AIM

Advanced Industrial Materials (AIM) Program
Office of Industrial Technologies
Energy Efficiency and Renewable Energy
U.S. Department of Energy (DOE)

Advanced Industrial Materials (AIM) Program

Compilation of Project Summaries and Significant Accomplishments

FY 1996

Date Published: April 1997

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MASTER

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Oak Ridge National Laboratory

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DISCLAIMER

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INTRODUCTION

The Advanced Industrial Materials (AIM) Program
Office of Industrial Technologies
Fiscal Year 1995

C. A. Sorrell, Program Manager

In many ways, the Advanced Industrial Materials (AIM) Program underwent a major transformation in Fiscal Year 1995 and these changes have continued to the present. When the Program was established in 1990 as the Advanced Industrial Concepts (AIC) Materials Program, the mission was to conduct applied research and development to bring materials and processing technologies from the knowledge derived from basic research to the maturity required for the end use sectors for commercialization. In 1995, the Office of Industrial Technologies (OIT) made radical changes in structure and procedures. All technology development was directed toward the seven "Vision Industries" that use about 80% of industrial energy and generated about 90% of industrial wastes. These are:

- Aluminum
- Chemical
- Forest Products
- Glass
- Metal Casting
- Refineries
- Steel

OIT is working with these industries, through appropriate organizations, to develop Visions of the desired condition of each industry some 20 or 25 years in the future and then to prepare Road Maps and Implementation Plans to enable them to reach their goals.

Recently, we began working with the forging, heat treating, welding and carbon products industries, which are cross-cutting industries to the seven. Each industry has decided to go through the process to develop a vision, road map, and implementation plan and OIT is working on ways to integrate them into the Industries of the Future, even though there will not be specific budget lines for them. We are pleased to have a part in this effort.

The mission of AIM has, therefore, changed to "Support development and commercialization of new or improved materials to improve productivity, product quality, and energy efficiency in the major process industries." Though AIM remains essentially a National Laboratory Program, it is necessary that each project have industrial partners, including suppliers to, and customers of, the seven industries. Now, well into FY 1996, the transition is nearly complete and the AIM Program remains healthy and productive, thanks to the superb investigators and Laboratory Program Managers.

We were fortunate to have the foresight to begin the transition in 1993 when, at the suggestion of the AIM Guidance and Evaluation Board, we began to develop assessments of materials needs and opportunities, beginning with the pulp and paper industry, following with the glass industry. We are now engaged in assessments of the metal casting and chemical industries. These assessments identified real needs of these industries and we have been able to follow through with several new projects. In FY 1996, we can honestly say that every project addresses a need identified by one or more of the seven industries. The challenge to retain the cross-cutting benefits of materials not only remains, but is even more important now than before the changes in OIT. All seven industries understandably have identified materials as important, particularly for high temperature strength, corrosion resistance, and wear resistance, and there are many common aspects to these industry needs that can best be addressed by a true cross-cutting materials program.

The same can be said of combustion, catalysts, separations, and sensors and controls, which also require materials development. Major advances in commercialization of new materials were made in 1995 and continue into 1996, particularly in iron and nickel aluminides and molybdenum disilicide, which are being tested in production environments of all seven industries, where they are proving to have remarkable high temperature fatigue resistance, strength, and corrosion resistance. Principal investigators for all the other projects are making excellent progress in the same direction. So far, we have been able to continue support for some of the more basic aspects of materials development that are required for applications engineering and development of new applications. This will become increasingly more difficult as budgets decrease and more funding is earmarked for specific industries, with rapid commercialization or near term problem solving as the major emphases.

This Compilation of Project Summaries and Significant Accomplishments Report contains the technical summaries of some very remarkable work by the best materials scientists and engineers in the world. It is hoped that this introduction places that work in the proper context and adequately describes the challenges facing AIM over the next few years. Congratulations from the Program Manager to those who have actually done real work and made him look good.

ADVANCED METALS AND COMPOSITES

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

WORK ELEMENT: High-Temperature Materials

PROJECT TITLE: Advanced Ordered Intermetallic Alloy Development

PHASE: Materials Capability Development

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATORS: C.T. Liu (423) 574-4459 and P.J. Maziasz (423) 574-5082

PHASE OBJECTIVE: To improve the tensile ductility and fracture toughness at ambient temperatures and the strength and creep and oxidation resistances at high temperatures of structural intermetallics based on TiAl, resulting in developing new light-weight structural materials for industrial use.

ULTIMATE OBJECTIVE: (1) To develop low-density, high strength, ductile ordered intermetallic alloys for structural applications in advanced energy conversion systems and heat engines, and (2) to help U.S. material industries to compete in the world market.

TECHNICAL APPROACH: Both macroalloying and microalloying processes are employed to improve metallurgical and mechanical properties of ordered intermetallic alloys. The selection of annoying additions will be based on physical metallurgy principles, structural maps and some empirical correlations. Emphasis will be placed on improving ductility and toughness at ambient temperatures and strength and creep and oxidation resistances at elevated temperatures through material processing and structural control.

PROGRESS: Grain size has been identified as the key microstructural parameter controlling the room temperature tensile properies of TiAl alloys with lamellar structures. The Hall-Petch analysis shows a good linear relation between tensile elongation and grain size. The mechanical properties of the TiAl alloys with ultra-fine lamellar structure produced by hot extrusion are much superior to advanced TiAl alloys developed recently.

Patents: 0 **Publications:** 3 **Proceedings:** 2
Books: 1 **Presentations:** 2

ACCOMPLISHMENTS:

Licenses: Discussions with several U.S. industries for potential licenses
Known Follow-on Product(s): Anticipared use in industrial and chemical energy conversion system.

INDUSTRY INTEREST: Several technical exchange meetings were held with U.S. industries including GE, Pratt & Whitney, Howmet Corporation, and Cummins Engine Company.

PROJECT SUMMARY (continued)

PROJECT TITLE: Advanced Ordered Intermetallic Alloy Development

CRITICAL ISSUES: (1) To improve the mechanical properties and weldability of TiAl alloys in cast conditions, (2) to improve impact resistance of TiAl alloys at room and elevated temperatures, and (3) to improve the tensile ductility and creep resistance of TiAl alloys at ambient temperatures.

FUTURE PLANS: (1) To increase the tensile ductility of cast TiAl alloys and to improve fracture resistance of these alloys by control of microstructure and alloy compositions, (2) to characterize oxidation and corrosion resistance of intermetallic alloys for industrial applications.

POTENTIAL PAYOFF: There are two major problems with many intermetallic alloys: poor room-temperature ductility and inadequate high-temperature creep resistance. If these problems are overcome, it will result in the development of a whole new class of ordered intermetallic alloys that have high-temperature properties that are superior to those of existing superalloys. The use of strong intermetallic alloys with light-weight would improve thermal efficiency and system performance of advanced engines and energy conversion systems, resulting in substantial energy savings.

SIGNIFICANT ACCOMPLISHMENT

SUBSTANTIAL IMPROVEMENT IN MECHANICAL PROPERTIES OF TiAl ALLOYS BY MICROSTRUCTURAL REFINEMENT

Advanced Industrial Materials (AIM) Program

PROBLEM: Two-phase TiAl alloys offer an attractive mix of low density (~4 g/cm^3), low thermal expansion, high melting point, and decent oxidation resistance at elevated temperatures. The major concerns for structural applications are limited ambient-temperature ductility and fracture resistance and high-temperature strength and creep resistance. The current development effort has been focused on mechanical property improvement by control of microstructure and alloy composition.

RESULTS: Grain size has been identified as the key mocrostructural parameter controlling the room temperature tensile ductility of TiAl alloys with lamellar structures (Fig. 1). The Hall-Petch analysis shows a good linear relation between tensile elongation and grain size (Fig. 2). The mechanical properties of the TiAl alloys with ultra-fine lamellar structure produced by hot extrusion are much superior to the advanced TiAl alloys (such as K-5; Ti-46.5 A1-2.1 Cr-3Nb-2W.at.%) developed recently (Fig. 3).

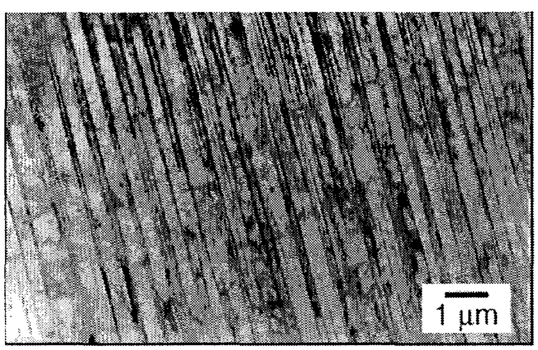


Fig. 1: Refined lamellar structure

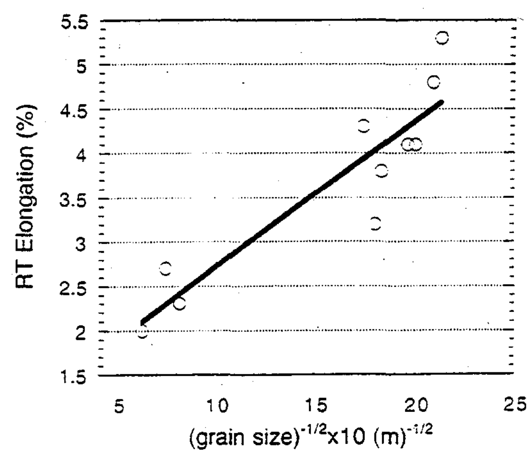


Fig. 2: Hall-Petch plot

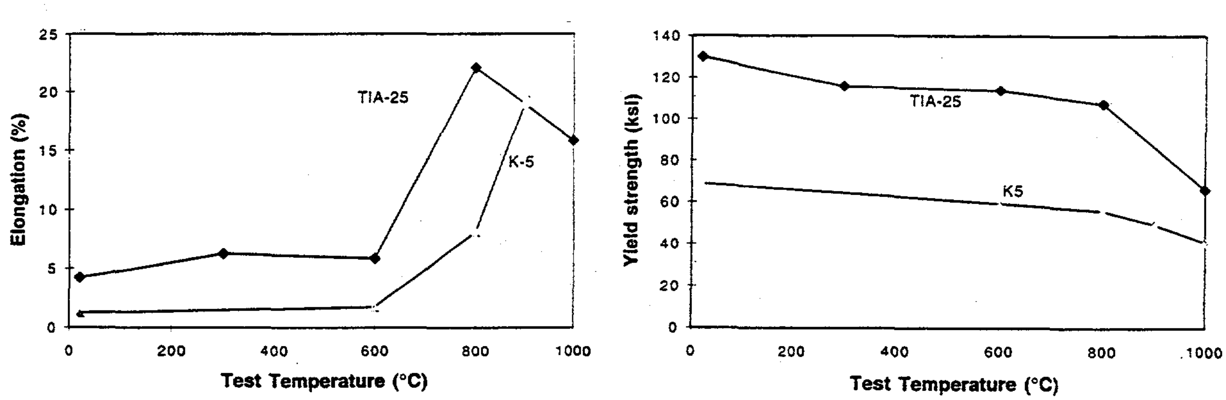


Fig. 3: Comparison of tensile properties of TiAl alloy, TIA-25, developed at ORNL with advanced alloy K5.

SIGNIFICANCE - FOR ENERGY EFFICIENCY: The development of light-weight, high strength TiAl alloys for high temperature applications is expected to substantially improve the performance of industrial and chemical energy conversion systems. All of these will result in a substantial energy savings for these systems.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Development of Weldable, Corrosion-Resistant Iron-Aluminide (FeAl) Alloys

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL)

PRINCIPAL INVESTIGATOR(S): P.J. Maziasz (423) 574-5082, G.M. Goodwin (423) 574-4809, X.L. Wang (423) 574-9164

PHASE OBJECTIVE: Develop FeAl compositions and metallurigical conditions (fabrication/microstructure) that enable weldability and corrosion-resistance with optimum mechanical properties. Develop both monolithic and weld-overlay cladding technology for FeAl.

ULTIMATE OBJECTIVE: Develop "super" corrosion-resistant FeAl alloys that are better than conventional heat/corrosion-resistant steels, stainless steels and Fe-Cr-Ni alloys. Produce FeAl material or components using commercial practice for industrial testing. Define applications for FeAl as monolithic material or weld-overlay cladding.

TECHNICAL APPROACH: Make micro-alloying additions of B, C, and Zr to enhance ductility and more ductile fracture at room-temperature, and ZrC formation and stability at high-temperatures. Control processing and heat-temperature conditions to produce microstructures that give the best combination of room-temperature and high-temperature mechanical behavior.

PROGRESS: Refining the processing-induced grain size and/or increasing the amount of fine ZrC precipitation are the keys achieving good room-temperature ductility and toughness, and good high-temperature strength and creep-resistance in FeAl. Heat-treatments to coarsen grain size and/or preoxidize FeAl produce the best high-temperature properties behavior. FeAl with good room-temperature ductility has also been found to be autogeneously weldable with no cold-cracking. FeAl solid- or powder-cored wire has been produced by Stoody for automated gas-metal arc (GMA) welding. FeAl weld-overlays can be made on various alloy steels, and some stainless steels. Optimizing the FeAl weld-deposit composition and processing conditions to eliminate cold-cracking is in progress.

Patients: 2
Books:
Publications:
Presentations: 11
Proceedings: 8
Awards: 2

PROJECT SUMMARY (continued)

PROJECT TITLE: Development of Weldable, Corrosion-Resistant Iron-Aluminide (FeAl) Alloys

ACCOMPLISHMENTS: INCO testing has found FeAl alloys to be carburization resistant. United Defense is casting grate-bars for ore processing.

Licenses:
Known Follow-on Product(s): Cast components, weld-overlays, P/M thin foil or filters.
Industry Workshop:

Technology Transfer or Industrial Interaction: FeAl material or components have been tested or are in test with 8-10 different companies, and discussions based on new corrosion or mechanical properties data have been initiated with several others.

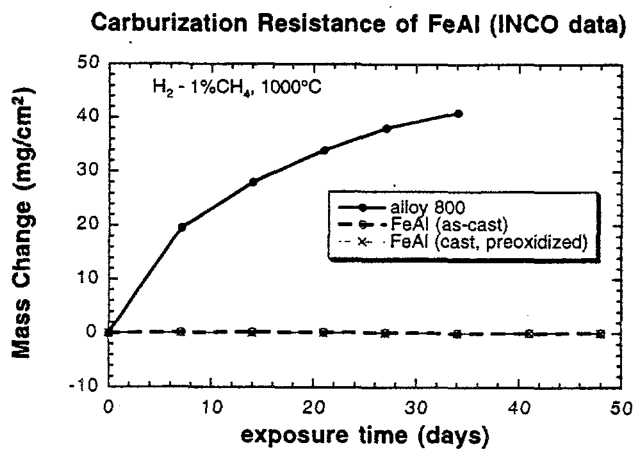
SIGNIFICANT ACCOMPLISHMENT

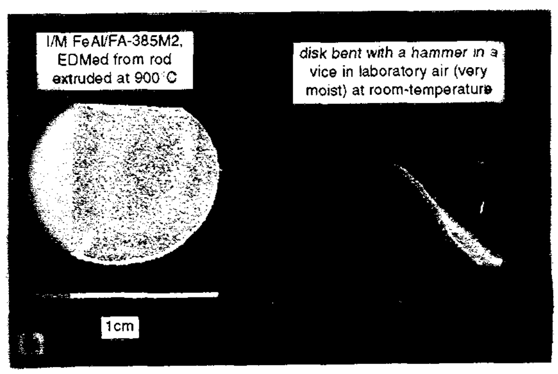
DUCTILE, TOUGH, WELDABLE FeAl ALLOYS ALSO RESIST CARBURIZATION

Advanced Industrial Materials (AIM) Program

ISSUE: FeAl iron-aluminides possess outstanding oxidation and sulfidation resistance based on their formation of a protective Al_2O_3 scale. Does that oxide scale protect against other kinds of high-temperature environments, like carburizing atmospheres? FeAl alloys with fine-grained processing-induced microstructures have been found to be quite tough and ductile at room-temperature in air. Can such materials be welded without cold-cracking?

RESULTS: Cast FeAl alloys (Fe - 36-38 at. % Al) were tested by INCO in carburizing atmospheres at 1000 and 1100°C that simulate industrial ethylene pyrolsis (shown below) or steam/methane reformer environments, and showed outstanding resistance, as measured by weight-change or subsurface carbide penetration. When such alloys are hot-extruded to refine the grain size to 30-50 μm, they have enough ductility and toughness in room-temperature air to be bent with a hammer in a vice (shown below). Such behavior is highly unusual for FeAl alloys which are usually quite brittle. Such ductile FeAl can also be autogeneously welded without cold-cracking, without any preheat or post-weld-treatment, which represents a significant breakthrough revelent to industrial applications.





ENERGY EFFICIENCY: FeAl iron-aluminides can also be melted by the Exo-Melt^{TM} process, which saves 50% of the energy used by conventional melting. Longer lifetime and radically lower metal wastage of "super" corrosion-resistant FeAl in aggressive high-temperature environments will save the energy used to produce and process conventional steels, stainless steels and heat/resistant Fe-Cr-Ni alloys for such applications. It will also save the wasted time and energy associated with down-time and lost production.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed-Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Materials for the Pulp and Paper Industry

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory, Pulp and Paper Research of Canada, and Institute of Paper Science and Technology.

PRINCIPAL INVESTIGATOR(S): James R. Keiser, 423-574-4453

PHASE OBJECTIVE: Measure residual stresses in unexposed and exposed 304L/SA210 composite tubes, predict the stresses in recovery boiler floor tubes during normal operation and during thermal transients, determine if the microstructure of an exposed tube has features characteristic of thermal cycling, measure the corrosivity of smelt, identify environments that can cause stress corrosion cracking of 304L stainless steel, determine the effect of thermal cycling on cracking, and continue the characterization of cracked tubes.

ULTIMATE OBJECTIVE: Identify an alternate material or materials or an operational approach that can be used to prevent cracking of composite floor tubes.

TECHNICAL APPROACH: Use standard metallographic examination techniques coupled with advanced analytical techniques to collect information on unexposed and exposed, cracked tubes. Use neutron and X-ray diffraction to measure the residual stresses in composite tubes, and use finite element modeling to predict stresses under operating conditions. Conduct laboratory studies to determine the corrosivity of molten smelt, to identify environments that can cause stress corrosion cracking, and to determine the effects of thermal cycling.

