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FY 1999

Progress Report for Propulsion Materials

Energy Efficiency and Renewable Energy
Office of Transportation Technologies
Office of Advanced Automotive Technologies
Energy Conversion Team

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CONTENTS

1. INTRODUCTION

Advanced Propulsion Materials R&D: Enabling Technologies to Meet Technology Program Goals

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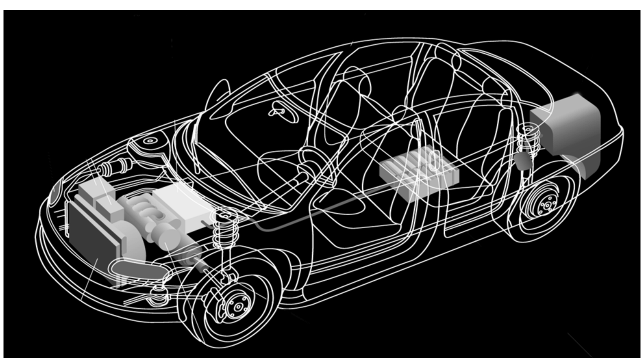
On behalf of the Department of Energy's (DOE's) Office of Advanced Automotive Technologies (OAAT), I am pleased to introduce the FY 1999 Annual Progress Report for the Automotive Propulsion Materials Research and Development Program. Together with DOE national laboratories and in partnership with private industry and universities across the United States, OAAT engages in high-risk research and development (R&D) that provides enabling technology for fuel-efficient and environmentally-friendly light duty vehicles.

The Automotive Propulsion Materials Research and Development Program supports the Partnership for a New Generation of Vehicles (PNGV), a government-industry partnership striving to develop by 2004 a mid-sized passenger vehicle capable of achieving 80 miles per gallon while adhering to future emissions standards and maintaining such attributes as affordability, performance, safety, and comfort. Automotive propulsion materials research is key to PNGV program success as it focuses on improving the materials used in propulsion systems components and subsystems. New propulsion materials will facilitate higher efficiencies, lower emissions, improved alternative fuel capabilities, and lower specific weight and volume, without compromising cost, safety, and recyclability.



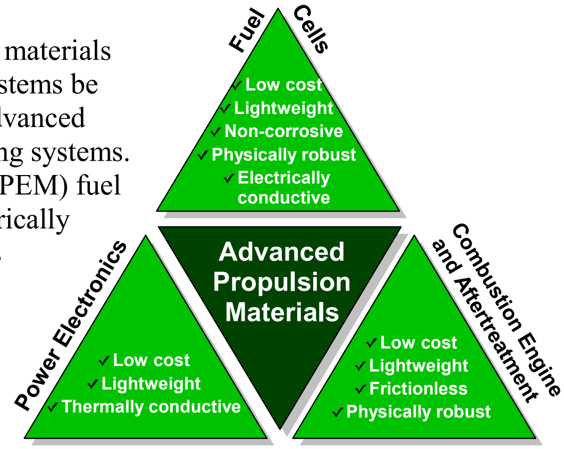
Advances in propulsion material technologies will impact all vehicle systems

Reorganized in FY 1998, the Automotive Propulsion Materials program is now an integral partner with the Power Electronics, the Advanced Combustion and Emissions Control, and the Fuel Cells for Transportation R&D programs. This change reflects the elimination of the gas turbine engine as a candidate for the 80-mpg automobile and the emphasis on direct-injection engines and fuel cell technologies as the selected candidate powerplants for 80-mpg hybrid electric vehicles. Projects within the Automotive Propulsion Materials program address materials concerns that directly impact the critical technical barriers in each of these programs—barriers such as thermal management, emissions reduction, and reduced manufacturing costs.

Enabling Technologies

The technologies developed in the Automotive Propulsion Materials program are what are known as enabling technologies—those necessary for the success of the power electronics, fuel cell, and combustion engine and aftertreament research programs. One of the most important technical barriers being addressed by the materials program, for example, is preventing the overheating and failure of vehicle electronics (thermal management). The components necessary for the high-fuel-economy, low-emission PNGV vehicles require high-power electronics to be smaller and lighter in weight. This R&D in electronics materials is enabling the Advanced Integrated Power Module program to address new requirements for vehicle electronics, such as controlling electricity generated from fuel cells and other hybrid-electric configurations. These requirements increase the temperatures realized by circuitry and challenge the ability to keep power electronics and capacitors from overheating. R&D for new thermal management materials is at the core of the activities in power electronics materials.

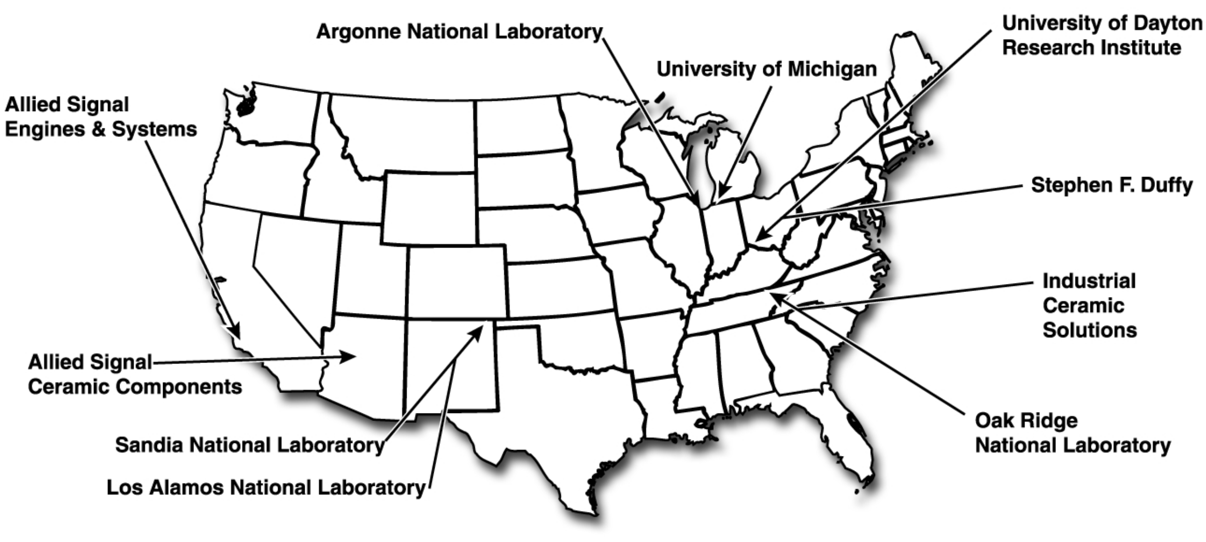
The successful development of fuel cells will require major materials breakthroughs. Not only must low-cost, durable fuel cell systems be developed, but also specific fuel cell components require advanced materials development to turn research concepts into working systems. The bipolar plates used in the proton-exchange membrane (PEM) fuel cell stack, for example, must be resistant to corrosion, electrically conductive, and physically robust. The propulsion materials program has included projects specifically tasked with developing less costly materials to provide these characteristics. Two successful bipolar plate projects have been transferred to the Fuel Cells for Transportation program, and materials work is now focusing on other critical materials-related barriers for fuel cells, such as the development of a high-temperature PEM.



Advanced Propulsion Materials Enable Other Program Areas to Meet Technical Goals

Compression-ignition, direct-injection (CIDI) engine and aftertreatment development will greatly benefit from the propulsion materials program through research in advanced component coatings and the development of improved particulate filters for diesel engines. Wherever there are moving parts within a system, there is concern with the amount of friction between these parts and how it places demands on overall durability and operating life. For both fuel cell compressors and CIDI engine applications, development of advanced materials for coatings can minimize friction to ensure long component life or reduced wear of components such as fuel injectors. Wear of components can lead to increased emissions, lower efficiency, and lower durability.

In addition, current CIDI engine technology faces the difficult balance of engine efficiency versus tailpipe emissions. The propulsion materials program is working to maximize efficiency while reducing emissions through the development of advanced filters to reduce particulate matter from combustion engines. The propulsion materials program is also investigating the development of other materials that can further reduce tailpipe emissions.



Advanced Propulsion Materials Program

Collaboration and Cooperation

As with other programs under PNGV, collaboration and cooperation across organizations is a critical part of the Advanced Propulsion Materials program. Across the materials projects, scientists at the national laboratories are collaborating with manufacturers to identify and refine the necessary characteristics for meeting performance requirements. Component manufacturers and scientists from national laboratories and contractors are also working together to identify the technological barriers to manufacturing optimal materials to meet component requirements.

Laboratory/contractor-industry collaboration

Laboratory	Industrial partners	
Argonne National Laboratory	Ability Engineering Technology, Inc.	DaimlerChrysler Corporation
	Atlas Cylinders, Inc.	Ford Motor Company
	Bronson and Bratton, Inc.	Lucas-Varity
	Cryomagnetics, Inc.	Purdue University
	CRUMAX	UGIMAG, Inc.
Los Alamos National Laboratory	Bulk Molding Compounds, Inc.	Plug Power, LLC
	Premix, Inc.	
Oak Ridge National Laboratory	AlliedSignal	Industrial Ceramic Solutions
	AVX	Kemet
	Bronson and Bratton, Inc.	Motorola
	Conoco Corporation	Murata
	Cryomagnetics, Inc.	Plug Power, LLC
	CRUMAX	UGIMAG, Inc.
	DaimlerChrysler Corporation	University of Dayton Research Institute
	Dow Chemical Company	University of Tennessee
	Ford Motor Company	University of Wisconsin
	Florida International University	
Sandia National Laboratory	AVX	Murata
	DaimlerChrysler Corporation	Pennsylvania State University
	Ford Motor Company	TAM
	General Motors	Tokay
	Degussa	TPC Ligne Puissance
	Ferro	TPL, Inc.
	Kemet	TRS Ceramics
	Materials Research Associates	

There is also cooperation among national laboratories to take advantage of the expertise of each facility. Argonne and Oak Ridge National Laboratories, for example, are collaborating in the development of a low-cost, high-energy-product permanent magnet. For this project, Argonne provides expertise in fabrication, while researchers at Oak Ridge characterize permanent magnets fabricated at Argonne, as well as those from other commercial manufacturers. In another project, Oak Ridge National Laboratory (ORNL) is providing ceramic materials support to Pacific Northwest National Laboratory for the development and fabrication of ceramic components for new non-thermal plasma after treatment systems to reduce diesel exhaust emissions.

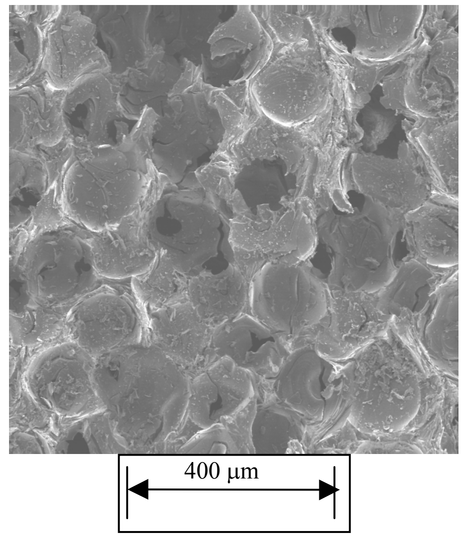
In addition to national laboratory and large industry participation, the FY 1999 Advanced Propulsion Materials program also included some breakthrough research and development conducted by a small business. Industrial Ceramic Solutions, LLC, located in Oak Ridge, Tennessee, is developing a ceramic filter to reduce particulate emissions from diesel engines. As in the collaborative efforts of national laboratories with industry, researchers at Industrial Ceramic Solutions are working closely with representatives from DaimlerChrysler, Ford, and General Motors to develop a filter that will help meet PNGV emissions targets.

Accomplishments

FY 1999 featured notable accomplishments in all three materials program areas. While the remainder of the report provides summaries of all of the Advanced Propulsion Materials projects, this section provides a highlight of some of the major accomplishments during FY 1999. Materials development in support of power electronics, for example, featured breakthroughs in the use of high-conductivity carbon foam for heat exchangers and heat sinks. Fuel cell–related materials activities demonstrated improvements in the capability to mass-produce low-cost composite material for fuel cell stack bipolar plates. Finally, materials research in the support of combustion engine and aftertreatment technologies led to the development of a microwave-regenerated exhaust particulate filter.

Power Electronics

One of the greatest challenges to the successful development of advanced power electronic devices is managing the heat generated by their operation. Currently, most heat sinks for cooling high-power electronics use a water-cooled aluminum or copper plate mounted below the electrical circuitry to transfer heat from the electronics to the water-cooled metal. Using high-conductivity carbon foam as the core material for these heat exchangers can significantly increase the effective transfer of heat while reducing the overall size and weight.



Carbon foam structure at high temperature (1000^{o}C)

During FY 1999, researchers at ORNL improved processing techniques for the production of carbon foam, increasing the thermal conductivity by more than 50% and meeting the program's goal. Collaborating with potential manufacturers, ORNL researchers defined targets and manufacturing requirements for using this highly conductive carbon foam in electronic component heat exchangers and heat sinks. Researchers varied processing conditions and characterized foam structures to understand the effects on thermal properties. As a result of these findings, ORNL researchers developed a new, faster process for fabricating carbon foams, eliminating several steps in the fabrication process.

The outcome of this project has generated positive responses. First, based upon confidence in this new technology, ORNL has successfully licensed the carbon foam material technology to Poco Graphite of Decatur, Texas, for large-scale commercial production. Second, extensive meetings are being conducted with DaimlerChrysler, Ford, Lockheed Martin, Boeing, Modine, Peterbilt, and a NASCAR racing team to develop this material for use in radiator systems and other electronics cooling applications. Third, there is potential for using carbon foam in desktop computers and laptops to better disperse heat, allowing the size of the computer to be reduced. Finally, it is expected that the same technology may be applied for use in fuel cell vehicles (to remove heat) and large trucks (smaller, lighter radiators make for more aerodynamically shaped trucks).

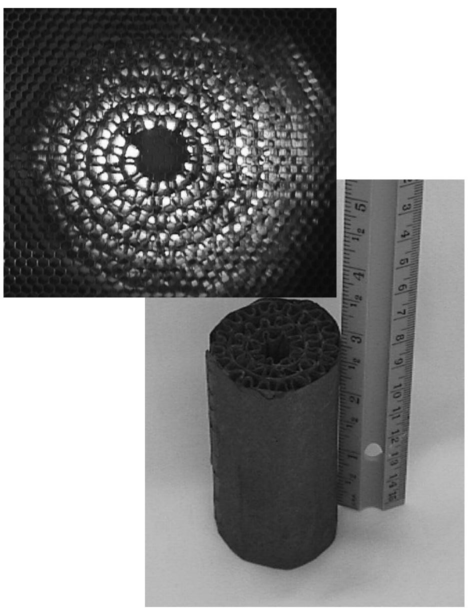
Fuel Cells R&D

The successful development of fuel cell technology in vehicles requires breakthroughs in cost, durability, size, and performance. During FY 1999, researchers at Los Alamos National Laboratory (LANL), in collaboration with Premix, Inc., and Bulk Molding Compounds, Inc., took the final steps necessary for mass production of composites for PEM fuel cell stack bipolar plates that are low-cost, corrosion-resistant, electronically conductive, and physically robust.

Although laboratory-scale plates produced at LANL in FY 1998 exhibited good properties, it was recognized that the processing of molding compounds would need to be improved prior to mass production. Using the manufacturing expertise of Premix and Bulk Molding Compounds, researchers worked together to produce new molding compounds that exhibited reduced cure times, extended shelf life, and more uniform flow. Researchers used vinyl ester resins in these compounds to minimize process cycle times and enhance plate resistance to corrosion. In addition, they eliminated machining requirements by forming plate molds, allowing for a single molding step. All of these accomplishments will lead to lower-cost production of stacks for PEM fuel cell systems. As a result of these breakthroughs, LANL has submitted an application for a U.S. patent for this advanced composite molding process technology.

Advanced Combustion Engine and Emissions R&D

A major PNGV goal is to develop a vehicle with outstanding fuel economy that meets stringent emissions standards. Balancing high fuel economy with low emissions is a challenge that is being addressed through the materials activities in support of the Advanced Combustion Engine and Emission Control R&D program. Specifically, work conducted at Industrial Ceramic Solutions has led to the development of an advanced exhaust filter system capable of capturing more than 90% of the carbon particulates from diesel engine exhaust.



Industrial Ceramic Solutions' microwave-regenerated ceramic fiber filter

Based upon characteristics identified by the PNGV representatives at DaimlerChrysler, Ford, and General Motors, researchers at Industrial Ceramic Solutions designed and fabricated a ceramic filter system. This system was demonstrated on the exhaust of the Ford 1.2 liter DIATA diesel engine. The filter system features a ceramic-fiber filter that can be automatically cleaned through the use of microwave power. Researchers tested the capability of the system to self-clean during engine idling, varying the temperature of operation, air flow through the filter, and microwave power input. As a result of the tests, Industrial Ceramic Solutions developed a prototype exhaust filter system that can capture more than 90% of diesel particulates from exhaust and be regenerated or cleaned under idle conditions.

This exhaust filter system signifies a breakthrough in emission control technology. If successful, it could be applied in a wide variety of diesel engines that generate very fine particulate matter. Beyond the application in diesel-powered cars, this technology could be applied to diesel engines used in pick-up trucks, sport utility vehicles, and large trucks. In addition, with the near-elimination of particulate emissions, the focus on engine optimization could be steered toward reducing other types of emissions, such as nitrogen oxides (NO_x), a major contributor to air pollution.

Awards and Achievements

Carbon foam thermal management *(ORNL)*	† License granted to Poco Graphite † Three Patent Applications Submitted
Near-frictionless coating *(ANL)*	† Argonne National Laboratory Directors Award—1999 † Patent Application Submitted

Future Directions

As this program focuses on enabling technologies to support technology program goals, the Advanced Propulsion Materials program will continue to work closely with PNGV partners and industry to understand propulsion materials-related requirements. Building upon the recent advances in materials technologies, many of this year's projects will be moved out of the laboratory and over to industry for testing. Projects such as the microwave regenerative exhaust filter will continue to optimize the technology design in preparation for vehicle testing. Other projects will continue to refine manufacturing requirements and characteristics necessary to meet the challenges of the PNGV program. Several technologies, such as the composite molding process technology for fuel cells, will be transferred to industry for commercialization.

The most promising new activity in the Advanced Propulsion Materials program for FY 2000 is the collaboration between Oak Ridge and Argonne National Laboratories in the development of smaller, lighter, and more efficient radiators. To reduce the size and weight of the radiator, heat transfer must be improved on the airside; once that is accomplished, heat transfer characteristics of the coolant must be improved. Carbon foam materials developed at Oak Ridge and nanofluids developed at Argonne are advanced heat transfer materials with significantly higher thermal conductivities and improved heat transfer characteristics than are presently available. Therefore, combining carbon foam technology with nanofluid technology could lead to a breakthrough in the design of advanced vehicle thermal management systems that can meet the needs to improve heat transfer on both the air side and coolant side of the radiator.

As advanced automotive technology developments uncover new challenges, the Advanced Propulsion Materials program will continue to provide breakthrough technology solutions. Collaborating with industry, PNGV partners, national laboratories, and small businesses, the Advanced Propulsion Materials program will continue to serve the needs of power electronics, fuel cells, combustion engine and aftertreatment, and all other critical technology areas.

Project Abstracts

The remainder of this report communicates the progress achieved during FY 1999 under the Automotive Propulsion Materials program. It consists of 14 abstracts of national laboratory projects—5 that address power electronics, 4 that address combustion and emission technologies, 4 that address fuel cells, and 1 that summarizes the closeout of the ceramic gas turbine activities. The abstracts provide an overview of the critical work being conducted to improve these systems, reduce overall cost, and maintain component performance. In addition, they provide insight into the challenges and opportunities associated with advanced materials for high-efficiency automobiles.

Patrick B. Davis

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2. POWER ELECTRONICS

A. Carbon Foam Thermal Management Materials for Electronic Packaging

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objectives

- Collaborate with potential manufacturers with regard to designing, testing, and manufacturing of smaller, lighter, and more efficient heat exchangers and heat sinks for power electronics, utilizing the high conductivity carbon foam.
- Utilize improved understanding of effects of processing conditions on foam structure to increase the thermal conductivities of high conductivity carbon foams by more than 50%.

OAAT R&D Plan; Task 4; Barriers B, C, D

Approach

- Vary processing conditions and characterize foam structures to gain understanding of effects of process conditions on structures that affect thermal properties.
- Work with industrial partners to define targets for foam-based heat exchangers.
- Develop joining/bonding techniques to laminate the foam to heat exchangers without sacrificing thermal conductivity.

Accomplishments

- Met program goal for increasing thermal conductivity by over 50%.
- Licensed the technology to Poco Graphite, Inc. to commercialize the material and scale up for production for large volume markets.
- Developed bonding techniques with epoxies and brazing for laminating foam to different materials.
- Developed electroplating technique for improving the ruggedness of the foam.

Future Direction

- Develop logic and system design for integration of the foam into application-specific devices.
- Improve understanding of pressure drop/density/thermal conductivity/heat transfer coefficient relationships to ensure optimum weight-efficiency tradeoffs.
- Increase heat flux/weight by up to 10-fold

Introduction

Two devices are currently used for thermal management: heat exchangers, which transfer heat energy from one area of a device to another; and heat sinks, which dissipate heat into the air. Currently, most cooling heat exchangers for high-power electronics use layers of water-cooled aluminum or copper plate mounted below the electrical circuitry to transfer heat from hotter areas to cooler areas. Using carbon foam as the core material for these heat exchangers, the effective transfer of heat can be significantly increased while the size and weight of the heat exchanger is reduced.

A new, less time-consuming process for fabricating mesophase pitch-based graphitic foams without the traditional blowing and stabilization steps has been developed at Oak Ridge National Laboratory (ORNL) and is the focus of this research. Initially these foams possess a thermal conductivity of 106 W/m·K at a relatively low density of 0.54 g/cm^3. Potentially, the process will lead to a significant reduction in the cost of carbon-based thermal management materials (i.e., foam-reinforced composites and foam core sandwich structures).

Experimental

In this research, two 100% mesophase pitches were used to produce graphitic foam: Mitsubishi ARA24 naphthalene-based synthetic pitch (melting point of 237°C) and a proprietary mesophase pitch from Conoco Corporation labeled "Conoco Dry Mesophase" (melting point of 355°C). All foam samples were carbonized at 0.2°C/min to 1000°C and then graphitized at 10°C/min in argon to 2800°C with a 2-hour soak, at temperature.

In order to develop a fundamental understanding of the foam structure and graphitic morphology, and therefore develop an ability to tailor the thermal properties, samples were examined using a JOEL scanning electron microscope. Also, the thermal conductivity, κ, of the foam was determined with a xenon flash diffusivity technique. The thermal diffusivity, α, was first measured on samples of 12-mm diameter by 12-mm thickness on a custom-built machine in the High Temperature Materials Laboratory at ORNL. The sample density, ρ, and specific heat capacity, C_p, (assumed to be 713 J/Kg·°C) were then used to calculate the thermal conductivity with the following relation:

$$\kappa = \alpha \cdot \rho \cdot C_p.$$

Finally, the same foam samples used for thermal diffusivity were machined to cylinders of 12-mm diameter by 6-mm thickness for X-ray diffraction studies, giving an understanding of the relationship between processing conditions and the graphitic structure of the foam.

