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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 1998

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INTRODUCTION

Introduction to the Advanced Industrial Materials (AIM) Program
Office of Industrial Technologies
Fiscal Year 1998

C. A. Sorrell, Program Manager

The Advanced Industrial Materials (AIM) Program is in the Office of Industrial Technologies (OIT), Energy Efficiency and Renewable Energy, U.S. Department of Energy (DOE). The mission of AIM is to ?support development and commercialization of new or improved materials to improve energy efficiency, productivity, product quality, and reduced waste in the major process industries.? AIM investigators in the DOE national laboratories are working closely with approximately 100 companies via a range of mechanisms, including Cooperative Research and Development Agreements (CRADAs), User Centers, and informal partnerships. Research and development is being performed in a wide variety of materials technologies, including metallic and intermetallic alloys, ceramic and metal matrix composites, inorganic membrane materials, and coatings. The emphasis within AIM is on high-temperature, corrosion-resistant alloys and membrane materials; continuous fiber ceramic composites and monolithic ceramics are covered primarily by DOE's Continuous Fiber Ceramic Composites Program and Advanced Turbine Systems Program.

The Office of Industrial Technologies concentrates on the major process industries through the Industries of the Future (IOF) strategy. OIT has encouraged and assisted these industries in developing visions of what they will be like in 20 or 30 years, defining the drivers, technology needs, and barriers to realization of their visions. The visions provide a strategic framework for development of technology roadmaps and implementation plans. OIT then (1) provides cost-shared support for research and development to meet the needs identified in the roadmaps and (2) works with other governmental agencies to leverage resources. The Industries of the Future are agriculture, aluminum, chemicals, forest products, glass, metalcasting, mining, and petroleum refining. Other industries that serve the IOF industries also have stepped forward to develop visions and roadmaps and are ready to respond to solicitations of the IOF industries. These support industries are forging, heat treating, carbon products, and welding. The Portland cement industry recently has expressed a strong interest in following these examples.

In this context, the AIM Program supports the Industries of the Future by conducting research and development on materials to solve problems identified in the roadmaps. This work is done by national laboratory/industry/university teams with the facilities and expertise needed to develop new and improved materials. Each project in the AIM Program has active industrial participation and support.

In FY 1998, several projects were transferred to the IOF teams for further development and demonstration in industry. The zeolite membrane work at Sandia National Laboratories, New Mexico, under a CRADA with Amoco, is now supported by the

Chemical Industry budget, as is the electrochemical reactor work at Los Alamos National Laboratory, under a CRADA with Dow Chemical. The refractories work at Oak Ridge National Laboratory (ORNL) is now being supported by the Glass Industry budget, along with the molybdenum disilicide work at Los Alamos, under a CRADA with Johns Manville, and the chemical vapor deposition work at Sandia National Laboratory, California, under a CRADA with Pilkington Libby Owens Ford. Recently, the Los Alamos work on molybdenum disilicide and the Sandia work at the Combustion Research Facility have received funding directly from the Glass Industry budget resulting from a Laboratory solicitation. A new user facility for modeling the glass-melting furnace also was funded by the Glass Industry budget. The Steel Industry team has continued funding work on intermetallic alloys for the industry, based on the successful demonstration of steel transfer rolls by Bethlehem Steel. So the transfer of AIM-sponsored work to the IOF industries is beginning to work, and AIM is receiving due recognition from OIT management.

The designation of the Metals Processing Laboratory (MPLUS) at ORNL as a DOE User Center has been successful beyond our expectations. Over 80 proposals have been received, and many have been completed. Industry has been very enthusiastic about the opportunity to work at MPLUS and the other centers at ORNL. The Aluminum and Metal Casting teams are now providing funding for MPLUS, and others are likely to follow. The MPLUS business plan calls for referring potential users to other laboratories, with funding appropriate to the needs of the users. We are nearly at a funding level to make this work.

No brief summary can do justice to the quality and relevance of the work done by the hard-working AIM investigators. The reader will have to go through this entire volume to appreciate the magnitude of what has been accomplished with a relatively modest budget. It is not likely that many other government programs have produced so much for so little. The Program Manager expresses his appreciation for the support of such a fine group of people.

