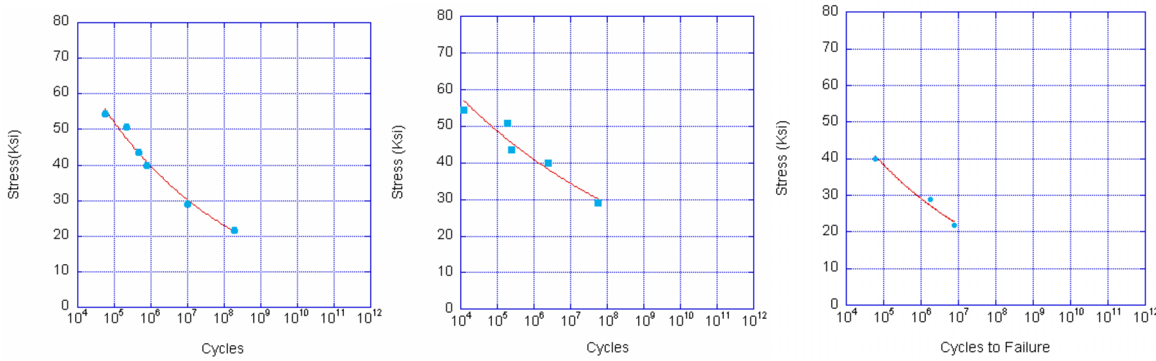
Technical Progress

Materials-by-Design of Advanced Materials:
In this quarter, work was continued on Ni-based alloys for valve applications. As reported earlier, using thermodynamic modeling, microstructure evaluation, and mechanical property evaluation, high temperature fatigue was identified as a property of critical interest in Ni-based alloy valve materials for the next generation automotive engines. An important part of the on-going work is to develop a database of mechanical properties as a function of alloy composition and microstructure (which is a function of processing and heat-treatment). In this quarter, work has continued on developing this mechanical property database and in particular developing data on the alloy currently used for automotive valves. IN 751 was supplied by Carpenter Technologies in the annealed condition and a two-step aging treatment was used to heat treat the alloys as shown in Table 1. Computational thermodynamic modeling was performed for the actual composition of this alloy and the amount of the strengthening phase γ' was determined.

Figure 1 shows the number of cycles to failure for IN 751 during fatigue testing at 1600^{o}F, subject to the heat-treatment shown in Table 1. Also shown for comparison are the data obtained earlier for Udimet 720 and Waspaloy. It is to be observed that IN 751 subject to the two step-aging treatment has a lower fatigue life at a given stress level than the other alloys shown in the figure. Figure 2 shows the variation in fatigue life as a function of the calculated amounts of γ'for various alloys tested in this work along with the position of IN 751 in comparison to the other alloys. The general trend of fatigue life as a function of the γ' content seems to be consistent with the trend observed in the previous data.

Table 1: Heat treatment conditions used for IN 751

Alloy	Condition Designation	Aging treatment
IN 751	IN751-carp	1600^{o}F/4 hrs/ Air cool 1350^{o}F/4 hrs/ Air cool



(a) (b) (c)

Figure 1. Cycles to failure as a function of stress in Ksi at 1600°F for (a) Udimet 720, (b) Waspaloy, and (c) IN 751.

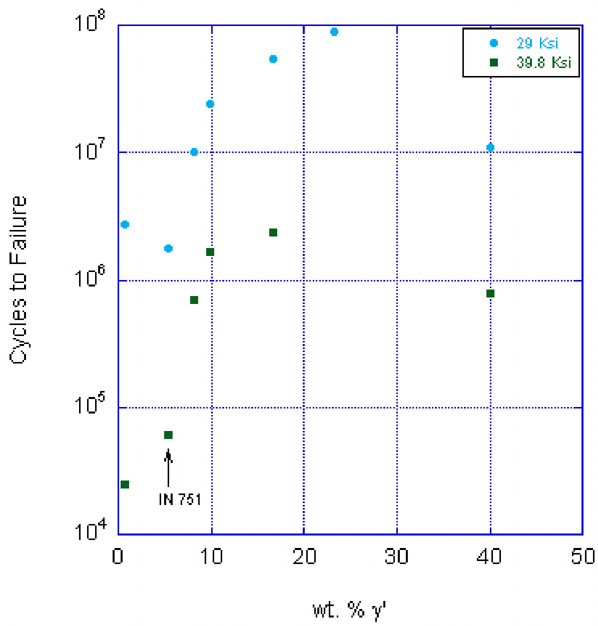


Figure 2. Cycles to failure observed at 870°C as a function of calculated γ' contents and fatigue stress. Note that the general trend is that the cycles to failure increase with increasing wt. % γ' except in Udimet 720. The new data is marked in the graph.

Milestones

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

Agreement 8697: Electrochemical NO_x Sensor for Monitoring Diesel Emissions

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

Objective/Scope

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

Technical Highlights

Previously, an impedance-based NO_x sensing technique was presented, and an evaluation of a prototype sensor in a variety of conditions (temperatures, O_2 concentrations, etc.) was performed. Criteria for materials and configurations suitable for impedancemetric NO_x sensing have been developed. Using the developed criteria, sensor prototypes consistently show reasonable stability (~500 hours) at the operating temperature (650°C), sensor speeds less than 10 sec., sensitivity down to 5 ppm NO_x, and minimal cross-sensitivity to water at the operating temperature of 650°C. Remaining issues include cross-sensitivity to oxygen, temperature sensitivity, and long-term stability (> 500 hours) as well as a suitable sensor platform for commercialization and manufacturability. Current progress has focused on characterizing two recent prototypes, one based on the Au/YSZ system that incorporates an alumina substrate and another based on the LSM/YSZ system. Prototype sensors underwent vehicle testing at Ford testing facilities, but only limited information about sensor performance was obtained due to unforeseen equipment malfunction (see "Problems Encountered" below). The role of the porous YSZ thickness was also investigated with implications for sensor design and operation. Preliminary results indicate that increasing the porous YSZ thickness up to a few hundred microns causes an increase in sensitivity towards NO_2, with no effect on NO sensitivity. No further NO_2 sensitivity enhancements were measured for thicker layers. Further testing will focus on developing improved prototype sensors for additional comprehensive laboratory testing and dynamometer testing.

Status of FY 2008 Milestones

The 1st quarter 2008 milestones were achieved and included dynamometer testing of FY07 prototypes at Ford, which was completed ahead of schedule in the 4th quarter 2007. Additional dynamometer testing of prototype sensors is scheduled for the 2nd quarter 2008. Major progress was also made in the development of criteria for appropriate materials and configurations. Prototype sensors are currently focused on two material systems, the Au/YSZ and the LSM/YSZ systems. Prototype sensors using an alumina substrate were also demonstrated, which allow more flexibility in terms of sensor configurations and manufacturability. Further work refining the sensor criteria will continue into the 2nd quarter 2008.

Communications/Visits/Travel

- A semiannual meeting with Ford collaborators was held in Dearborn, MI (4th Quarter 2007, August 15) to present research updates, evaluate progress, and modify future research plans. The meeting also provided the opportunity to conduct vehicle dynamometer testing at the Ford facilities using prototype sensors.

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

- Leta Woo and Bob Glass attended the 13th Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Aug. 12-16, 2007, in Detroit, MI.

Problems Encountered

Data from vehicle testing of the prototype sensor at the Ford testing facilities in the 4th Quarter 2007 provided limited information due to unforeseen equipment malfunction. The malfunction occurred in a commercial NGK NO_x sensor located next to the prototype sensor. When operating correctly, the NGK sensor provides an independent measure of the NO_x concentration that can be used to evaluate the performance of the prototype sensor. Due to the malfunction of the NGK sensor, only limited data for the vehicle exhaust was available for interpreting the performance of the prototype sensor. Future engine and vehicle dynamometer testing will include measurements from an operational commercial NGK sensor in order to fully assess the prototype sensor.

Publications/Presentations/Awards

- The following manuscript has been published:
  L.Y. Woo, L.P. Martin, R.S. Glass, W. Wang, S. Jung, R.J. Gorte, E.P. Murray, R.F. Novak, and J.H. Visser. "Effect of electrode composition and microstructure on impedancemetric nitric oxide sensors based on YSZ electrolyte." *J. Electrochem. Soc.*, **155**(1):J32-40, 2008.

- The following manuscript has been accepted for publication:
  E.P. Murray, R.F. Novak, D.J. Kubinski, R.E. Soltis, J.H. Visser, L.Y. Woo, L.P. Martin, and R.S. Glass. "Investigating the stability and accuracy of the phase response for NO_X sensing 5% Mg-modified $LaCrO_3$ electrodes. *ECS Transactions*, accepted, 2007.

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

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

George Fenske
Argonne National Laboratory

Objective/Scope

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

Technical Highlights

- Continued metallurgical evaluation of NVD coatings applied to commercial nozzles

Status of FY 2008 Milestones

- Milestones on-schedule

Communications/Visits/Travel

- Teleconference with Weber Manufacturing discuss NVD coating results and establish plan for next stage
- Teleconference with US EPA for future flow visualization studies.

Problems Encountered

- N/A

Publications/Presentations/Awards

- George Fenske, John Woodford, Jin Wang, Ronald Schaefer and Fakhri Hamady, "Fabrication and Characterization of Micro-Orifices for Diesel Fuel Injectors", 2008 SAE International Powertrains, Fuels and Lubricants Congress, Shanghai, China; Jun 23-25, 2008
- Fenske, G., "Fabrication of Micro-Orifices for Diesel Fuel Injectors," *2007 Annual Progress Report, Automotive Propulsion Materials,* U.S. Department of Energy, Washington, D.C., 2008.
- Annual Report of Laboratory-Directed Research and Development Program Activities for FY 2007.

Agreement 11754: Hydrogen Internal Combustion Engine Material Performance Modeling "H_2ICE-MPM" (PNNL/Ford/Westport)

James Holbery
Pacific Northwest National Laboratory

Objective/Scope

- Understand and predict the fundamental material degradation / aging mechanisms in hydrogen service environment.
- Analyze the mechanisms and modes that lead to early injector wear or failure with the goal of predicting material performance.
- Develop accelerated test methods and durability procedures for materials/coatings used on hydrogen injectors.
- Correlate injector test rig results to PNNL material results and engine testing

Technical Highlights

- **Needle-Nozzle Materials Compatibility Testing.** Hydrogen test device is fully operational; first *in-situ* data set complete. Currently several needle-nozzle tests continue. The data indicates that the localized hydrogen diffusion reduces the wear track and overall material removal, a positive development in the tests we have conducted.
- **Friction-Wear:** DLC characterization using Raman spectroscopy has been conducted at PNNL. Tribology measurements have been correlated with Penn State to verify *in-situ* apparatus.
- **DLC Coating Development.** M2 samples have undergone heat-treatment, surface finished, and have been shipped to suppliers for coating. Test plan has been approved by Westport and Ford.
- **PNNL Coating Test Development.** An unbalanced magnetron sputtering apparatus has been received and is installed. PNNL has produced over 120 samples of three different substrate materials. PNNL is currently coating these samples with a series of nano-laminates that will be integrated into the DLC test plan.

Status of FY 2008 Milestones

1. Complete 100% hydrogen *in-situ* sliding wear tests to quantify injector friction coefficient and resulting material embrittlement with the goal of understanding and predicting the fundamental material degradation / aging mechanisms in hydrogen service environment.
Status: Wear tests are underway on base materials; coatings are currently being manufactured and will follow.

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

3. Model the diffusion of hydrogen into engine component materials via atomistic models complemented with experimental neutron backscattering data generated on component materials.
Status: This effort will begin with the arrival of a Post-Doc in March, 2008.

4. Complete *in-situ* and *ex-situ* sliding-impact testing of needle-seat combination to understand the failure mechanism on injector seat materials.
Status: Samples are being manufactured, anticipated start date May, 2008.

Communications/Visits/Travel

- Westport Innovations visited PNNL on December 13. Discussions ensued to address test plan, Ford testing, new designs, and coating development. We have requested additional piezo samples from Westport to test specifics of hydrogen interaction with PZT materials.
- PNNL is in contact with Morgan Diamonex and Ion Bond and will send samples to be DLC coated in January.
- PNNL will send samples to be DLC coated to ANL in January.