PROGRESS: Stresses in operating composite tubes can be predicted, and studies are finding environments that can cause stress corrosion cracking. Studies are also addressing the possibility of thermal fatigue causing cracking of tubes.

Patents: --	**Publications:** 6*	**Proceedings:** --
Books: --	**Presentations:** 10**	**Awards:** --

* One paper published in conference proceedings, drafts of two laboratory reports submitted for review, and 3 manuscripts have been submitted for review for open literature publication

** Not including presentations made at triannual program review meetings

PROJECT SUMMARY (continued)

PROJECT TITLE: Materials for the Pulp and Paper Industry

ACCOMPLISHMENTS:

Licenses: --

Known Follow-on Product(s): --

Industry Workshop: Program review meetings are held three times per year.

Technology Transfer or Industrial Interaction: Fourteen paper companies, four recovery boiler manufacturers, and two two fabricators are active program participants.

CRITICAL ISSUES: Determination of dominant cracking mechanism(s), identification of materials that are resistant to dominant mechanism(s)

FUTURE PLANS: Continue to examine cracked tubes provided by paper companies, and work with paper companies to collect smelt samples, wash water samples, and temperature data.

POTENTIAL PAYOFF: The financial cost to paper companies resulting from recovery boiler material problems is enormous due to maintenance costs and the value of lost production. Identification of alternate materials, process changes and/or modifications of operating conditions should lessen or eliminate this financial burden.

ESTIMATED ENERGY SAVINGS: Kraft recovery boilers are the energy sources for pulp and paper facilities. Improved materials will have significant energy improvement and competitiveness impact.

OTHER SOURCES:

A CRADA has been established with a paper company
Four MPLUS proposals with paper companies and a boiler manufacturer were funded during the past year

SIGNIFICANT ACCOMPLISHMENT

PREPARATION OF STATE-OF-THE-ART REPORT ON COMPOSITE TUBE CRACKING

Advanced Industrial Materials (AIM) Program

ISSUE: Considerable information exists in public and private documents on the cracking of co-extruded tubes in black liquor recovery boiler. It was important to gain access to all of this information and to prepare a report summarizing what is known.

RESULTS: Information was obtained from an extensive list of sources including tube manufacturers, boiler manufacturers, public domain literature, companies operating kraft recovery boilers, consultants, failure analysis laboratories, and failure analyses conducted specifically for this project. A report was prepared such that sources were not identified but information from these sources could be presented in a public document. This report should serve as an important reference for recovery boiler manufacturers and operators as well as for future researchers in this area.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Ni_3Al Technology Transfer

PHASE: FY: 1996 **PHASE COMPLETION DATE**:

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL)

PRINCIPAL INVESTIGATOR(S): V.K. Sikka (423)574-5112, S. Viswanathan (423)576-6917, M.L. Santella (423)574-4805, R.W. Swindeman (423) 574-5108 and G. Aramayo (423)574-6503

PHASE OBJECTIVE: To promote the technology transfer of nickel-aluminide alloys in the broadest spectrum of industry possible.

ULTIMATE OBJECTIVE: To take advantage of excellent oxidation and carburization resistance and higher strength of nickel aluminides for a broad range of manufacturing-related industry applications. The applications identified to date include: furnace furniture (trays, fixtures, transfer rolls, belts, conveyors) and hot-pressing or forging dies.

TECHNICAL APPROACH: Since castings are most likely near-term applications, the technical approach has been to address issues related to castings. These include: (1) optimization of high-strength castable composition; (2) castability (mold type, fluidity, hot-shortness, porosity, and solidification modeling); (3) weld repairability of castings, welding for component fabrication and weldment properties; and (4) workability of cast or powder metallurgy product to sheet, bar, and wire.

PROGRESS: The Exo-Melt™ process developed for melting of nickel-aluminide alloys was transferred to casting producers such as United Defense LP/FMC, Sandusky International, and Alloy Engineering & Casting Company. Since the transfer of the Exo-Melt™ technology, over 100,000 lb of the Ni_3Al-based alloy castings have been commercially sold. The mold fillings and solidifcation analysis completed for the base tray was extended to centrifugal castings. The base-metal chemistry was further refined to make it consistently weldable. The chemistry refinement included control of carbon, sulfur, silicon, and boron.

Patents: 1	**Publications:** 3	**Proceedings:** 7
Books: 1*	**Presentations:** 6	**Awards**: 1

*Book chapter, entitled "Oxidation and Corrosion of Intermetallic Alloys," in *Physical Metallurgy and Processing of Intermetallics*, authored by Gerhard Welsch and Pramod D. Desai, was published by CINDAS/Purdue University, West Lafayette, Indiana.

PROJECT SUMMARY (continued)

PROJECT TITLE: Ni_3Al Technology Transfer

ACCOMPLISHMENTS:

Licenses: Two additional licenses were given to United Technologies/FMC to melt, cast, and commercialize nickel aluminides. One was exclusive for dies and the other for foreign sales.

Other Successful Technology Transfer Activities as Evidence of Industry Interest: (1) Cast and supplied six batch-furnace trays and two pusher-furnace assemblies. Three of the batch-furnace trays and one of the pusher-furnace assemblies were supplied in the preoxidized condition (1100 °C exposure in air for 3 h). (2) Completed two years of commercial testing of transfer rolls in a steel company. (3) Completed testing of nickel-aluminide die for hammer forging application for 100,000 parts. To date, the die has exceeded the life of a currently used die material by a factor of ten.

CRITICAL ISSUES: Although significant progress was made during FY 1996, welding of nickel aluminides still continues to be a critical issue.

FUTURE PLANS: Continue Ni_3Al-based alloy technology transfer through solving technical issues, prototype manufacturing, and in-plant testing.

POTENTIAL PAYOFF: Nickel-aluminide components for a range of applications with major benefits of U.S. industry gaining the competitive position in the world. Industries benefiting from nickel-aluminide technology are automotive, steel, chemical, heat treating and forging, and manufacturing.

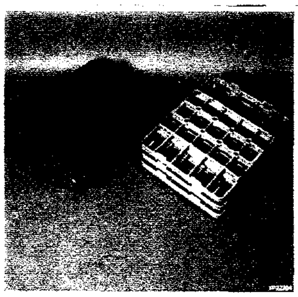
SIGNIFICANT ACCOMPLISHMENT

COMMERCIAL AVAILABILITY OF Ni_3Al-BASED ALLOY CASTINGS PAVES THE WAY FOR ITS BROAD-BASED INDUSTRIAL APPLICATIONS

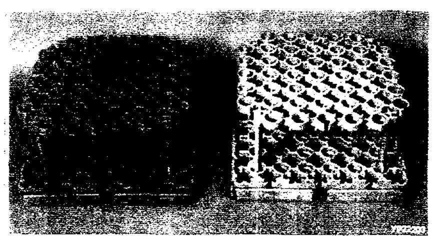
Advanced Industrial Materials (AIM) Program

ISSUE: Nickel-aluminide-based alloy castings offer superior combination of high-temperature strength and resistance to high-temperature oxidation, carburization, and chlorination. However, in spite of their excellent properties, the lack of commercial availability has been the main issue to their broad-based industrial applications.

RESULTS: The commercial availability issue has been addressed in five steps: (1) the development of a highly efficient and cost-effective process known as Exo-Melt™ for air melting nickel aluminides, (2) training staff of selected foundries on the Exo-Melt™ process, (3) providing the key property data needed for potential applications, (4) working closely with users of the casting under commercial operating conditions, and (5) working closely with suppliers of castings such as United Defense LP/FMC, Sandusky International, and Alloy Engineering & Casting Company. The outcome of these activities have resulted in cast components shown in the figure below. Over 100z000 lb of nickel aluminide were sold during FY 1996.

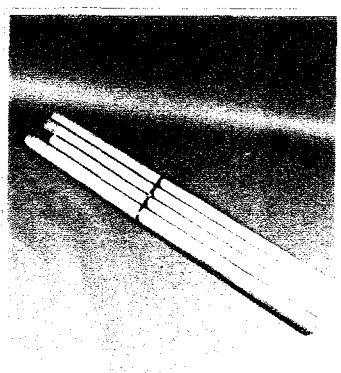


Batch Furnace Trays



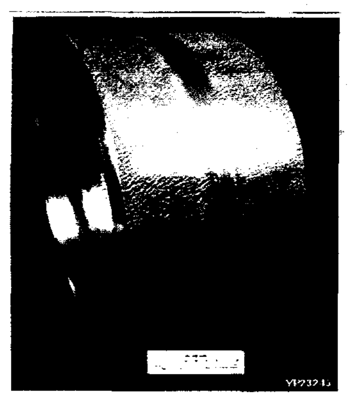
Pusher Furnace Assemblies

Return Bends



Radiant Burner Tubes

Roll Trunnion



Welded Roll Rings

ENERGY EFFICIENCY: The Exo-Melt™ process saves 50% of energy required to melt nickel aluminide as opposed to the conventional melting process. The use of nickel aluminide for dies with approximately ten times the life of conventional alloys, with furnace fixture life improvements by three to five times, and similar improvements in chemical industry applications result in substantial savings in energy by not having to melt significant quantities of the conventional alloys.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-960R22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Synthesis and Design of Silicide Intermetallic Materials

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Los Alamos National Laboratory (LANL)

PRINCIPAL INVESTIGATOR(S): J.J. Petrovic (505)667-0125, R.G. Castro (505)667-5191

PHASE OBJECTIVE: Conduct CRADA with Schuller International on $MoSi_2$ materials for fiberglass processing components. Development and characterization of $MoSi_2$-Si_3N_4 and $MoSi_2$-SiC composites, the plasma spraying of $MoSi_2$-based materials, and the joining of $MoSi_2$ materials to metals.

ULTIMATE OBJECTIVE: To develop $MoSi_2$-based high temperature structural silicide materials with optimum combinations of properties for applications of importance to U.S. processing industries, and particularly the glass processing industry.

TECHNICAL APPROACH: Develop $MoSi_2$-based high temperature structural materials, with focus on $MoSi_2$-Si_3N_4, $MoSi_2$-SiC, and $MoSi_2$-oxide composites. Develop processing methods for $MoSi_2$-based materials, with emphasis on plasma spraying and plasma spray forming. Develop $MoSi_2$-based prototype fiberglass processing components.

PROGRESS: CRADA No. LA95C10271-A001 "Advanced High Temperature Materials for Glass Applications" with Schuller International Inc. was formally executed on 19 March 1996. This is a three-year CRADA targeted at the area of $MoSi_2$-based high temperature materials and components for fiberglass melting and processing applications.

Patents:		**Publications:**	12	**Proceedings:**	3
Books:		**Presentations:**	5	**Awards:**	2

ACCOMPLISHMENTS: The plasma spray processing parameters for $MoSi_2$ spraying have been examined in detail, in order to optimize the quality of plasma sprayed coatings and plasma-spray formed materials. Residual stresses in plasma-spray formed $MoSi_2$ tubes have been measured and modeled. $MoSi_2$-Si_3N_4 and $MoSi_2$-SiC powders from the Exotherm Corporation have been characterized and the indentation creep properties of composites formed from these powders determined. $MoSi_2$ has been joined to stainless steel using Nb and Ni interlayers, and to itself using an Al braze.

PROJECT SUMMARY (continued)

PROJECT TITLE: Synthesis and Design of Silicide Intermetallic Materials

CRITICAL ISSUES: Identification, fabrication, testing, and evaluation of $MoSi_2$-based materials for prototype fiberglass processing components in association with the CRADA with Schuller International.

FUTURE PLANS: We are working to develop an interaction with the Institute of Gas Technology (IGT), to develop $MoSi_2$-based materials for gas-fired radiant heaters that have significant applications in glass processing and heat treating furnace applications. We are developing the near-net-shape directed light fabrication approach for silicide materials.

POTENTIAL PAYOFF: The potential payoff for industrial applications of high temperature $MoSi_2$-based structural silicides is very high. Major industrial applications exist in the areas of glass and metal processing equipment, industrial gas burners and lances, furnace heating elements and radiant gas heaters, and high temperature industrial components. An environmental payoff also exists since $MoSi_2$-based radiant burners and heaters that can burn mixtures of pure oxygen and natural gas will reduce NO_x and CO_2 emissions.

ESTIMATED ENERGY SAVINGS: Potential energy savings of 0.2 Quads (1 Quad = 10^{15} btu) will occur from the use of $MoSi_2$-based materials in industrial applications.

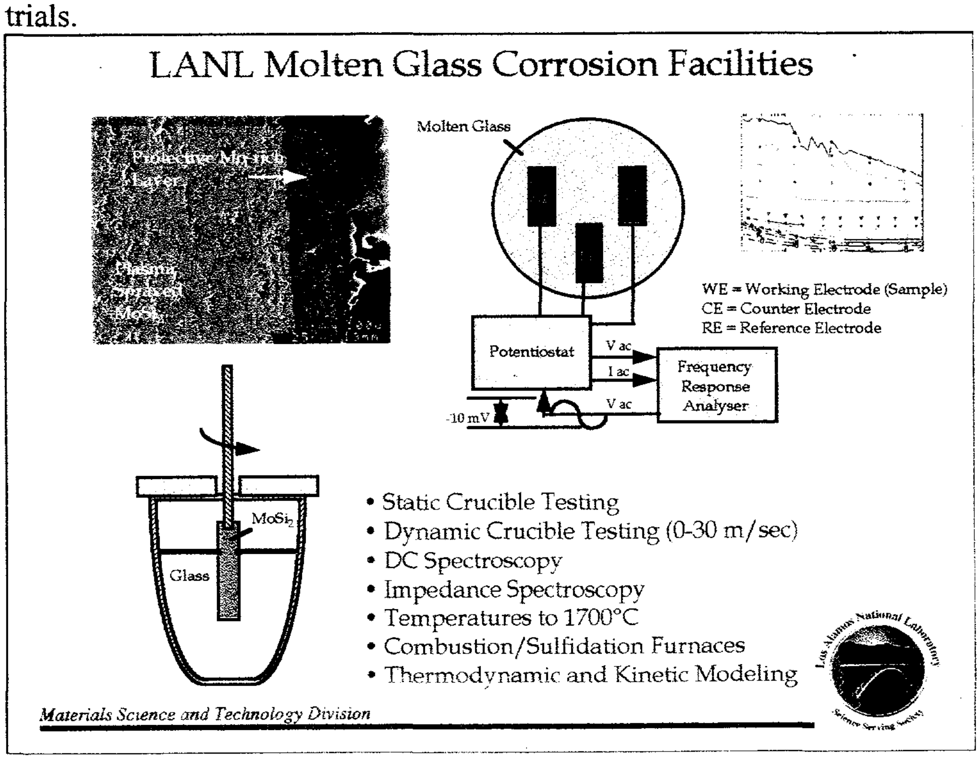
SIGNIFICANT ACCOMPLISHMENT

APPLICATION OF $MoSi_2$-BASED MATERIALS IN MOLTEN GLASS ENVIRONMENTS

Advanced Industrial Materials (AIM) Program

ISSUE: $MoSi_2$ is a candidate material for containment of and protection from molten glass. Understanding the rates and mechanisms of corrosion is key to the successful adoption of $MoSi_2$-based materials in industrial glass practices.

RESULTS: LANL has set up several new and made use of existing capabilities for evaluating the corrosion resistance of $MoSi_2$-based and other refractory materials under a variety of conditions relevant to the glass industry. These capabilities include static and dynamic glass testing as well as state-of-the-art electrochemical corrosion systems. It has been demonstrated that $MoSi_2$ shows great resistance to corrosion both below and above the glass line due to the formation of a protective Mo-rich layer and a highly viscous SiO_2 layer, respectively. Work is in progress to improve or mitigate the more rapid corrosion observed at the glass line. Components have been introduced into industrial field trials.



Research sponsored by the U.S. Department of Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program. It is being conducted at the Los Alamos National Laboratory.

SIGNIFICANT ACCOMPLISHMENT

NEAR-NET-SHAPE FABRICATION OF $MOSi_2$ COMPONENTS FOR GLASS APPLICATIONS

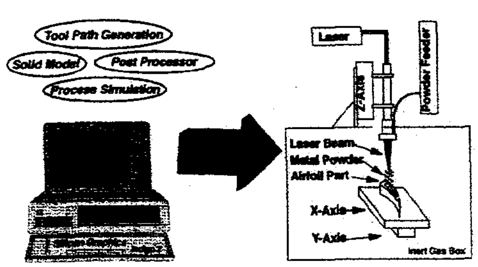
Advanced Industrial Materials (AIM) Program

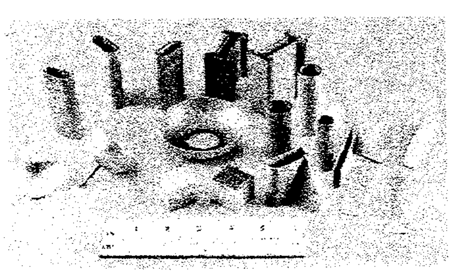
ISSUE: Near-net-shape processing of $MoSi_2$-based components for glass and heat-treating applications is being investigated using Directed Light Fabrication (DLF). Applications include burner nozzles, gas injection tubes, thermocouple tubes, gas ignitors and sensing elements.

RESULTS: The Directed Light Fabrication (DLF) process provides a one step fabrication of fully dense, near-net-shape $MoSi_2$-based components directly from supplied powders. $MoSi_2$ and other intermetallic components can be fabricated by first developing a solid model design using a commercial software package. From this design, a tool path is created, which directs a multi-axis position system. A laser beam, transmitted through beam delivery optics attached to the positioning system, scans the part cross-section while metal powder particles are fed into the laser focal spot where they melt and resolidify in a thin layer. Successive layers are stacked until the entire part is built. Wire and tube products of $MoSi_2$-based materials are currently being produced by this processing method.

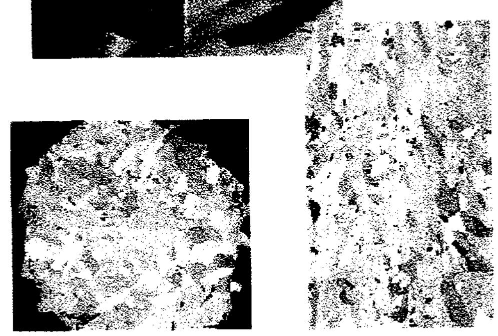
DLF- Directed Light Fabrication of $MoSi_2$

A directed metal deposition process that transforms a digital design into a 3-dimensional, fully dense, solid object





Various structures produced by DLF



Microstructure of DLF $MoSi_2$ wire and tube products

Research sponsored by the U.S. Department of Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program. Research being conducted at the Los Alamos National Laboratory.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

WORK ELEMENT: Powder and spray forming of high-temperature materials.