ADVANCED CERAMICS AND COMPOSITES

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Advanced Manufacturing of Ceramics by Chemical Vapor Deposition Methods

PHASE: Technology Proof-of-Concept **COMPLETION DATE:**

PERFORMING ORGANIZATION: Sandia National Laboratories, Livermore, California

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

PHASE OBJECTIVE: To develop predictive computational models, process-control algorithms, and sensors for designing, optimizing, and operating coating processes for depositing energy-efficient coatings on float glass for architectural and automotive uses.

ULTIMATE OBJECTIVE: To improve the competitiveness of the U.S. float-glass industry by developing new, cost-effective uses of glass. In addition, this project strives to reduce the costs of ceramic composites so that they can be applied more widely to corrosion, wear, and high-temperature problems in industrial settings.

TECHNICAL APPROACH: Industrial methods for the deposition of coatings on float glass are simulated using a high-temperature, variable-pressure flow reactor constructed as part of this project. Parallel development of computational models of physical and chemical mechanisms of deposition also is conducted.

PROGRESS:

- Developed a database located on the Internet of gas-phase thermodynamic and kinetic information needed to develop models of coating processes.
- Characterized the thermal stability and reactivity of indium-containing precursors used in float-glass coating operations.
- Designed and constructed a laboratory version of a system for monitoring precursors and reaction by-products used in float-glass coating operations.

Patents: None. **Publications:** 5 **Presentations:** 4

ACCOMPLISHMENTS:

Technology Transfer: Completed the second year of a 3-year, $1.06M CRADA with Libbey-Owens-Ford Co. (including $540K of direct and in-kind funding from LOF). Provided LOF with data concerning the thermal stability and reactivity of new indium-containing precursors and assisted their staff in conducting pilot-scale tests of a new coating process for the production of indium tin oxide coatings at their Ottowa, Illinois, float-glass facility.

PROJECT SUMMARY (continued)

PROJECT TITLE: Advanced Manufacturing of Ceramics by Chemical Vapor Deposition Methods

Licenses: None.

CRITICAL ISSUES: In the production of float glass, increasing the energy efficiency of fenestration through high-performance on-line coatings is an important technological objective, not only for glass producers, but also window fabricators, architects, HVAC engineers, automobile manufacturers, and utilities. A more detailed understanding of the high-temperature processes occurring prior to coating formation is necessary to effect a quantum leap in coating performance.

FUTURE PLANS: Field tests in a float-glass facility owned by LOF are planned for FY 1999. Initially, we will use the sensor to monitor the delivery rate of precursors used in the production of tin oxide coatings and the production of reaction by-products. The first set of tests are scheduled for mid January, 1999, with a second and possibly third set planned for later in the year, depending on the initial performance of the sensor. We also are exploring areas outside coating operations for applying this new tool and are in discussion with LOF regarding the possibility of using the sensor to monitor combustion gases in its glass-melting operations.

POTENTIAL PAYOFF: Use of the experimental data and computational models developed here is expected to shorten the time required to design, optimize, and scale up new coating processes and to facilitate extension of existing technology to new materials. New sensor hardware currently under development will increase the efficiency of coating operations by notifying operators of conditions that lead to sudden process upsets, thus minimizing downtime.

ESTIMATED ENERGY SAVINGS: New coatings on float glass developed in this project will save 1.4×10^{19} Btu/year when installed in place of clear glass windows.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

Development of an Economical Sensor for Monitoring Process Gases in Float-Glass Coating Operations

PROBLEM: On-line coating of float glass is a complex process involving many coordinated elements, including vacuum pumps, mass-flow controllers, and temperature-controlled precursor storage units and delivery lines. Variations in the operation of any one of these components can lead to nonuniformities in coatings and an unacceptable product. Sudden upsets caused by blockage of delivery or exhaust lines can waste expensive precursors, reduce product quality, and create conditions that may damage reactor hardware.