Problems Encountered

- There is a need for a Post-Doc researcher on the project. A requisition has been released, potential candidates are currently under final evaluation, with the expected start date 3.1.08.

Publications/Presentations/Awards

- Jim Holbery has been invited to attend the H-ICCE meeting at Sandia-Livermore to present work on Feb. 11, 2008.
- Jim Holbery will present a project review at the DOE Merit Review Meeting in Bethesda, MD February 25, 2008.

Agreement 16304: Materials for Advanced Engine Valve Train

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

N. Phillips
Caterpillar, Inc.

Objective/Scope

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

Highlights

Caterpillar, Inc.

Caterpillar completed testing and characterization on an initial set of exhaust valves and their matching seats. Caterpillar then provided fresh exhaust valves and seats to match with those wear-tested in the lab-test rig to ORNL for further microstructural and mechanical characterization and analyses.

ORNL

ORNL and Caterpillar have discussed the various technical aspects of the initial engine and lab-test rig exhaust valve and seat wear data, and have discussed and planned the next set of tests at Caterpillar and follow-on work at ORNL to begin this CRADA project.

Technical Progress, 1st Quarter, FY2008

Background

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

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

Technical Progress – Caterpillar, Inc.
The CRADA began this quarter. Caterpillar completed their initial testing and characterization on an initial set of exhaust valves and their matching seats in the "Buettner Rig" for engine simulation wear testing with controlled testing conditions (i.e., iso-thermal) at the Caterpillar Technical Center. Caterpillar has also obtained similar valves and seats with long-term wear from various diesel engines, and characterized those to provide a baseline for correlation with the rig-tested components. Caterpillar then provided fresh exhaust valves and seats to match with those wear-tested in the lab-test rig or from engine-service to ORNL for further microstructural and mechanical characterization and analyses.

Technical Progress – ORNL
ORNL obtained the various fresh and engine-exposed or test-rig worn valve and seat components late this quarter, and further evaluation has begun. ORNL will also age pieces of fresh valve and seat components to provide un-worn control surface and sub-surface microstructures for comparison to the various worn components. This effort will continue next quarter.

Communications/Visits/Travel
Detailed team communications between ORNL and Caterpillar occur regularly in multi-party conference calls. Caterpillar plans to extend discussions to include various commercial component suppliers, as needed.

Status of Milestones (ORNL for DOE)
New CRADA project that started this quarter.

Publications/Presentations/Awards
None – new CRADA project in FY2008.

Agreement 13329: Mechanical Reliability of Piezo-Stack Actuators

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

Objective/Scope

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

Technical Highlights

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

The development and adaptation of accelerated test methods is underway and software was acquired that will enable controlled increases in applied voltage amplitudes as a function of time. It will be used with our existing actuator test facility and also those additional ones that will be constructed in FY08.

Designs for a “piezo dilatometer” were conceived and its fabrication will commence during the second quarter. It will be used to measure expansion of piezoceramics as a function of applied voltage and also enable the study of changes in that expansion under high voltages.

Testing was completed and fatigue responses of a lead zirconate titanate (PZT) multilayer actuator with a plate-through electrode configuration were studied under an electric field (1.7 times that of a coercive field of PZT material) and a concurrent mechanical preload (30 MPa). A total one billion cycles were carried out on the actuator; at 50 Hz, it took approximately 8 months to accumulate that many cycles. Variations in charge density and mechanical strain under a high electric field and constant mechanical loads were observed during the fatigue test. The dc and the first harmonic (at 10 Hz) dielectric and piezoelectric coefficients were subsequently characterized by using fast Fourier transformation. Both the dielectric and the piezoelectric coefficients exhibited a monotonic decrease prior to 286 million cycles, and then fluctuated to a certain extent beyond that. Both the dielectric loss tangent and the piezoelectric loss tangent also exhibited the fluctuations after a certain amount of drop but at different levels relative to the pre-fatigue.

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

Communications/Visits/Travel
Wereszczak, Lin, and D. R. Johnson visited Cummins Inc. (Columbus, IN) on December 12 to discuss piezoactuator issues.

Problems Encountered
None.

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

A manuscript entitled "Fatigue Response of a PZT Multilayer Actuator under High-Field Electric Cycling with Mechanical Preload" by H. Wang, A. A. Wereszczak, and HT Lin, was composed and is presently undergoing ORNL internal review. It will be submitted to the open literature.

References
None.

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

Peter Blau
Oak Ridge National Laboratory

Objective/Scope

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

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

Technical Highlights

Improvements to the HTRI. Two improvements were made to the high-temperature repetitive impact (HTRI) valve materials testing system during the past quarter. A new specimen holder was designed and installed. It enables simple cylindrical samples to be tested, making possible additional studies of candidate alloys and surface treatments without having to machine production-dimensioned valves as test specimens. Figure 1 shows two inclined cylindrical pins resting on flat specimen surfaces to either side of the new holder. Contact stresses for this geometry have been calculated as a comparison with valve seat stresses. As many as four tests can be performed on each of the flat specimens simply by rotating them 90 degrees into a new position. During testing the cylindrical specimens lift off and are lowered onto the flat specimens by a cam and roller mechanism located below the furnace chamber. The second improvement was the design and installation of a lever fixture to enable more rapid and convenient calibration and adjustment of the down-force on the contact surfaces.

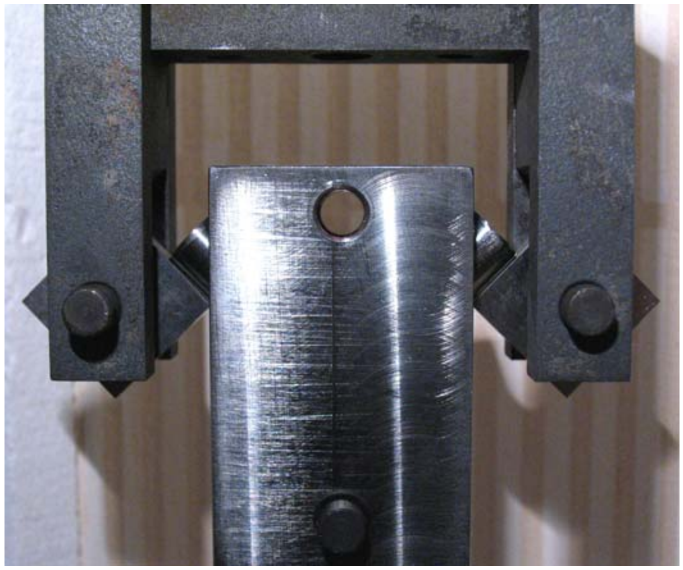


Figure 1. The tips of two cylindrical pins are just visible on opposite sides of the specimen holder and can be seen resting on the sides of square specimens that simulate the valve seat.

Oxide growth and healing of impact-damaged surfaces. The hotter a valve gets, the faster the surface reacts with the surrounding environment. Metallurgical changes also occur within the alloys, and alloying elements diffuse more quickly. Changes in composition and microstructure are especially promoted in the neighborhood of the surface because oxygen and other species at the valve/exhaust interface react or create driving forces for inter-diffusion. If, in addition, one impacts a surface or otherwise mechanically works it, that extra mechanical work can alter oxide kinetics and lead to the formation of structurally complex layers. In summary, the an oxide layer that forms under repetitive impact conditions does not have the same stoichiometry (composition) or defect structure as that which forms under free-surface exposure to the same environment.

In order to better understand how valve materials form oxides on mechanically damaged surfaces, an experiment has been designed using a production diesel exhaust valve made from a high-Ni alloy. A valve head has been sectioned into six parts, and each segment will be given a different thermal and mechanical treatment (repetitive impacting or abrasion). Segments will be exposed to a temperature of 850^{o} C in air. Certain segments will be removed, their surfaces damaged, and replaced into the furnace, while others will remain undamaged as ‘witness specimens.’ At the conclusion of the experiment, metallurgical cross-sections of the surfaces will be prepared to compare oxide growth morphology, composition, and re-healing behavior.

In addition to the oxide damage experiment, a series of tests of Fe-, Ni- and Co-based candidate valve alloys in the HTRI will begin. Cylinder-on-flat impact conditions, shown in Fig. 1, will be used. Both the scale-healing test results and HTRI data will be used to develop a model for the role of wear and oxidation in the recession of valve/seat combinations.

Future Plans

1) Complete experiments on oxide regrowth after contact damage.

2) Begin a new series HTRI tests using Fe-, Ni-, and Co-based alloys.

3) Begin to develop a framework for a wear-oxidation model for valve surface recession.

Travel

None

Status of Milestones

1) Complete experiments on the effects of surface damage on oxide formation and prepare a paper for journal submission. **(03/08)**

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

Publications and Presentations

None.

Agreement 9089: NDE of Diesel Engine Components

J. G. Sun and N. Phillips*
Argonne National Laboratory
***Caterpillar, Inc.**

Objective/Scope

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

Technical Highlights

Work during this period (October-December 2007) focused on acquisition and analysis of laser-scatter NDE data for 10 Si_3N_4 valves after an engine-duration test.

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

Ten Si_3N_4 and four TiAl valves had been successfully tested for 500-hr in a Caterpillar G3406 generator set at NTRC in 2006, and were installed again for the final phase of 500-hr engine test. However, on June 20, 2007 after 55 hours at full load operation, a Si_3N_4 intake valve located in Cylinder 6 (#22) failed, causing the rest of the valves in that cylinder been destroyed. The ceramic debris was also sucked into other cylinders, damaging all other ceramic and TiAl valves. The failure was later identified to be due to a worn metal valve-groove keeper that allowed the ceramic valve to be dropped inside the cylinder and crashed with the piston. As a result, the engine test was ended. The 10 engine-tested Si_3N_4 valves were analyzed by NDE at ANL during this period and will be destructively tested at ORNL. Figure 1 shows a photograph of these valves; note that the damaged valve head for all ceramic valves in Cylinder 6 has been removed prior to the NDE examination.

Fig. 1. Photograph of Si_3N_4 engine valves at end of engine duration test.

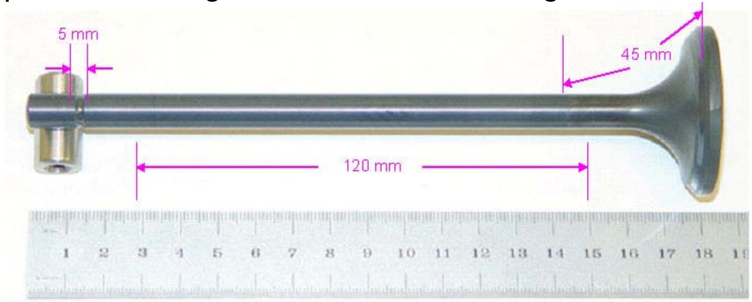


Fig. 2. Laser-scatter scanned regions for each Si_3N_4 engine valve.

Laser-scatter NDE scans were performed at three surface regions for each Si_3N_4 engine valve, as illustrated in Fig. 2. The NDE results for the 120-mm stem regions of the valves were presented in the previous report. Typical scan results for the valve-head and keeper-notch sections are presented and discussed below.

Figure 3 shows the laser-scatter image of the valve-head surface of intake valve I#12 that was installed in Cylinder 3. A large chip has spalled off, seen in the inserted valve photograph, likely due to an impact on the valve face surface by a large amount of debris. The scatter image shows that the edges of the broken region are clean, without cracks emanating from the broken region. Within and around the contact surface (which matches the seat-insert surface), a few subsurface damages were detected. Figure 4 shows detailed NDE images and photomicrographs of two prominent subsurface damages within the contact surface. They are up to 1-mm long and have different optical-scatter intensities representing different levels of damage severity and depth. These damages were apparently come from scratches or impacts by smaller debris. It is interesting to note that, near the second damage feature shown in the right column in Fig. 4, another apparent scratch (at the top region in the bottom-right micrograph) did not induce subsurface damage as seen in the corresponding NDE image. In addition, the NDE image in Fig. 3 also indicates many other damage features (circled) on the fillet and nearby stem surfaces. However, the presence of surface contamination and the difficulty to visually examine the curved (fillet) surfaces prevented a visual confirmation of these features.

