

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 1995

Date Published: April 1996

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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 1995

Date Published: April 1996

Coordinated by Peter Angelini
Compiled by HSRD\BEIA\Information Management Technology Group
Oak Ridge National Laboratory

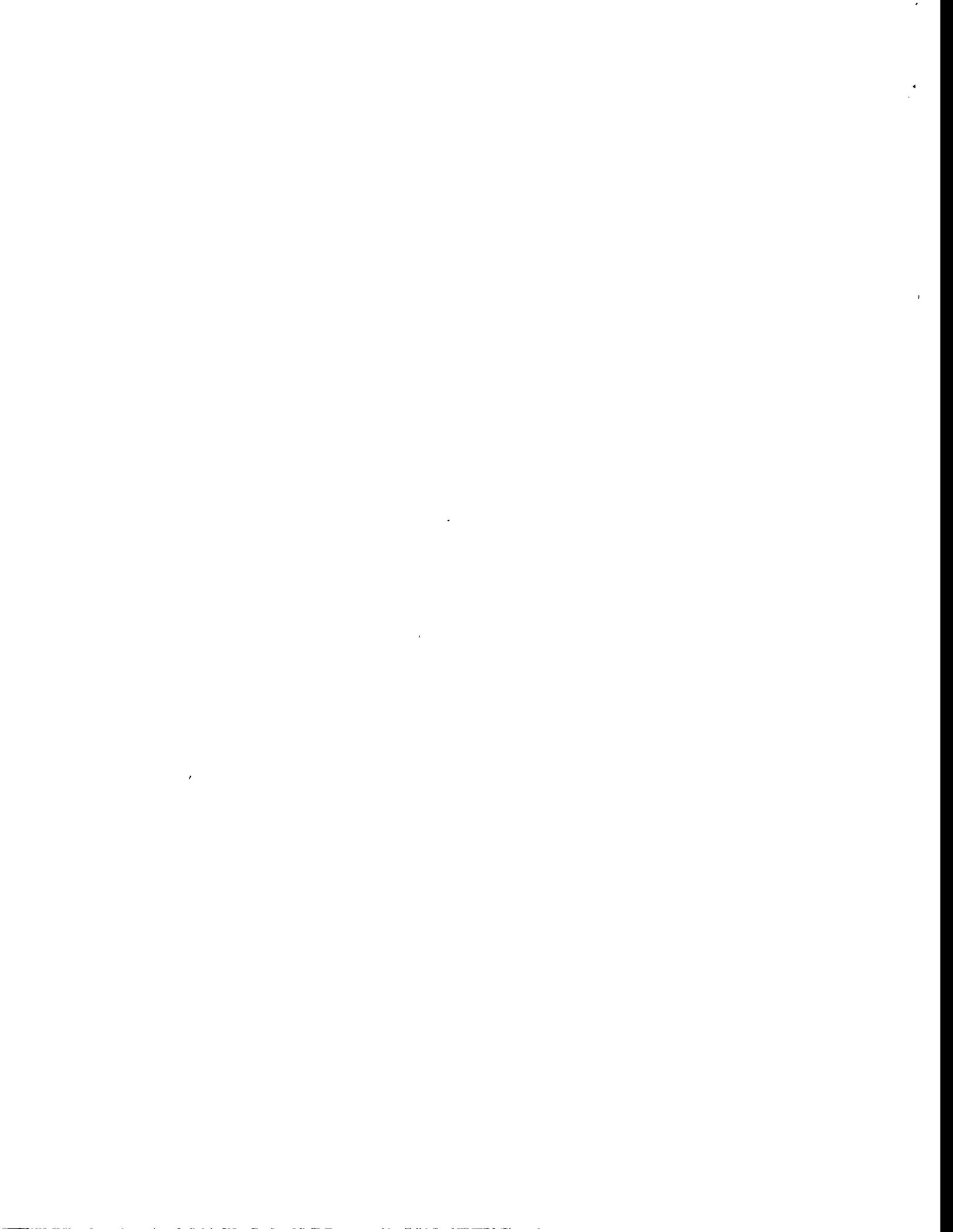


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INTRODUCTION



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:

- o Forest Products
- o Steel
- o Aluminum
- o Metal Casting
- o Chemicals
- o Refineries
- o Glass

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, and welding 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.

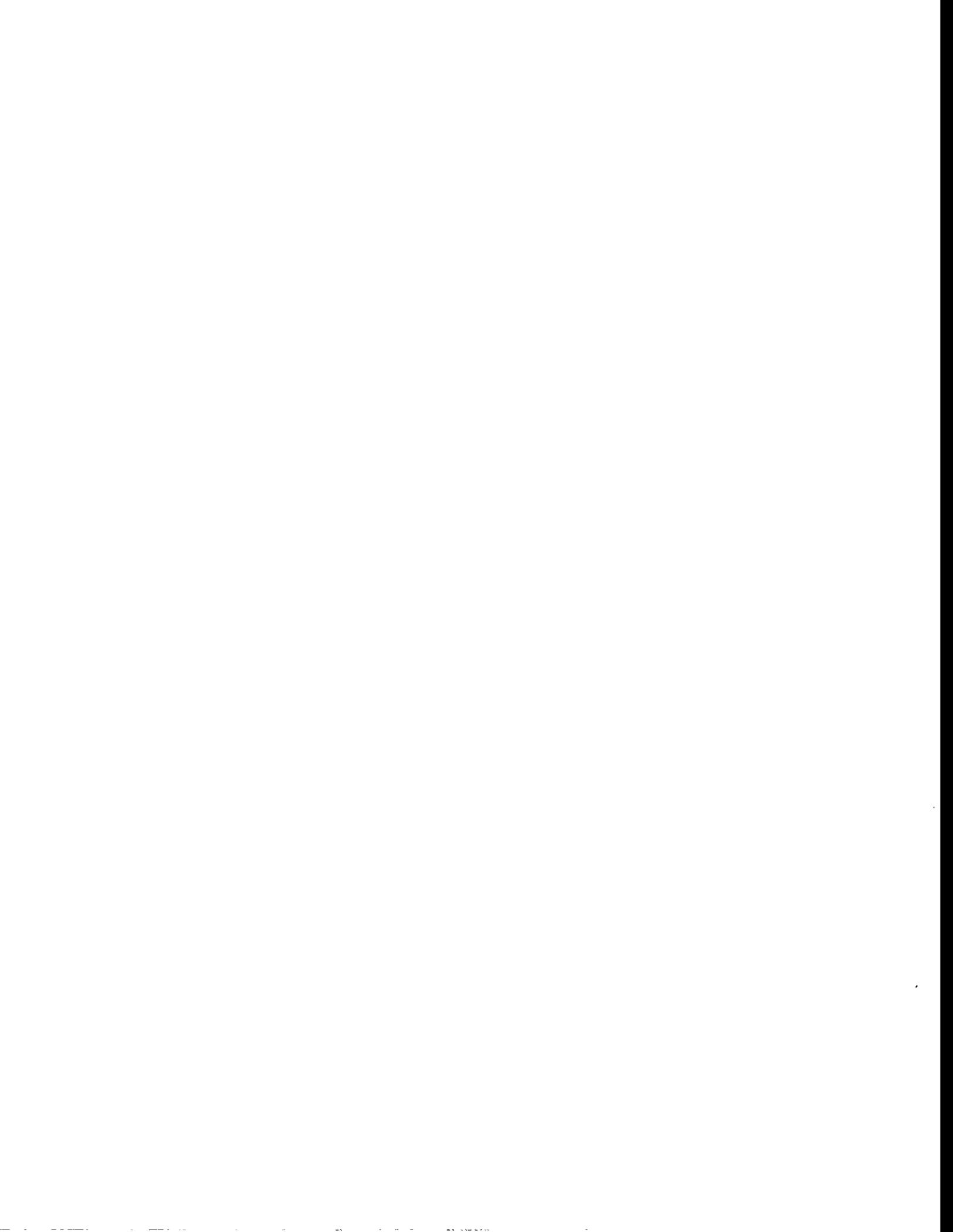
The mission of AIM has, therefore, changed to "Support development and commercialization of new or improved materials to improve productivity, product quality, and energy efficiency in the major process industries." Though AIM remains essentially a National Laboratory Program, it is essential that each 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 reasonably 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 resistant, 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 Project Summaries and Significant Accomplishments Report contains the technical details 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

PRINCIPLE INVESTIGATORS: C. T. Liu (423) 574-4459, P. J. Maziasz (423) 574-5082, and J. H. Schneibel (423) 576-4644.

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 alloying 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: Our studies indicate that the microstructure of two-phase TiAl alloys can be controlled by material processing, heat treatment, and composition control. The TiAl alloys with refined lamellar colony size (50 μm) and ultra-fine interlamellar spacing (0.2 μm) exhibited excellent strength at room and elevated temperatures. Also, the alloys with the optimum microstructure showed excellent fracture toughness ($\sim 60 \text{ MPa}\sqrt{\text{m}}$) at room temperature.

Patents: 3

Publications: 19

Proceedings: 19

Books: 9

Presentations: 21

ACCOMPLISHMENTS:

Licenses: Discussions with several U.S. industries for potential licenses

Known Follow-on Product(s): Anticipated use in heat engines, turbine engines, and other energy conversion and industrial systems.

OTHER SUCCESSFUL TECHNOLOGY TRANSFER ACTIVITIES AS EVIDENCE OF INDUSTRY INTEREST: Several technical exchange meetings were held with U.S. industries including GE, Pratt & Whitney, Howmet Corporation, and Cummins Engine Company.

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 fracture 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 increase the tensile ductility and fracture toughness of TiAl-base alloys by control of grain size and lamellar structure, and (3) 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.

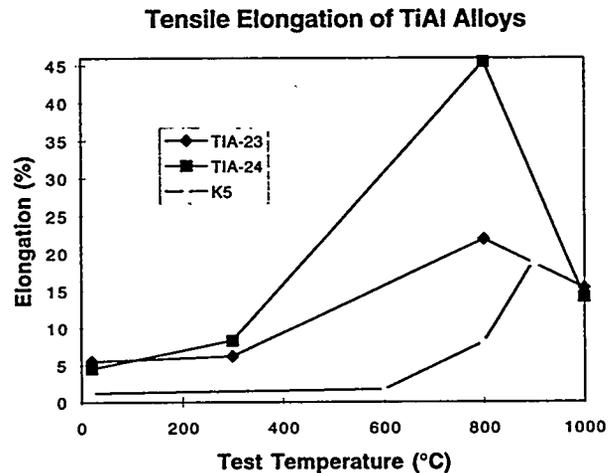
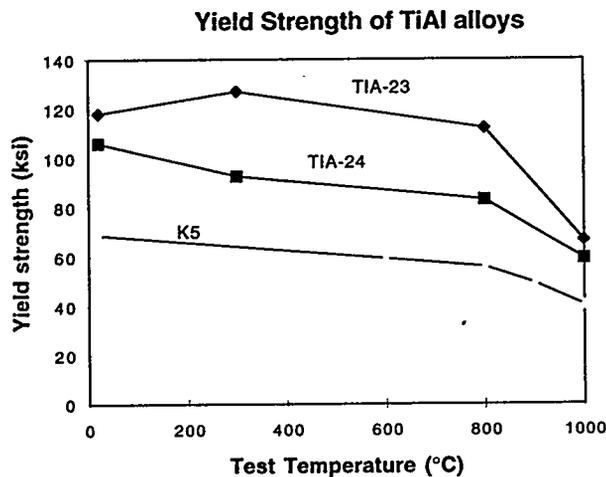
TiAl ALLOYS WITH CONTROLLED MICROSTRUCTURES SHOW EXCELLENT TENSILE PROPERTIES AND FRACTURE TOUGHNESS AT ROOM AND ELEVATED TEMPERATURES

Problem:

Two-phase TiAl alloys offer an attractive mix of low density ($\sim 4 \text{ g/cm}^3$), low thermal expansion, high melting point, and decent oxidation resistance at elevated temperatures. The research efforts so far have not yet developed adequate mechanical properties for structural use. The major concerns are ambient-temperature ductility and fracture resistance and high-temperature strength and creep resistance.

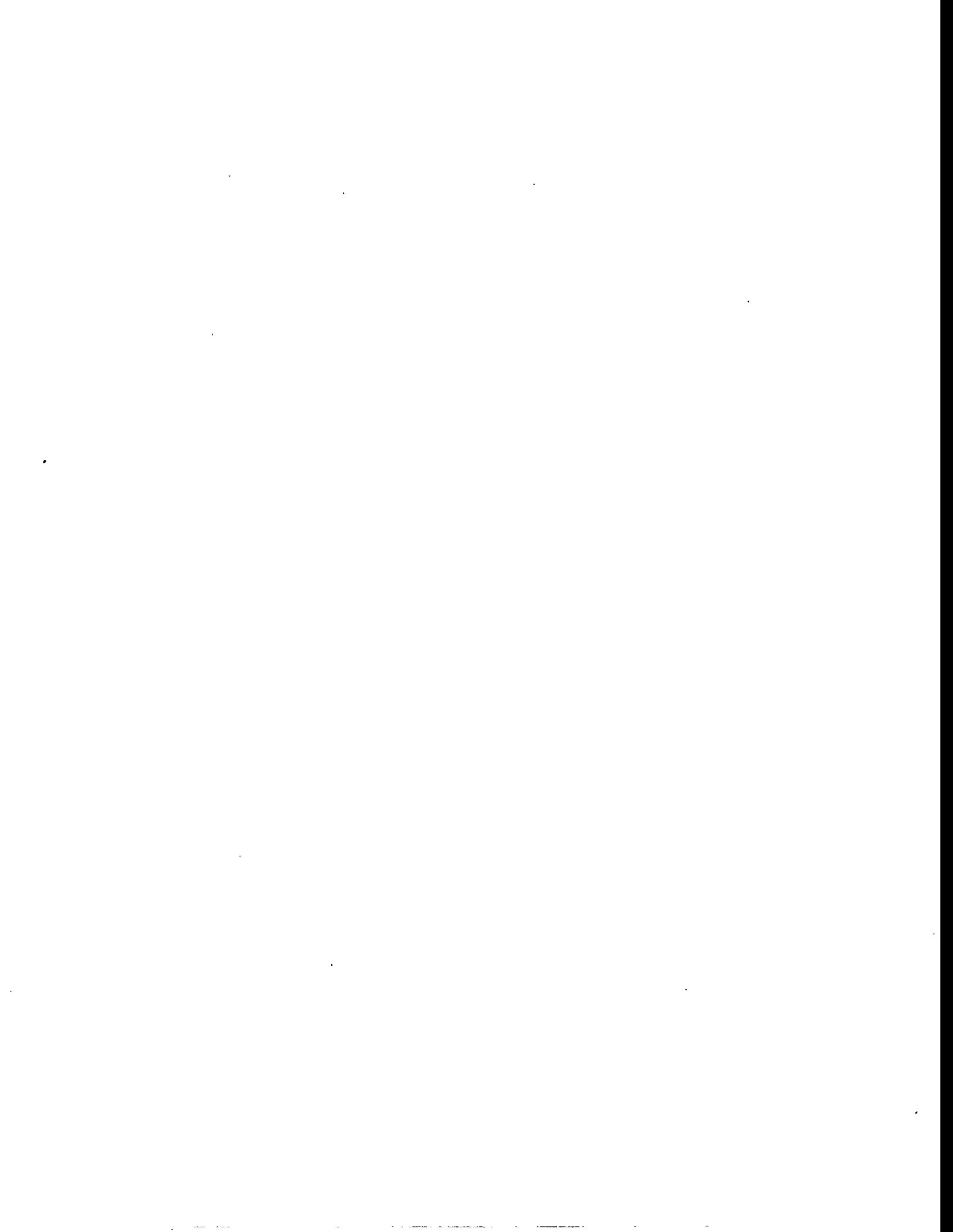
Results:

Our studies indicate that fully lamellar microstructures of TiAl alloys can be controlled by hot extrusion of the alloys at temperatures above 1300°C . The TiAl alloys with refined lamellar colony size ($50 \mu\text{m}$) and ultra-fine interlamellar spacing ($0.2 \mu\text{m}$) exhibited excellent ductility and strength at room and elevated temperatures (see Fig. 1). The alloy TIA-23 developed at ORNL is almost 100% stronger and more ductile than the best existing TiAl alloy (K5) developed recently. Also, the alloy with the optimum microstructure showed an excellent fracture toughness, $\sim 60 \text{ MPa}\sqrt{\text{m}}$, at room temperature.



Significance - For Energy Efficiency:

The development of light-weight, high-strength TiAl alloys for high-temperature applications is expected to significantly improve the performance (in terms of thermal efficiency, material durability, etc.) of heat and turbine engines and energy conversion systems. All of these will result in a substantial energy savings for these engineering systems.



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Development of Materials for Black Liquor Recovery Boilers

PHASE: FY 1995

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR: J.R. Keiser (423) 574-4453

PHASE OBJECTIVE: Characterize the microstructural and residual stress state of as-fabricated composite tubing. Use measured residual stress data in finite element models to predict the stress state of composite floor tubes during boiler operation.

ULTIMATE OBJECTIVE: Utilize various characterization techniques and laboratory fatigue and corrosion testing methods to determine the mechanism(s) responsible for cracking of black liquor recovery boiler composite floor tubes. Measure the residual stresses in unexposed tubes, and use finite element modeling methods to predict the stresses in composite tubes under operating conditions. Using the information gathered from these studies, identify a material or operational approach that can be used to prevent cracking of composite floor tubes.

TECHNICAL APPROACH: Standard metallographic examination techniques coupled with advanced analytical techniques can provide significant information about both unexposed tubes and exposed, cracked tubes. Neutron and X-ray diffraction can be used to determine the residual stresses in composite tubes.

PROGRESS: Microstructural studies of unexposed tubes defined the interfacial region in composite tubes. Adjacent to the interface in the austenitic material there is a carbide-rich region while the ferritic material has a carbon-depleted region along the interface. Many tubes that had cracked during exposure were examined, and a tendency for branching to develop in the cracks and for the cracks to turn and proceed parallel to the interface were noted. Neutron diffraction measurements established that residual stresses in composite tubes had patterns that were characteristic of the tube manufacturer. Finite element modeling considered the effects of residual stresses from fabrication as well as stresses produced by weld attachment of membranes, internal pressurization, and exposure to the high boiler temperatures.

Patents: _____

Publications: _____

Proceedings: _____

Books: _____

Presentations: 17

ACCOMPLISHMENTS:

Licenses: none

Industrial Interest: Ten paper companies, five recovery boiler manufacturers, and one composite tube fabricator are actively participating in the program by contributing information, samples, and materials.

CAUSE OF FAILURE OF CARBON STEEL RECOVERY BOILER FLOOR TUBES IDENTIFIED

Problem:

Studded carbon steel tubes are frequently used as floor tubes on slope-floored black liquor recovery boilers. However, there have been many cases of ruptures in such tubes. By determining the cause of these failures, it may be possible to identify alternate materials or operating conditions or procedures that will lessen the chance of such failures.

Results:

Macro- and microscopic examinations were used to identify changes that had occurred to the dimensions and microstructure of three recovery boiler tubes as a result of their exposure. These examinations revealed extensive corrosion on the outside of the tubes had significantly reduced the wall thickness. Microstructural studies showed changes that indicated the tubes had reached temperatures many hundreds of degrees above their normal operating temperature. As a result of the reduction of cross section caused by corrosion and the reduction in strength caused by operation at higher than design temperature, the load on the tubes exceeded the strength of the remaining material and ductile rupture occurred.

Significance:

Protection of carbon steel floor tubes from the corrosive smelt environment and prevention of large temperature spikes should lessen the probability of carbon steel tube rupture thus improving the safety and reliability of recovery boiler operation.

Development Of Materials For Service In Kraft Recovery Boilers

The Project Incorporates a Strong Team Effort

Pulp and Paper

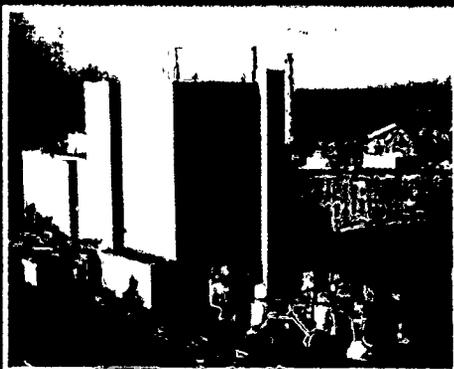
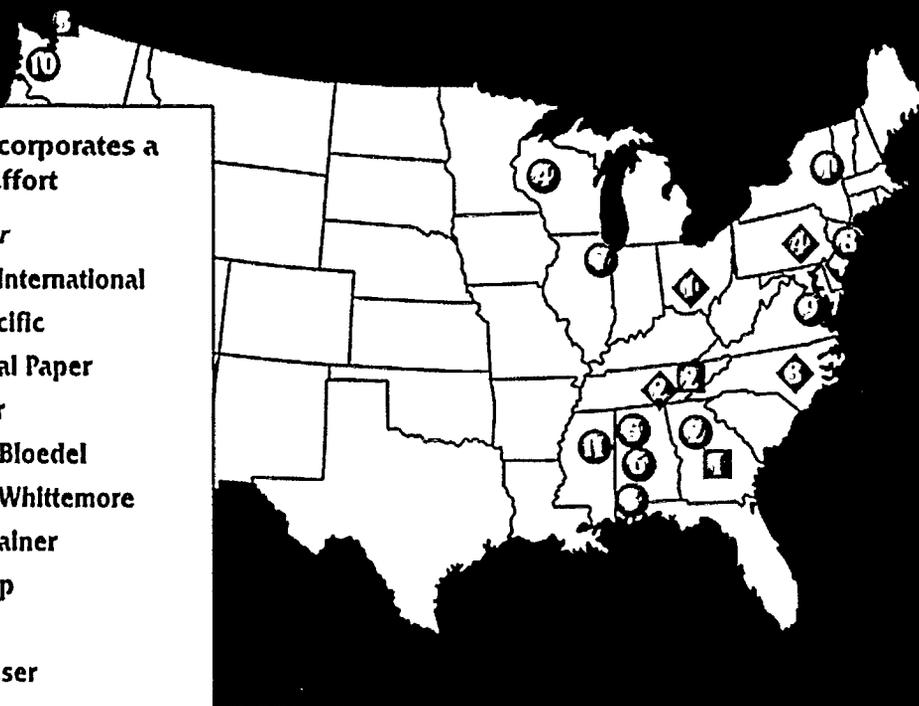
- ① Champion International
- ② Georgia-Pacific
- ③ International Paper
- ④ James River
- ⑤ MacMillan Bloedel
- ⑥ Parsons & Whittemore
- ⑦ Stone Contalner
- ⑧ Union Camp
- ⑨ Westvaco
- ⑩ Weyerhaeuser
- ⑪ Weyerhaeuser

Suppliers

- ① Babcock & Wilcox
- ② Combustion Engineering
- ③ Kvaerner
- ④ Sandvik

Research Sites

- ① Institute for Paper Science and Technology
- ② Oak Ridge National Laboratory
- ③ Pulp and Paper Research Institute of Canada



Approach _____

- Identification of degradation mechanisms, and selection of improved technologies/materials
- Evaluation of alternative design/materials
- Manufacturing and testing of components

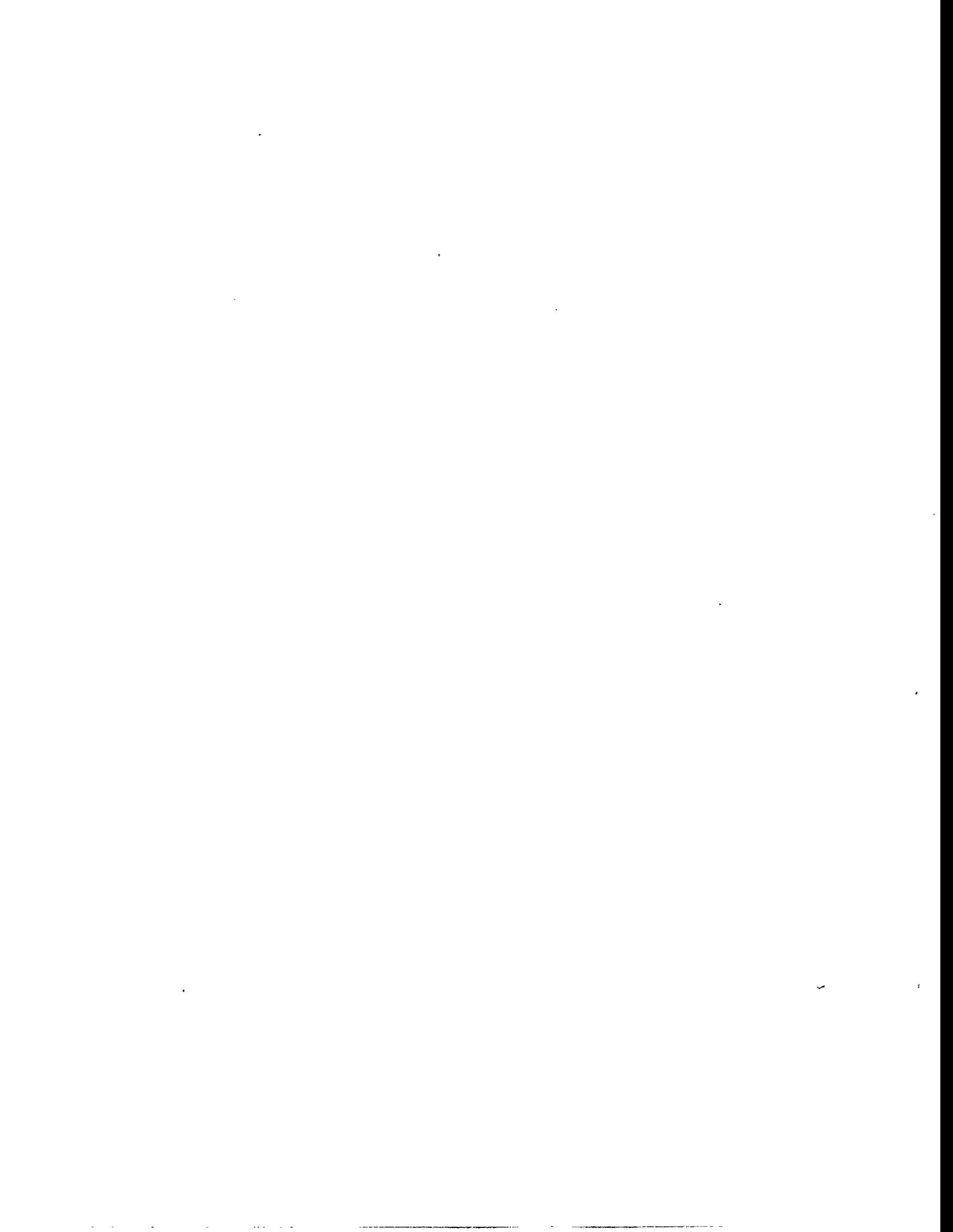
The project is a direct result of the "Materials Needs And Opportunities" assessment of the AIM Program.