RESULTS: A field-portable residual gas analyzer system (RGA) was designed and constructed that can detect reactant and product gases present during float-glass coating. The system incorporates both a precision RGA, capable of collecting high-resolution mass spectra from 0 to 300 amu, and a low-resolution but economical Ferran Micropole™ analyzer (MPA), a novel device originally developed by NASA. Laboratory tests demonstrate both devices could be useful in an on-line process-monitoring scheme. Field testing in a float-glass facility is planned for early 1999.

Fig. 1. Photograph of field-portable residual gas analyzer system

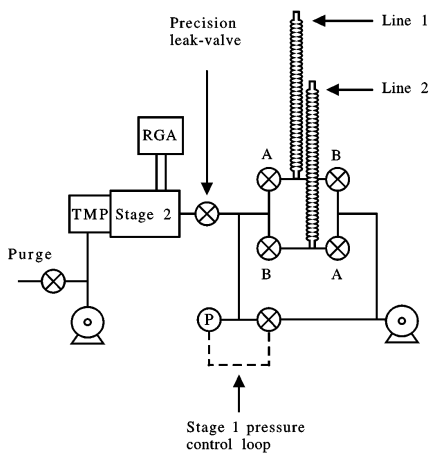


Fig. 2. Schematic of field-portable RGA system.

SIGNIFICANCE – FOR ENERGY EFFICIENCY: In North America, 2.6 Mtons/year of float glass are used in residential and commercial construction. Use of low-emissivity ("low-E") coatings on this glass can dramatically improve the energy efficiency of this material. New coatings developed in this project will save 1.4×10^{19} Btu/year when installed in place of clear glass windows.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: High Temperature Particle Filtration Technology

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATORS: Theodore M. Besmann (423-574-6852) and R. L. Martin (423-574-4929)

PHASE OBJECTIVE: The main objective of the current year's work was to perform bench-scale testing of the compatibility of high-temperature filters in Dow Corning applications.

ULTIMATE OBJECTIVE: The ultimate objective is to demonstrate utilization of high-temperature filtration in two Dow Corning applications related to dimethyldichlorosilane production.

TECHNICAL APPROACH: The approach of the program is to acquire filter specimens from manufacturers and perform bench-scale compatibility testing. After prioritizing the filter samples based on the testing, full-scale filters will be used in a small process unit at Dow Corning as a proof-of-concept evaluation.

PROGRESS: During this period, we completed modification of a furnace system for bench-scale testing of the filter samples. A large number of filter samples were acquired, and all were tested for 24 h under simulated conditions for one Dow Corning application.

Patents: None. **Publications:** None. **Proceedings:** None. **Books:** None.

Presentations:

T. M. Besmann, "High Temperature Particle Filtration," Advanced Industrial Materials Program Annual Meeting, Jackson Hole, Wyoming, June 23–25, 1998.

D. J. Bennett, "Hot Gas Filters," NACE International, Ceramics: Cutting Edge Solutions for Corrosion Control, Houston, Texas, June 29–30, 1998.

Awards: None.

ACCOMPLISHMENTS: Determined that a significant number of commercial filter concepts are likely to perform well in one of the Dow Corning application environments.

Technology Transfer or Industrial Interaction: Information is provided to Dow Corning regarding the stability of the filters in their environments.

PROJECT SUMMARY (continued)

PROJECT TITLE: High Temperature Particle Filtration Technology

CRITICAL ISSUES: Developmnent of slip-stream and pilot-scale testing at Dow Corning facilities.

FUTURE PLANS: Continue bench-scale testing for 1000 h for the thermal-oxidizer environment.

POTENTIAL PAYOFF: The payoff will be the application of high-temperature filtration to major process systems used by Dow Corning and its suppliers.

ESTIMATED ENERGY SAVINGS: Potential 12 trillion Btu/year by the year 2010.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

High Temperature Particle Filtration Technology

ISSUE: Improve energy efficiency of a process for producing a silicone precursor feedstock, dimethyldichlorosilane.