PROJECT TITLE: Uniform-Droplet Spray Forming

PHASE: FY: 1996 **PHASE COMPLETION DATE**:

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL), Massachusetts Institute of Technology, and Tuffs University

PRINCIPAL INVESTIGATOR(S): C.A. Blue (423) 574-4351, V. K. Sikka (423) 574-4351, J. H. Chun (617) 253-1759, and T. Ando (617) 628-5000 ext. 5163

PHASE OBJECTIVE: To translate the uniform-droplet spray-forming process to high-temperature materials (aluminides) and promote technology transfer of the process to the broadest spectrum of industry as possible.

ULTIMATE OBJECTIVE: To take advantage of the extremely uniform droplet and size distribution produced by the process for a broad range of manufacturing-related industrial applications. The applications identified to date include: ball-grid array (BGA) type integrated circuit (IC) packaging, water filtration systems (bronze), shot production, spray forming, ballbearing production, and powder production.

TECHNICAL APPROACH: Since many applications exist for uniform droplets of high-temperature materials, the technical approach has been to address issues relating to the development of a high-temperature uniform system. These include: (1) development of a low and medium temperature system to identify a potential high-temperature assembly, (2) determine the low and medium temperature optimum spraying conditions for materials with melting points between 230 and 1250°C, (3) verify size distribution and repeatability of droplets, (4) identify and resolve any problem encountered with the low and medium temperature systems, and (5) translate acquired knowledge to the construction of a high-temperature uniform-droplet system.

PROGRESS: The uniform-droplet program requires that three droplet heating systems, one for low-temperature metals (T_m<400°C), one for medium-temperature metals (T_m 400 to 1250°C), and one for high-temperature metals (T_m 1250 to 1650°C) be assembled. The fabrication of the low-temperature system provided a basis for the design of the medium-temperature unit. Construction of the low-, medium-, and high-temperature uniform-droplet systems at ORNL has been completed. Over 90 runs have been completed to date and further tailoring of these systems is ongoing. The tailoring of the system includes elimination of orifice clogging, large-diameter uniform-droplet formation (>750 μm), and proper charging of high-temperature materials. The large-diameter work was accomplished in line with the possible development of a new/additional funding source.

PROJECT SUMMARY (continued)

PROJECT TITLE: Uniform-Droplet Spray Forming

Preliminary Temperature System Results

All of the initial experimentation with the high-temperature system utilized aluminum, bronze,and copper as the materials of choice pending arrival of the high-temperature crucible.

High-Temperature System

The high-temperature apparatus has been assembled, and preliminary testing is in progress. This system has allowed for the fabrication of uniform droplet of materials with melting points as high as 1082°C. These materials include aluminum, bronze, and copper. Also, this system was designed for higher volume melts (15 to 20 lb, materials dependent). Therefore, this system will aid in the development of the uniform-droplet system for industrial practices. The successful and timely construction of both the low- and medium-temperature systems allowed the meeting of milestones and set the stage for designing and constructing the high-temperature system.

Patents: 0 **Publications: 2** **Proceedings: 0**
Presentations: 5

CRITICAL ISSUES: Orifice clogging, large-diameter bearing fabrication, and high-temperature charging of dropletts.

FUTURE PLAN: Continue acquiring knowledge through solving technical issues with the medium- and high-temperature uniform droplet. Apply the uniform-droplet system technology to near-net-shape fabrication of parts. Also, continue developing interest in the industrial sector, and transfer technology of the low-, medium-, and high-temperature systems.

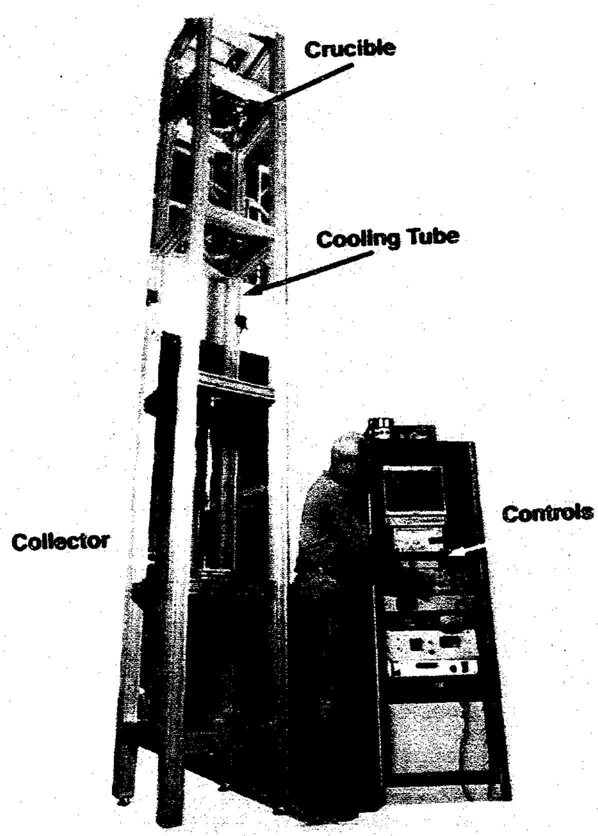
SIGNIFICANT ACCOMPLISHMENT

COMPLETED FABRICATION OF A MEDIUM-TEMPERATURE (1250tC) UNIFORM-DROPLET SPRAY SYSTEM

Advanced Industrial Materials (AIM) Program

ISSUE: A uniform-droplet spray (UDS) process has been developed at Massachusetts Institute of Technology, Northeastern University, and the Oak Ridge National Laboratory for spraying low-melting-point materials. However, the most potential for the UDS process is in the production of medium to higher melting temperature alloys.

RESULTS: Experience gained with the low-temperature (400°C) UDS system has been extended to the design and construction of a medium-temperature (1250°C) system shown below. The new system is essentially the same as the low-temperature system with the exception that it has a long droplet cooling tower, higher temperature crucible, and higher temperature furnace. The controls and video imaging equipment are the same for the medium-temperature system as that used for the low-temperature system. The new system has already been checked for making uniform-size powders of aluminum, copperphosphorus eutectic, and recently pure copper.



SIGNIFICANCE - FOR ENERGY CONSERVATION: The UDS process allows for fabrication of mono-sized powders near 100% yield which eliminates the sieving of powder as performed with present powder-forming technologies. The elimination of sieving translates into reduction of overall production cost through saving energy. This process can also be used for near-net shaping of complex shapes. It can also allow for formation of part from materials that are inherently difficult to machine and/or casts The scenario stated above demonstrates massive energy savings and the utilization of new materials.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-960R22464 with Lockheed Martin Energy Research Corporation.

ADVANCED CERAMICS AND COMPOSITES

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Advanced Methods for Processing Ceramics

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATOR: W.B. Carter, (404) 894-6762

PHASE OBJECTIVES: To deposit lanthanum phosphate via combustion chemical vapor deposition and produce modified thermal barrier coatings (TBCs) incorporating combustion CVD deposited interlayers between bond coat and ceramic.

ULTIMATE OBJECTIVE: To develop combustion chemical vapor deposition as an alternative coating process for industrial applications.

TECHNICAL APPROACH: Optimize the combustion chemical vapor deposition process for the deposition of oxide coatings by a systematic investigation of process parameter variation. Develop alternative combustion CVD variants utilizing various combinations of fuels, flames types, and reagent delivery schemes. Evaluate the performance of the coatings in systems such as TBCs using industrial tests.

PROGRESS: The combustion chemical vapor deposition of several potentially useful oxides was developed. These include lanthanum phosphate and magnesium-aluminum spinel. Theta phase alumina deposited via combustion CVD showed promise as an interlayer material in TBCs. Thermal barrier coatings incorporating the alumina interlayers and subjected to a vacuum anneal prior to ceramic deposition displayed thermal fatigue lifetimes over 60% longer than control specimens.

Patents: 1 Pending	**Publications:** 2 Theses	**Proceedings:** 2
Books:	**Presentations:** 5	**Awards:**

ACCOMPLISHMENTS:

Licenses: -
Known Follow-on Product(s): -
Industry Workshop: -
Technology Transfer or Industrial Interaction: Working with General Electric Power Generation on a DOE funded program to develop improved thermal barrier coatings for use in land based gas turbines. Collaborating with Allison Engine Company, and the South Carolina Energy Research & Development Center and Solar Turbines Incorporated in developing additional programs for thermal barrier coating research.

PROJECT SUMMARY (continued)

PROJECT TITLE: Advanced Methods for Processing Ceramics

CRITICAL ISSUES: Increasing the deposition rate and uniformly coating large, non-simple shaped surfaces as well as the many fibers in a tow are critical issues.

FUTURE PLANS: Continue work on fiber coatings and pursue applications in thermal barrier coatings with industrial partners.

POTENTIAL PAYOFF: Since coatings are ubiquitous in many areas of technology, the development of a less expensive, simpler, alternative coating process for specialized applications will have obvious benefits. Economic savings should result from the non-necessity of the furnaces and vacuum equipment associated with conventional CVD processing. The potential ability to easily coat certain types of substrates continuously, such as fibers, would also be advantageous.

ESTIMATED ENERGY SAVINGS: The combustion chemical vapor deposition process should reduce energy consumption by replacing conventional coating methods for certain applications. The elimination of furnace and vacuum hardware and their concomitant energy requirements should more than offset the consumption of inexpensive organic solvents and gases. Often, less expensive reagents can be used with combustion CVD than are required for conventional CVD processes. The substantially smaller capital investment anticipated for the combustion CVD process relative to conventional techniques will also entail less energy expenditure up front in equipment production. As the process is presently in the early stages of development and those applications to which it may ultimately be applied are uncertain, it is not possible to produce a quantitative estimate of potential energy savings.

OTHER SOURCES: *The U.S. Department of Energy's Advanced Gas Turbine Program and Georgia Tech

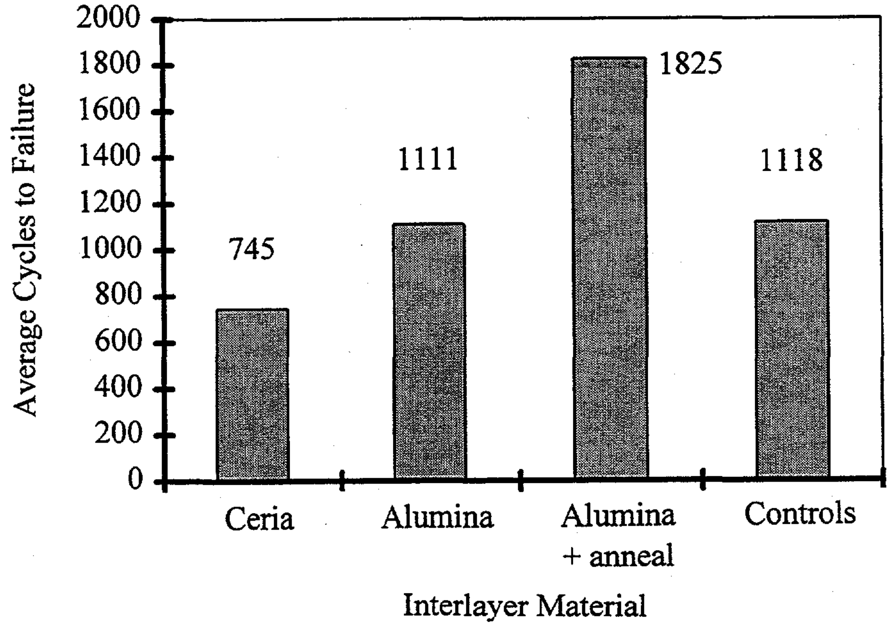
SIGNIFICANT ACCOMPLISHMENT

COMBUSTION CVD DEPOSITED INTERLAYERS SHOW PROMISE IN INCREASING THERMAL BARRIER COATING LIFETIMES

Advanced Industrial Materials (AIM) Program

ISSUE: Thermal barrier coatings (TBCs) are used to coat components in the hot sections of gas turbines. By maintaining a temperature differential as large as 150°C, TBCs allow for higher turbine operating temperatures (producing concomitant gains in thermodynamic efficiency) and/or prolonged component lifetimes. Thermal barrier coating performance often restricts the time between overhauls of gas turbines. Improved TBCs are needed to extend the operating lifetimes and efficiencies of gas turbines.

RESULTS: Combustion CVD coatings were incorporated into thermal barrier coatings and subjected to furnace cycle testing (FCT). Both ceria and theta alumina were deposited via combustion CVD directly onto NiCrAlY bond coated single crystal N5 substrates. Some of the alumina coated specimens were vacuum annealed for four hours at 1080°C. All specimens were then air plasma sprayed with 8 wt. % yttria stabilized zirconia. Control and modified TBC specimens were furnace cycle tested in air to 1093°C. The figure below displays the FCT results.



ENERGY EFFICIENCY: Improved thermal barrier coatings that can withstand higher temperatures will allow gas turbines to operate at increased temperatures resulting in increased thermodynamic efficiencies. The use of combustion CVD to produce modified TBCs should yield significant energy savings over alternative coating processes.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-84OR21400 with Lockheed Martin Energy Research Corporation and by the U.S. Department of Energy, Morgantown Energy Technology Center, Cooperative Agreement No. DE-FC21-92MC29061.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Characterization of Three-Way Automotive Catalysts

PHASE: FY 1996 **COMPLETION DATE:** FY 1996

PERFORMING ORGANIZATIONS: Lockheed Martin Energy Research (LMER) and Delphi Automotive Systems (formerly General Motors - AC Delco Systems)

PRINCIPAL INVESTIGATORS: E. A.. Kenik (423) 574-5066 and W. LaBarge (313) 257-0875

PHASE OBJECTIVE: Characterization of microstructural and chemical state of noble metals (Pt, Rh, Pd), washcoat oxides, and interactions between the catalyst and catalyst support materials. Correlate catalyst structure for advanced catalyst formulations under poisoning conditions with conversion efficiencies and degradation under engine dynamometer ageing.

ULTIMATE OBJECTIVE: Critically evaluate catalytic materials in as-produced and aged conditions and correlate materials and systems developments to improve catalyst performance and lifetime while decreasing emissions.

TECHNICAL APPROACH: Characterize the microstructural and chemical state of both noble metals and substrate in as-produced catalyst materials with a wide range of techniques. Compare to that of materials aged in either test stands or operating vehicles. Correlate observed evolution of microstructural and chemical state of catalyst material with changes in catalytic performance. Identify manufacturing processes which produce optimum catalyst performance and lifetime.

PROGRESS: Characterization of as-prepared and both vehicle- and dynamometer-aged materials has identified several levels of microstructural evolution during ageing of catalytic convertors. Several microstructural changes have been identified which contribute to the deactivation of the catalyst during ageing, including sintering and transformation/growth of washcoat component oxide phases, growth of the precious metal clusters (PMCs), and encapsulation of both ceria and PMCs by sintering and growing washcoat oxide phases and by poison element reaction layers.

Patents: Pending **Publications:** 3 **Proceedings:**
Presentations: 19

ACCOMPLISHMENTS:

Known Follow-on Product: CRADA aimed at improving performance and lifetime of catalytic convertors and reducing emissions.

Technology Transfer or Industrial Interaction: Joint research between Delphi and LMER under CRADA No. ORNL92-0115.

PROJECT SUMMARY (continued)

PROJECT TITLE: Characterization of Three-Way Automotive Catalysts

CRITICAL ISSUES: 1) Relation of microstructural and chemical state of catalyst and substrate to the performance, lifetime, and emissions of the catalytic convertor. 2) Can manufacturing processes be optimized to produce catalytic convertor with improved performance, lifetime, and/or cost? 3) Do advanced catalyst formulations resist degradations observed in earlier formulations. The noble metals and ceria are expensive and critical materials. Can their utilization in catalytic convertors be improved with resultant material conservation and lower cost?

POTENTIAL PAYOFF: CRADA goals of improved performance for catalytic convertors would permit U.S. automobile manufacturer to meet stronger emission and lifetime regulations and could reduce weight of emission system and thereby improve automobile fuel economy. Improved utilization of critical materials would reduce consumption, wastage, and recycling costs.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Chemical Vapor Infiltration of TiB_2 Fibrous Composites

PHASE: FY 1996 **COMPLETION DATE:** FY 1996

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR: Theodore M. Besmann, 423/574-6852

PHASE OBJECTIVE: Efforts this period were devoted to scaling up the process and providing demonstration composite plates to Alcoa for evaluation.

ULTIMATE OBJECTIVE: This program is designed to develop a Hall-Heroult aluminum smelting cathode with substantially improved properties at competitive costs.

TECHNICAL APPROACH: The current work is designed to develop a Hall-Heroult aluminum smelting cathode with substantially improved properties. It is suggested that a fiber reinforced-TiB_2 matrix composite by chemical vapor infiltration (CVI) would have the requisite wettability, strength, strain-to-failure, cost, and lifetime to solve this problem. The overall program is designed to evaluate potential fiber reinforcements, fabricate test specimens, and test the materials in a static bath, lab-scale Hall cell, and pilot-scale facilities.

PROGRESS: Bench-scale testing of a section of the 8x8 inch disk provided to the Alcoa Technical Center revealed excellent electrical, wetting, and aluminum production capability. Problems arose from the delamination of the composite, indicating inadequate interlaminar shear strength. To solve this problem multidimensional preforms were investigated and were procured for fabricating scale-up samples for Alcoa. Continued failures prompted a microprobe study of the a polished cross-section of composite which indicated that there was a slight excess of titanium in the TiB_2. This may be the cause of the poor stability.

Patents:	**Publications:**	**Proceedings:**
Books:	**Presentations:** 1	**Awards:**

ACCOMPLISHMENTS:

Licenses: License no. 128
Known Follow-on Product(s):
Industry Workshop:
Technology Transfer or Industrial Interaction: Continued interaction with Alcoa.

PROJECT SUMMARY (continued)

PROJECT TITLE: Chemical Vapor Infiltration of TiB_2 Fibrous Composites

CRITICAL ISSUES: Alcoa Technical Center has ceased testing of small-scale specimens and now requires large plates for testing.