Research and Development Sponsored by

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





PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: Metallic and Intermetallic Alloys/Composites

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

PHASE: FY 1995

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPLE INVESTIGATORS: P.J. Maziasz (615) 574-5082, G.M. Goodwin (615) 574-4809

PHASE OBJECTIVE: Develop weldable FeAl alloys with good properties. Develop the best fabrication technology for optimum mechanical properties (room-temperature ductility and high-temperature strength) for monolithic applications of such weldable FeAl alloys. Develop coating/cladding (ie., weld-overlay cladding) technology for conventional code-approved structural steels and alloys.

ULTIMATE OBJECTIVE: Take advantage of the outstanding high-temperature oxidation/sulfidation resistance, corrosion resistance in molten salts or molten aluminum, and potential carburization/nitriding resistance of FeAl alloys. Produce components for industry to test. Develop fabrication technology for monolithic FeAl components equivalent to commercial steels or coating/cladding technology for code-approved structural steels and alloys.

TECHNICAL APPROACH: Micro-additions of carbon and boron impart the best weldability, room-temperature ductility and high-temperature strength to FeAl alloys. Develop the technology to produce FeAl weld-overlay cladding on conventional steels and alloys using industrially-produced weld consumables. Develop I/M and P/M fabrication technology for producing FeAl components for industry testing.

PROGRESS: Fe-sheath/Al-core weld-wire (1.6 mm diam) has been produced by Stoodly and was used to make good crack-free FeAl on 2½Cr-1Mo steel. Neutron diffraction studies indicate that substantial tensile residual stresses are found in FeAl weld-clad, and FeAl must be strong, ductile and resistant to hydrogen embrittlement to survive. I/M and P/M processing of FeAl that significantly refines the grain structure achieves all of these. Boron micro-alloying additions further improve the hydrogen embrittlement resistance of FeAl and its high-temperature strength. As-cast FeAl has a significant strength advantage over type 316 stainless steel at up to 800°C.

Patents: 1 (+1)

Publications: 3

Proceedings: 6

Books:

Presentations: 5

ACCOMPLISHMENTS: Licenses: Ametek, is interested in extending licensing of Fe₃Al to FeAl.

Known Follow-on Products: FeAl is in test by GE, Rocketdyne and Thixomat (semi-solid injection molding of Al). INCO is willing to test for carburization/nitriding resistance. Radiant heating tubes have been centrifugally-cast by Alloy Engineering and Casting Company.

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

CRITICAL ISSUES: Weldability, room-temperature ductility (hydrogen-embrittlement resistance in air), and high-temperature strength are critical parameters that must be improved for FeAl alloys. FeAl weld consumables and I/M or P/M components must be produced commercially. FeAl cladding/coating need to be made on code-approved steel and alloy components. Industry testing of FeAl in aggressive service environments is required.

POTENTIAL PAYOFF: FeAl alloys are optimum materials for forming thin, adherent and protective Al_2O_3 films, which is the basis for their outstanding high-temperature oxidation/sulfidation/corrosion resistance. FeAl coated steels or monolithic FeAl can perform at conditions where conventional steels and Fe-based alloys cannot to save energy and material wastage. They can save substantial energy by enabling new and improved materials processing technologies. FeAl alloys have improved corrosion and wear-resistance and are Cr- and Ni-free relative to 300-series stainless steels and most heat-resistant alloys.

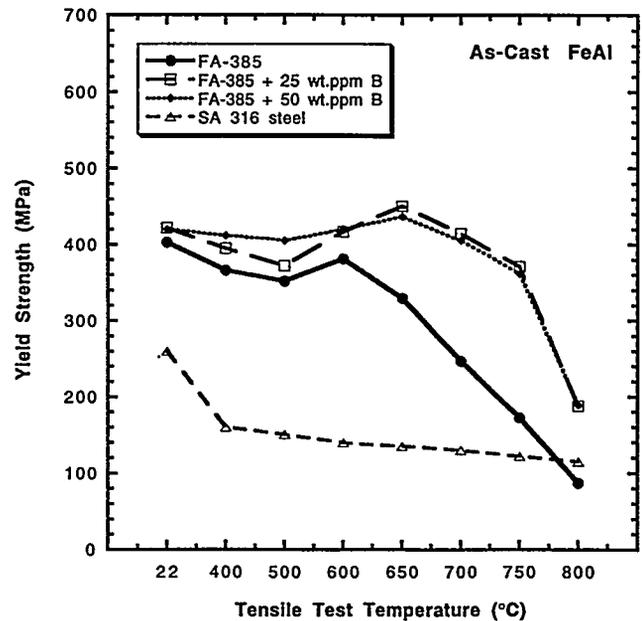
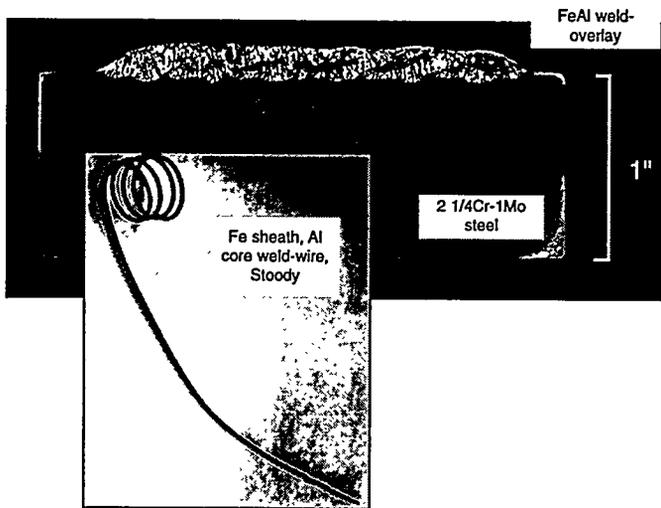
BORON MICRO-ALLOYED FeAl HAS SIGNIFICANTLY IMPROVED WELDABILITY, STRENGTH, DUCTILITY AND TOUGHNESS

Problem:

Improve the weldability, room-temperature ductility and hydrogen-embrittlement, and high-temperature strength of FeAl to take advantage of the outstanding oxidation/sulfidation and corrosion resistance that these Al_2O_3 -forming materials offer.

Results:

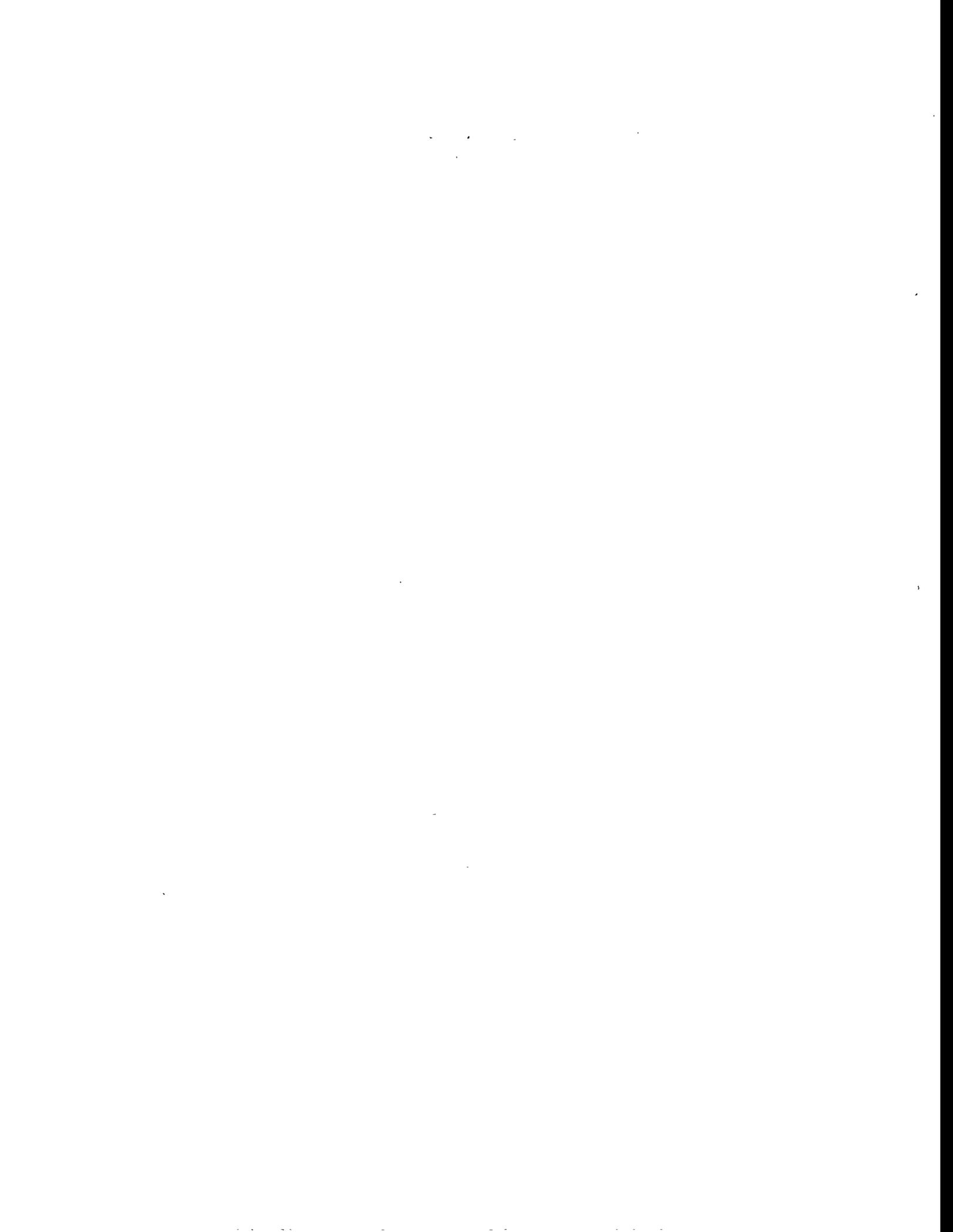
FeAl weld-wire for automated welding was produced commercially by Stoodly and found to make crack-free welds on steel. Boron micro-alloying has been found to improve the room-temperature ductility and high-temperature strength of FeAl. FeAl radiant-heating tubes have been centrifugally-cast commercially using the EXO-MELT technology. I/M and P/M extrusions of FeAl have been found to have outstanding ductility, strength and toughness at room-temperature.



Significance - For Energy Conservation:

FeAl alloys have oxidation/sulfidation resistance, resistance to dissolution in molten aluminum and the potential for carburization/nitriding resistance that cannot be found in conventional steels and alloys. They are 25% less dense and have much higher electrical resistivity than steels. They can save significant energy by improving existing processes or new, more efficient technologies for producing or processing materials.

(R&D performed at Oak Ridge National Laboratory (ORNL) under DOE-EE-AIM Program support)



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: High-Temperature Materials

PROJECT TITLE: Ni₃Al Technology Transfer

PHASE: FY 1995

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, and R. W. Swindeman (423) 574-5108

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 application identified to date include: furnace furniture (trays, fixtures, transfer rolls, belts, conveyors) and hot-pressing or forging dies.

TECHNICAL APPROACH: Since castings are the 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 reparability 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 during 1994 was further optimized, and its utility extended to the melting of iron and titanium aluminide. The Exo-Melt™ process won the R&D 100 award for 1995. The process details were transferred to several foundries with a specific license to United Defense/FMC. Since the transfer of Exo-Melt™ technology and licensing to United Defense/FMC, over 35,000 lb of nickel aluminide have been commercially melted. Mold filling and solidification analyses were completed for the base tray. The video animation output of the results was shared with commercial foundries.

Patents: 1
Books: 1*

Publications: 2
Presentations: 6

Proceedings: 4
Awards: 1

*Book entitled "Physical Metallurgy and Processing of Intermetallics," authored by N. S. Stoloff and V. K. Sikka, was published by Chapman & Hall.

PROJECT TITLE: Ni₃Al Technology Transfer

ACCOMPLISHMENTS:

Licenses: One license was given to United Technologies/FMC to melt, cast, and commercialize nickel aluminides.

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 nearly two years of commercial testing of transfer rolls in a steel company.
3. Completed testing of nickel-aluminide die for hammer forging application for 35,000 parts. To date, the die has exceeded the life of a currently used die material by a factor of seven.

CRITICAL ISSUES: Welding of nickel aluminides still continues to be a critical issue.

FUTURE PLANS: Continue Ni₃Al-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.

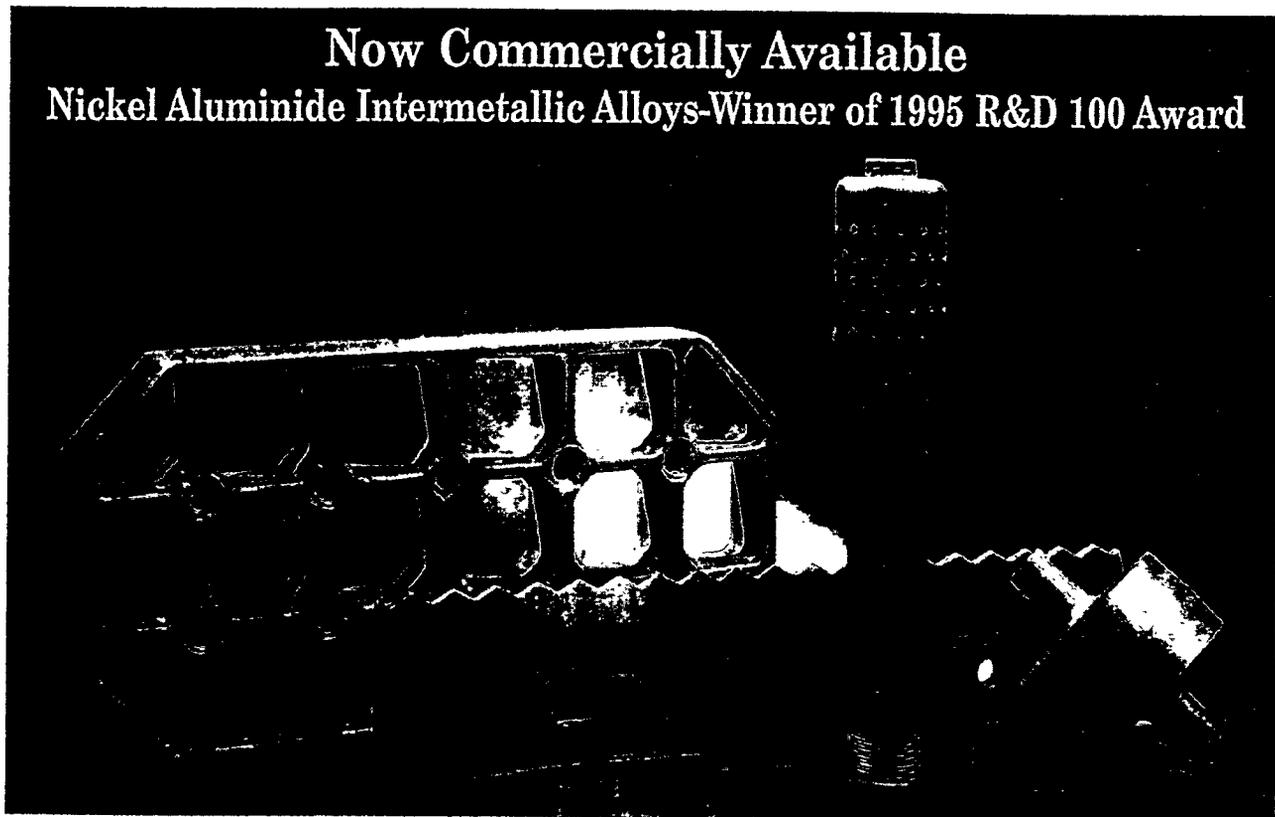
LICENSING AGREEMENT WITH A FOUNDRY PAVES THE WAY FOR COMMERCIAL AVAILABILITY OF Ni₃Al-BASED ALLOY CASTINGS

Problem:

Nickel aluminides have superior high-temperature strength and have been known to possess excellent resistance to high-temperature oxidation and carburization. However, in spite of their excellent properties, the lack of commercial availability of the castings has been the main hindrance to their applications.

Results:

The commercial availability of nickel-aluminide castings has been addressed in three steps: (1) developing a highly efficient and cost-effective process known as Exo-Melt™ for air melting nickel aluminides, (2) educating the selected foundries about the Exo-Melt™ process, and (3) selecting and licensing United Defense/FMC (Anniston, Alabama) to use the Exo-Melt™ process for melting and casting nickel aluminides. The result of licensing United Defense/FMC has been advertisements in technical journals such as the one shown below.



Significance - For Energy Conservation:

The Exo-Melt™ process saves 50% of the energy required to melt nickel aluminides as opposed to the conventional melting process. Using nickel aluminides for dies and furnace components allow longer life and requires less melting and processing of conventional materials for the same applications.

(R&D performed at Oak Ridge National Laboratory (ORNL) under DOE-EE-AIM Program support)

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: Metallic and Intermetallic Alloys/Composites

PROJECT TITLE: Synthesis and Design of Silicide Intermetallic Materials

PHASE: FY-1995

PERFORMING ORGANIZATION: Los Alamos National Laboratory (LANL)

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

PHASE OBJECTIVE: Develop $\text{MoSi}_2\text{-SiC}$, $\text{MoSi}_2\text{-Si}_3\text{N}_4$, and $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite materials for industrial applications. Develop the groundwork for a CRADA with Schuller International on MoSi_2 materials for fiberglass processing components.

ULTIMATE OBJECTIVE: To develop MoSi_2 -based high temperature structural silicide composite materials with optimum combinations of elevated temperature strength/creep resistance, low temperature fracture toughness, and high temperature oxidation resistance for applications of importance to the U.S. processing industries, and particularly the glass processing industry.

TECHNICAL APPROACH: Develop MoSi_2 -based high temperature structural materials, with focus on $\text{MoSi}_2\text{-SiC}$, $\text{MoSi}_2\text{-Si}_3\text{N}_4$, and $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites. Develop processing methods for MoSi_2 -based materials, with emphasis on plasma spraying/plasma spray forming and electrophoretic deposition. Develop MoSi_2 -based prototype industrial components such as fiberglass processing components, gas injection tubes, and fuel burners.

PROGRESS:

Patents: 1 (2 pending)

Publications: 11

Presentations: 4

Awards/Honors: 5

ACCOMPLISHMENTS: Net-shape microlaminates of $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites have been produced by plasma spray forming and their mechanical properties determined. The fabrication, microstructures, and mechanical properties of $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composites have been investigated as a function of MoSi_2 phase size, volume fraction, and densification aid. SHS powders produced by the Exotherm Corporation have been investigated for potential plasma spray coating and structural use in glass melting applications. The electrophoretic deposition process has been shown to be feasible for MoSi_2 and $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composites. The mechanical properties of MoSi_2 plasma spray formed tubes have been determined at Penn State University. A Partial Transient Liquid Phase method has been demonstrated for joining MoSi_2 to stainless steel. In collaboration with Schuller International, refractory bricks for glass melting have been successfully coated with MoSi_2 and the corrosion resistance of MoSi_2 in molten alkali-borosilicate glass has been determined.

Licenses: None

Known Follow-On Products: Fiberglass processing components. Industrial gas burners and lances.

PROJECT TITLE: Synthesis and Design of Silicide Intermetallic Materials

CRITICAL ISSUES: Identification, fabrication, testing, and evaluation of MoSi₂-based materials for prototype fiberglass processing components, as well as the processing of other types of glasses. Finalization of the CRADA with Schuller International.

FUTURE PLANS: To develop MoSi₂-based materials for the industrial applications, particularly in the glass processing industry.

POTENTIAL PAYOFF: The potential payoff for industrial applications of high temperature MoSi₂-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 high temperature industrial components. The potential for an energy savings of 0.2 Quads (1 Quad = 10¹⁵ btu) exists in these applications. An environmental payoff also exists since MoSi₂-based radiant burners that can burn mixtures of pure oxygen and natural gas will reduce NO_x and CO₂ emissions. With regard to economic benefits, if these materials can be inserted as processing components the savings in the glass industry alone are estimated at \$38M annually.

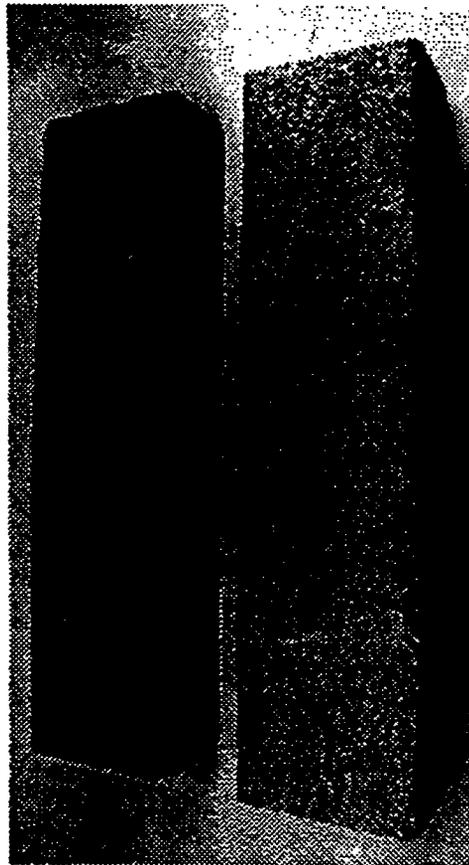
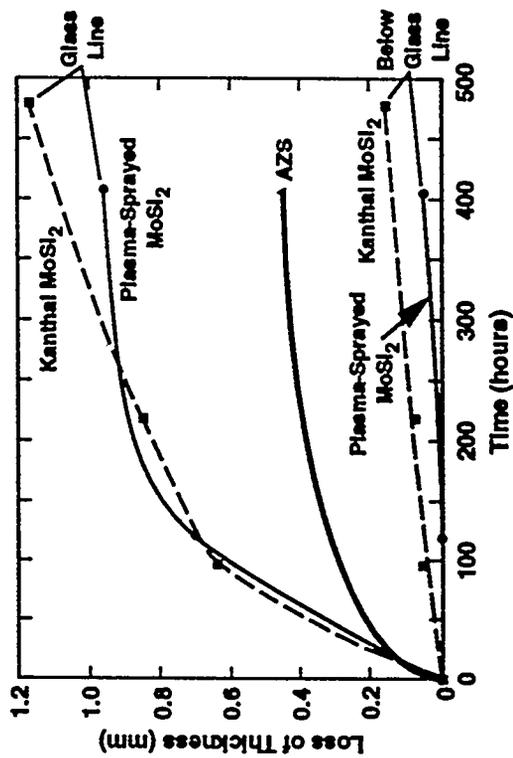
ESTIMATED ENERGY SAVINGS: Potential energy savings of 0.2 Quads (1 Quad = 10¹⁵ btu) will occur from the use of MoSi₂-based materials in industrial applications.