Several 38.1-mm-thick foam blocks were made from AR mesophase pitch with the standard ORNL process. Sandwich panels were constructed from 12.7-mm-thick, 152.4-mm-diameter foam core sections machined from the thick blocks. Both aluminum 3003-H14 and copper 110, 0.635-mm-thick, were used as face sheets. A thermally conductive film adhesive, T-gon 1/KA-08-128 (0.203 mm, 8 W/m·K), was used to bond the face sheets to the foam core with a cure at 0.241 MPa, 150°C for 30 minutes. Although a slightly higher pressure was recommended for curing the film adhesive, 0.241 MPa was found to be sufficient for bonding to the foam.

Flexural tests were conducted on 107-mm by 27.9-mm samples according to ASTM C393-94 for 4-point bending with two-point loading and one-quarter span. This specimen geometry was chosen to produce core shear or bond failure. Compression testing was conducted at 5.08 mm/min for 19-mm-square samples.

The thermal conductivity of the laminated samples was determined by the same method as that used for the basic foam.

Results and Discussion

Figures 1 (a) and (b) are scanning electron micrographs of the pore structure of the Mitsubishi ARA24- and Conoco-derived foams, respectively, heat treated at 1000°C. The Conoco pitch yielded foams with marginally higher densities than foams produced with the ARA24 mesophase pitch. The ARA24 pitch-derived foams exhibited a larger mean pore size than the Conoco pitch-derived foams (275 µm vs. 60 µm). The higher melting temperature of the Conoco pitch yields higher viscosities during processing, and therefore smaller bubble sizes.

Both foams exhibit a spherical cell structure with open, interconnected pores (P in Figure 1) between most of the cells. It is evident from the images in Figure 1 that the graphitic structure in both foams is oriented parallel to the cell walls and highly aligned along the axis of the ligaments (L in Figure 1).

It can be seen in the ARA24-derived foams that the graphitic structure is less aligned in the junctions between ligaments (J in Figure 1) and possesses more folded, mosaic texture. It is postulated that this arises from the lack of stresses at this location during forming.

Figure 2 is the X-ray diffraction spectra for both foams. The d_{002} spacing was calculated to be 0.3355 nm for the ARA24 foam and 0.3360 nm for the Conoco-derived foam. This is significantly better than in existing high-performance carbon fibers such as K1100 (0.3366) and vapor-grown carbon fibers (0.3366) and better than most synthetic carbons. The crystallite sizes (L_a and L_c) were similar to typical high-thermal-conductivity carbon fibers.

The thermal conductivity of the ARA24 foam graphitized at 10°C/min ranged from 50 to 150 W/m·K, and the Conoco derived foams exhibited thermal conductivities ranging from 40 to 135 W/m·K (Figure 3). These conductivities are remarkable for materials with such low densities, 0.27 to 0.57 g/cm^3 (density was varied by varying processing conditions).

Under close examination of the scanning electron microscope images in Figure 1, microcracks and delaminations of the graphite planes can be observed. These are most likely due to the thermal stresses induced during carbonization and graphitization as a result of the low thermal conductivity of the foam prior to graphitization. It was postulated that reducing the heating rates during this process would minimize thermal gradients, and thus minimize thermal

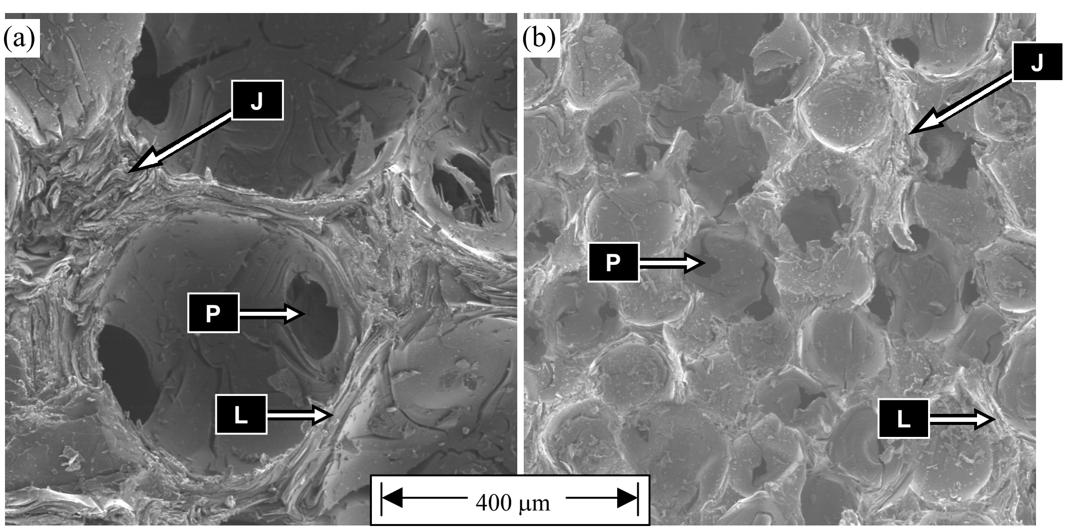

Figure 1. Structure of (a) Mitsubishi ARA and (b) Conoco Mesophase pitch-derived carbon foams carbonized at 1000°C.

stresses, resulting in fewer microcracks and delaminations. In fact, when the graphitization rate was slowed to 4°C/min, the thermal conductivity of the ARA24-derived foams increased significantly to nearly 190 W/m·K (Figure 3). This is significantly better than the targeted 50% increase in thermal conductivity.

Four sandwich panels were fabricated for testing: two with aluminum face sheets and two with copper face sheets. The flexure specimens exhibited classic shear failure with only a slight delamination of the foam from the face sheet. The core shear stress ranged from 1.49 to 2.35 MPa, while the shear modulus ranged from 47.9 to 111 MPa. The values for panels with copper face sheets had a significantly higher core shear stress and core shear modulus that has not been explained.

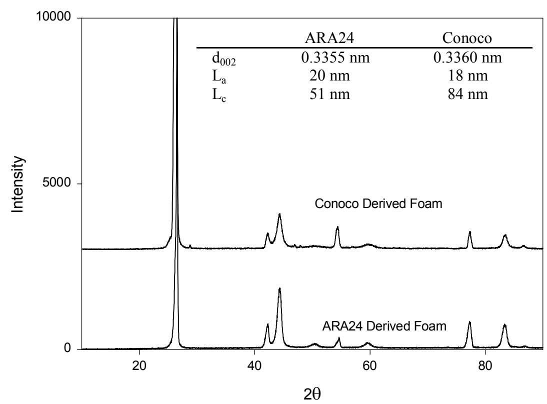

Figure 2. X-ray diffraction patterns of ARA24 and Conoco derived foams graphitized at 2800°C.

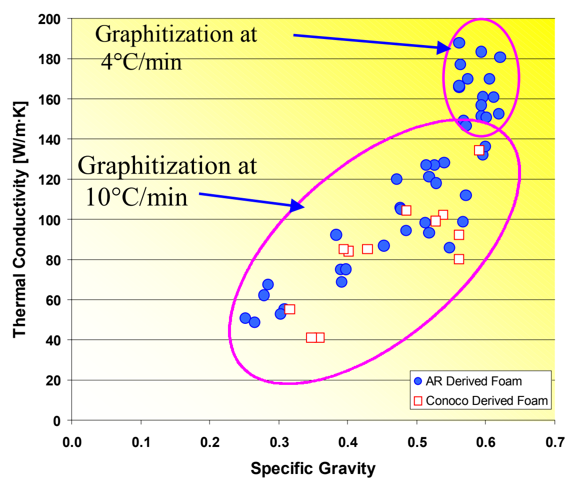

Figure 3. Thermal conductivity of ARA24 and Conoco derived foams as a function of density.

A typical load-displacement curve for the compression tests shows that the foam core crushes with a fairly uniform load over a large displacement. The compression strength and modulus ranged from 1.2 to 2.5 MPa and 44 to 176 MPa, respectively.

The results of the thermal conductivity testing of the sandwich panels indicated that the sandwich specimens had a through-the-thickness thermal conductivity of between 50 and 65 W/m·K with little difference between the aluminum and the copper sandwich panels. Although the thermal conductivity was lower than that of the basic foam because of the relatively low-conductivity adhesive, the specific conductivity of the sandwich panels is comparable to that of aluminum.

The average adhesive thickness in the sandwich panels was between 0.127 and 0.203 mm. With a thermal conductivity of only 8 W/m·K, the interface was the limiting factor for the through-thickness conductivity. Methods to improve the through-thickness thermal conductivity include using a higher-conductivity adhesive and decreasing the adhesive thickness. Several additional sandwich panels have been successfully bonded with thinner bond lines of filled epoxies (approximately 0.0254 mm). Also, a brazing technique has been developed for bonding aluminum face sheets (thermal conductivity of the brazing material is approximately 45 W/m·K).

Applications

Since the foam is open cellular, it is a prime candidate for use as a porous media heat exchanger for a power electronics substrate. Currently, most substrates for high-power electronics include a water-cooled aluminum or copper plate mounted below the circuitry. It can be shown that the effective heat transfer coefficient can be raised from ~ 250 W/m^2·K for current designs to over 10,000 W/m^2·K for flow through a porous graphite foam. It was proposed that a once-through foam core/aluminum-plated substrate be fabricated to replace the current substrates (see Figure 4). The foam core thickness, geometry, channel patterns, foam cell size, and heat treatment temperature will be

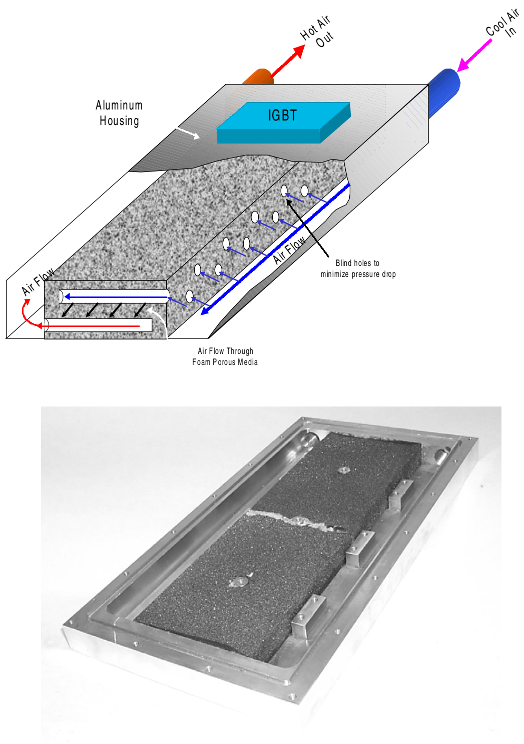

Figure 4. Schematic and photograph of design for foam-based heat exchanger substrate for power electronics cooling.

evaluated to give optimum heat removal at the lowest flow rate of cooling fluid.

In a separate test, heat transfer coefficients for a shell-and-tube heat exchanger with carbon foam as the core were measured as high as 11,000 $W/m^2 \cdot K$. This test validated the capability of the foams to remove large amounts of heat with cooling air instead of water.

Furthermore, independent tests of the foam material at Florida International University have confirmed the dramatic improvement in heat transfer coefficients when the foam is used as a porous heat transfer medium. The major conclusion of this research is that natural convection is not enough to improve the heat transfer: the air must be forced through the foam to realize the full potential of the material.

A closed-form mathematical model was developed at the University of Tennessee to predict the thermal conductivity of the foam based on the structure and density. This model is being expanded to study the heat transfer characteristics of the foam under forced flow.

Last, extensive meetings are being conducted with DaimlerChrysler, Lockheed Martin, Boeing, Modine, Peterbilt, and a NASCAR racing team to develop this material for radiator systems and other electronic cooling applications.

Conclusions

The manufacture and properties of high-thermal-conductivity carbon foams have been reported. It was shown that pitch precursor characteristics will affect foam structure and properties such as bubble size, ligament structure, and thermal conductivity. The highly aligned ligaments have similar structures to high-thermal-conductivity carbon fibers, such as K1100 and VGCF. In fact, the d-spacing was less than that of VGCF, which has exhibited thermal conductivities as high as 1950 W/m·K. These properties, combined with the continuous graphitic network, result in a specific thermal conductivity of up to 6 times greater than that of copper. Through this essential materials characterization, it was determined that slower heating rates during carbonization and graphitization would result in a dramatic improvement in thermal conductivity, nearly 75% better than the initial values. Hence, the main program objective was met.

Standard laminating techniques were shown to be viable for producing foam core sandwich panels. However, either thin bond lines or brazed interfaces were found necessary to preserve the high thermal conductivity. With further development, carbon foam can replace honeycomb in applications that require high thermal conductivity and low weight.

High heat-transfer coefficients have been measured, and heat exchangers have been designed and built with the knowledge learned in this program. In future research, extensive tests and redesigns will be conducted to build a proper heat exchanger substrate for power electronics cooling and other cooling applications for the Partnership for a New Generation of Vehicles.

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B. dc Buss Capacitors for PNGV Power Electronics

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Contractor: Sandia National Laboratory, Albuquerque, New Mexico
Prime Contract No.: 04-94AL85000

Objectives

- Develop a replacement technology for the presently used aluminum electrolytic dc buss capacitors for year 2004 new-generation vehicles.
- Develop a high-temperature polymer dielectric film technology that has dielectric properties technically superior to those of Al electrolytic dc buss capacitors and is of a comparable or smaller size.
- Develop a low-cost, multilayer ceramic technology that results in capacitors that are technically superior to presently used Al electrolytic capacitors.

OAAT R&D Plan; Task 4; Barriers A, B, C, D

Approach

- Contact automobile design and component engineers, dielectric powder and polymer film suppliers, and capacitor manufacturers to determine state-of-the-art capabilities and to define market enabling, technical goals.
- Synthesize conjugated polyaromatic chemical solution precursors that result in dielectric films with low dielectric loss and excellent high-temperature dielectric properties.

- Use a molecular engineering approach to create higher polarizabilities in polymer films, leading to higher dielectric constants, by substitution of side groups and bridging molecules.
- Fabricate, microstructurally analyze, and electrically characterize barium titanate and lead-based ceramics dielectrics in layers of suitable thickness for use in 2004 automobiles.

Accomplishments

- Determined critical issues for dc buss capacitors: (1) cost and hard breakdown for ceramic multilayers and (2) higher dielectric constants for polyfilm capacitors.
- Developed technologies for single-layer deposition thickness of 3 μm for polyfilm capacitors and layer thickness ranging from 20 μm to 50 μm for ceramic capacitors using computer-controlled micro-pen and tape cast technologies (these would be suitable for 600-V dc buss capacitor operation).
- Designed and fabricated polyfilm dielectrics with dielectric constants of 4 and dielectric loss less than 0.003, which exceeded the properties of state-of-the-art polyphenylene sulfide.
- Fabricated ceramic dielectrics with high permittivity that met or exceeded manufacturer's specifications and that were compatible with low-cost electrode approaches (ultralow fire and base metal electrode). Performed a trade-off study of performance versus electrode cost for low-fire barium titanate dielectrics.

Future Directions

- Enhance dielectric constant of polymer film dielectrics to greater than 6 and keep dissipation factor below 0.01. Commercial manufacturers have stated that these properties would spur commercial development.
- Develop low-cost electrode, ceramic dielectric capacitor technology that can withstand high electrical breakdown fields.
- Fabricate multilayer polyfilm and ceramic dielectrics that meet PNGV electric field operation criteria to reduce size of units.

Introduction

Sandia National Laboratories (SNL) has actively interacted with a number of representatives from the automobile industry to obtain their perspective on what is needed for 2004 automobiles. These representatives included Gary Crosbie and Paul Crosby (Ford), Balarama Murty and Jim Nagashima (General Motors), and Alvin White (Daimler Chrysler). Sandia has also actively interacted with a variety of capacitor manufacturers and dielectric powder suppliers. These suppliers included AVX, Murata, Kemet, Degussa, TAM, Ferro, TPL Inc., TRS Ceramics, Materials Research Associates, Tokay, and TPC Ligne Puissance.

These interactions led us to the conclusion that the two most viable replacement technologies for the electrolytic dc buss capacitors by 2004 were multilayer ceramic and multilayer polymer film capacitors. Although the greatest concern regarding the multilayer ceramic capacitors (shown in Figure 1) was the cost, reducing the size of the polymer capacitors was most often cited by automobile design engineers as a needed technology-enabling breakthrough. Thus, Sandia is targeting technical solutions that will reduce the cost of ceramic multilayer capacitors and that will increase the dielectric constant of the polyfilm dielectrics, thereby leading to smaller capacitors. The industry would like to have higher field operation for low-cost multilayer ceramic technologies, such as base metal (BME)

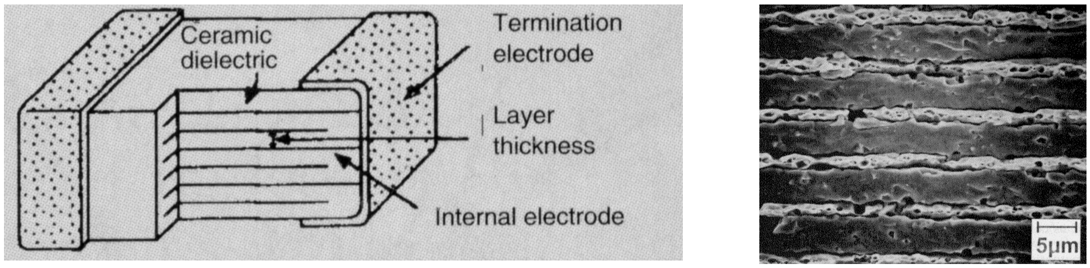

Figure 1. Multilayer ceramic capacitor schematic and micrograph of cross-sectional view.

and ultra-low-fire (ULF) dielectrics. A dielectric constant of 1000 at a dc field of 200 kV/cm has been stated as a goal for power electronics by AVX and the Center for Dielectric Studies at Penn State. Both the BME and ULF technologies substantially reduce the cost of multilayer ceramic capacitors by permitting the use of lower-cost Ni or Ag electrodes instead of high-Pd-content electrodes. The electrodes comprise roughly 95% of the total cost of a ceramic multilayer capacitor. Other considerations expressed by the auto manufacturers were cost, hard breakdown behavior in ceramics, and the high-temperature performance of polymer film capacitors. Inverter designs and operating conditions for dc buss capacitors vary from manufacturer to manufacturer. We presented our assumption of 450-volt dc operation with 125-volt spike voltages for a nominal 500 µF dc buss capacitor, which was well received at the DOE Merit Review Meeting.

Based on these criteria, an individual dielectric layer thickness of approximately 3 µm for polyfilm and 40 µm for ceramic capacitors is projected. Operating field strengths of 2 MV/cm and 150 kV/cm are projected for polyfilm and ceramic dielectric capacitors, respectively. Based on these assumptions and on measurement of presently available commercial capacitors, size comparisons of 500 µF dc Buss capacitors for different technologies were obtained (Figure 2).

While size and outstanding temperature performance are advantages for the ceramic technologies, soft breakdown behavior and lower cost are assets for polymer film capacitors.

Polymer Film Dielectric Development

SNL polymer film dielectric development has been based on the request from manufacturers that the new polyfilm dielectrics have voltage and temperature stability that is equivalent to present polyphenylene sulfide (PPS) technology. Thus, a structural family of polymer dielectrics has been designed and synthesized to meet two of the most stringent PNGV requirements: (1) low dielectric loss and (2) extremely good temperature stability. Figure 3 shows a schematic diagram of Sandia's conjugated, polyaromatic-based structure and indicates the large number of molecular modifications to this structure that are possible. Our present effort emphasizes molecular engineering of higher-polarizability structures that will enhance dielectric constants, yet retain acceptable dielectric loss characteristics. A patent disclosure has been issued covering the design and synthesis techniques for this polymeric

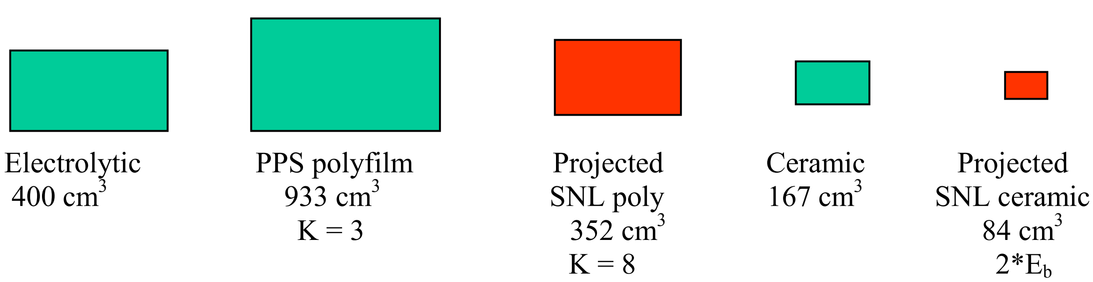

Figure 2. Size diagram of 500 µF dc buss capacitors of different technologies.

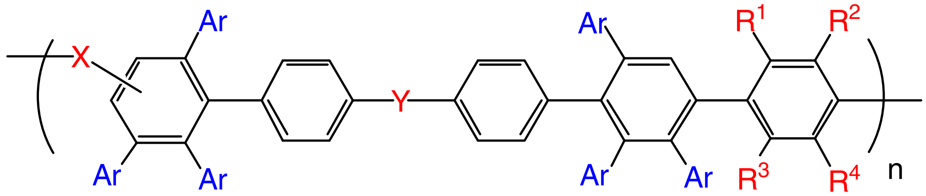

Figure 3. Schematic diagram of SNL conjugated polyaromatic film base structure.

family. Three initial molecular modifications to the base structure were made: (1) propyl bridge substitution, (2) sulfur bridge substitution and (3) replacement of R side groups with high-electronegativity fluorine ions to enhance polarizability.

The initial dielectric properties of a series of films of approximately 0.4 µm thickness are shown in Table 1. The industry standard high-temperature performance polyfilm dielectric, PPS, has a dielectric constant of 3, a dissipation factor of 0.003 and a breakdown field of 2.2 MV/cm at 25°C. We have increased the dielectric constant to approximately 4, while maintaining similar loss and breakdown field characteristics. Breakdown field is very much a function of the processing environment and, in production-type environments, it is anticipated that the breakdown field will be substantially enhanced. An example is shown in the bottom row of the table for polyvinylidene fluoride (PVF2) films that were processed using a chemical vapor deposition technique at Sandia. Breakdown fields of 5.5 MV/cm were obtained for these films and indicate the potential 6-fold increase in energy density possible for the next generation of chemically deposited polyfilms. Although the fluorine substitutions did not yield the hoped-for enhancement in dielectric constant, numerous other promising molecularly modified polymer dielectrics will be synthesized in FY 2000.

