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ADVANCED INDUSTRIAL MATERIALS PROGRAM

ANNUAL PROGRESS REPORT FOR FY 1993

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TABLE OF CONTENTS

INTRODUCTION

Introduction to the Advanced Industrial Materials (AIM) Program (C. A. Sorrell)	3
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ADVANCED METALS AND COMPOSITES

Advanced Ordered Intermetallic Alloy Development	7
Development of Weldable, Corrosion-Resistant Iron-Aluminide Alloys	37
Evaluation of the Mechanism of Room Temperature Embrittlement of Aluminides	51
High-Temperature Precipitation-Strengthened Iron Aluminides and Other Intermetallic Alloys	55
Modeling Fracture of Advanced Ceramic Materials	73
Superior Metallic Alloys Through Rapid Solidification Processing by Design	89
Synthesis and Design of Intermetallic Materials	101
Ni ₃ Al Technology Transfer	131

ADVANCED CERAMICS AND COMPOSITES

Advanced Methods for Processing Ceramics	151
Characterization of CVI Densification of Ceramic Composites	171
Characterization of Three-way Automotive Catalysts	183
Chemical Vapor Infiltration of TiB ₂ Composites	195
Development of Chemical Vapor Composite (CVC) Materials	203
Development of New Composite Aerogel Materials	215

High Deposition Rate Ceramics Synthesis	225
Metallic and Intermetallic-Bonded Ceramic Composites	241
Microwave Assisted Chemical Vapor Infiltration	253
Synthesis and Processing of Composites by Reactive Metal Infiltration	267
Three-Dimensional X-Ray Tomography of Crack-Resistant Composites	289
POLYMER AND BIOBASED MATERIALS	
Chemical Recycling of Mixed Waste Plastics	301
Composites and Blends from Biobased Materials	311
Conducting Polymers: Synthesis and Industrial Applications	321
Magnetic Field Processing of Inorganic Polymers	337
Polymerization and Processing of Organic Polymers in a Magnetic Field	351
NEW MATERIALS AND PROCESSES	
Advanced Microwave Processing Concepts	371
Biomimetic Thin Film Synthesis	379
Materials R&D—Student Internships	391
Microwave Processing of Ceramic Oxide Filaments	397
Microwave Joining of SiC	413
Microwave Processing of Materials: Glass-Ceramics	425
Polymeric Materials with Improved Surface Properties	443
Selective Inorganic Thin Films	455
Silicon Carbide Powder Synthesis	469

INTRODUCTION

INTRODUCTION TO THE ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM*

C. A. Sorrell, Department of Energy (DOE) Program Manager

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The AIM Program is a part of the Office of Industrial Technologies (OIT), Energy Efficiency and Renewable Energy in the Department of Energy. The mission of the AIM Program is to conduct applied research, development, and applications engineering work, in partnership with industry, to commercialize new or improved materials and materials processing methods that will improve energy efficiency, productivity, and competitiveness. AIM is responsible for identifying, supporting, and coordinating multidisciplinary projects to solve identified industrial needs and transferring the technology to the industrial sector. Program investigators in the DOE National Laboratories are working closely with approximately 100 companies, including 15 partners in Cooperative Research and Development Agreements. Work is being done in a wide variety of materials technologies, including intermetallic alloys, ceramic composites, metal composites, polymers, engineered porous materials, and surface modification.

The Program supports other efforts in the OIT to assist the energy consuming process industries, including pulp and paper, glass, iron and steel, non-ferrous metals, casting, materials processing, chemicals, and refineries. To support OIT's "Plants of the Future" initiatives and to improve the relevance of materials research, assessments of materials needs and opportunities in the process industries are being made. These assessments are being used for program planning and priority setting; this will be followed by support of work to satisfy those needs.

Many new materials that have come into the marketplace in recent years, or that will be available for commercial use within a few more years, offer substantial benefits to society. The promise is for greater industrial efficiency, reduced energy consumption, greater reliability and product life, and new products for better productivity and leisure activities. From a national standpoint, it is important to remember that any nation excelling in advanced materials, and sharing the technologies and/or products resulting from those technologies at the appropriate commercial moment, will realize optimum benefits for its investments in addition to providing useful technologies for the world as a whole. Any nation that builds a leadership position in these technologies and subsequently retains or expands that technological strength can feel secure about sharing commercialization.

Materials are enabling for virtually any improvement in manufacturing efficiency and energy consumption but, even though the U.S. leads the world in development of new materials and synthesis methods, identification of the benefits of new materials and application of these to manufacturing have not received adequate attention from U.S. industry. A recent report from the National Research Council concludes that while the U.S. leads in materials science, a serious gap exists in synthesis and processing needed to carry the technology to the market place. Consequently, while the U.S. discovers the new materials, other nations do the necessary applied research to commercialize them and benefit from the economic advantage.

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Of the more than \$1.8 billion spent by the U.S. government on materials research in FY 1993, the expenditures are overwhelmingly devoted to basic research. Only the small efforts in Energy Efficiency and Renewable Energy in the Department of Energy and the National Institute for Standards and Technology presently involve significant cooperation with non-military industries to carry materials technologies forward to actual applications. It is widely recognized that direct cooperative efforts between government and industry are crucial to the efficiency and competitiveness of U.S. industry. The vision of the AIM Program is the successful formation of National Laboratory/industry/university teams to bring materials from basic research, through applied research, development, and engineering, to industrial application to strengthen the competitive position of U.S. industry and save energy. Ideally, the Program can serve as a prototype for other cooperative efforts between the public and private sectors.

In order to realize this vision, the Program takes the following tactical or procedural steps:

- Works with materials suppliers and users to identify opportunities for improved efficiency and energy savings by use of new materials and determine properties needed for identified applications. Supports OIT's "Plants of the Future" initiatives including: pulp and paper, iron and steel, non-ferrous metals, casting, materials processing, chemicals and refining.
- Identifies customers for materials technologies prior to initiation of work; customers may be industry, end-use programs within Energy Efficiency and Renewable Energy, or other government programs. Identify energy and economic savings to be realized. At the same time, the Program will identify promising areas for pioneering work in materials and support them.
- Forms applied research and development teams, consisting of staff from industry, the DOE National Laboratories, and universities, to solve engineering problems attendant to industrial use of the materials. At any given time, the goal is to fund a variety of materials and processing efforts with a range of maturities and anticipated times to completion.
- Works with Energy Research to identify materials technologies offering potential for commercialization but needing applied research, development, and applications engineering.

ADVANCED METALS AND COMPOSITES

ADVANCED ORDERED INTERMETALLIC ALLOY DEVELOPMENT

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INTRODUCTION

Many ordered intermetallics possess unique properties and have the potential to be developed as new materials for energy-related applications. The objective of this task is to develop low-density, high-strength intermetallic alloys for engineering use in advanced energy conversion systems and heat engines. Current efforts are focused on five alloy systems (1) NiAl aluminides, (2) TiAl aluminides, (3) shape-memory alloys based on NiAl/Ni₃Al compositions, (4) Ni₃Si alloys, and (5) reaction synthesis of NiAl and Ni₃Al alloys.

The NiAl aluminide has a high-melting point ($T_m = 1640^\circ\text{C}$), low density (5.86 g/cm^3) and excellent oxidation and corrosion resistance. The structural use of NiAl, however, has been limited by its low ductility and poor fracture toughness at ambient temperatures, and inadequate strength at high temperatures. Our early study indicated that the grain boundary in NiAl is intrinsically brittle at ambient temperatures. We had found that microalloying with boron is able to completely suppress intergranular fracture. The mechanical properties of NiAl are sensitive to alloying additions. Alloying with a couple of percents of elements can substantially improve the

ductility at ambient temperatures and the strength and creep resistance at elevated temperatures. Current effort on NiAl alloy development is concentrated on optimizing alloy compositions and evaluating mechanical properties of selected cast NiAl alloys.

A subcontract has been established with Polytechnic University on study of TiAl alloys prepared by rapid solidification. Some limited results indicate that TiAl alloys produced by rapid solidification possess tensile ductilities as high as 8% at room temperature, the highest tensile ductility ever reported for γ titanium-aluminide alloys. The objective of this task is to verify the result obtained from thin-section materials by preparation and evaluation of bulk materials. It is our intention to further improve the ductility and toughness of TiAl alloys by control of precipitation and processing.