Table 1. Summary of Filter Specimen Test Results Showing Burst-Strength Measurements

Manufacturer	Type	Control		FBR		Therm. Ox.
			24 h	72 h	1000 h	24h
		(MPa)	(MPa)	(MPa)	(MPa)	(MPa)
Dupont-Lanxide	SiC/SiC	37.36	41.39	45.85	31.55	30.64
Dupont-Lanxide	PRD-66C	6.75	6.6	7.86	6.12	6.37
Dupont-Lanxide	PRD-66M	4.72	5.41	6.42	6.67	5.7
3M Company	SiC/Nextel	11.34	9.64	13.14	10.65	Incomplete
Techniweave	Carbon/SIC	11.4	11.34	11.41	12.23	FBR Only
Techniweave	Mullite/Mextel 610	22.19	Thermal Oxidizer Only			22.37
Techniweave	Mullite/Nextel 720	14.69	Thermal Oxidizer Only			13.57
Smart Ceramics	Oxide	28.59	32.69	26.37	24.84	29.23
McDermott Technologies	Oxide	8.94	9.11	-	8.87	8.32
Amercom	SiC	1.15	0.56	**		
Amercom	Oxide	0.75	0.64	**		
Blasch	Oxide	4.62	4.65	**		
Pall Corporation	Hastelloy X	205.71	256.86	260.85	208.4	FBR Only
Pall Corporation	Hastelloy C276	65.6	60.37	*		FBR Only
Pall Corporation	Inconnel 600	144.35	148.21	*		FBR Only
Pall Corporation	Vitripore 326	15.57	Thermal Oxidizer Only			14.48
*Dropped since not commercially available						
**Eliminated by properties						

RESULTS: Completed bench-scale testing of filter specimens for the fludized bed reactor (FBR) and the 24-h tests for the thermal-oxidizer environment.

ENERGY EFFICIENCY: Potentially 12 trillion Btu/year by the year 2010.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

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

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATOR: 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 at 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 for producing the desired pore structure. Separations of hydrocarbon gas mixtures with these membranes have been demonstrated.

ACCOMPLISHMENTS:

Licenses: None. **Known Follow-On Products(s):** None. **Industry Workshop:** None.

Technology Transfer or Industrial Interaction: This effort will continue in 1999 as a joint research effort with Amoco Chemical Company. 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.

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.

PROJECT SUMMARY (continued)

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

POTENTIAL PAYOFF: There are important benefits that will result from the success of the proposed CRADA effort. 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, U.S. 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 by-products 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 such flue-gas pollutants 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 U.S. 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 Btu per year for an olefins complex: this corresponds to a potential annual savings of nearly $8 million.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

Membrane Systems for Energy Efficient Separation of Light Gases

ISSUE: Ethylene and propylene are two of the largest commodity chemicals in the United States. and are major building blocks for the petrochemicals industry. These olefins are separated currently by cryogenic distillation, which demands extremely low temperatures and high pressures. Over 75 billion pounds of ethylene and propylene are distilled annually in the United States. at an estimated energy requirement of 400 trillion Btu. Nondomestic olefin producers are rapidly constructing state-of-the-art plants. These energy-efficient plants are competing with an aging U.S. olefins industry in which 75% of the olefins producers are practicing technology that is more than 20 years old. New separation opportunities, therefore, are needed to continually reduce energy consumption and remain competitive.

RESULTS: We have shown that oblique-angle vapor deposition techniques can be used to produce thin films with pores in the desired range of 4 to 5 nm. We have tested a number of systems of interest consisting of C1 through C4 hydrocarbons with nitrogen and hydrogen. Good separation factors along with permeability have been obtained.

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 Btu 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 TITLE: New Method for Synthesis of Metal Carbides, Metal Nitrides, and Metal Borides

PHASE: FY1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION: Southern Illinois University at Carbondale

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

PHASE OBJECTIVE: To promote the transfer of the technology developed under the AIM program. The technology deals with a new process for producing high-purity, submicron, non-agglomerated metal-carbide (SiC, TiC, WC), metal-nitride (TiN, Si_3N_4), and metal-boride (TiB_2) powders.