Ceramic Dielectric Layer Fabrication and Characterization

Ceramic dielectric layers were fabricated using two different techniques: (1) conventional tape casting and (2) computer-controlled micropen technology. For the micropen deposition, a ceramic slurry in the form of a 30-micron-diameter tube is deposited onto the desired substrate (Figure 4). We have demonstrated high-quality dielectric layers of thickness as low as 20 microns using this technique. Both chemically prepared barium titanate–based dielectric powders from Degussa and conventional state-of-the-art mixed oxide powders from TAM have been fabricated into dielectric layers using this technique. Further, an initial study to determine dielectric properties as a function of firing temperature has been completed. Dielectric layers processed at 850°C had lower dielectric constants, but they could be processed using inexpensive electrodes with high Ag content. Layers processed at higher temperatures had higher dielectric constants but required more expensive electrodes with high Pd

Table 1. SNL polyfilm dielectric properties for initial molecular modifications

Sample description	Dielectric constant	Dissipation factor	Breakdown field (MV/cm)
Propyl bridge	4.0	.003	1.9
Sulfur bridge	3.8	.002	1.7
Fluorine side group substitution	3.9	.001	1.8
PVF2 vapor deposited	4.1	.005	5.5

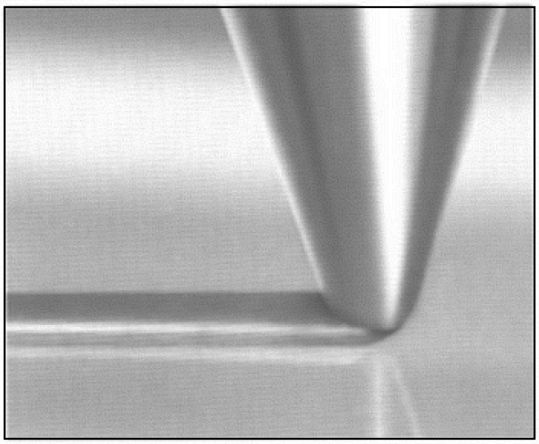

Figure 4. Micropen CAD/CAM Direct Write (30 µm to 500 µm lines).

content for compatibility. The layers processed at high temperature (1320°C) had dielectric constants of 3000, while films processed at lower temperature (900°C) had dielectric constants of 1000. Studies of breakdown strength versus temperature are in progress for the layers produced by the different processes.

In addition to micropen deposition, conventional tape casting processes were developed. Presently, a 40-µm-per-layer process has been optimized for high-altitude depositions and has resulted in dielectric layers with properties comparable to those specified by commercial manufacturers in state-of-the-art multilayer ceramic fabrication facilities. Table 2 shows the dielectric constants obtained from chem-prep (Degussa) and mixed oxide (TAM) barium titanate–based powders using different deposition methods.

Summary

Critical economic and technical issues for improvements of dc buss capacitors for new-generation vehicles were determined through discussions and visitations with automobile design engineers and capacitor manufacturers. We have been able to fabricate new polymer film dielectrics with a 33% increase in dielectric constant compared with industry standards, while maintaining voltage and dielectric loss stability. The goal in FY 1999 is to increase the dielectric constant of the Sandia-designed polyfilms by 100% while keeping losses below 1%. Thus, the polymer film task is at the stage where the appropriate foundation or backbone chemistry development is completed. In the future, molecular modifications to this backbone chemistry should lead to substantial enhancements in dielectric constant.

Two different techniques were developed to fabricate ceramic layers of a thickness suitable for high-voltage dc buss capacitor applications. Dielectric properties of both tape-cast and micropen-deposited layers were equivalent to state-of-the-art commercial multilayer dielectrics. Thus, the foundation has been formed for the evaluation and enhancement of both ULF and BME ceramic dielectrics via proper selection of dopants and low-level additives in FY 2000.

References/Publications

None.

Table 2. Dielectric properties of micropen and tape cast layers

Sample	K, commercial multilayer	K, SNL micropen	K, SNL tape cast	K, SNL bulk ceramic
Degussa, X76 CP, 1310°C	3200	3200	3400	2595
TAM X7R 262L, 1140°C	2242	2240	2056	2062

C. Mechanical Reliability of Electronic Ceramics and Electronic Ceramic Devices

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objectives

- Develop testing algorithms that can be used to assess electronic ceramic (EC) and electronic ceramic device (ECD) mechanical reliability.
- Mechanically characterize EC and ECD alternatives that are less expensive and that can be used to promote device miniaturization.

OAAT R&D Plan: Task 4; Barriers A, D

Approach

Utilize micromechanical testing and ceramic-specific-characterization testing facilities to measure in situ mechanical properties of ECs in the ECDs.

- Characterize presently used and developmental EC and ECDs supplied from their manufacturers or their end-users.
- Use already-developed ceramic component prediction codes (whose development was funded by the Office of Transportation Technologies/Ceramic Technology Project for structural ceramics) and their statistical analysis capabilities in analyzing the mechanical strength and fatigue of ECs and ECDs.
- Provide results and insights back to manufacturers that will result in the improved reliability of ECs and ECDs.

Accomplishments

- A mechanical properties microprobe (MPM) was used to characterize $BaTiO_3$ dielectrics in snubber multilayer capacitors (MLCs). It was found that mechanical performance (e.g., fracture toughness, strength) of ceramic dielectrics can be significantly different in equivalent snubber MLCs.
- Strength and fatigue of two alumina substrates and an aluminum nitride substrate were characterized and mechanical design data were generated for use with ECDs.

- The fatigue and strength testing of candidate tape-cast aluminas for automotive gas exhaust sensors was initiated in a collaboration with Motorola.

Future Direction

- Acquire commercially available dc buss MLCs and measure the in situ mechanical performance of their dielectric ceramics. Collaborate with Sandia National Laboratories in the characterization of the dielectric ceramic in their developmental dc buss MLCs for automotive power electronics building blocks.
- Characterize less expensive Ni-electrode snubber MLCs.
- Study the utility of non-destructively measuring residual stresses in MLCs with piezospectroscopy and non-destructively identifying damaged MLCs with resonant ultrasound spectroscopy.

Introduction

A lack of mechanical reliability of ECs in ECDs can often limit the reliability of their electronic function. Three classes of ECs or ECDs that this project examined in FY 1999 were multilayer capacitors (MLCs), EC substrates, and oxide ceramics for automotive exhaust gas sensors; the service life of all three can in fact be limited by their mechanical reliability. The application of ceramic life prediction codes (developed for structural ceramic component design in high-temperature gas turbine engines) is used in concert with the mechanical testing analyses of the ECs because they portray the probabilistic strength and fatigue properties of ECs in an appropriate (but underutilized) manner.

One MLC manufacturer states that 40–50% of its capacitor failures are mechanically induced. Although its MLC failure rate is only on the order of 1 part per million, since the company manufactures 30–40 million capacitors a day, this failure rate is actually significant. Therefore, the company (and its customers) have a vested interest in improving MLC mechanical reliability. A goal of this project is to help MLC manufacturers improve this reliability.

Measuring the mechanical performance of dielectric ceramics in MLCs is not trivial because of their very small size. An MPM in the Mechanical Characterization and Analysis Group was used to measure in situ fracture toughness of the dielectric ceramic in equivalent, commercially available, snubber MLCs. Although the MLCs had equivalent capacitances, the fracture toughnesses of their dielectrics were statistically different, as shown in Figure 1. Fracture toughness is an indicator of mechanical robustness, and an end-user of these three MLCs (an automobile manufacturer) stated that it had experienced increasing reliability with the MLCs in this examination with higher fracture toughnesses. These results suggest that MLCs that have a dielectric ceramic with maximum toughness will offer better mechanical reliability.

Additional techniques to assess mechanical robustness of MLCs were also examined and developed. Image analysis was coupled with fracture mechanics and Weibull theory to "calculate" the strength distribution of dielectric ceramics in MLCs. This technique, along with fracture toughness measurement, helps portray the whole mechanical performance of dielectric ceramics.

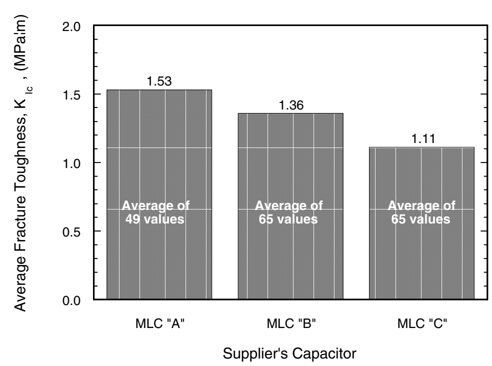

Figure 1. The fracture toughness of the dielectric ceramic in equivalent snubber multilayer capacitors was different. The difference was statistically significant.

The strength and fatigue of three commercially available ceramic substrates were characterized. Two of the substrates were aluminas (a tape-cast and a roll-compacted material), and the third material was an aluminum nitride (AlN). The tape-cast alumina (Al_2O_3) was stronger and more fatigue-resistant than the roll-compacted Al_2O_3 (commonly used in ECDs), but it was more costly. The AlN was not as strong as the tape cast Al_2O_3, but it was stronger than the roll-compacted Al_2O_3 and much more fatigue-resistant, as compared in Figure 2 (and was the most expensive of the three). The results from this study will help end-users of ceramic substrates appropriately design with and choose them.

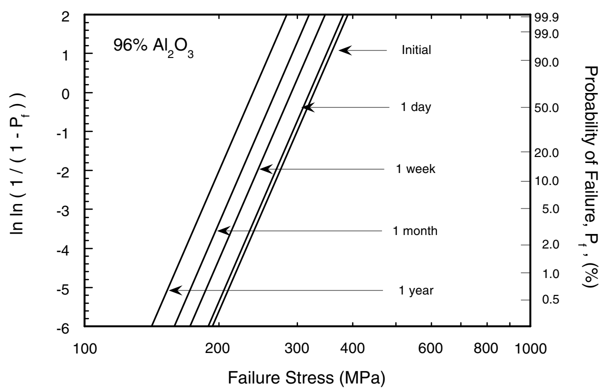

Figure 2a

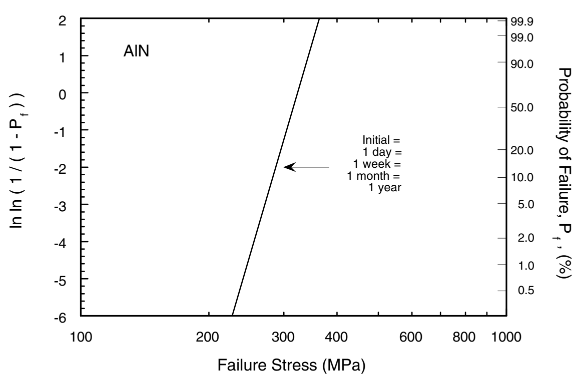

Figure 2b

Figures 2 a and b. A 96% alumina material (2A) was found to be susceptible to fatigue at 20°C, while AlN (2B) was not. The alumina tested is a commonly used ceramic substrate; the AlN substrate is more costly but has better thermal conductivity and a thermal expansion similar to that of silicon.

Motorola is developing an automotive exhaust gas sensor; this project is assisting its development. The sensor is a multilayer design and will be using Al_2O_3 as a matrix; however, an alumina with optimum strength and fatigue (which is also inexpensive) has not yet been identified. The mechanical testing of three Al_2O_3s was initiated during FY 1999 to measure their strength as a function of temperature, as well as their fatigue performance. The highest purity of Al_2O_3 examined had the lowest strength at room temperature, while the least pure Al_2O_3 had the highest strength at room temperature, as shown in Figure 3. However, recent results show that the lowest-purity Al_2O_3 has the worst fatigue resistance of the three and was no longer the strongest Al_2O_3 of the three at 1000°C (an expected service temperature of the sensor).

Summary

The present project's FY 1999 mechanical testing results, characterization, and analyses of all three classes of these ECs and ECDs will help manufacturers (1) identify ECs that will prolong the service life of ECDs and (2) design their ECDs so that deleterious stresses are not imposed within them during their manufacture or service. Fracture toughness and strength results and analyses of dielectric ceramics in MLCs are being used by MLC manufacturers to improve the overall mechanical robustness of their MLCs. Strength and fatigue results and analyses of Al_2O_3

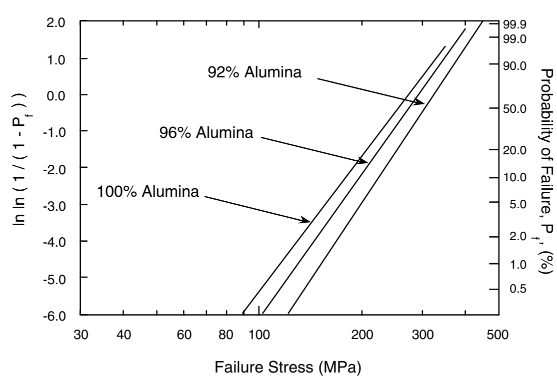

Figure 3. The 20°C strength of 92% alumina was the highest, followed in turn by the 96% and 100% aluminas. All aluminas are candidates for Motorola's automotive exhaust gas sensor.

and AlN ceramics will help ECD manufacturers choose an appropriate ceramic substrate (and design) for their ECD that promotes longer service life. Finally, high-temperature strength and fatigue results and analyses of candidate Al_2O_3s will help this original equipment manufacturer identify the optimum and best-performing Al_2O_3 for their developmental automotive exhaust sensor.

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D. Low-Cost, High-Energy-Product Permanent Magnets

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Contractor: Argonne National Laboratory, Argonne, Illinois
Prime Contract No: W-31-109-Eng-38

Objectives

- Develop a low-cost process to fabricate NdFeB permanent magnets with up to 25% higher strengths. The higher-strength magnets will replace ones made by traditional powder metallurgy and enable significant size and weight reductions of traction motors for hybrid vehicles.

- Utilize high-strength superconducting magnets to improve the magnetic alignment of grains prior to pressing and sintering, therefore producing higher-strength magnets.
- Collaborate with magnet manufacturers, who will provide powder, sinter the green compacts, and perform characterizations of the engineering magnetic properties.

OAAT R&D Plan: Task 3; Barriers B, C, D

Approach

- Develop facilities to align magnetic domains of NeFeB powders within a high-strength magnetic field, created by a superconducting magnet, during forming operations.
- Characterize, compare, and correlate engineering and microscopic magnetic properties of magnets processed under varying conditions, including some in current production.
- Utilize a reciprocating feed to automate insertion of loose and compacted magnet powder into and out of the steady field of a superconducting solenoid.

Accomplishments

- Completed design of an axial-die press for making 1- to 2-cm-diameter permanent magnets in a batch mode.
- Fabricated and assembled an Axial-Die Press facility at Argonne National Laboratory that includes a 9-Tesla superconducting magnet.
- Characterized magnetic properties of permanent magnets provided by manufacturers.

Future Directions

- Optimize fabrication processing and powders from different industrial partners using axial-die and isostatic pressing in batch mode operations.
- Design, fabricate, and operate a reciprocating press in a continuous mode to demonstrate the feasibility of competitive factory operation.
- Optimize fabrication processing and powders from different industrial partners, using transverse-die pressing and a reciprocating press.
- Provide design rules for the fabrication of permanent magnets, including knowledge for scale-up to larger size magnets at commercial rates of production.

A Cryomagnetics, Inc., superconducting solenoid has been specified and purchased, after consultation with permanent magnet manufacturers. The magnitude of the steady field in the bore of the solenoid can be continuously varied up to 9 Tesla. Magnet powder can be aligned in a field that is uniform within 5%, over a volume that is large enough to axial-die press 1- to 2-cm-diameter cylindrical magnets that have similar lengths. Alternatively, a 2.5-cm-diameter by 12.5-cm-long volume of powder, contained in a rubber mold, can be aligned for subsequent isostatic pressing.

The axial-die and punch set shown in Figure 1 was designed in consultation with the permanent-magnet manufacturer UGIMAG, Inc. and the tooling fabricator Bronson and Bratton, Inc. The set was made using very low-magnetic-permeability material (<1.002), which will not affect significantly the uniformity of the

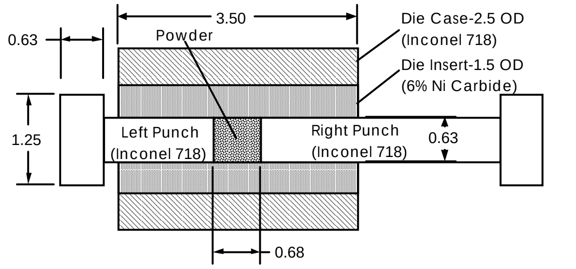


Figure 1. Axial-die and punch set for 5/8 in. magnet; powder shown is compacted.

superconducting solenoid's magnetic field or the alignment of the magnet powder. However, self-demagnetization fields are inherent in short cylinders of magnet powder and can affect the applied field uniformity and grain alignment of permanent magnets. This happens in current production, where, typically, electromagnets provide alignment fields of less than 2 Tesla, which approaches the saturation limit of the steel present in commercial presses. Vector field electromagnetic code calculations were made that showed demagnetization effects were still pronounced up to applied alignment fields of 7 Tesla, which can be exceeded with the superconducting solenoid purchased.

An unorthodox press-in-tube method for axial-die pressing in a batch mode was devised and built by Ability Engineering Technology, Inc., which met the magnetic, geometric and program cost constraints associated with using superconducting solenoids (see Figure 2). The press tube and ram are made from very low-magnetic-permeability materials (< 1.002). The hydraulic cylinder was custom made, by Atlas Cylinders, Inc., from stainless steel with a low permeability (< 1.010). The length of the press tube was made sufficient to locate the more magnetic hydraulic cylinder in the far field of the solenoid, where the magnetic-field gradient is weak, and to access the solenoid, which is thermally shielded deep within its helium Dewar. Electromagnetic code calculations were made to determine the far magnetic field and maintain minimal magnetic forces between the solenoid and the axial-die press.

The press insertion mechanism enables complete and controlled removal of a green compact from the Dewar's warm-bore tube, while the superconducting solenoid is operating and the hydraulic cylinder is activated. This feature allows the experimental determination of extraction and insertion forces, which will be used to calibrate electromagnetic code models already developed. Understanding the forces and their minimization is key to the design of a reciprocating press. Also, the mechanism allows rotation of the end of the press tube into the solenoid's weak fields (< 250 Gauss) for removal of the green compacts.

The capability to move the axial-die press into the far field of the solenoid allows exploration of another processing method. In isostatic pressing, the powder is aligned separate from the pressing operation. Argonne National Laboratory maintains an isostatic press that exceeds the capabilities of magnet manufacturers. Discussions with manufacturers and a review of the journal and patent literature indicates that the greater alignment fields of superconducting solenoids will be less effective in energy-product improvement, because self-demagnetization effects are much less for the long, powder-filled cylindrical rubber molds used in isostatic pressing. Also, because the commercial electromagnetic alignment solenoids are separate

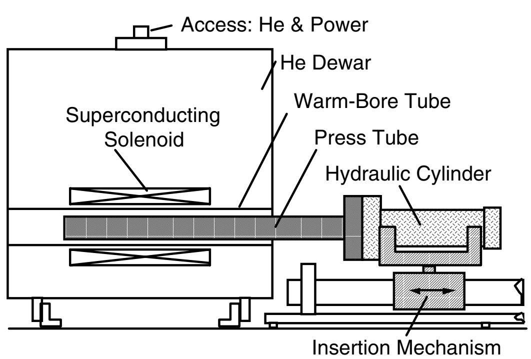
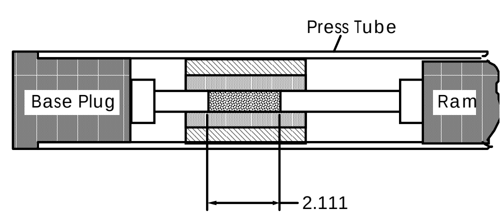


Figure 2 (a). Axial-die press in the solenoid.



2 (b). Press-tube interior; no compaction.

from the press and can be isolated from ferromagnetic material, they can provide multiple, higher-field alignment pulses (< 6 Tesla) to the powder. In addition, enhancements can be achieved by mechanical manipulation of the rubber molds. Currently, isostatic pressing is claimed to produce permanent magnets that are within 5–10% of having optimal alignment and magnetic properties. However, the alignment of powder has never been attempted in the steady, high fields available with the superconducting solenoid. Other processing improvements may be possible, such as an ability to align a more economical powder that has a wider particle-size distribution. The magnet producer CRUMAX will participate in identifying any benefits.

The magnet manufacturers provided characterized permanent magnets: transverse-die pressed 26-mm cubes and two sets of isostatically pressed cylindrical magnets with diameters of 14–15 mm. The energy products of the cubes were 41 MGOe. One set of cylinders had a 45-MGOe energy product, which was significantly different from the other's 35 MGOe. The two sets were made using different processes. At Argonne, the remnant induction of each magnet was measured by rotating it in a Helmholtz coil. The manufacturer's values, which ranged from 1.2 to 1.35 Tesla, were confirmed.

At Oak Ridge, an examination of microstructure and preferred orientation revealed clear differences between samples. Electron microprobe analysis of each manufacturer's products showed the composition of their grain boundary phases to be slightly different; however, the primary phase was chemically identical. X-ray diffraction pole figures were used to characterize the texture on the face normal to the magnetization axis.

Data were collected at 5-degree tilt and rotation increments using Cu k-alpha X-ray radiation with 1-mm diameter incident beam collimation. The strongest preferred orientation was observed for one of the isostatically pressed cylindrical magnets, as shown in Figure 3, whereas the other cylindrical magnet had the weakest texture, as shown in Figure 4. Both of

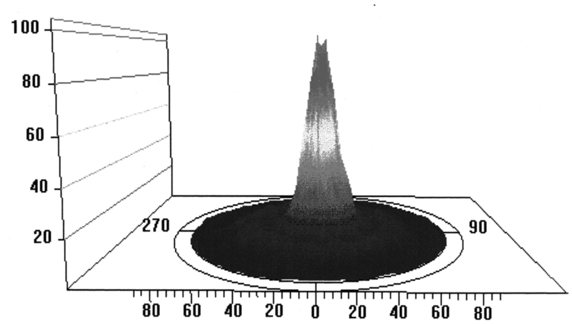


Figure 3. Oblique view of 006 pole figure of the cylindrical sample showing axial symmetry characteristic of strong "fiber" texture. Peak height = 105 cps.

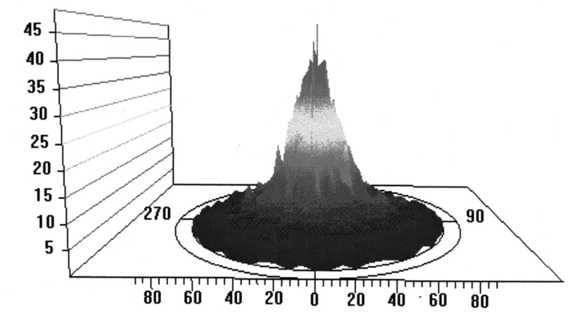


Figure 4. Oblique view of 006 pole figure for the cylindrical sample showing axial symmetry characteristic of moderate "fiber" texture. Peak height = 49 cps.

these showed a fiber texture with cylindrical symmetry.

The cube samples were strongly textured, only slightly less so than the strongest cylindrical sample, and both were nearly identical. Their texture was not perfectly cylindrical, as shown in Figure 5. This was not unexpected for transverse-die pressing, where compaction is unidirectional and normal to the direction of magnetization.

The correlation of these texture measurements with the energy product and methods of pressing is a clear demonstration of the importance of improved grain alignment and the utility of microstructure analysis, in particular, X-ray diffraction analysis, in quantifying subtle variations in texture produced by different methods of processing.

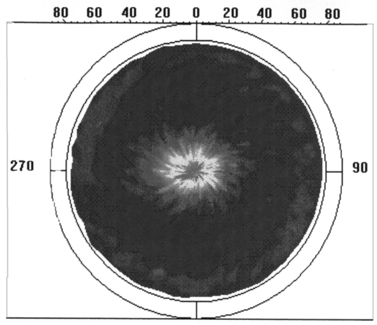


Figure 5. Top view of 006 pole figure for a cube sample, showing slightly distorted cylindrical symmetry. Peak height = 100 cps.

E. Lead-Free Solders for Automotive Electronics

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objective

- Support development of lead-free, high-temperature "engineered" solder alloys for automotive electronics applications such as power electronics devices by systematically determining the effects of alloying on the properties, soldering characteristics, and microstructure of Sn alloys.