FUTURE PLANS: Project terminated

POTENTIAL PAYOFF: Low cost, high efficiency inert cathode for aluminum smelting.

ESTIMATED ENERGY SAVINGS: Between 10% and 18% of the power consumed in aluminum reduction (0.75 and 1.35×10^{10} kWhr/y) could be saved by the use of TiB_2 electrodes.

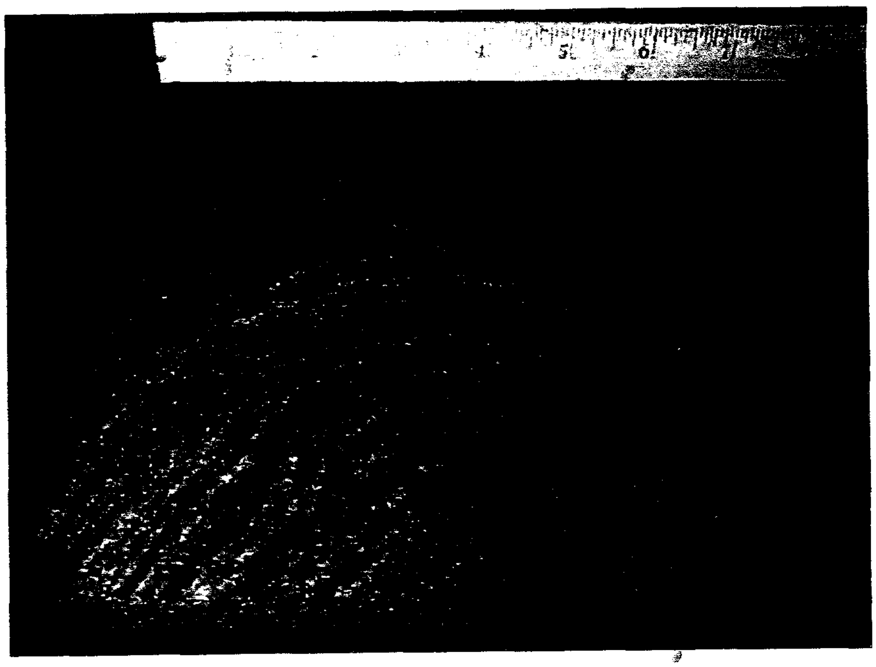
SIGNIFICANT ACCOMPLISHMENT

CHEMICAL VAPOR INFILTRATION OF TiB_2 FIBROUS COMPOSITES

Advanced Industrial Materials (AIM) Program

ISSUE: Delamination of the composite in molten aluminum.

RESULTS: Use of three-dimensional weave and non-woven preforms attempted to solve the problem. The preforms, due to geometrical considerations were difficult to infiltrate. This is being addressed via a modeling exercise.



Carbon-bonded, carbon fiber preform (non-woven) for infiltration by TiB_2.

ENERGY EFFICIENCY: Between 10% and 18% of the power consumed in aluminum reduction (0.75 and 1.35×10^{10} kWhr/y) could be saved by the use of TiB_2 electrodes.

Research sponsored by the U. S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-ACo5-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Development of High Toughness, High Strength Aluminide-Bonded Carbide Ceramics

PHASE: FY 1996

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR: Paul F. Becher, (423) 574-5157

PHASE OBJECTIVE: The development of 'near-net shape' fabrication routes for inter-metallic bonded carbides, continued assessment of properties, and collaborations with industry on their application

ULTIMATE OBJECTIVE: This program is designed to develop a range of wear resistant composite materials that can be employed in applications requiring good corrosion resistance and the retention of high strength at elevated temperatures (1000 °C).

TECHNICAL APPROACH: The present program was initiated to develop new composite materials to replace WC/Co in environments were corrosion or application temperature was a problem. Direct substitution of the ductile intermetallic Ni_3Al for Co was suggested to overcome both of these limitations. Initial observations on hot-pressed WC/Ni_3Al and TiC/Ni_3Al composites demonstrated that this hypothesis was sound, with an order of magnitude improvement in corrosion resistance in acidic environments noted over WC/Co composites, and high strengths that are retained to elevated temperatures (~ 1.4 GPa at ~ 1000 °C). In addition these new materials exhibit similar toughness and strength values to WC/Co. In addition, the use of Ti-based carbide and boride matrices allow composites with lower theoretical densities to be developed. The overall aim of the program further encompasses the development of industrially viable processing techniques for these new composite materials, as well as assessing the effects of further refinement of the Ni_3Al alloy composition upon mechanical behavior.

PROGRESS: Both reaction sintering and melt-infiltration processes were developed to fabricate near-net shaped components. In addition, these composites can be machined using more economical electrical discharge machining (EDM) methods. The mechanical and thermal properties are comparable to those of commercial WC-Co systems while the oxidation and acidic corrosion resistances are superior.

Patents: 2 **Publications:** 9 **Proceedings:** 7
Presentations: 8 **Invention Disclosures:** 2 **Awards:**

PROJECT SUMMARY (continued)

PROJECT TITLE: Development of High Toughness, High Strength Aluminide-Bonded Carbide Ceramics

ACCOMPLISHMENTS:

Licenses: None

Industrial Interactions: Numerous discussions held with representatives of metal forming and working, deep drilling, and petrochemical industries. Composite samples have been prepared for evaluation as extrusion dies for aluminum tubing by Reynolds Metals, in wear applications by Cummins Engines, in wear/drill applications by Kennametal, Latrobe, PA; and by Thixomat for evaluation in liquid aluminum environments.

CRITICAL ISSUES: None

FUTURE PLANS: Continue industrial interactions

POTENTIAL PAYOFF: The ability to employ these materials at elevated temperatures and in agressive chemical environments offer considerable payoff in increased productivity in metal forming/working and petrochemical industries.

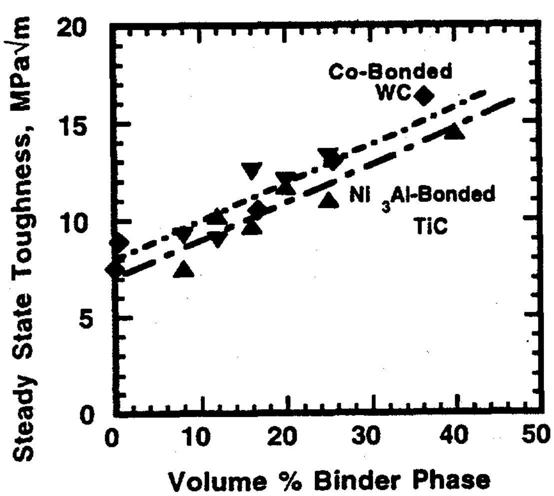
SIGNIFICANT ACCOMPLISHMENT

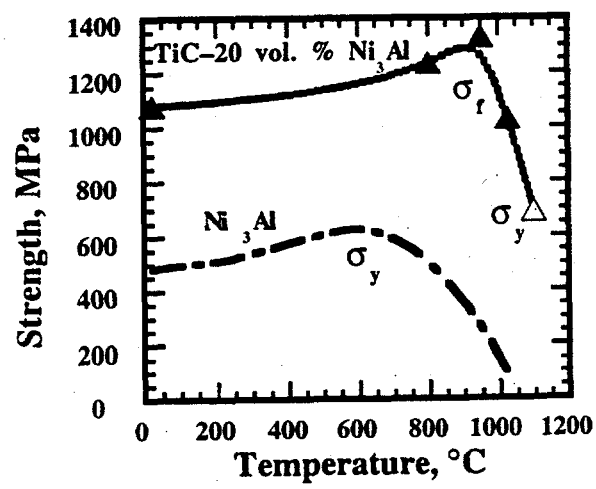
HIGH TOUGHNESS, HIGH STRENGTH ALUMINIDE BONDED CARBIDE CERAMIC COMPOSITES

Advanced Industrial Materials (AIM) Program

ISSUE: Cobalt bonded 'cemented carbides' (e.g., WC or TiC) are widely used in applications where resistance to abrasion and wear are important (particularly in combination with high strength and stiffness) particularly in the chemical, petrochemical, and deep well drilling industries. However, these materials often exhibit poor resistance to oxidation and aqueous/acidic corrosion, and also a reduction in strength at elevated temperatures.

RESULTS: The substitution of the ductile intermetallics, e.g. nickel or iron aluminides (Ni_3Al, FeAl), for cobalt as a binder phase for carbides, borides, and nitrides offers exciting improvements. For instance, the resistance to acidic corrosion and to oxidation is improved, and their high fracture strengths (> 1 GPa) are retained at temperatures 1000 °C. In addition, their fracture toughness values are comparable to those of commercial cobalt-bonded carbides. The thermal expansion coefficients can also be tailored (ranging from ~ 7 to 15 x 10^{-6}/ °C) depending on composition. Finally, they can be fabricated by either melt-infiltration or reaction sintering and exhibit good electrical conductivity allowing them to be machined by electrical discharge machining (EDM) processes.





Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Gelcasting Polycrystalline Alumina

PHASE: FY 1996 **COMPLETION DATE:** FY 1998

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL)

PRINCIPAL INVESTIGATOR(S): Mark A. Janney, 423-574-4281

PHASE OBJECTIVE: Develop gelcasting of optical grade alumina for lamp applications

ULTIMATE OBJECTIVE: The purpose of the CRADA with Osram-Sylvania Inc. is to determine the feasibility of making polycrystalline alumina items having sufficient optical quality that they are useful in lighting applications using gelcasting.

TECHNICAL APPROACH: Gelcasting is an advanced powder forming process. It is most commonly used to form ceramic or metal powders into complex, near-net shapes. Turbine rotors, gears, nozzles, and crucibles have been successfully gelcast in silicon nitride, alumina, nickel-based superalloy, and several steels.

Osram-Sylvania would like to explore using gelcasting to form PCA tubes for Lumalux® lamps, and eventually for metal halide lamps (known as quartz-halogen lamps). Osram-Sylvania, Inc. currently manufactures PCA tubes by isostatic pressing. This process works well for the shapes that they presently use. However, there are several types of tubes that are either difficult or impossible to make by isostatic pressing. It is the desire to make these new shapes and sizes of tubes that has prompted Osram-Sylvania's interest in gelcasting.

PROGRESS: A series of gelcasting slurries was made using Osram-Sylvania proprietary powders. These were cast into thin-walled tubes, dried and fired. The optical properties of the fired gelcast parts was deemed acceptable for lamp applications. An extensive study of slurry-mold-mold release agents was conducted to determine the combination best suited to this gelcasting application.

Patents: -	**Publications:** -	**Proceedings:** -
Books: -	**Presentations:** -	**Awards:** -

PROJECT SUMMARY (continued)

PROJECT TITLE: Gelcasting Polycrystalline Alumina

ACCOMPLISHMENTS:

Licenses: -

Technology Transfer or Industrial Interaction: Osram-Sylvania is actively pursuing applications of gelcast tubes to their product line.

CRITICAL ISSUES: Developing a manufacturing line from successful laboratory tests will be critical to the successful transfer of this technology. Also, development of methods to make complex-shaped tubes needs to be demonstrated.

FUTURE PLANS: Develop gelcasting systems appropriate for thin-walled, complex shaped tubes.

POTENTIAL PAYOFF: Gelcasting could eliminate several geometric constraints on the manufacture of arc tubes. Potential increases in lighting efficiency of 3% are predicted.

SIGNIFICANT ACCOMPLISHEMENT

GELCASTING POLYCRYSTALLINE ALUMINA FOR HIGH PRESSURE SODIUM ARC LAMPS

Advanced Industrial Materials (AIM) Program

ISSUE: High-pressure sodium vapor arc lamps are used for industrial, highway, and street lighting. The key to the performance of these lamps is the polycrystalline alumina (PCA) tube that is used to contain the plasma that is formed in the electric arc. Currently, there are severe shape limitations on the alumina tubes. Gelcasting tubes should eliminate most of the geometric constraints on fabricating lamp tubes. Successful completion of the work done under this cooperative research and development agreement (CRADA) with Osram-Sylvania Inc. could result in a new family of energy-saving lamps. Lighting efficiency increases up to 3% are predicted

RESULTS: We have formulated slurries at 45 to 50 vol % solids using standard gelcasting formulations based on methacrylamide monomer and methylene bisacrylamide crosslinker. These slurries were made using proprietary powders supplied by OSI. Good flow behavior was achieved; viscosities were on the order of 200 cps.

The slurries were successfully cast as thin-walled tubes (0.3 inch OD, 0.020 inch wall, 2 inch long) in molds supplied by OSI. The tubes were fired using a standard schedule and produced translucent material

Research sponsored by the U.S. Department of Energy, Assistnat Secretary for Energy Efficiency and Renewable Energy, Office of industrial Technologies, Advanced Industrial Materials Program, under contract DE-ACOR-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Membrane Systems for Energy Efficient Separation of Light Gases

PHASE: FY 1996

PERFORMING ORGANIZATION(S): Los Alamos National Laboratory

PRINCIPAL INVESTIGATOR(S): David J. Devlin (505) 667-9914

PHASE OBJECTIVE: Development of a process based on vapor deposition techniques for the fabrication of membrane systems for light gas separation.

ULTIMATE OBJECTIVE: Development of a membrane system suitable for operation in a pilot scale system for the separation of C1 to C4 hydrocarbons from hydrogen.

TECHNICAL APPROACH: The technical approach involves the use of vapor deposition techniques to tailor pore size and shape in porous substrates. The pore properties will be engineered to effect capillary condensation of hydrocarbons near ambient temperatures and pressures less than 250 psig.

PROGRESS: A method for developing carbon pores for capillary condensation of hydrocarbons has been devised. Experiments demonstrate the feasibility of oblique angle vapor deposition as a means producing the desired pore structure. A joint work statement with Amoco was prepared and approved by the DOE. The CRADA has been reviewed by Amoco's legal department and has requested minor changes. These are now being processed and we expect to have the CRADA in place by January of 96.

ACCOMPLISHMENTS:

Technology Transfer or Industrial Interaction: This effort will continue in 1996 as a joint research effort with Amoco's Olefins R&D group. Amoco will develop characterization capabilities and design criteria for the membrane systems. With their guidance we will develop the materials and processing for the fabrication of these of membranes. Amoco's goal is a materials system capable of scaling for use in a pilot plant system.

PROJECT SUMMARY (continued)

PROJECT TITLE: Membrane Systems for Energy Efficient Separation of Light Gases

CRITICAL ISSUES: The precise control of pore structure in membrane materials.

FUTURE PLANS: Development of materials by vapor deposition techniques with engineered pore size and shape. Characterization and performance testing of developed materials by Amoco Olefins R&D.

POTENTIAL PAYOFF: There are important benefits that will result from the success of the proposed CRADA effort. The US. hydrocarbon industry has experienced a loss in competitiveness over the last decade that has resulted in the loss of nearly 500,000 jobs and has severely affected the US. balance of trade. Improvements in hydrocarbon-light gas separation processes represent the largest area for potential cost reductions for the entire hydrocarbon industry that includes natural gas processing, oil refining, and petrochemicals. For example, new grass-roots olefins units cost upward of $750 million; the separation section accounts for approximately 75% of this capital investment. Because of the high capital costs and market competitiveness, US. olefins producers have relied on de bottlenecking of existing units to meet capacity increases required to maintain market share. Shortly, these activities will not be feasible because of compressor train capacity limitations. Non-cryogenic breakthrough technologies for separating light gas byproducts from olefinic mixtures could lead to inexpensive capacity increases of 50%; this would significantly reduce manufacturing costs and promote industry growth. Also, the development of energy-efficient gas separation processes will have a positive impact on the environment. Lower energy consumption translates into less fuel burning to generate power resulting in a significant reduction in flue gas pollutants such as hazardous nitrogen and carbon oxides. Reducing pollutants is critical in the major industrial regions that have become non-attainment areas based on the National Ambient Air Quality Standards. Growth and job creation in these regions are dependent on reducing these emissions. Lower energy consumption would create the opportunity to expand and still meet the environmental guidelines while lessening the US. dependence on energy imports.

ESTIMATED ENERGY SAVINGS: Initial economic analyses have shown that the commercialization of this novel separation concept could result in an energy reduction potential of 5 trillion BTUs per year for an olefins complex: this corresponds to a potential annual savings of nearly $8 million.

SIGNIFICANT ACCOMPLISHMENT

MEMBRANE SYSTEMS FOR ENERGY EFFICIENT SEPARATION OF LIGHT GASES

Advanced Industrial Materials (AIM) Program

ISSUE: Ethylene and propylene are two of the largest commodity chemicals in the US. and are major building blocks for the petrochemicals industry. These olefins are separated currently by cryogenic distillation which demands extremely low temperatures and high pressures. Over 75 billion pounds of ethylene and propylene are distilled annually in the United States at an estimated energy requirement of 400 trillion BTU's. Non-domestic olefin producers are rapidly constructing state-of-the-art plants. These energy-efficient plants are competing with an aging US. olefins industry in which 75% of the olefins producers are practicing technology that is over twenty years old. New separation opportunities are therefore needed to continually reduce energy consumption and remain competitive.

RESULTS: We have shown that oblique angle vapor deposition techniques can be used to reduce pore size and tailor the shape of pores. The precise control of both pore size and shape is critical to the development of separation processes based on capillary condensation. Working with Amoco we are developing materials to separate C2 to C4 hydrocarbons from hydrogen at near ambient temperatures and low pressures.

ENERGY EFFICIENCY: Initial economic analyses have shown that the commercialization of this novel separation concept could result in an energy reduction potential of 5 trillion BTUs per year for an olefins complex: this corresponds to a potential annual savings of nearly $8 million.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program. Research and development performed at the Los Alamos National Laboratory (LANL), Los Alamos, New Mexico.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Process Simulation for Advanced Composites Production

PHASE: FY 1996

PERFORMING ORGANIZATION(S): Sandia National Laboratories, Livermore, California

PRINCIPAL INVESTIGATOR(S): Mark D. Allendorf (510)294-2895

PHASE OBJECTIVE: To develop predictive computational models, process-control algorithms, and sensors for designing, optimizing, and operating coating processes for depositing boron nitride (BN) layers on continuous fiber ceramic composites (CFCCs). Optimization and scale-up of new BN deposition processes is of great interest due to the effectiveness of this material as a interfacial (debonding) layer in the manufacturing of CFCCs.

ULTIMATE OBJECTIVE: To reduce the costs of ceramic composites so that they can be applied more widely to corrosion, wear, and high-temperature problems in industrial settings.