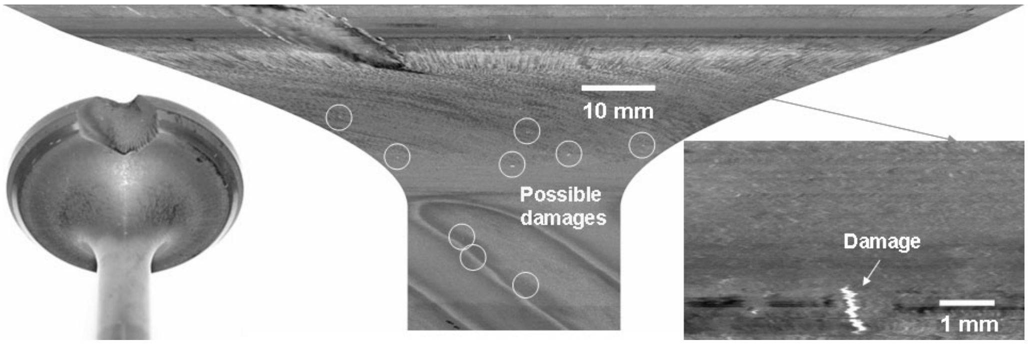


Fig. 3. Laser-scatter scan image of intake valve I#12 at end of engine test.

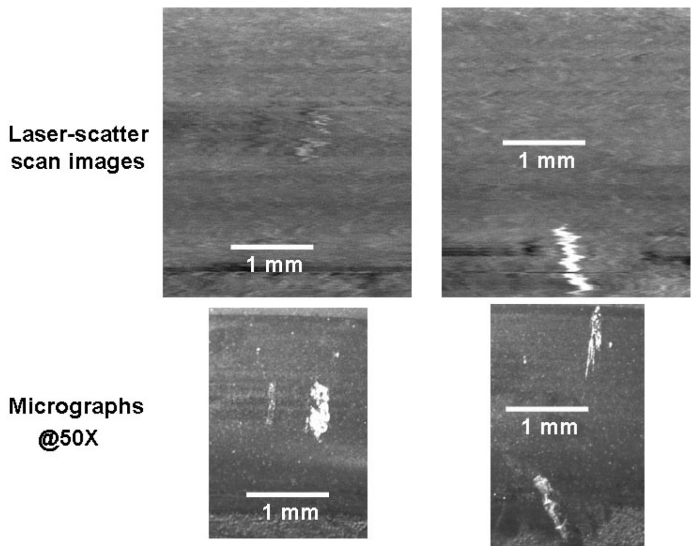


Fig. 4. Detailed laser-scatter NDE images and photomicrographs of two prominent damages within the contact surface of intake valve I#12.

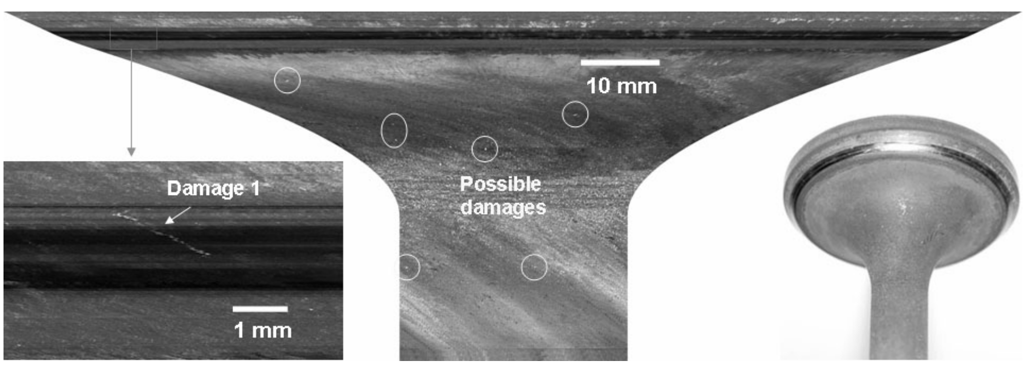


Fig. 5. Laser-scatter scan image of exhaust valve E#1 at end of engine test.

Figure 5 shows the laser-scatter image of the valve-head surface of exhaust valve E#1 that was installed in Cylinder 1. Within the contact surface, two prominent subsurface damages (up to 1 mm long) were detected. Figure 6 shows detailed NDE images and photomicrographs of these subsurface damages. These damages were likely due to scratches or impacts by smaller debris. Similar to the intake valve I#12 and all other valves, many other damage features (circled) were detected on the fillet and nearby stem surfaces, as seen in Fig. 5. They, however, were not further confirmed by visual examination due to difficulties cited above.

The keeper-notch region of all Si_3N_4 valves was scanned for a 5-mm axial length in the entire circumference. Figure 7 shows the laser-scatter scan image for the notch surface of exhaust valve E#5 which was installed in Cylinder 2. In the image, the darker horizontal stripes were surface contamination (possibly embedded fine metal particles) due to contact with the metal keeper. A prominent damage was detected at the bottom edge (towards the valve head side). From the enlarged NDE image and the corresponding photomicrograph shown in Fig. 8, it is apparent that this damage is a crack of ~1-mm long with a few small dents along its length. This damage was probably generated during the engine-test failure process; no such damage was found on other Si_3N_4 valves. However, smaller material defects and original machining damages were detected at notch-groove edges; one larger defect, ~70 µm in size (likely a porous pore), is shown in Fig. 9.

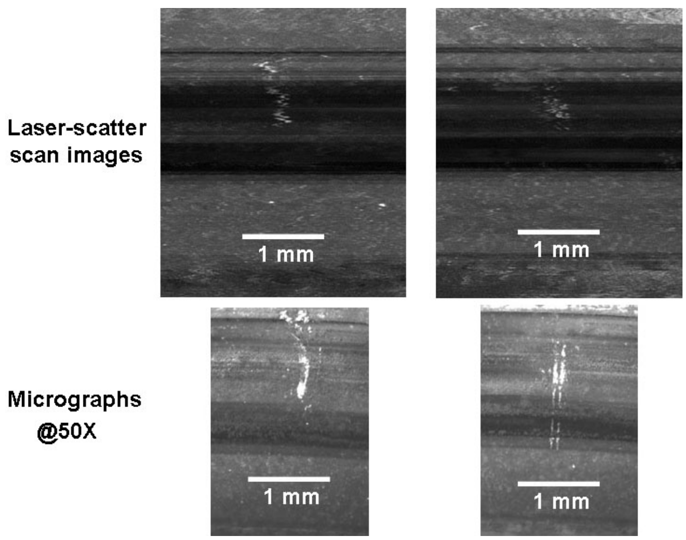


Fig. 6. Detailed laser-scatter NDE images and photomicrographs of two prominent damages within the contact surface of exhaust valve E#1.

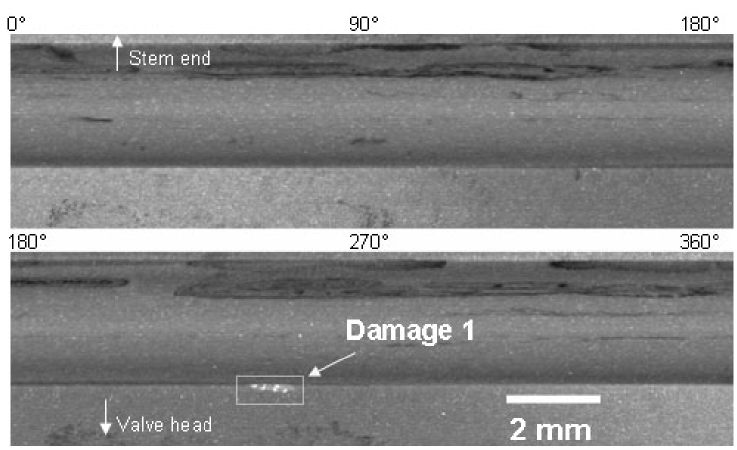


Fig. 7. Laser-scatter image in keeper notch region of exhaust valve E#5.

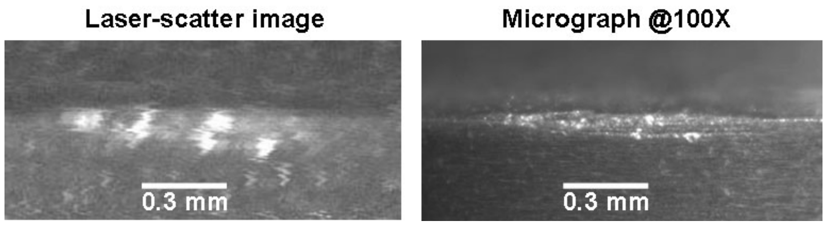


Fig. 8. Detailed NDE image and micrograph of damage at notch edge of exhaust valve E#5.

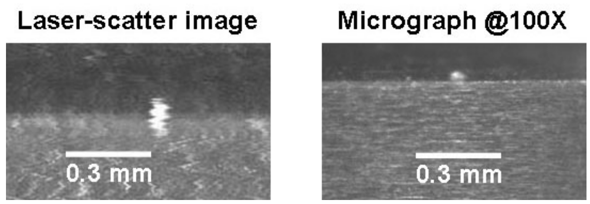


Fig. 9. Detailed NDE image and micrograph of a defect at notch edge of an intake valve.

Status of Milestones

Current ANL milestones are on schedule.

Communications/Visits/Travel

J. G. Sun plans to present a paper at the 32nd International Conference & Exposition on Advanced Ceramics and Composites to be held Jan. 27-Feb. 1, 2008, in Daytona Beach, FL.

J. G. Sun plans to participate the DOE Vehicle Technologies Annual Merit Review to be held Feb. 25-28, 2008, in Bethesda, MD.

Problems Encountered

None this period.

Publications

None this period.

Agreement 15050: Materials-enabled High Performance Diesel Engines

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

Objective/Scope

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

Highlights

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

Technical Progress, 1st Quarter, FY2008

Background

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

Approach

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

Communications/Visits/Travel
Detailed team communications between ORNL and Caterpillar occur regularly in multi-party conference calls.

Status of Milestones (ORNL for DOE)
New CRADA project being negotiated.

Publications/Presentations/Awards
None

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

Amit Shyam and Thomas R. Watkins
Oak Ridge National Laboratory

Objectives/Scope

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

Highlights

- The effect of washcoating and soot-loading on the temperature dependence of the elastic modulus of porous cordierite substrates (for DPFs) was determined.
- The effect of catalyst loading on the elastic properties of cordierite substrate (for catalysts) was examined.

Technical Progress

The thermal shock resistance of DPFs is determined in part by the elastic modulus of the substrate. Procedures for high temperature elastic modulus determination for DPF filter walls by resonant ultrasound spectroscopy (DPF) have been reported earlier. Flat plates of porous cordierite (40 x 20 x 0.275 mm) were prepared by dry grinding methods that have also been reported earlier. The temperature dependence of the elastic modulus of the plate for three grades of cordierite termed B-0, B-1 and B-2 is reported in Figure 1. While B-0 represents a bare (uncoated) cordierite, B-1 represents a B-0 type cordierite with a catalytic washcoating and B-2 represents a B-0 type cordierite with a washcoating and soot loading. It is important to understand the influence of washcoating and soot-loading on the mechanical properties of porous cordierite. The temperature dependence of elastic modulus for the three grades of cordierite is unusual, in that the modulus values increase with temperature up to 1000^{o}C. Similar results for other grades of cordierites have been reported earlier. While the room temperature elastic modulus values of B-0 and B-1 material are similar at 9.5 GPa, the room temperature elastic modulus value of B-2 cordierite is slightly higher at 10.2 GPa. The rate of increase of the modulus values with temperature is the highest for B-2 material, followed by B-1 and the lowest for B-0 material. It is known that the modulus increase with temperature is due to the partial healing or complete closure of microcracks that form during cooling from the processing temperature. Results presented in Figure 1 suggest that the washcoating and soot particles interact with the microcracks at elevated temperature and change the modulus dependence of temperature.

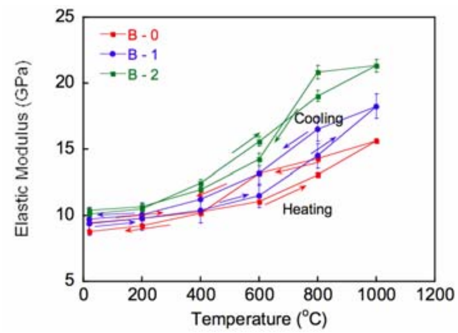


Figure 1. The temperature dependence of the elastic modulus of porous cordierite. The test specimens were subjected to a maximum temperature of 1000°C. Error-bars represent root mean square errors of fit for one test under each condition.