Currently used shape memory alloys (SMAs) based on Ni-Ti are limited to ambient-temperature applications. If alloys that can operate at higher temperatures are developed, numerous new applications will be forthcoming (e.g., in sensors, actuators, HVAC systems, under-the-hood automobile applications, heat engines for waste heat recovery, etc.). Because of their relatively higher transformation temperatures, specifically their martensite-start (M_s) and austenite-start (A_s) temperatures, NiAl-base alloys have the potential to be developed as next-generation SMAs, provided ways can be found to overcome their poor low-temperature ductility. The specific goals of this task are to develop NiAl-base SMAs with $M_s > 100^\circ\text{C}$, and room-temperature ductilities in the range of 2-4% total elongation to fracture.

The intermetallic compound Ni_3Si has several properties which make it a material for potential applications. It has excellent corrosion resistance to certain acid solutions as well as many of the attractive mechanical properties of some L_{12} structure intermetallics. The major problem with Ni_3Si , as is common to most intermetallics, is its limited ductility. In order to improve the room temperature and elevated temperature ductility of Ni_3Si several alloy development programs have focused on this intermetallic. A series of Ni_3Si -base alloys have been developed at ORNL which have high strength, superplastic formability, reasonable room-temperature ductility and corrosion resistance. More research is needed to optimize the compositions of the promising alloys and to understand the alloying and microstructural features which control the properties of interest.

The proposed research will address these problems of structure-property relationships in Ni_3Si alloys as influenced by composition modifications. Three topics have been chosen for initial study. These are: (1) oxidation behavior of selected Ni_3Si -base alloys in the temperature range of 600 to 1000°C; (2) the influence of certain alloying additions, for example cerium, on the oxygen-induced embrittlement observed in tensile tests at about 600°C; (3) the influence of thermal treatment on the microstructure and properties of certain Ni_3Si -base alloys, e.g., those with niobium alloying additions.

The feasibility study of reactive sintering of aluminide alloys developed at Oak Ridge National Laboratory was initiated in August 1993. Reactive sintering has the potential to be a low cost, energy saving alternative to melt processing because of the use of inexpensive elemental powders and low furnace temperatures. Research during this period has been carried out initially by a post-doctoral research associate, Dr. T. R. Smith, and is now being performed by a graduate research assistant, C. Sainio. The two alloys chosen for initial study are NAL-109 and IC-221M. Compositions (in weight percent) are as follows:

(1) IC-221M: 81.09% Ni, 8.0% Al, 7.7% Cr, 1.7% Zr, 1.43% Mo, 0.08% B,

(2) NAL-109: 67.76% Ni, 31.0% Al, 0.14% Zr, 0.43% Mo, 0.29% Fe.

TECHNICAL PROGRESS FY 1993

Summary

1. The Milestone "Completion of Mechanical-Property Characterization and Evaluation of Environmental Effects of Cast NiAl Alloys" was completed in August 1993. The tensile properties of cast NiAl alloys are sensitive to both cast defects and microstructure. Removal of second-phase network at grain boundaries by high-temperature annealing results in significant increases in fracture strength at room temperature and 1000°C. Test environment basically does not affect the mechanical properties of cast NiAl alloys.
2. An ingot of TiAl alloy ($\text{Ti}_{0.52}\text{Al}_{0.48}$) $_{99.5}\text{Ni}_{0.5}$ was prepared by consolidation of melt spinning ribbons via HIPing and hot forging at 1000°C. Metallographic examination and electron microprobe analyses of the consolidated pancake indicate contamination of the alloy by molybdenum particles, which reduce the tensile ductility at room temperature.

3. Shape-memory alloys based on Ni-Al-Fe-B were prepared by both conventional and innovative methods. The materials prepared by both methods show thermally activated shape-memory effects at temperatures below A_p , the austenite formation temperature (as high as 180°C). Further studies are required to stabilize the metastable martensitic phase at temperatures above 100°C.
4. The oxidation behavior of Ni-19 at. % Si, Ni-19% Si-8% Cr, and Ni-19.1% Si-3.26% Cr-0.3% Hf was studied at 500 to 900°C in air. Chromium additions substantially reduce the oxidation rate at temperatures below 800°C but not above that temperature. The oxidation results can be explained in terms of formation of silicon and chromium oxides at elevated temperatures.
5. Reaction synthesis of NAL-109 (Ni-49.8Al-0.2Mo-0.2Fe-0.8Zr, at. %) was performed at temperatures 400 to 610°C. The samples sintered at 575 and 610°C exhibited extreme shape loss, while the samples sintered below 575°C showed no indication of combustion reaction.

Milestones

1. Complete mechanical properties characterization and evaluate environmental effects of cast NiAl alloys and prepare a letter report. Start 10/92. End 8/93.

Based on the early work on development of wrought NiAl alloys, five alloys are selected for study of cast properties, with their compositions (wt %) given below:

1. NAL-76: Ni-30.28Al-1.53Mo-0.85Nb-0.47V-0.9Ta,
2. NAL-108: Ni-30.60Al-1.54Mo-0.85Nb-0.17Zr-0.26Fe,
3. NAL-115: Ni-30.60Al-1.54Mo-0.85Nb-0.17Zr-0.26Fe-0.01B-0.005C,
4. NAL-116: Ni-30.60Al-1.54Mo-0.85Nb-0.17Zr-0.26Fe-0.02B, and
5. NAL-112: Ni-23.40Al-12.11Fe-1.46Mo-0.81Nb-0.16Zr-0.005B.

The first four alloys contain 0 to 0.2 at. % Fe and the last alloy is modified with 10 at. % Fe. Alloy ingots weighing 450 to 5000 g were prepared by either vacuum induction melting or inert-gas arc melting. After melting, the ingots were cast into ZrO₂ crucible, cast iron mold, graphite mold, or copper mold. All the alloy ingots contain some degrees of cast porosities, and the amount

of porosity varies with alloy composition and cast method. In general, the ingots prepared by drop casting into copper mold have less visible cast defects.

The microstructure of the alloy ingots was studied in as-cast and heat-treated conditions. The heat treatments involve annealing in the temperature range of 1100 to 1500°C for 1 to 24 h. All the cast ingots show a network of second phases formed along grain boundaries [Fig. 1(a)]. The second-phase network starts to breakdown when annealed at temperatures above 1200°C. The network disappears and spherical particles within grains are formed when annealed at 1500°C [Fig. 1(b)]. The annealing at temperatures above 1300°C results in grain growth. Significant grain growth was observed at and above 1400°C, in particular, for drop-cast ingots with fine grain structure. The composition of the second phases in the alloy NAL-115 was determined by electron microprobe analyses. The matrix has the composition: Ni-29.3Al-0.1Mo-0.0Nb-0.2Fe-0.1Zr (wt %). The solubility of niobium in NiAl is virtually zero. Two distinct compositions are identified for the second-phase particles. One is a molybdenum-rich solid solution containing essentially 25.8% Nb (Mo-25.8Nb-3.6Ni-1.0Al-0.2Fe-0.3Zr). The other phase has a composition (Ni-28.2Al-11.9Zr-6.7Nb-1.6Mo) similar to the Heusler phase Ni(Al,X), where X = Zr, Nb, and Mo.

The mechanical properties of the alloys in the as-cast and heat-treated conditions were determined by tensile testing at room temperature and 1000°C. Table 1 summarizes the tensile properties of the three alloys annealed 1 d/1100°C plus 1h/800°C and tested at room temperature and 1000°C. The NAL-76 specimens were electro-discharge machined from a vacuum induction-melted ingot weighing 5000-g. All three alloys fractured prior to macroscopic yielding, with the best fracture strength obtained from NAL-108. This result suggests that the fracture strength of NiAl alloys depend on both microporosity and alloy composition. NAL-108 and 112 showed extensive ductilities (>49%) whereas NAL-76 exhibited no appreciable plastic deformation at 1000°C. Among the three alloys, NAL-108 has the best mechanical properties at room temperature and 1000°C.

Fig. 1. Effect of annealing on microstructure of cast NAL-108. (a) Annealed 1d/1100°C + 1h/800°C, and (b) annealed 1h/1500°C + 1h/800°C.

Table 1. Tensile properties of cast NiAl alloys tested in air

Alloy number	Test temperature (°C)	Strength (MPa)		Ductility (%)
		Yield	Tensile strength	
NAL-76	RT	*	156	*
NAL-108	RT	*	278	*
NAL-112	RT	*	142	*
NAL-76	1000	*	167	*
NAL-108	1000	232	265	49.3
NAL-112	1000	199	214	135

*Fractured prior to macroscopic yielding.