OAAT R&D Plan; Task 4; Barrier D

Approach

- A series of binary alloys are formulated to determine the effects of individual alloying elements on mechanical properties, the wetting behavior on copper, and melting characteristics.
- A micromechanical testing technique is being used to determine the mechanical properties of solder alloys in situ in solder joints.

Accomplishment

- The feasibility of using automated ball indentation testing to measure the tensile properties of solder bumps was demonstrated. This indicates that measurement of solder joint properties is also feasible.

Future Direction

- The effects of major alloying elements such as Bi, Cu, In, Sb, and Zn on tensile properties, wetting behavior, microstructure, and melting characteristics will be determined.
- Alloying elements will be identified that improve the ductility of Sn, as this is expected to favorably impact solder joint reliability and the resistance to fillet lifting in through-hole connections.
- Some effort will be directed toward perfecting micromechanical testing of solder joints.

Introduction

Lead is recognized as a significant threat to both the environment and public health, and pending legislation could result in the banning of lead from a wide variety of products, including electronics. The overall objective of this project is to develop lead-free, high-temperature "engineered" solder alloys that will increase the operating temperature of automotive electronic packages from 120°C to 180°C. The initial emphasis is on studying the properties and characteristics of tin alloys because they are most likely to form the basis of high-temperature soldering alloys such as eutectic Sn-Ag.

During FY 1999, significant progress was made toward determining the feasibility of using automated ball indentation (ABI) testing to measure the tensile properties and strain rate sensitivity of solder joints. Because of its importance to reliability, the mechanical behavior of existing and newly developed solder alloys is a key concern in the design and engineering of advanced electronic components. Standard tensile testing is commonly used to determine alloy strength and ductility properties, but there is concern that tensile testing may not provide an accurate indication of actual solder joint performance. Part of the basis for this concern is that the thermal processing conditions experienced during joint manufacturing may not be accurately reproduced in bulk alloy tensile specimens. This means that the mass transport conditions and chemical reactions that occur in joints and that will influence their properties are unlikely to be reflected in standard test data. The ABI testing was viewed as a novel way to measure the mechanical properties of actual joints.

Subsized tensile specimens were made from 1.5-mm-thick rolled sheets of pure Sn, Sn–3.5Ag, Sn-37Pb, and Pb–5Sn (nominal compositions wt %). The Pb alloys were included as standard reference alloys. These specimens were tested at room temperature to determine baseline tensile properties.

Subsequently, ABI tests were performed on the shoulder areas of the same specimens as indicated schematically in Figure 1.

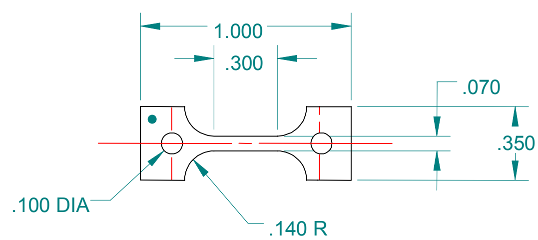

Figure 1. Schematic of solder alloy tensile specimen showing relative size of ABI indent on specimen shoulder (dot on upper left corner).

Images of the ABI indentations taken in a scanning electron microscope (SEM) are shown in Figure 2. The indentations are circular, as required for data analysis, and the plastic zones surrounding them are evident. During the tests, both the load and indentation depth are very accurately measured and used to determine a plastic flow curve where the true strain, ε_p, and the true stress, σ_p, are given by

$$\varepsilon_p = 0.2\frac{d_p}{D} \qquad \sigma_p = \frac{4P}{\pi d_p^{\,2}\delta} \quad .$$

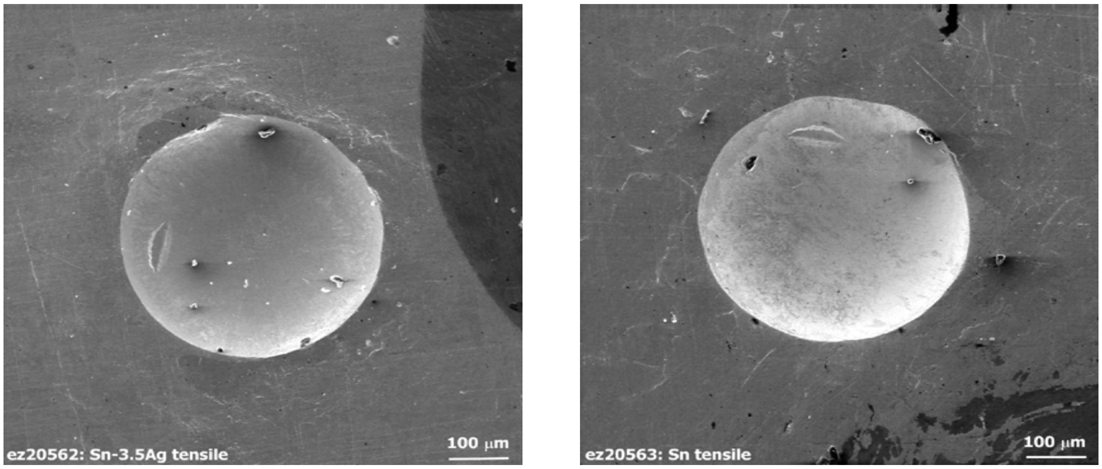

Figure 2. ABI indentations on tensile specimens of pure Sn (right) and Sn–3.5 Ag solder alloy (left).

The quantity d_p is geometrically related to indentation depth, D is the indenter diameter, P is the applied load, and δ is a constant determined from the test data. The yield strength is also determined from the ABI test using a separate calculation.

Overall, however, there was good agreement between the two data sets. The ABI test was originally developed for use on steels, for which it provides very accurate measurements of tensile properties. This experiment established that the ABI test was also capable of determining tensile properties of solder alloys with reasonable accuracy (see Figure 3).

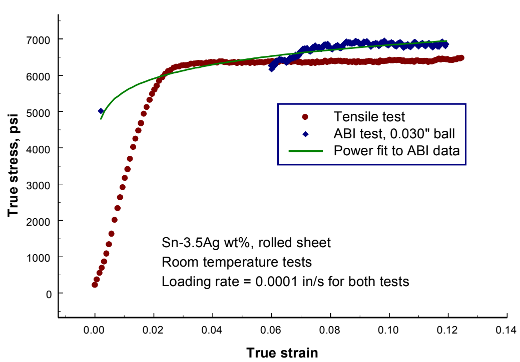

Figure 3. Comparison of tensile and ABI test data from bulk specimen of Sn–3.5Ag solder alloy.

Next, small FR4 printed-circuit test boards were obtained that contained arrays of solder bumps made with Sn–3.5Ag solder alloy. The solder bumps had nominal dimensions of 2.5 mm length by 0.8 mm width by 0.30–0.50 mm thickness. The ABI test requires a flat surface for accurate measurements, so flat spots were made on the solder bumps using a polishing technique. The sizes and shapes of the solder bumps before and after preparation of flat spots are shown in Figure 4.

The appearance of several solder bumps after ABI testing is presented in Figure 5. The indentations on the bumps at the top left position and bottom right position of Figure 5 show uniform circular impressions that are consistent with obtaining acceptable data. The indentation on the lower left has an irregularity on its diameter that was produced by a defect in the solder bump. The impression on the upper right is actually a porosity defect in the solder bump rather than an indentation from testing. The existence of defects was unexpected, and they only became apparent in the solder bumps as the ABI tests were being conducted. Figure 5 further illustrates the accuracy with which the ABI indentations can be located on small specimens.

ABI test results from the solder bumps agreed well with those from the tensile specimen shoulders, as shown in Figure 6. Compared with the ABI data from the tensile specimens, the solder bump data showed slightly higher flow stresses and work hardening rate. Also, the yield strength determined for the solder bump was strength determined for the solder bump was higher than that of the bulk alloy.

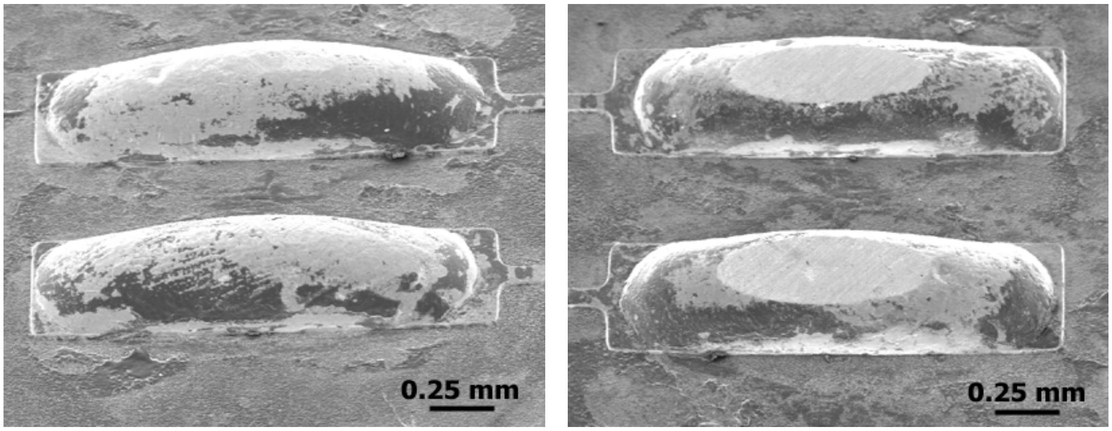

Figure 4. Sn-3.5Ag solder bumps on FR4 test board before (left) and after (right) polishing.

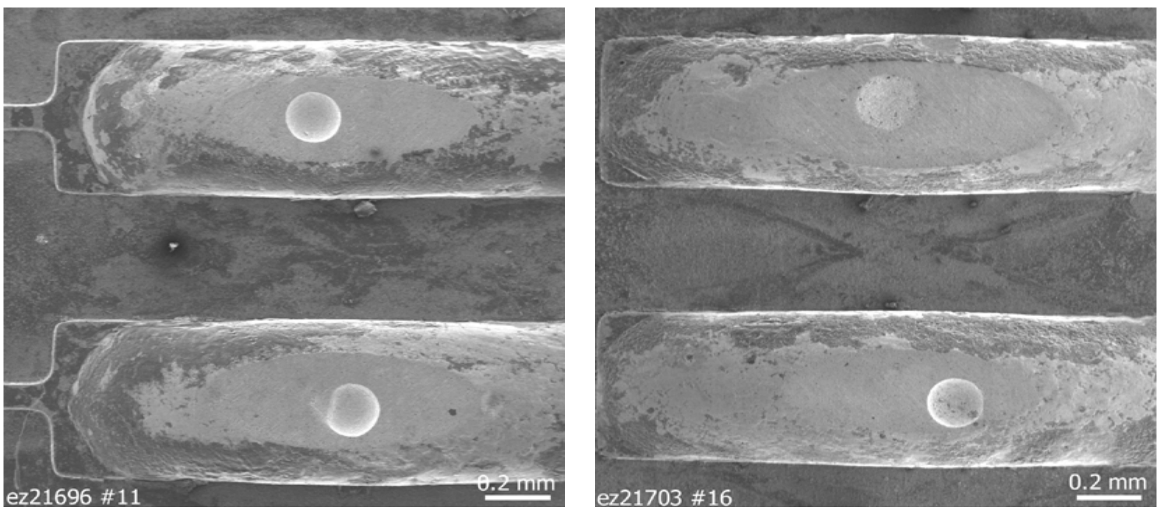

Figure 5. ABI indentations on Sn-3.5Ag solder bumps.

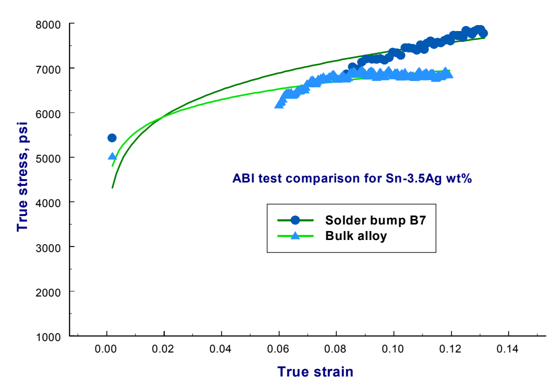

Figure 6. Comparison of ABI results from the bulk alloy and a solder bump of Sn-3.5Ag solder alloy.

There are a number of possible reasons for the discrepancies between the tensile data and the ABI data sets. Calculation of the yield strength and the flow curve from the ABI data uses empirical constants that are determined from the materials being tested. Confidence in the values of these constants increases proportionately with the amount of available tensile test data and ABI test data. Also, specific tests, which were not performed in this experiment, may be done to determine the values of some of the constants. Another source of error relates to the strain rate sensitivity of the solder alloys, which is relatively high. The strain rate during tensile testing is nearly constant until the onset of necking. However, during ABI testing, the strain rate decreases by over an order of magnitude because of the geometry of the deformation under the indenter. Traditionally, controlling strain rate during ABI testing was not a concern because it is not important for determining the properties of steels.

Another source of error in the ABI tests on the solder bumps is defects in the material. A radiograph of the FR4 test board used for this experiment (Figure 7) indicates that most of the bumps contain porosity defects, as indicated by the dark spots. Arrows are used in Figure 7 to indicate the bumps that were ABI tested; while some of the spots are indentations, most of them are porosity defects. Finally, one important difference between the data from the bulk alloy and that from a solder bump (Figure 6) is that the solder bump has chemically reacted with the copper on the test board. It is possible the combined effects of reaction with the Cu and the different thermal processing of the bump produced a measurable difference in properties.

These results show that valid ABI tests can be conducted on relatively small volumes of solder alloys, and that the data from such tests agree well with tensile test data from the bulk material. The results indicate the reasonable possibility of obtaining valid tensile property measurements on actual solder joints.

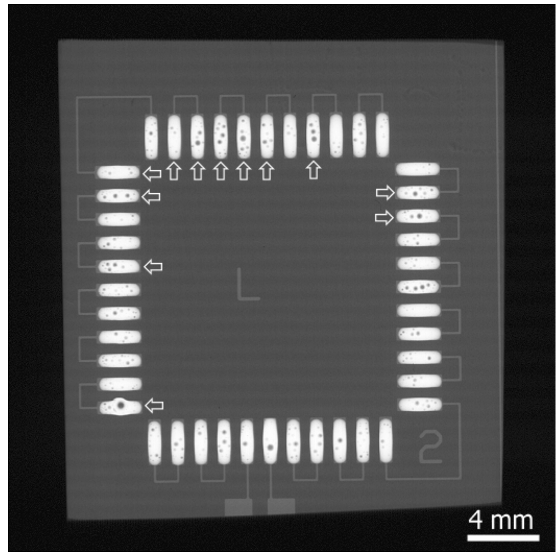

Figure 7. Radiograph of FR4 test PC board used for ABI testing.

3. FUEL CELLS RESEARCH AND DEVELOPMENT

F. Composites for Bipolar Plates

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Contractor: Los Alamos National Laboratory, Los Alamos, New Mexico
Prime Contract No.: W-7405-Eng-36

Objective

- Develop low-cost, mass-producible composites for fuel cell stack bipolar plates that are corrosion-resistant, electronically conductive, and physically robust.

OAAT R&D Plan; Task 13; Barrier B

Approach

- Use low-cost, commercially available raw materials (graphite powder and polymeric resin binder).
- Use thermosetting vinyl ester resins for corrosion resistance and short process cycle times.
- Eliminate machining requirements by forming net shape plates (including fluid flow channels) in a single compression, injection, or injection-compression molding step.

Accomplishments

- Collaborated with industry to provide materials suitable for mass production with enhanced properties and processability.
- Submitted U.S. Patent application.

Future Direction

- Transfer technology to industry and continue to provide feedback, especially in the areas of fiber reinforcement and corrosion resistance.

A major focus area of FY 1999 research was improvement of the processability and mechanical properties of our baseline composite material. Although laboratory-scale plates produced at Los Alamos National Laboratory (LANL) exhibited good properties, it was recognized that mass production would require significant improvements in the processability of the molding compound. To achieve these improvements, we have been collaborating with Premix, Inc., and Bulk Molding Compounds, Inc. (BMC), both of which have expertise in manufacturing vinyl ester molding compounds. Both companies produced molding compounds with reduced cure times (2–5 minutes compared with 10–15 minutes for LANL formulations), extended shelf lives (several weeks compared to several hours for LANL formulations), and more uniform flow. In addition, both companies have utilized mold release agents within their compounds. This prevents parts from sticking to the mold, while avoiding the time- and labor-intensive application of a release agent to the mold surfaces before each part is molded. Such internal mold release agents will be especially critical in molding fluid flow fields directly into bipolar plates. A mold designed by Plug Power, LLC, was used to mold plates with fluid flow channel dimensions on the order of 1 mm from LANL compounds in FY 1998 and from Premix compounds in FY 1999. To date, even though the feasibility of direct flow field molding has been demonstrated, the bipolar plates used for fuel cell testing have had machined flow fields because of frequent design changes and the high cost of tooling.

Although compression molding has been the intended processing route for these graphite/vinyl ester compounds because of their high solids content, other manufacturing alternatives now appear feasible. Premix has developed molding compounds that, with slight modifications, it expects to be suitable for injection or injection-compression molding. BMC has already produced plates successfully from some of its compounds using injection-compression molding. Although the injection-compression–molded plates had an electrical conductivity somewhat lower than our historical target value of 100 S/cm, good performance in fuel cells can be achieved with plates of lower conductivity. Figure 1 compares the fuel cell performance of graphite plates and Premix composite plates with a conductivity of 85 S/cm. Recent feedback from the fuel cell community indicates that conductivities of 60 S/cm, or possibly as low as 15 S/cm, may be acceptable for bipolar plates. With these lower conductivity targets, the solids content of the molding compounds can be reduced so that injection molding is more easily achieved.

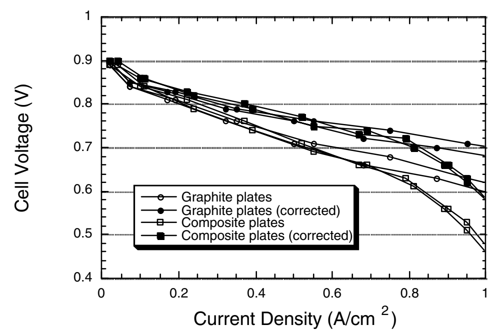

Figure 1. Polarization curves obtained from single fuel cell tests using POCO graphite plates and Premix composite plates.

In LANL formulations developed in FY 1998, the incorporation of certain fibers into the baseline bipolar plate material resulted in significant strength improvements. However, similar improvements were not observed with compounds from BMC and Premix incorporating the same fibers; in fact, the incorporation of these fibers actually appeared to affect composite strength negatively in the new formulations. Two possible reasons have been postulated. First, the LANL compounds were based on a fairly dilute, low-viscosity vinyl ester resin. In the case of cotton fibers, strengthening presumably resulted from resin absorption by the fibers and the subsequent formation of an essentially continuous fiber-matrix interphase. The cotton fibers may not be able to imbibe the thicker resins used by the compounders. Second, the LANL formulations did not incorporate mold release agents. The lubricating action of the internal mold releases used by Premix and BMC may hinder fiber-resin adhesion. Thus, the utility of fiber additives remains a topic of investigation.

However useful fiber reinforcements eventually prove to be, the strength of composites with high particulate loading is determined primarily by the matrix material. Significant improvements in strength can be achieved with the use of different resin binders. However, changing the resin system often requires adjustments to the graphite loading level to maintain the target electrical conductivity. A composition of 68% graphite in a fairly dilute vinyl ester resin provided good conductivity in tests at LANL, and it served as a "baseline" for subsequent formulations developed by Premix. But when other binder systems were used, the different rheologies and reduced extrusion during molding resulted in significantly lower conductivities. When graphite loading was increased, good conductivities were regained, and higher strengths were still obtained by capitalizing on the improved resin systems. If conductivity requirements can be relaxed as expected, graphite content can be reduced to give even stronger plates, since the resin matrix is the determining factor in composite strength. Typical properties of composites using different resin systems with and without cotton fiber reinforcement are shown in Figure 2.

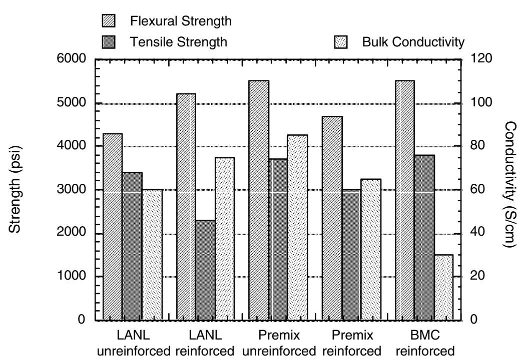

Figure 2. Property comparison for composites using three different resin binders, with and without cotton fibers.

Corrosion in the fuel cell environment is a major issue in bipolar plate material development. Vinyl esters are widely known and used in the chemical process industry for their superior corrosion resistance, and therefore they are excellent matrix material candidates for composite bipolar plates. Indeed, none of the graphite/vinyl ester samples subjected to corrosion testing sustained measurable weight loss or visible degradation. However, degradation of mechanical properties during exposure is a potential problem, especially in the case of direct methanol fuel cells. While vinyl esters in general are quite corrosion resistant, some vinyl esters are adversely affected by methanol. In preliminary tests, the tensile and flexural strengths of one material were reduced to about 60% of their original values after exposure to 6M methanol at 80°C for 500 hours. Although the methanol concentration in an actual fuel cell would be much lower, this strength reduction is still of significant concern, and more extensive tests are planned.

Besides physical corrosion or weakening of the bipolar plate, the leaching out of ions from resin additives may also be problematic if these ions bind to the proton exchange membrane. Resin additives such as mold release agents often contain heavy atoms such as calcium, magnesium, or zinc. Based on elemental analysis of the liquid solutions and Nafion membranes used in corrosion testing, no ions were leached from the resin additives. However, significant amounts of calcium and iron were leached out of ash impurities in the graphite powder, in some cases tying up as many as 20% of the active sites in membranes immersed with composite samples. Purifying the graphite powder prior to compounding would eliminate these impurities, but such an extra processing step would be costly, time consuming, and probably unnecessary. The observed effect of leachants is exaggerated, since the samples and membranes were immersed for a period of 3–6 weeks in liquids that were not circulated or changed. Long-term fuel cell testing has not indicated any adverse effects from leachable ions binding to the proton exchange membrane, probably because the continuous flow of liquid in an operating fuel cell prevents the ions from reaching and/or binding to the membrane.

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G. Carbon Composite for PEM Fuel Cells

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objectives

- Develop a low-cost slurry molded carbon fiber material with a carbon chemical-vapor-infiltrated sealed surface for proton exchange membrane fuel cell stack bipolar plates
- Collaborate with potential manufacturers with regard to testing and manufacturing of such components.

OAAT R&D Plan; Task 13; Barrier B

Approach

- Fabricate fibrous component preforms for the bipolar plate by slurry molding techniques using carbon fibers of appropriate lengths and filler.
- Fabricate hermetic plates using filler and a final seal with chemical-vapor-infiltrated carbon.
- Develop commercial-scale components for evaluation.

Accomplishments

- Fabrication of prototypical 100-cm^2 active area plate (single- and two-sided)
- Measured high strength (175 MPa in biaxial flexure) and observed good flexibility
- Demonstrated ability to impress/emboss features
- Material of very low density: 0.96 g/cm^3

- Initial production cost estimates within specification
- Single-sided specimens provided to industry for evaluation
- Program goal exceeded for material electronic conductivity of greater than 200 S/cm.
- Program goal met of less than 1 $cm^3/cm^2/h$ leakage under 2 atm. of hydrogen.
- Single-cell test indicating good kinetics and very low cell resistance

Future Direction

- Scale to 15 x 15-cm plates
- Transfer technology to partners such as Plug Power, AlliedSignal, and others.