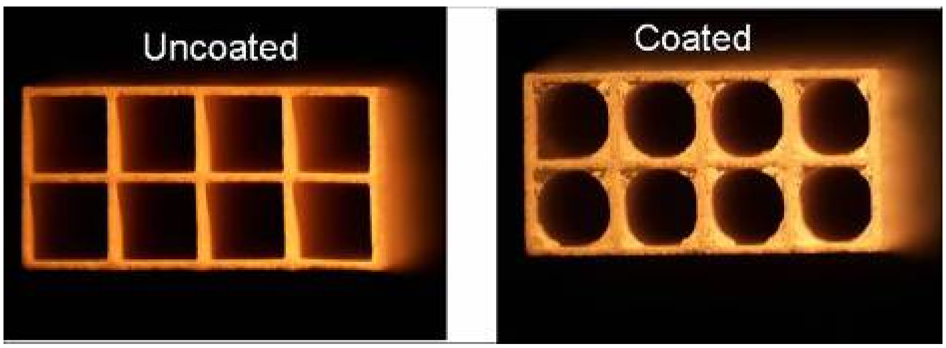


Figure 2. 4 x 2 cellular specimen cross-sections for evaluation by dynamic mechanical analysis (DMA). The difference in the shape of the cells for the coated and uncoated specimens is to be noted.

The effect of catalytic coating on the elastic modulus of porous cordierite (with ~ 40 % porosity) for catalysts was evaluated in the reporting period. The thickness of the walls of the catalyst substrate (shown in Figure 2) is ~150 µm. DPF substrates whose elastic modulus values have been reported earlier have an initial wall thickness of ~300 µm. The lower thickness of the catalyst substrate walls presents an added challenge for preparing specimens. Dynamic mechanical analysis (DMA) was utilized to obtain the elastic modulus of the coated and uncoated specimens. As shown in Figure 2, 4 x 2 cellular specimens were prepared and the difference in the shape of the cells (square for uncoated specimens and elliptical for coated specimens) was accounted for in the corrected moment-of-inertia calculations. Two kinds of specimens, namely short specimens with a length of 16 mm and long specimens with a length of 60 mm were tested in three-point bend loading fixtures with spans of 10 mm and 50 mm, respectively. The obtained elastic modulus values are compared in Figure 3. The elastic modulus values of the short and the long specimens are comparable with the uncoated specimens having an elastic modulus of ~19.3 GPa and the coated specimens having a slightly lower modulus of ~17.0 GPa. The change in the modulus of the coated specimens is attributed to the fact that the washcoat has lower modulus compared to the cordierite substrate and that effectively lowers the elastic modulus of coated specimens.

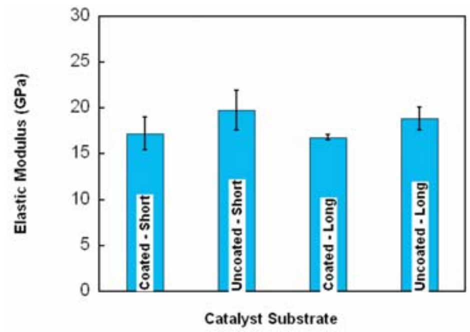


Figure 3. The effect of coating on the elastic modulus of cordierite for catalysts. Coating leads to a small decrease (~10-15%) in the elastic modulus values. One specimen each was tested for the two short specimens, two specimens for the coated long specimens and three specimens for the uncoated long specimens. Three repetitions were performed for each specimen and the blue bars represent the average of the values while the error-bars represent the standard deviation of the values.

Publications

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

Meetings

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

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

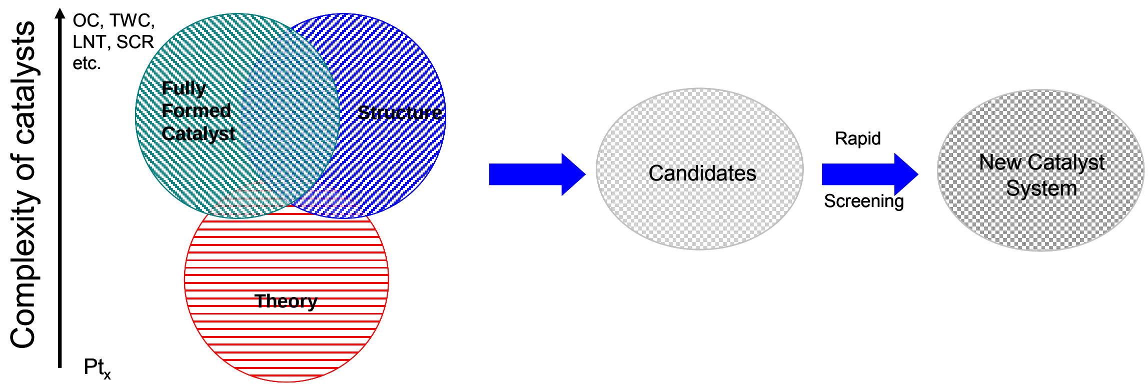
C. Narula, M. Moses and L. Allard
Oak Ridge National Laboratory

Objective/Scope

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

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

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



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

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

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

Our goals are as follows:

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

- This approach will allow us to identify the catalyst sites that are responsible for CO, NO_x, and HC oxidation. We will then address support-cluster interaction and design of new durable catalysts systems that can withstand the prolonged operations.

Technical Highlights

Our results on experimental studies of Platinum-Alumina Systems and their nanostructural changes under CO-oxidation conditions are summarized in the following paragraphs. We have initiated our study of nanostructural changes in this catalyst system during hydrocarbon oxidation also.

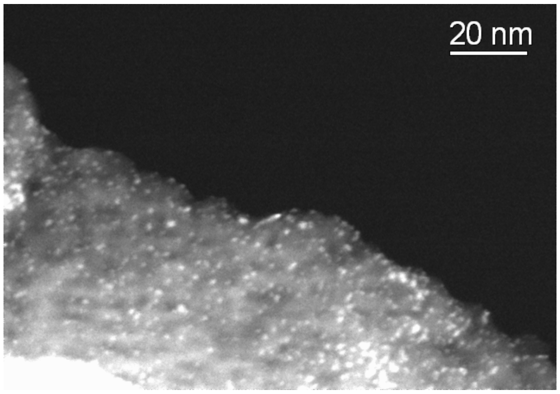
Experimental Studies

CO Oxidation: In previous reports, we have summarized our study on the microstructural effect of the Pt cluster/particle size on the 2%Pt/γ-Al_2O_3 catalysts demonstrated that fresh 1 nm and smaller Pt clusters agglomerate quickly even under CO oxidation initiation conditions and continue to exhibit sintering through 3 cycles of quantitative CO oxidation. Large particles (based on our tests of supported 12 nm Pt particles), on the other hand, are more stable and do not significantly change after 3 cycles of CO oxidation. These results suggest that the efforts to obtain nanometer and sub-nanometer Pt particles do not offer a significant advantage for CO oxidation.

We also studied the effect the substrate plays on the Pt microstructure under CO oxidation conditions by studying 1 nm 2%Pt/θ-Al_2O_3. While we found that there is a significant difference in activity, surprisingly, our microstructural studies show no structural differences in Pt particles supported on γ and θ alumina in fresh samples. Furthermore, agglomeration and sintering for both types of samples under various CO oxidation conditions were almost identical. In this report, we summarize our results on the impact of synthetic routes.

1 nm 2%Pt/γ-Al_2O_3 – Impact of Synthetic Routes

While the nanoparticles of precious metals are fairly easy to prepare, the monodisperse particles are extremely difficult to obtain, especially, by tradition wet synthetic routes. In our efforts to narrow the distribution of Pt particles, we employed Platinum(0) bis(dibenzylideneacetone), $Pt(C_6H_5CH{=}CHCOCH{=}CHC_6H_5)_2$, to prepare the supported catalyst. Experimentally, Platinum(0) bis(dibenzylideneacetone) was dissolved in THF and added to commercial γ-Al_2O_3. After removal of solvent, the catalyst was heated to 400ºC to remove organics.



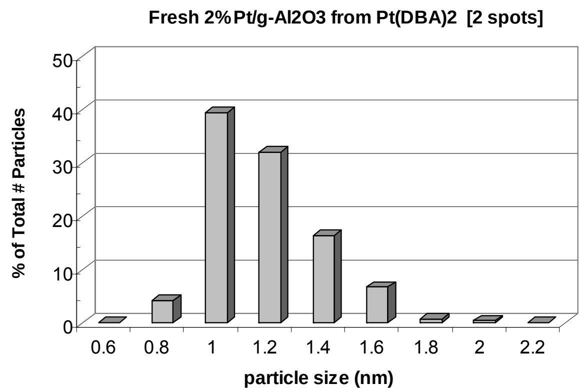


Figure 1: The STEM Image of Pt/γ-Al_2O_3 and Pt particle size distribution

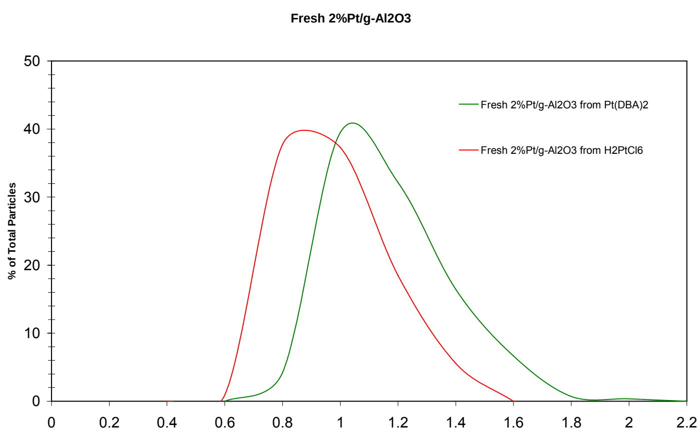


Figure 2: Pt particle size comparison for catalysts obtained from H_2PtCl_6 and $Pt(DBA)_2$

The STEM images (Figure 1) show that the Pt particles are in 0.8-1.8 nm range. This range is somewhat broader than the one in catalyst samples prepared from H_2PtCl6 impregnation of γ-Al_2O_3 (Figure 2). The CO oxidation on the fresh catalyst, derived from $Pt(DBA)_3$, initiates at 150ºC and completes at 180ºC. The third cycle of CO shows changes (initiation at 180ºC and completion at 210ºC) suggesting that catalyst has undergone some changes.

Interestingly, the synthetic method does not appear to have much impact on the performance or durability of the catalyst. After 3 cycles of CO oxidations, the catalysts prepared from $Pt(DBA)_2$ and H_2PtCl_6 have very similar Pt particle distribution (Figure 4).

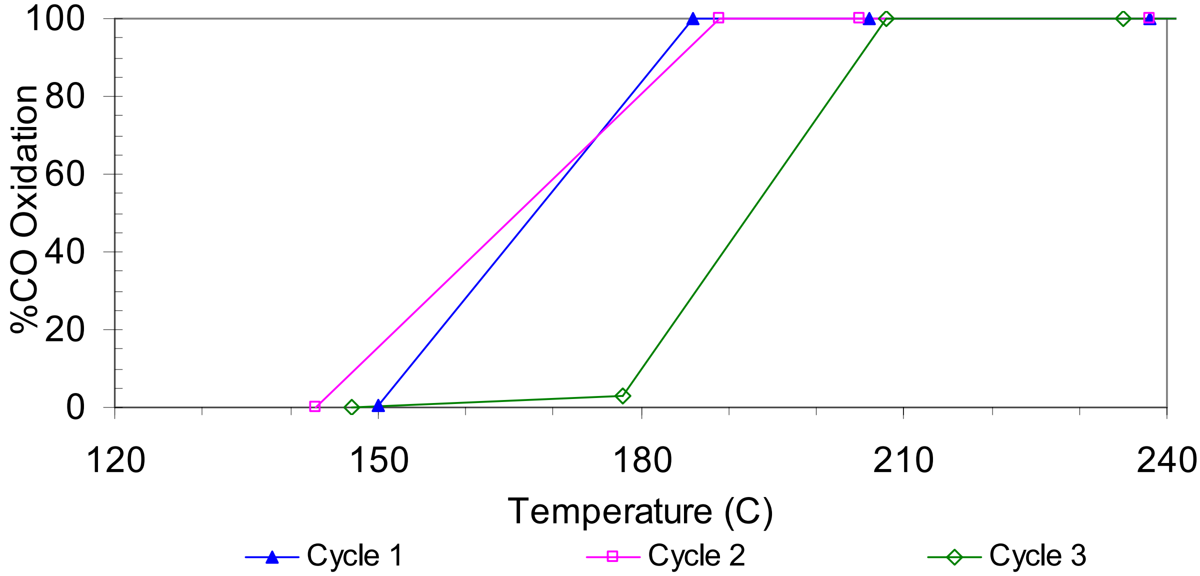


Figure 3: Three cycles of quantitative CO oxidation as a function of temperature on 1nm Pt on γ-Al_2O_3 prepared from $Pt(DBA)_2$ impregnation.