The mechanical properties of NAL-108 were determined as a function of heat treatment. The mechanical properties were not changed much when annealed below 1300°C. Annealing at 1400°C results in breaking the second-phase network at the grain boundary and improves the tensile strength at room temperature and 1000°C. For instance, NAL-108 shows an increase in the yield and ultimate tensile strengths at 1000°C from $\sigma_y = 232$ MPa and $\sigma_{ul} = 265$ MPa to $\sigma_y = 338$ MPa to $\sigma_{ul} = 372$ MPa when annealed for 2 h at 1400°C. The significant grain growth at 1400°C reduces the tensile ductility of NAL-108 from 49.3 to 3.6%. Thus, the heat treatment has a profound effect on mechanical properties of cast NiAl alloys.

The tensile properties of intermetallic alloys, such as Ni₃Al-based alloys, show severe environmental embrittlement at ambient and elevated temperatures. The environmental embrittlement involves moisture-induced hydrogen at ambient temperatures and oxygen penetration along grain boundaries at elevated temperatures. To evaluate the effect of test environment on mechanical properties, the tensile properties of NiAl alloys were determined in air and vacuum at room temperature and 1000°C. All the results indicate that the tensile properties are not significantly affected by test environment. It is thus concluded that NiAl alloys are not prone to environmental embrittlement at room and elevated temperatures.

2. Rapid solidification processing, consolidation and characterization of new γ TiAl-Ni alloys.

Start 10/92, End 7/93.

The objective of this task is to process and evaluate the structure and property of TiAl alloys containing nickel prepared by rapid solidification. Ribbons of $(\text{Ti}_{.52}\text{Al}_{.48})_{99.5}\text{Ni}_{0.5}$ were prepared by a melt spinning technique developed at Polytechnic University. Because of the brittle nature of the alloy, all ribbons produced broke into a few cm long pieces with a thickness in the range of 20-80 μm . The cross section of the ribbons (80 μm) parallel to the surface exhibits the cellular structure of 10-20 μm in diameter. The cross section perpendicular to the longitudinal axis of the ribbon shows a featureless structure at the bottom, which appears to be caused by a high solidification rate during the contact with the substrate.

The rapidly solidified ribbons were pulverized into powders by a commercially available hammer mill. The powders were screened with standard mesh screens. The results are given below:

Under mesh	40 (over)	45	60	80	100	140	200
(%)	10.2	77.4	38	14.5	9.35	3.4	1.26

The cold-pressed powder compact exhibited an apparent density of 50% which is considered to be relatively low for direct HIPing. As a result, the cold-pressed powder were first hot pressed at 1000°C at 190 MPa, followed by hot isostatically pressing (HIPing) at 1000°C for 3 h. The ingots were then forged at 1000°C with a total of 75% reduction in thickness. Figure 2 shows the forged alloy pancake with a size of 13-cm-diam and 1.5-cm thick. The pancake was shipped from Polytechnic University to ORNL for evaluation in July 1993.

Fig. 2. Forged TiAl+Ni alloy pancake with a size of 13-cm diam and 1.5-cm thick.

Optical metallography of the forged Ti-Al-Ni pancake prepared by Polytechnic University revealed large inclusions that were as much as 200 μm in length by as much as 100 μm wide, with reaction zones between the inclusions and matrix. Microprobe analysis indicated that the inclusions were about 40 at. % Ni, 40% Mo, and 20% Fe. The amounts of titanium and aluminum in the reaction zones increased as the analysis spot was moved in steps from the inclusion to the matrix. The matrix itself was roughly 55 at. % Ti and 45% Al, with small amounts of nickel and iron. Tensile specimens (0.5 in. gage length) were cut from the pancake using electrical discharge machining, and three tensile tests were conducted in air at room temperature using a strain rate of $3.3 \times 10^{-3}/\text{sec}$. All three specimens failed before macroscopic yield in a brittle manner with no indication of plastic strain. It is believed that the large Ni-Mo-Fe inclusions are contributing to the brittle nature of this alloy. Subsequent one-hour heat treatments at temperatures of up to 1200°C have not resulted in total dissolution of the inclusions.

3. Development and characterization of Ni-Al-Fe-B alloys for shape-memory applications,
Start 10/92, End 9/94.

Shape-memory alloys based on Ni-Al-Fe alloys were prepared by both conventional and innovative methods. Shape-memory alloys (SMA) of Ni-Al-Fe doped with boron have been cast into wire shape directly from the melt by the in-rotating-liquid technique. Much of the present and proposed applications of SMA require wire and/or spring configurations. The advantages of this method is obvious in that the production of net-shape wire avoids the difficult and costly problem of fabricating bulk castings. The alloy is first melted in a quartz crucible then ejected by an over pressure of argon gas through an orifice into a layer of rotating water.

Rapidly solidified wires of 0.1 to 0.5 mm diam. and lengths to 2 m have been produced from a number of different SMA alloys. The alloys were first prepared by arc melting and drop casting, examined for macro-segregation, and cut into small pieces for melt spinning. Compositions of these alloys include Ni-(20~30)Al-(6~20)Fe with small additions of boron. The method produces circular wires with diameters to 0.25 mm while larger ones are somewhat oval in cross-section. The effects on the wires of processing parameters such as ejection and coolant velocity, the incident angle of nozzle to coolant, and nozzle to coolant length, are also investigated. Optimum conditions were achieved through control of these parameters.

Typical cross sections of wires examined by optical and SEM metallography reveal columnar surface grains and dendritic structures with the presence of a second phase in the center area. X-ray studies of SMA-48 showed the presence of martensitic body-centered orthorhombic structure along with the NiAl B2 phase and some L1₂. After cold work, the B2 phase largely transformed to the tetragonal martensitic phase.

The material is ductile and can be cycled through full 180 degree bends. The shape-memory behavior was measured as a function of temperature to 600°C by the degree of recovery of specimens bent around a 2.5-mm mandrel. Specimens cycled repeatedly show full recovery at the austenite formation temperature, A_p, of 180°C. There is no apparent embrittlement in the alloys below 300°C. Bend test results are generally consistent with differential scanning calorimeter (DSC) measurements of the martensitic transformation temperature.

Wire samples produced by in-rotating-liquid melt spinning were thermally cycled in a tensile machine to determine the amount of the shape memory effect (Fig. 3). Using a current of 6 A, wire specimens of SMA-48 were self-heated to 250°C then cooled to 100°C in 20-s cycles. A constant load of 965 MPa was applied, and the tensile strain versus time was measured. The shape-memory effect resulted in a shortening of the wire. The measured amount of length change of 0.3% includes thermal expansion. The true shape-memory recovery is therefore higher, however, this setup is similar to many applications. The length change ceased after the temperature reached 250°C. Upon cooling, the wire returned to its original length. The 0.3% strain recovery remained unchanged through 40 cycles.

Cyclic shape-memory-recovery tensile tests were also performed on the alloy SMA-48 prepared by a conventional melting and casting method. The specimen fabricated by hot rolling and oil-quenching from 1300°C was deformed 2% prior to the shape-memory-recovery cycling. The first tensile cycle showed a recovery of 0.86% and the start and finish temperatures corresponded well with the DSC measurement. The shape recovery began at 153°C and ended at 185°C. A two-way shape-memory effect was indeed found in this alloy, although it took nine training cycles to stabilize the effect. After stabilization, the shape recovery averaged around

Fig. 3. Recoverable strain of SMA-48 wire specimens as a function of cycling between 100 and 250°C.

0.65% and the start of the recovery was around 130°C with an applied load of approximately 200 MPa. Unfortunately, the shape recovery was not as sharp as in alloy SMA-23 (another reference alloy) and required about 80°C to produce most of the recovery. Interestingly, the prior cold work (2% tensile deformation) along with the cycling under load has resulted in a two-way effect with transformation temperatures lower than expected according to DSC on undeformed specimens but approximately equal to that of SMA-23.

A major problem of using Ni-Al-Fe-B alloys as shape-memory material is that the metastable martensitic phase further transforms into the stable Ni_5Al_3 and B2 phases at temperatures above 100°C. In order to increase the stability of the martensitic phase, two new alloys SMA-55 and 56, were prepared by arc melting and drop casting. The alloy ingots were hot fabricated into sheets at 1000°C, followed by oil-quenching from 1300°C. The quenched specimens were then aged at either 100 or 200°C for different times. Periodically, X-ray diffraction scans are made to check the stability of the quenched martensitic phase. At approximately two months no definite trend can be detected, indicating that the martensitic phase is possibly stable at these temperatures.