In FY 1999, the ORNL carbon composite bipolar plate effort has achieved several programmatic goals in scaling, electrical properties, cell performance, strength, and of particular importance, weight (0.96 g/cm^3). Single-sided components 1.5 mm in thickness and two-sided plates 2.5 mm in thickness with a 00-cm^2 active area have been produced. Sample components have been tested at Los Alamos National Laboratory (LANL) and have been provided to Plug Power and AlliedSignal for their evaluation. Previously it was demonstrated that projected costs would meet program goals.

Fibrous component preforms for the bipolar plate are prepared by slurry molding techniques using 400-µm carbon fibers (Amoco DKD-x mesophase pitch fiber) in water containing phenolic resin (Figure 1). The approach is such that a vacuum molding process produces a low-density preform material. A phenolic binder is used to provide green strength, and also assists in providing geometric stability after an initial cure.

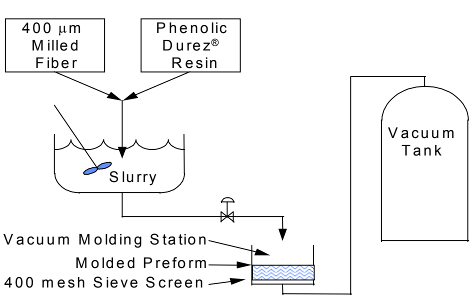

Figure 1. Schematic of slurry-molding system.

The surface of the preform is sealed using a chemical vapor infiltration (CVI) technique in which carbon is deposited on the near-surface fibers sufficiently to make the surface hermetic. This is accomplished by placing the preforms in a furnace (Figure 2) which is heated to 1400–1500°C and allowing methane under reduced pressure to flow over the component. The hydrocarbon reacts and deposits carbon on the exposed fibers of the preform, and when sufficient deposition has occurred, the surface becomes sealed. Thus the infiltrated carbon provides both an impermeable surface and the necessary electrical conductivity so that power can be obtained from the cell. Processing times are in the range of 5 h.

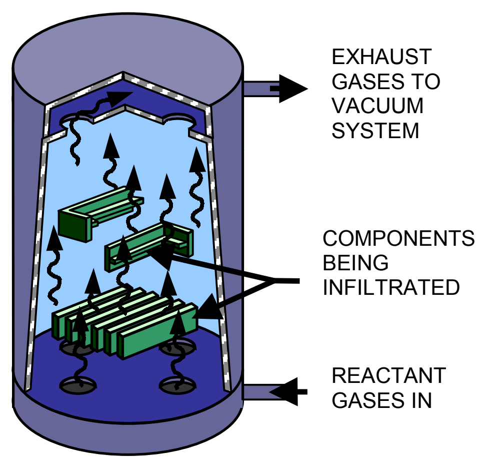

Figure 2. CVI system for carbon infiltration.

Initial specimens were provided to LANL for determining bulk conductivity. The values were measured by four-point probe to be 200–300 S/cm. Surface resistivity measured at ORNL was

12.2±4.2 Ω/cm, compared with POCO graphite having 7.8±2.62 Ω/cm.

During this period, 100-cm^2 active area plates were prepared to the specifications provided by LANL (Figure 3). The flow field was machined for these initial developmental components.

Figure 4 is a polished cross-section of a single-sided plate sample showing the flow field channels and the sealed surface. Also apparent is the low-density volume (> 50 vol % of void volume) of the component, which consists of fibers bonded by the CVI carbon.

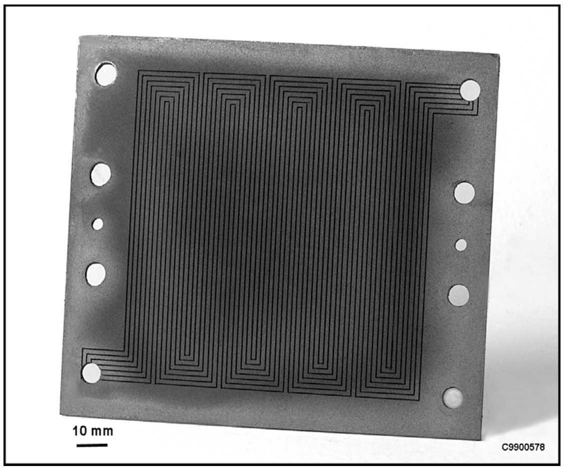

Figure 3. A fabricated, 100 cm^2 active area plate showing the flow field.

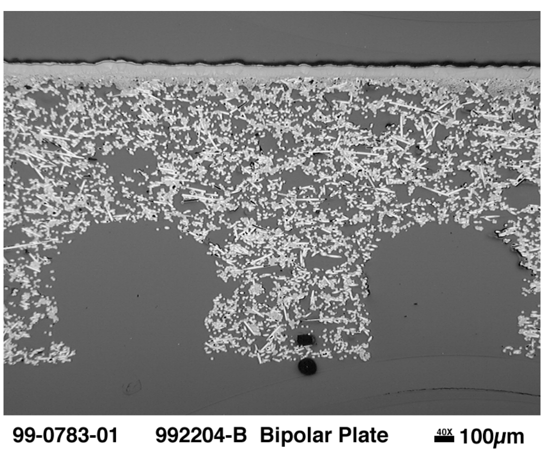

Figure 4. Optical image of a cross-section of a single-sided plate.

A single-sided, 100-cm^2 active area plate was prepared and forwarded to LANL for evaluation in a proton exchange membrane fuel cell. The plate tested very well, exhibiting good kinetics and exceptional low cell resistance (Figure 5). An observed drop-off in cell voltage at high currents was likely due to leakage from seals around the edge of the plate in the cell.

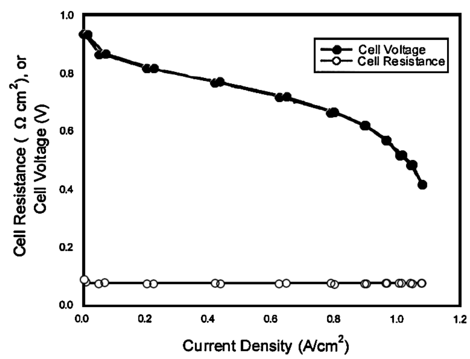

Figure 5. Fuel cell resistance and voltage test results from LANL using the 100-cm^2 active area bipolar plate sample.

The mechanical properties of the bipolar plate material were tested in biaxial flexure. Samples of material 3.8 cm in diameter (disks) and 1.5 mm in thickness, with one side sealed, were prepared. A biaxial load fixture was fabricated that applies a load to a ring centered on the disk, with the edge of the opposite side of the disk supported by a second ring. The stress is applied so that the sealed surface is in tension. The results indicate the material has a strength of 175±26 MPa (25.3±26 ksi), and Figure 6 is an example of the stress-displacement curve. To indicate the onset of cracking, the fixture was fitted with an acoustic detector; and acoustic emissions did indicate cracking at relatively low loads (Figure 6). However, samples that had been subjected to 100-MPa stresses and that emitted acoustic signals during testing were found not to suffer through-thickness gas leakage. Thus the material can be stressed to close to failure strength without loss of integrity. A wetted plate was also tested under freeze-thaw conditions and remained undamaged.

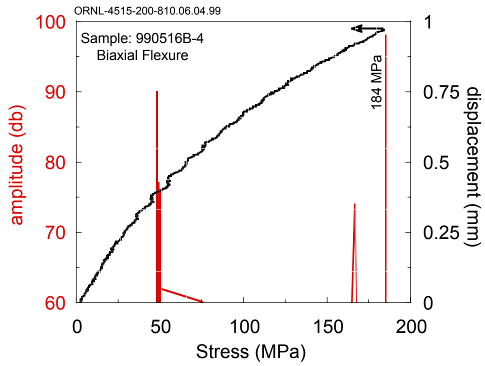

Figure 6. Stress-displacement curve for the composite bipolar plate material, also indicating measured acoustic emissions.

The bipolar plates tested to date have been fabricated with machined flow fields. In production, these plates would need to use embossed or otherwise impressed features, as machining would be too costly. A preliminary evaluation of the capability to emboss features in the composite material prior to infiltration with carbon was performed. A small aluminum mold was fabricated with channels 0.78 mm (31 mil) deep and wide. The mold was used to impress channels into the preform material, with the result seen in Figure 7. As is apparent, the preform material can take impressed features with the necessary tolerances and dimensions.

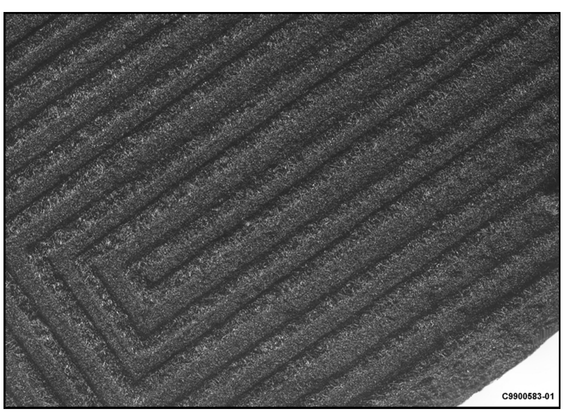

Figure 7. Example flow field impressed on the carbon composite bipolar plate preform material.

In summary, as of the end of FY 1999, it has been established that the carbon composite bipolar plate approach results in a component with

- significantly higher strength than competing materials
- component weight about half that of other materials
- very high electronic conductivity
- very low cell resistance
- good cell kinetics
- gas impermeability
- low cost
- scalability to prototype dimensions

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H. Cost-Effective Metallic Bipolar Plates Through Innovative Control of Surface Chemistry

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objective

- Demonstrate "proof of principle" for producing proton exchange membrane fuel cell stack bipolar plates by forming corrosion-resistant and electrically conductive nitride scales via elevated temperature exposure of model alloys in a nitrogen-containing gas.

OAAT R&D Plan; Task 13; Barrier B

Approach

- Form nitride scales on two model metallic alloys by elevated temperature exposure in a nitrogen-containing gas.
- Determine if through-thickness defects are present in the nitride scales by immersion in an acid environment aggressive to the substrate metallic alloys but not the nitride scales.
- Supply nitrided coupons to AlliedSignal (H. Dai) for potentiodynamic evaluation of corrosion resistance in a pH 5 sulfuric acid solution; corrosion current of less than 1×10^{-6} A/cm^2 at 900 mV vs SCE is desired.

Accomplishments

- Acid exposures showed no evidence of through-thickness "pin-hole" defects typical of conventional coating processes.
- The current AlliedSignal goal of a corrosion current of less than 1×10^{-6} A/cm^2 at 900 mV vs SCE was met.
- Proof of principle for protection of metallic bipolar plates alloys via thermally grown scales was established.

Future Directions

- Demonstrate the formation of a corrosion-resistant and electrically conductive thermally grown scale on either a commercially available alloy or a “custom” designed alloy that can meet the cost goals set by OAAT for metallic bipolar plates in proton exchange membrane fuel cell applications.
- Demonstrate that metal bipolar plates treated in this manner will exhibit better cell performance than graphite bipolar plates or composite bipolar plates currently under development.

For proton exchange membrane (PEM) fuel cells, thin metallic bipolar plates offer the potential for lower weight and significantly lower cost than graphite bipolar plates. However, inadequate corrosion resistance can lead to high electrical resistance and/or contaminate the PEM. Metal nitrides, carbides, and borides (e.g. TiN, NbC) offer electrical conductivities that are up to an order of magnitude greater than those provided by graphite and are highly corrosion-resistant. However, conventional coating methods leave “pin-hole” defects that result in accelerated local corrosion.

Pin-hole-type defects are generally not observed in thermally grown oxide scales because both kinetic and thermodynamic considerations strongly favor complete conversion of surface metal to oxide. Such defects are also not expected for thermally grown nitride, carbide, or boride scales. Rather, the key issues are scale cracking, adherence and morphology (discrete internal precipitates vs. continuous external scales). These factors can be controlled through proper selection of alloy compositions, alloy microstructure, and elevated temperature gas reaction conditions. The goal of this effort was to demonstrate proof of principle for forming defect-free, corrosion-resistant nitride scales via gas nitridation (Figure 1).

Two alloys were selected for study: alloy A (commercially available refractory alloy) and alloy B (model alloy designed to be nitrided). To determine if through-thickness pin-hole defects were present, nitrided coupons were immersed for 24–72 hours in an acid environment aggressive to the substrate metallic alloys but not to the nitride scales. Nitrided coupons were also supplied to AlliedSignal (H. Dai) for potentiodynamic evaluation of corrosion resistance in a pH 5 sulfuric acid solution. The initial goal set by AlliedSignal was a corrosion current of less than 1 H 10^{-6} A/cm^2 at 900 mV vs SCE.

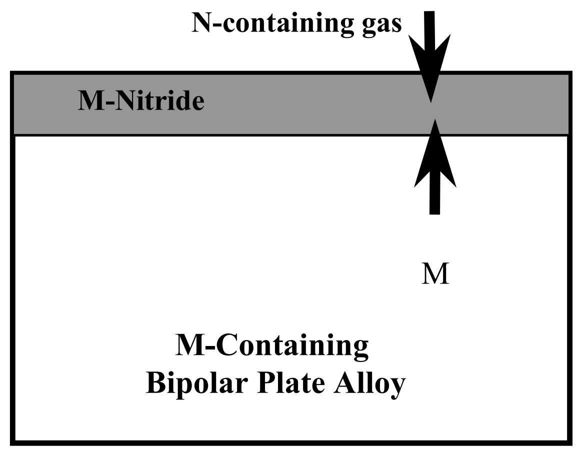


Figure 1. Schematic of gas nitridation approach.

No acid attack on the substrate was detected in nitrided alloy A, which suggests that the nitride layer was defect-free (Figure 2). Pin-hole-type defects were also not detected in nitrided alloy B. However, acid attack was evident at sharp edge regions where surface preparation was poor (Figure 3). Such edge susceptibility likely can be eliminated by rounding sharp edges prior to nitridation and/or modifying nitriding conditions. Preliminary potentiodynamic data in pH 5 sulfuric acid solution indicated that nitrided alloy A and nitrided alloy B both meet the target goal of less than 1 H 10!^{6} A/cm^2 at 900 mV vs SCE (Figures 4 a and b).

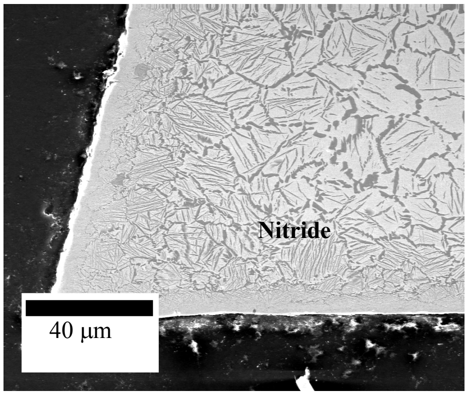


Figure 2. SEM cross-section of nitrided Alloy A after 46 h exposure in a HF solution.

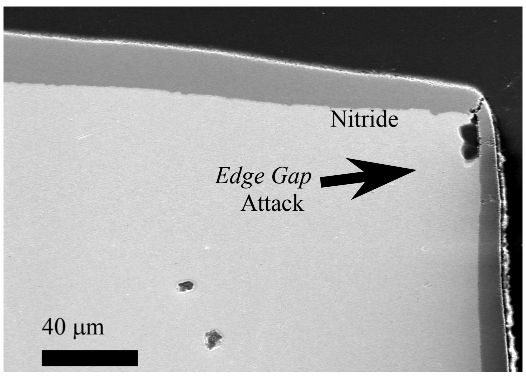
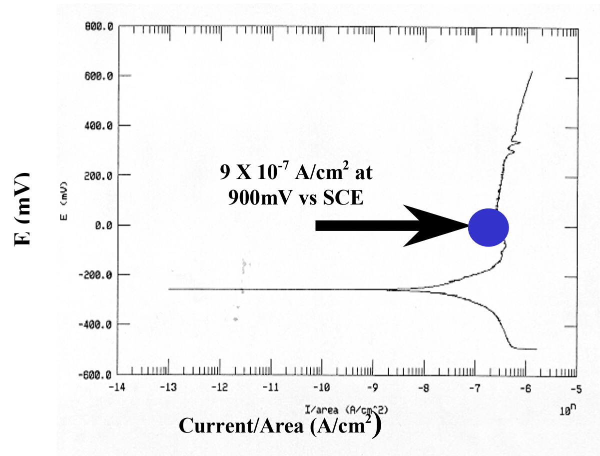


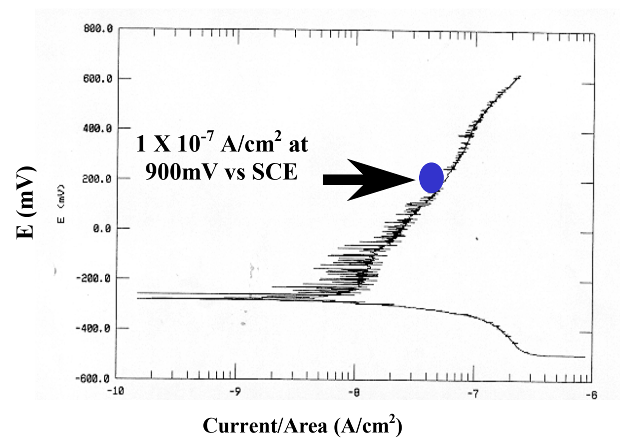
Figure 3. SEM cross-section micrograph of Alloy B after 64 h in a HNO_3 solution.

The results of this preliminary study suggest that thermally grown nitride scales can effectively protect the underlying metallic substrate from corrosion (i.e., pin-hole defects typical of coating processes are not formed). Future work will seek to demonstrate the formation of a corrosion-resistant and electrically conductive thermally grown scale on either a commercially available alloy or a "custom"-

4 a. Nitrided Alloy A



4 b. Nitrided Alloy B



Figures 4 a and b. Preliminary potentiodynamic data in pH 5 sulfuric acid solution (data of H. Dai of AlliedSignal).

designed alloy that can meet the cost goals set by the Office of Advanced Automotive Technologies for metallic bipolar plates in PEM fuel cell applications.

I. Low-Friction Coatings for Fuel Cell Air Compressors/Bearings

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Contractor: Argonne National Laboratory, Argonne, Illinois
Prime Contract No.: W-31-109-Eng-38

Objectives

- Develop and evaluate the friction and wear performance of low-friction coatings and materials for fuel cell air compressor/expander systems.

  —Specific goals—50 to 75% reduction in friction coefficient

  —One order of magnitude reduction in wear
- Transfer developed technology to DOE industrial partners.

OAAT R&D Plan; Task 13; Barrier D

Approach

- Identify appropriate compressor components requiring low friction and wear.
- Optimize near-frictionless carbon (NFC) coatings for the identified components.
- Conduct laboratory benchtop evaluation of friction and wear performance of the NFC coating.
- Conduct component testing of NFC-coated compressor/expander parts.
- Develop and evaluate friction and wear properties of boric acid coating and composite materials.

Accomplishment

- The radial air bearings and thrust bearings of Meruit's turbo compressor were identified as components that require both low friction and low wear rate for satisfactory performance.
- Thrust washer wear tests showed that NFC coating reduced the friction by about four times and wear rate by two orders of magnitude. Both met and exceeded the project goals.
- A procedure was developed for laboratory fabrication of polyphenylene sulfide and B_2O_3 polymer matrix composite. A preliminary wear test showed a significant reduction in friction coefficient with addition of B_2O_3.

Future Directions

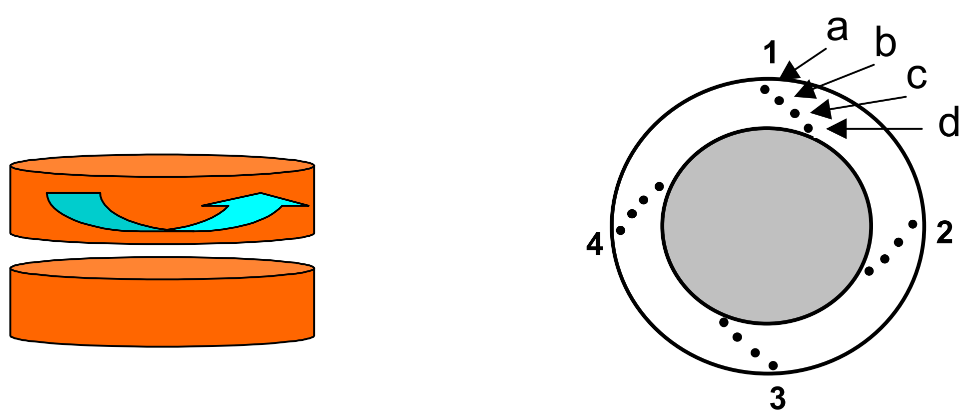
- Continue benchtop testing of NFC coatings and boric acid–based solid lubricant. The effect of various contact parameters, such as speed and load, will be assessed.
- Optimize NFC coating process for Meruit's turbo compressor air bearings.
- Conduct component rig testing of NFC-coated turbo compressor air bearings for reliability and durability improvement.
- Optimize boric acid lubricant–based polymer composites. This will include friction and wear testing of various compositions.
- Conduct component rig testing of boric acid–based coating and composites.

Fuel cell technology air management subsystems consisting of compressors and expanders have many critical components with tribological challenges. The seals and bearings in these devices will require good lubrication for friction and wear control. Recent activities at Argonne National Laboratory have lead to the discovery of a new class of amorphous carbon coatings (near frictionless carbon or NFC) that exhibit extremely low friction coefficients (<0.001 in dry nitrogen or dry argon environments). Wear rates of test samples coated with NFC films are also extremely low (approximately 5 to 6 orders of magnitude lower than those of uncoated test samples). These results have been achieved under dry sliding conditions. Earlier research at Argonne has also demonstrated that certain boric acid–based compounds can be made to be extremely lubricious under the proper conditions. Under humid conditions, such as those found in fuel cell air compressors, friction coefficients of as low as 0.02 can be achieved. The main objective of this project is to apply these lubrication technologies to address the tribological challenges in the fuel cell compressors and expanders.

Different components requiring lubrication have been identified in compressor and expanders being developed by Vairex, A.D. Little, and Meruit. Results presented in this report are from the work done for the lubrication of Meruit turbocompressor radial journal and thrust air bearings. Under normal operation, a thin film of high-pressure air separates the load-bearing surfaces of an air bearing. However, fuel cell air compressors are expected to undergo numerous start/stop cycles during which the load-bearing surfaces will contact each other and be subjected to wear. To minimize wear during start/stop cycles (and during off-normal transients and bumps), the surfaces of the air bearings are often treated with a low-friction wear-resistant coating. Argonne's NFC coating is being evaluated for this application.

Benchtop thrust washer tests were conducted for NFC-coated and uncoated 440 C stainless steel material. The tests duplicate the tribological conditions expected in a thrust bearing contact interface. Figure 1a shows the schematic contact configuration of the test. Two discs were loaded against each other. One of the discs had a recess in the middle, as shown in Figure 1b. During the test, one disc was stationary while the other was rotated at a constant speed. Dimples of known depth were created on the disc with a recess (Figure 1b). Linear wear was measured by monitoring the changes in the dimple height. Tests were conducted at load of 1.25 N, speed of 1000 rpm, room temperature and relative humidity of 34–45%.