MoSi₂ Coatings for Improved Refractory and Component Lifetime for Glass Applications



- Use of MoSi₂-Based Materials can Provide:
- Lower cost rebuilds of glass melting furnaces
 - Longer glass melting operations
 - higher daily pulls of glass products
 - better glass quality
 - Reduce disposal of glass refractories in landfills

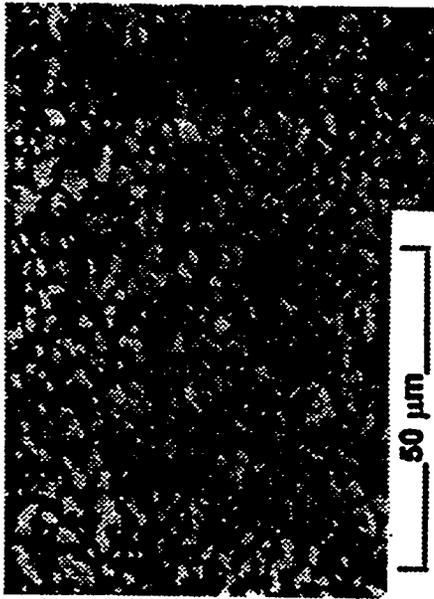
Static Corrosion in Alkali Borosilicate, 1065°C



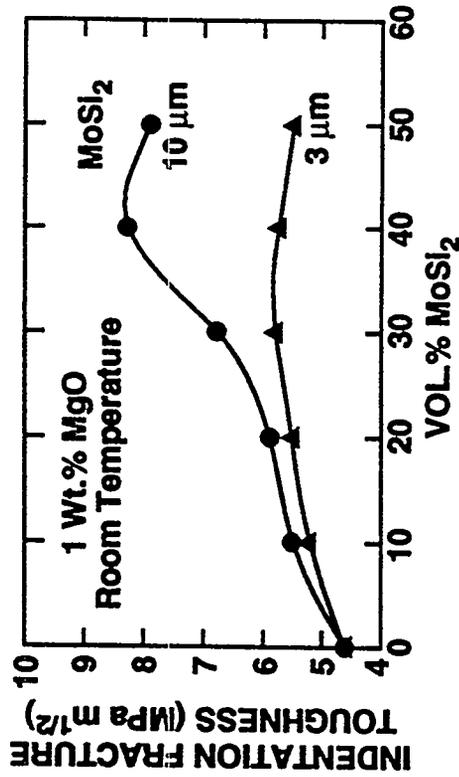
Beryllium Atomization
and Thermal Spray Facility

Los Alamos
Materials Science and Technology

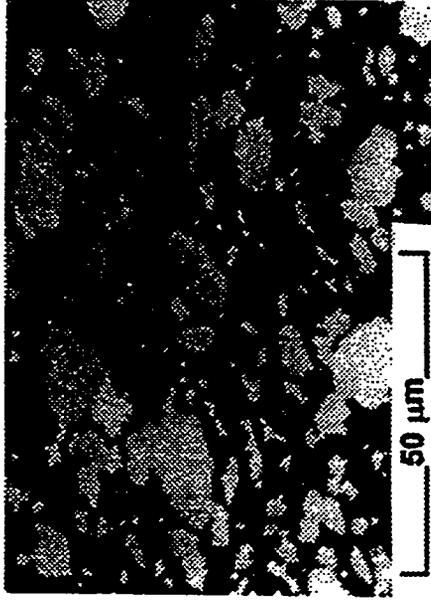
Los Alamos $\text{MoSi}_2\text{-Si}_3\text{N}_4$ Composites Exhibit Excellent Strength and Fracture Toughness for Industrial Applications



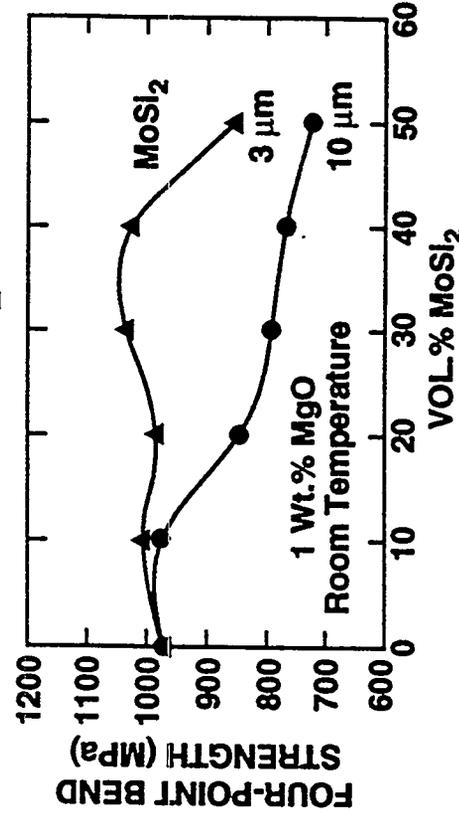
3 μm -40 vol.% MoSi_2 Composite



Fracture Toughness



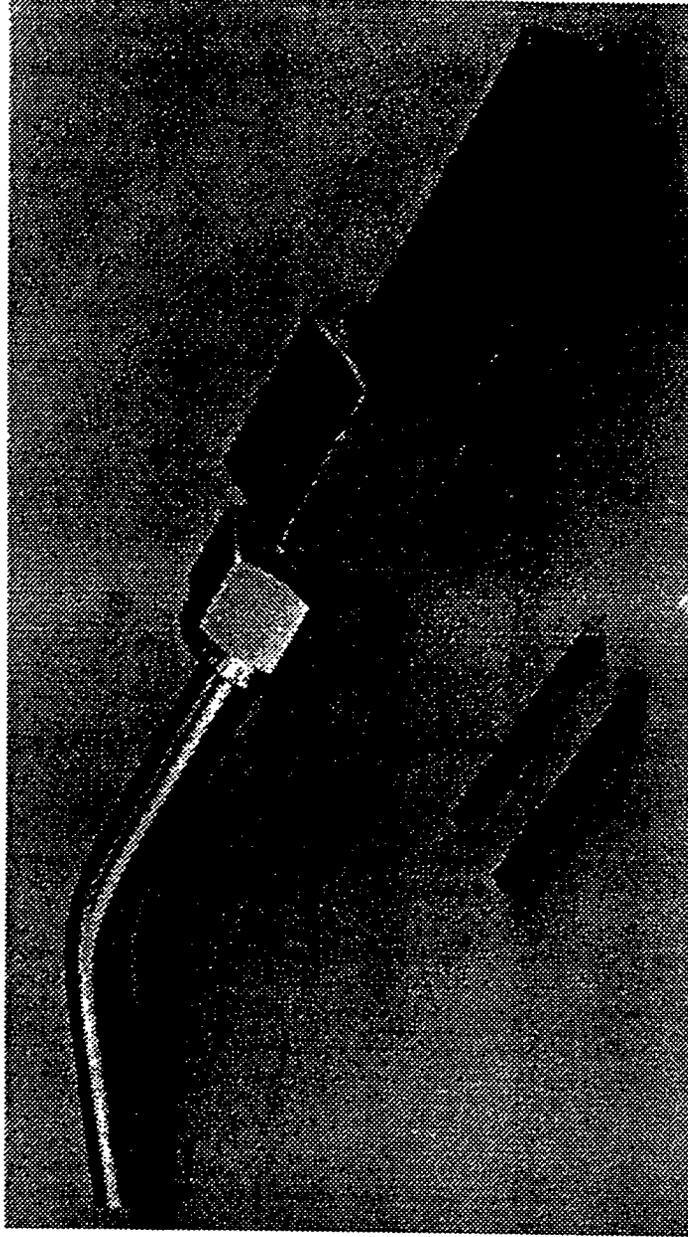
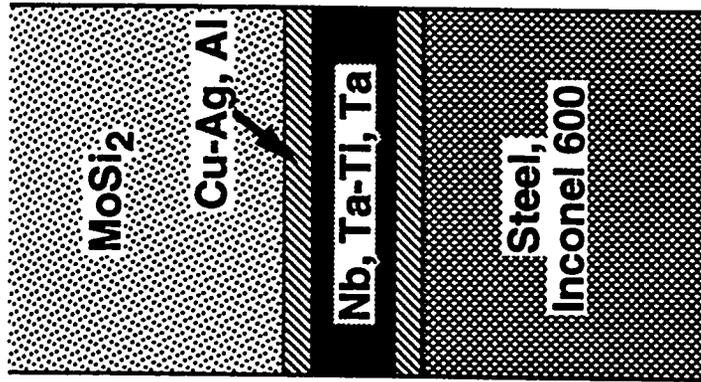
10 μm -40 vol.% MoSi_2 Composite



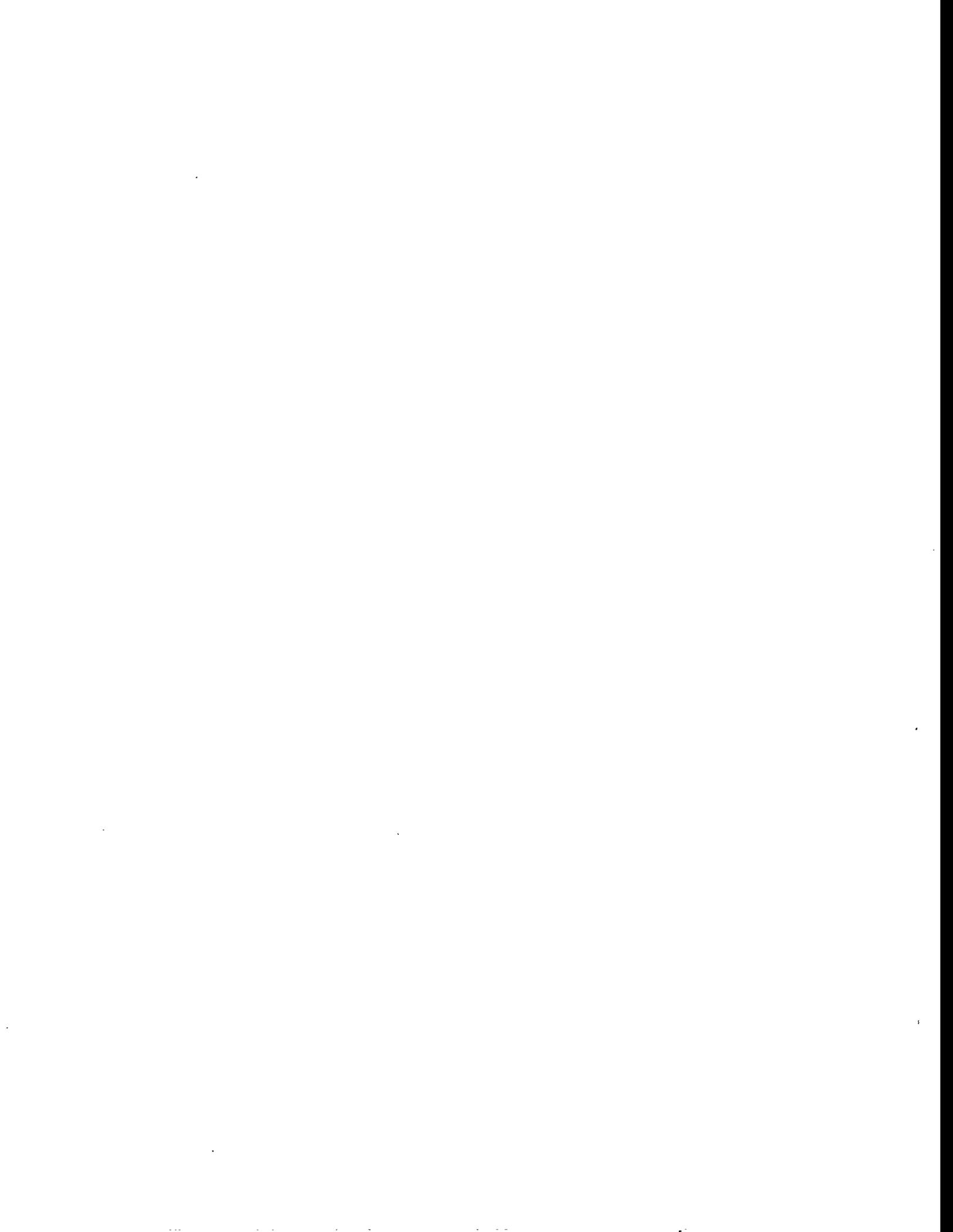
Strength

- $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composites can also be electro-discharge machined, for lower cost industrial components

MoSi₂ Joining Using Transient Liquid Phase Technique



- Low Temperature Process
- Reproducible joint quality, minimum preparation
- Joint strengths of at least 200 MPa
- Variable materials and geometries



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: 1995

PHASE COMPLETION DATE:

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

PRINCIPAL INVESTIGATOR(S): V. K. Sikka (423) 574-5112, C. A. Blue (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, shot production, spray forming, ball bearing 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 problems 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-temperature uniform droplet system at ORNL was completed in June 1995. A similar system is near completion at Tufts University, which will be used for solidification modeling. Over 36 runs have been completed using the ORNL system to date and further tailoring of this system is ongoing. The tailoring of the system includes elimination of orifice clogging, completed, and large-diameter uniform-droplet formation (> 750 μ m). The large-diameter work was accomplished in line with the possible development of a new/additional funding source.

Preliminary Low-Temperature System Results

All of the initial experimentation with the low-temperature system utilized tin as the material of choice. Preliminary size distribution data revealed an average diameter of 168 μ m and a standard deviation of 2 μ m.

PROJECT TITLE: Uniform-Droplet Spray Forming

Medium-Temperature System

The medium-temperature system has been assembled, and preliminary testing is in progress. This system will allow for the fabrication of uniform droplet of materials with melting points as high as 1250 °C. Also, this system was designed for higher volume melts (15 to 20 pound, materials dependent). Therefore, this system will aid in the development of the uniform droplet spray 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: 3

Proceedings: 2

Presentations: 5

CRITICAL ISSUES: Orifice clogging, large diameter bearing fabrication, and successful operation of a high temperature system.

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

FABRICATION OF LOW- (400°C) AND MEDIUM-TEMPERATURE (1250°C) UNIFORM-DROPLET SPRAY FACILITIES AT ORNL TO ALLOW FOR THE DEVELOPMENT OF A HIGH- TEMPERATURE FACILITY AND FULL DEVELOPMENT OF THE PROCESS

Problem:

A uniform-droplet spray process (UDS) developed at Massachusetts Institute of Technology (MIT) produces monosize metallic powders. The monosize droplets offer the potential for new structures during the spray-casting process and designed structures through powder-metallurgy processes. However, the UDS is currently available only for low-melting-point metals, although the potential for applications is the most for high-temperature materials. Significant progress has been made towards the goal for having a high-temperature system.

Results:

Both a low and medium UDS system have been fabricated at Oak Ridge National Laboratory (ORNL). All of the initial experimentation with the low-temperature system utilized tin as the material of choice. Preliminary-size distribution data for a 45- μm orifice revealed an average diameter of 168 μm and a standard deviation of 2 μm . The UDS process allows for the fabrication of powders of a single size with no sieving and spraying of materials with identical masses and thermal histories. Figure 1 shows a scanning electron micrograph of tin powder fabricated by ORNL's UDS system. Significant progress has also been made towards understanding the UDS process at MIT and Tufts University, the partners in the development of the process.

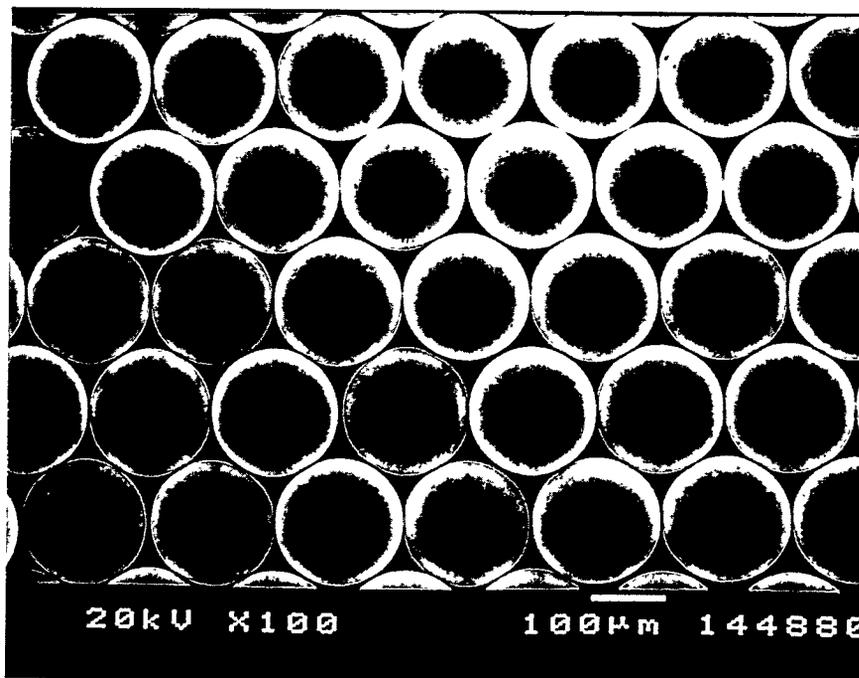
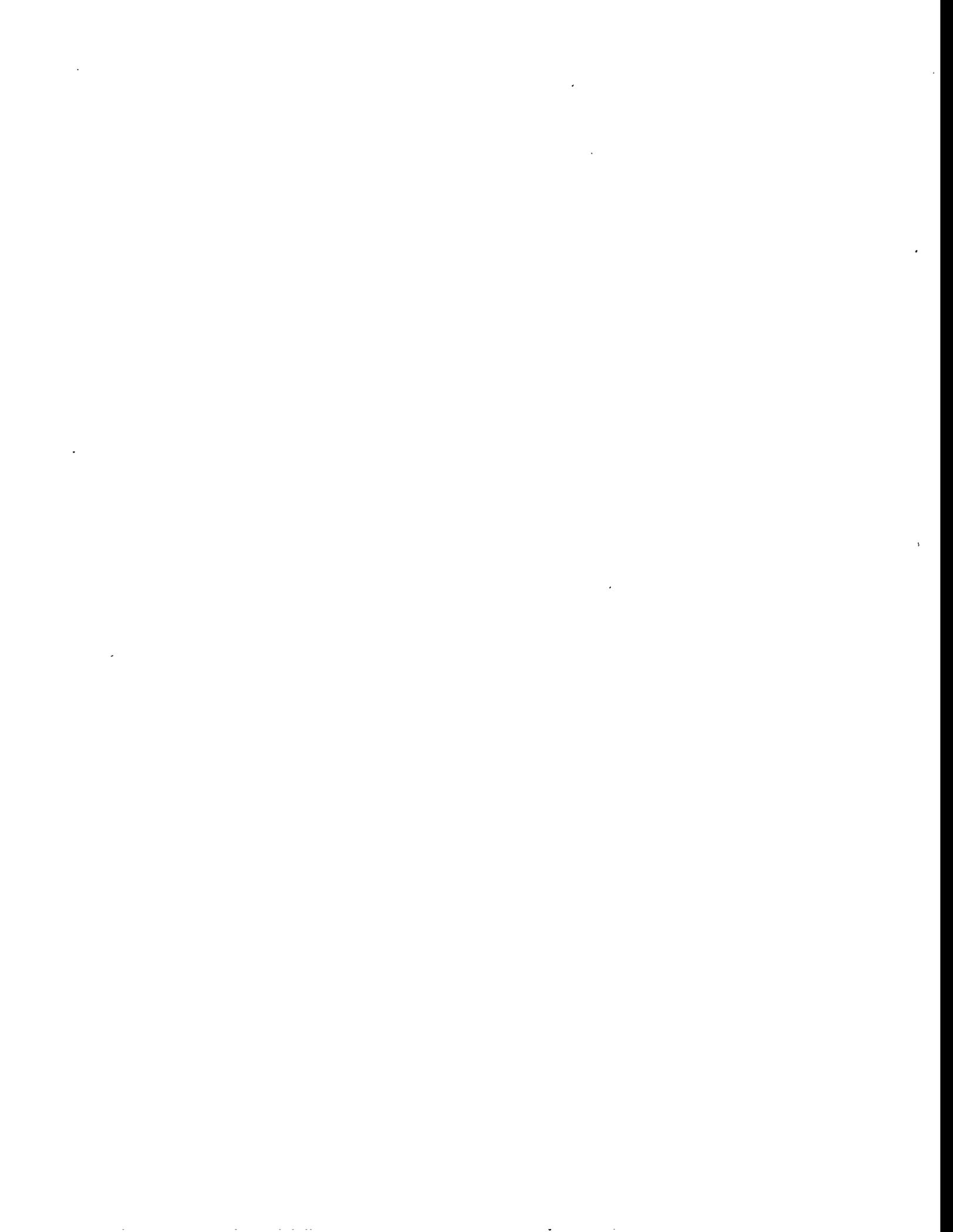


Fig. 1. Droplets produced by the Uniform-Droplet Spray system at the Oak Ridge National Laboratory.

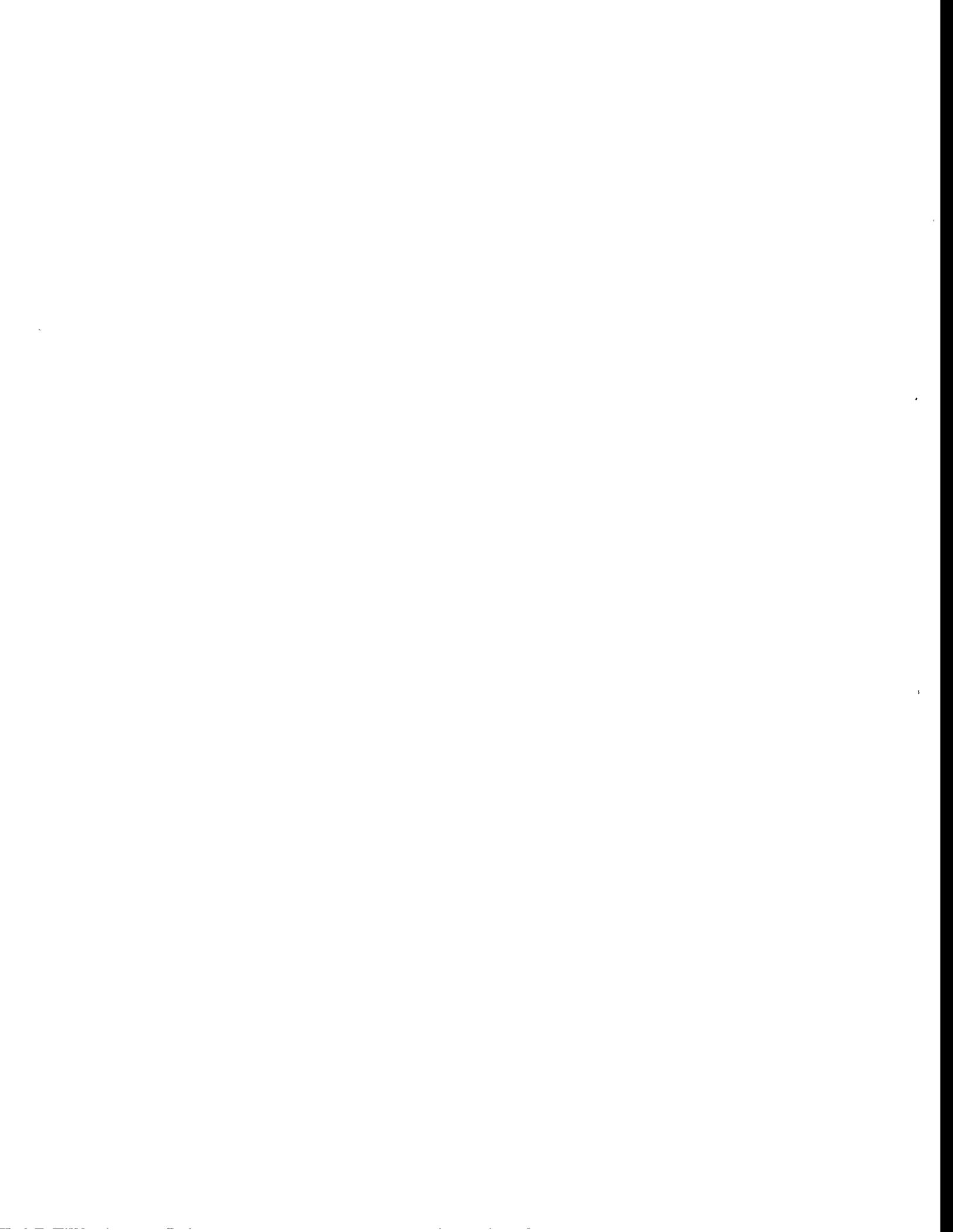
Significance - For Energy Efficiency:

Energy savings will result from: (1) a reduced need for remelting unwanted powder size as is the case for the conventional process, (2) the production of near-net shape, which requires either none or minimum hot processing to final thickness or size; and (3) enhancing the life of the powder metallurgy or sprayed component and, thus, requiring less processing of the material.