The shape-memory effects of SMA-55 and 56 were characterized by thermal cycling tests. Figure 4 shows a plot of tensile strain versus time from cycles 46 through 49 from SMA-56. The alloy specimen was tensile strained 2% at room temperature before the cyclic testing began. A constant load of 165 MPa was then applied to the specimen. In this plot when the specimen reached 165°C, the shape recovery began and the specimen shortened. At approximately 210°C the length change ceased. The amount of strain recovery is typically 0.8% but depending on history can drop to 0.4%. In this apparatus, the heating from 165 to 210°C required about 4 seconds while cooling required about 16 seconds. The current was cycled between 17 amps to heat to 250°C, then to 7 amps until the specimen had cooled to 120°C. The specimen showed no indication of change in the shape-memory effect after 100 cycles.

Fig. 4. The shape-memory effect is shown here in SMA-56 initially strained 2% in tension at room temperature. Plot of tensile elongation versus time as the temperature is cycled from 120 to 250°C.

Note also a slight bend to the strain vs. time curves in Fig. 4 during the transformations. These correspond to the endothermic transformation during heating which would absorb energy and thereby slow the length change. Upon cooling the exothermic peak would give up heat and likewise slow the transformation. Upon cooling the temperature range for this bend in the plot was 210 to 180°C. With no load, i.e. bend type test, the strain recovery appears instantly as the specimen is heated. However, for a tensile load range from 41 MPa to 207 MPa, no difference occurs in the amount of shape recovery.

4. Complete the characterization of the oxidation behavior of the selected Ni₃Si-base alloys and prepare a draft report for publication. Start 7/92. End 8/93.

Research is required to optimize the compositions of Ni₃Si-base alloys which are promising materials for elevated-temperature and corrosion-resistance applications. The first topic to be addressed in this research program is the oxidation behavior of selected Ni₃Si-base alloys in the temperature range of 500 to 1000°C.

The isothermal oxidation of Ni-19 at. % Si at 500, 600, 700, 800 and 900°C was conducted using a Perkin Elmer TGA apparatus. Figure 5 shows that for this base alloy the oxidation rate increases as the temperature increases from 500 to 700°C; however, the oxidation rate is lower at 800 and 900°C. The angle lapping technique was used for microscopic examination of the oxides formed. Grinding at an inclined angle of 5'44" to the specimen surface is used. Optical micrographs are consistent with Fig. 5 showing weight gain as a function of temperatures. The unetched samples oxidized at 500, 600, and 700°C show two distinct oxide layers and internal oxides. The size of the internal oxide grains increases with temperature. The unetched samples oxidized at 800 and 900°C show a reverse trend with smaller grain size of internal oxides at 900°C and larger grain size at 800°C.

Fig. 5. Weight change of Ni-19 at. % Si as a function of exposure time and temperature in air.

The isothermal oxidation behavior of Ni-18.8 at. % Si-8.06 at. % Cr is shown in Fig. 6. In comparison to the base alloy discussed above, Ni-18.8 at. % Si-8.06 at. % Cr has a lower oxidation rate in the corresponding temperature range with the maximum weight gain of about 0.10 mg/cm² at 900°C. For this alloy the oxidation rate increases as the temperature increases from 600 to 900°C. The results of the isothermal oxidation for the alloy containing Ni-19.1 at. % Si-3.26 at. % Cr-0.3 at. % Hf are illustrated in Fig. 7 showing the weight gain as a function of time at various temperatures. It can be noted that the maximum weight gain is about 0.09 mg/cm² at 900°C. Although the weight gain increases with temperature, the weight gain at 800°C is less than the weight gain at 700°C. The oxidation rates for the base alloy, Ni-19 at. % Si, are higher than for the alloy containing chromium (either 3.2 at. % or 8.2 at. %) at temperatures of 600 to 900°C.

The specimens of Ni-19% Si and Ni-18.8% Si-8.06% Cr oxidized at 500-900°C were examined by scanning electron microscopy and electron microprobe analysis. As mentioned above, the maximum oxidation rate for Ni-19% Si was obtained at 700°C. The oxides which formed in this alloy at temperatures <700°C consisted of external NiO layers and oxides which penetrate into the two-phase (L1₂ + fcc) regions of the microstructure adjacent to the sample surface. The decrease in oxidation rate observed for oxidation temperatures >700°C is attributed to the formation of a continuous SiO₂ protective oxide films at the base of the NiO layers. The formation of chromium-oxides appears to dominate the oxidation behavior of the Ni-19 at. % Si-8 at. % Cr alloy. The oxidation rates for the chromium-containing alloy were lower than those for the Ni-19% Si base alloy at temperatures <800°C. However, at temperatures ≥800°C the oxidation rates were larger than those in the base alloy, suggesting that the chromium-oxide scale is less protective than the SiO₂ scale which forms in the base alloy in this temperature range.

5. Complete the feasibility study of reaction synthesis of nickel aluminide alloys, Start 8/93, End 10/94.

Elemental powders were obtained from the vendors. The powders were opened in the glove box under high pressure argon and weighed to the appropriate amounts for the desired alloy

Fig. 6. Ni-18.8 at. % Si-8.06 at. % Cr.

Fig. 7. Ni-19.1 at. % Si-3.26 at. % Cr-0.3 at. % Hf.

compositions. 200 g samples were prepared for each of the two alloy compositions. The NAL-109 alloy powder was cold pressed into tensile specimens. Two samples were pressed--sample one at 45,3000 lbs and sample two at 152,000 lbs. Sample one was sintered at 610°C in air; sample two was sintered at 505°C in air. Both samples exhibited extreme shape loss and appeared to have melted at the selected sintering temperatures.

Additional tensile specimens of NAL-109 were then cold pressed. All samples were pressed at 45,500 lbs. Because of the extreme deformities encountered previously with sintering temperatures over 500°C, sintering began at 400°C. Samples were sintered in air at 400°C, 450°C, and 495°C without any indications of the shape loss experienced earlier. However, the samples did not appear to sinter at all. Only signs of oxidation were evident on the samples. Sample 6 was sintered in air at 550°C. At this temperature, signs of the beginning of sintering were apparent. However, the sample did not completely sinter. As with the previous three samples, there was no shape loss. Sample 7 was sintered at 575°C. The sample sintered but the shape loss previously experienced occurred. As before, the sample seemed to have melted. This discrepancy in sintering temperature at which shape loss occurs has not been resolved.

In order to avoid the difficulties cited above, we have decided to mix some prealloyed powders with elemental powder in an attempt to dampen the reaction. The NAL-109 powder was mixed with 30 weight percent of +15/-38 μm grade prealloyed NiAl powder. Also, sintering will take place in argon to eliminate oxidation. Samples of the new powder (70 weight percent NAL-109 and 30 weight percent prealloyed NiAl) were cold pressed at 45,5000 lbs. Upon heating this sample in a vacuum furnace, the furnace tube fractured. Sintering of the NAL-109 alloy will be delayed until a new furnace tube arrives. In the meantime, tensile specimens of Ni₃Al alloy IC-221M will be cold pressed.

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LICENSES

1. General Electric (GE) Corporation, General Motors (GM) and Metallamics are interested in the ORNL work on alloy development of NiAl alloys. We have maintained a close contact with these companies on alloy development of NiAl alloys.
2. Memory Metals, Inc. and Pratt and Whitney are interested in the higher temperature shape memory alloys. We had a couple of meetings with Dr. L. M. Schetky, Memory Metals to discuss the possibility of forming a CRADA to work on new high-temperature shape memory alloys based on Ni-Al-Fe-B.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

We had several contacts with General Motors (GM), General Electric (GE), NASA, Memory Metals, Cummins Engine Company and Metallamics to discuss the potential use of NiAl-base alloys for various industrial applications.

ESTIMATED ENERGY SAVINGS

1. The development of high-temperature aluminides and silicides will lead to improvement in performance (such as thermal efficiency, durability, etc.) of advanced energy conversion systems and heat engines, resulting in substantial energy saving.
2. High-temperature shape memory alloys have the potential to be used as new industrial materials in many energy-related control systems (such as sensors, actuators, HVAC systems, under-the-hood automobile application, heat engines for waste heat recovery, etc.). All these potential applications will lead to substantial energy saving.