TECHNICAL APPROACH: Industrial methods for the production of ceramics materials are simulated using a high-temperature, variable-pressure flow reactor constructed as part of this project. The reactor provides an environment in which process parameters such as temperature, pressure, chemical composition, and reactant mass flow rates are tightly controlled. In addition, access for mass spectrometric sampling and laser diagnostics is provided. Parallel development of computational models of physical and chemical mechanisms of deposition is conducted. Experimental data provide insight into the mechanism controlling deposition rates and deposit properties and are also used to test and verify the computational models. Ultimately, new reactor designs may be developed and optimized over broad parameter ranges using such models.

PROGRESS:

- Developed a model to predict deposition of BN layers on ceramic-fiber preforms. The model accounts for all relevant transport phenomena as well as gas-phase and surface chemical reactions and predicts BN growth rates as a function of reactor temperature, pressure, reactant concentration, and preform geometry.
- Verified model predictions by using scanning electron microscopy to measure BN coating thicknesses on sample preforms provided by DuPont Lanxide Composites (Newark, DE). Samples covering factors of two in operating pressure, temperatures, reactor size, and preform thickness were examined. The model is in excellent agreement with experiment in all cases, giving confidence that the model can be used to suggest strategies for process optimization.

PROJECT SUMMARY (continued)

PROJECT TITLE: Proces Simulation for Advanced Composites Production

PROGRESS (continued):

- Characterized gas-phase and surface processes occurring during the deposition of BN. Data provide new insight into the temperature, pressure, and concentration dependence of BN formation rates. Results of the investigation are being incorporated into the preform coating model to improve the accuracy of predictions and expand the generality of the model.

Patents: none **Publications:** 6 **Presentations:** 6

ACCOMPLISHMENTS

- **Technology Transfer:** A three-year, $1.06 M CRADA was signed with Libbey Owens Ford Co. (LOF) of Toledo, OH, to begin Oct. 1, 1996 (including $540 K of direct and in-kind funding from LOF). Project goals are to obtain kinetic data and design computer models needed to develop new processes for manufacturing of energy-efficient coatings on float-glass.

CRITICAL ISSUES: The costs of ceramic composite materials are currently too high to permit widespread use in industrial settings. One way to reduce these costs is to reduce the time required to develop, optimize, and scale up new processes for producing ceramic composites. Computational models that predict deposition rates and deposit composition, if they were available, would be invaluable tools in this process. Research during FY96 resulted in an experimentally verified process model that simulates BN formation in chemical vapor deposition processes used to coat ceramic-fiber preforms. Application of this model is already providing insights into coating process operation that would be difficult and expensive to obtain through experiments.

FUTURE PLANS: Research efforts in the immediate future (FY97) will be directed toward application of the process model developed in FY96 to the fiber-preform coating process used commercially by DuPont Lanxide Composites Inc. (DLC). Experimental and modeling investigations will continue to be conducted at Sandia during this phase of the project. A PC version of the model will be constructed in FY97, which will be licensed to DLC for direct use by their process engineers. In addition to ongoing model development, candidates for process-control sensors will be examined this year. A non-disclosure agreement between Sandia and DLC is in place; a CRADA is presently under negotiation.

POTENTIAL PAYOFF: Use of the computational models developed here is expected to shorten the time required to design, optimize, and scale up new fiber-coating processes and to facilitate extension of existing technology to new materials. Since these processes contribute as much as 40% of the manufacturing cost of CFCCs, improvements in their efficiency will have a significant impact on the cost of CFCCs. For example, predictions by manufacturers suggest that a 50% increase in reactor yield will lead to a factor of three to four reduction in CFCC manufacturing costs.

PROJECT SUMMARY (continued)

PROJECT TITLE: Process Simulation for Advanced Composites Production

OTHER SOURCES: Additional funding was received in FY96 from the Sandia Laboratory Directed Research and Development Program to develop process models for titanium nitride thin films and coatings.

ESTIMATED ENERGY SAVINGS: Energy benefits associated with widespread use of CFCCs are large. Examples include: up to 0.52 Quads/year in gas turbines, 0.5 Quads/year in high-pressure heat exchangers, 0.1 Quads/year in hot-gas cleaning systems, and 0.5 quads/year in radiant burners used in the metals and glass industries.

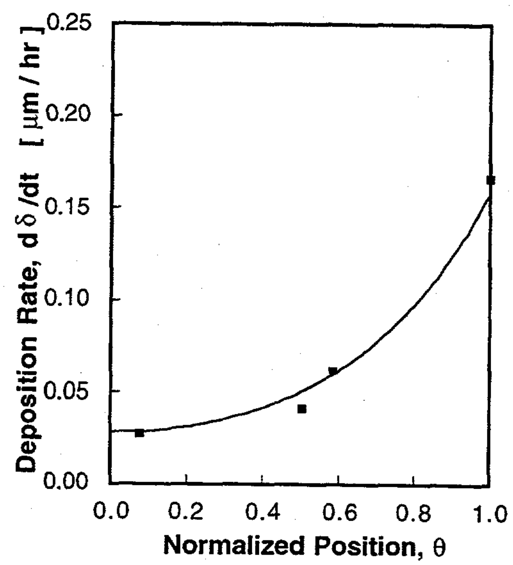
SIGNIFICANT ACCOMPLISHMENT

COMPUTATIONAL MODEL PREDICTS THICKNESS AND UNIFORMITY OF FIBER COATINGS USED IN CFCC MANUFACTURING

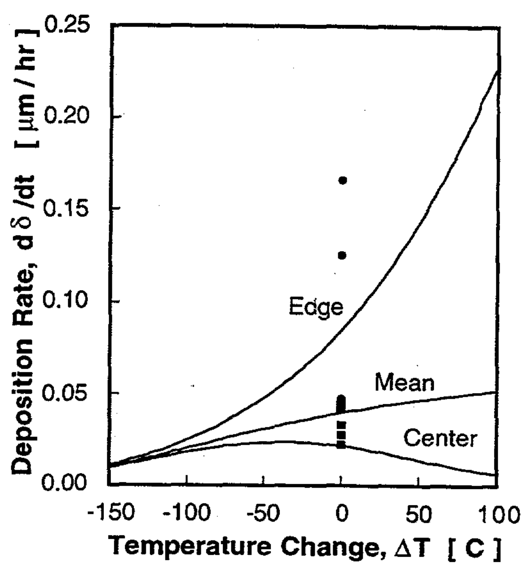
Advanced Industrial Materials (AIM) Program

PROBLEM: Coatings such as boron nitride (BN) and graphite are deposited on fiber preforms used to make continuous fiber ceramic composites (CFCCs), providing a debond layer that allows fibers to pull out from the matrix under load. Coating processes contribute as much as 40% of CFCC manufacturing costs, providing a driving force for improving their operating efficiency.

RESULTS: A computational model of preform infiltration that accounts for all relevant transport processes as well as gas-phase and surface chemical reactions was used to predict BN coating rates and thickness profiles. To verify model predictions, BN thicknesses as a function of depth within a preform were measured on samples provided by DuPont Lanxide Composites (DLC). Comparisons over a range of pressures, temperatures, reactant flow rates, and preform thicknesses show that the model accurately predicts both thickness and uniformity as a function of location within the preform. The model is now being used by DLC to optimize its reactor conditions.



BN growth rate as a function of normalized position within the part. $\theta = 0$: part center; $\theta = 1$: part outside surface. Points represent the average of several measurements; the curve is the model prediction.



Deposition rate as a function of temperature relative to current operating conditions.($\Delta T = 0$). Circles: measurements made at the outside surface of a part; Squares: measurements at the center of a part. Curves: model predictions of thickness profiles at the part edge, mean, and center position.

SIGNIFICANT ACCOMPLISHMENT (continued)

COMPUTATIONAL MODEL PREDICTS THICKNESS AND UNIFORMITY OF FIBER COATINGS USED IN CFCC MANUFACTURING

SIGNIFICANCE - FOR ENERGY CONSERVATION: The energy efficiency of many industrial processes is limited by the materials exposed to heat and corrosive environments. CFCCs can withstand higher temperatures and more hostile environments than existing alloys, permitting manufacturing operations that employ gas turbine power generators, high-pressure heat exchangers, and radiant fire tubes, which are common in energy-intensive industries such as paper and glass manufacturing, to operate in more efficient regimes.

SIGNIFICANCE - FOR MATERIALS TECHNOLOGY: Achievement of high strength in CFCCs requires accurate control of fiber debond layer thickness and microstructure. However, the complexity of manufacturing processes used to deposit these layers makes it very difficult to obtain the necessary level of control and reproducibility. The model developed here predicts effects of changing process variables on thickness and uniformity, minimizing the need for expensive batteries of experiments and allowing coating processes to be developed far more rapidly.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program. Research and development performed at the Sandia National Laboratories, Livermore, California.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Synthesis and Processing of Composites by Reactive Metal Penetration

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Lead Organization: Sandia National Laboratories(SNL) Subcontractors: University of New Mexico (UNM), New Mexico Institute of Mining and Technology (NMIMT), and SRI International (SRI).

PRINCIPAL INVESTIGATOR(S): Ronald E. Loehman (SNL: 505-272-7601), Kevin G. Ewsuk (SNL: 505-272-7620); Subcontractor PIs: UNM: William G. Fahrenholtz (505-272-7626); NMIMT: Ping Lu (505-835-5731); SRI: Sylvia M. Johnson (415-859-4277).

PHASE OBJECTIVE: To identify compositions favorable for making composites by reactive metal penetration and to understand the mechanism(s) by which these composites are formed.

ULTIMATE OBJECTIVE: To learn to make high-quality composites and composite coatings economically, and to apply the results to problems of interest to the aluminum industry.

TECHNICAL APPROACH: Composites are made by reacting molten metals with ceramics under controlled conditions. Results are analyzed by a variety x-ray and electron analytical techniques to develop mechanisms consistent with thermodynamic calculations and phase diagram data. We use those results to make test specimens for determining physical properties.

PROGRESS: We measured a fracture toughness of 10.5 $MPa\bullet m^{1/2}$ for a composite prepared by reacting Al with porous mullite, and a toughness of 8.4 $MPa\bullet m^{1/2}$ for Al reacted with porous kaolin. We developed processes for making composites containing alumina and either $MoSi_2$, $Mo(Si,Al)_2$, or $Mo(Si,Al)_2$-Mo_3Al_8. Processing parameters were optimized to form $MoSi_2$, $Mo(Si,Al)_2$, and Mo_3Al_8, and samples were prepared for subsequent property evaluations.

Patents: -	**Publications: 5**	**Proceedings: -**	
Books: -	**Master's Theses: 2**	**Presentations: 16**	**Awards: -**

Technology Transfer or Industrial Interaction: R. Loehman and K. Ewsuk visited the Alcoa Technical Center and Reynolds Metals Co. to discuss applicability of their results to problems relevant to aluminum processing. Discussions on CRADAs or other interactions are underway.

PROJECT SUMMARY (continued)

PROJECT TITLE: Synthesis and Processing of Composites by Reactive Metal Penetration

CRITICAL ISSUES: Reliability and cost are critical issues for any new material. Learning how to control wetting and reactivity of ceramic preforms by molten metals is critical to developing reliable materials. Understanding reaction mechanisms and rate-limiting processes are necessary for development of a wider range of composites, such as those that contain $MoSi_2$ formed by in-situ reaction.

FUTURE PLANS: In-situ formation of phases such as $MoSi_2$ will be pursued because of the potential for composites with improved properties. Recent very promising TEM results will be followed -up to give new insights into reaction mechanisms. Much of what we are learning about molten metal wetting is applicable to the aluminum industry because of the potential for increasing lifetime of refractories. We are pursuing a CRADA with one or more aluminum and refractory companies.

POTENTIAL PAYOFF: Composites made by RMP could replace cast iron for many applications with significant savings due to their lower density. Improved refractories for aluminum processing would lead to large increases in process efficiency. We are learning that reactive metal penetration could be an economical process for manufacturing many of the advanced ceramic composites that are needed for light-weight structural and wear applications. Near-net-shape fabrication of parts has the additional advantage that costly and energy intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.

OTHER SOURCES: Cost sharing has been primarily in the form of continuing collaborations that are maintained at no cost to the project. For example, A.P. Tomsia and his associate, Eduardo Saiz, use internal funding from LBL to support their contributions to the collaboration. Graduate students working on the project with support from their home institutions (U. WA and UT, El Paso) represent an in-kind level of ~$50,000.

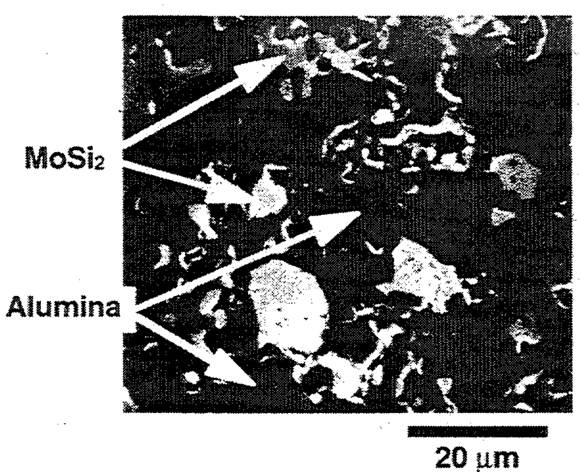
SIGNIFICANT ACCOMPLISHMENT

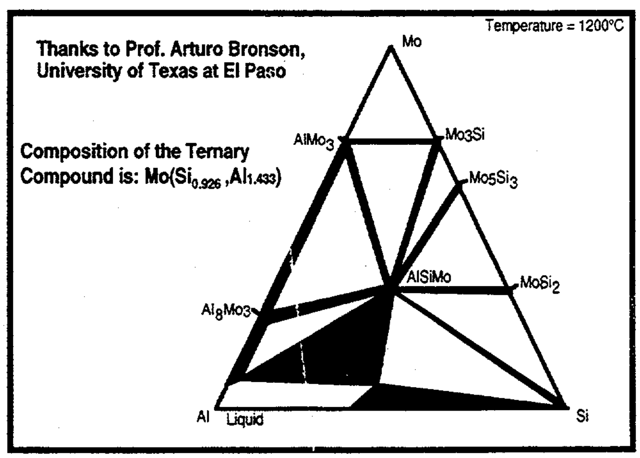
$MoSi_2$ - CERAMIC COMPOSITES PREPARED BY IN-SITU REACTION

Advanced Industrial Materials (AIM) Program

ISSUE: Composites containing $MoSi_2$ are of considerable interest because they may lead to light-weight structural materials with significant improvements in high temperature toughness and oxidation resistance. Techniques for forming $MoSi_2$ in-situ have many advantages, including better control of composite microstructure and the ability to make parts to near-net-shape, which would provide materials with better properties at lower cost.

RESULTS: We have made composites containing $MoSi_2$ according to the reaction:
$8Al + 3Al_6Si_2O_{13} \rightarrow 13Al_2O_3 + 3MoSi_2$. Control of the process required determining the phase relations in the system. A composite containing 18 vol% $MoSi_2$ and 82 vol% Al_2O_3 had a density of 96% of theoretical (4.22 g/cm^3). The 4-point bend strength was 453 MPa, the modulus was 382 GPa and the hardness was 13.8 GPa.





ENERGY EFFICIENCY: Finishing and machining operations can represent up to 90% of the cost of making advanced ceramics and ceramic composites. Net shape forming, such as is provided by many in-situ processing methods offers the prospect of significantly reducing or even eliminating many finishing and grinding operations. In addition, availability of materials with strength and toughness at high temperatures will allow higher operating temperatures in many industrial processes, which will increase their thermodynamic efficiencies.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC04-94AL85000 with Sandia National Laboratories.

POLYMERS AND BIOBASED MATERIALS

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Conducting Polymers: Synthesis and Industrial Applications

(New focus starting FY-1997: Energy Efficient Electrochemical Reactors Based on Polymer Electrolyte Membrane/Electrode Assemblies)

PHASE: FY-1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Los Alamos National Laboratory

PRINCIPAL INVESTIGATOR(S): Shimshon Gottesfeld, (505) 667-0853

PHASE OBJECTIVES: Establish asymmetric membranes for gas separation, based on integrally skinned polyaniline structures, with a selectivity of ~10 and a throughput satisfying the demands in commercial applications.

ULTIMATE OBJECTIVES: (1) Establish asymmetric membranes for gas separation, based on integrally skinned polyaniline structures, with a selectivity of ~10 and a throughput satisfying the demands in commercial applications -- this ultimate objective achieved in FY -1996. Ultimate objective of new task, starting FY- 1997: to develop and test prototype electrochemical reactor (ECR) for industrial liquid feed streams, based on polymer membrane/electrode assembly (MEA) and oxygen or air electrode, of energy consumption lower by, at least, 40% vs. present day industrial ECRs.

TECHNICAL APPROACH: High molecular weight polyaniline powder were used to prepare asymmetric membranes and permeabilities through optimally structured and doped membranes measured with automated gas-permeator system. For ECRs for the chemical industry, novel ECR configurations, based on MEAs and effective oxygen electrodes developed at LANL, were assembled and tested at LANL. Collaboration is planned with a major US chemical industry, to ensure full and meaningful comparison with present day technology and assist in industrial implementation.

PROGRESS: We completed this year our Ultimate Objective in the field of Conducting polymer membranes for gas separation: Establish asymmetric membranes for gas separation, based on integrally skinned polyaniline structures, with a selectivity of ~10 and a throughput satisfying the demands in commercial applications -- described in detail in Annual Report.

PROJECT SUMMARY (continued)

PROJECT TITLE: Conducting Polymers: Synthesis and Industrial Applications

PROGRESS (continued): In preliminary tests of a cell based on an MEA and oxygen electrode, we have demonstrated energy consumption lower by 47% vs. industrial state of the art chlor-alkali cells. Optimization of the MEA and operation conditions to achieve high current efficiency and longer tests with larger cells are main themes of future work.

Patents: 1	**Publications:** 3	**Proceedings:** 1
Books: -	**Presentations:** -	**Awards:** -

ACCOMPLISHMENTS: Asymmetric membranes of polyaniline with porous base and apparent skin thickness of 2 μm, prepared this year at LANL, demonstrated throughput enhancement by factor 50-80 compared with thick and dense membranes of the same conducting polymer material and fully maintained the high selectivity in pair gas separation. This chapter of our R&D work for the AIM program has been brought to a point of successful conclusion.