(R&D performed at ORNL under DOE-EE-AIM Program support.)



ADVANCED CERAMICS AND COMPOSITES



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: Inorganic Coatings

PROJECT TITLE: Advanced Methods for Processing Ceramics

PHASE: FY 1995

PERFORMING ORGANIZATION: Georgia Institute of Technology

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

PHASE OBJECTIVE: Develop the combustion chemical vapor deposition process for the deposition of high quality ceramic coatings.

ULTIMATE OBJECTIVE: Develop a containerless chemical vapor deposition process that is economically advantageous for certain applications, e.g., for the coating of ceramic fiber tows.

TECHNICAL APPROACH: Optimize the CCVD process for the deposition of oxide coatings by a systematic investigation of process parameter variation. Develop alternative CCVD variants utilizing various combinations of fuels, flames types, and reagent delivery schemes. Evaluate the properties of the resulting coatings.

PROGRESS: The oscillating capillary nebulizer (OCN) was found useful for performing combustion CVD. Ceria (CeO_2) coatings produced by the combustion of smaller, more uniform aerosols produced by the OCN displayed higher quality at lower deposition temperatures than coatings produced with a perfume sprayer-type nebulizer. Prior to investigating the feasibility of the OCN a gaseous fuel combustion CVD process was developed for depositing ceria. Polycrystalline, textured zirconia-yttria coatings have been deposited with a perfume sprayer-type nebulizer using different reagent concentrations and compositions and their thermal aging behavior studied.

Patents: __

Publications: __

Proceedings: 3

Books: __

Presentations: 3

ACCOMPLISHMENTS:

Licenses: None

Known Follow-on Products: Combustion CVD coatings are being investigated for use with thermal barrier coating systems. Platinum coatings are being developed to provide high temperature oxidation resistance.

CRITICAL ISSUES: To further develop the CCVD process for coating substrates of technological interest. To minimize the substrate temperature required for producing quality coatings. To increase the size and uniformity of the deposition zone.

PROJECT TITLE: Advanced Methods for Processing Ceramics

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.

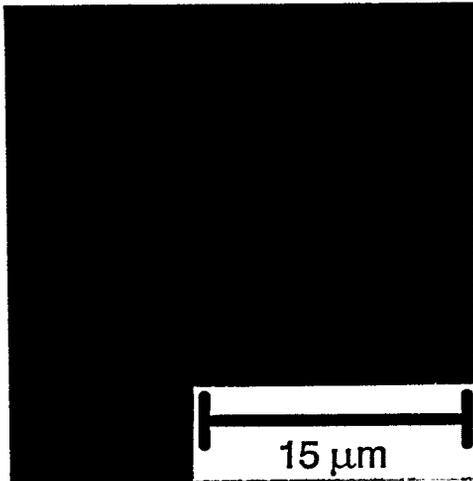
**OSCILLATING CAPILLARY NEBULIZER PROVIDES GREATER CONTROL
OVER COMBUSTION CHEMICAL VAPOR DEPOSITION PROCESS
AND PROMOTES HIGHER QUALITY COATINGS**

Problem:

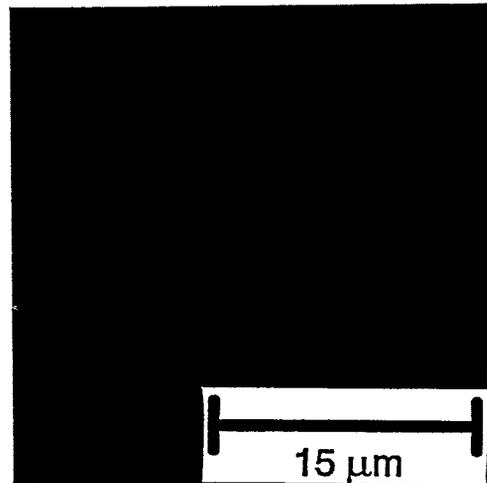
Wide distribution of droplet sizes in aerosol used for combustion chemical vapor deposition results in inefficient deposition process. Low coating precursor concentrations are required to prevent homogeneous nucleation.

Results:

The oscillating capillary nebulizer (OCN) produces an aerosol with a narrower size distribution than conventional perfume sprayer type pneumatic nebulizers. By configuring the OCN to produce an aerosol with a small Sauter mean diameter, it is possible to produce higher quality ceria coatings at lower substrate temperatures than when using a conventional pneumatic nebulizer.



Ceria coating produced with 11 μm Sauter mean diameter aerosol.



Ceria coating produced with 2.3 μm Sauter mean diameter aerosol.

Significance - For Energy Conservation:

The oscillating capillary nebulizer allows the use of higher coating precursor concentrations with the combustion chemical vapor deposition process. This reduces the amount of solvent (fuel) required to apply a specified coating with attendant energy savings.

(R&D performed at the Georgia Institute of Technology under DOE-EE-AIM Program support.)



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Aerogel Nanocomposite Materials

PHASE: FY 1995

PERFORMING ORGANIZATION: Lawrence Berkeley Laboratory

PRINCIPAL INVESTIGATOR: Arlon J. Hunt, (510) 486-5370

PHASE OBJECTIVE: Develop aerogel composites for industrial thermal insulation and explore new composite aerogel materials.

ULTIMATE OBJECTIVE: Utilize the unusual properties of nanocomposite aerogels to develop new materials and processes to reduce energy use, weight and space requirements for insulating and other applications.

TECHNICAL APPROACH: Develop processes to make new aerogel-based composite materials with uniquely useful properties. Use Chemical vapor Infiltration to improve the thermal and physical performance of aerogel insulation for higher temperature industrial applications. Explore the use of aerogel's unusual properties to develop new materials and processes such as gas separation and metal matrix composites.

PROGRESS: Large samples of thermally enhanced silica aerogel composites were produced using chemical vapor infiltration methods. A new instrument developed at LBL, the VICTOR (Vacuum Thermal Conductivity Tester), was used to characterize the thermal properties of these and other aerogels. The carbon composite materials displayed improved thermal properties and strength. The aerogel CVI process was extended to produce a wide variety of new composite materials. Post processing was found to be useful in modifying their characteristics and producing new materials. The new composites displayed very different characteristics from silica aerogel such as magnetism, photo-luminescence, and electrical conductivity.

Patents: 1 Publications: 11 Proceedings: 5
Presentations: 7

ACCOMPLISHMENTS:

Licenses: Aerojet Corporation has option to license the opacification method.

Known follow-on products: Aerojet will begin production of silica aerogel for commercial applications using the LBL carbon dioxide process under a CRADA providing technical transfer from LBL to Aerojet.

Enhanced Nanocomposite Aerogels

Problem:

Silica aerogel is one of the best thermal insulating materials. However, at ambient and higher temperatures the heat transfer due to infrared radiation contributes significantly to the overall conductivity. To improve the thermal resistance and reduce aerogel costs the radiant transfer must be blocked. We use Chemical Vapor Infiltration (CVI) to block the infrared by opacifying silica aerogel. In earlier work, the thermal conductivity of regular and opacified aerogel was determined from heat transfer models and infrared measurements on small samples. However, good measurements of thermal conductivity require large samples and accurate instrumentation, neither of which existed for aerogel research.

Results:

Equipment for the CVI of large samples was built and tested. To characterize the thermal properties of superinsulating aerogel a precision instrument was designed and constructed to measure the thermal conductivity of large aerogel slabs as a function of pressure and temperature. The Vacuum Insulation Conductivity Tester (VICTOR) provides absolute measurements of thermal conductivity with an accuracy of about 5 percent.

Significance - For Energy Conservation:

Opacified aerogel for intermediate temperature applications has significantly improved thermal performance over currently used materials. The new process lowers costs, increases R-Value, and reduces the required thicknesses.

Significance - For the Environment:

Aerogel can replace thermal insulation in many space sensitive applications, significantly reducing the use of CFC's that are widely used in industrial and appliance insulation.

(R&D performed at Lawrence Berkeley Laboratory (LBL) under DOE-EE-AIM Materials Program support.)

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT SUMMARY: CHEMICAL VAPOR INFILTRATION OF TiB₂ COMPOSITES

PHASE: FY 1995

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-TiB₂ matrix composite would have the requisite wettability, strength, strain-to-failure, cost, and lifetime to solve this problem. The approach selected to fabricate such a cathode material is chemical vapor infiltration (CVI). This process produces high purity matrix TiB₂ without damaging the relatively fragile fibers. The overall program is designed to evaluate potential fiber reinforcements, fabricate test specimens, and test the materials in a static bath and lab-scale Hall cell. Process improvements are also pursued in order to produce cost-competitive materials. Finally, the process must be scaled to produce usable demonstration components.

PROGRESS: Until the current period only small specimens of TiB₂-matrix composites could be prepared. Yet under a DOE/Alcoa program to evaluate wettable cathodes for the production of aluminum it was necessary to provide relatively large plates for demonstration cells. The scale-up of the chemical vapor infiltration process to produce usable 20 x 20 cm plates required increasing the component size by a factor of 20.

Patents: none

Publications: one

Proceedings: none

Presentations: one

ACCOMPLISHMENTS:

Licenses: one

Industrial Interest: Alcoa is incorporating the scale-up TiB₂ composite plates in their DOE demonstration program.

SCALE-UP OF CHEMICAL VAPOR INFILTRATION OF TiB₂ WILL LEAD TO LOW-COST COMPOSITES FOR IMPROVED ALUMINUM SMELTING CATHODES

Problem:

Current carbon cathodes are not well wetted by molten aluminum and thus cause substantial turbulence in the cathodic aluminum pad. This effect results in significant power losses during aluminum reduction. TiB₂ is highly electrically conductive and is wet by aluminum, but is extremely brittle and particulate composites with greater toughness have been shown to be susceptible to corrosive attack. Toughened TiB₂ composites have demonstrated good mechanical properties and are wetted and produce aluminum in bench-scale cell tests. The current issue is to scale the process to produce 20 x 20 cm plates from the 5-cm diameter disks which had been developed.

Results:

Most recently, the process for producing composite material was successfully scaled to provide 20 x 20 cm plates for evaluation in a DOE/Alcoa wettable cathode program. The best plate had approximately 90% density and was processed in typically rapid forced chemical vapor infiltration. The plate was provided to the Alcoa Technical Center for evaluation

Significance:

Until the current period only small specimens of TiB₂-matrix composites could be prepared. Yet under a DOE/Alcoa program to evaluate wettable cathodes for the production of aluminum it was necessary to provide relatively large plates for demonstration cells. The scale-up of the chemical vapor infiltration process to produce usable 20 x 20 cm plates required increasing the component size by a factor of 20. This was successfully accomplished and sample plates are being evaluated at Alcoa. Between 10% and 18% of the power consumed in aluminum reduction (0.75 and 1.35x10¹⁰ kWhr/y) could be saved by the use of TiB₂ electrodes.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Improved Catalyst System Materials for use with Conventional Fuels - CRADA No. ORNL92-0115

PHASE: FY 1995

COMPLETION DATE: FY 1996

PERFORMING ORGANIZATIONS: Martin Marietta Energy Systems (MMES) and Delphi Automotive Systems (formerly General Motors - AC Delco Systems)

PRINCIPAL INVESTIGATORS: E.A. Kenik (615) 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 with manufacturing processes and formulation and identify optimum processing routes for further evaluation. Characterize vehicle-aged catalyst for comparison to dynamometer-aged catalysts.

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. Identify processes responsible for degradation of performance/lifetime and possible mechanisms for minimizing their influence.

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 dynamometer- and vehicle-aged materials has identified several levels of microstructural evolution during ageing. Several process variations have been shown to influence on the distribution of precious metals and subsequent formation of clusters. Several microstructural changes have been identified which may contribute to the deactivation of the catalyst during ageing.

Patents: -
Presentations: 17

Publications: 3

Proceedings: -

ACCOMPLISHMENTS:

Licenses: -

Known Follow-on Product: CRADA aimed at improving performance and lifetime of catalytic convertors and reducing emissions. Delphi is currently and will continue to incorporate developments from this CRADA into their product line.

Industry Workshop: -

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

PROJECT TITLE: Improved Catalyst System Materials for use with Conventional Fuels - CRADA No. ORNL92-0115

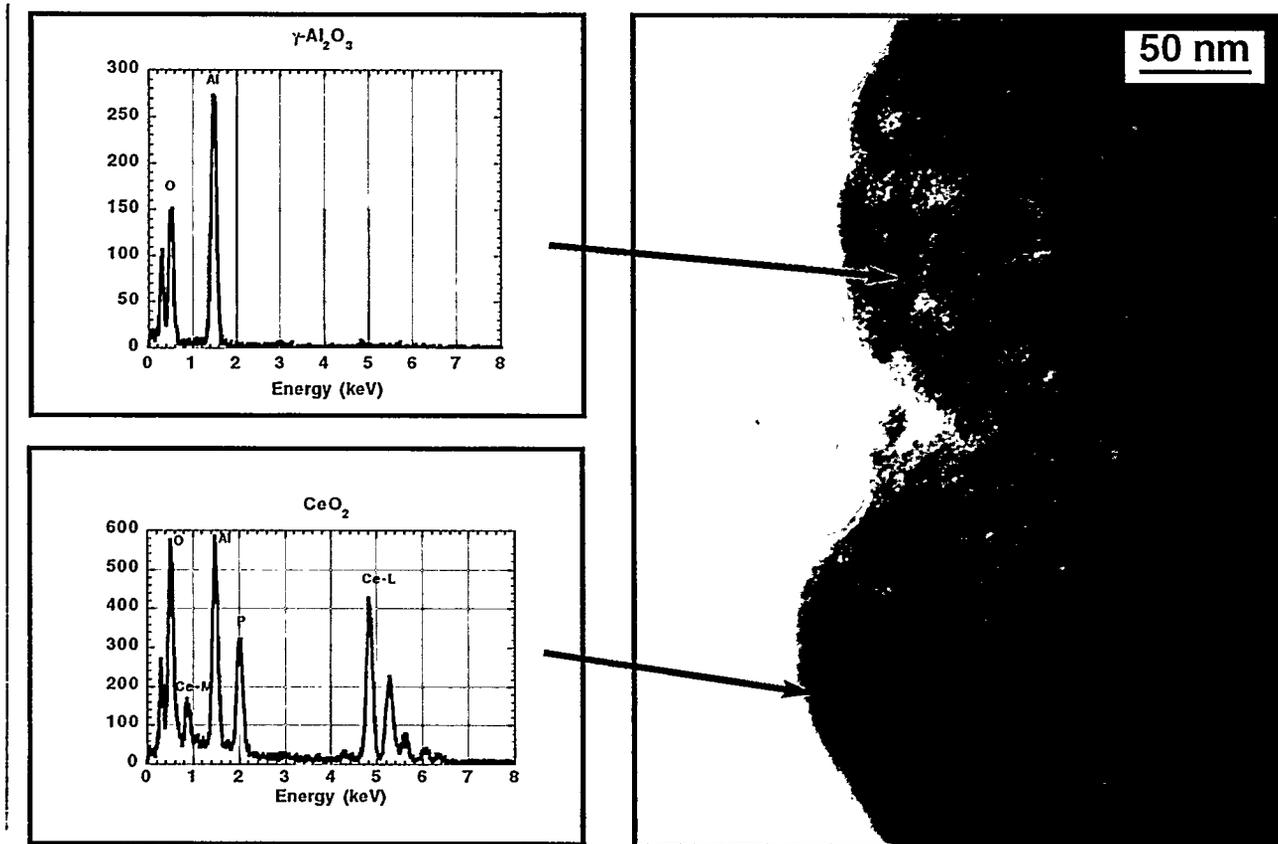
CRITICAL ISSUES: 1) Relation of microstructural and chemical state of catalyst and substrate to the performance, lifetime, and emissions of the catalytic convertor. 2) Can manufacturing processes be optimized to produce catalytic convertor with improved performance, lifetime, and/or cost? The noble metals 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.

DEVELOPMENT OF IMPROVED AUTOMOTIVE CATALYST SYSTEMS

Problem: Current Pt/Rh based three-way-catalysts (TWC) may have problems meeting the more stringent emission standards to be imposed in the near future, which demand improved performance/service life from these catalysts. One limit to service life is poisoning of the active catalyst by impurities (P, Zn, Ca) in the exhaust gas stream.

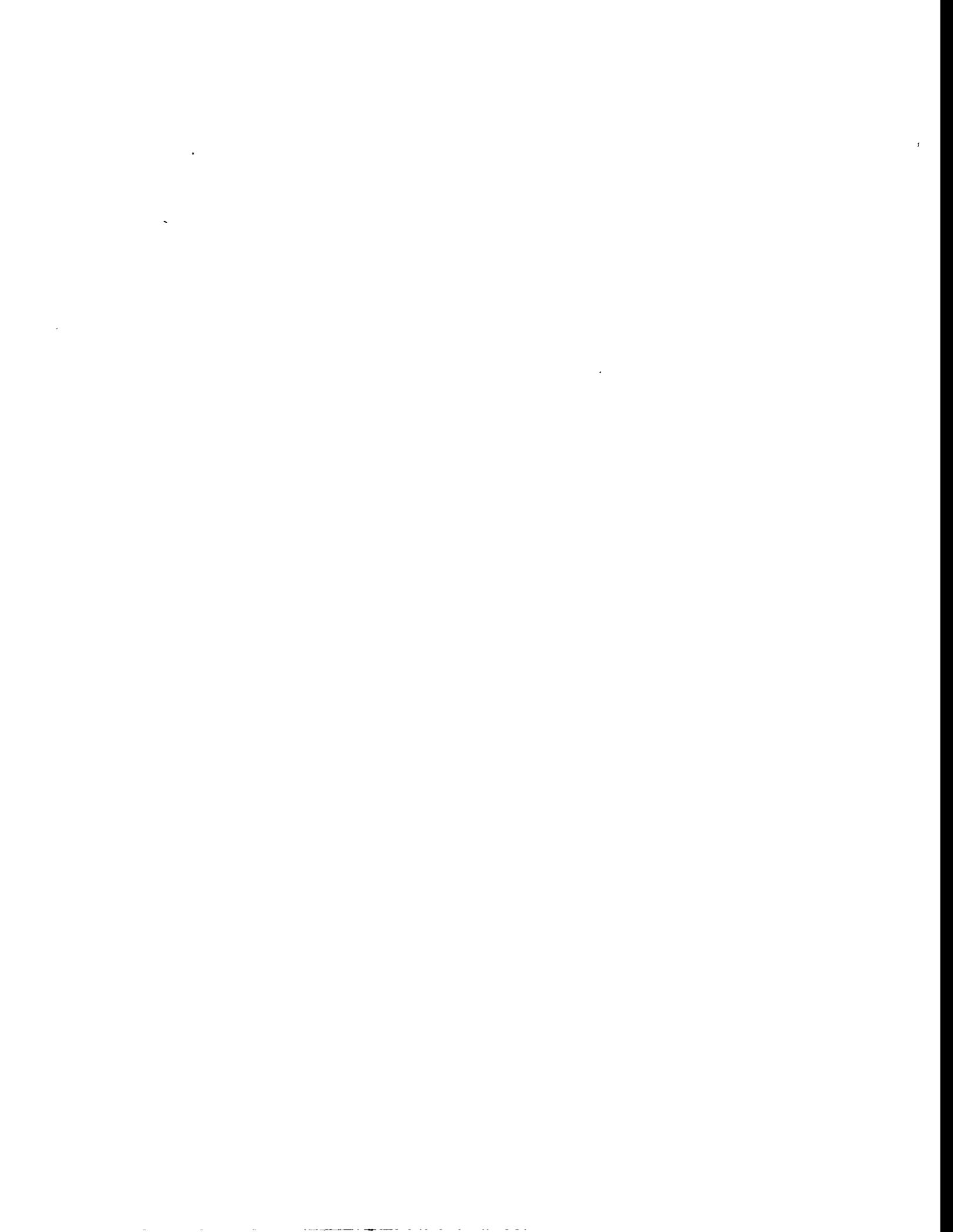
Results: Phosphorus enrichment on the washcoat surface of dynamometer-aged catalysts was localized to ceria particles and not present on alumina. Such preferential interaction would result in both decreased oxygen storage capability of the ceria and the loss of catalytic activity of those platinum/rhodium clusters associated with the ceria.



Energy dispersive X-ray spectrometry (EDS) indicates the association of high phosphorus levels with ceria particles and not with alumina washcoat matrix

Significance - For Energy Conservation

If the influence of impurity poisons on the conversion efficiency and lifetime can be minimized by fuel/oil additives or washcoat modifications, improved performance and lifetime requirements could be achieved in a cost-effective manner, while conserving precious and strategic materials and permitting new emission standards to be met.



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT SUMMARY: Metallic and Intermetallic-Bonded Ceramic Composites

PHASE: FY 1995

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 intermetallic bonded carbides and continued assessment of mechanical and chemical properties

ULTIMATE OBJECTIVE: This program is designed to develop a range of wear resistant composite materials that can replace WC/Co composites in applications requiring good corrosion resistance and the retention of high strength at elevated temperatures (800°C).

TECHNICAL APPROACH: The present program was initiated to develop new composite materials to replace WC/Co in environments where corrosion or application temperature was a problem. Direct substitution of the ductile intermetallic Ni₃Al for Co was suggested to overcome both of these limitations. Initial observations on hot-pressed WC/Ni₃Al and TiC/Ni₃Al 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 a 30-40 % increase in retained high temperature strength. In addition these new materials exhibit similar toughness and strength values to WC/Co. 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 Ni₃Al alloy composition upon mechanical behavior.

PROGRESS: Prior to the current period all intermetallic materials were fabricated by hot-pressing, which is not an industrially viable fabrication route, due to shaping limitations. In the present period two distinct 'pressureless' densification routes have been developed, which allow the fabrication of complex shaped components. Additionally, these routes both produce materials with mechanical properties comparable to, and often better than, the earlier hot-pressed composites.

Patents: One

Publications: One

Proceedings: Two

Presentations: Four

Invention Disclosure: Two

ACCOMPLISHMENTS:

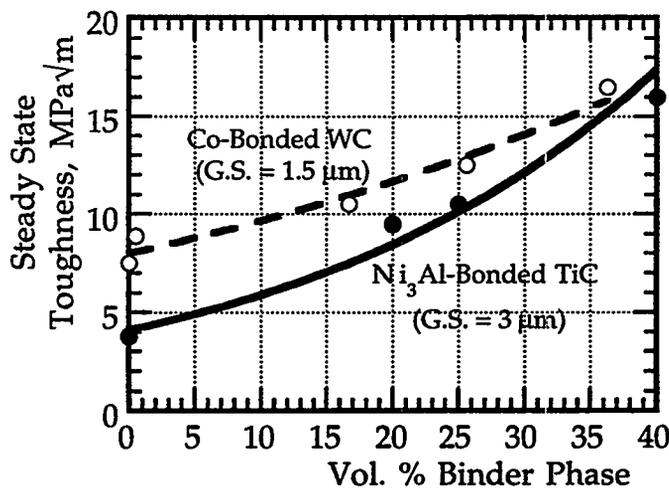
Licenses: None

Industrial Interest: A recently published news release brought inquiries from over 30 companies, both domestic and foreign, that have interest in the technology. These companies represent most of the world's hardmetals industries. In addition a number of informal collaborations/discussions are ongoing.