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS PROGRAM

WORK ELEMENT: High-Temperature Materials

PROJECT TITLE: Advanced Ordered Intermetallic Alloy Development

PHASE: Materials Capability Development **PHASE COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory (ORNL), and The University of Tennessee (UT)

PRINCIPAL INVESTIGATOR(S): C. T. Liu (615) 574-4459, J. A. Horton (615) 574-5575, E. P. George (615) 574-5085, C. C. Koch (919) 515-7340, and S. H. Whang (718) 260-3144, N. S. Stoloff (518) 276-6371

PHASE OBJECTIVE: To improve the ductility and fracture toughness at ambient temperatures and the strength and creep resistance at high temperatures (to 1200°C) of structural intermetallics NiAl, TiAl, TiAl₃ and Ni₃Si and to enhance the ductility and performance of high-temperature shape-memory alloys based on NiAl+Fe+B

ULTIMATE OBJECTIVE: (1) To develop low-density, high-strength, ductile ordered intermetallic alloys for structural and functional 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 resistance at elevated temperatures.

PROGRESS: We have completed the initial evaluations of microstructure, mechanical properties of cast NiAl alloys in different environments. Chromium additions substantially reduce the air oxidation rate of Ni-19% Si alloy at temperatures below 800°C but not above that temperature. Shape-memory alloys based on Ni-Al-Fe-B have been prepared by both conventional and innovative methods. The materials prepared by both methods show thermally activated shape-memory effects at temperatures close to 200°C.

Patents: 3

Publications: 13

Proceedings: 18

Books: 8

Presentations: 18

ACCOMPLISHMENTS:

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

Known Follow-On Product(s): Anticipated use in heat engines, jet engines, glass industries, and energy control systems.

Industry Workshop: The results were presented at the Nickel and Iron Aluminide Workshop held at Oak Ridge.

Other Successful Technology Transfer Activities as Evidence of

Industry Interest: Several technical exchange meetings were held with U.S. industries including GE, GM, Metallamics, Eaton Corporation, Cummins Engine Company, Memory Metals, etc.

PROJECT TITLE: Advanced Ordered Intermetallic Alloys

CRITICAL ISSUES: (1) To improve the mechanical properties and weldability of NiAl alloys in cast conditions, (2) to improve impact resistance of NiAl alloys at room and elevated temperatures, and (3) to eliminate aging embrittlement and to sharpen the shape-memory characteristics in NiAl+Fe+B alloys.

FUTURE PLANS: (1) To increase the tensile ductility of cast NiAl and to improve impact resistance of these alloys by control of microstructure and alloy compositions, (2) to increase the incipient melting point and to improve oxidation resistance of Ni₃Al base alloys by control of alloying elements, and (3) to characterize oxidation and corrosion resistance of Ni₃Si alloys for industrial applications.

POTENTIAL PAYOFF: There are two major problems with many ordered intermetallics: 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 new shape-memory alloys with high operation temperatures have the potential for many new applications in energy-related control systems.

Chromium Additions Effectively Improve the Oxidation Resistance of Ni₃Si-Base Alloy in Air at Temperatures Below 800°C

- The oxidation rate can be explained in terms of formation of protective chromium and silicon oxides at different temperatures.

Shape-Memory Alloys Based on NiAl+Fe+B Prepared by Both Conventional and Innovative Methods Show Thermally Activated Shape-Memory Effects at Temperatures Below the Austenitic Formation Temperature (A_p)

- The shape-memory effect is shown in SMA-56 as functions of time and thermal cycles between 120 and 250°C.
- Additional work is needed to increase the long-term stability of the martensitic phase below 250°C.

DEVELOPMENT OF WELDABLE, CORROSION-RESISTANT IRON-ALUMINIDE ALLOYS

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INTRODUCTION

Corrosion-resistant, weldable FeAl alloys are being developed with improved high-temperature strength for structural applications. These alloys are currently also being evaluated for weld-overlay coating applications on conventional structural steels and alloys. The goals of this project are to complete alloy development efforts to maximize weldability and properties improvements in FeAl alloys for structural applications, and to develop the potential of weldable FeAl alloys for use in weld-overlay cladding applications. In FY 1993, this task was further broadened to include neutron scattering experiments to measure residual stress distributions in FeAl weld-overlay cladding.

TECHNICAL PROGRESS - FY 1993

Summary

1. Weldability of FeAl Alloys:

A series of small (500 g) heats of modified FeAl alloys (FA-385-M1 through -M7) derived from the weldable FA-385 base alloy composition, and another series (FA-385-M8 through -M11) based on the creep-resistant FA-328/mod. 11 alloy composition, were melted and fabricated during FY 1992. The initial weldability (hot-cracking) testing has been completed and the results are summarized in Figure 1. The alloys showing the best weldability were FA-385M1, -385M2, -385M3, and -385M9, with threshold hot-cracking stresses comparable to type 316 austenitic stainless steel. Eight new larger (6.83 kg) heats of these most weldable alloys, and additional alloys with minor impurity modifications thereof, were also melted and fabricated into sheet-stock during FY 1993.

Fig. 1 - A histogram of the threshold hot-cracking stress determined from Sigmajig weldability testing, plotted for the various different FeAl alloy compositions tested.

Weldability and mechanical properties testing (see the section "High-Temperature Precipitate-Strengthened Iron-Aluminides and Other Intermetallic Alloys" elsewhere in this report).

Another series of six new small heats, three based on the creep-resistant FA-328/mod.11 base composition, and three lower aluminum (30 at.% Al), based on the weldable FA-385-M2 and -M3 alloy compositions, were also melted and fabricated during FY 1993, and testing will be done next year. Larger heats of these same six alloys were also melted to evaluate the properties of as-cast material.

2. Weld-Overlay Cladding Applications:

Weld-overlay cladding was a new thrust in this project that began in FY 1992 and continued in FY 1993. The initial FeAl weld-deposits were made onto a type 304L austenitic stainless steel substrate using the moderately weldable FA-372, -385 and -388 alloys, showing that such an application was feasible. Weld pad desposits of the various new weldable FeAl alloys (FA-385-M1 through -M11) were also made onto type 304L stainless steel substrates, and some were weld-deposited onto a 2¼Cr-1Mo bainitic steel substrate during FY 1992 and 1993. No hot-cracking during weld-deposition was observed, but all the FeAl alloys exhibited some degree of delayed cold-cracking during cooling for cladding tests made on type 304L stainless steel. A second series of tests with 200°C preheat, but no post-weld heat-treatment, showed that FA-385 and the FA-385-M1, -M2 and -M3 and -M9 single-layer weld pads on the 304L substrate were crack-free. Similarly, single-pass weld-overlay deposits of the FA-385 alloy onto the 2¼Cr-1Mo bainitic steel substrate also showed no delayed cold-cracking with preheat only.

Some filler-wire of FeAl/FA-385-M1 alloy was fabricated at ORNL during FY 1993 (see the next section below), and was used to produce multiple-layer GTA weld-deposits on thicker (25.4 mm) substrates of 304L austenitic stainless steel, 2¼Cr-1Mo bainitic/martensitic steel, and an

Fe₃Al/FA-129 iron-aluminide alloy. The FeAl weld-deposits made onto the thicker 304L steel substrate all showed some surface cold-cracking in the fusion zone even with a preheat of 200°C, and a postweld heat-treatment of 400°C. Good, crack-free weld-deposits of FA-385-M1 on 2¼Cr-1Mo steel were obtained with a preheat of 200°C, a minimum interpass temperature of 350°C, and a postweld heat-treatment of 800°C (followed by furnace cooling). Weld deposits of FeAl made onto the Fe₃Al/FA-129 substrate cracked very badly, with the cladding not adhering to the substrate at all. This initial data demonstrates that welding parameters and procedures can be adjusted to avoid hydrogen-related cold cracking, at least in some situations. Optimized weld-overlay cladding parameters and procedures need to be tailored to the particular substrate, especially defining the lowest possible post-heat temperatures needed. The current data do demonstrate the feasibility of at least FeAl weld-overlay cladding on 2¼Cr-1Mo steels.

3. FeAl Filler-Wire Development

One method used to produce FeAl filler-wire of FeAl (FA-385-M1 with 36 at.% Al) for GTA welding at ORNL in FY 1993 was extrusion of a large (6.83 kg) heat of that material (clad in mild steel) at 1000°C to a final wire diameter of 3 mm. This, however, is not a commercially viable process for producing weld filler-wire.