Preliminary tests demonstrated a prospect for highly energy efficient electrochemical reactors (ECRs) for various processes in the chemical industry. An important Accomplishment in this new chapter of our work has been the interest expressed by a major chemical industry to collaborate with us in the further development of such ECRs.

CRITICAL ISSUES: We demonstrated very low cell voltage for a very small scale ECR working in chlor-alkali mode. The critical issues are to show that the same energy efficiency, or similar, can be maintained while ensuring also high current efficiency and long-term performance in cells of sizes more relevant to industrial dimensions.

FUTURE PLANS: Together with industrial partner, test viability of concept demonstrated this year for chlor-alkali ECRs based on polymer membrane/electrode assembly (MEA) and oxygen/air electrode. The test will focus on optimization of MEA to maximize current efficiency and on testing of larger cells.

POTENTIAL PAYOFF: The chlor-alkali industry alone consumes 1-2% of all electric power generated in the US. The ECR concept demonstrated this year and the focus of our work in FY-97, has the potential to reduce the electric energy consumption in this process by 50%.

ESTIMATED ENERGY SAVINGS: Potential energy savings estimated at 1 quad/yr. are expected from introduction of conducting polymer based ultracapacitors in power trains of electric and hybrid vehicles. Conducting polymer based gas separation membranes provide a potential for energy savings in the US estimated at 1 to 3 quads/yr.

SIGNIFICANT ACCOMPLISHMENT

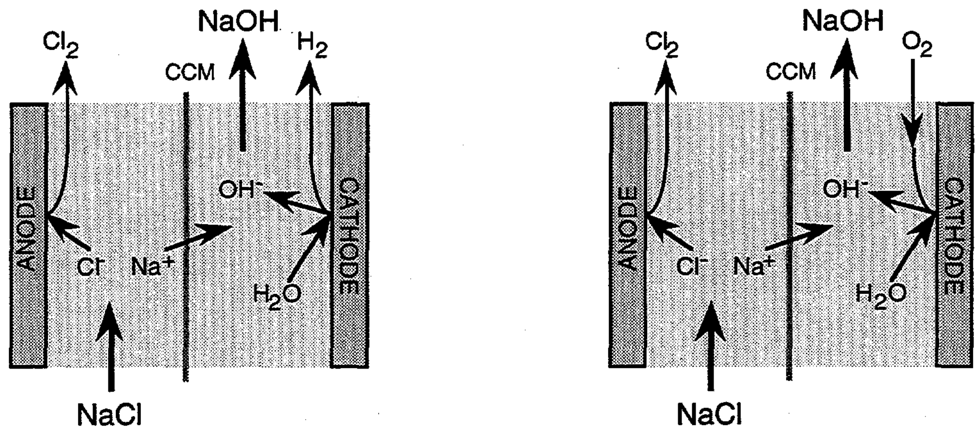
ENERGY EFFICIENT ELECTROCHEMICAL REACTORS (ECRs)

Advanced Industrial Materials (AIM) Program

PROBLEM: The volume of the clor-alkali industry is such that it consumes 1-2% of the total electric power generated in the U.S. The products at the cathode are NaOH and hydrogen gas, and gaseous chlorine is generated at the anode. The cell voltage required for significant electrolysis rate (typically 300 A/ft^2) is 3.2-3.3V. This cell voltage directly reflects the electric energy consumption perton of chlorine (or caustic) product. Lowering of the cell voltage is, therefore, an important energy savings target for this particular industrial process, as well as several other industrial processes involving electrochemical oxidations.

RESULTS:

a) Conventional Chlor-Alkali Cell b) Chlor-Alkali Cell with Oxygen Cathode



(V_{cell} = 3.2 V) **(V_{cell} = 2.3 V)**

The figure shows on the left the conventional configuration of an ECR used in the chlor-alkali industry, generating chlorine and caustic soda by electrolysis of sodium chloride brine. The cell voltage required at a typical production rate of 300 Amperes/ft^2 is 3.2-3.3V. If the hydrogen evolving cathode were replaced by an oxygen consuming cathode (fig. 3b), the voltage of the cell could be reduced, in principle, by about 0.9V. We have developed in recent years at LANL advanced oxygen/air electrodes bonded to polymer electrolyte membranes, and adaptation of this technology for such ECRs seemed possible. A first-demonstration-cell (1996) showed a cell voltage as low as 1.7V at 300 A/ft^2. The additional lowering in cell voltage seems to originate from an effective cell configuration. Such a cell voltage amounts to savings in electric power consumption of close to 50% (!) Compared with present day chlor-alkali cells.

ENERGY EFFICIENCY: Potential to save 50% of the electric energy consumed by an industry which uses 1-2% of the total electric power generated in the U.S.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program. Research and development performed at Los Alamos National Laboratory (LANL).

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT SUMMARY: Polymerization and Processing of Polymers in Magnetic Fields

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATOR: Brian C. Benicewicz

PHASE OBJECTIVE: See FY 1996 Annual Report.

NEW MATERIALS AND PROCESSES

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Advanced Industrial Materials (AIM) Fellowship Program

PHASE: FY 1996

PERFORMING ORGANIZATION: Oak Ridge Institute for Science and Education, Virginia Polytechnic Institute and State University, University of Cincinnati, Lehigh University Center for Advanced Technology for Large Structural Systems (ATLSS), Oak Ridge National Laboratory.

PRINCIPAL INVESTIGATORS: Deborah Duncan McCleary, Oak Ridge Institute for Science and Education; B.D. Dickerson, X. Zhang and S.B. Desu, Virginia Polytechnic Institute and State University; A. Jordan and O.N.C. Uwakweh, University of Cincinnati; A.B. Magee and J.H. Gross, Lehigh University Center for Advanced Technology for Large Structural Systems (ATLSS); E.A. Kenik, P.J. Maziasz, R.D. Stout and B. Radhakrishnan, Oak Ridge National Laboratory.

PHASE OBJECTIVE: The Graduate Fellowship Program focused toward helping students who are currently under represented in the nation's pool of scientists and engineers, enter and complete advanced degree programs.

ULTIMATE OBJECTIVE: The objectives of the program are to: 1) establish and maintain cooperative linkages between DOE and professors at universities with graduate programs leading toward degrees or with degree options in Materials Science, Materials Engineering, Metallurgical Engineering, and Ceramic Engineering, the disciplines most closely related to the AIM Program at Oak Ridge National Laboratory (ORNL); 2) strengthen the capabilities and increase the level of participation of currently under represented groups in master's degree programs, and 3) offer graduate students an opportunity for practical research experience related to their thesis topic through the three-month research assignment or practicum at ORNL.

The program is administered by the Oak Ridge Institute for Science and Education (ORISE). The following abstracts summarize the activities of two of the participants.

TECHNICAL APPROACH: Offer fellowships for masters degree program in materials science-related academic fields.

PROGRESS: Three fellowship recipients are involved in the project. (See attached Significant Accomplishments.)

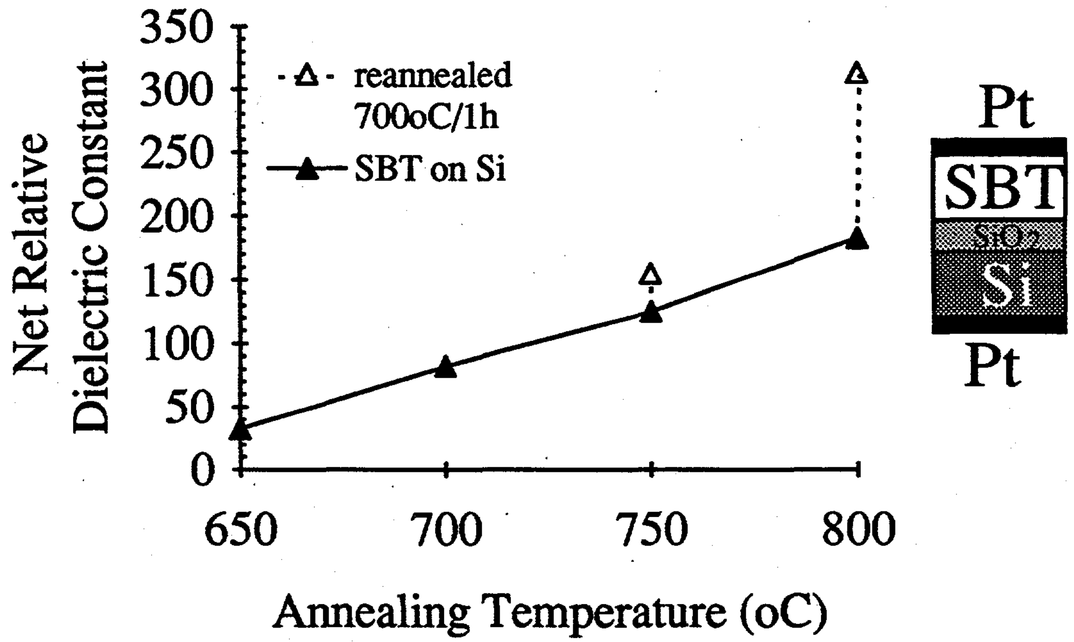
SIGNIFICANT ACCOMPLISHMENT

SECTION 1.
INTERFACIAL REACTIONS AND GRAIN GROWTH IN FERROELECTRIC $SrBi_2Ta_2O_9$ (SBT) THIN FILMS ON Si SUBSTRATES

Advanced Industrial Materials (AIM) Program

ISSUE: Traditional infrared cameras require expensive, immobile, cryogenic cooling systems to eliminate thermal noise. Alternatively, pyroelectric cameras (based on ferroelectrics) can be simpler and more portable since they operate at room temperature without cryogenic cooling systems. Depositing ferroelectric sensors directly on silicon image processing chips further promotes mass production and availability of uncooled infrared cameras.

RESULTS: The feasibility of depositing ferroelectric $SrBi_2Ta_2O_9$ (SBT) thin films directly on Si was demonstrated. Previous electircal property limitations in SBT on Si have been attributed to a reaction layer between SBT and Si. This reaction layer was identified as amorphous SiO_2 fromnanoprobe EDAX, from diffuse scattering in TEM, and from the activation energy for reaction layer growth. Despite the reaction layer, double annealing in O2 (1 hour at 800 °C followed by 1 hour at 700 °C) produced relative dielectric cnstants higher than 300 in SBT infrared pixels deposited directly on Si wafers.



ENERGY EFFICIENCY: Uncooled infrared cameras are desired to monitor high temperature materials processing for improved energy efficiency and quality control.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation and administered by the Oak Ridge Institute for Science and Education (ORISE). Research performed at the Virginia Polytechnic Institute and State University.

SIGNIFICANT ACCOMPLISHMENT

SECTION 2.
FORMATION OF AN FeSi PHASE IN MECHANICALLY ALLOYED Fe-Zn-Si SYSTEM

Advanced Industrial Materials (AIM) Program

ISSUE: Fe-Zn coatings are of technological interest, because they offer excellent resistance to corrosion during the Zn application of steel. However, the coating formed during galvanization of Si-bearing steels has an adverse affect which leads to a decrease in corrosion protection and un-controlled coating thickness.

RESULTS: The formation of an FeSi phase and the invariant reactions in the Fe-Zn-Si ternary system proved to be beneficial in understanding how Si-bearing steels behave during galvanization. The results obtained were addressed in the following manner: (1) using a high energy technique such as ball-milling to prepare the homogenous alloys being studied and, (2) using various characterization techniques (i.e., Differential Scanning Calorimetry and X-Ray Diffraction) to evaluate the stability of the FeSi phase formed. Results concerning this issue have been submitted to various technical journals for future publication.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation and administered by the Oak Ridge Institute for Science and Education (ORISE). Research performed at the University of Cincinnati.

SIGNIFICANT ACCOMPLISHMENT

SECTION 3.
OPTIMIZATION OF A 550/690-MPa HIGH-PERFORMANCE BRIDGE STEEL

Advanced Industrial Materials (AIM) Program

ISSUE: This project to develop a high-performance bridge steel was intended to avoid susceptibility of the steel to weld heat-affected-zone cracking and therefore minimize the requirement for preheat and to increase its fracture toughness at service temperatures. Previous studies by the Lehigh University Center for Advanced Technology for Large Structural Systems have suggested that a Cu-Ni steel with the following composition was an excellent candidate for such a bridge steel.

C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V	Cb
0.070	1.50	0.009	0.005	0.25	1.00	0.75	0.50	0.50	0.06	0.010

To confirm that observation, 227-kg heats of the candidate steel were melted and processed to 25- and 50-mm-thick plate by various thermomechanical practices, and the weldability and mechanical properties determined. To evaluate the feasibiity of reduced alloy content, two 227-kg heats of a lower hardenability steel were melted with C reduced to 0.06, Mn to 1.25, and Mo to 0.25 and similarly processed and tested.

RESULTS: The results indicate that the steels were not susceptible to hydrogen-induced weld-heat-affected-zone cracking when welded without preheat. Jominy end-quench tests of the higher-hardenability steel indicate that a minimum yield-strength of 690 MPa should be readily attainable in thicknesses through 50 mm and marginally at 100 mm. Mechanical-property tests of conventionally quenched and tempered plates confirmed these yield-strength observations and showed that a transition temperature lower than -85C was typical for plates through 50 mm. In addition, a yield strength of 690 MPa can be obtained upon accelerated cooling after rolling. The toughness of the steel readily met AASHTO specifications for Zone 3 in all conditions and thicknesses, and may be sufficiently tough so that the critical crack size will minimize fatigue-crack-extension problems. The results of the Jominy tests on the lower-alloy lower-hardenability steel indicate that a yield strength of 690 MPa could be achieved only through 12-mm think plate, marginally at 25 mm and a yield strength of 80 ksi through 100 mm. Mcehanical-property tests confirmed these observations and showed that the toughness was excellent for 12-mm plate but diminished as the plate-thickness increased. A production heat of the candidate steel should be melted and tested in plates through 100 mm to confirm the excellent combination of strength and toughness that was obtained in laboratory heats studies of the interaction between carbon and various alloying additions is recommended to optimize the composition of a 70W steel.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation and administered by the Oak Ridge Institute for Science and Education (ORISE). Research performed at the Lehigh University Center for Advanced Technology for Large Structural Systems (ATLSS).

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Advanced Microwave Processing Concepts

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR(S): R. J. Lauf (423) 574-5176, A. D. McMillan (423) 241-4554

PHASE OBJECTIVE: To determine the curing behavior of thermosetting resins and polymer-matrix composites under microwave heating conditions. To determine the quantitative effect of frequency variation or bandwidth on power uniformity in a multimode microwave cavity.

ULTIMATE OBJECTIVE: To demonstrate and commercialize the Variable Frequency Microwave Furnace. To demonstrate microwave curing as a way to lower the cost and speed production of polymer products, including resins, composites, and adhesives.

TECHNICAL APPROACH: Determine the cure time, physical properties, and uniformity of polymeric articles as a function of microwave heating conditions such as average frequency, bandwidth, and power. Characterize the power distribution in a multimode microwave cavity as a function of frequency and bandwidth, using both numerical modeling and direct thermal mapping.

PROGRESS: We are currently exploring the use of microwave cured adhesives for joining lightweight materials, metal-to-metal, metal-to-polymer, or metal-to-ceramic. A proprietary epoxy-based adhesive from B.F. Goodrich and a commercially available sheet adhesive manufactured by Cyanamid (FM73) are being examined individually. Preliminary data is encouraging.

Patents: 2	**Publications:** -	**Proceedings:** 2
Books: -	**Presentations:** 2	

ACCOMPLISHMENTS:

- Two patents were issued in 1996, one of which is licensed to Lambda Technologies, Inc.
- Lambda introduced a new line of microwave furnace products and sold several large systems to industrial customers.

POTENTIAL PAYOFFS: Industries benefiting from VFMF-cured polymeric materials are pulp and paper, glass, and manufacturing, automotive, and aircraft.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Advanced Powder Processing

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL)

PRINCIPAL INVESTIGATOR(S): Mark A. Janney, (423) 574-4281

PHASE OBJECTIVE: Develop gelcasting of metal powders.

ULTIMATE OBJECTIVE: Develop wide application of the gelcasting ceramic forming process to all type of sinterable materials. Applications include tool steels, stainless steels, superalloys, and non-ferrous metals such as aluminum.

TECHNICAL APPROACH: Gelcasting is an advanced powder forming process. It is most commonly used to form ceramic or metal powders into complex, near-net shapes. Turbine rotors, gears, nozzles, and crucibles have been successfully gelcast in silicon nitride, alumina, nickel-based superalloy, and several steels. Gelcasting can also be used to make blanks that can be green machined to near-net shape and then high fired. Green machining has been successfully applied to both ceramic and metal gelcast blanks.

Recently, we have used gelcasting to make tooling for metal casting applications. Most of the work has centered on H13 tool steel. We have demonstrated an ability to gelcast and sinter H13 to near net shape for metal casting tooling. Also, blanks of H13 have been cast, green machined into complex shape, and fired. Issues associated with forming, binder burnout, and sintering are addressed.

PROGRESS: Gelcasting was successfully applied to H13 tool steel. All slurry processing was conducted in water-based suspensions and binder removal was accomplished in air at temperatures between 200 and 350°C. Sintered properties such as density, hardness, carbon content, and oxygen content were comparable for H13 that was gelcast and H13 that was sintered starting from a tapped powder stack.

Patents: none	**Publications:** 1	**Proceedings:** 2
Books: none	**Presentations:** 3	**Awards:** none

ACCOMPLISHMENTS:

Licenses: none
Technology Transfer or Industrial Interaction: Gelcasting has been licensed to three companies so far. Additional interactions are on-going

PROJECT SUMMARY (continued)

PROJECT TITLE: Advanced Powder Processing

CRITICAL ISSUES: Interactions of metal powders with aqueous gelcasting solutions need to be investigated to determine way to minimize reactions such as oxidation and hydrogen generation.

FUTURE PLANS: Develop gelcasting sytems tailored to metal particle systems.

POTENTIAL PAYOFF: Gelcasting is becoming an accepted forming method for making large and complicated parts in ceramic powder systems. It is still new to the metals industry. With sufficient work, it could help extend the range of size large, complex parts made from metal powders.