ULTIMATE OBJECTIVES: To develop a novel synthesis method for producing high-quality, low-cost metal-carbide, metal-nitride, and metal-boride powders using carbon-coated precursors. To demonstrate the advantages of the process and understand the formation of submicron powders from carbon-coated precursors. To perform initial investigation on the sintering behavior of these powders.

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

PROGRESS: The carbon-coating method developed for production of submicron TiC powders from carbon-coated TiO_2 powders was investigated using high-temperature TGA, DSC, XRD, and SEM/TEM. Liquid-phase sintering of the produced TiC powders was studied in flowing Ar and Ar + 10% H_2 as a function of carbon content in the precursor and nickel binder content. The produced submicron TiC powders were sintered to near-theoretical density in flowing argon at 1500°C for 2 h with only 3 wt % Ni.

PROJECT SUMMARY (continued)

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

Patent: U.S. 5,417,952	**Publications:** 3	**Proceedings:** 1
Books: None.	**Presentations:** 4	**Awards:** 2

ACCOMPLISHMENTS

Awards: R. Koc, Recipient of Sigma Xi Research Award, 1998.

Technology Transfer or Industrial Interaction:

ART has licensed the SiC patent to produce SiC powders.
Greenleaf Inc. is in process of licensing TiC patent.
Kennametal Inc. is in process of licensing WC technology.

CRITICAL ISSUES: Applicability of the process to synthesis of other metal-carbides, -nitrides, and -borides with high quality and low cost.

FUTURE PLANS: Investigate the formation of submicron powders from carbon-coated precursors using a high-temperature TGA-DTA/DSC unit. Characterize the resulting powders and provide information about their sinterability.

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

ESTIMATED ENERGY SAVINGS: This technology will improve energy efficiency when compared to conventional ones because it does not require high-reaction temperatures for production of these powders.

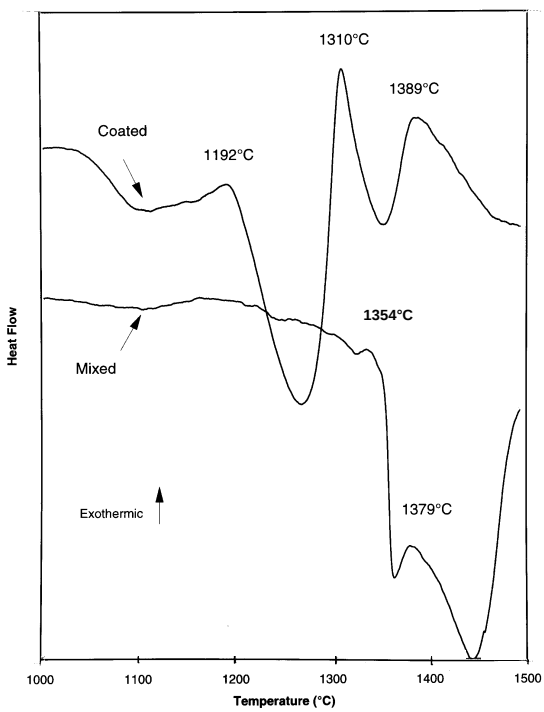
SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

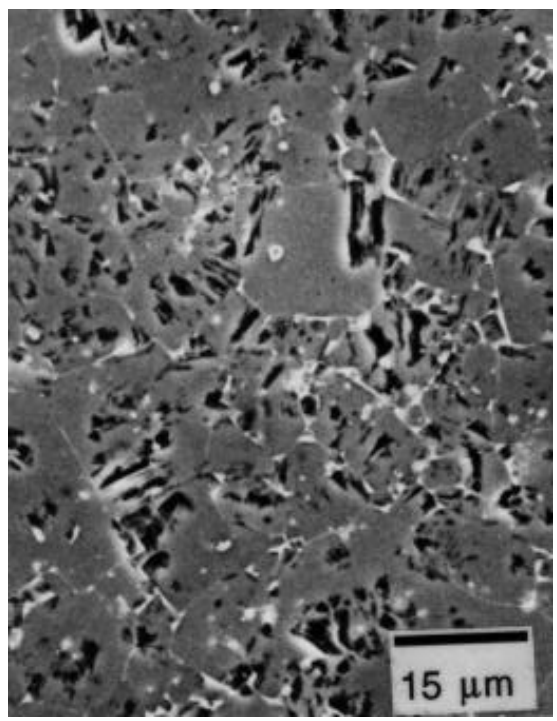
New Method for Synthesis of Metal Carbides, Metal Nitrides, and Metal Borides