Efforts to develop weld-consumables using commercial or commercially-viable processes also began in FY 1993. Previously, Devasco International, Inc. (Houston, TX) began developing shielded-metal-arc (SMA) electrodes, formulated on the FA-385 FeAl base alloy composition, and electrodes were received for testing at ORNL. These new SMA electrodes exhibited excellent welding characteristics, but their aluminum content was much lower than intended, which caused both hot- and cold-cracking. Another effort to produce filler-metal rods was initiated with Haynes International (Kokomo, IN) during FY 1993. Three heats of a nearly optimized FeAl alloy composition (best for

deposition on 2¼Cr-1Mo steel, based on or related to the weldable FA-385, FA-385-M1, and FA-385-M2 alloys, as noted above) were aspiration-cast into quartz tubes to produce weld-rods. These aspiration-cast FeAl filler-rods contain more than 36 at.% Al to compensate for the loss of Al that can occur during the GTA weld-deposition process. Several large single-layer weld deposits were made onto a 2¼Cr-1Mo steel substrate and found to be completely free of cold-cracks, using a 200°C preheat and a high-temperature post-weld heat-treatment, with furnace cooling. A metallographic cross-section is shown in Figure 2. These successful weld deposits using the Haynes FeAl filler rods have been cut from the substrate and will be analyzed for chemical composition and tested for oxidation resistance next year. More heats of FeAl will be produced during FY 1994 to better define the useable range of compositional variation for each alloying element for the aspiration-casting process, and to tailor the FeAl alloy clad compositions for other substrate materials as well.

4. Residual Stress Measurements in FeAl Weld-Overlay Cladding

To support the FeAl weld-overlay cladding effort, efforts to measure residual stresses and their distributions in the weld-clad and in the base-metal substrate using neutron diffraction methods began in FY 1993. Special specimens were made using the weldable FeAl/FA-385-M1 alloy (ORNL filler wire) to produce a large (75mm × 84mm × 3mm) single-pass GTA weld-clad deposit onto a 2¼Cr-1Mo steel plate. The 2¼Cr-1Mo steel was in the normalized and tempered condition prior to welding, and the weld-overlay clad deposit was produced using a 200°C preheat and a 700°C post-weld heat-treatment, with furnace cooling to prevent cracks. Optical examination revealed that the weld clad was crack-free.

Residual strains were mapped in the ferrite base-metal underneath the FeAl clad, using the neutron diffraction system at the High Flux Isotope Reactor (HFIR) at ORNL. The beam sampling volume was 8 mm³ [(2 mm)³], and elastic strains were mapped parallel and perpendicular to the

Fig. 2 - GTA weld-overlay deposit of FeAl (FA-385), made with new aspiration-cast weld rods produced by Haynes International, on a 2¼Cr-1Mo steel substrate (25.4 mm thick), with 200°C preheat and an 800°C post-weld heat-treatment (metallographically polished and etched). No cold-cracking was found in the FeAl weld-clad deposit or in the steel substrate.

welding direction in the plane of the cladding. Mapping of the strain in the FeAl clad, normal to the clad/steel interface will be done next year. The in-plane strains in the center of the steel were fairly isotropic, and similar in directions parallel and perpendicular to the welding direction. Strain mapping as a function of specimen rotation angle confirmed the isotropic strains. The average in-plane strain also scanned through the thickness of the steel beneath the FeAl clad, as shown in Figure 3. The ferritic base-metal substrate showed compressive strains. Since the FeAl clad has a much higher coefficient of thermal expansion, its contraction during cooling is counteracted by the ferritic steel base metal. This data implies that the FeAl weld-clad is in tension, and further neutron diffraction strain mapping will confirm the FeAl weld-clad stress state.

MILESTONES DURING FY 1993

AIC Supplemental Milestone 93CC-55: Identify materials and processes for developing FeAl weld overlay coatings on steels substrates and prepare draft publication or report (August, 1993).

This milestone was completed and satisfied by invention disclosure entitled "High-Temperature Corrosion-Resistant Iron-Aluminide (FeAl) Alloys Exhibiting Improved Weldability," (Maziasz, Goodwin and Liu) that was submitted to the ORNL Patent Section of Martin Marietta Energy Systems, Inc.

Fig. 3 - A through-thickness scan to measure in-plane strains parallel to the FeAl-steel interface as function of depth using a neutron diffraction method. Distance is measured from the FeAl weld-clad surface, with the FeAl layer being about 3 mm thick. Strains were measured in the 2½Cr-Mo ferritic steel substrate underneath the FeAl clad, and were found to be compressive below the interface.

PUBLICATIONS

Journals

1. P.A. Ferguson and C.T. Liu, "Environmental Embrittlement and Cutting Cracks in FeAl(40% Al)." *Scripta Metallurgica et Materialia*, 26 (1992) 1669-1674.
2. P.J. Maziasz, G.M. Goodwin, C.T. Liu and S.A. David, "Effects of Minor Alloying Elements on the Welding Behavior of FeAl Alloys for Structural and Weld-Overlay Cladding Applications," *Scripta Metallurgica et Materialia*, 27 (1992) 1835-1840.
3. C.G. McKamey, P.J. Maziasz, G.M. Goodwin and T. Zacharia, "Effects of Alloying Additions on the Microstructures, Mechanical Properties and Weldability of Fe₃Al-Based Alloys," accepted for publication in *Materials Science and Engineering Journal* in 1993.

Other Publications

1. C.T. Liu, "Moisture-Induced Environmental Embrittlement of Ordered Intermetallic Alloys at Ambient Temperatures," NATO Proc. *Ordered Intermetallics - Physical Metallurgy and Mechanical Behavior*, eds. C.T. Liu, R.W. Cahn and C.T. Santhoff, NATO ASI Series vol. 213, Kluwer Academic Publishers (1992) pp. 321-334.

2. P.F. Tortorelli and P.S. Bishop, "Corrosion of Aluminides in Molten Nitrate Salt," submitted for publication in *Proc. Symp. Environmental Effects on Advanced Materials*, TMS, Warrendale, PA, 1991 (in press).

3. G.M. Goodwin, C.G. McKamey, P.J. Maziasz and V. Sikka, "Weldability of Iron Aluminides," *Proc. of the 7th Annual Conference on Fossil Energy Materials*, CONF-9305135, ORNL/FMP-93/1 (July, 1993) pp. 181-188.

PRESENTATIONS

Oral Presentations

1. G.M. Goodwin, C.G. McKamey, P.J. Maziasz and V. Sikka, "Weldability of Iron Aluminides," presented at the 7th Annual Conference on Fossil Energy Materials, sponsored by the Fossil Energy (AR&TD) Materials Program, US-DOE, held in Oak Ridge, TN on May 11-13, 1993.

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

1. C.T. Liu, C.G. McKamey, P.F. Tortorelli and V.K. Sikka, "FeAl Aluminides for Structural Use," invention disclosure, ESID No. 726-X; DOE patent case No. S-70469.

2. P.J. Maziasz, G.M. Goodwin and C.T. Liu, "High-Temperature Corrosion-Resistant Iron-Aluminide (FeAl) Alloys Exhibiting Improved Weldability," invention disclosed to the ORNL Patent Section of Martin Marietta Energy Systems, Inc. on August 27, 1993.

LICENSES

None

INDUSTRIAL INPUT and TECHNOLOGY TRANSFER

Air Products was interested in Fe_3Al and FeAl alloys for the MOLTOX process, and they have tested the alloys in a molten salt environment. Air Products participated in meetings and development with ORNL and with Timken.

Work began with Devasco International, Inc. of Houston, TX for the development of shielded-metal-arc (SMA) electrode formulations for the FA-385 FeAl type alloy composition. Such production of weld-electrodes is an important step in enabling FeAl for weld-overlay cladding applications.

Work also began with Haynes International (Kokomo, IN) to produce filler-metal weld rods via aspiration casting methods based on the most weldable FA-385 series alloy compositions. Weld rods of several compositional variants have been produced and weld-overlay cladding deposits have been made to test these alloys. Initial results are good and analysis of weld-clad test pads is in progress.

COST SHARING

Timken and Latrobe are estimated to have spent about 150 \$K on melting and processing of FeAl alloys. Air Products contributed about 150 \$K in their testing efforts on FeAl alloys.

ESTIMATED ENERGY SAVINGS

The development of low-cost, low-density, corrosion-resistant, fabricable and weldable FeAl aluminide alloys should enable their application to advanced energy conversion, to stationary or mobile heat-engines, or to high-temperature materials processing equipment in aggressive environments. All such applications will save energy (better thermal efficiency, durability and lifetime, or allow more efficient processes to operate). In addition, heat-resistant alloys made of mainly iron and aluminum are environmentally beneficial because iron and aluminum are recyclable and are major components of the recycled metals scrap streams today. Furthermore, iron and aluminum are not RCRA waste hazards like nickel and chromium, which are major constituents of heat-resistant claddings or coatings today. The development of weld-overlay cladding of FeAl alloys on conventional structural steels should enable their near-term application in various engineering or processing systems.