HIGH TOUGHNESS, HIGH STRENGTH NICKEL ALUMINIDE BONDED CARBIDE CERAMIC COMPOSITES

Problem: Cobalt bonded 'hard-metals' (or 'cemented carbides'), for example WC or TiC, are particularly widely used in applications where resistance to abrasion and wear are important (particularly in combination with high strength and stiffness). However, these materials exhibit poor resistance to oxidation and aqueous/acidic corrosion, and also limited high temperature strength retention. Consequently it is desirable to find an alternative binder phase to cobalt, that offer comparable room temperature properties with improved resistance to corrosion/oxidation and increased elevated temperature strength retention. A potential solution is the substitution of the ductile intermetallics, e.g. nickel aluminide (Ni_3Al), for cobalt. Initial results indicate this approach is sound, consequently emphasis has been placed upon developing industrially viable fabrication routes (i.e. pressureless-sintering of complex shapes) and optimization of mechanical properties.

Results: Two methods have been developed to allow the low-cost fabrication of complex shaped parts, namely; vacuum-sintering (liquid phase sintering) of pressed powder mixtures, and a novel combined melt-infiltration/liquid phase sintering process. Both routes allow the fabrication of components with sintered densities greater than 98 % of theoretical, and equipment requirements are identical to those presently used in the 'hard-metal' industry. The mechanical properties of these materials were comparable to previously reported hot-pressed Ni_3Al binder 'hard-metals'. Additionally, these new vacuum-sintered carbides exhibit toughness values comparable to the highly developed sinter-HIP processed 'hard-metals' (i.e. WC-Co).



Corrosion resistance in either nitric or sulfuric acid solutions was improved one order of magnitude over materials prepared with a cobalt binder, and high temperature (800°C) flexure strengths were comparable, and sometimes higher, than those obtained at room temperature (this is a significant improvement over the behavior of cobalt based materials, which typically show a strength reduction of 30-40 % when tested at 800°C).

Significance for Energy Conservation: Hard materials, which combine high toughness and strength with improved corrosion/oxidation resistance, are needed in a variety of 'vision' industries. Notably, these include; pulp and paper, metal forming, glass forming and chemical industries. In each case the implementation of new materials are required to increase production efficiency or expand the service life of equipment.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS PROGRAM

WORK ELEMENT: High Temperature Materials

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

PHASE: FY1995

PERFORMING ORGANIZATION: Southern Illinois University at Carbondale

PRINCIPAL INVESTIGATOR: Rasit Koc (618) 453-7005

PHASE OBJECTIVE:

To develop a novel synthesis method for producing high purity, submicron, nonagglomerated powders of metal-carbide systems (TiC-TiN; WC-WN).

ULTIMATE OBJECTIVE:

(1) To provide a process for synthesizing metal carbide, nitride and carbonitride powders possessing high purity, narrow particle size distribution, and stoichiometry for use in making components and composites for structural and electronic applications, and (2) To help U.S. ceramic material and composite industries to advance in the world market.

TECHNICAL APPROACH:

The method is based on carbothermal reduction of carbon coated precursors and uses a gas-phase hydrocarbon as the carbon source, therefore impurities are not introduced into the final product. There is also a more uniform distribution of carbon, resulting in a final product with finer particle size.

PROGRESS:

The developed process was applied to synthesize submicron TiC powders. The process was capable of producing high quality TiC powders suitable for making ceramic materials and composites-highly pure powder with submicron particles. We have delivered 200grams of submicron TiC powders to ORNL and 60 grams to 3M Ceramic Technology Center for evaluation.

Patent: 1

Publications: -

Proceedings: 1

Presentations: 2

ACCOMPLISHMENTS:

Licenses: None

Known Follow-on Product: None

Project Title: New Method for Synthesis of Metal Carbides, Nitrides and Carbonitrides

Critical Issues:

Metal carbides, nitrides and carbonitrides are the leading advanced engineering ceramics used in metal-working, electronics, ceramic 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. Processes include production of the advanced ceramic powders (powder synthesis); shaping (consolidation to engineering shape); sintering (densification/microstructural development) steps. Each step has the potential for introducing a detrimental heterogeneity during sintering. If reliable advanced ceramics are to be fabricated, powder synthesizing methods must be developed to ensure that heterogeneities are eliminated from powders and they should not be reintroduced in subsequent processing steps. In addition, the cost of high quality powders is a major factor hindering the wide commercialization of metal carbide, nitride and carbonitride components. Present methods of synthesizing these powders require expensive steps that yield only small quantities of the product. The method for production of submicron TiC powder developed at SIU has potential as a low cost high quality powder synthesis route.

Future Plans:

Steps will be taken to apply the process towards producing submicron WC powders. We will clearly demonstrate the advantages of the process and provide information on the applicability of the process for synthesizing related advanced ceramic powders.

Potential Payoff:

This work will demonstrate the capability of producing high purity, high surface area, low cost metal carbide, nitride and carbonitride powders utilizing the carbon coating method. From a technical standpoint the carbon coating process is a leap forward in the technology for producing nonoxide advanced ceramic powders. This technology will improve energy efficiency because it does not require high reaction temperatures for production of these powders. From an economic standpoint American Industries will stand to benefit greatly from this technology, because they have had to rely on expensive powders provided only by foreign suppliers.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Process Simulation For Advanced Composites Production

PHASE: Technology Proof-of-Concept

PERFORMING ORGANIZATION: Sandia National Laboratories, Livermore, California

PRINCIPAL INVESTIGATOR: Mark D. Allendorf Tel: (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 scaleup of new BN deposition processes is of great interest due to the effectiveness of this material as a debond layer in CFCCs.

ULTIMATE OBJECTIVE: To reduce the costs of ceramic materials 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 predicting coating rates and thickness profiles in ceramic-fiber preforms used in the manufacture of CFCCs. The model is simple to apply and can be used to optimize reactor operating conditions (temperature, pressure, and precursor concentration) to produce coatings with the desired thickness and uniformity.
- Verified preform-model predictions by measuring boron nitride (BN) coating thicknesses on preforms provided by DuPont Lanxide Composites (Newark, DE). Comparisons show that the model predicts both the coating thickness and the thickness uniformity as a function of location within the preform.
- 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: 1 disclosure **Publications:** 4 **Presentations:** 6

ACCOMPLISHMENTS

- **Technology Transfer:** A short-term research project was initiated with Libbey Owens Ford Glass Company (LOF; Toledo, OH) to characterize the high-temperature behavior of chemical precursors used in the coating of float glass. The cost of this project (\$5 K) was born by LOF. This interaction is expected to continue in FY96, with funds provided by LOF.
- **Licenses:** none.

PROJECT TITLE: Process Simulation For Advanced Composites Production

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. One material of particular interest for debond layers in CFCCs is BN. Research during FY95 provided data of both an experimental and theoretical nature necessary for developing models that simulate BN formation in chemical vapor deposition processes used to coat ceramic-fiber preforms.

FUTURE PLANS: Research efforts in the immediate future (FY96) will continue to be directed toward development of a simulation capability for the fiber-preform coating process used commercially by DuPont Lanxide Composites Inc. (DLC). Experimental and modeling investigations are being conducted at Sandia during this phase of the project. In addition to model development, candidates for process-control sensors will be examined this year. A non-disclosure agreement between Sandia and DLC is in place.

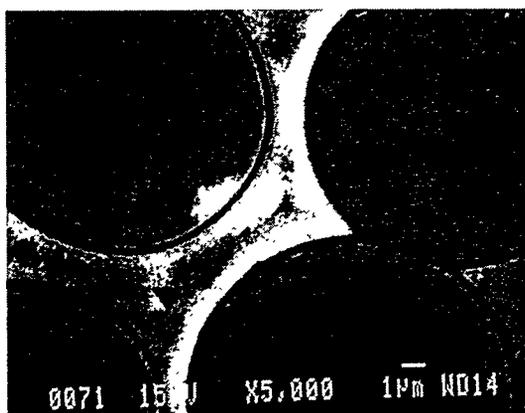
POTENTIAL PAYOFF: Use of the computational models developed here is expected to shorten the time required to design, optimize, and scale up new fiber-coating processes and to facilitate extension of existing technology to new materials. Since these processes contribute as much as 40% of the manufacturing 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.

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.

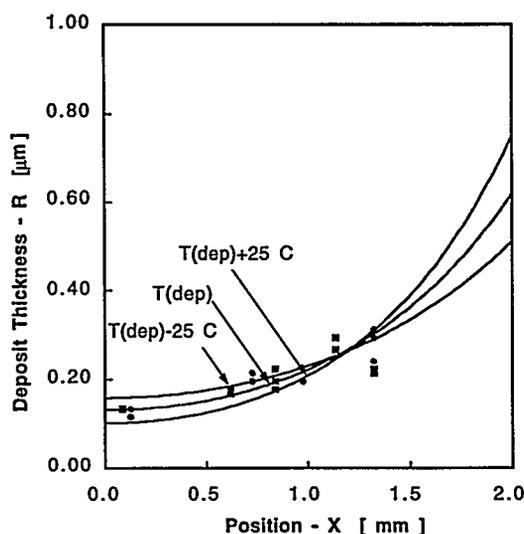
COMPUTATIONAL MODEL PREDICTS THICKNESS AND UNIFORMITY OF FIBER COATINGS USED IN CFCC MANUFACTURING

Problem: Coatings such as boron nitride (BN) and graphite are deposited on continuous fiber ceramic composites (CFCCs) to provide 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 new model has been developed that predicts coating rates and thickness profiles in ceramic-fiber preforms used in the manufacture of CFCCs. Model predictions were verified by comparing them with measurements of boron nitride (BN) coating thickness as a function of depth within a preform. Comparisons show that the model accurately predicts both the coating thickness and the thickness uniformity as a function of location within the preform. The model is simple to apply, with results obtainable from a pocket calculator or spreadsheet program. It can be used to optimize reactor operating conditions (temperature, pressure, and precursor concentration) to produce coatings with the desired thickness and uniformity.



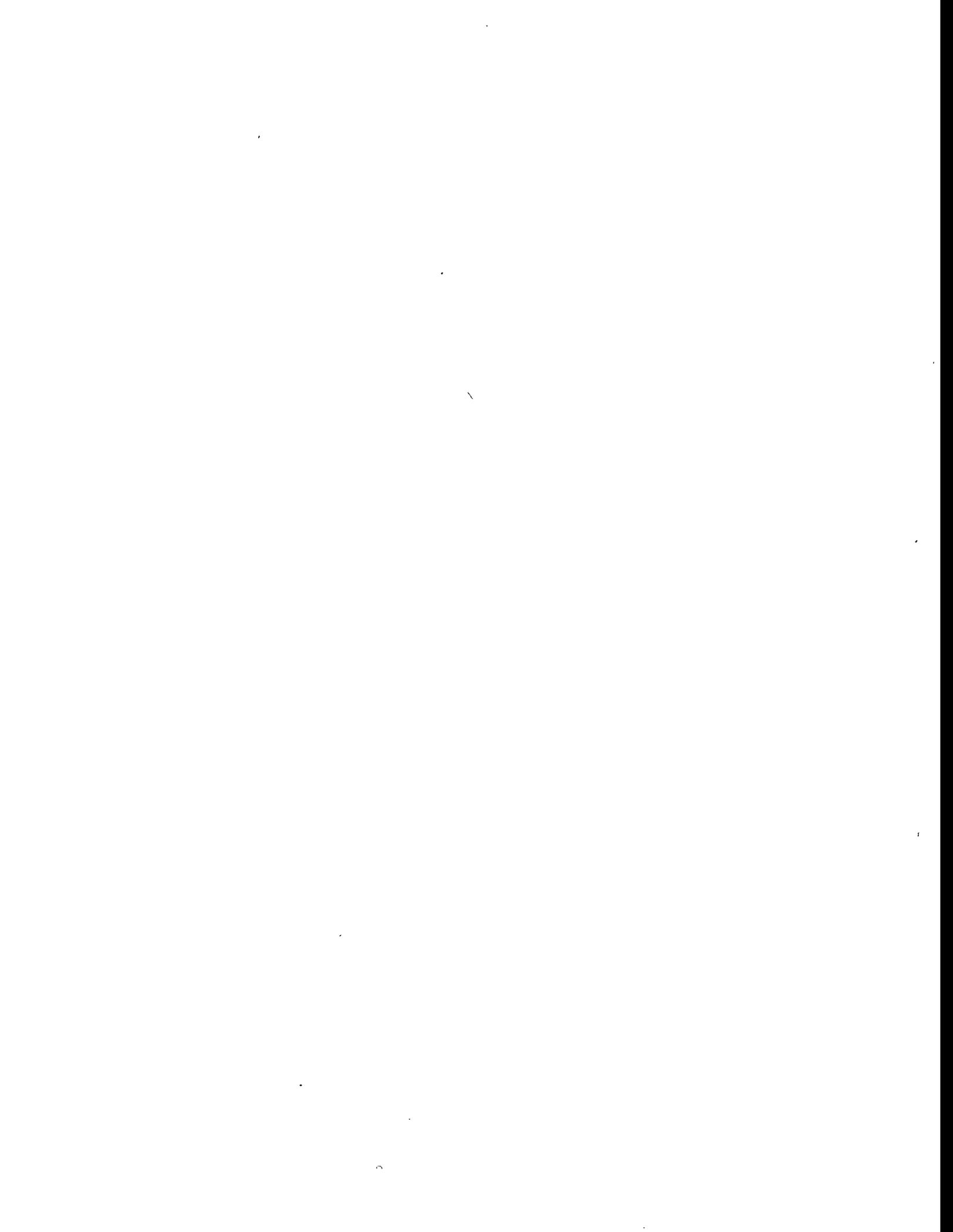
Scanning electron micrograph of SiC-fiber-reinforced alumina composite at 5,000X magnification, taken approximately 100 μm below the sample surface.



Depth profiles of the predicted BN deposit thickness (solid lines) compared with measurements of coating thickness for each of the two samples (points). $T(\text{dep})$ is the reactor temperature during deposition.

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 the thickness and microstructure of the fiber debond layer. 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 provides physical insight into the effects of process variables on thickness and uniformity without requiring expensive batteries of experimental measurements, which will allow development of new coating processes to occur much more rapidly than is currently feasible.



Project Summary

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: Advanced Ceramics and Composites

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

PHASE: FY 1995

PERFORMING ORGANIZATION: Sandia National Laboratories

PRINCIPAL INVESTIGATORS: Ronald E. Loehman (505) 272-7601 and Kevin G. Ewsuk (505) 272-7620

PHASE OBJECTIVES: The objectives for this year were to use results of wetting and TEM experiments to refine our model for the reactive penetration mechanism; to investigate the potential for using kaolin as an inexpensive ceramic precursor material; to investigate reactive penetration of NiO and TiO₂ ceramics; and to demonstrate net-shape forming using porous ceramic preforms that produce a wider range of composite metal contents.

ULTIMATE OBJECTIVE: The overall objectives of the program are: 1) to identify compositions favorable for making composites by reactive metal penetration; 2) to determine the mechanisms that control the process; and 3) to optimize the process so that composites and composite coatings with commercial potential can be made.

TECHNICAL APPROACH: Composites are made by reacting molten metals with ceramics under controlled conditions. Cross sections of reaction fronts are examined by x-ray and electron analytical techniques to identify compositions and microstructures. Those results are compared with data from wetting and penetration experiments using the sessile drop technique and are analyzed using thermodynamic calculations and phase diagram data. We use those results to make test specimens for determining composite physical properties.

PROGRESS: We have made ceramic composites of Al₂O₃/Ti₃Al and Al₂O₃/Ni₃Al by reactive hot-pressing. We discovered that kaolin can serve as a low-cost ceramic preform for making Al₂O₃/Al composites to near-net-shape. We learned how to improve the pressureless infiltration of molten Al into porous mullite and kaolin, which allows us to obtain composites with a much wider range of metal concentrations than when using dense ceramic preforms.

Patents:

Publications: 7

Proceedings: 3

Books:

Presentations: 19

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

CRITICAL ISSUES: The potential market for advanced ceramic-metal composites is as substitutes for existing materials. Even though their properties may be substantially better than existing materials, experience has taught us that the advanced materials are unlikely to penetrate commercial markets unless their cost is competitive with what is in current use. Because advanced materials by their nature are new, they generally lack a design history and data base on properties and reliability sufficient to persuade designers to specify the new material. Thus, the critical issues for any new material are reliability and cost. Ceramic-metal composites made by reactive metal penetration are no exception.

POTENTIAL PAYOFF: Wider use of ceramic-metal composites requires improvements in synthesis and processing so that high-performance parts can be produced more economically. Reactive metal penetration produces ceramic-metal composites that exhibit high stiffness-to-weight ratios, good fracture toughness, and their electrical and thermal properties can be varied through control of their compositions and microstructures. 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.

Significant Accomplishment

Reactive Penetration Process Produces Ceramic-Metal Composites to Net-Shape Using Low-Cost Raw Materials

Problem

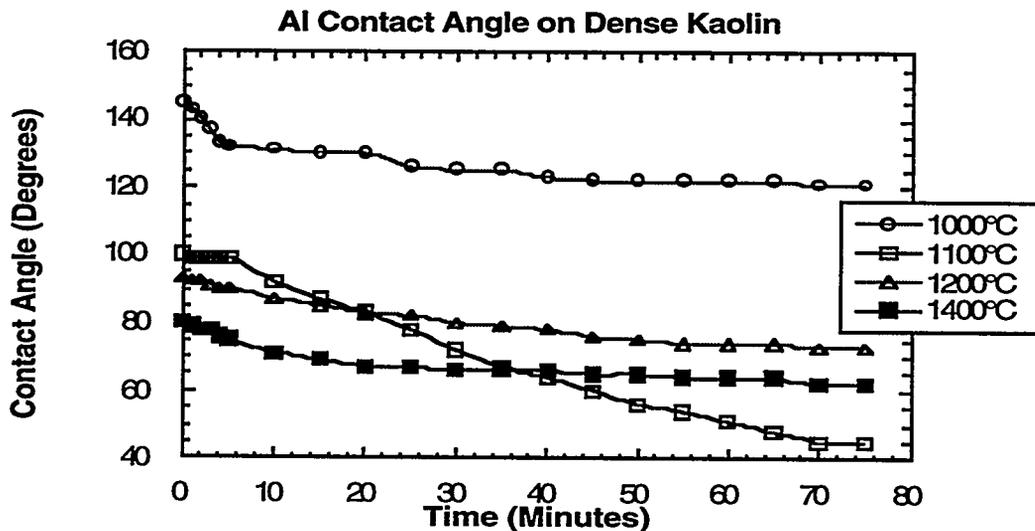
Ceramic-metal composites are candidate materials for advanced structures and components because of their high stiffness-to-weight ratios and excellent fracture toughness. However, their raw materials costs can be high and they generally are expensive to make in finished shapes.

Results:

Reactive metal penetration, the process by which a reactive metal penetrates a dense ceramic preform and converts it to a ceramic-metal composite, appears to be an inherently net-shape process. In the Al/mullite system the molar volumes of reactants and products are such that the stoichiometric reaction exhibits no net change in volume. However, even off-stoichiometry reactions are found to have less than a 2% volume change from reactants to products. The reason seems to be a reaction mechanism in which the dense ceramic preform maintains the overall shape of the part while the reaction proceeds.

Recently it was discovered that kaolin can be used as the ceramic preform for these reactively-formed composites. The reaction of Al with kaolin is similar to that with mullite, except that kaolin has a higher silica content, which is reflected in the reaction product:

$(8 + x) \text{ Al} + \text{Al}_6\text{Si}_2\text{O}_{13} + 4 \text{ SiO}_2 \rightarrow 7 \text{ Al}_2\text{O}_3 + 6 \text{ Si} + x \text{ Al}$. Wetting and penetration of kaolin by Al is as favorable as with mullite. Kaolin can produce composites with higher Al contents than does mullite, which extends the range of available metal contents using dense preforms.



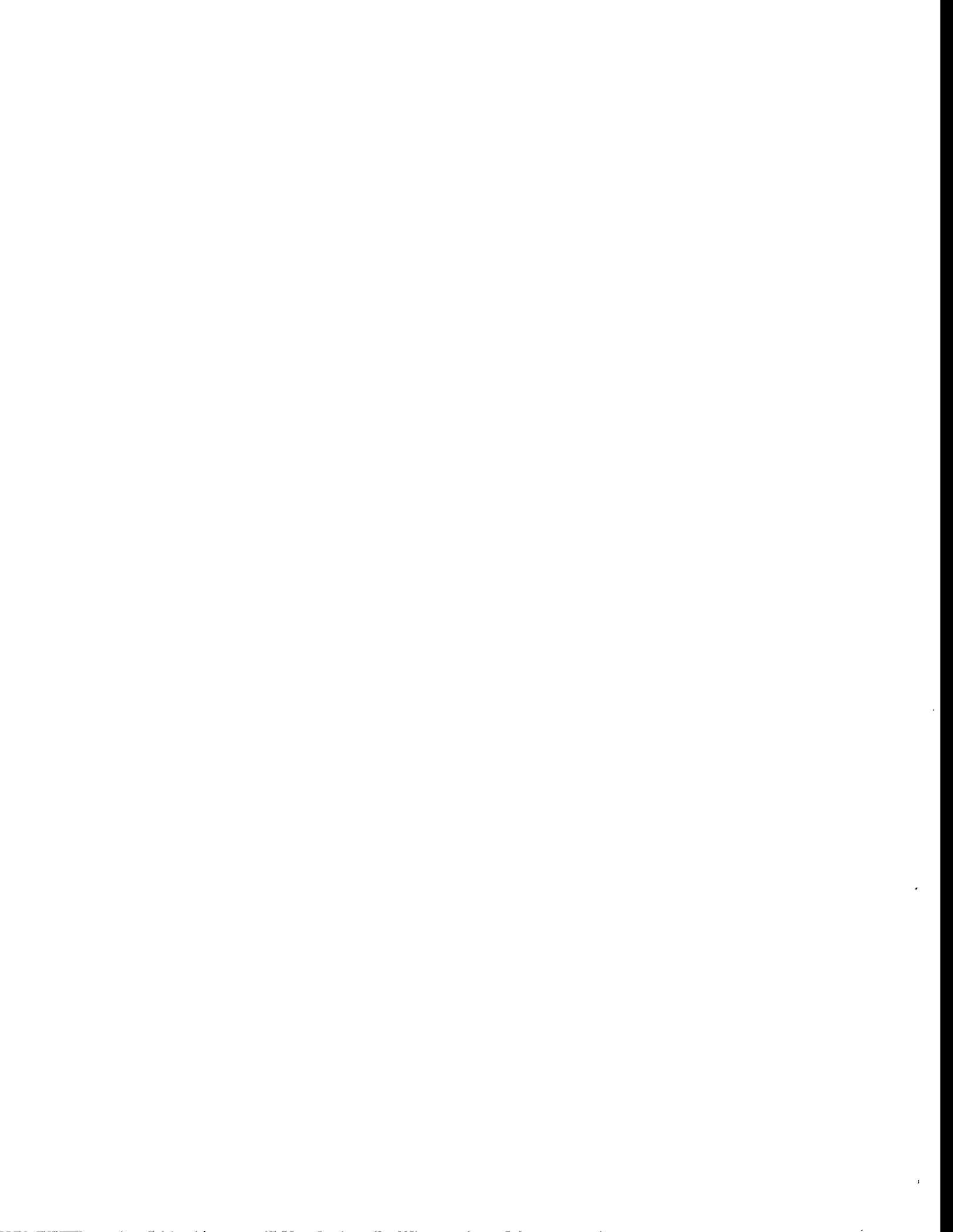
Contact angle of aluminum on dense kaolin.