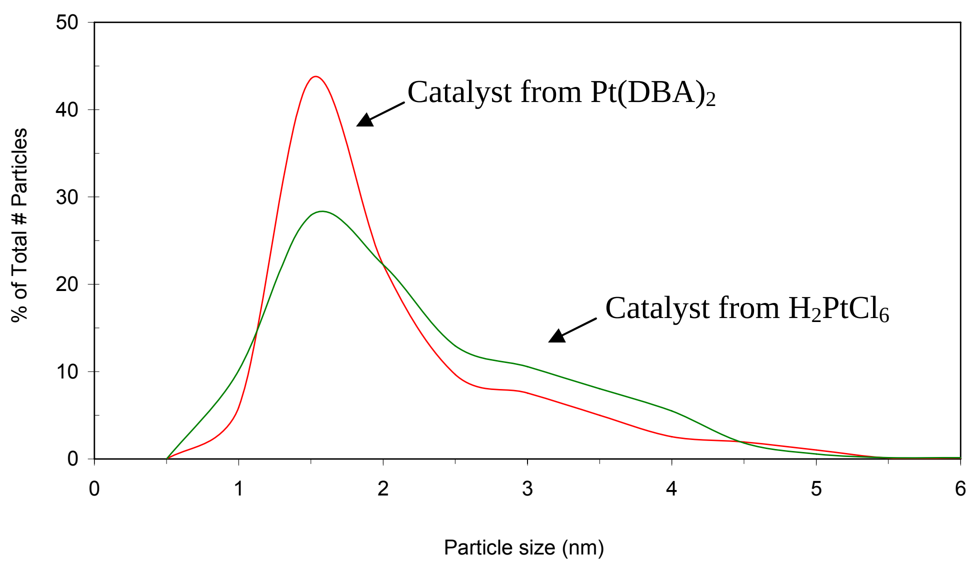


Figure 4: Changes in 1 nm 2%Pt/ γ-Al_2O_3 particle size from fresh to 3-cycles of quantitative CO oxidation.

HC Oxidation: A fresh sample of 1 nm 2%Pt/γ-Al_2O_3 catalyst was exposed to a hydrocarbon mixture of 500 ppm propene and propane in 2:1 ratio, 10% O2 and balance N2 at a space velocity of 25k h^{-1} and hydrocarbon conversion was recorded [Figure 5].

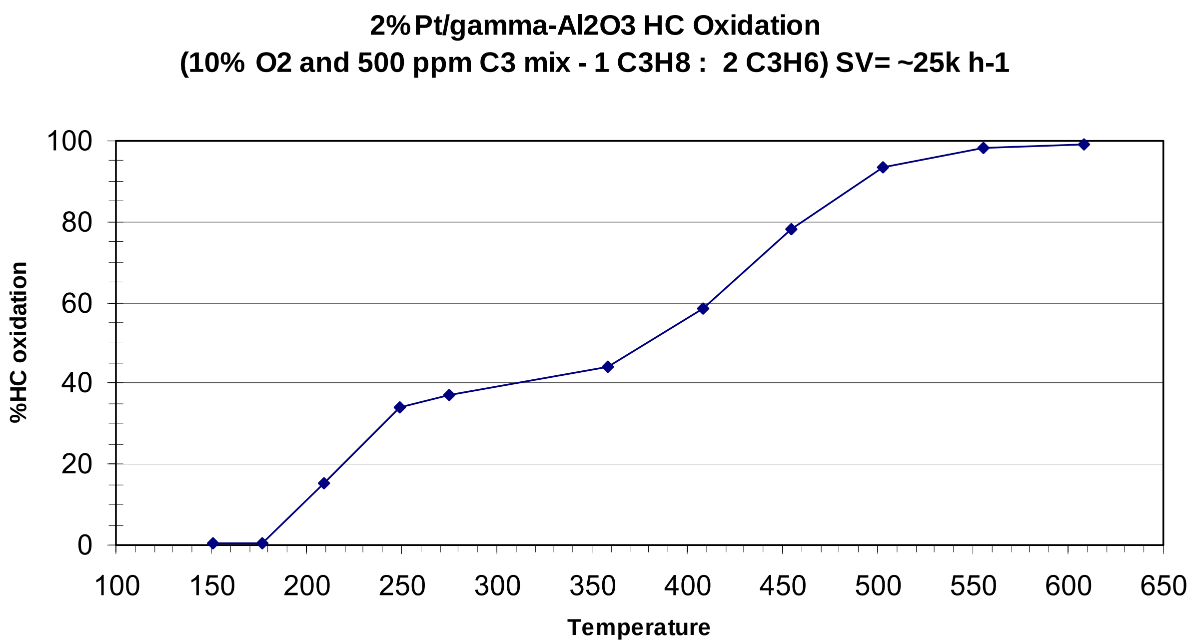


Figure 5: Hydrocarbon oxidation on 1 nm 2%Pt/γ-Al_2O_3

As expected, hydrocarbon oxidation begins at 180ºC with propene oxidizing first and completes with the complete oxidation of propane. The sample was collected and is being examined by TEM.

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

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

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

Other Activities

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

Communication/Visitors/Travel

C.K. Narula presented a talk titled "Catalyst by Design - Bridging the Gap between Theory and Experiments" at management meeting of Süd-Chemie Corporation.

Publications

1. C.K. Narula, "Catalyst by Design – Bridging the Gap between Theory and Experiments at Nanoscale Level" Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008 (invited).
2. C.K. Narula, L.F. Allard, D.A. Blom, M. Moses-DeBusk, "Bridging the Gap between Theory and Experiments – Nano-structural Changes in Supported Catalysts under Operating Conditions" SAE-2008-01-0416.
3. C.K. Narula, L.F. Allard, D.A. Blom, M.J. Moses, W. Shelton, W. Schneider, Y. Xu, "Catalysis by Design - Theoretical and Experimental Studies of Model Catalysts", SAE-2007-01-1018 (invited).
4. C.K. Narula, M.J. Moses, L.F. Allard, "Analysis of Microstructural Changes in Lean NO_x Trap Material Isolates Parameters Responsible for Activity Deterioration" SAE 2006-01-3420.
5. Y. Xu, W.A. Shelton, and W.F. Schneider, "The thermodynamic equilibrium compositions, structures, and reaction energies of Pt_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. Narula, C.K.; Allard, L.F.; Blom, D.A.; Moses-DeBusk, M.; "Bridging the Gab between Theory and Experiments – Nanostructural Changes in Supported Catalysts under Operating Conditions," Society of Automotive Engineers – International Congress, April 2008 (invited)
2. Narula, C.K.; Moses, M.J.; Xu, Y.; Blom, D,A,; Allard, L.F.; Shelton, W.A.; Schneider, W.F.; 'Catalysis by Design – Theoretical and Experimental Studies of Model Catalysts', Nanomaterials for Automotive Applications, Society of Automotive Engineers – international Congress, March 2007 (invited)
3. Blom, D.; Allard, L.; Narula, C.; Moses, M.; "Aberration-Corrected STEM ex-situ Studies of Catalysts" 8/8/07 Wednesday, Microscopy and Microanalysis Meeting, 2007, August 5-9, Ft. Lauderdale, Florida. *(Invited)*.
4. Narula, C.K.; Moses, M.J.; Blom, D,A,; Allard, L.F.; 'Catalysis by Design – Bridging the Gap Between Theory and Experiments'– DEER 2007, Detroit, MI
5. Allard, L.F.; Blom. D.A.; Narula, C.K.; Bradley, S.; Catalyst Characterization via Aberration-Corrected STEM Imaging, 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007

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

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

L. F. Allard, C. K. Narula, M. A. O'Keefe, M. J. Yacaman and S. A. Bradley
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 (Prof. M. Jose-Yacaman and students). Studies of the behavior of Pt species on oxide substrates are also being conducted with colleague S. A. Bradley of UOP Co.

Technical Progress

In-Situ electron microscopy: In this quarter, a number of interesting experiments were conducted with the new Protochips in-situ heater chips, on the JEOL 2200FS-AC ACEM. To review briefly, Protochips Inc. provides a novel heater technology, comprising a thin (~100 nm) 500 nm square conductive ceramic film suspended on a 3 mm diameter Si chip. When installed in a special-made specimen rod, electrical leads contact two electrode pads on the Si chip, providing current that heats the film. Because of its low mass, a heating rate of 1 million degrees per second is reached. The relatively large mass of Si surrounding the film acts as a thermal sink for cooling, so nearly the same rate for cooling is achieved. This means that the film can be cycled from RT to say 1100°C in one millisecond, with a similar path for return to RT. The symmetry of the overall sample assures that there is virtually no X-Y shift during heating, and, most extraordinarily, essentially no image drift at the highest magnifications. This gives the new heater assembly an outstanding capability for recording images at the ultimate resolution capability of the microscope. The only significant observable sample motion we have found is a change in sample height in the microscope (i.e., Z position), which causes a change in focus of the image. Because an equilibrium temperature is reached in fraction of a second, high-resolution images can be recorded immediately after a simple height adjustment and re-focusing operation. To illustrate the stability, Figure 1 shows a high-angle annular dark-field (HA-ADF) image of a dispersion of $FePt_3$ catalyst nanoparticles, during which recording the power to the chip was cycled periodically to take the film from RT to 700°C. The in-focus bands show the instantaneous return to and holding of the focus condition, within the time of a single scan line (32 ms/line). It is difficult to overstate the significance to the microscopist and to the potential research results of this overall paradigm for *in-situ* heating. In the following example, heating experiments using highly dispersed Au-Pd 3-layer nanoparticles (work with Prof. M.-J. Yacaman, UTexas-Austin) are detailed. Additional experiments with Dr. Steven Bradley of UOP Corp. were also conducted, but not shown here due to space limitations.

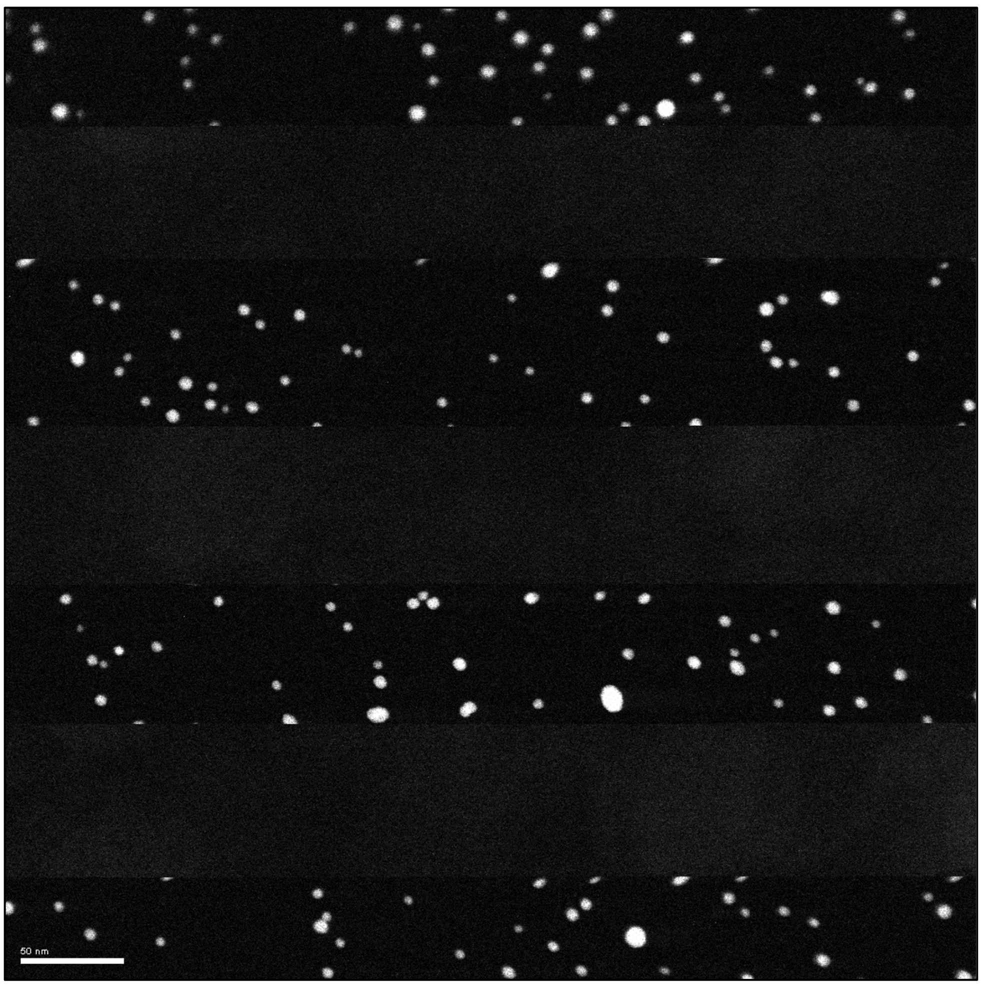


Fig. 1 $FePt_3$ nanoparticle dispersion, with the in-focus bands recorded while the sample was at a nominal 700°C, and the out-of-focus bands recorded with the power to the heater chip turned off so the chip returned to a nominal RT.