HIGHLIGHTS

WELDABLE FEAL ALLOYS CAN BE USED AS WELD-OVERLAY CLAD ON STEELS - Recent work has revealed that several complex FeAl alloys have good weldability, in some cases as good as found in type 316 or 304 austenitic stainless steel. These alloys, with appropriate welding-technique modifications, have been used to produce overlay weld-deposits on commercially available structural steel substrates. Similar crack-free weld-clad deposits have been made with commercially-produced FeAl weld consumables, with appropriate pre-heat and post-weld heat-treatments to eliminate the hydrogen effects which can cause delayed cold-cracking during cooling.

NEW, WELDABLE FeAl IRON-ALUMINIDES SHOW PROMISE FOR WELD-OVERLAY CLADDING APPLICATIONS ON STRUCTURAL STEELS

Problem:

FeAl type iron-aluminides show outstanding oxidation resistance at $>1000^{\circ}\text{C}$, but lack strength above 600°C , but can be difficult to fabricate and to weld. The challenge was to improve the weldability of FeAl alloys, and to be able to apply them as corrosion-resistant weld-overlay cladding to protect conventional structural steels and alloys at high temperatures.

Results:

Commercial FeAl weld consumables (rods) of the most weldable FeAl alloys (modified FA-385 alloys) have been produced and used to produce weld-overlay cladding deposits on $2\frac{1}{4}\text{Cr-1Mo}$ steel. Proper modifications of the welding practice (preheat and post-weld heat-treatments) have produced crack-free weld-deposits.

Significance - For Energy Conservation:

Weldability of FeAl alloys that enables the use of those alloys high-temperature corrosion/oxidation resistant weld-overlay cladding on conventional structural steel and alloy substrates. This will accelerate their use in systems that are more efficient and save energy at higher service or process temperatures.

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

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

WORK ELEMENT: Metallic and Intermetallic Alloys/Composites

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

PHASE: FY 1993

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

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

PHASE OBJECTIVE: Determine the effects of minor alloying additions on the weldability of FeAl alloys. Determine the best combination of weldability and mechanical properties behavior (room-temperature ductility and high-temperature strength) in FeAl type alloys for structural applications. Use the most weldable FeAl as weld-overlay cladding on conventional structural steels and alloys.

ULTIMATE OBJECTIVE: Take advantage of the outstanding oxidation/sulfidation/molten salt corrosion resistance exhibited by FeAl alloys at high-temperatures, through either monolithic structural or weld-overlay cladding applications in advanced energy conversion systems, processing systems, or heat engines. Improved weldability is essential for any applications of FeAl alloys.

TECHNICAL APPROACH: Determine the effects of minor alloying or impurity elements on weldability of FeAl alloys. Test the ability to produce crack-free weld-deposits of weldable FeAl alloys on a variety of structural steel and alloy substrates. Evaluate the corrosion and mechanical behavior of these weld-overlay composites under potential service conditions.

PROGRESS: Several new modifications of the FeAl/FA-385 base alloy composition were found to have good weldability and mechanical behavior. These FeAl alloys are nearly as weldable as 300 series austenitic stainless steels. Weld-clad deposits of these weldable FeAl alloys have been made onto type 304L austenitic stainless and 2¼Cr-1Mo bainitic/martensitic steel substrates, and with proper preheat and post-weld heat-treatments such weld-deposits are crack-free.

Patents: 1

Publications: 3

Proceedings: 3

Books:

Presentations: 1

ACCOMPLISHMENTS:

Licenses: none

Known Follow-on Products: Commercial FeAl weld-consumables are being studied. (This work is directly relevant to all other technology-transfer efforts on iron-aluminides that are ongoing at ORNL)

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

CRITICAL ISSUES: To find minor alloying or impurity elements additions maximize the weldability of FeAl alloys without adversely affecting mechanical properties. To take the most weldable FeAl alloys and find welding methods that enable these to be used as weld-overlay cladding on commercial structural steels and alloys. To produce FeAl weld consumables commercially. To determine the in-service properties of FeAl weld-overlay cladding/substrate composites

POTENTIAL PAYOFF: Weldability is necessary for almost any potential application of FeAl alloys. Improved weldability that does not come at the expense of mechanical properties makes FeAl alloys more attractive as high-temperature structural materials. Weldable FeAl alloys can also find almost immediate application as corrosion-resistant alumina-forming weld-overlay cladding on conventional structural steels and alloys. FeAl alloys are made from cheap and abundant constituents that are the major components of metals recycling waste-streams today, and should themselves also be recyclable. FeAl are environmentally beneficial in that they provide outstanding oxidation/corrosion resistance without the use of Ni and Cr, which are classified as hazardous RCRA waste.

EVALUATION OF THE MECHANISM OF ROOM TEMPERATURE EMBRITTLEMENT OF ALUMINIDES

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INTRODUCTION

The deformation and fracture of aluminides has been found to be reduced by exposure to water vapor and aqueous solutions. Research has shown that this "embrittlement" is the result of aluminum metal reacting with water to form atomic hydrogen and aluminum oxide on the surface (or aluminum ions in aqueous solutions). As a result, one would expect that any environment containing water should also cause embrittlement of aluminides. However, for nickel aluminide this is not the case. The objective of this work is to find out why some environments that contain water do not cause embrittlement of nickel aluminide in the hope that this knowledge will enable the fabrication of intermetallic compounds that are not susceptible to embrittlement by water at room temperature.

SUMMARY

The first hypothesis examined to explain this phenomena was that ordering resulted in altering the chemical activity of aluminum sufficiently that hydrogen evolution did not occur in the aqueous solutions where embrittlement is not observed. Thermodynamic calculations indicated that this is not the case and that for any stoichiometry near Ni_3Al hydrogen evolution should occur whenever aluminum metal comes into contact with water.

The second hypothesis examined was that ordering results in a physical barrier which prevents aluminum metal from reacting with water at the surface of the intermetallic compound. That is, in the L1_2 structure of nickel aluminide, the aluminum atoms have only nickel nearest neighbors and nickel atoms must be removed for hydrogen production by aluminum dissolution to continue for more than a quarter of a monolayer (though surface

diffusion may allow slightly more than the stoichiometrically predicted quarter of a monolayer). If this is the case, aqueous solutions which do not attack nickel will not cause embrittlement. If this hypothesis is correct, some interesting corollaries follow. First, since continuous dissolution may be possible at the grain boundaries especially if they are rich in aluminum, then segregation of aluminum to the grain boundaries will result in promoting embrittlement. Second, alloys slightly substoichiometric in aluminum should be more resistant to embrittlement than stoichiometric or hyperstoichiometric alloys. Third, alloying elements that promote segregation of aluminum to the grain boundaries should also promote embrittlement while the reverse should be true for alloying elements that displace aluminum at the grain boundaries. Fourth, a disordered layer at the grain boundaries may enable slip accommodation but, it may also promote hydrogen evolution and embrittlement.

To evaluate this second hypothesis, scratch tests were conducted on samples of nickel aluminide alloy and a Ni-Fe alloy heat treated either to yield a random solid solution or to yield completed ordered ($L1_2$) Ni_3Fe . In contrast to the Ni_3Al system, it is relatively easy to obtain ordered and random solutions at room temperature in the Ni_3Fe system. The Ni-Fe samples were examined with X-ray diffraction to confirm the presence or absence of ordering. The scratch tests were conducted in aqueous solutions found to not cause embrittlement of nickel aluminide and the potential of the sample with respect to a reference electrode (and the potential for hydrogen evolution) were recorded. The results found that for ordered sample the potential transient during scratching never went below that observed for pure nickel while lower potential were observed for the disordered material. These results are in complete agreement with the hypothesis that ordering results in a physical barrier to aluminum dissolution that can only be overcome in solutions where nickel is removed from the surface by dissolution or moves rapidly on the surface by surface diffusion.

PUBLICATIONS

None.

PRESENTATIONS

None.

HONORS AND AWARDS

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

None.

COST SHARING

NIST

Danish Engineering Academy

HIGHLIGHTS

Results confirm the hypothesis that ordered influences chemical behavior indicating means for reducing susceptibility to room temperature embrittlement of aluminides.

HIGH-TEMPERATURE PRECIPITATION-STRENGTHENED IRON ALUMINIDES AND OTHER INTERMETALLIC ALLOYS

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INTRODUCTION

The purpose of this work is to explore precipitate-strengthening effects for improved high-temperature strength in various intermetallic alloys, starting with FeAl-type (B2 phase) iron-aluminides. This project expanded in FY 1991 to explore similar microstructural effects in Fe₃Al-type (FA-129) alloys. In FY 1992, the alloy development goals broadened to include improved weldability and balancing processing/heat-treatment conditions to improve the combination of room-temperature ductility and high-temperature strength. These mechanical behavior and weldability studies were also supported by microcharacterization, phase/structure, and physical properties studies (including Ni₃Al) during FY 1993.