Significance

The discovery that kaolin can be used as a raw material for the preparation of ceramic-metal composites may have enormous impact on the commercialization of such materials. Kaolin, the main mineral constituent of common clay, is a low-cost raw material that is available in nearly unlimited quantities. In raw material cost alone, there is nearly a three order-of-magnitude savings for kaolin as compared to mullite, with additional savings due to the fact that kaolin is easier to handle, requires fewer organic processing aids, and requires lower firing temperatures than does mullite, which extends the range of available metal contents using dense preforms.

(R&D performed at Sandia National Laboratories under DOE-EE-AIM support.)

**POLYMERS AND BIOBASED
MATERIALS**



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT SUMMARY: Chemical Recycling of Mixed Waste Plastics

PHASE: FY 1995

PERFORMING ORGANIZATION: National Renewable Energy Laboratory

PRINCIPAL INVESTIGATOR: K. Tatsumoto, (303) 384-6138

PHASE OBJECTIVE: This period was devoted to process optimization of nylon 6 waste carpet recycling for the CRADA agreement with AlliedSignal Company. Further work was carried out on three other plastics, polyethylene terephthalate, polyurethane, and polycarbonate, to convert them to valuable chemicals.

ULTIMATE OBJECTIVE: This program is design to develop selective catalytic-thermal processes to convert waste plastics mixtures into monomers or other high value-products. The processes can then be transferred to industries for their use to reduce waste and develop new sources of chemicals. Cost-effectiveness is essential for any potential application.

TECHNICAL APPROACH: The initial, screening research is carried out on the NREL pyrolysis-molecular beam mass spectrometer (MBMS) to analyze the products of reaction in real time. The MBMS is used to identify reaction conditions to produce valued chemicals in a single stream from plastic mixtures in high yield. The conditions used to effect differences in reaction rates include catalyst and support, temperature control, and coreactants. The information is used: (1) to develop a technology base to guide the chemical recycling of mixed plastics, and (2) to identify promising applications of this method to specific waste streams by applying our multivariate data analysis tools.

After the initial screening experiments are done, larger-scale, engineering tests are run to validate the results from the MBMS and refine the operating conditions. During the engineering experiments, both a technoeconomic assessment of potential applications and a market analysis of waste supplies and end-products use are incorporated as integral parts of this program's experimental approach. From the earliest stages these assessments are used to identify target applications that have potential for economic success.

PROGRESS: Tests performed on the waste nylon 6 carpets this year are the most advanced and extensive. The 10-cm, circulating, fluidized-bed reactor was modified to include a catalyst withdrawal port for the catalyst recycling and a side sample feeder to optimize the engineering parameters. The material feeding system has been modified to accommodate variations of the carpet feed and the catalyst. The yields and purity of the monomer, ϵ -caprolactam, from the waste nylon 6 carpet have increased. A possible alternative to the purification procedure has been discovered. The 5-cm quartz, fluidized-bed reactor was fabricated to observe the physical pyrolytic

phenomenum. It was used to test any changes made to the nylon 6 carpet process and transfer the MBMS results to small engineering experiments. In other parts of this program, improvements in the conversion and yield were made on:

- (1) poly(ethylene terephthalate) (PET) to its monomer, dimethylterephthalate from polyester fiber blends found in waste textiles;
- (2) bisphenol A from polycarbonate from electronics parts and;
- (3) diamines and oxygenates from polyurethane foam.

The intelligent chemical processing system has demonstrated the quantitative and qualitative ability to analyze carpet mixtures, and moved closer to the seamless, on-line, multivariate data analysis system. The data base has expanded to include all the plastic samples.

Patents: 3 ISSUED AND 5 FILED

Publications: K. Tatsumoto, C.C. Elam, M.J. Looker, and R.J. Evans, "Tertiary Recycling of Waste Polyurethane Car Seat Foam," Proc. of the Polyurethane 1995 Conference, (September 1995) pp. 270-274.

Proceedings: NONE

Meetings: Quarterly AlliedSignal CRADA Meetings were held on October 17-18, 1994, January 23-24, May 4-5, August 17-18, November 2-3, 1995 with AlliedSignal, DSM, Hazen Research Inc. and NREL.

Presentations: American Textile Bobbin Show at Atlanta, GA, October 1994; the IEEE Workshop at IBM Research Center, Yorktown Heights, NY, October 1994; the MBMS Workshop, Estes Park, CO, October 1994; the Electronic Products Disposition Workshop, Austin, Texas, January 12-13, 1995; the American Plastics Council (APC), January 25, and March 17, 1995; Angelica Uniform Group, St. Louis, MO, March 7, 1995; OIT/AIM Annual Meeting, Washington, D.C., June 14-16, 1995; Frontiers of Pyrolysis: Biomass Conversion and Polymer Recycling, Breckenridge, CO, June 26-30, 1995; Gordon Research Council on Fiber Science, July 7-14, 1995; Polyurethane '95 Conference, Chicago, IL, September 27-29, 1995.

ACCOMPLISHMENTS: The parameter optimization of fluidized-bed reactor experiments has improved using post-consumer waste carpets. Our selective pyrolysis process was applicable to recycling textile blend fabrics of polyester. This accomplishment and work on the cellulose fractionation, done under other program, enhanced the possibility of NREL's involvement with the American Apparel Manufacturers Association.

CRITICAL ISSUES: This program has dealt with products that require environmental, safety, and health (ES&H) awareness. In the next few years we will be dealing with more products requiring greater ES&H awareness that requires greater care and diligence by us. To accomplish these future goals, more safety equipment and a larger, more knowledgeable labor force will be required to run the experiments.

FUTURE PLANS: Our plan for the next two years is to further develop the polycarbonate, polyurethane and PET data base at the MBMS level and engineering level tests. In addition, if these recycling systems prove to be technoeconomically feasible, technology transfer activities will be

undertaken with industries. At the same time on the MBMS level, researches will continue to progress on other plastic wastes such as post-consumer waste that includes polyethylene, polystyrene, PET, polyvinyl chloride and polypropylene, and valuable chemicals such as styrene and bisphenol-A from engineering blends and composites.

POTENTIAL PAYOFF: The goals of the chemically recycling mixed plastics project are to develop processes that are cost-effective, consume less energy, than conventional systems of chemical s from oil, reduce fossil fuel dependence, be environmentally safe, and reduce disposal. On energy savings alone for caprolactam from waste nylon, we expect a 50% reduction in fossil fuel in terms of raw materials needed and process fuel used. With the maturation of plastic recycling technology, an improvement in the economy is possible because new jobs will be created and other related opportunities will be fostered.

CHEMICAL RECYCLING OF MIXED WASTED PLASTICS

Problem:

Increased use of plastics in many industries and by consumers requires cost-effective and environmentally-safe recycling or disposal methods. Especially important is treating mixed plastics streams to minimize waste and recover the intrinsic chemical value of the waste materials.

Results:

This process uses selective, catalytic pyrolysis to convert one component of a mixture to monomers or high-value products, while other components of the mixture are left unreacted. Subsequent reaction conditions can then be used and the residual materials are either converted to valuable chemicals, reacted to produce a product of secondary value such as a liquid fuel, or burned to generate process energy, steam, or electric power. Currently, the process is primarily used to recover ϵ -caprolactam from post-consumer nylon 6 waste carpet, toluenediamine and oxygenated hydrocarbons from waste polyurethane foam, dimethyl-terephthalate from post-consumer, mixed plastics containing polyethyleneterephthalate and textile fabrics made from polyester/cotton or any other plastic/cotton blends, and bisphenol A from electronic components containing polycarbonate or epoxies.

Significant Accomplishment:

Under the CRADA agreement with AlliedSignal Co. on nylon 6 waste carpet recycling, the engineering experiments were conducted at 200 gram to 1000 gram per hour scales. The feed has progressed from clean carpet to dirty post-consumer carpets and yields have increased steadily. The process development unit currently being designed is sponsored by the Pollution Prevention Program.

Significance

- For Energy Conservation:

A new technology for chemical recycling mixed plastics has been designed which promises to be cost-effective. The process can be energy self-sufficient and provide substitute plastic precursors thus replacing monomers made from fossil fuels.

- For Materials Technology:

This technology will be used to recycle high-value, engineering materials such as polymer composites and blends. This will foster the use of these light-weight materials in applications where weight reduction and high performance are critical.

PROJECT SUMMARY
ADVANCED INDUSTRIAL MATERIALS PROGRAM

PROJECT SUMMARY: Composites and Blends from Biobased Materials

PHASE: FY 1995

PERFORMING ORGANIZATION: National Renewable Energy Laboratory

PRINCIPAL INVESTIGATOR: Stephen S. Kelley, ph (303) 384-6123, fax (303) 384-6103, e-mail kelleys@tcplink.nrel.gov

PHASE OBJECTIVE: Improve the permselective and compaction properties of cellulose ester gas separation membranes through the development of organic/inorganic hybrid materials, cellulose mixed ester copolymers and cellulose ester polymer blends.

ULTIMATE OBJECTIVE: Develop composites and blends from biobased materials for use as membranes, plastics and lightweight composites. Because of the potential for a significant energy savings, gas separation membranes have been selected as the initial target application.

TECHNICAL APPROACH: Significant progress has been made this year in increasing our understanding of the structure-property relationships and phase behavior of cellulose esters in several complex systems. This understanding has allowed for the development of novel cellulose ester materials as potential gas separation membranes.

PROGRESS: Cellulose esters have been used to prepare novel composites and blends. These composites and blends have improved permselective or compaction properties relative to unmodified cellulose esters.

Patents: none **Publications:** three **Proceedings:** one **Presentations:** nine

ACCOMPLISHMENTS: CA OIH materials with improved properties have been developed. Dow Chemical Company has evaluate the properties of the CA-OIH membranes and found significant increase in the selectivity of the materials.

CRITICAL ISSUES: To further optimize the properties of the CA OIH materials for important commercial separation applications such as CO₂/CH₄ and O₂/N₂. To develop a fundamental understanding of the effects of inherent material properties and membrane formation conditions on the resistance of a microporous material to mechanical creep or compaction. To evaluate the potential of cellulose ester blends for gas separation applications.

FUTURE PLANS: Use experimental and molecular modeling approaches to assist with the development of novel CA OIH materials and CME copolymers that can be used for new separation applications. Work with university and industrial researchers to continue to improve the permselective properties of CA OIH materials for gas separation applications of commercial interest.

POTENTIAL PAYOFFS: The United States has an estimated 357,000 bscf of reserves of low grade, natural gas that contain carbon dioxide (CO₂) contaminants at high levels that can not be economically removed with current technology. Improved cellulose ester membranes that would allow the use of only 5 percent of these known domestic reserves would provide more than 22,000 bscf of new domestic energy resources.

Composites and Blends from Biobased Materials

Problem: Naturally occurring polymers are an underutilized raw material that show potential for commercial development. This program focuses on the development of composites and blends from biobased materials for use as membranes, high value plastics, and lightweight composites. Biobased materials include, cellulose derivative microporous materials, cellulose derivative blends and novel cellulose derivatives. This year research focused on developing an improved understanding of the molecular features that control the permeation of gases through cellulose derivatives, and then use this understanding to design cellulose based materials with improved properties for gas separation applications.

Results: Cellulose ester based organic/inorganic hybrid (CA-OIH) membrane materials have been prepared and evaluated. These CA-OIH materials show an increase in pure gas and mixed gas selectivity for CO₂ over CH₄. The solvent resistance, mechanical properties and thermal stability of the CA-OIH materials are also improved, relative to unmodified cellulose esters. The morphology of the OIH materials can also be varied over a very wide range: from optically clear films with nanometer sized inorganic domains to microporous materials with micrometer sized voids. A joint research project between researchers at NREL, the University of Colorado's NSF Industry/University Cooperative Research Center for Separations Using Thin Films, and Dow Chemical Company has begun an investigation of the effects of material properties membranes formation conditions and resistance to mechanical creep and compaction.

A series of homogeneous cellulose ester blends were also prepared as potential membrane materials. The addition of a high strength second polymer increases the strength of the membrane, however, the addition of the second polymer did not significantly improve the CO₂/CH₄ selectivity of these blends. Studies to crosslink the blends, similar to the approach successfully taken with the CA-OIH materials are underway.

Significance for Energy Conservation: The United States annually uses about 17,500 billion standard cubic feet (bscf) of clean burning natural gas to heat homes, produce chemicals, and for industrial power generation. To supply this energy need the United States has 95,000 bscf of known, domestic reserves of natural gas. In addition, there are an estimated 357,000 bscf of reserves of low grade, natural gas that contains CO₂ contaminants that can not be economically removed with current technology. Improved cellulose ester membranes that would allow the use of only 5 percent of the low grade natural gas in known domestic reserves, and new fields would provide more than 22,000 bscf of new domestic energy resources.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Magnetic Processing Of Inorganic Polymers

PHASE: FY 1995

PERFORMING ORGANIZATION(S): Idaho National Engineering Laboratory (INEL)

PRINCIPAL INVESTIGATORS(S): Dennis C. Kunerth (208-526-0103)
Eric S. Peterson (208-526-1521)

PHASE OBJECTIVE: Demonstrate the capability of magnetic field processed (MFP) polyphosphazene membranes for industrial applications.

ULTIMATE OBJECTIVE: Develop, and understand the use of, magnetic field processing to modify the properties of inorganic-based polymers; and transfer this technology to American industry.

TECHNICAL APPROACH: Demonstrate the chemical separation properties of magnetically-processed polyphosphazene membranes using geometries and chemical species of interest to industry.

PROGRESS: Tube-in-shell membrane modules with MFP membranes fabricated on the inside of tubular ceramic substrates surrounded by an external shell were developed and characterized. A simple permanent magnet yoke system was used to process the membranes during fabrication.

A CRADA between the INEL and ChromatoChem, Inc., Missoula, Montana, to jointly develop a chemical separation system having extended capabilities demonstrated the ability to fabricate and use MFP membranes for industrial applications. ChromatoChem's current system is very efficient at separating metal ions from process streams but cannot separate trace organics. Mating MFP membranes (having improved flux properties) with ChromatoChem's current technology produced a hybrid chemical separation system having expanded capabilities. The test results of the hybrid magnetically-processed membrane/column system are provided in Table 1.

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

ACCOMPLISHMENTS:

Technology Transfer or Industrial Interaction: ELF ATOCHEM, N.A. supplied the polyphosphazene materials used in the experiments. A CRADA between ChromatoChem, Inc., Missoula, Montana, and the INEL has been completed.

PROJECT TITLE: Magnetic Processing Of Inorganic Polymers

CRITICAL ISSUES: Critical program issues included the need to fabricate MFP membranes in a functional geometry, characterize transport properties, and demonstrate improved performance in an industrial application.

FUTURE PLANS: The successful demonstration of MFP membranes for an industrial application has addressed the goals of this program. No further work is presently planned.

POTENTIAL PAYOFF: Magnetic field processing has the potential to significantly improve the material properties of various polymer systems, thereby extending their service life and possible applications. Of particular interest is the development of improved chemical separation membranes, which can yield significant energy savings via more efficient separation processes. Current work has demonstrated that magnetically-processed polyphosphazene membranes have improved flux characteristics, which will significantly improve the economics of membrane chemical separation.

Improvement of membrane transport properties has the potential to achieve significant energy savings by making industrial implementation feasible. A recent DOE study (DOE/NBM-80027730) states that an annual energy savings of over one quad (equivalent to 170 million barrels of oil) could be achieved if membrane separations were fully used in only one application, liquid-to-vapor separations.

Table 1. Hybrid System Capabilities

Metal Ion Removal.

Metal	Initial Concentration (ppm)	Final Concentration (ppm)	Break Through (Bed Vols.)	Percent Metal Recovery
Cu	2700	No Detect	12	73
Ni	500	No Detect	150	97
Zn	510	No Detect	180	89

Methylene Chloride Removal.

Percent MeCl in Feed	Percent MeCl in Permeate	Percent MeCl Recovery	MeCl Flux L/m-Hr	Separation Factor
0.5	99.5	93	0.07	3800

MAGNETIC FIELD PROCESSING OF INORGANIC POLYMERS

PROBLEM:

Electromagnetic fields applied to polyphosphazene-based chemical separation membranes during fabrication improved transport properties in test samples. Magnetically-processed membranes have not been demonstrated in an industrial application.

RESULTS:

Joint work performed under a CRADA between ChromatoChem, Missoula, MT, and the Idaho National Engineering Laboratory demonstrated that combination of ion exchange and magnetically-processed membrane technologies provides a chemical separation system having extended capabilities. Table 1 is a summary of capabilities for extracting both trace metals and organics of a second generation hybrid membrane/column separation system.

TABLE 1. HYBRID SYSTEM EXTRACTION CAPABILITIES

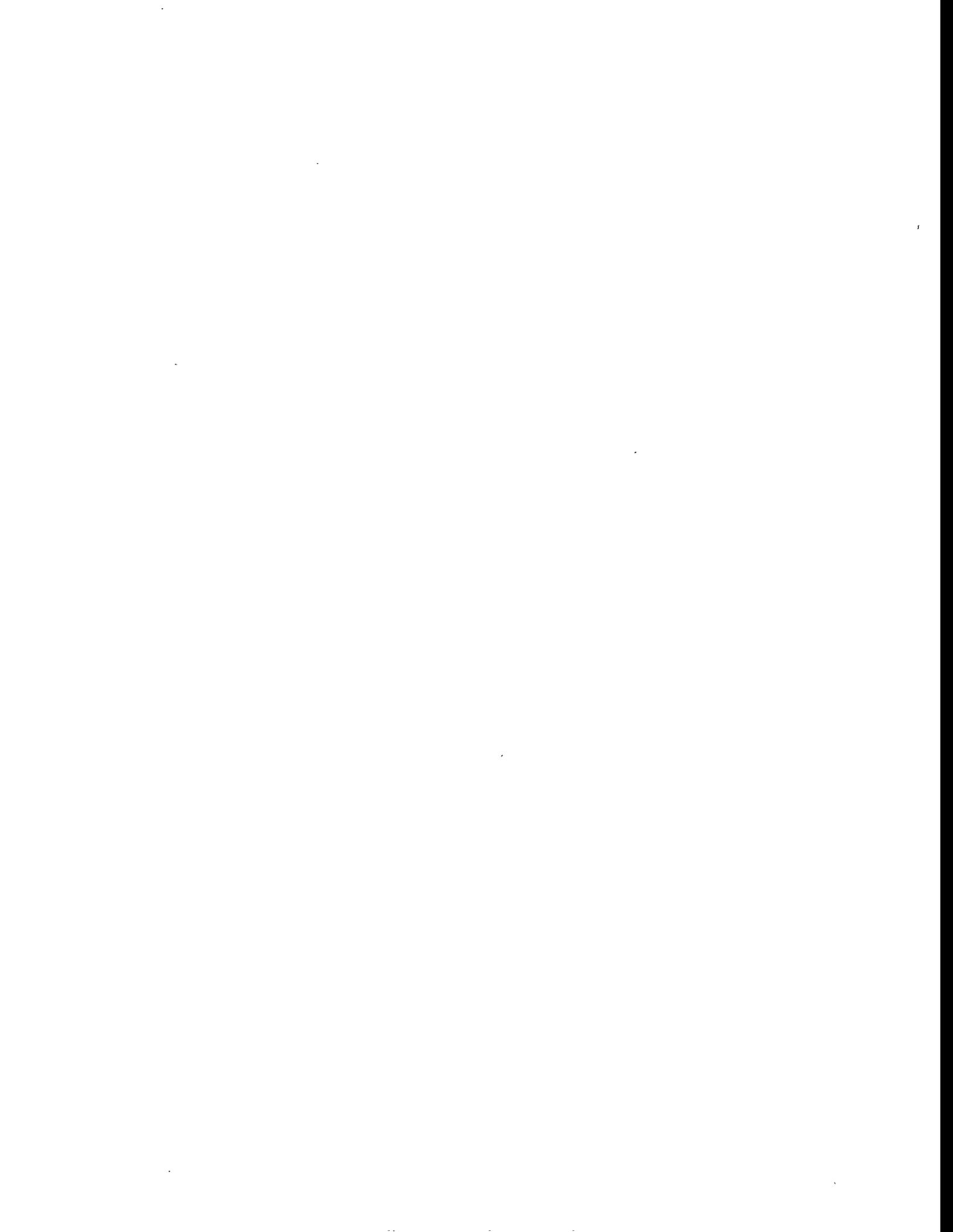
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Methylene Chloride Removal				
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0.5	99.5	93	0.07	3800

SIGNIFICANCE - FOR ENERGY CONSERVATION:

Improvement of polymer properties through magnetic processing so that they can be used in separation membranes has potential to achieve significant energy savings. A recent DOE study (DOE/NBM-80027730) states that an annual energy savings of over 1 quad (equivalent to 170 million barrels of oil) could be achieved if membrane separations were fully utilized in only one application, liquid-to-vapor separations.

(R&D performed at the Idaho National Engineering Laboratory under DOE-AIM Materials Program under DOE Idaho Operations Office Contract DE-AC07-941D13223.)



PROJECT SUMMARY
ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAMS

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

PHASE: FY95

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:

Licenses: none

Known Follow-on Products(s): none

Industry Workshop: none

Technology Transfer or Industrial Interaction: This effort will continue in '96 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 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.

MEMBRANE SYSTEMS FOR ENERGY EFFICIENT SEPARATION OF LIGHT GASES

Problem:

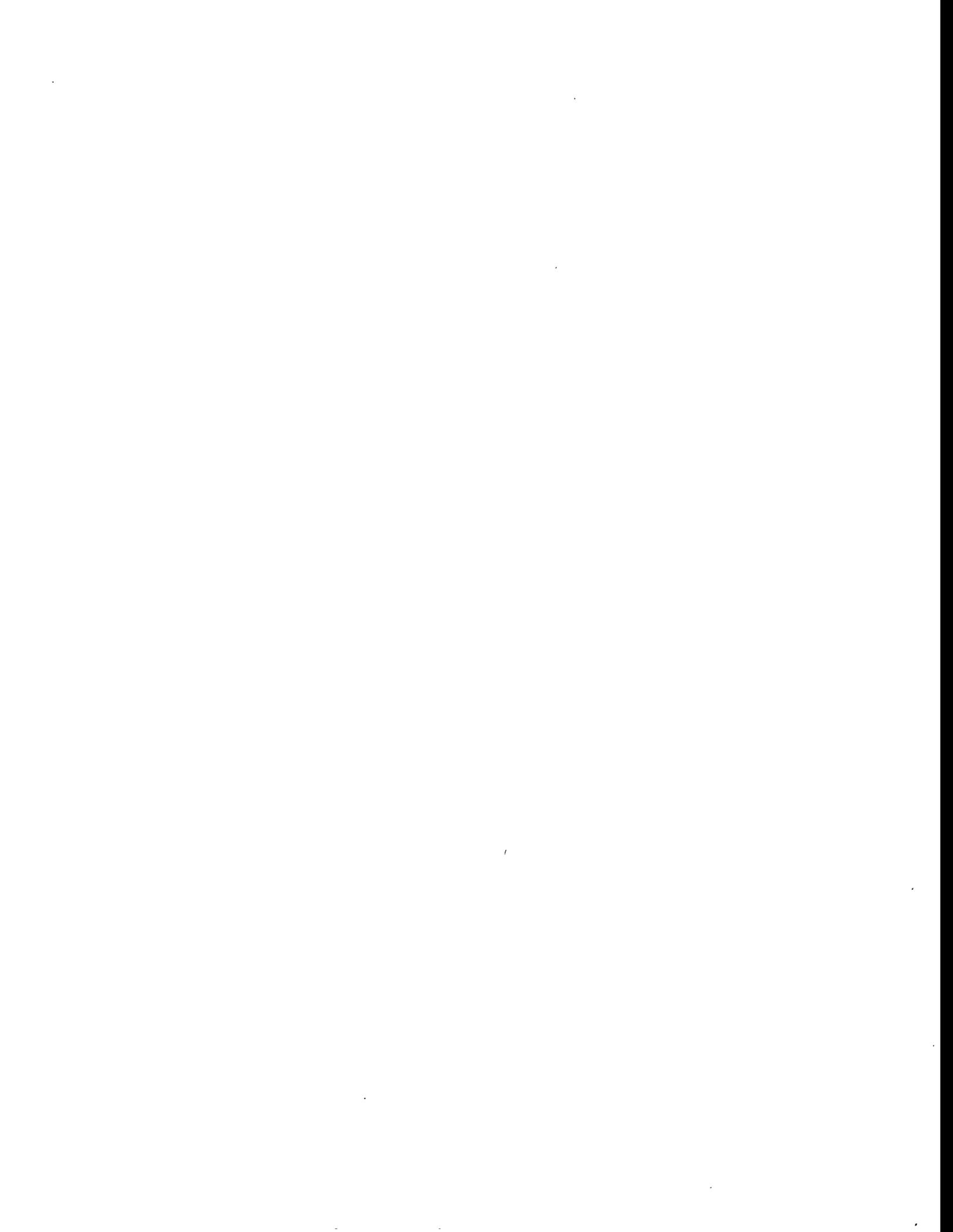
Ethylene and propylene are two of the largest commodity chemicals in the US. and are major building blocks for the petrochemicals industry. These olefins are separated currently by cryogenic distillation which demands extremely low temperatures and high pressures. Over 75 billion pounds of ethylene and propylene are distilled annually in the US. 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 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.