Au-Pd Heating Experiment: We have reported on the novel structure of bimetallic ~10 nm gold-palladium particles [1, and annual report 2007], which exhibit a core/inner-shell/outer-shell structure of, respectively, Pd-rich, Au-rich, and Pd-rich layers. It is of interest to understand the behavior of bimetallics such at this, especially in the nanometer domain, in order to better understand the mechanisms that may occur in “real” catalyst systems. The Au-Pd nanoparticles were dispersed from an ethyl alcohol suspension onto a Protochips heater chip with a 20-nm thick amorphous holey carbon film as the support surface. This sample was carried through a heating experiment, with temperatures increasing through the range of 350°C to 900°C, in increments of first 100°C, then 50°C from 550°C to 900°C. HA-ADF and bright-field (BF) images were recorded at magnifications from 8 Mx to 500 kx. Sets of images from each magnification, recorded at the different temperatures, were collected into “movies,” frames from which are shown in the sequences that follow. The details observed with each set are explained in the captions. The sets comprise 3 images each; the top image (2a etc.) represents the particle distribution at 350°C early in the run; the middle image (2b etc.) shows a mid-run stage, at 550°C, and the bottom image (2c etc.) is an example of the distribution late in the run, at a temperature of 700°C.

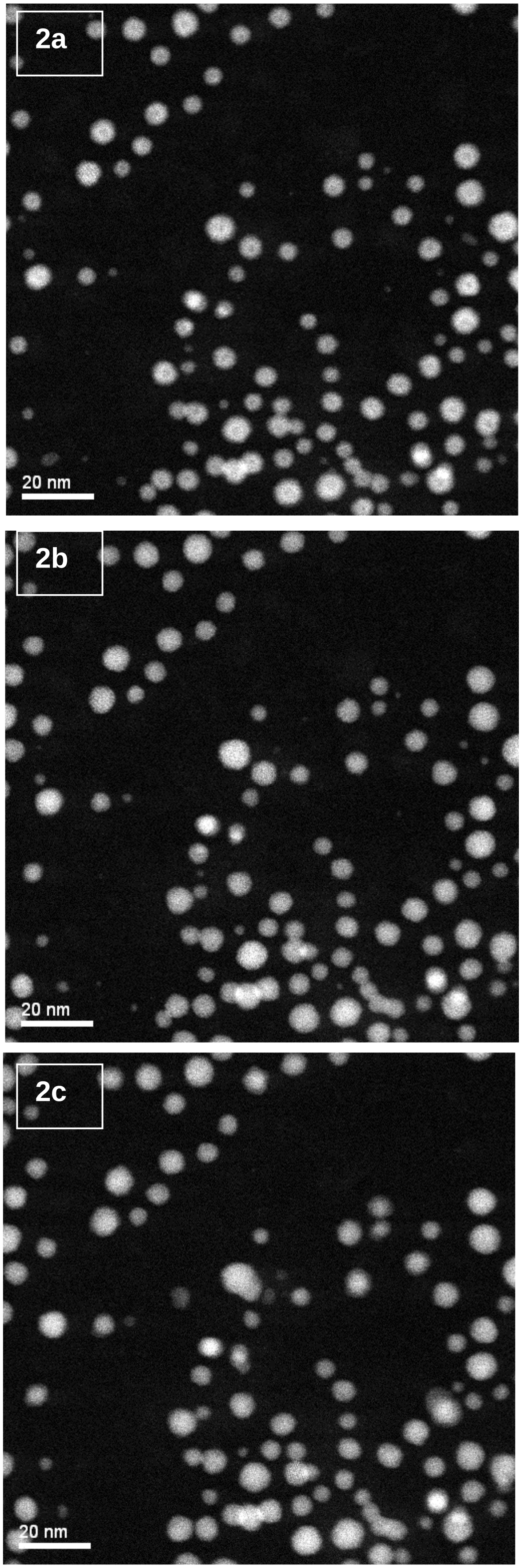


Fig. 2. HA-ADF images of overall area at original magnification of 500kx.

a) T = 350°C. $AuPd_3$ particles range in size from 1 to 7nm. A dark core can be seen in each particle, due to its Pd-rich composition.

b) T = 550°C. Core contrast is diminished, suggesting homogenization (alloying) is beginning to occur.

c) T = 700°C. Some small particles begin to disappear, and some larger particles grow (arrows). Area in white box is featured in higher magnification sets below.

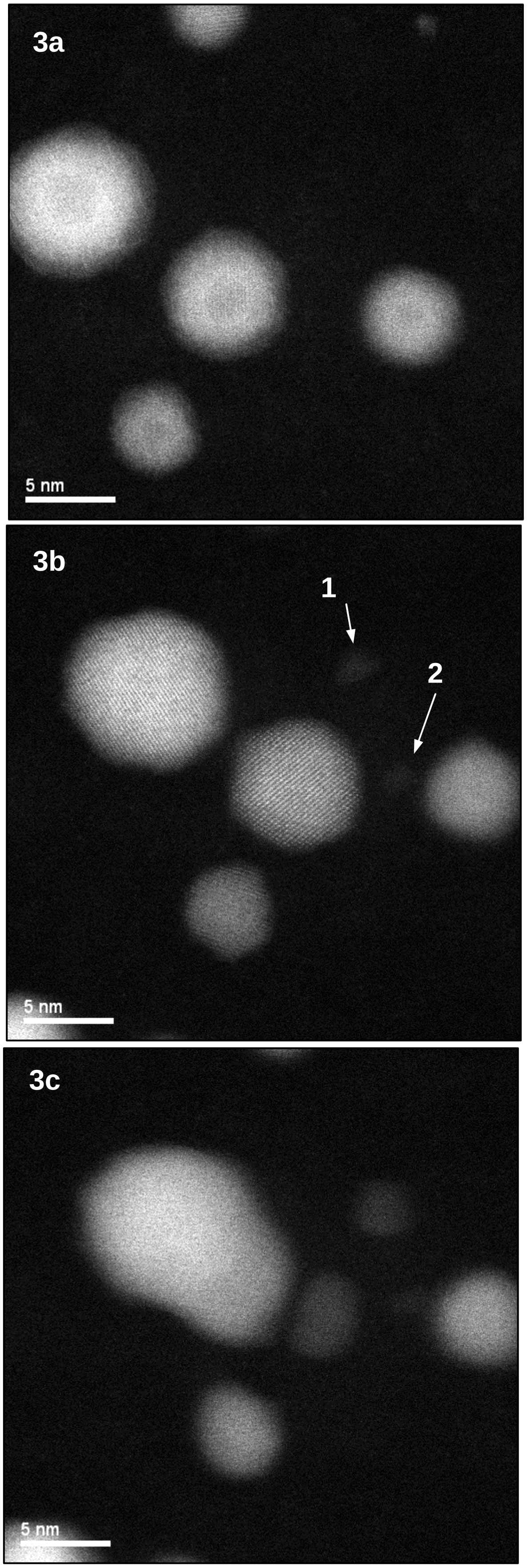


Fig. 3. HA-ADF images of central region of Fig. 2.

a) T = 350°C. The Pd-rich core, Au-rich inner shell, and Pd-rich outer shell are clearly visible.

b) T = 550°C. Distinct core-shell regions are disappearing at this temperature. New aggregates of Pd-Au atoms are forming (1,2), perhaps as a result of migration of ultra-fine clusters and single atom species not seen at this magnification. Large particles at center and upper left appear to increase slightly in size, and the separation decreases. Note the lattice fringes in the large particles; in HA-ADF images such as these, lattice is seen only when a crystal is very close to a good orientation with the electron beam.

c) T = 700°C. Remarkably, the center particle diminishes greatly in size, with the growth of a new grain on the adjacent surface of the larger particle. The two particles remained separated throughout the entire run, even though they were only a nanometer or less apart at any time. New particle 1 grew also, but new particle 2 did not change appreciably after its initial formation at the lower temperature. The core-shell structure was not apparent in any particle, suggesting full alloying after time at the higher temperature.

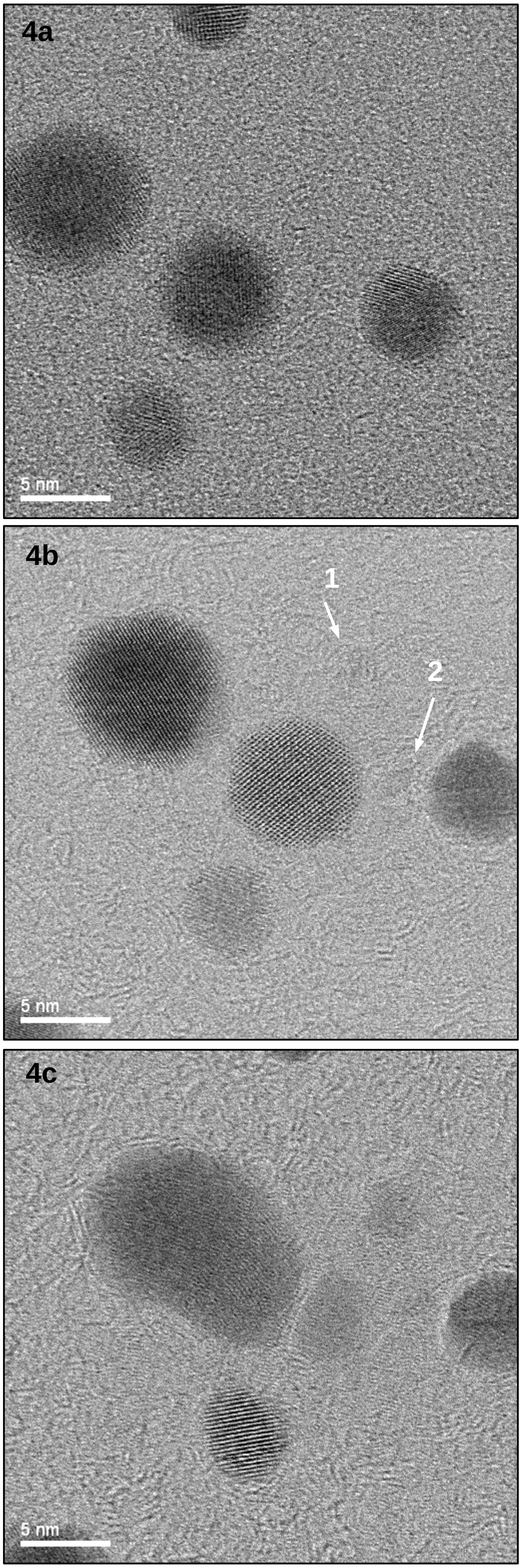


Fig. 4. Bright-field (BF) images acquired simultaneously with the respective images of Fig. 3.

a) Crystal lattice can be resolved in BF images at orientations somewhat farther away from a good orientation required for HA-ADF images.

b) Particles 1 and 2 from the HA-ADF images are faintly seen in the equivalent BF image. The beginnings of growth of the largest particle are apparent, where the new material is not at the same crystal orientation as the original particle, which shows its crystal lattice.

c) The large particle shows faint crystal lattice in this image, and is apparently 2 separate grains. The center particle is again nearly fully depleted. Changes in lattice structure visible from one image to the next are largely due to slight shifts in orientation of the particles due to the thermal effects.