ISSUE: The formation of TiC using the carbon-coated TiO_2 precursor was investigated. The use of TGA/DSC and XRD was instrumental in this research. Also, investigation of the liquid-phase sintering behavior of produced TiC powder was investigated.

RESULTS: The activation energy of TiC formation was calculated as 731.6 kJ/mol. Also, DSC demonstrated the superiority of using coated precursors rather than mixed precursors. The coated precursor experiences three complete reactions, forming pure TiC (confirmed by XRD), under 1500°C, while the mixed had only two, producing TiC_xO_y. The produced TiC powder was sintered to more than 99% TD using only 3 wt % Ni in flowing Ar + 10% H_2.



DSC curves for TiO_2-C.



SEM of TiC–3 wt % Ni sintered in Ar+10% H_2.

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

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

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

PHASE: FY 1998 **COMPLETION DATE:**

PERFORMING ORGANIZATIONS: Sandia National Laboratories (SNL); Subcontractors: University of New Mexico (UNM), New Mexico Institute of Mining and Technology (NMIMT), and SRI International (SRI)

PRINCIPAL INVESTIGATORS: Ronald E. Loehman/SNL (505-272-7601), Kevin G. Ewsuk/SNL (505-272-7620); Subcontractor PIs: William G. Fahrenholtz/UNM (505-272-7626),: Ping Lu/NMIMT (505-835-5731), Sylvia M. Johnson/SRI (650-859-4277).

PHASE OBJECTIVE: To identify compositions favorable for making composites and coatings by in situ reactive methods and to understand the mechanism(s) by which they are formed.

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

TECHNICAL APPROACH: Composites are made by reacting molten metals with ceramics under controlled conditions. Coatings are made from organometallic polymers filled with ceramic and metal powders that are converted to adherent films. Mechanistic process models are developed from kinetic, microstructural, and phase-diagram data combined with thermodynamic calculations. We use those results to make test specimens for determining physical properties.

PROGRESS: We discovered that heating rate can be used to control reaction rate in composite formation, which allows us to prepare dense, high-strength composites with compositions that previously were inaccessible, for example, Al_2O_3-$MoSi_2$, Al_2O_3-Ni, and Al_2O_3-Cu. Al_2O_3-Nb composites exhibited excellent strengths of 524 MPa, which possibly is due to lower internal stresses because of the close thermal-expansion match of the phases. We developed a correlation between residual Si in Al_2O_3-Al composites and their toughness and showed that Si-free composites exhibit desirable resistance-curve behavior in which toughness increases with increasing crack length. We investigated a wide range of composite coating formulations. Coatings of Al/Al_2O_3, Zn/SiO_2, and TiO_2/Al_2O_3 combined excellent corrosion resistance and hardness. Coating chemistry was varied to cure at room temperature to improve surface adhesion. Chemical surface treatment also was assessed to improve the bonding of the coatings to steel. Some surface-treated coatings survived over 1000 h of salt-spray test and had hardnesses of 6H to 9H.

PROJECT SUMMARY (continued)

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

Patents: 1	**Publications:** 4	**Proceedings:** 2
Books: None.	**Master's Thesis**: 1	**Presentations:** 17

Technology Transfer or Industrial Interactions: We have signed nondisclosure agreements for exchange of technical information with National Refractories and Minerals Corp. of Livermore, California, and BFD, Inc., of Columbus, Ohio. Sandia and National have agreed in principle on a CRADA in the area of developing improved refractories for the aluminum industry. SRI has established small evaluation projects with four companies for assessing its coating technology for different applications.