NFC coating significantly improved the friction and wear behavior of the 440 C steel material. The frictional force was reduced by four times, and the linear wear rate was reduced by two orders of magnitude, as shown in Figure 2. Oxidative wear mechanism was predominant in the uncoated steel surfaces and was accompanied by the generation of abrasive oxide wear debris. Polishing was the primary mode of wear in the NFC-coated surfaces. The resulting improvement in the surface roughness is expected to be beneficial as time passes.



1a. **1b.**

Figures 1 a and b. Thrust washer test configuration.

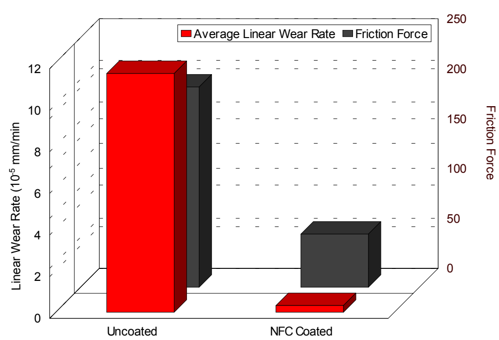


Figure 2. Friction and wear of uncoated and NFC-coated 440 C steel surfaces.

With the very good friction and wear results from the bench test, the plans are under way to run component tests with NFC-coated turbo compressor journal bearings. This is a high priority because of some recent results of the compressor bearing tests that indicated the occurrence of localized wear. High friction at startup of the compressor has also been problematic for the bearing test.

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J. Inorganic Proton Exchange Membrane Electrode/Support Development

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objectives

- Develop electrically conducting metallic electrodes/supports and catalytically active ceramic sandwich layers for use in ceramic electrolyte proton exchange membranes for fuel cells. These inorganic membranes should be less costly because of reduced Pt loading and should minimize CO poisoning because of the higher operating temperatures.
- Collaborate with Professor Marc Anderson’s project on microporous inorganic membranes at the University of Wisconsin. The membrane electrodes/supports and sandwich layers developed in this project will be evaluated in the Wisconsin project, which will provide valuable feedback for the design and development of advanced membrane electrodes/supports and sandwich layers.

OAAT R&D Plan; Task 13; Barrier B

Approach

- Fabricate initial electrodes/supports using sintered tape-cast nickel foils coated with a titania sandwich layer having a pore size of about 0.1 μm. A blend of submicron and nanosized titania particles has been tested and determined to be appropriate for the sandwich layer.
- Deposit platinum in the sandwich layer from an aqueous solution of chloroplatinic acid or aminoplatinum.

Accomplishment

- Developed techniques for tape casting and sintering porous nickel foils.
- Developed appropriate titania powder compositions for a sandwich layer that sinters at <400°C.
- Developed a technique for coating nickel substrate with a titania sandwich layer.

Future Direction

- Develop similar sandwich layer for carbon fiber paper electrodes.
- Develop complete bipolar configuration for fuel cell based on the Wisconsin inorganic proton exchange membrane.

Microporous inorganic membranes are being developed by Professor Marc Anderson at the University of Wisconsin as proton exchange membranes (PEMs) for fuel cells. These new membranes will operate at temperatures in excess of 100°C, will retain water at these elevated temperatures, and will provide proton conductivities of the same order of magnitude as the presently employed Nafion® membranes. More important, these membranes should reduce the cost of the membrane by substantially reducing the amount of Pt catalyst required to operate a fuel cell, and they should minimize CO poisoning of the Pt by operating at these elevated temperatures. The goal of this project is to develop electrically conducting metallic electrodes/supports and catalytically active ceramic sandwich layers for use in ceramic electrolyte PEM membranes based on nanoparticles of TiO_2 and Al_2O_3. This project was initiated in the last quarter of FY 1999 and is being conducted in coordination with Anderson's project on microporous inorganic membranes at the University of Wisconsin. The membrane electrodes/supports and sandwich layers developed in this project will be evaluated in the Wisconsin project, which will provide valuable feedback for the design and development of advanced membrane electrodes/supports and sandwich layers.

The initial electrode/support is based on a tape-cast, sintered porous nickel foil. The sintered nickel support is not a long-term solution. It will, however, allow us to provide a workable electrode/support system to the University of Wisconsin in a timely fashion, which will allow them to conduct electrochemical tests with their membranes. The sintered nickel foil has a porosity of about 55 vol % and an average pore size of about 1–2 μm. A sandwich layer having a similar porosity and a pore size of about 0.1 μm is deposited on top of the electrode foil. The small pore size of the sandwich layer provides an appropriate surface upon which to deposit the nanoparticle membrane. A blend of submicron and nanosized titania particles has been tested and determined to be appropriate for the sandwich layer. This blend produces a desirable pore size (about 0.1 μm) and can be sintered to reasonable strength at temperatures of as low as 300°C. In addition, the sandwich layer will be platinized. The platinum is deposited on the sandwich layer from an aqueous solution of chloroplatinic acid or aminoplatinum. The sandwich layer will be characterized with respect to microstructure, including pore size and distribution, particle bonding, and Pt particle size (SEM and TEM), surface area (BET gas adsorption), surface finish (atomic force microscopy or profilometry), and Pt content (chemical analysis).

Once the sintered nickel foil–based substrates can be made repeatably and reliably, we will start developing the sandwich layer on a better porous conducting support to replace the sintered nickel foil support. One promising candidate is carbon fiber paper, which is currently used in the Nafion-based PEM fuel cells. These papers have been shown to have the physical and chemical characteristics required of the PEM fuel cell electrode/support structure. We have tested the carbon papers and shown them to be thermally stable at temperatures of up to at least 500°C in both oxidizing and neutral atmospheres. The low firing temperatures (<400°C) we have demonstrated for the blended submicron/ nanoparticle titania sandwich layer compositions allow us to contemplate using the carbon fiber paper as the electrode/support for the inorganic PEM membranes. We can thermally process the membrane and the sandwich layer to bond and strengthen them without fear of damaging the carbon fiber paper. Platinizing will again be done either in the slurry state or after the substrate layer is bonded to the metal support.

4. ADVANCED COMBUSTION ENGINE AND EMISSIONS R&D

K. Microwave-Regenerated Diesel Exhaust Particulate Filter

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Contractor: Industrial Ceramic Solutions, Oak Ridge, Tennessee
Prime Contract No: 80X-SZ896V

Objectives

- Develop a ceramic filter capable of removing particulate matter (PM) from diesel engine exhaust streams at greater than 90% efficiency.
- Develop a microwave cleaning system capable of regenerating the filter cartridge during diesel engine idle condition operation.
- Use technology and materials that are cost-effective and scalable to large-volume commercial production.

OAAT R&D Plan; Task 16; Barrier B

Approach

- Test a bench-scale microwave ceramic filter system in the laboratory during 15 cfm air flow conditions (idle condition for a 1.9-liter Volkswagen Passat diesel engine) to measure the heating capability of the filter during engine idle.
- Test a more sophisticated microwave ceramic filter system on the exhaust of a 1.2-liter Ford DIATA diesel engine to measure the PM removal filtration efficiency in the exhaust stream and the microwave cleaning efficiency of the ceramic filter cartridge during engine operation.

Accomplishments

- Designed and fabricated the bench-scale microwave ceramic filter system for measuring heating capability under forced air flow conditions.
- Conducted a parametric study with *air flow through the filter* and *microwave power input* as the independent variables, measuring *temperature increase* in the ceramic filter cartridge.
- Proved in bench-scale testing that the filter cartridge could reach 600^{o}C carbon combustion temperatures in less than a minute under engine idle conditions.

- Designed and fabricated a microwave ceramic filter capable of operating on the exhaust of the Ford 1.2-liter DIATA diesel engine.
- Conducted a debugging test of the engine filter system on a Ford Motor Company test cell dynamometer.
- Achieved greater than 90% elimination of diesel particulates from the exhaust stream and better than 90% microwave regeneration recovery (cleaning) of the filter cartridge.
- Refined and improved Ford test cell system for August testing at the Ford Motor Company.

Future Direction

- Optimize the materials properties of the ceramic filter media, filter insulation package, microwave power source input, and filter cartridge design for mechanical strength, filter particulate control efficiency, and microwave energy minimization.
- Produce microwave-regenerated diesel exhaust particulate filters for vehicle testing.
- Enlist engineering assistance from automobile and aftertreatment systems suppliers to refine a system, based on vehicle test results, to a viable commercial device for controlling particulate exhaust emissions.

Introduction

This was the first year of funding for this diesel exhaust particulate control project by the DOE OAAT Program. The primary concern of the automotive partners in the Partnership for a New Generation of Vehicles (PNGV) program regarding the microwave-regenerated diesel exhaust particulate filter was the ability of the invention to reach carbon combustion temperatures (600^{o}C) during diesel engine operation. Several thermodynamic models had shown that over 30 kW of microwave power would be required to heat the ceramic filter to the proper temperature for cleaning during exhaust flow. Therefore, a first step toward proving the concept, before moving ahead with the project, required heating a ceramic filter cartridge to 600^{o}C under engine idle exhaust flow conditions at a reasonable microwave power input. A survey of existing small diesel engines revealed that the 1.9-liter Volkswagen Passat idles at 15 cubic feet per minute (cfm) of exhaust flow. The 1.2-liter Ford DIATA diesel engine idles at 10 cfm exhaust flow. Industrial Ceramic Solutions (ICS) chose the 15-cfm flow rate for the laboratory bench-scale testing.

Heating Efficiency of the Microwave-Regenerated Diesel Exhaust Particulate Filter

Filter cartridge specifications were determined in meetings with PNGV representatives from DaimlerChysler, Ford, and GM. A filter cartridge size of 2 in. in diameter by 3 in. in length was selected according to the partners' specifications. The filter was fabricated, and a microwave system to accommodate the ceramic filter was designed, constructed and tested. A schematic of the microwave-regenerated filter test system (Figure 1) and a picture of the actual experimental system (Figure 2) are shown.

The assumption by most scientists who evaluated this technology was that all microwave energy converted to heat energy by the unique silicon carbide fibers would be immediately transferred to the exhaust gases. Fortunately, the silicon carbide fibers convert the microwave energy to thermal energy much faster than the heat transfer to the exhaust stream occurs. For example, a prototype ceramic filter was installed in the system (Figure 2) with 15 cfm of air flowing through the filter. After the microwave was turned on at a very low 0.8 kW of power, the temperature of the filter increased rapidly to nearly 800°C in only 40 seconds. Obviously, the power required to heat the filter was much less than the calculated 30 kW. A graph of the experimental data is exhibited in Figure 3.

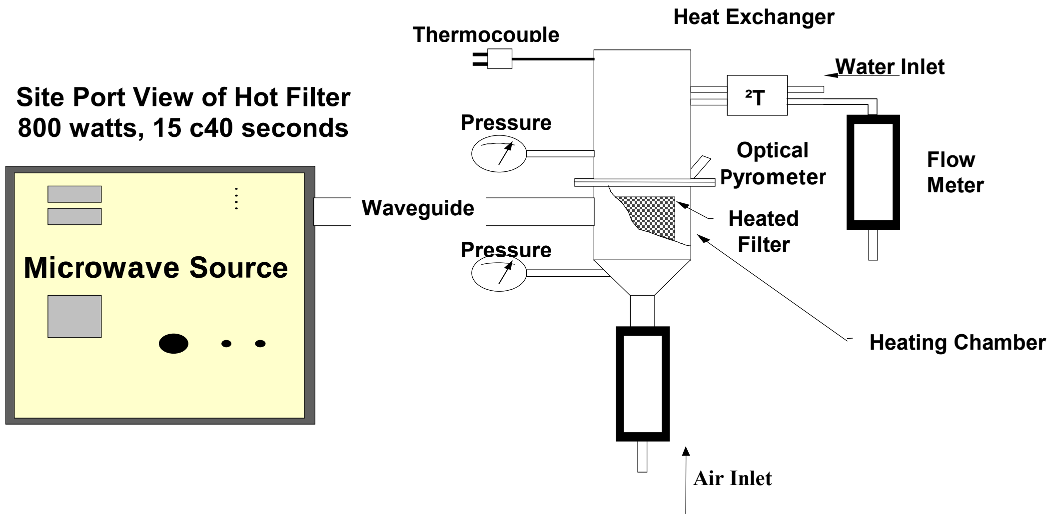

Figure 1. Demonstrated Industrial Ceramic Solutions exhaust filter can achieve regeneration temperatures at engine idle conditions.

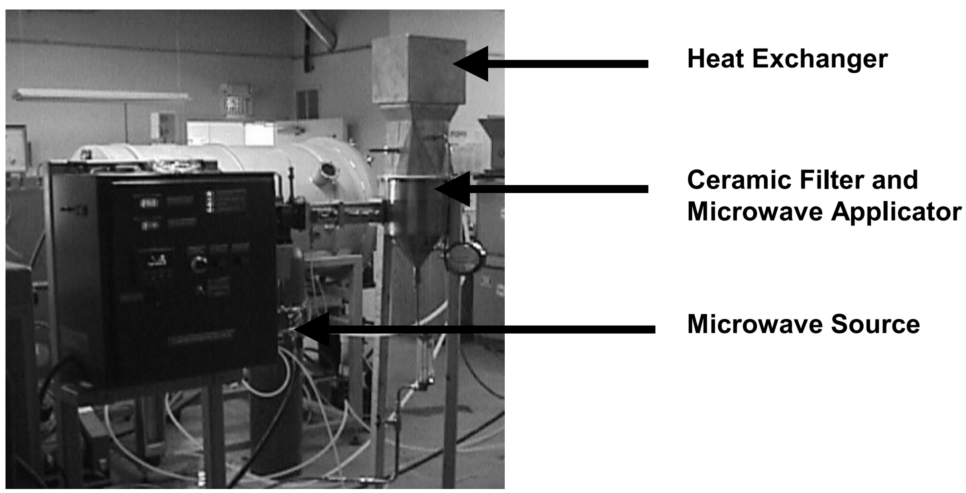

Figure 2. Heating efficiency device test.

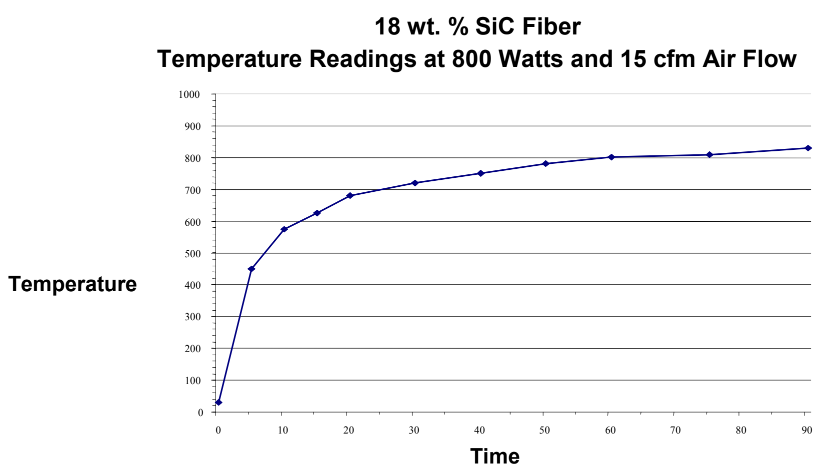

Figure 3. Graph of experimental data.

Diesel Engine Testing on the Ford Motor Company's 1.2-Liter DIATA Diesel

A microwave-regenerated diesel exhaust filter system was designed and fabricated to be tested in the Ford test cell #5 DIATA engine dynamometer. This system is shown in Figure 4 installed on the DIATA engine. The analytical equipment in the Ford test cell measures the percentage of smoke removal in Bosch smoke units. Figure 5 illustrates that the prototype particulate filter removed nearly 100% of the particulates at 1800 rpm or less. The efficiency of the filter decreased slightly at higher engine rpm.

The ceramic filter was regenerated by microwaves over three exhaust loading cycles. In each regeneration cycle, the filter returned to its "clean" condition for the next round of filtration. A microwave regeneration cycle is shown in Figure 6.

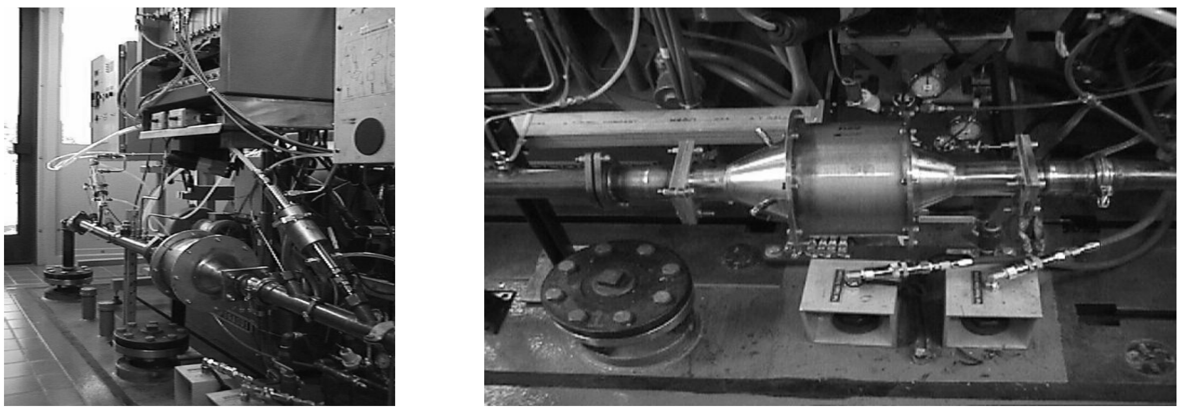

Figure 4. Industrial Ceramic Solutions microwave-regenerated ceramic filter installed on Ford DIATA engine test cell.

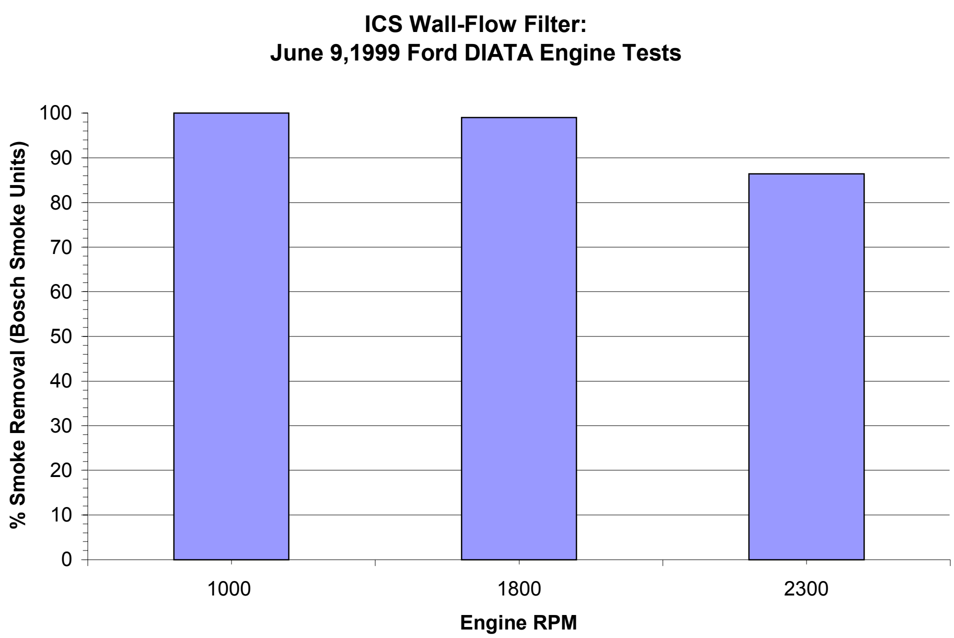

Figure 5. Percentages of particulates removed at different speeds.

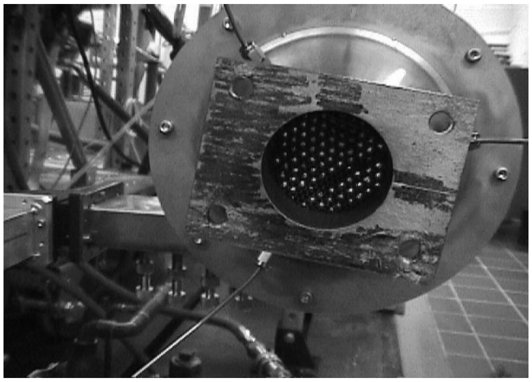

Figure 6. Microwave regeneration cycle in process.

Conclusions

The work has proved that concerns regarding the ability of the ceramic filter to reach carbon combustion temperatures under diesel engine idle conditions are not a critical problem. The microwave ceramic filter achieved regeneration temperatures at a fraction of the microwave power calculated to be necessary.

The initial testing at Ford's test cell #5 on the DIATA diesel engine was a debugging test. A number of issues arose related to the parties at Ford and Industrial Ceramic Solutions learning each other's procedures and equipment. Those issues have been resolved. ICS recognized several areas for potential improvements to the product technology during these debugging tests. The most important of these are filter cartridge shape design and microwave distribution within the filter during regeneration. These improvements are currently being addressed in the ICS laboratory to ensure that the next tests at Ford will include the engineering refinements. ICS expects significant data from future testing at Ford to positively influence the future of the microwave-regenerated diesel exhaust filter. The company is currently focusing its efforts to ensure that the improvements are ready and tested before proceeding with the next opportunity at Ford.

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L. Rapid Surface Modification of Aluminum Engine Block Bores by a High-Density Infrared Process

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-96OR22464

Objectives

- Aluminum engine blocks for compression-ignition, direct-injection engines offer an advantage over conventional iron materials because of the significant weight savings. Unfortunately, wearing of the relatively soft aluminum cylinder walls results in increased emissions and reduced fuel economy as the engine wears. The objective of this work is to develop a new, durability-enhancing coating for aluminum engine block cylinder bores using an innovative yet inexpensive, rapid infrared surface modification process.
- Treat the cylinder internal bores to enhance wear resistance and reduce friction in order to eliminate the need for heavy cast iron cylinder liners.
- Collaborate with potential end users of the technology to enhance the effectiveness of the project while identifying other potential applications.

OAAT R&D Plan; Task 5; Barrier C

Approach

- Identify a candidate coating system capable of matching or exceeding the performance of heavy cast iron cylinder liners.
- Apply the candidate coating on both 4340 steel and aluminum substrate materials and optimize the high-density infrared (HDI) fusing process using metallurgical analysis and hardness testing.
- Perform appropriate wear testing to verify the performance of the coating system.
- Assist the original equipment manufacturer in the development of the necessary down-hole infrared fusing hardware.
- Collaborate with the automotive industry to ensure that approaches are in line with industrial practices.

Accomplishments

- The HDI processing equipment, manipulators, and facility have been received at Oak Ridge National Laboratory and installation has been completed.
- Coating systems have been identified and applied.
- Optimization of HDI fusing for 4340 steel specimens has been completed and wear testing initiated.
- Initial fusing of coating systems on aluminum has been accomplished.
- Discussion and collaboration with Ford Motor Company and DaimlerChrysler Corporation have been enhanced and other potential projects identified.
- Down-hole hardware development has been initiated.

Future Direction

- Improve coating adherence to aluminum through elemental additions to coating metal matrix system.
- Improve coating adherence to aluminum through minor fluxing addition, similar to that used by Ford with thermal spraying.
- Continue wear testing of coating systems on both steel and aluminum.
- Continue down-hole hardware development.
- Further develop related applications with automotive and other industries.