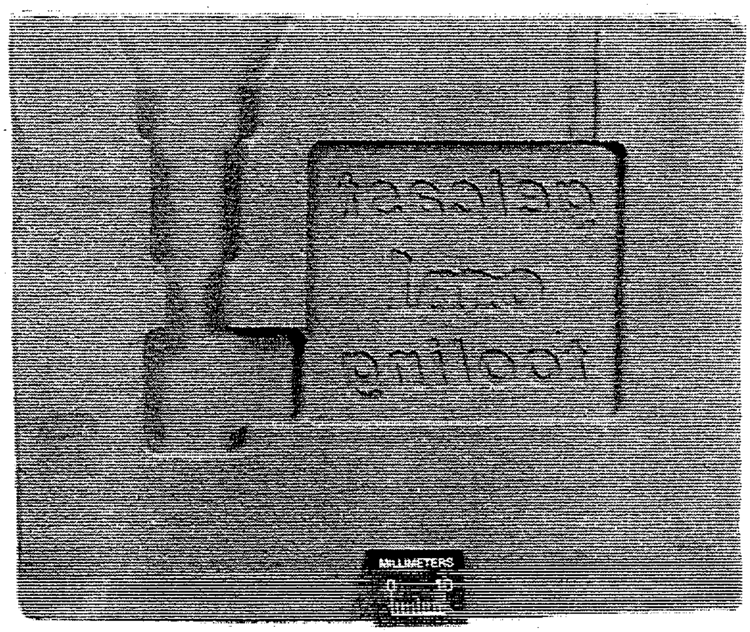
SIGNIFICANT ACCOMPLISHMENT

GREEN MACHINING GELCAST H13 TOOL STEEL PAVES WAY FOR RAPID PRODUCTION OF DIE CASTING MOLDS

Advanced Industrial Materials (AIM) Program

ISSUE: H13 tool steel is the preferred material for fabricating molds for die casting aluminum alloys. However, fabricating dies from H13 using conventional machining of H13 stock is difficult and expensive. Using gelcast H13 and machining the dies in the green state would provide a new, potentially lower cost route to prototype die fabrication.

RESULTS: Commercial H13 tool steel powder was evaluated for gelcasting. Several technical challanges had to be overcome including developing proper binder burnout conditions to produce the appropriate carbon content in the sintered parts. It was demonstrated that sintered gelcast H13 with good density, hardness, and chemistry could be made by gelcasting. Further, it was demonstrated that gelcast H13 could be machined in the green state to form complex parts. One of these, a demonstration part for die casting aluminum is shown below.



Research performed at the Oak Ridge National Laboratory (ORNL) and sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-ACOR-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Control Technology for Surface Treatment of Materials Using Induction Hardening

PHASE: FY 1996 **COMPLETION DATE:** FY 2001

PERFORMING ORGANIZATION: Sandia National Laboratories (SNL).

PRINCIPAL INVESTIGATOR(S): J. Bruce Kelley (505) 845-3105; Russell D. Skocypec (505) 845-8838.

PHASE OBJECTIVE: To support the establishment of an induction hardening consortium consisting of Delphi Saginaw Steering Systems/General Motors, Ford, and Chrysler Corporation; their first-tier suppliers as appropriate; with an advisory board from the heat treating, steel, casting, and forging industries

ULTIMATE OBJECTIVE: Broaden the range of materials, processing conditions and part geometries applicable for intelligent induction hardening by: developing integrated process models, developing advanced intelligent process control systems, and optimizing processes and components; generating significant improvements in energy efficiencies and environmental benefits.

TECHNICAL APPROACH: CRADA research tasks were defined in the following areas: computational process modeling, materials characterization, process characterization and sensor development; controller development; and product/process optimization.

PROGRESS: Established an induction hardening consortium consisting of Delphi Saginaw Steering Systems/General Motors, Ford, and Chrysler Corporation; and their first-tier suppliers as appropriate.

Patents: --	**Publications:** --	**Proceedings:** --
Books: --	**Presentations:** 1	**Awards:** 2

ACCOMPLISHMENTS: The CRADA with the above consortium was developed.

TECHNOLOGY TRANSFER OR INDUSTRIAL INTERACTION:
The CRADA has an industrial advisory board consisting of representatives of the heat treating, steel, casting, and forging industries through appropriate professional societies or trade associations (Forging Industry Association (FIA), the American Iron and Steel Institute (AISI), the Steel Founders Society (SFS) and ASM International (ASMI) have agreed to date). A poster was displayed at the Advanced Industrial Materials (AIM) conference in June. Discussions about the project were held with representatives of the FIA, SFS, and the North American Die Casting Association (NADCA), as well as with a number of interested industrial companies.

PROJECT SUMMARY (continued)

PROJECT TITLE: Control Technology for Surface Treatment of Materials Using Induction Hardening

CRITICAL ISSUES: Tailoring of material properties through intelligent, energy efficient and environmentally benign inductive processing continues to be a critical issue, as identified in a number of industry roadmaps.

FUTURE PLANS: Continue development of intelligent systems for induction hardening processes through the induction hardening consortium consisting of Delphi Steering, Ford, and Chrysler; their first-tier suppliers as appropriate; with an advisory board from the heat treating, steel, casting, and forging industries. (The US automotive industry represents about 50% of the induction heating and hardening market.) The work with this consortium will provide the basis for expanding the application base to the broad industrial heat treatment market segment.

POTENTIAL PAYOFF: Hundreds of millions of dollars worth of products are produced annually using the induction hardening process, including shafts, bearings, and gears. Induction hardening is typically performed on components which are fully machined. It is estimated that tens of millions of dollars in savings could be generated annually (just in the automotive industry) if induction hardening could be more widely used and more precisely controlled. The use of induction hardening and heating could grow significantly compared to alternative heat treating technologies. This is due to the inherent advantages of induction, the cleanliness of the process, the energy efficiency of the process, and the ability to put the process in-line with other manufacturing processes. Improved ability to design products using induction hardening, and the ability to streamline the manufacturing and quality control operations, could increase the number of applications for this energy efficient and environmentally benign process. This can be achieved without the need for additional investment in plant and capital equipment, and without the need to develop manufacturing bases associated with new materials and processes.

ESTIMATED ENERGY SAVINGS: The potential energy savings of 90% compared to competing technologies makes broader application of this technology of great importance to the heat treating, steel, forging, casting, paper and pulp, and aluminum industries. Direct energy savings of 630 trillion BTUs, and total energy savings of about 1 quadrillion BTUs, are possible over 20 years in the heat treating industry alone. The forging and steel industries have identified significant additional energy savings opportunities for induction heating technology if uniform and reliable heating can be achieved.

SIGNIFICANT ACCOMPLISHMENT

CONTROL TECHNOLOGY FOR SURFACE TREATMENT OF MATERIALS USING INDUCTION HARDENING

Advanced Industrial Materials (AIM) Program

ISSUE: Induction hardening is a widely used industrial process to enhance the strength, wear resistance, and toughness of components made from medium and high carbon steels. Commonly hardened components include drivetrain and chassis components such as axles, gears, and crankshafts, as well as industrial equipment components such as pump shafts, bearing races, ball screws and wear pins. Induction hardening is extensively used because it is a very fast in-line heat treating technology that applies energy only to the volume of material required to be hardened. The ability to heat treat parts rapidly with in-line technology results in lower direct energy costs, shorter manufacturing lead times, and decreased amounts of distortion when parts are quenched. Additionally, induction is an environmentally benign process because no endothermic atmospheres, plating processes or stripping tanks are required. However, induction hardening is not as widely used as it could be. Current limitations of the process as used commercially include the lack of closed-loop process control, unidentified process and material variations which cause continual adjustment of the process parameters, coil and process development by trial and error, and an inability to monitor coil condition. Destructive examination of parts, required with open-loop control, costs tens of millions of dollars annually in the automotive industry alone. Improvement and optimization of the induction hardening process is limited by an inadequate understanding of process fundamentals and material/process interactions.

RESULTS: A CRADA has been established with Ford, Chrysler, and Delphi Saginaw Steering Systems/General Motors; and their first-tier suppliers as appropriate, to: (1*) develop components of an integrated process model* to speed the design process, improve process precision, enable process optimization to produce lighter-weight higher-performance parts, make the process more agile over a broader range of operating conditions, and speed coil and process development; (2) *develop advanced intelligent process control systems*, which enable the knowledge generated in the integrated process model to be realized in the processing of induction-heated parts, and provide improved precision and accuracy, real time verification of the process, and compensation for material variations within a given class of material; and (3*) optimize processes and components* with the aid of the process control technology and process modeling tools.

ENERGY EFFICIENCY: The energy savings makes application of this technology of great importance to the heat treating, steel, forging, casting, paper and pulp, and aluminum industries. *Direct* energy savings of 630 trillion BTUs, and *total* energy savings of about 1 quadrillion BTUs, are possible over 20 years in the heat treating industry alone. The forging and steel industries have identified significant additional energy savings opportunities for induction heating technology if uniform and reliable heating can be achieved.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program. Research performed at Sandia National Laboratories, Albuquerque, New Mexico.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Development of Improved Refractories

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL) and the Center for Glass Research (CGR) Satellite Refractory Center at the University of Missouri at Rolla (UMR); the latter is a NSF center.

PRINCIPAL INVESTIGATOR(S): Andrew A. Wereszczak/ORNL (423)574-7601, Mattison K. Ferber/ORNL (423)576-0818, Kenneth C. Liu/ORNL (423)574-5116, and Robert E. Moore/UMR (573)341-4401

PHASE OBJECTIVE: To design high temperature mechanical testing frames that can be used for compressive creep and dynamic loading testing of refractories, and procure hardware for the frames' construction.

ULTIMATE OBJECTIVE: To generate an engineering database on the high temperature mechanical properties of commercial refractories that are candidate materials for glass-melting furnace superstructures.

TECHNICAL APPROACH: The proposed refractory high temperature testing facilities will be equipped with the necessary instrumentation to accurately control and monitor refractory creep and high temperature modulus of elasticity (MOE) tests. A minimum of two test frames, one solely dedicated to compression creep testing and another capable of either creep or high temperature MOE measurements, will be used for this task. Each of these testing stations will be comprised of a testing frame, a computer and appropriate software for test control and data acquisition, a furnace and load train capable of achieving and maintaining loads and temperatures to 3300°F, and a high temperature extensometer to monitor strain as a function of time or stress. High temperature test conditions will be selected that mimic those of refractory service (determined through consultation with CGR-UMR members). Success of this subtask will be demonstrated when representative engineering creep and high temperature MOE data become available to those scientists, engineers, and technicians, and academicians requiring it for use in materials development and structural design.

PROGRESS: The majority of procured hardware was received for the two testing frames, and the construction of the units were initiated. The project was initiated 1 July 1996, so only three months were available for progress for FY96.

Patents:	-	**Publications:**	-	**Proceedings:**	-
Books:	-	**Presentations:**	1	**Awards:**	-

PROJECT SUMMARY (continued)

PROJECT TITLE: Development of Improved Refractories

ACCOMPLISHMENTS: See Progress Section.

CRITICAL ISSUES: Getting consensus from refractory vendors on which materials to test in FY97.

FUTURE PLANS: For FY97, a system checkout of the two constructed test frames will be conducted at elevated temperatures to confirm consistency and repeatability. A letter report will be submitted to the Program Manager describing the constructed testing systems and preliminary test results.

POTENTIAL PAYOFF: More efficient and economical designs of glass-melting furnace superstructures will be a consequence of this project, because accurate engineering data will be available to describe the high temperature mechanical performance of candidate refractory materials. Data such as this is either non-existent in the literature, or what little data that is available was generated by questionable means.

ESTIMATED ENERGY SAVINGS: The technology to be developed in this project will enable the use of oxy-fuel firing in glass melting furnaces, thus permitting energy savings and environmental benefits.

SIGNIFICANT ACCOMPLISHMENT

DEVELOPMENT OF IMPROVED REFRACTORIES

Advanced Industrial Materials (AIM) Program

ISSUE: The project was initiated July 1, 1996. Measurement systems were designed and the majority of procured hardware was received for two testing frames that are to be constructed for the project's use. Preliminary construction of the units occurred.

Research performed at the Oak Ridge National Laboratory (ORNL) and sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-ACOR-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Metals Processing Laboratory User Center (MPLUS)

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Metals and Ceramics Division,Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831.

PRINCIPAL INVESTIGATOR(S):
Gail Mackiewicz-Ludtka ((423)-576-4652) and H. Wayne Hayden ((423)-574-6936)

PHASE OBJECTIVE: To pilot a new Metals Processing Laboratory User (MPLUS) Center and assess its value to U.S. industry.

ULTIMATE OBJECTIVE: MPLUS is designed to assist key U.S. industry improve energy efficiency and enhance the competitiveness of U.S. industries in the global market by partnering with U.S. industries.

TECHNICAL APPROACH: Initially pilot the MPLUS User Center concept within a small scale organizational framework to determine whether a need exists for such a program, and if so, demonstrate its value.

PROGRESS: The industrial and academic response to this piloted MPLUS User Center has grown tremendously *within less than a year.* As of September 30, 1996, a total of 31 MPLUS Proposals were received from 27 companies and universities representing 17 states (Figure 1). Of these 31 proposals, 22 were reviewed, 18 were approved, while the others were either still under development, or were being modified. Two (2) projects were completed, and 12 User Companies had already utilized the MPLUS facilities.

Due to industrial requests/needs, MPLUS has expanded to incorporate not only the original Engineering Section within the Metals and Ceramics Division, but has continually branched out to include: first, other ORNL User Centers (e.g., HTML and CCII), then, to provide industrial partners with access to additional facilities within other Divisions, e.g., Fusion Energy. The *amazing growth* of this MPLUS User Center has demonstrated that industry considers the MPLUS User Center to be an extremely valuable asset. MPLUS has provided a timely technical response mechanism for industries to address important issues and/or resolve current industrial problems/concerns in a short time. Without MPLUS support, these issues probably would have had to have been ignored, delayed, and/or more costly.

Patents:	**Publications:** 5	**Proceedings:**
Books:	**Presentations:** 3	**Awards:** 1

PROJECT SUMMARY (continued)

PROJECT TITLE: Metals Processing Laboratory User Center (MPLUS)

ACCOMPLISHMENTS: Established the importance of MPLUS to U.S. industry.

> **Licenses:** -
> **Known Follow-on Product(s):** Additional industrial interactions with user companies.
> **Industry Workshop:** -
> **Technology Transfer or Industrial Interaction:** Occurs with every project.

CRITICAL ISSUES: Is MPLUS needed?

FUTURE PLANS: Expand MPLUS to incorporate non-ORNL facilities and expertise.

POTENTIAL PAYOFF: Restoration of U.S. industry's competitive edge in the global market.

ESTIMATED ENERGY SAVINGS: --

SIGNIFICANT ACCOMPLISHMENT

METALS PROCESSING LABORATORY USER CENTER (MPLUS)

Advanced Industrial Materials (AIM) Program

ISSUE: Pilot test a User Center geared toward Metals Processing Needs primarily related to the seven Vision Industries identified and supported by DOE.

RESULTS: The tremendous success of this pilot effort is evidenced by the phenomenal technical support requests and timely responses that MPLUS has been able to provide. The industrial and academic response to this piloted MPLUS User Center has grown tremendously *within less than a year.* As of September 30, 1996, a total of 31 MPLUS Proposals were received from 27 companies and universities representing 17 states (Figure 1). Of these 31 proposals, 22 were reviewed, 18 were approved, while the others were either still under development, or were being modified. Two (2) projects were completed, and 12 User Companies had already utilized the MPLUS facilities.
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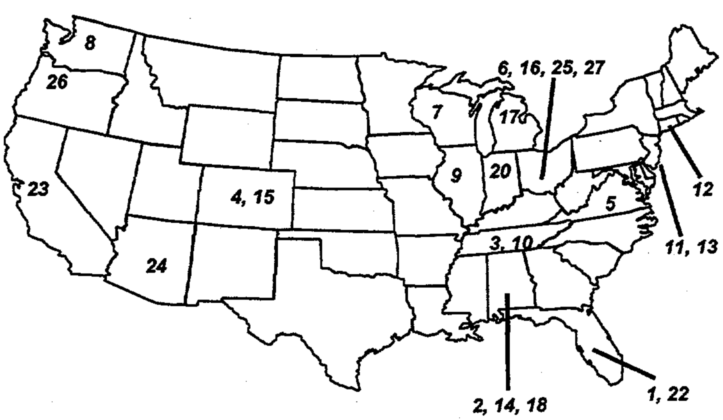
As of September 30, 1996, 17 States and 27 Companies have Requested MPLUS.

1. **Westinghouse**
2. **Reynolds**
3. **ForMat Industries**
4. **Schuller Int'l.**
5. **E.R. Johnson**
6. **Sandusky Int'l**
7. **Waukesha Electric**
8. **Weyerhauser**
9. **A.Finkl**
10. **Jeffrey Chain Corp.**
11. **Materials Technologies**
12. **ABB C-E Services**
13. **Union Camp Corp.**
14. **United Defense**
15. **Colorado School of Mines**
16. **Doehler-Jarvis**
17. **General Motors**
18. **University of Alabama**
19. **Cornell University**
20. **Cummins Engine**
21. **Bethlehem Steel**
22. **Anchor Glass**
23. **FMC Corp.**
24. **Arizona State University**
25. **Ohio State University**
26. **Goldendale Aluminum**
27. **Lincoln Electric Corp.**



ENERGY EFFICIENCY: This amount is different for each individual MPLUS project.

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Microwave Joining of SiC

PHASE: FY 1996 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): FM Technologies, Inc.

PRINCIPAL INVESTIGATOR(S): Richard Silberglitt, (703) 425-5111

PHASE OBJECTIVE: To investigate use of polymer precursors to form SiC interlayers in situ during microwave joining.

ULTIMATE OBJECTIVE: To identify and develop the most effective microwave joining methods for scale-up to large tube assemblies of silicon carbide that are required for industrial applications.

TECHNICAL APPROACH: Strong joints have already been demonstrated for reaction bonded SiC in an air environment. In order to join sintered SiC and continuous fiber-reinforced (CFCC) SiC/SiC composites, polymer precursor decomposition in an inert environment is required. This required design and fabrication of a new microwave applicator capable of vacuum baking and back-filling with inert gas, and large enough to allow insertion of tubes up to 10 cm (~ 4") in diameter.

PROGRESS: A new multimode applicator, approximately 16" in diameter and 16" long, to be used with the existing 6 kW 2.45 GHz microwave source, was designed, fabricated and tested. It is capable of evacuation and backfilling to establish any required environment for production of SiC or other interlayers from chemical reactions in situ. This applicator was used to join commercial SiC/SiC composite plates using a commercial polymer precursor to form a SiC interlayer in situ.