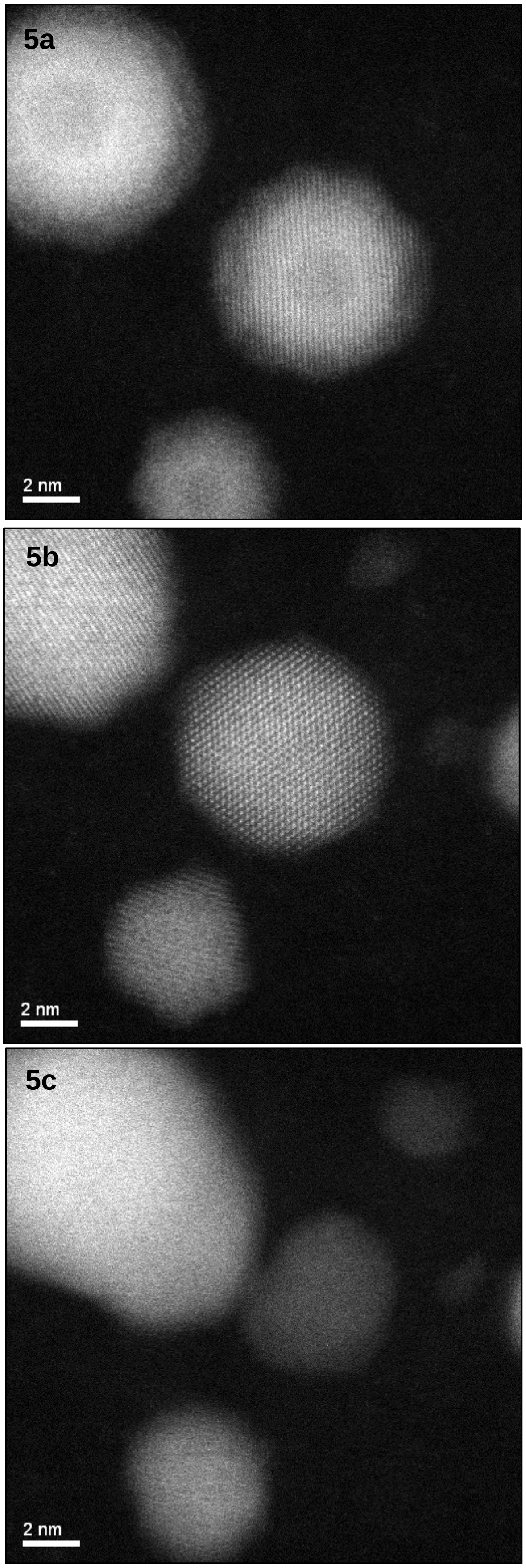


Fig. 5. HA-ADF images at original magnification of 8Mx. These images were acquired one to two minutes **prior to** the respective images of the earlier sets.

a) T = 350°C. Shell structure is very apparent. Some single atoms are seen.

b) T = 500°C. Core-shell structure not apparent. Center particle is nearly perfectly oriented to a zone axis. Note the tendency for the large center and upper left particles to form a "neck," but they do not join to form a single particle.

c) T = 700°C. In this image, the large particles appear to touch, but they never merged to form a single particle. The observed behavior was that the center particle gradually supplied atoms to grow the larger particle, without an apparent sintering effect occurring. Note the interesting observation that the center particle actually separates from the larger particle in the image of Fig. 4c, which was recorded just after this image.

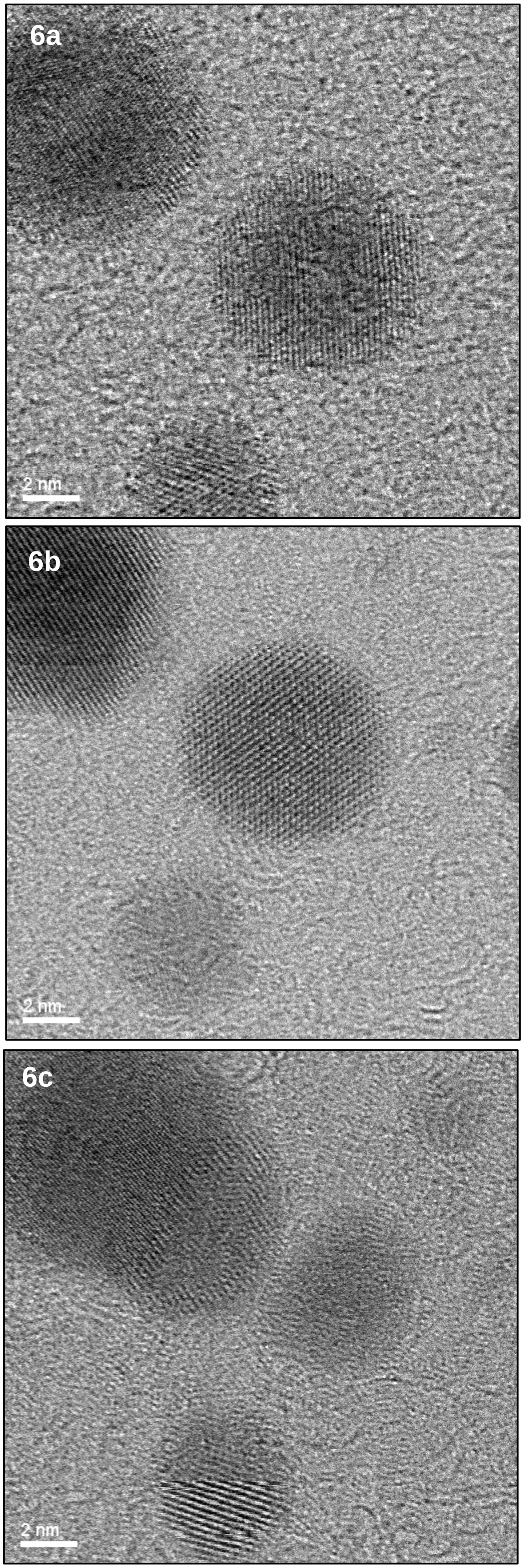


Fig. 6. BF images acquired simultaneously with images of Fig. 5.

a) T = 350°C. Core-shell structure evident.

b) T = 550°C. The crystal lattices of both large particles is seen more clearly in this BF image.

c) T = 700°C. Center and upper left particles are within a few Ångströms. The growth of the second grain on the large particle is clearly evident by the resolved lattice fringes in this image.

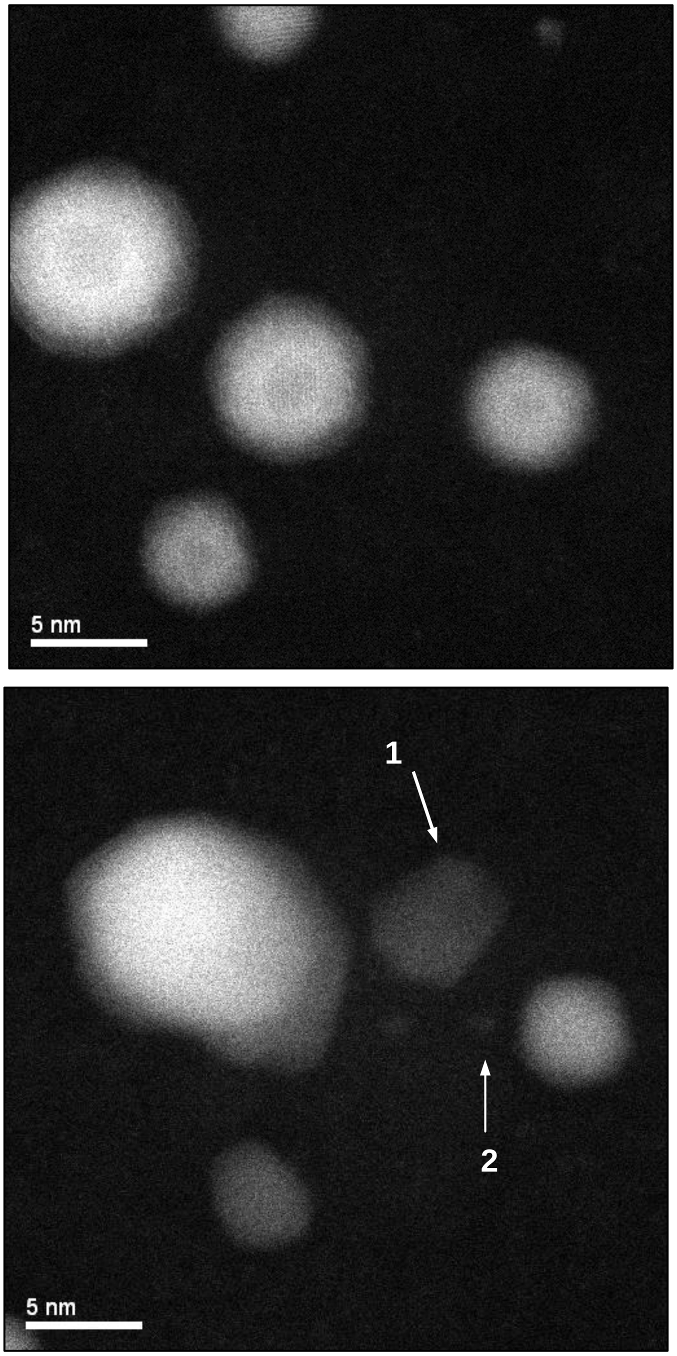


Fig. 7. Final result, after heating to 900°C. The Au-Pd *in-situ* heating experiment was continued to higher temperatures, up to 900°C. The final configuration of the particles is shown in Fig. 7b, and is interesting to compare again to the starting particle array at 350°C.

a) Original HA-ADF image at 350°C, to compare to b).

b) Final HA-ADF image, at 900°C. The new particle (arrow 1) grew continuously during the experiment, whereas the tiny new particle (arrow 2) did not increase in size during the entire experiment. The largest particle shows additional material of low contrast, suggesting that it might be composed primarily of Pd species. The other two primary particles showed a small diminishment in size over the course of the experiment, suggesting that they supplied material to the larger particle, instead of exhibiting growth as might be expected from usual experience.

Summary observations

The example shown in detail here represents one of our earliest experiences in using our new *in-situ* heating capability for characterizing the behavior of catalytic materials. It is the precursor work to a future capability we are developing to allow *in-situ* studies at elevated temperatures with appropriate gaseous environments (i.e., an "environmental cell" capability). We recognize that in the present case, the nanoparticles are supported on a thin carbon film rather than on a "real" support material; that the heating takes place in a vacuum environment; and finally that there is an unavoidable component of the incident electron beam which might have an influence on the details of the experiment. However, experiments like this are necessary to allow us to better understand future results, and they provide tantalizing observations that may be important clues to the behavior of fine particles in real systems. It is of great interest, for example, that particles of equivalent size can come essentially into contact, and not exhibit a tendency to sinter. Why two particles can nucleate (e.g., particles 1 and 2 in Fig. 3a) but only one grows and the other does not is also of interest. These and other questions that result from our early experiments will form the basis for further studies.

References

[1] D. Ferrer, et al., "Three-layer core-shell structure in Au-Pd nanoparticles," *Nano Letters* **7**(6), 2007

Status of Milestones

On schedule

Communications/Visits/Travel

Visit to BASF Co., Woodbridge, NJ. LFA presented seminar "Characterization of Catalysts via Aberration-Corrected Electron Microscopy.

Publications

D. Ferrer, D.A. Blom, L.F. Allard, S. Mejia, E Periz-Tijerina and M.J. Yacaman, "Atomic Structure of Three-Layer Au/Pd Nanoparticles Revealed by Aberration-Corrected Scanning Transmission Electron Microscopy," submitted to *J. Materials Chemistry*.

Agreement 9110: Life Prediction of Diesel Engine Components

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

Nate Phillips and Jeff Jensen
Caterpillar, Inc.