Significance - For 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.



Project Summary Advanced Industrial Materials (AIM) Program

Project Summary: Polymerization and Processing of Organic Polymers in a Magnetic Field

Phase: 1995

Performing Organization: Los Alamos National Laboratory

Principal Investigator: Elliot P. Douglas, 505-665-4828

Phase Objective: This period was devoted to measurement of the mechanical properties of liquid crystalline thermosets oriented in high magnetic fields.

Ultimate Objective: The demonstration of a beneficial effect of magnetic fields in materials processing.

Approach: Test the ability of a high magnetic fields to orient melts of liquid crystalline thermosets during processing. Magnetic fields offer the advantage over other techniques of acting to orient the bulk of the material rather than just the surface.

Progress: Use of magnetic fields to orient liquid crystalline thermosets during processing has resulted in significant improvements in mechanical properties compared to materials processed in the absence of a field. The typical tensile modulus for a material processed at 18 Tesla is 1174 ksi with an orientation parameter of 0.90, compared to 443 ksi and 0.00 for the material processed in the absence of a field. These are the highest fields used to date for alignment of liquid crystalline molecules, and the degree of order obtained is higher than previously reported.

Patents: None

Publications: None

Proceedings: None

Accomplishments: We have performed the first measurements of the mechanical properties of liquid crystalline materials processed in magnetic fields.

Licenses: None

Critical Issues: To demonstrate the minimum field strengths needed to obtain orientation and desired improvements in properties of liquid crystalline polymers.

Potential Payoff: The potential benefits of this CRADA to the U.S. are significant. Several U.S. companies supply structural materials to industries ranging from construction to automotive. Successful application of our technology to manufacturing processes will result in a new class of high strength, light weight structural materials.

SIGNIFICANT ACCOMPLISHMENT

Polymerization and Processing of Organic Polymers in a Magnetic Field

Problem:

There is an important interaction between magnetic fields and large molecules in simple liquid crystal systems. This interaction results in orientation of magnetically anisotropic units. To date there have been no studies on the effect of high magnetic field processing on the mechanical properties of liquid crystalline systems. This lack of information is due to the great difficulty in preparing large samples that can be used for mechanical testing. We have been able to design a new type of mold which is used to prepare large plaques of liquid crystalline thermosets in high magnetic fields. As a result, we have been able to provide the first data on the tensile properties of highly anisotropic liquid crystalline polymers.

Results:

In this report we provide the first description of the orientation of liquid crystalline thermosets (LCT's) in field strengths of up to 18 T, as well as the first report of tensile properties for both unoriented and oriented LCT's. The LCT we have chosen for study is the diglycidyl ether of dihydroxy- α -methylstilbene cured with the diamine, sulfanilamide. Table I below shows the tensile properties of macroscopically oriented and unoriented materials. Orientation in magnetic fields leads to an increase of almost three times the modulus compared to the unoriented material. These values are much greater than can be obtained with conventional thermosets. The strain at break is also significantly affected by the chain orientation. The coefficient of thermal expansion and x-ray diffraction of oriented samples show high degrees of anisotropy, indicating significant chain alignment in the magnetic field. We are working to further understand the field dependence of orientation and properties plus the mechanisms of the alignment process.

Table I: Tensile Properties

	0 T	15 T	18 T
modulus (ksi)	443 (32)	1081 (93)	1174 (166)
strain at break (%)	8.9 (1.6)	0.8 (0.3)	1.0 (0.03)
stress at break (psi)	13,010 (621)	8117 (1105)	9985 (500)

Significance for Energy Conservation:

This project has the potential for energy savings through the introduction of processing techniques to create high strength, light weight structural materials. Additional energy savings could result from the use of self-reinforcing liquid crystalline polymers in manufacturing processes. Liquid crystalline polymers do not require the use of reinforcements or fillers, resulting in less wear on manufacturing equipment, elimination of compounding as a processing step, and more efficient recycling of materials.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: SYNTHESIS AND INDUSTRIAL APPLICATIONS OF CONDUCTING POLYMERS

PHASE: FY-1995

Performing Organization: Los Alamos National Laboratory

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

PHASE OBJECTIVES: (1) Demonstrate model capacitor with active conducting polymer material with 3V per unit cell and 1000 charge/discharge cycles
(2) 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) Develop model electrochemical capacitor device of >7 Wh/kg @ 2kW/kg based on conducting polymer active material, with cyclability extended beyond 10^4 times (2) 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

TECHNICAL APPROACH:

- (1) Ultracapacitors: Conducting polymer active materials are prepared by electropolymerization of specialty monomers synthesized in house. Electrodes loaded with such active materials used to prepare model ultracapacitor cells for testing under multicycling conditions
- (2) Conducting polymer membranes for gas separation: High molecular weight polyaniline powder used to prepare asymmetric membranes and permeabilities through optimally structured and doped membranes are measured with automated gas-permeator system

PROGRESS: (1a) We demonstrated this year a model Type III ultracapacitor based on conducting polymer active materials with very high short term performance, satisfying combined energy & power density requirements from advanced ultracapacitors for electric vehicles; (1b) Extension of the cycle life of Type III ultracapacitors by modification and purification of the electrolyte has been demonstrated;

(2) Mechanical and microporosity characteristics of asymmetric conducting polymer membranes for gas separation have been significantly improved

Patents: One awarded, November 1994

Publications: 6

Proceedings: 5

ACCOMPLISHMENTS:

(1) The Type III electrochemical capacitor developed under the AIM program has been selected for further development for telecommunications applications in a joint project with a major US industry

(2) We have demonstrated this year the potential applicability of a technology developed and patented earlier in this AIM project -- the chemical polymerization of conducting polymer films on insulating substrates -- , for new needs in electronics microfabrication.

PROJECT TITLE: SYNTHESIS AND INDUSTRIAL APPLICATIONS OF CONDUCTING POLYMERS

CRITICAL ISSUES: (1) The stability of conducting polymer materials under multicycling charge/discharge conditions is a critical issue in their complete demonstration for electrochemical capacitor applications. (2) The development of asymmetric membranes of conducting polymers with combined high throughput and selectivity is critical for their demonstration as real candidates for industrial gas separation processes. Skin integrity and its reproducibility need to be improved.

FUTURE PLANS: (1) Demonstrate together with new industrial partner applicability of Type III electrochemical capacitors for telecommunications applications; use this niche for market entry followed by further development for larger scale applications. (2) Continue optimization of fabrication and optimized doping of asymmetric membranes of polyaniline for gas separation, strengthening the interaction with gas technology industries towards a collaborative agreement.

POTENTIAL PAYOFF: For both items (1) and (2) above- energy savings of the order of several quads per year could be achieved.

ESTIMATED ENERGY SAVINGS:

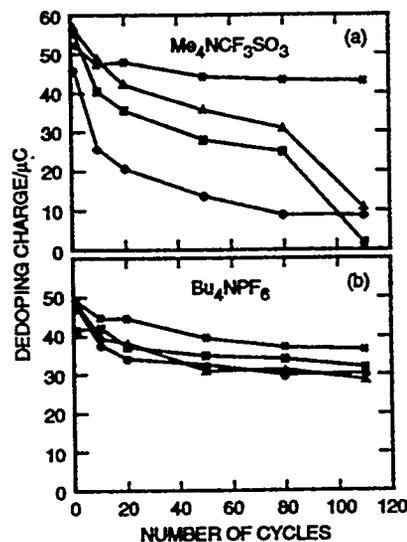
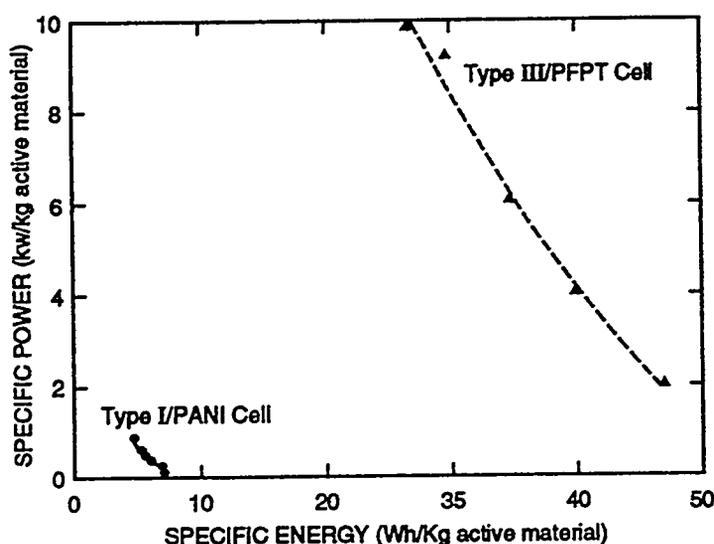
(a) Potential energy savings estimated at 1 quad/yr. expected from introduction of conducting polymer based ultracapacitors in power trains of electric and hybrid vehicles.

(b) Conducting polymer based gas separation membranes provide a potential for energy savings in the US estimated at 1 to 3 quads/yr.

THE APPLICATION OF CONDUCTING POLYMER ACTIVE MATERIALS IN ELECTROCHEMICAL CAPACITORS

PROBLEM: Energy storage devices are needed in several applications that require significant power outputs for durations in the range of 10 ms - 10 s. This usually defines combined requirements of device power density in the range 1-2 kW/kg and device energy density in the range 5-10 Wh/kg. For most applications, added requirements are highly extended charge/discharge cycling and minimized cost. Electrochemical capacitors could probably answer the combined requirements of power and energy density if further developed, and thus provide a basis for advanced industrial technologies and high energy savings.

RESULTS: A new family of active materials -- electronically conducting polymers -- has been synthesized and developed as part of this AIM program to provide a basis for the production of electrochemical capacitors of high energy/ power densities, extended cyclability, ease of manufacturing and reduced cost. Our most promising technology, based on a Type III ultracapacitor with p- and n-dopable conducting polymer active materials, has been advanced this year in two critical areas: demonstrated energy/power densities in a model device, and clarification of electrolyte nature and electrolyte purity effects on cyclability. The figures below show (left) a power density vs. energy density plot obtained for a model device tested this year (Type I device performance also shown for comparison), and (right) improved cyclability achieved by optimization of electrolyte composition.



SIGNIFICANCE:

This family of electrochemical energy storage devices has high potential significance in several fields of developing industrial technologies, ranging from electric vehicles to advanced telecommunications. US energy savings of one quad per year are expected from devices of this type at relatively early stages of implementation of electric and/or hybrid vehicles, rising two-three times higher with further development of advanced transportation technologies.

(R&D performed at Los Alamos National Laboratory (LANL) under the DOE-EE-AIM Materials Program support.)

NEW MATERIALS AND PROCESSES



PROJECT SUMMARY

ADVANCED INDUSTRIAL (AIM) MATERIALS PROGRAM

WORK ELEMENT: Microwave Processing of Materials

PROJECT TITLE: Advanced Microwave Processing Concepts

PHASE: FY 1995

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

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

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

ULTIMATE OBJECTIVE: Demonstrate and commercialize the Variable Frequency Microwave Furnace. 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 metal-to-metal or 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) have been examined individually. Preliminary data are encouraging.

Patents: 1

Publications:

Proceedings: 2

Books:

Presentations: 2

ACCOMPLISHMENTS:

A new CRADA was signed in June with Lambda Technologies, Inc. Additionally, Lambda executed a Sole Commercial License for microwave curing of polymers (ESID 1378-X, patent pending).



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAMS

PROJECT TITLE: Intelligent Systems For Induction Hardening Processes

PHASE: FY 1995

COMPLETION DATE: FY 2000

PERFORMING ORGANIZATION: Sandia National Laboratories

PRINCIPAL INVESTIGATORS: Russell D. Skocypec and J. Bruce Kelley

PHASE OBJECTIVE: Assess the potential to develop a consortium of industrial companies to further develop Intelligent Induction Hardening.

ULTIMATE OBJECTIVE: Develop Intelligent Induction Hardening systems which are functional across a broad range of materials, geometries, and processes, thus enabling broader use of the induction hardening process.

TECHNICAL APPROACH: A multidisciplinary team is organized around four task areas, process characterization, materials characterization, computational modeling, and closed-loop controller development. New materials, geometries, and processes will be addressed on a year-by-year basis.

PROGRESS:

Patents: None

Presentations: "Intelligent Systems For Induction Hardening Processes" presented at the First International Conference on Induction Hardened Gears and Critical Components, May 1995, Indianapolis

ACCOMPLISHMENTS:

Licenses: None

Known Follow-on Products: None

Industry Workshop:

Technology Transfer or Industrial Interactions: Presentations to technical management at Thompson-Saginaw Ball Screw Company, Black and Decker Corp, and Caterpillar Corp.

PROJECT TITLE: Intelligent Systems For Induction Hardening Processes

CRITICAL ISSUES: Coupling Electromagnetic, Thermal, and Materials Transformation models to create an integrated model which can be used for process tryout in a desktop environment. Development of high speed neural network controllers for a variety of material, geometry, and process variations, i.e. scanning, high frequency, and tempering processes. Development of metrics for the on-heating transformation process which are meaningful and easy to quantify, useful for both the modeling and process control tasks.

FUTURE PLANS: Technical efforts will progress in four task areas, Process Characterization, Materials Characterization, Computational Modeling, and Neural Net Control Development. Publicity from this activity may create market pull for technology transfer through formation of an industrial consortium or through licensing of technology.

POTENTIAL PAYOFFS: Reduced product realization lead times. Agile and robust manufacturing process control technology. Significantly wider use of the most energy efficient, environmentally benign case hardening process using the existing plant, machine tool, and materials infrastructure.

ESTIMATED ENERGY SAVINGS: 630 Trillion BTUs direct energy savings over 20 years. Up to 1 quadrillion BTUs total energy savings over 20 years.

COMPANIES EXPRESS INTEREST IN CONSORTIUM TO FURTHER DEVELOP INTELLIGENT SYSTEMS FOR INDUCTION HARDENING AND HEATING PROCESSES

Problem:

Induction hardening is an energy efficient, environmentally benign, fast and flexible in-line manufacturing process which is run in open loop control mode because closed-loop control technology was not previously available. The feasibility of closed-loop control has been demonstrated under a CRADA with Delphi Saginaw Steering Systems but further technology development needs to occur for significantly broader use of this energy efficient, environmentally benign process can occur.

Results:

Significant interest in formation of an industrial consortium to broaden the applicability of *intelligent* induction hardening systems was expressed by industrial companies such as Black and Decker, Caterpillar Thompson-Saginaw Ball Screw, and John Deere. Extending intelligent induction hardening to be applicable new materials, processes, and geometrics will enable optimization of a much broader range of processes and products, allowing substitution of this process for more commonly used processes like carburizing and nitriding. The approach of adding intelligence to enable science-based process control could also enable near term implementation of impulse drying for the pulp and paper industry, a dramatically more energy efficient paper and pulp drying process.

Significance For Energy Efficiency:

Significant energy savings will accrue as *intelligent* induction hardening is substituted for carburizing other case hardening processes used to case harden critical components like shafts, ball screws, bearings, and gears used in a wide variety of industrial equipment. Direct energy savings of up to 630 trillion BTUs are possible over 20 years, with total energy savings (direct and indirect) of up to 1 quadrillion BTUs. The net use of impulse drying, enabled by intelligent induction heating, would enable savings of an additional 80 trillion BTUs over 30 years.



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Materials R&D — Student Internships

PHASE: FY 1995

COMPLETION DATE: —

PERFORMING ORGANIZATION: Ames Laboratory

PRINCIPAL INVESTIGATORS: R. Bruce Thompson, 515-294-9649
Scott Chumbley, 515-294-7903
David C. Jiles, 515-294-9685

PHASE OBJECTIVE: To continue programmatic research of minority students.

ULTIMATE OBJECTIVE: The conduct of programmatic research of the Advanced Industrial Concepts Materials Program while training minority graduate students in the process.

TECHNICAL APPROACH: The approach for involving minorities involves recruiting students for participation in the program, matching them with projects of programmatic interest to the Advanced Industrial Concepts Materials Program, conduct of the research, continuous mentoring and graduation.

The specific technical approach will depend on the projects selected. The primary work in the current year is direct towards the development of magnetostrictive materials with enhanced dynamic energy transfer efficiencies for transducers and actuators and development of plasma torch techniques for production of nanocrystalline materials in large quantities and for depositing Cr layers without hazardous baths.

PROGRESS: Through the addition of 1% Al and Si, it has been possible to realize a 125% increase in resistivity and a 55% increase in the energy conversion efficiency of the highly magnetostrictive material Terfenol. An experimental design has been completed to determine the optimum parameters for the deposition of Cr films, and initial results show that thicknesses range from 0.1 nm to 500 nm.

Patents: 1 disclosure filed

Presentations: 2

ACCOMPLISHMENTS:

Licenses: —

Known Follow-on Product(s): —

Industry Workshop: —

Technology Transfer or Industrial Interaction: Meeting with Edge Technologies, the leading supplier of Terfenol, to discuss possible implementation of the new method for producing highly energy efficient magnetostrictive materials for high frequency applications.

PROJECT TITLE: Materials R&D — Student Internships

CRITICAL ISSUES: Identifying appropriate students and assisting them in what can be a significant transition from their undergraduate institution to a major research university.

FUTURE PLANS: Continued recruitment and education of minority students.

POTENTIAL PAYOFF: Increasing the fraction of the population available to perform technical jobs for the nation.

ESTIMATED ENERGY SAVINGS:

55% increase in the efficiency of energy conversion in the highly magnetostrictive material Terfenol at kilohertz frequencies.

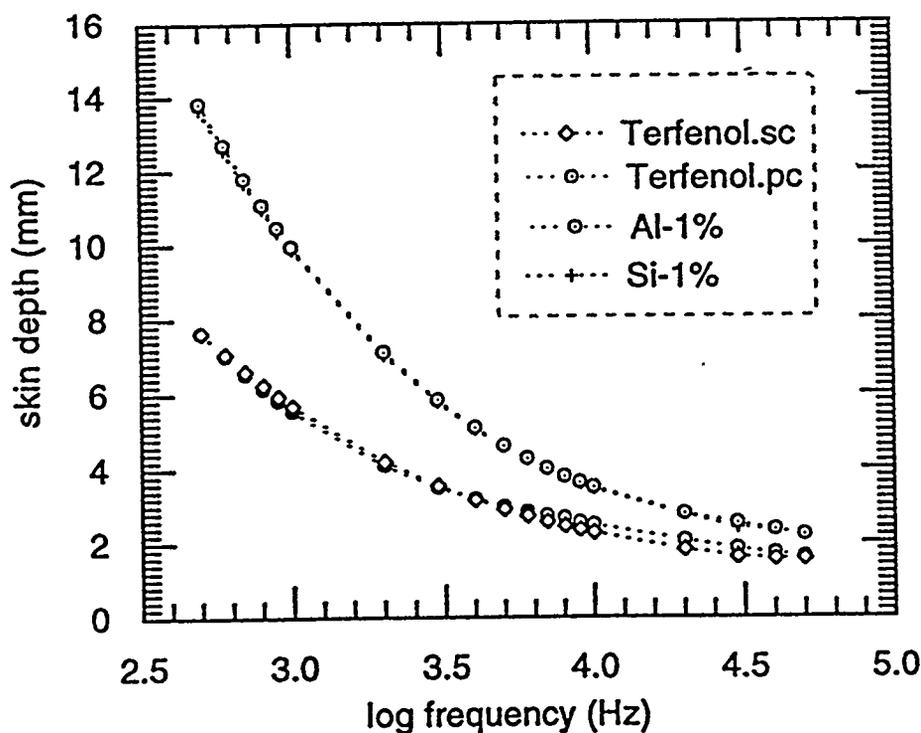
IMPROVEMENTS IN THE EFFICIENCY OF ENERGY CONVERSION IN THE HIGHLY MAGNETOSTRICTIVE MATERIAL TERFENOL

Problem:

Magnetostrictive materials are used in a wide range of applications, ranging from active vibration control to sonar projectors, where large displacements are controlled. However, the presence of electrical resistivity limits their efficiency of operation and maximum operating efficiency.

Results:

Terfenol, a rare-earth alloy containing Tb, Dy and Fe, exhibits one of the largest known magnetostrictive effects. Through the addition of 1% Al and Si, it has been possible to realize a 125% increase in resistivity. As shown below, this leads to a greater penetration of the exciting fields into the material (skin depth), with attendant increases in efficiencies.



Significance — For Energy Efficiency:

A 55% increase in the magnetomechanical coupling coefficient was observed, leading to increases in energy conversion efficiency for frequencies up to 36 kHz.

(R&D performed at Ames Laboratory (AL) under DOE-EE-AIM Program support.)



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Microwave Joining of SiC

PHASE: FY 1996

COMPLETION DATE: August 31, 1998

PERFORMING ORGANIZATION(S): FM Technologies, Inc., George Mason University, Los Alamos National Laboratory.

PRINCIPAL INVESTIGATOR(S): Richard Silbergitt (FMT) (703) 425-5111, W. Murray Black (GMU) (703) 993-4069, Joel D. Katz (LANL) (505) 665-1424.

PHASE OBJECTIVE: Identify the most effective joining methods for scale-up to large tube assemblies.

ULTIMATE OBJECTIVE: Develop and optimize joining method that can be applied to large scale fabrication of components such as radiant burner tubes and high temperature, high pressure heat exchangers.

TECHNICAL APPROACH: Previous research has demonstrated the effectiveness of microwave joining for small samples of reaction bonded SiC (RBSC) and sintered SiC and for short tube sections with diameters up to approximately 5 cm (2"). Two research avenues are currently being explored to support scale-up and application to commercial materials: (1) use of polymer precursors to form SiC in situ; and (2) design and development of new cavity applicators suitable for joining of long tubes of 4" and greater diameter.

PROGRESS: SiC was formed in situ from pyrolysis of polycarbosilane (PCS) using microwave heating and sintered SiC specimens were joined with in situ material. Fracture toughness measurements on test bend bars machined from reaction bonded SiC tubes joined using hybrid (microwave plus radiant) heating in a multimode applicator demonstrated strength equal to or greater than as-received material.

Patents: -

Presentations: 18

ACCOMPLISHMENTS: Microwave joining of RBSC and sintered SiC has been demonstrated for tubes up to 5 cm (2") in diameter. Joints are leak-tight at service temperature, and have adequate mechanical strength for desired applications. Formation of SiC in situ during joining provides a mechanism for filling gaps due to tolerance mismatch with large tubes.

Licenses: none

Industrial Interaction: Materials supplied for test joints and mechanical testing performed by Golden Technologies, Inc., the Coors company responsible for advanced ceramics R&D. Actively working with Golden Technologies and other companies to define a prototype demonstration for the scale-up of the technique.

PROJECT TITLE: Microwave Joining of SiC

CRITICAL ISSUES:

- ♦ Identification of appropriate precursors for SiC;
- ♦ Achievement of uniform temperatures at interface;
- ♦ Development of applicators for long and large diameter specimens that can be cost-effectively fabricated and operated.

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. Golden Technologies has identified a radiant burner tube assembly application in the steel industry.

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 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 CO₂ emissions and a 90% reduction in SO_x emissions.