Patents:[-] **Publications:**[-] **Proceedings:**[-]
Books:[-] **Presentations:**1 **Awards:**[-]

ACCOMPLISHMENTS:

Licenses: [-] **Known Follow-on Product(s):**[-] **Industry Workshop:**[-]

Technology Transfer or Industrial Interaction: Discussions with Stone & Webster concerning potential for microwave joining in the fabrication of components for the high pressure heat exchange system (HiPHES). A work scope has been developed and a contract is under negotiation for microwave joining of tube sections supplied by Stone & Webster that will be tested at ORNL under environmental conditions that simulate the service environment. Presentation of joining results on CFCC SiC/SiC composites was planned for the CFCC Review Meeting and BES/CFCC Workshop in San Diego, CA on October 16-18, 1996.

PROJECT SUMMARY (continued)

PROJECT TITLE: Microwave Joining of SiC

CRITICAL ISSUES: Identification and optimization of polymer precursors for strong and adherent SiC interlayers, as well as the development of applicators for cost-effective fabrication of long and large diameter specimens.

FUTURE PLANS: Joining of test specimens supplied by industrial collaborators that properly simulate the components to be fabricated, followed by tests conducted by the industrial collaborators that simulate performance environments, and then scale-up to fabricate prototype components, and prototype testing. Commercialization agreements will be based upon licensing or contract manufacturing, as appropriate.

POTENTIAL PAYOFF: The markets for SiC radiant burner tubes and heat exchangers have been estimated to be greater than 100 million dollars annually. These components cannot currently be cost-effectively fabricated in lengths and shapes required. Microwave joining could be an enabling technology by allowing fabrication through the joining of several small, simply shaped pieces. Development of a transportable microwave applicator would provide the capability for on-site fabrication and repair of ceramic tube assemblies, which would further enhance the cost-effectiveness of this approach.

ESTIMATED ENERGY SAVINGS: Natural gas savings are estimated at $172,892 per year due to 4-7% higher efficiency of SiC radiant burner tubes. Use of SiC tube heat exchanger in externally fired combined cycle coal power plants is projected to produce a 20% increase in thermal efficiency, together with a 20% reduction in CO_2 emissions and a 90% reduction in SO_x emissions. Energy savings through the reduction of feedstock consumption and decoke fuel and steam requirements with an advanced ethylene production process using HiPHES are projected by Stone & Webster at 63.9 trillion BTUs per year.

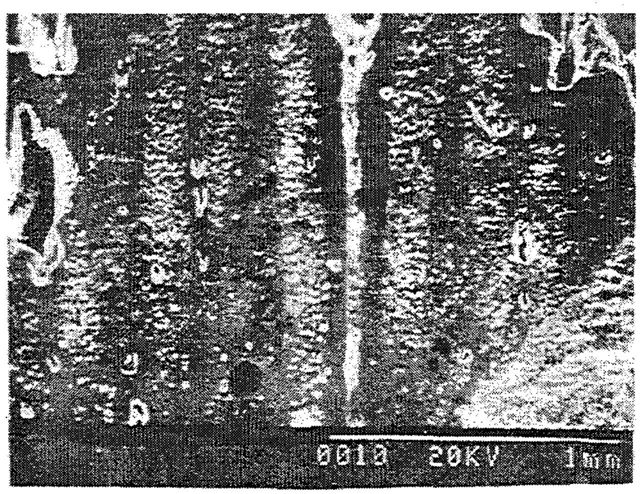
SIGNIFICANT ACCOMPLISHMENT

MICROWAVE JOINING OF CONTINUOUS FIBER CERAMIC COMPOSITES (CFCCs) DEMONSTRATED

Advanced Industrial Materials (AIM) Program

ISSUE: Continuous fiber ceramic composite (CFCC) materials can increase service temperatures of turbines, heat exchangers and other energy system components, while avoiding the brittle failure problems of monolithic ceramic materials. Joining methods are needed to allow large CFCC structures to be fabricated cost-effectively from small, simply shaped pieces.

RESULTS: Microwave heating was used to join specimens of CFCC SiC/SiC composite plates via decomposition of a polymeric precursor to form a SiC interlayer in situ. The rapid heating and increased effectiveness of microwaves in producing SiC at lower temperature, as compared to conventional heating, were used to minimize SiC fiber degradation.



ENERGY EFFICIENCY: Natural gas savings are estimated at $172,892 per year due to 4-7% higher efficiency of SiC radiant burner tubes. Use of SiC tube heat exchanger in externally fired combined cycle coal power plants is projected to produce a 20% increase in thermal efficiency. Energy savings through the reduction of feedstock consumption and decoke fuel and steam requirements with an advanced ethylene production process using a high pressure SiC heat exchanger are projected at 63.9 trillion BTUs per year.

Research performed by FM Technologies, Inc.-George Mason University-Los Alamos National Laboratory and sponsored by DOE Advanced Industrial Materials (AIM) Program.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: New Method for Synthesis of Metal Carbides, Nitrides and Carbonitrides

PHASE: FY1996

PERFORMING ORGANIZATION: Southern Illinois University

PRINCIPAL INVESTIGATOR(S): Rasit Koc (618) 453-7005

PHASE OBJECTIVE: To investigate the reaction mechanisms and phase evolution during the formation of TiC powders from carbon coated titania precursors and to produce submicron TiC powders with desired stoichiometries.

ULTIMATE OBJECTIVE: To develop a novel synthesis method using a carbothermic reduction reaction of carbon coated precursors for producing high purity, submicron, non-agglomerated powders of metal-carbide, metal-nitride and metal-boride systems. We also want to demonstrate the advantages of the process and provide information on the applicability of the process for synthesizing related advanced ceramic powders (e.g. SiC, WC, TiN, TiB_2). From a technical standpoint the carbon coating method is a leap forward in the technology for producing nonoxide advanced ceramic powders. From an economic standpoint American industries have been/will be standing to benefit greatly from this technology. Because they have had to rely on an expensive powders provided only by foreign suppliers.

TECHNICAL APPROACH: The process developed in this project utilizes a carbothermic reduction reaction of novel coated precursors that has potential as a low cost powder synthesis route. It minimizes kinetic barriers by improving the way carbon is introduced to the reactants. The process consists of two steps. The first step is the coating of titanium containing powders with carbon by decomposing a hydrocarbon gas at temperatures of 400°- 600°C. The second step involves the formation of TiC powders by promoting the carbothermal reduction of the carbon-coated titanium containing particles in an inert atmosphere at temperatures of 1200°-1600°C. This way of increasing contact area between reactants results in a more complete reaction and a purer product at comparatively lower temperatures. The complete separation of the titanium containing particles by coated carbon and the low temperature processing results in products with less particle agglomeration and uniform particle size.

PROJECT SUMMARY (continued)

PROJECT TITLE: New Method for Synthesis of Metal Carbides, Nitrides and Carbonitrides

PROGRESS: The carbon coating method developed for production of submicron TiC powders during 1995 was further improved, and its application extended to the synthesis of tungsten and tungsten monocarbide powders. The carbon coating method for production of SiC powders won the R&D 100 award for 1995. The technology was transferred to Advanced Refractories Technologies (ART), Inc. This technology also received Federal Laboratory Consortium Award for Technology Transfer for 1996.

Patent : U.S. 5,417,952	**Publications**: 2	**Proceedings**: 1
Books: 0	**Presentations**:4	**Awards**: 2

ACCOMPLISHMENTS:

Licenses: ART Inc. has licensed the SiC patent. Greenleaf Inc. is in the process of licensing the TiC patent.

Other Successful Technology Transfer Activities as Evidence of Industry Interest:

1. The synthesized submicron TiC powders with desired stoichiometries have been supplied to ORNL for evaluation in fabrication of intermetallic-TiC composites. They have achieved densification at 1350°C and 1610°C, somewhat higher temperature than that required for commercial powder. Since there is no submicron TiC powder supplier in the world market, these submicron TiC powders will result in the production of components with unique (better) properties than those achieved with commercial powders. ORNL researchers would like to have larger (500grams -1 kg) amounts of submicron TiC powders.

2. The produced submicron TiC powders were supplied to Greenleaf Corporation for evaluation in their proprietary Al_2O_3 - TiC composites. The resulting microstructure was very encouraging and they are requesting an additional 300 grams of the same material. They are also interested in a joint program to pursue the possibility of manufacturing this material.

3. The produced submicron TiC powders were supplied to 3M Ceramic Technology Center for evaluation in their specific application. They would like to license the process.

4. The synthesized submicron TiC powders were also supplied to Bayer (Dr. Reimer Holm-Germany) for evaluation. They concluded that the TiC powders have submicron particles, high stoichiometry, low oxygen content, some free carbon, and moderate agglomeration. Their report indicated that these powders will broaden the areas of application for TiC based materials.

5. Southern Illinois University Office of Research Development and Administration has started the application of a patent and commercialization of the process for the production of tungsten or tungsten monocarbide powders.

PROJECT SUMMARY (continued)

PROJECT TITLE: New Method for Synthesis of Metal Carbides, Nitrides and Carbonitrides

CRITICAL ISSUES: Applicability of the process to synthesize other metal carbides, nitrides and borides.

FUTURE PLANS: Continue TiC and WC powder technology transfer by providing information on the process. Clearly demonstrate the advantages of the process over the conventional process.

POTENTIAL PAYOFF: Acquisition of a new process for nonoxide advanced ceramic powders that will provide a supply of low-cost, high quality (high purity, fine particle size) powders. The low cost powders will have a major impact on the cost of finished products that may expand current markets.

ESTIMATED ENERGY SAVING: This technology will improve energy efficiency because it does not require high reaction temperatures for production of these powders.

SIGNIFICANT ACCOMPLISHMENT

NEW METHOD FOR SYNTHESIS OF METAL CARBIDES, NITRIDES AND CARBONITRIDES

Advanced Industrial Materials (AIM) Program

ISSUE: Metal carbides (TiC,SiC, WC), nitrides (TiN, Si_3N_4, WN) and borides (TiB_2) are the leading advanced ceramics used in metal-working, electrical and electronics, chemical and refractory industries. This is due to their high temperature strength retention, excellent oxidation resistance, low thermal expansion coefficient, high wear resistance, and light weight. Fabrication of these advanced engineering ceramics involves a series of process steps that are designed to produce dense components. Process include production of the advanced ceramic powders (powder synthesis); mixing and milling (powder preparation for consolidation); shaping (consolidation to engineering shape); sintering (densification/microstructural development) steps. Each step has the potential for introducing a detrimental heterogeneity which will persist during further processing or develop into a new heterogeneity during sintering. If reliable advanced ceramics are to be fabricated, powder synthesizing methods must be developed to ensure that the heterogeneities are eliminated from advanced ceramic powders and they should not be reintroduced in subsequent processing steps. In addition, the cost of high quality (high purity and high surface area) powders is a major factor hindering the wide commercialization of metal carbide, nitride and boride components. Present methods of synthesizing these powders require expensive steps that yield only small quantities of product.

RESULTS: A novel cost - effective synthesis method using a carbothermic reduction reaction of carbon coated precursors for producing high purity, submicron, non-agglomerated, and low cost powders of metal carbide, metal nitride and metal boride systems have been developed. We have demonstrated the advantages of the process and provided information on the applicability of the process for synthesizing TiC, SiC and WC. Steps are also taken to investigate the reaction mechanisms and phase evolution during the formation of TiC from carbon coated titania precursors and to produce submicron TiC powders with desired stoichiometries. Depending on the carbon content in the coated titania precursor, TiC powder was produced with different stoichiometries (different amount of oxygen and free carbon). The synthesized submicron TiC powders with desired stoichiometries have been supplied to ORNL, 3M Ceramic Technology Center, and Greenleaf for evaluation. The personnel at 3M Ceramic Technology Center are interested in the results of our program with respect to application of submicron TiC based materials in their specific products. We have supplied 3M with materials and consultation for their particular needs. Greenleaf has expressed great interest in the properties of TiC synthesized using the new process for utilizing in advanced Al_2O_3/TiC ceramic composites. They are also interested in a joint program with us to pursue the manufacture of this material.

ENERGY EFFICIENCY: This technology will improve energy efficiency because it does not require high reaction temperatures for production of these powders.

This research was sponsored by the U.S. Department of Energy, Office of Industrial Technologies, as part of the Advanced Industrial Materials Program, under contract DE-AC05-84OR21400 with Lockheed Martin Energy Research Corporation.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Selective Inorganic Thin Films

PHASE: Materials Development **COMPLETION DATE:** Open

PERFORMING ORGANIZATIONS: Sandia National Laboratories,University of Washington, University of New Mexico,University of Western Australia

PRINCIPAL INVESTIGATOR: Mark L. F. Phillips, Dept. 1815, MS 0367,phone: (505) 844-8969,fax: (505) 844-4816

PHASE OBJECTIVE: Study inorganic membranes capable of separating light gases and mixtures of arene isomers via molecular sieving. Investigate methods for crystallizing zeolite films from sol-gel, clay, and metal precursor films on porous substrates. Confine permeability of film to zeolite crystals by increasing density of coverage and reducing gas permeability of matrix. Enhance permeability by decreasing film thickness while maintaining continuous coverage.

ULTIMATE OBJECTIVE: Develop new class of inorganic membranes for light gas separation and possibly catalysis. Use this technology to improve upon separation efficiencies and thermal stability currently available with polymer or oxide membranes, emphasizing application to petroleum and natural gas refining. Transfer technology base to industry.

TECHNICAL APPROACH: Use computational modeling to select appropriate microporous phases for desired separation. Nucleate and crystallize zeolite and microporous zinc phosphate phases from sol-gel, clay, and metallic films, using porous filters and gas membranes as supports for these films. Investigate novel microporous zinc phosphates as molecular sieves.

PROGRESS: We studied methods for synthesizing and caulking Zeolite A membranes extensively. We made cesium zinc oxide phosphate ($CsZn_2OPO_4$) molecular sieve membranes on porous zinc oxide wafers. These membranes are permeable to water and helium, but not to gases with larger kinetic diameters. Thin films were also made of zinc oxide phosphates with the larger-pore $M_3Zn_4O(PO_4)_3$ structure type. We discovered a methylammonium zinc oxide phosphate phase that remains microporous after the water and template are removed by calcination; this was synthesized as a thin film as well. We have developed a phase detection system for surface plasmon resonance sensors that uses an optical heterodyne design, increasing detection sensitivity by an order of magnitude.

PROJECT SUMMARY (continued)

PROJECT TITLE: Selective Inorganic Thin Films

ACCOMPLISHMENTS:

Publications: 5 **Presentations:** 4 **Disclosures:** 2

CRITICAL ISSUES:

1. Improving permeabilies of zinc phosphate films by reducing film thickness while maintaining complete substrate coverage.

2. Improve techniques for eliminating intercrystalline gaps and porosity in Zeolite A films via the caulking process.

FUTURE PLANS:

1. Continue studying alkali zinc phosphate membranes for hydrogen recovery, organic zinc phosphates for natural gas purification.

2. Continue to improve methods for caulking Zeolite A membranes.

3. Model permeation of mixtures of xylene isomers through known zeolite phases. Synthesize membranes containing phases with optimum selectivity. Measure relative permeabilities of xylenes through these membranes.

POTENTIAL PAYOFF: The petroleum and natural gas refining industries would significantly benefit from high permeability molecular sieve films capable of separating light, fixed gases, particularly if the membranes can be used at high temperatures. The alkali metal zinc phosphates that we have synthesized as membranes are stable up to 700 °C, which is compatible with hydrogen recovery. With sufficiently high permeability and low unit area cost, energy savings of several quad/yr could be achieved when all feasible applications of inorganic membranes are considered.

We are negotiating a CRADA with Amoco Chemical Co. to study the feasibility of using shape selective molecular sieve membranes to enrich *p*-xylene from mixtures of the isomers. If these membranes eliminate the first crystallization step in *p*-xylene production worldwide, approximately 0.070 quad/yr will be saved, principally in the form of decreased natural gas consumption.

SIGNIFICANT ACCOMPLISHMENT

ZINC PHOSPHATE MOLECULAR SIEVES

Advanced Industrial Materials (AIM) Program

ISSUE: Separating valuable light gases such as methane and hydrogen from other constituents of natural gas and refinery process streams (such as N_2, CO_2, C_2H_2, H_2S) using polymer membrane technology is difficult, particularly at high temperatures. Membranes capable of separating gases based on kinetic diameter (molecular sieves) promise high separation factors, but previously reported zeolitic films have not been sufficiently durable or permeable to be useful for large-scale gas refining.

RESULTS: We have shown that zinc phosphates can act as molecular sieves in a fashion similar to zeolites, and that molecular sieve membranes can be made from zinc phosphate films. For example, we have deposited films of microporous cesium zinc oxide phosphate onto porous zinc oxide wafers. These membranes are permeable to helium and water, but not to hydrogen or to other light, fixed gases. The films can also be synthesized from metallic zinc coatings, which should be compatible with commercially available alumina gas filters. In addition, we modeled gas permeabilities in several zinc phosphates with the general formula $M_3Zn_4O(PO_4)_3$ (M=Li, Na, K), and found that the lithium and sodium phases can selectively permeate hydrogen in the presence of other gases. Films of the potassium phase were deposited onto ZnO wafers and ion exchanged to yield the lithium and sodium phases.

We have also synthesized a new organic zinc oxide phosphate phase from which the organic template (methylamine) and water may be removed via calcination without altering the structure of the zinc phosphate framework. This is the first organic zinc phosphate for which nondestructive template removal has been demonstrated. The pore size of this phase is being determined crystallographically. It is likely that the pores of this phase are larger than those of the inorganic phases; this is significant for methane purification. Films of this phase were successfully grown onto ZnO wafers and thermally detemplated.

SIGNIFICANCE: The petroleum and natural gas refining industries would benefit significantly from high permeability molecular sieve films capable of separating light, fixed gases, particularly if the membranes can be used at high temperatures. The alkali metal zinc phosphates that we have synthesized as membranes are stable up to 700 °C, which is compatible with hydrogen recovery. With sufficiently high permeability and low unit area cost, energy savings of several quad/yr could be achieved when all feasible applications of inorganic membranes are considered.

This work was sponsored by the U. S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program under contract DE-AC04-95AL85000 with the Sandia Corporation, a Lockheed Martin company.

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