Objective/Scope

There has been considerable interest in the extensive potential use of advanced ceramics and intermetallic alloys for applications in advanced diesel engine systems because of their superior thermomechanical properties at elevated temperatures in oxidative and corrosive environments. The implementation of components fabricated from these advanced materials would lead to significant improvement in engine efficiency, long-term durability, and reduction in NO_x and CO exhaust emission as required in the 21^{st} Century Truck Program. This interest has focused primarily on research aimed at characterization and design methodology development (life prediction) for advanced silicon nitride ceramics and TiAl alloys in order to manufacture consistent and reliable complex-shaped components for diesel engine applications. The valid prediction of mechanical reliability and service life is a prerequisite for the successful implementation of these advanced materials as internal combustion engine components.

There are three primary goals of this research agreement, which contribute toward successful implementation: the generation of mechanical engineering database from ambient to high temperatures of candidate advanced materials before and after exposure to simulated engine environments; the microstructural characterization of failure phenomena in these advanced materials and components fabricated from them; and the application and verification of probabilistic life prediction methods using diesel engine components as test cases. For all three stages, results will be provided to both the material suppliers and component end-users to refine and optimize the processing parameters to achieve consistent mechanical reliability, and validate the probabilistic design and life prediction of engine components made from these advanced materials.

Technical Highlights

Advanced silicon nitride valves after final engine testing (~534 hrs) have been successfully examined by NDE at ANL and then machined for subsequent retained strength evaluation at ORNL. Half cylindrical samples were machined from the stem region for mechanical testing in flexure. Also, valve heads would be fractured to assess the effect of engine environment on the material reliability as well. The mechanical data generated from these engine-tested valves would allow end user to confirm its long-term life prediction results carried out for these valve components subjected to engine application condition.

Previous studies on the TiAl turbo wheel showed that the characteristic strength of biaxial discs extracted from airfoils with as-processed surface exhibited strength that was 34% lower than those discs machined from hub region and tested with as-machined surface. Also, the discs with as-processed surfaces exhibited relative low

Weibull modulus than those with as-machined surface. Thus, detailed of electronic microscopy studies were carried out to elucidate the cause of the lower mechanical performance of as-processed discs from airfoils. Results showed that the strength limiting flaws present in the as-processed discs, in general, were mainly from those large rough surface regions due to the processing, and those critical machined groves were noted for those as-machined discs. Note that all of the as-processed discs completely fractured into two half discs, while the as-machined discs fractured only in the central discs region and other region still remained intact. The difference in the fracture characteristic (brittle fracture for the as-processed discs versus ductile fracture for the as-machined discs) could probably result from the difference in the grain boundary chemistry of materials near the subsurface region.

Long-term creep studies on TiAl alloys provided by different material suppliers and also with different processing conditions were continued during this reporting period. This long-term creep database provides a very important input for the probabilistic turbo wheel design and life prediction for advanced diesel engine applications.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

Communications via phone and e-mails with Nate Phillips of CAT regarding the progress of destructive evaluations of both silicon nitride and TiAl valves after final engine testing.

Communications with Nan Yang of CAT regarding the updates of long-term tensile creep tests of TiAl alloys.

Problems Encountered

None

Publications/Presentations/Awards

None

References

None

Agreement 14957: Thermoelectrics Modeling

Andrew Wereszczak and Hsin 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

Over 700 test specimens of p- and n-type bismuth telluride were purchased (Marlow Industries Inc., Dallas, TX) and received for thermomechanical characterization during the present reporting period. One rationale behind this test plan is this thermoelectric material is mature and its testing will provide a reference database that can be used to compare developmental thermoelectric materials too. The measurement of Young's Modulus, Poisson's ratio, CTE, thermal conductivity, and uniaxial and biaxial flexure strength as a function of temperature will commence during the second quarter. The large number of specimens will enable the generation of statistically significant strength data. Any anisotropic variation of E, ν, CTE, and strength will also be explored. Fractography of tested strength specimens will be performed and failure initiation sites and strength-limiting flaw types will be identified. The uniaxial and biaxial flexure strength test methods will enable us to censor the data according to edge-type and surface-type, and perhaps even volume-type flaws.

In preparation for this testing, fixturing was designed and fabricated to enable the valid strength testing of these specimens. A custom-length sapphire standard was also fabricated for dual-rod dilatometry of these bismuth telluride specimens.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

Numerous communications were held with staff at Marlow Industries, Dallas, TX.

Problems Encountered

None.

Publications/Presentations/Awards
O. M. Jadaan and A. A. Wereszczak, “Probabilistic Design Optimization and Reliability Assessment of High Temperature Thermoelectric Devices,” in proceedings review, 32nd International Cocoa Beach Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, 26 January - 01 February 2008.

References
None.

Agreement 16308: Themoelectric Materials

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

Technical Highlights

(1) Na_xCoO_2 and other oxide phases:

We completed work on the origin of the magnetic field dependence of the thermopower in Na_xCoO_2. This allowed us to explain the reduction in the Seebeck coefficient which was associated with spin-entropy and to establish that the thermopower can be quantitatively predicted based only results from first principles calculations, specifically the band structure and Boltzmann transport theory. A paper detailing some of these results was published in Physical Review. The understanding of the properties of Na_xCoO_2 from these results is that its thermoelectric performance is determined by the narrow d band electronic structure and the fact that it can be doped with a high density of carriers. As is well known, practical difficulties with its application are the high cost and the strong anisotropy of its thermoelectric and mechanical properties. However, based on the fact that the properties of Na_xCoO_2 can be quantitatively determined, we can use the lessons learned from these results to find other more favorable compositions. Accordingly, we started looking for alternate materials that would also have narrow d bands but with potentially lower cost and less anisotropy. Since the O-Co-O bond angles are found to play a key role in Na_xCoO_2 we focused on crystal structures with a similar topology. Based on these considerations and the fact that the mixed valence of Ti often leads to conductivity in titanates, we selected some spinel based titanates as candidates. These are Mg_2TiO_4 and Zn_2TiO_4, which according to literature order in a tetragonal structure when appropriately annealed. Furthermore, while the Ti has valence IV in these compounds, Ti III is also a common valence, and so it seems reasonable to suppose that these compounds could be effectively doped either by excess Ti or by O vacancies to produce an n-type oxide thermoelectric. We started calculations for those materials, and find that indeed they have narrow d bands with charge transfer type band gaps. This is favorable for high thermopower. We are planning to calculate transport properties to determine whether this is in fact so and also to calculate other properties of these materials to better assess their potential as inexpensive practical oxide thermoelectrics.

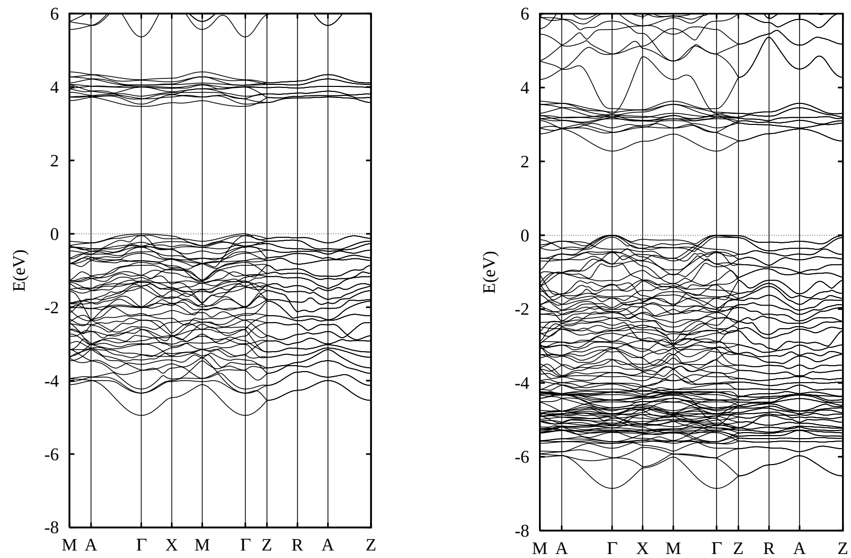

Fig. 1: Calculated band structure of ordered Mg_2TiO_4 (left) and Zn_2TiO_4 (right). Note the narrow d-bands at +2 to +4

(2) Non-oxide materials:

La_3Te_4 is a known high ZT thermoelectric that is under investigation for power generation. However, little is known about its electronic structure or the origin of its high power factor or the doping dependence. It is however known that the material can be synthesized over a wide stoichiometry range from La_3Te_4 to La_2Te_3 while retaining the same structure. We are performing a series of electronic structure and Boltzmann transport calculations to assess whether this material can have high ZT at temperatures important for waste heat recovery. One interesting feature of this system is that similar phases can be made with a variety of rare earths, which suggests that there is room for further optimization via rare earth alloying. Results so far show that the operating temperature of this material can be lowered, but more quantitative calculations are needed to establish this.

(3) Thermal conductivity:

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

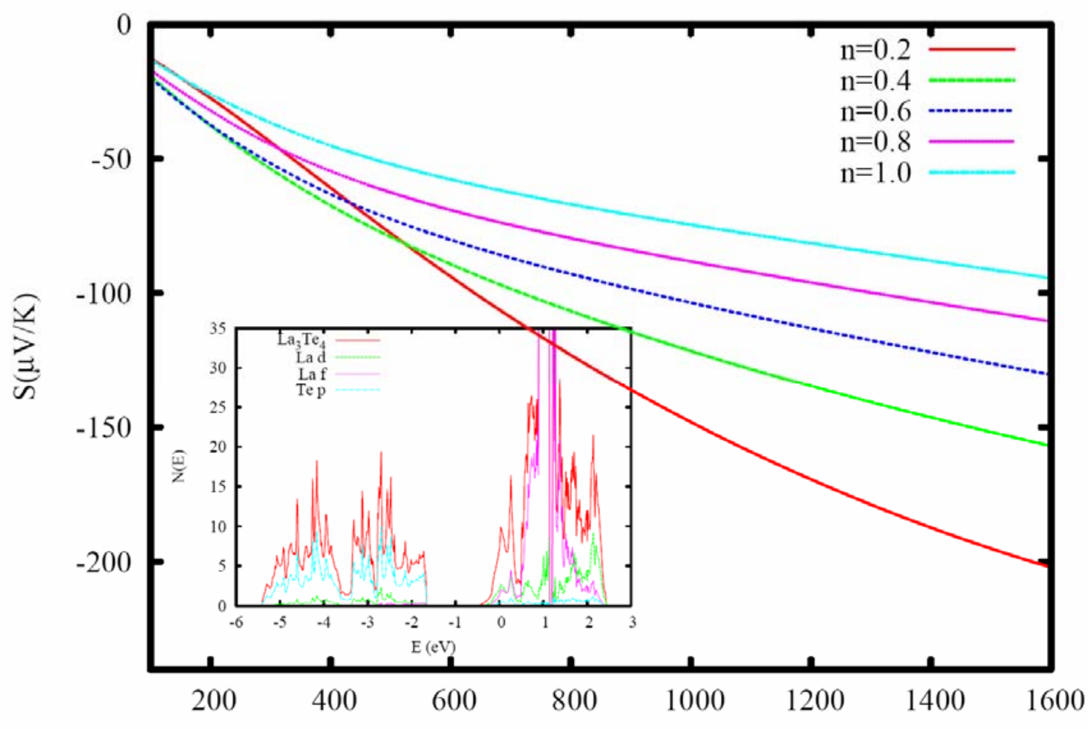

Fig 2: Calculated thermopower as a function of temperature for various carrier concentrations and density of states (inset) for La_3Te_4.

Status of FY 2008 Milestones

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

Communications/Visits/Travel

1. D.J. Singh: Travel to Materials Research Society Meeting, Boston, MA to attend Symposium U: Thermoelectric Power Generation

Problems Encountered

No significant problems encountered this quarter.

Publications/Presentations/Awards

Publications:

1. H.J. Xiang and D.J. Singh, "Suppression of thermopower of Na_xCoO_2 by an external magnetic field: Boltzmann transport combined with spin-polarized density functional theory" *Physical Review B* **76**, 195111 (2007).

Presentations:

1. “Oxide Thermoelectrics”, David J. Singh, Materials Research Society Meeting, Boston, MA, November 2007 – **Invited Talk**

References