Introduction

Cast aluminum alloys have been used to reduce the weight of internal combustion engine blocks conventionally made of cast iron. To maintain adequate wear and frictional characteristics, cast-iron cylinder liners are often installed within aluminum blocks. Eliminating the need for these heavy liners requires developing a cost-effective surface treatment for the aluminum alloy surfaces where they mate with the sliding piston rings. The cast iron liners currently used cost approximately $5 per liner installed, resulting in a cost of $40 for a V-8 engine. Their wall thickness is approximately 3 to 4 mm for cast-in and 2 to 3 mm for press fit liners. Eliminating these liners is expected to reduce engine weight by at least 8 to 12 lb., and several more pounds could be cut by reducing the engine size because less space would be needed.

A high-density infrared (HDI) transient-liquid coating (TLC) process to produce wear-resistant coatings has been developed at the Oak Ridge National Laboratory (ORNL). The application of this process on aluminum cylinder bore surfaces could result in weight reductions through the elimination of cast iron liners and a potential reduction in overall engine size. Initial calculations indicate that an electrical cost of 2 to 3 cents per bore will be necessary to fuse the chosen coating. The coating process, performed at room temperature, should cost in the range of $1 per bore. This is an 80% reduction in cost in addition to a weight reduction of approximately 10 lb per engine.

Experiment

This project will develop and demonstrate the use of a unique, ORNL-developed HDI TLC process to produce wear-resistant coatings on aluminum cylinder bore surfaces. The TLC process, which uses a high-intensity infrared heat source to fuse wear-enhancing additives into a surface, will offer attractive manufacturing speed advantages over spot-type methods that must raster back and forth to get full coverage, or other methods that require long line-of-sight paths or complex gas plasma-generating systems. Also, this process will treat the full bore at one time, with a processing time of 1 to 5 seconds, eliminating the reannealing that occurs with other methods. Therefore, an entire engine block could be treated in less than 30 seconds with a single apparatus. A conceptual design of the final HDI fusing apparatus is shown in Figure 1.

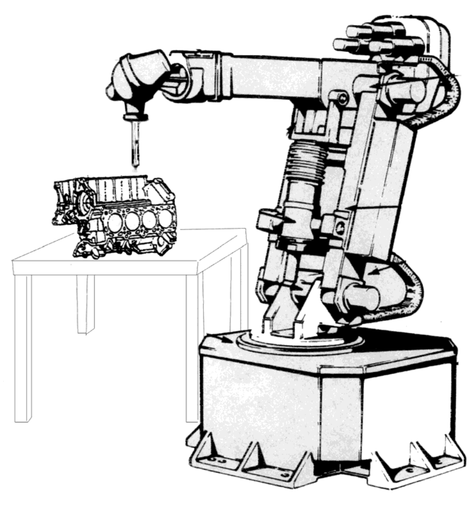

Figure 1. Conceptual design of the final high-density infrared fusing apparatus.

The experimental approach for this project will involve the following three stages.

Select and test a surface alloying system. Material compositions that are most likely to provide wear resistance, desired frictional behavior, compatibility with engine lubricants, and manufacturability will be selected. The selection will be based on the knowledge of ORNL infrared processing and tribology staff in light of current wear-resistant coatings technology. Test coupons of candidate HDI-synthesized materials on 4340 steel and aluminum will be analyzed in terms of microstructure and hardness. The best compositions and processing parameters will be selected for the next phase.

Figure 2 compares the reduced wear rates achievable for a variety of coatings with the wear rates of aluminum and cast iron.

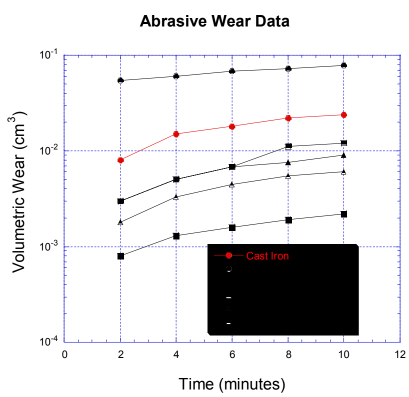

Figure 2. Comparison of wear rates.

Optimize HDI TLC for cylindrical surfaces. Test coupons of candidate infrared-synthesized materials will be subjected to reciprocating wear and friction tests under hot, lubrication-starved conditions to simulate the piston/cylinder interface. Also, ring materials provided by Ford Motor Company containing plasma-sprayed coatings will be incorporated in the testing. HDI fusing of candidate coating materials on aluminum substrates will continue because of inherent interfacial issues, which are anticipated as a result of the presence of alumina. Microstructure and hardness of the treated surfaces will be characterized, and the best candidate compositions and processing parameters will be selected for additional optimization on aluminum.

Demonstration using aluminum alloy engine block. ORNL will work cooperatively with an auto company to demonstrate the coating technique on curved surfaces followed by an aluminum engine block. Wear tests on the treated cylindrical surfaces will be conducted by ORNL's Tribology Group. Actual piston rings will be used as the sliders. Tests will be run at a variety of contact loads and reciprocating speeds to assess the sensitivity of coating performance metrics to imposed operating conditions. Plans are to provide the HDI-treated engine block to an engine testing facility to verify its performance under conditions comparable to actual service.

Discussions will continue between materials engineers from the automotive industry and ORNL infrared processing and senior tribology staff throughout the research to enhance the project through industrial insight. Hardware development for down-hole HDI TLC will be initiated with the original equipment manufacturer.

Results and Discussion

Twelve tungsten-carbide particulates, 20 and 60 to 70 vol %, and Cr_2C_3, 70 vol %, combined with a nickel-boron-silicon-iron-chromium powder, were sprayed on 4340 steel substrates. These coatings were fused using the HDI TLC process to initiate the wear testing. The installation at ORNL used for the process is shown in Figure 3. The nickel base binder system with the WC reinforcement was used because these types of systems are being explored by other fusing techniques such as laser fusing and thermal spray. Both of these techniques have extreme draw backs: fusing overlap and time consumption for laser fusing, and lack of interfacial bonding and porosity for thermal spray.

Through optimization, it was found that processing parameters of 1000 W/cm^2 at a translation speed of 0.5 cm/s were necessary to obtain a liquid metal matrix and allow for wetting of the 4340 base material. The microstructure of the room-temperature-sprayed, tungsten-carbide/nickel-based, HDI-processed sample is shown in Figure 4. The coating is metallurgically bonded to the base material and has been shown to be extremely adherent even under repeated temperature cycling to 660°C.

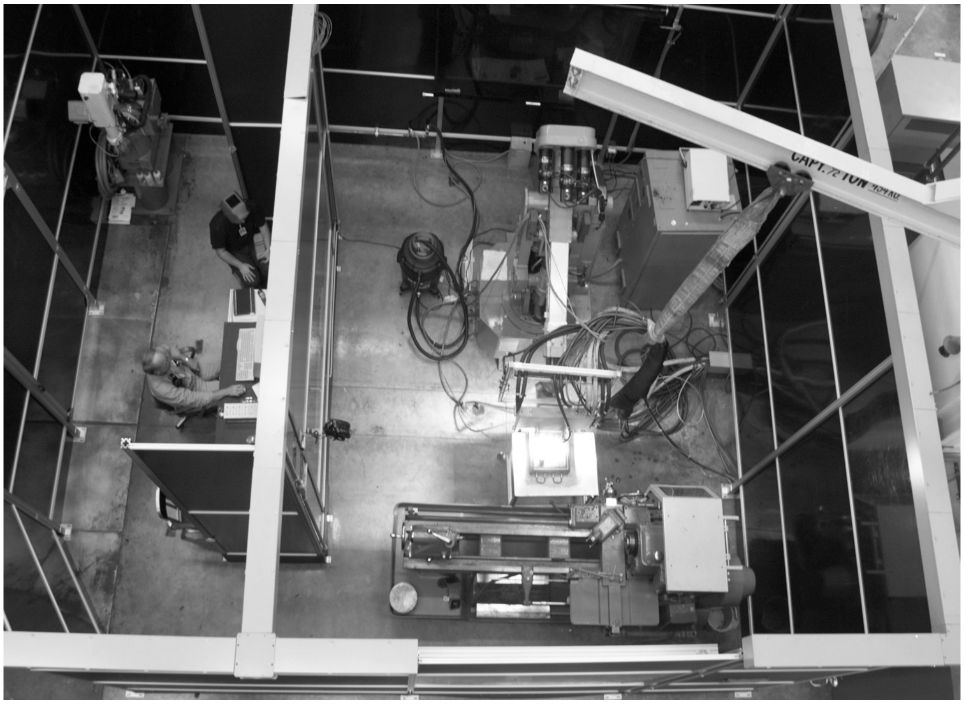

Figure 3. High-density infrared processing facility at the Oak Ridge National Laboratory.

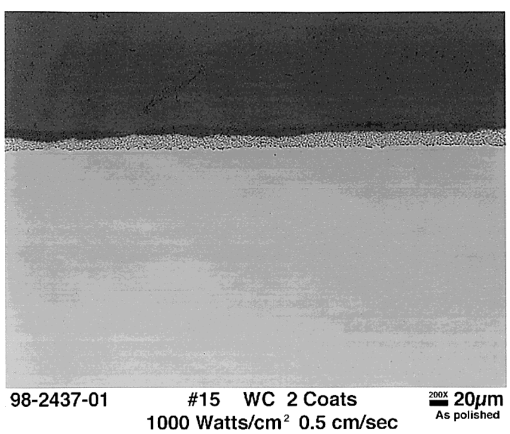

Figure 4. Tungsten-carbide-reinforced coating produced by fusing nickel-based matrix onto 4340 steel.

Hardness testing of the HDI-fused coating revealed that a coating hardness of 1100 HV is typical, and thicknesses from 10 to 100 μm are easily achievable.

The same fusing process on the aluminum base material resulted in a fused coating, but adherence with the base material was an issue. This result was expected because of the inherent Al_2O_3 that forms on the aluminum. This wetting issue has been further studied. Two approaches have been explored: (1) the addition of active elements into the metal power matrix, which is being fabricated by an outside vender; and (2) the addition of minor amounts of fluxing material. The fluxing material to be used is similar to that presently used by an automotive manufacture during coating of aluminum engine bores.

Applications

The automotive industry, coating industry, and ORNL identified several other applications for this process in addition to coating of cylinder bores. They include the following:

- Auto companies
  - — Ford Motor Company (proposal stage)
    - Robert C. McCune
      - – Surface alloying—corrosion resistance
      - – Wear-resistant surfaces on aluminum alloys
      - – Advanced joining of lightweight materials

[Collaboration with Ford Motor Company also includes a potential coating system for engine bores. Ford has supplied ORNL with compression rings with a plasma-sprayed molybdenum (nickel-chromium) composite for incorporation into wear testing.]

—DaimlerChrysler Corporation
- Rosa Paulo
  –Ceramic coatings (boron carbide)

- Industrial Companies

—Dow Chemical Company
- Ceramic coatings

—Electric Boat Corporation
- Cladding work
- Postheat treatments

—DOE Idaho Operations Office
- Yevgeny Macheret
  – Powder metallurgy

—Cincinnati Milicron
- Wear-resistant coatings
- Down-hole hardware being developed

Conclusion

An HDI TLC process to produce wear-resistant coatings has been developed at ORNL. The application of this process on aluminum cylinder bore surfaces could result in engine weight reduction through the elimination of cast iron liners and reduction of overall engine size. Initial calculations indicate that an electrical cost of 2 to 3 cents per bore will be necessary to fuse the chosen coating. Performed at room temperature, the coating process should cost in the range of $1 per bore. This estimate represents an 80% reduction in cost, in addition to a weight reduction of approximately 10 lb. per engine This process will eliminate the interfacial and porosity issues involved in many metal spray techniques, while eliminating the overlap and surface roughness encountered with laser techniques.

The new HDI TLC facility has been installed and producing coatings for several months. Candidate coating systems have been selected for the engine bore application through a literature survey and collaboration with the automotive industry. Successful coating deposition has been accomplished on 4340 steel. Coating fusion has been accomplished on aluminum but has experienced some interfacial bonding issues as a result of the inherent alumina present on the aluminum substrates. Two different approaches have been taken to enhancing the interfacial properties between the coating and substrate. Wear testing on coatings deposited on 4340 has been initiated to produce a base line for the aluminum-based material work. Also, because of the salient advantages of the HDI TLC process, several other applications with the automotive industry are at the proposal stage, and potential applications in other industries have been identified. One industrial partner is driving the need for the down-hole hardware that is presently being studied and developed with Vortek Industries, the original manufacturer of the plasma infrared equipment.

M. Optimization of NFC Coatings for Light-Duty CIDI Applications

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Contractor: Argonne National Laboratory, Argonne, Illinois
Prime Contract No.: W-31-109-Eng-38

Objectives

- Develop low-friction coatings to improve performance and durability of critical engine components that will run on low-sulphur diesel and dimethyl ether fuels as well as lubricating oils and greases.
- Evaluate friction and wear performance of Argonne's near frictionless carbon (NFC) coatings under conditions prototypical of compression-ignition direct-injection (CIDI) engine components.
- Optimize coating microstructure and chemistry to obtain maximum friction and wear performance on light-duty CIDI applications.

OAAT R&D Plan; Task 5; Barriers A, B

Approach

- **Determine deposition conditions** needed to achieve optimum friction and wear performance. Vary deposition parameters and determine the optimum coating conditions for components used in fuel injection systems (such as those being developed by Lucas-Varity and Bosch). The major deposition parameters will include gas composition, substrate bias, substrate material, and coating thickness.
- **Use bench-top test machines to determine the effects** of load, speed, and temperature (as well as type of motion - e.g. unidirectional sliding, reciprocating motion, and rolling) on friction and wear performance. Characterize worn surfaces and determine failure mechanisms. Use experimental and analytical findings to maximize the friction and wear performance of materials operating on low-sulfur diesel fuels.
- **Test coated components under conditions prototypical** of advanced CIDI engines being designed by Ford and Chrysler for their PNGV contracts. The major parameters will include: engine lubricant (parafinic and synthetic base stocks, and commercial products with additives, and new vs. used oil), fuels (conventional diesel, low-sulphur diesel, and DME).
- **Evaluate NFC coatings in actual fuel injection rigs:** Fuel injection components coated with NFC coatings will be tested in component test rigs to quantify the effect of NFC coatings on mechanical energy losses and component durability. These tests will be performed on instrumented test rigs in conjunction with Lucas-Varity and AVL.

Accomplishments

- NFC coatings were successfully produced on test materials and on some actual fuel injection components. Their chemical and microstructural characterizations were completed. Uniform coating thickness was achieved over the entire surface of the test materials and actual components.
- Deposition conditions were further optimized to improve coating adhesion. Different bond layers and layer thickness were tried.
- Demonstrated dramatic improvements in friction and wear of NFC coated test pieces in low sulfur diesel fuels and in a variety of oils (basestock and formulated).

Future Directions

- Continue benchtop testing of NFC coated test pieces in clean diesel fuel and in a variety of dirty oils recovered from engines.
- Optimize deposition conditions to achieve maximum improvements in friction and wear.
- Perform rig testing of NFC in actual engines and/or instrumented testers that simulate actual engine applications (such as Lucas-Varity and AVL).
- Scale up and transfer optimized products to industrial companies.

Compression ignited direct-injected engines are one of several energy conversion concepts being pursued for hybrid passenger vehicles due to their high thermal efficiency. However, emission of NOx and particualtes from CIDI engines may prohibit their use. Combustion and aftertreatment approaches are being pursued to overcome these emission barriers and the efforts described below focus on the development of low-friction, wear-resistant coatings to improve the durability of critical engine components required for these new approaches.

In this project, we are exploring the properties and light-duty CIDI applications of a near-frictionless carbon (NFC) film developed at Argonne National Laboratory. The project aims to optimize the growth conditions and tribological performance of these films and to transfer the optimized process to industry for use in critical CIDI applications. The overall goal is to increase energy efficiency, improve component reliability, and reduce toxic emissions to environments. Research to date has shown that the NFC films have the potential to overcome many of the friction and wear problems experienced by various engine components (such as fuel injectors operating in sulfur-free diesel and gasoline fuels) under sever running conditions. The film has exceptional wear resistance and durability with a coefficient of friction 0.001 when measured in a dry nitrogen atmosphere. Deposition process is very versatile and the film can be deposited on CIDI components at fairly low temperatures (room temperature to 200°C) without risking damage to the base materials. Fuel lubricity tests in a specially designed friction and wear test machine indicated that NFC coatings were compatible with ethanol and sulfur-free diesel fuels and provided dramatically improved friction and wear performance. These coatings seem to work exceptionally well in ethanol, methanol, and low-sulfur diesel fuels and under dry or marginally-lubricated conditions. These findings have led to the conclusion that the NFC films hold high promise for light-duty CIDI engine applications. A series of recent tests evaluated the effects of various lubricating oils on friction and wear of NFC-coated test pieces. In these tests, we have been using several base stock and formulated oils. We have been also evaluating the effects of various oil additives on friction and wear. Tests under lubricated reciprocating contact conditions. at room temperature have indicated that the NFC films are very compatible with base mineral oils and have the capacity to lower friction by 40%. Figure 1 shows the lubricated friction coefficients of uncoated and NFC coated 52100 steel samples. Steel against steel under lubricated condition can provide a friction coefficient of about 0.13 at room temperature, but with the NFC coating, the friction coefficient is reduced to 0.07 level. Wear on the uncoated surfaces are quite severe, but on the coated surfaces, it is minimal. These initial results indicated that the NFC films are quite effective in reducing both friction and wear under lubricated test conditions.

The results presented in Figure 1 are quite remarkable, in that the NFC coating seems to have a synergistic effect on the lubricity of base oil. As is known, on lubricated surfaces friction is very much determined by the viscosity and the nature of the boundary films formed on sliding surfaces. It looks that the NFC coating is quite compatible with base stock oil. Results of other tests run with different oils and oil additives are summarized in Table 1. Tests with synthetic and dirty oils are planned and will be performed over

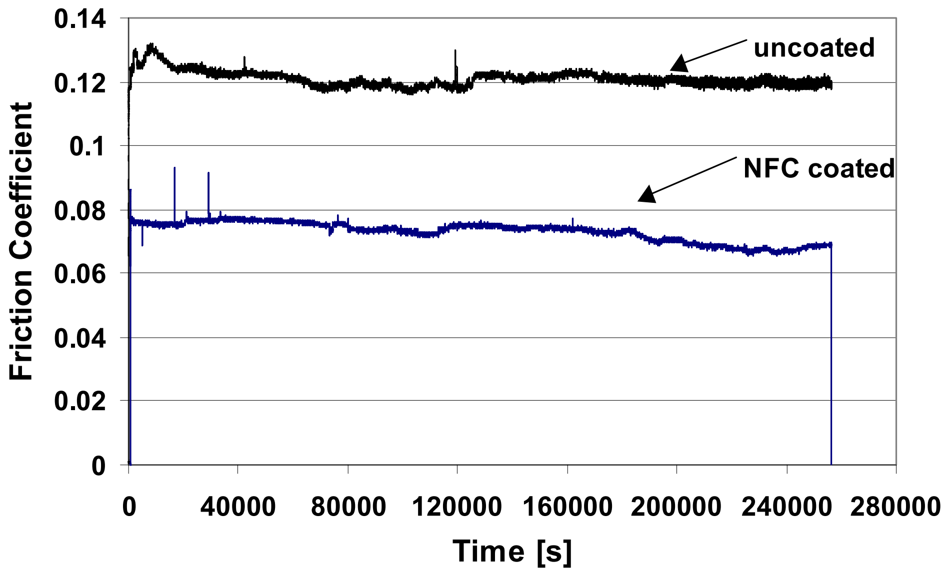

Figure 1. Effect of mineral oil on friction coefficients of uncoated and NFC-coated steel surfaces.

a wide temperature range (i.e., room temperature to 160°C).

Experimental studies with diesel fuels have also continued and concentrated on the effectiveness of the NFC films on reducing wear. For this purpose, we utilized two test machines; one reciprocating ball on flat (very popular in Europe) and a ball on three flats (favored in the United States). Initially, we ran tests with conventional (high-sulfur diesel containing about 500 ppm sulfur) and low sulfur (containing 140 ppm sulfur) diesel fuels. The results obtained so far are very encouraging. As shown in Figure 2, the NFC film effectively reduced the wear of the 52100 steel flats in low- and high-sulfur diesel fuels. Figure 3 shows the size-of-wear scars formed on uncoated and NFC-coated flats during tests in a low-sulfur diesel fuel.

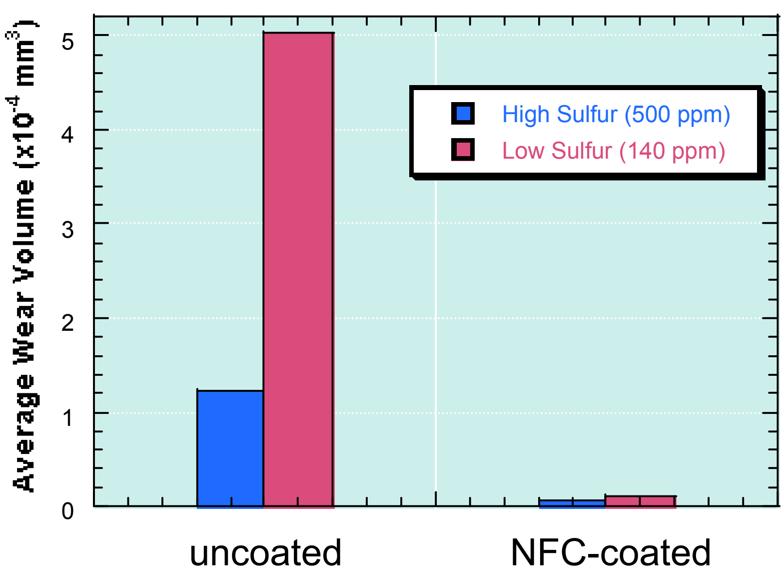

Figure 2. Effect of NFC coating on the wear of 52100 steel disks tested in low- and high-sulfur diesel fuels.

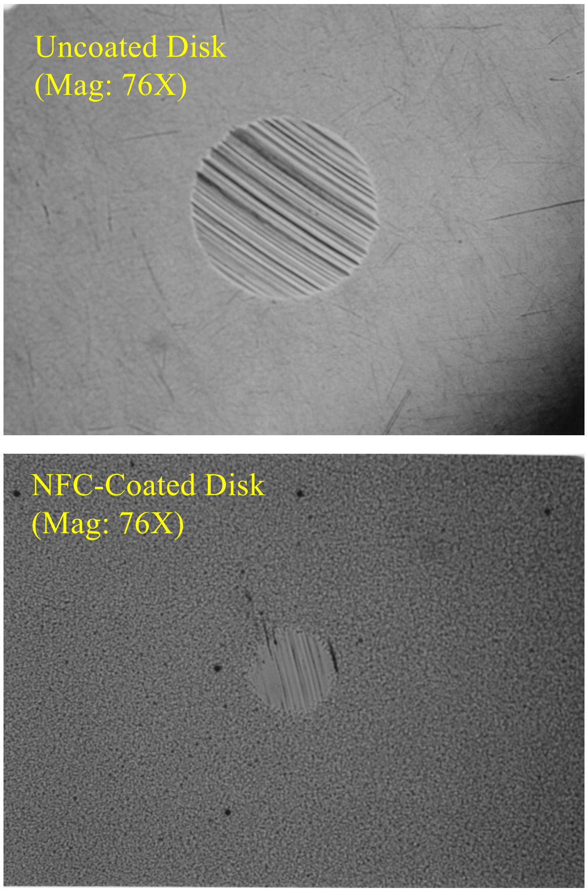

Figure 3. Effects of sulfur content of diesel fuel on wear scar diameters of uncoated and NRC-coated 52100 flats.