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

FUTURE PLANS: A major part of the FY 1999 effort will be devoted to the CRADA work with National Refractories. We will continue developing novel ceramic composites. SRI will continue improving process behavior, determine characteristics and performance of high-temperature coatings, and optimize formulations for high-temperature use.

POTENTIAL PAYOFF: Composites made by RMP could find many applications with significant savings due to their lower density. Improved refractories for aluminum processing would lead to large increases in process efficiency. Near-net-shape fabrication of parts has the additional advantage that costly and energy-intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.

OTHER SOURCES: Cost sharing has been primarily in the form of continuing collaborations that are maintained at no cost to the project. For example, A. P. Tomsia and his associate, Eduardo Saiz, use internal funding from Lawrence Berkeley National Laboratory to support their contributions to the collaboration. Graduate students continue to work on the project with support from their home institutions (University of Washington), representing an in-kind level of ~$50,000.

SIGNIFICANT ACCOMPLISHMENT

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

Al_2O_3-Al Composites Exhibit Desirable R-Curve Toughening Behavior

ISSUE: One way to improve ceramic reliability is by incorporating metal reinforcements because during crack propagation the metal ligaments bridge the crack faces, thereby creating closing forces across them. This results in an increasing toughness with increasing crack length that is known as resistance-curve or R-curve behavior. It is believed that materials with steep R-curves (i.e., those that reach their plateau toughness over a short increase in crack length) will show reduced flaw sensitivity and improved reliability.

RESULTS: Recently, composites with precise metal contents have been made by control of preform composition and processing conditions that exhibit improved toughness. These composites had microstructures with metal ligaments that can bridge any cracks that might develop in use. Figure 1 shows measured R-curves for two composites with 18 vol % metal, one processed to contain bridging ligaments and one without. Both of the samples have relatively steep R-curves that plateau after 300 to 500 μm of crack growth. One can see that the heat-treated composite (with low Si and bridging Al ligaments) has a higher plateau in toughness than the untreated material (high Si and no bridging ligaments). Figure 2 compares the R-curves for samples with 18 and 25 vol % metal, both of which were heat-treated to promote ligament formation. As expected, the plateau toughness increases (from 5 to 7 $MPam^{1/2}$) with increasing metal content. Both R-curves are relatively steep and plateau after 500 to 700 μm of crack growth.

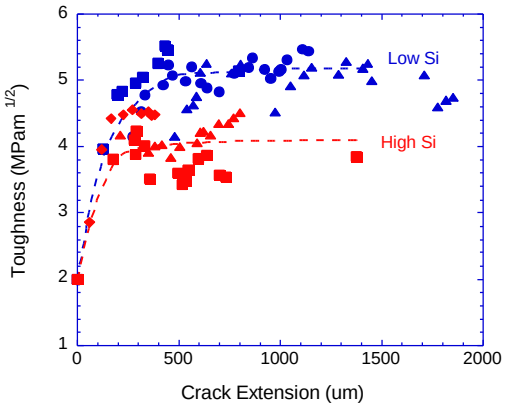


Fig. 1. Lowering the residual Si content in the composite increases the bridging metal ligaments and composite fracture toughness

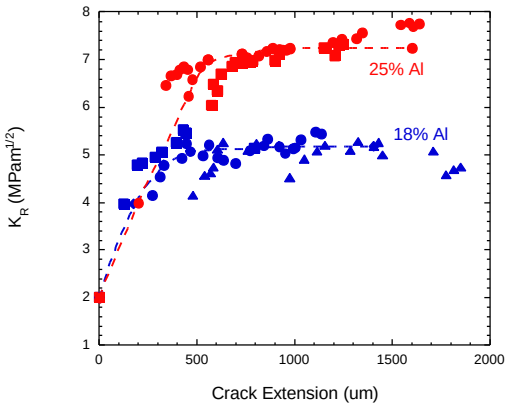


Fig. 2. Increasing Al content increases the plateau value of the R-curve and toughness of the composite