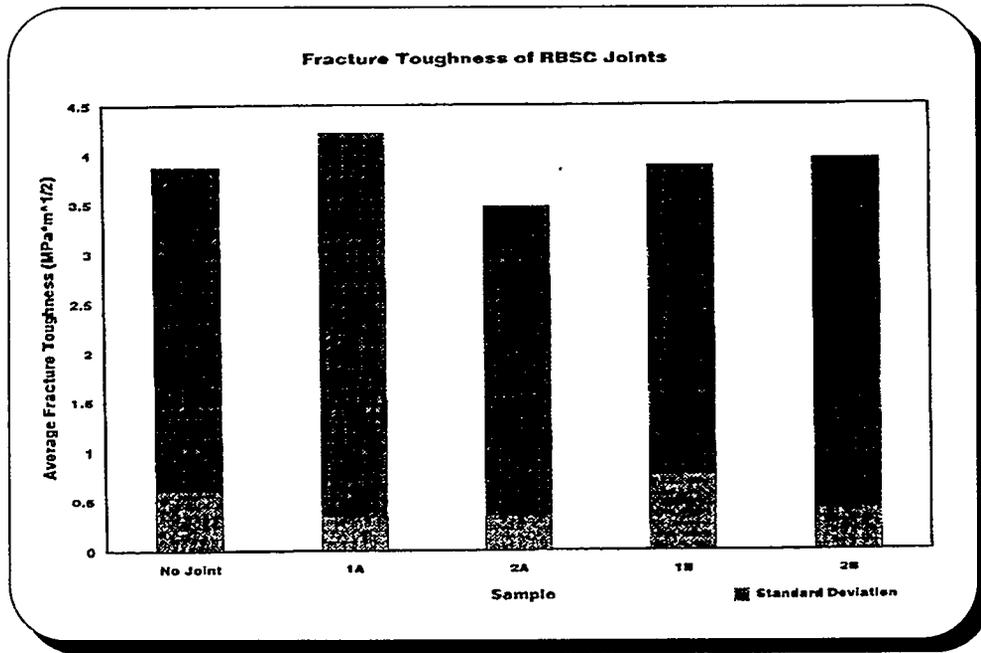
FRACTURE TOUGHNESS OF MICROWAVE JOINED SiC EQUAL TO OR GREATER THAN THAT OF ORIGINAL MATERIAL

Problem:

Markets for SiC radiant burner tubes and heat exchangers are 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.

Results:

Microwave heating was used to join tube sections of reaction bonded SiC greater than 1" outer diameter. Test bend bars were sectioned from the joined tubes, and the fracture toughness of these bars was measured and compared to that of bars sectioned from the original material. The fracture toughness of the SiC joined at temperatures in the range of 1420°C-1515°C was determined to be equal to or greater than that of the original material.

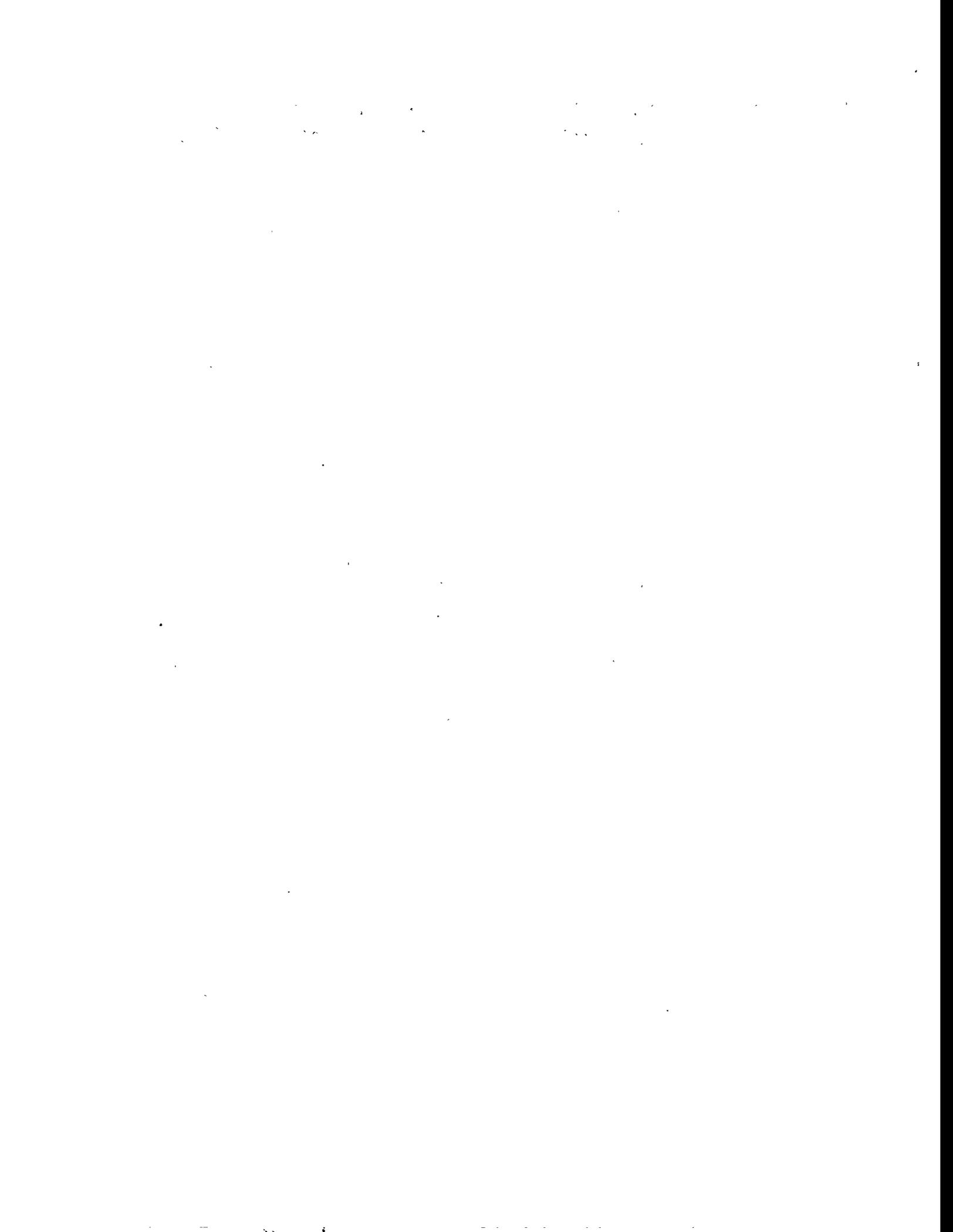


Fracture Toughness of SiC Joints (Joining Temperatures:
Specimen 1A, 1465°C; Specimen 2A, 1565°C; Specimen 1B, 1515°C; Specimen 2B, 1420°C)

Significance:

The demonstration that microwave joining retains or increases the fracture toughness of tubes with greater than 1" outer diameter qualifies this method for fabrication of SiC tube assemblies for radiant burners and heat exchangers.

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



PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: MICROWAVE PROCESSING OF CONTINUOUS CERAMIC OXIDE FILAMENTS

PHASE: FY 1995

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATORS: Gerald J. Vogt, 505/665-4988

PHASE OBJECTIVE: Develop microwave sintering and drying processes for 3M prototype continuous ceramic filament tows.

ULTIMATE OBJECTIVE: Develop economic microwave processing technology for the complete manufacturing of continuous ceramic oxide filament tows from extruded solution-based sols with greater energy efficiency than conventional thermal processing and for the manufacturing of new fibrous products.

TECHNICAL APPROACH: Use volumetric microwave absorption to heat ceramic oxide filament tows in order to drive process drying, prefiring, and sintering in the preparation of continuous tows from solution-based sols. The potential energy and economic advantages of microwave processing will be evaluated through direct comparison with conventional thermal processing. The technical goal is to demonstrate more rapid filament processing by microwave heating with less energy and at a lower cost, but with the same quality as conventional thermal processing.

PROGRESS: A universal hybrid microwave heating technique was demonstrated for controlled microwave sintering of the prototype filament tows. Microwave heating can be initiated without breaking the continuous filament tow or stopping the process. A microwave-driven heating zone can be maintained and propagated along continuous filaments moving through the microwave cavity. A prototype microwave drying system has been designed, constructed, and operated for the drying of continuous filaments extruded from inorganic sols. The prototype microwave drying system has successfully dried a single continuous filament, hundreds of meters in length.

Patents: none **Publications:** 3 **Proceedings:** 3 **Presentations:** 5

ACCOMPLISHMENTS:

Licenses: none

Known follow-on Products: one under consideration

Industry Workshops: none

Technology Transfer or Industrial Interaction:

1. CRADA with the 3M Company for the microwave processing of continuous ceramic oxide filaments.
2. Exploratory microwave heating tests on Babcock & Wilcox filaments to evaluate the feasibility of microwave heating for the material.

PROJECT TITLE: MICROWAVE PROCESSING OF CONTINUOUS CERAMIC OXIDE FILAMENTS

CRITICAL ISSUES: 1) The sintering temperature for the prefired filaments must be controlled at 1000°-1100°C to retain the submicron grain size necessary for the desired flexibility and mechanical strength. 2) Filament drying must be accomplished without splitting or bursting the individual filaments.

FUTURE PLANS: To carry out the CRADA work with the 3M Company for microwave processing of continuous proprietary filament tows. We will develop microwave techniques for drying, organic burn out, and sintering of prototype sol-gel filament tows. The energy efficiency and economics of microwave processing will be directly compared to those of conventional thermal processing. Microwave processing has the potential to produce new products not available by conventional processing.

POTENTIAL PAYOFF: Continuous ceramic filaments have important applications in aerospace and automotive structural composites, as well as woven, shaped fabrics for high temperature combustion, catalyst support, filtration, refractory insulation, and consumer products. Continuous ceramic filaments are a principal component in many advanced high temperature materials like continuous fiber ceramic composites (CFCC) and woven ceramic textiles. Continuous ceramic filaments can be used in CFCC radiant burners, gas turbines, waste incineration, and hot gas filters in U.S. industry and power generation. Microwave filament processing offers significant improvements over conventional processing in faster processing, lower manufacturing and capital costs, and energy savings with direct volumetric heating.

ESTIMATED ENERGY SAVINGS: Microwave sintering for specific filament tows can be carried out with energy savings over conventional processing with large electrical furnaces to slowly sinter inorganic filament tows for several hours. Better than 95% of the energy in conventional processing is needed to maintain a stable furnace temperature, with less than 1% of the energy being used in heating the filament tows. Microwave energy is directly absorbed by the inorganic filaments without the need to heat bulky furnace insulation. Also, microwave processing may require only seconds-to-minutes to complete a processing step, compared to hours by conventional processing.

Continuous ceramic filaments are a principal component in many advanced high temperature materials like continuous fiber ceramic composites (CFCC) and woven ceramic textiles. The use of continuous ceramic filaments in CFCC radiant burners, gas turbines, waste incineration, and hot gas filters in U.S. industry and power generation is estimated to save at least 2.16 quad/yr by year 2010 with energy cost savings of at least \$8.1 billion. By year 2010, continuous ceramic filaments and CFCC's have the potential to abate pollution emissions by 917,000 tons annually of nitrous oxide and 118 million tons annually of carbon dioxide (DOE Report OR-2002, February, 1994).

Woven textiles are used in hot gas filtration, high-temperature insulation in aircraft firewalls and engine cowls, zone dividers and furnace curtains in metal processing, oil boom covers to burn off oil spills, and many other applications. Seamless ceramic fiber filter bags can operate up to 1100°C to remove more than 99.9% of the pollution particulates in a variety of corrosive gas environments. Annual energy savings of 0.1 quad/yr are possible from the combustion of coal alone. Hot gas filters will reduce nitrous oxide and carbon dioxide emissions by thousands of tons annually. Filtered hot gas will also help prevent erosion of turbines.

MICROWAVE PROCESSING OF CONTINUOUS CERAMIC OXIDE FILAMENTS

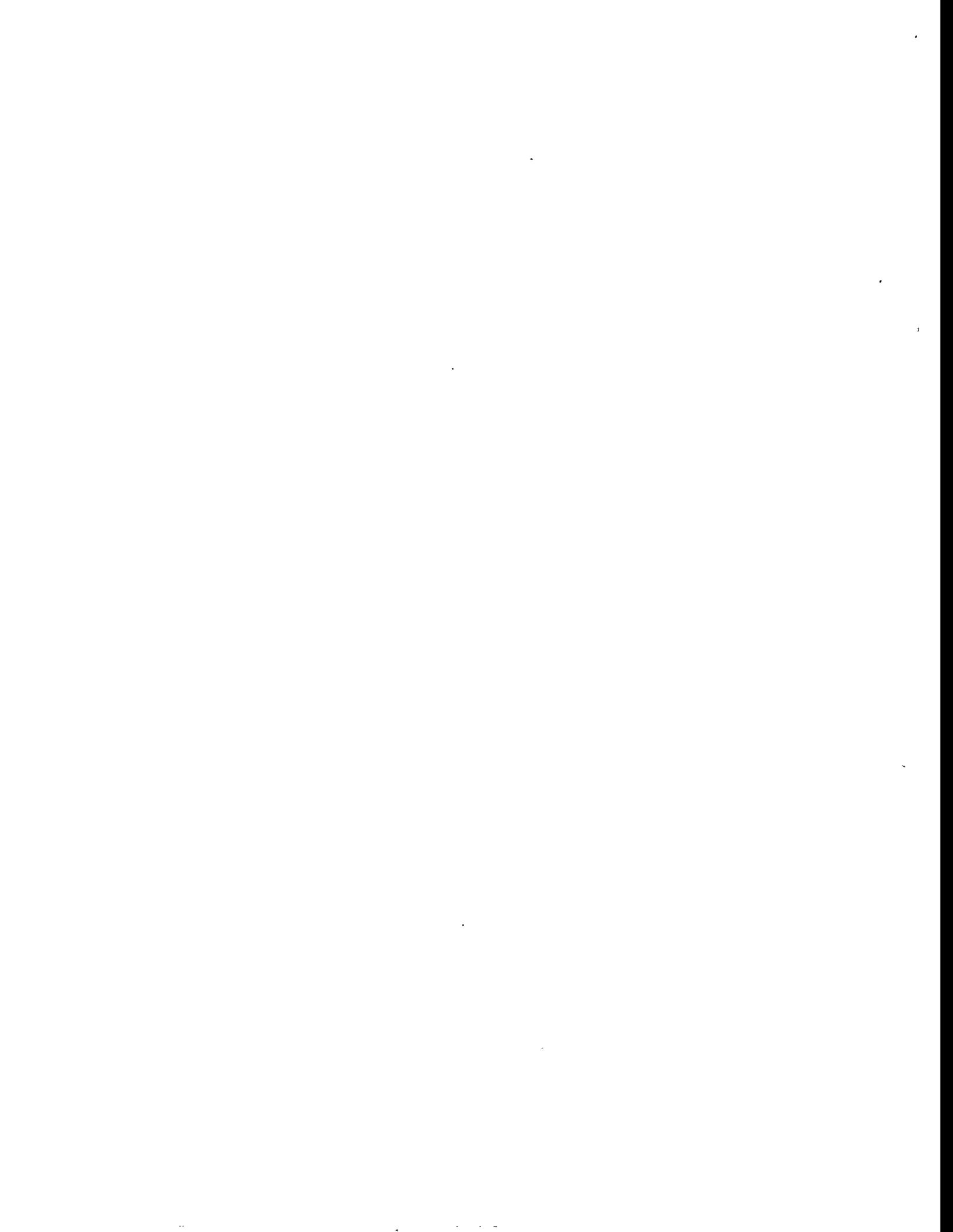
Problem: Conventional manufacturing of continuous ceramic oxide filaments has a low energy efficiency due to the need to electrically heat large furnaces to prepare a product with a relatively low thermal mass and to process unit lengths for 1 hour or more. Conventional processing is also practically limited to producing very small diameter (1-30 μm) filaments due to the diffusional nature of heat transfer in this technology.

Results: Microwave energy is volumetrically absorbed by oxide filaments to selectively dry, to remove organic residue by combustion, and to sinter. The energy is delivered directly to the filament tows without the need to heat an external furnace. Many different oxide filaments can be heated to sintering temperatures by a hybrid microwave heating technique. Microwave drying can rapidly dry continuous filaments in commercial lengths.

Significance - For Energy Conservation: Microwave sintering for specific filament compositions can save more than 90% of the energy currently used in conventional processing. The use of continuous fiber ceramic composites in radiant burners, gas turbines, waste incineration, and hot gas filters in U.S. industry and power generation is estimated to save at least 2.16 quad/yr by year 2010 with an energy cost savings of at least \$8.1 billion.

Significance - For Materials Technology: Microwave processing offers the possibility of improved filament quality and consistency at a lower cost over that available from conventional processing technology.

(Work performed at Los Alamos National Laboratory with DOE-AIM support)



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
Northern Illinois University

PRINCIPAL INVESTIGATOR: Mark L. F. Phillips, Dept. 1846, MS 0333
phone: (505) 844-8969
fax: (505) 844-4816

PHASE OBJECTIVE: 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. Develop sensor techniques for characterizing physical properties and enhancing chemical selectivity of films.

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: Nucleate and crystallize zeolitic phases from sol-gel, clay, and metallic films, using porous filters and gas membranes as supports for these films. Develop new techniques for characterizing physical and surface chemical properties of precursor and product films. Adapt these techniques for use as chemical sensors.

PROGRESS (FY95): Zeolite films have been synthesized on porous substrates from bilayer sol-gel films and clays. Gas permeation data have been obtained from both film types. Zeolite films made from kaolinite have been made free of macroscopic defects, but still contain microscopic intercrystalline gaps. Films from sol-gel precursors have been made free of cracks and pinholes, and separation factors are better than those from uncoated supports (Knudsen diffusion). Surface plasmon resonance (SPR) has been established as a film characterization method, and sol-gel films have been used to enhance performance of SPR-based sensors.

FY95: Publications: 3 Presentations: 3 Disclosures: 3

ACCOMPLISHMENTS:

Licenses: --
Known follow-on products: --
Industry Workshops: --

PROJECT TITLE: Selective Inorganic Thin Films

CRITICAL ISSUES:

1. Synthesize crystalline molecular sieve films with complete surface coverage and high permeability on porous substrates.
2. Develop a means for eliminating intercrystalline gaps and porosity, using a "caulking" phase.

FUTURE PLANS:

1. Continue optimizing conditions for zeolite membrane processing. Characterize high-temperature gas separation performance of supported zeolite membranes.
2. Continue developing metallic and clay films as nutrients for zeolite film crystallization.
3. Continue to derivatize SPR sensors with modified sol-gel films to enhance sensor specificity.

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. With sufficiently high permselectivities and low unit area cost, energy savings of several quad/yr could be achieved.

ZEOLITE-BASED MOLECULAR SIEVE MEMBRANES

Mark L. F. Phillips, Lori A. Weisenbach, Teresa V. Bohuszewicz, and C. Jeffrey Brinker
Department 1846, Sandia National Laboratories
Albuquerque, NM 87185-0333

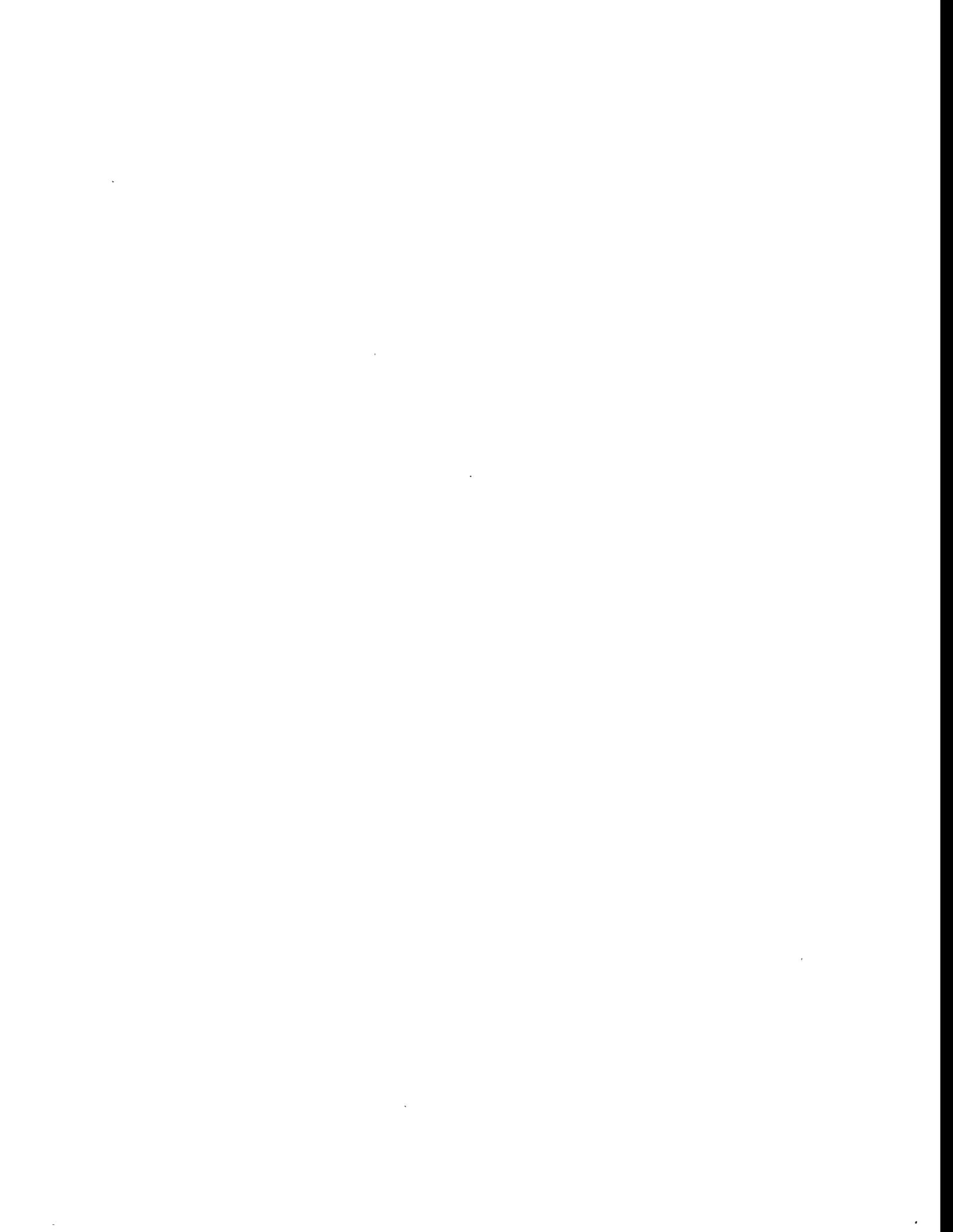
PROBLEM: Separating valuable light gases such as methane and hydrogen from other constituents of natural gas and refinery process streams (such as N_2 , CO_2 , C_2H_2 , H_2S) using polymer membrane technology is difficult, particularly at high temperatures. Membranes capable of separating gases based 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.

RESULT: We have demonstrated techniques for depositing sol-gel and clay (kaolinite) coatings onto mesoporous alumina supports, and hydrothermally converting these coatings to zeolite films. The films from sol-gel consist of zeolite crystals grown from the amorphous matrix, and are an order of magnitude thinner than other reported zeolite films. We have also synthesized kaolinite-derived Zeolite A films that are free of macroscopic defects. In both cases the zeolite-alumina composite membranes can be heated to at least 500 °C without apparent film cracking or zeolite decomposition.

We have recently shown via gas permeation measurements that the zeolite films crystallized from sol-gel precursor films can be made free of microscopic defects such as gaps, cracks, or pinholes. Separation factors are greater than those obtained from the uncoated substrate, though residual porosity in the remaining sol-gel phase prevents the membranes from acting as molecular sieves. Gas flow through the kaolinite-derived films is dominated by intercrystalline gaps. We are addressing these issues by using successive hydrothermal treatments and sol-gel "caulking" films to plug intercrystalline gaps and mesoporosity. These methods are expected to increase separation factors by allowing gases to flow only through the zeolite pores.

SIGNIFICANCE: These results represent substantial advances toward the goal of making inexpensive, thermally robust molecular sieve membranes based on zeolite films. The petroleum and natural gas refining industries would significantly benefit from high-permeability molecular sieve membranes capable of separating light, fixed gases, particularly if the membranes can be used at high temperatures. With sufficiently high permselectivity and low unit area cost, energy savings of several quad/yr could be achieved.

This work was performed at Sandia National Laboratories under DOE-EE Advanced Industrial Materials Program support (contract no. DE-AC04-95AL85000).



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