As is clear from Figures 2 and 3, the NFC coating is very effective in reducing wear, especially in a low-sulfur diesel fuel environment. A synthetic diesel fuel containing essentially no sulfur is on order and will also be used in our test program. Lubricated tests will also continue and concentrate on the effects of temperature and dirtiness of the oils (i.e., heavily sooted oils drained from actual engines). As can be seen from Table 1, presence of certain additives makes significant difference in the friction and wear performance of uncoated steel samples in poly-alpha-olefin (PAO) oil. However, when used on NFC coated samples, the effect of additives is diminished. In fact, the base stock PAO oil seems to work rather well, thus raising the prospect for the elimination of some of the unwanted sulfur, chlorine, or phosphorous bearing additives from formulate oils.

In the near future, we will approach end-user companies to jointly determine the optimum film properties that will required for their specific applications. We will deposit, characterize, and qualify coatings on their specific test pieces for further tests in their labs. If the results look promising, we will help scale-up the process for pilot size production and use in actual engines.

Table 1. Friction and wear performance of uncoated and NFC coated steel samples in various oils.

Test conditions: 1 km, 20 cm/s, uncoated parts, room temp and humidity unless otherwise noted

Test Fluid	Average Wear (mm)			Average Friction Coefficient		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Dry	0.835[1]			0.543		
PAO	0.715	0.793		0.121	0.114	
1% TCP	0.355	0.335	0.293	0.099	0.105	0.113
1% ZDDP	0.778	0.745		0.122	0.121	
1% Moly	1.048	1.005		0.132	0.131	
1% Moly & 1% TCP	0.793	0.665		0.126	0.121	
1% Moly & 1% ZDDP	0.273	0.285		0.107	0.070	
1% TCP & 1% ZDDP	0.648	0.478[2]	0.713	0.115	0.130	0.129
1% TMS	0.880	0.855		0.117	0.112	

[1] Test run for only 0.1 km
[2] More oil applied

Test conditions: 1 km, 20 cm/s, NFC-coated parts, room temp and humidity unless otherwise noted

Test Fluid	Average Wear (mm)			Average Friction Coefficient		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Dry	0.275[3]	0.218		0.097	0.105	
PAO	0.158	0.158		0.084	0.070	
1% TCP	0.155	0.160		0.067	0.076	
1% ZDDP	0.293[3]	0.283[3]		0.085	0.100	
1% Moly	0.233[3]	0.225[3]		0.079	0.077	
1% Moly & 1% TCP	0.185	0.175		0.063	0.071	
1% Moly & 1% ZDDP	0.168	0.178		0.070	0.071	
1% TCP & 1% ZDDP	0.273[3]	0.308[3]		0.077	0.067	
1% TMS	0.190[4]	0.145		0.087	0.079	

[3] Film appears to have worn out
[4] Film thickness slightly less than for test 2

Publications

1. "Tribology of Hard Carbon Films under Extreme Sliding Conditions," Ali Erdemir, Invited Keynote Lecture at the Cost-516 Tribology Symposium, Helsinki, Finland, May 14–15, 1998, pp. 38–57.

2. "Friction and Wear Performance of Diamond-like Carbon Films Grown in Various Source Gas Plasmas," A. Erdemir, I. B. Nilufer, O. L. Eryilmaz, M. Beschliesser, and G. R. Fenske, Presented at International Conference on Metallurgical Coatings and Thin Films, April 12–16, 1999, San Diego, CA.

3. "Effect of Source Gas Chemistry on Tribological Performance of Diamond-like Carbon Films,"A. Erdemir, O. L. Eryilmaz, I. B. Nilufer, and G. R. Fenske, Presented at the 10th European Diamond Conference, Prague, Czech Republic, September 12–17, 1999.

N. Material Support for Non-Thermal Plasma Development

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No. DE-AC05-96OR22464

Objective

- Provide ceramic material support to Pacific Northwest National Laboratory (PNNL) for development and fabrication of new proprietary ceramic component designs for use in non-thermal plasma reactors for the treatment of diesel exhaust gases.
- Fabricate and ship components to PNNL for testing and evaluation in prototype non-thermal plasma reactors.

OAAT R&D Plan; Task 1B; Barrier A, B

Approach

- Utilize the gelcasting forming method to fabricate complex-shaped ceramic components that meet PNNL design specifications.
- Modify processing as needed to accommodate material and design changes.
- Evaluate metallization materials and processes to apply electrodes to the ceramic components.

Accomplishments

- Fabricated and shipped ceramic components having two design variations to PNNL for testing and evaluation.
- Identified a metallizing material for use in forming electrodes on the ceramic components.

Future Direction

- Fabricate metallized ceramic components for testing at PNNL.
- Modify processing as necessary to meet material and design modifications.
- Evaluate commercially viable processes for component fabrication.

Complex-shaped ceramic components for a new design of non-thermal plasma (NTP) reactors were successfully fabricated and sent to Pacific Northwest National Laboratory (PNNL) for testing and evaluation. NTP reactors have shown great potential as an effective means of eliminating unwanted exhaust gas emissions from diesel engines. Researchers at PNNL are developing new design configurations for NTP reactors that build on past experimental work. To improve effectiveness, these designs include ceramic components having complex configurations. Oak Ridge National Laboratory (ORNL) has extensive experience in the fabrication of complex ceramic shapes, primarily based on prior work related to developing ceramic components for gas turbine engines. ORNL's gelcasting process for forming ceramic shapes was used in the fabrication of components for the new NTP reactors.

A well-defined processing procedure was developed for gelcasting the ceramic shapes. Careful control of the ceramic slurry preparation, the casting mold preparation and assembly, and the casting and gelling procedure were required to produce satisfactory green ceramic parts. The subsequent drying and sintering steps were also critical in producing parts that were free of defects such as cracking and distortion. The casting molds were designed to produce an oversize part to account for the shrinkage of the ceramic component during densification. The optimum solids content of the ceramic slurry, the organic monomers for gel formation, and the polymerization initiator were determined experimentally to produce high-quality gelcast components. High-purity ceramic raw materials were used to maintain high dielectric strength and uniform dielectric properties in these components.

Three metal alloy systems were evaluated for forming the electrodes on the ceramic components. These included a magnesium-based alloy, a powdered titanium-based paste, and a moly-manganese silk screening ink. The magnesium and titanium materials were selected for their lower processing temperatures. Experiments on sample parts, however, indicated that the fired-on moly-manganese ink provided the best metallization on the ceramic component material. Tests were conducted under varying heat treatment conditions. The effects of both firing temperature and furnace atmosphere were evaluated.

Components will continue to be produced and provided to PNNL for testing. As component testing at PNNL proceeds, any necessary material and design changes will be incorporated in future ceramic component fabrication at ORNL. Now that an appropriate material has been identified, a well-defined process for applying the metal electrodes to the ceramic components will be developed and electroded components will be provided to PNNL. Alternative processing approaches, which may be more amenable to commercial production of the ceramic components, will be assessed.

O. Nanofluids for Thermal Management Applications

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Contractor: Argonne National Laboratory, Argonne, Illinois
Prime Contract No.: W-31-109-Eng-38

Objective

- To develop nanofluid technology for increasing the thermal transport of engine coolants and lubricants. The research in FY 1999 focuses on demonstration of the heat transfer potential of nanofluids, for application in thermal management systems for advanced vehicles.

OAAT R&D Plan; Task 5; Barrier C

Approach

- Modify an existing small-channel heat transfer test apparatus. Perform bench-scale testing using various nanofluids and several different particle loadings. Measure and report heat transfer coefficients and pressure drop.

Accomplishments

- An existing hot-wire cell requires about 500 ml of nanofluids to measure the thermal conductivity of nanofluids. In efforts to reduce the volume of testing samples, a small hot-wire cell that requires only 60 ml of nanofluids is being designed and fabricated. In addition, a new heat transfer test section is being designed and fabricated.

Future Direction

- Perform heat transfer experiments using various nanofluids and several different particle loadings.
- Develop smaller and lighter nanofluid/carbon foam radiators.

Conventional automotive heat transfer fluids, such as lubricants and engine coolants, are inherently poor heat transfer fluids. There is a strong need to develop advanced heat transfer fluids with significantly higher thermal conductivities and improved heat transfer. Combining nanophase technology with heat transfer technology provides a new class of heat transfer fluids, called nanofluids, that are engineered by dispersing nanometer-size solid particles in traditional heat transfer fluids to increase thermal conductivity and heat transfer performance. The potential benefits of the application of nanofluid technology include automotive heat exchangers that are smaller, lighter in weight, and more efficient than conventional units and have a reduced inventory of fluid.

The objective of this activity is to develop nanofluid technology for increasing the thermal transport of engine coolants and lubricants. This is a new activity started in April 1999. Previous research with nanofluids has demonstrated that nanofluids are stable and that thermal conductivity can be substantially enhanced over the base fluid. For example, improvements in thermal conductivity of up to 40% of the base fluid have been demonstrated for a relatively low metallic nanoparticle loading (<0.3 vol %). The increase in thermal conductivity will result in an increase in heat transfer over that of the base fluid without dispersed nanoparticles. In preliminary research, Argonne National Laboratory (ANL) has shown that the heat transfer capability of water increased by 20% with the dispersion of less than 1 vol % copper oxide nanoparticles. Even greater improvements in heat transfer are expected for nanofluids that contain metals (such as Cu and Ag) rather than oxides. In FY 1999, the research focuses on demonstration of the heat transfer potential of nanofluids for application in thermal management systems for advanced vehicles.

In May, Xinwei Wang, a Ph.D. candidate from Purdue University, started working at ANL. During the reporting period, Wang focused his efforts on further development and evaluation of the transient hot wire technique for measuring thermal conductivity of nanofluids. An existing hot-wire cell requires about 500 mL of nanofluids to measure the thermal conductivity of nanofluids. In efforts to reduce the volume of testing samples, a small hot-wire cell that requires only 60 mL of nanofluids is being designed and fabricated. In addition, a new heat transfer test section is being designed and fabricated.

On May 5, Marty Wambsganss and Steve Choi visited DaimlerChrysler in Madison Heights, Michigan. Choi made a presentation titled “Nanofluids for Thermal Management.” Based on our discussions with experts in fuel cell technology at ANL and at the auto makers, it appears that the near-term application of nanofluid technology for cooling fuel cell systems would be in the secondary coolant loop. That loop uses a conventional coolant and includes the radiator and a liquid-to-liquid heat exchanger. The application of nanofluid technology to improve the heat transfer characteristics of the coolant will lead to smaller heat exchangers and a reduced fluid inventory. In the long term, it may be possible to identify nanoparticle materials and nanofluid production methods that would allow nanofluids to directly cool the fuel cell stack without adversely affecting operation of the stack.

The heat rejection requirements of a fuel cell–powered vehicle can be significantly greater than those of a conventional vehicle because nearly 100% of the waste heat goes to the cooling system, compared with only 30% for conventional vehicles. In addition, the fuel cells must operate at temperatures of 80°C or less, resulting in a smaller driving temperature difference for heat transfer in the radiator. These conditions require much larger radiators and lead to the conclusion that a conventional cooling system will not work. As a result, thermal management can be considered an enabling technology for fuel cell–powered vehicles.

The heat transfer coefficient on the air side is inherently low; therefore, a large air side surface area is required. The heat transfer characteristics of the coolant are also relatively poor; for example, the thermal conductivity of a water/ethylene-glycol mixture is about one-half that of water. To reduce the size and weight of the radiator, there is a need to improve heat transfer on the air side. Once that is accomplished, the heat transfer characteristics of the coolant need to be improved. Carbon foam materials and nanofluids are advanced heat transfer materials with significantly higher thermal conductivities and better heat transfer characteristics than are presently available. Therefore, combining carbon foam technology with nanofluid technology could lead to a breakthrough in advanced vehicle thermal management system design that can meet the strong need to improve heat transfer on both the air side and coolant side of the radiator.

Oak Ridge National Laboratory and ANL plan to develop carbon foam radiators that use nanofluid coolants. The purposes of the planned joint research are to develop combined nanofluid and carbon-foam technology for application in advanced vehicle thermal management systems, and to demonstrate that the combined carbon foam and nanofluid technology can significantly reduce the size and weight of radiator systems for fuel cell–powered vehicles, heavy vehicles, hybrid-electric vehicles and other performance-driven systems.

References/Publications

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2. Wang, X., X. Xu, and U. S. Choi, "Thermal Conductivity of Nanofluids," accepted for publication in the Journal of Thermophysics and Heat Transfer, 1999

5. CERAMICS FOR GAS TURBINES

P. Agreement to Bring into Production and Commercialize a Manufacturing Process for Silicon Nitride Turbomachinery Components

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Contractor: AlliedSignal Ceramic Components, Torrance, California
Prime Contract No: N0014-95-2-0006

Objective

- Develop, demonstrate, and verify the ceramic technology necessary to produce large quantities of high-quality silicon nitride components for automotive gas turbine engines at costs acceptable to the automobile industry.

OAAT R&D Plan; Task 1; Barrier A

Approach

- Provide improvements in yield, quality, and cost of Si_3N_4 components.
- Develop and implement automated forming, statistical process control, and intelligent processing control.
- Demonstrate a gelcasting manufacturing process capable of supplying engine-quality hardware in typical production volumes.

Accomplishments

- Designed, fabricated, and installed automated equipment capable of gelcasting 500 to 1000 complex-shaped silicon nitride turbine wheels per month.
- Developed an improved AS800 silicon nitride gelcasting system that demonstrates more consistent gelation that results in higher yields, reduced cycle times, improved part quality, and reduced costs.

The gas turbine engine was eliminated as a candidate for the 80-mpg Partnership for a New Generation of Vehicles automobile in FY 1998. Work on this contract continued through FY 1999, using funds from previous fiscal years.

Structural ceramics, which traditionally have been based upon non-oxides such as silicon carbide or silicon nitride, have long been considered primary candidates for hot-section components in advanced gas turbines. Initial property limitations such as low strength, low Weibull modulus, and poor creep resistance were successfully addressed in a number of materials development programs. However, the commercialization of silicon nitride has been limited because of the high cost of these components.

Technical Progress

A local supplier that specializes in systems design, integration, and fabrication of automated equipment was identified to design and build automated equipment for the large-scale manufacturing of complex-shaped Si_3N_4 components. A fully automated system was designed with only minimal operator interaction required. The system currently requires two operators; the goal is to reduce the number of operators to one. A closed-loop conveyor system was designed for the movement of gelcast molds through the process stations. The Gel*Fast* ™ system was installed at AlliedSignal Ceramic Components in FY 1998 and debugged and integrated into a full operating system during FY 1999. Figure 1 shows the system prior to installation of heat station #2.

The production demonstration using the automated Gelcasting equipment was delayed for 6 months because of problems associated with the completion of the automated system by the equipment manufacturer. The demonstration was completed during FY 1999, and a steady state cycle time of 15 minutes per wheel was achieved. The automated gelcasting of a Teledyne M304 turbine wheel is shown in Figure 2.

The cost study for a dedicated facility to fabricate large quantities of turbine wheels has been completed. The study was based on an annual production of 50,000 turbine wheels for an industrial turbogenerator. The predicted drop in cost per wheel was exponential up to 10,000 wheels, whereupon the cost began to drop slowly with each additional 5,000 wheels produced per year. The predicted unit cost for the ceramic wheel was 2–3 times the cost of the

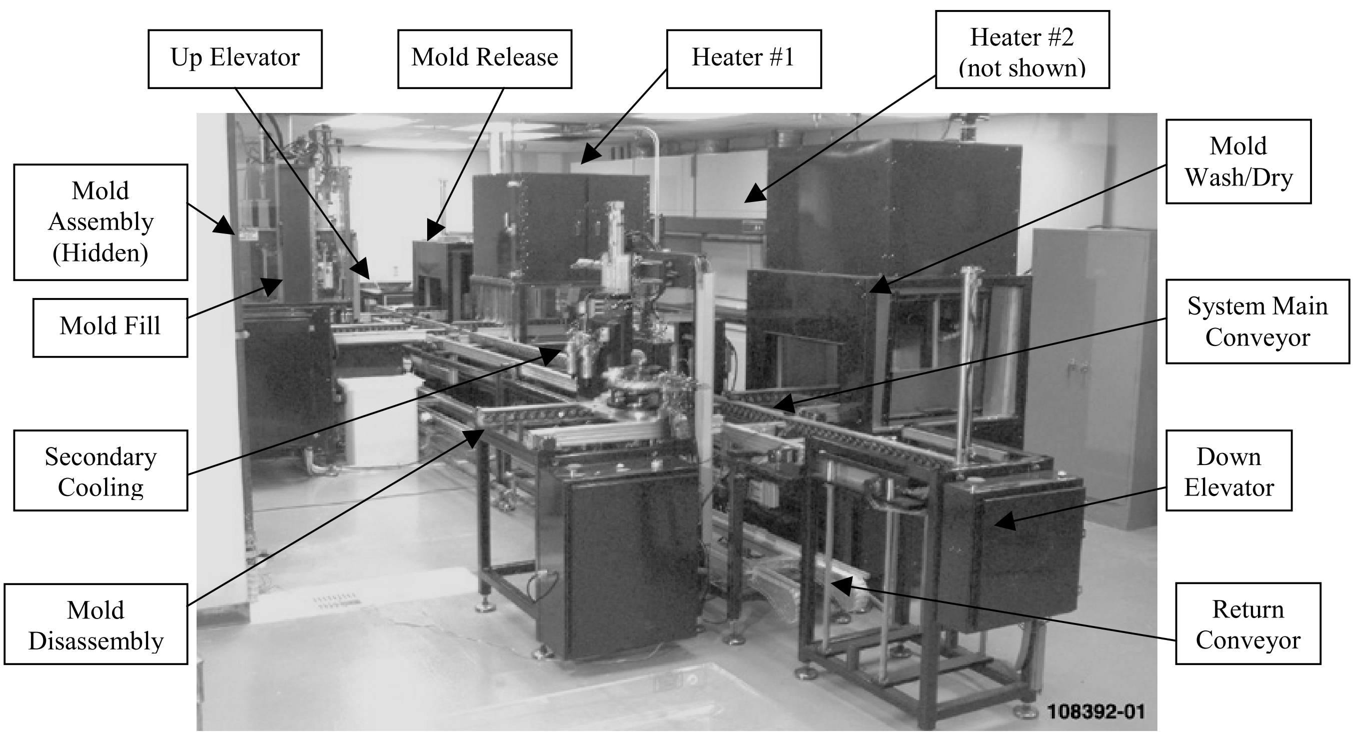

Figure 1. Automated gelcasting system, Gel*Fast* ™.

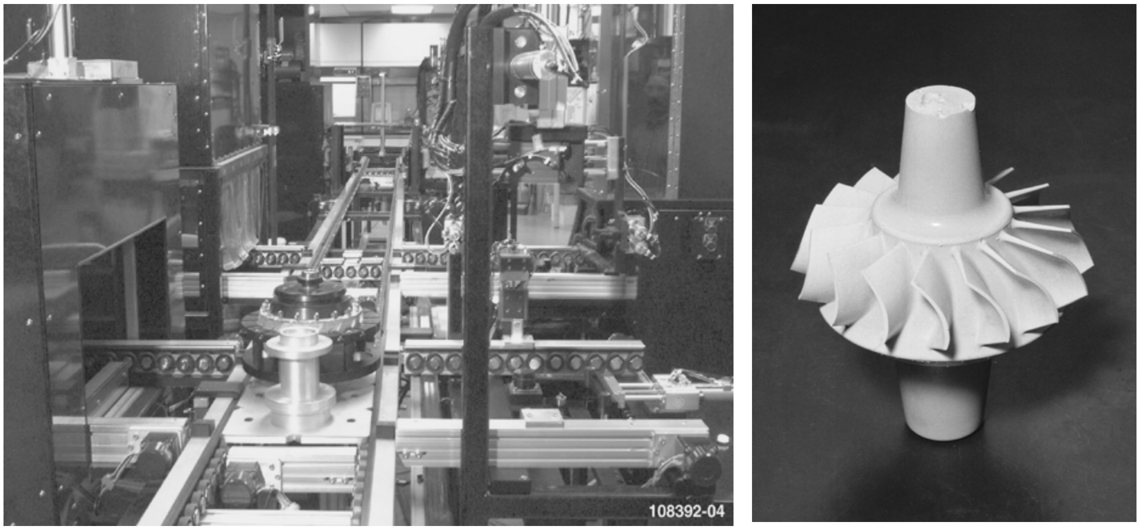

Figure 2. Automated gelcasting of a Teledyne M304 turbine wheel.

metallic wheel. However, the life of the ceramic wheel is predicted to exceed the life of the engine, while the metallic wheel would have no useful life under these operating conditions.

A number of process refinements to the original gelcasting process were investigated in FY 1999. An optimized AS800 silicon nitride gelcasting system was developed and demonstrated. The system demonstrated much more consistent gelation than the previous system; and a wide variety of parts including test plates, Teledyne M304 turbine wheels, and turbine nozzles were successfully fabricated. Optimization activities have focused on part quality and yield, cost reduction, and cycle time reduction.

A binder burnout cycle for gelcast M304 turbine wheels was also developed for the new system. Wheels were reproducibly densified using this cycle (no M304 wheels made using the previous gel system achieved density using the old pyrolysis cycle), and mechanical properties were verified. The pre-sintering cycle was eliminated, contributing to reduction of cost and cycle time. The use of optical pyrometers for optimized temperature monitoring in the furnace is being employed as a cost reduction measure.

The high cost of gelcasting molds has been a detriment to making production of complex-shape gelcast parts feasible. Advanced mold technology was pursued this year. Alternate mold materials were identified and shown to be compatible with the optimized gelcast system. The alternative techniques have reduced the lead time required for mold fabrication and have therefore reduced costs.

The industrial turbogenerator wheel was successfully redesigned during the year with a simplified single-pull vector used for the airfoil slides. The original design had a complex three-dimensional twist to the airfoil, which required multiple pull vectors to be engaged during fabrication of the part. The original design was cost-prohibitive and high-risk for production operations. The revised design will save approximately 50% in tooling costs.

APPENDIX A: ABBREVIATIONS, ACRONYMS, AND INITIALISMS

ABI	automated ball indentation
AlN	aluminum nitride
Al_2O_3	alumina or aluminum oxide
ASTM	American Society for Testing and Materials
BMC	Bulk Molding Compounds, Inc.
BME	base metal
CIDI	compression-ignition, direct-injection
CTP	Ceramic Technology Project
CVI	chemical vapor infiltration
dc	direct current
DME	dimethyl ether
DOE	U.S. Department of Energy
EC	electronic ceramic
ECD	electronic ceramic device
GM	General Motors
HDI	high-density infrared
ICS	Industrial Ceramic Solutions
LANL	Los Alamos National Laboratory
MLC	multilayer capacitor
MPM	mechanical properties microprobe
NFC	near-frictionless carbon
NO_x	oxides of nitrogen
NTP	non-thermal plasma
OAAT	Office of Advanced Automotive Technologies
ORNL	Oak Ridge National Laboratory
OTT	Office of Transportation Technology
PAO	poly-alpha-olefin
PEBB	power electronics building block
PEM	proton exchange membrane
PM	particulate matter
PNGV	Partnership for a New Generation of Vehicles
PNNL	Pacific Northwest National Laboratory
pps	polyphenylene sulfide
R&D	research and development
SEM	scanning electron microscope
SNL	Sandia National Laboratories
TLC	transient-liquid coating
ulf	ultra low fire