TECHNICAL PROGRESS - FY 1993

Summary

1. Mechanical Properties Behavior - FeAl alloys:

Twelve new small heats of modified FeAl-type alloys based on the weldable FA-385 alloy composition were melted and fabricated into sheet stock. Initial weldability (SIGMAJIG hot-cracking) tests were completed in FY 1992 and the results reported. Mechanical properties testing, including tensile-testing at room-temperature (22°C) (Table 1) and 600°C (Table 2), and creep-rupture testing at 600°C/207 MPa (30 ksi) (Table 3) began late in FY1992 and continued during FY 1993. The most weldable FeAl alloys (FA-385-M1 and -M2, see the section "Development of Weldable, Corrosion-Resistant Iron-Aluminide Alloys" elsewhere in this report) also show the best

Table 1 - Room Temperature Tensile Data on FeAl Alloys

Alloy	Test Temperature (°C)	Strength (MPa)		Total Elongation (%)
		Yield	Ultimate	
FA-324	22	355	409	2.2 ^a
FA-385	22	336	519	4.4 ^a
	22	357	483	3.3 ^a
FA-388	22	417	465	1.8 ^b
	22	318	406	1.8 ^a
	22	315	355	1.3 ^a
	22	434	434	<0.1 ^b
	22	467	533	2.0 ^b
FA-385-M2	22	461	473	1.1 ^b
FA-385-M3	22	359	395	1.2 ^b
FA-385-M4	22	340	364	0.8 ^b
FA-385-M5	22	339	339	<0.1 ^b
FA-385-M6	22	325	342	2.0 ^b
FA-385-M7	22	241	281	0.5 ^b
FA-385-M8	22	349	358	0.6 ^b
FA-385-M10	22	324	324	<0.1 ^b
FA-385-M11	22			

a - heat-treated for 1h/800°C + 1h/700°C

b - hot-rolled at 900°C, heat-treated for 1h at 750°C + 1h at 1000°C

Table 2 - Tensile Data on FeAl Alloys Tested at 600°C

Alloy	Test Temperature (°C)	Strength (MPa)		Total Elongation (%)
		Yield	Ultimate	
FA-324	600	312	353	49.3 ^b
	600	332	394	20.1 ^a
FA-385	600	346	495	20.9 ^a
	600	400	493	11.0 ^b
	600	422	510	8.3 ^b
	600	389	481	10.1 ^b
	600	357	451	14.6 ^c
FA-388	600	359	475	9.3 ^a
	600	418	487	9.9 ^b
	600	357	453	9.9 ^c
FA-385-M1	600	487	592	7.9 ^b
	600	481	558	5.6 ^b
FA-385-M2	600	484	555	8.2 ^b
	600	480	567	9.6 ^b
FA-385-M3	600	475	578	14.0 ^c
	600	478	542	2.1 ^b
	600	489	590	3.2 ^b
FA-385-M4	600	404	536	17.0 ^c
	600	390	482	9.1 ^b
	600	395	503	6.9 ^b
FA-385-M5	600	370	476	14.7 ^c
	600	416	521	11.4 ^b
	600	389	487	4.4 ^b
FA-385-M6	600	351	466	13.6 ^c
	600	402	482	18.5 ^b
	600	401	477	12.2 ^b
FA-385-M7	600	333	449	10.7 ^c
	600	398	482	24.5 ^b
	600	335	482	4.5 ^b
FA-385-M8	600	328	461	5.4 ^c
	600	384	477	5.7 ^b
	600	369	473	4.1 ^b
FA-385-M9	600	365	475	9.1 ^c
	600	379	458	13.2 ^b
FA-385-M10	600	375	405	0.9 ^b
	600	393	456	3.1 ^b
	600	420	521	3.3 ^b
FA-385-M11	600	397	535	7.5 ^c
	600	347	447	3.4 ^b
	600	313	315	2.5 ^b

a - heat-treated for 1h/800°C + 1h/700°C

b - hot-rolled at 900°C, heat-treated for 1h at 750°C

c - hot-rolled at 900°C, heat-treated for 1h at 750°C + 1h at 1000°C

tensile strength at 600°C (Table 2), and by far the best creep-strength at 600°C/207 MPa (Table 3 and Fig. 1). These rupture life values ranging from 260 to 430 h for FeAl during creep at 600°C/207 MPa are comparable to or better than the creep strength of type 304 austenitic stainless steel, an important measure-of-goodness for this program. The room-temperature tensile ductility of FA-385-M2 is 2% (in air) after a heat-treatment of 1h at 1000°C, which is comparable to or better than the base alloys (FA-385 and -388) or most of the other alloys in this series given the same heat-treatment (Table 1). However, because room-temperature ductility of FeAl alloys is very sensitive to alloy composition, heat-treatment and environmental embrittlement (hydrogen) effects, work will continue in FY 1994 to study these effects and determine the heat-treatments that provide the best creep-rupture resistance, the best room-temperature ductility, and the best combination of those two properties in those FeAl alloys with the best weldability.

During FY 1993, scale-up efforts based on the previous results included melting of seven new larger (15 lb) heats of the FeAl/FA-385 alloy series compositions that were most weldable (FA-385-M1, -M2, -M3 and -M9). These alloys were fabricated into a) thin-sheet stock for weldability and mechanical properties testing, b) rod-stock for mechanical properties testing and for use as welding rods. Mechanical properties testing and weld-overlay cladding evaluation will continue during FY 1994. Three additional new small heats, based on the FeAl/FA-328 alloy compositions shown previously to have outstanding creep-rupture resistance at 600°C/30 ksi, were melted during FY 1993 for weldability testing.

Finally, new efforts began during FY 1994 to produce small and large heats of Fe-30Al alloys to attempt to combine the high-temperature strength and weldability of the best FeAl/FA-385 series alloys with best combinations of properties found in Fe₃Al/Fe-28Al series alloys (room-temperature ductility, weldability, high-temperature strength and processability). The new Fe-30Al alloys are expected to remain essentially B2-phase at high and low temperatures, thus they are categorized as

Table 3. Creep-rupture properties of new modified FA-385 FeAl-type alloys

Alloy	Processing/Heat-Treatment Condition	Creep Conditions		Rupture		Minimum Creep-rate (%/h)
		Temp. (°C)	Stress (ksi)	Time (h)	Elongation (%)	
FA-385	HR-900°C/1h-750°C	600	30	11	62.8	1.7
		600	30	10.3	56.3	3.1
FA-388	HR-900°C/1h-750°C + 1h-1000°C	600	30	7.8	47.5	3.7
		600	30	6.5	40.5	3.8
FA-385 -M1	HR-900°C/1h-750°C	600	30	295.7	15.7	0.02
		600	30	434	14.5	0.01
FA-385 -M2	HR-900°C/1h-750°C	600	30	271	9.5	0.015
		600	30	267	16.3	0.015
FA-385 -M3	HR-900°C/1h-750°C	600	30	20.1	56.4	0.9
FA-385 -M4	HR-900°C/1h-750°C	600	30	11.2	24.3	2.2
		600	30	16	32.5	1.4
FA-385 -M5	HR-900°C/1h-750°C	600	30	12.3	33	1.0
		600	30	26.3	32.4	0.6
FA-385 -M6	HR-900°C/1h-750°C	600	30	11.4	33.5	1.9
		600	30	13.1	38.8	1.6
FA-385 -M7	HR-900°C/1h-750°C	600	30	14.6	47	1.9
FA-385 -M8	HR-900°C/1h-750°C	600	30	15.9	29	1.1
FA-385 -M9	HR-900°C/1h-750°C	600	30	8.1	38.1	2.8
FA-385 -M10	HR-900°C/1h-750°C	600	30	24.4	35	0.8
FA-385 -M11	HR-900°C/1h-750°C	600	30	7.9	21.4	1.6

Fig.1 - Plots of creep-strain versus time for FeAl/FA-385 alloys creep-rupture tested at 600°C/207 MPa (30 ksi), a) FA-385-M1, and b) FA-385-M2.

FeAl type. New efforts will also extend to evaluating properties of these alloys in both the as-cast as well as in the as-wrought conditions.

2. Mechanical Properties Behavior and Weldability - Fe₃Al alloys:

ORNL research efforts on iron-aluminides were coordinated between the AIM and the Fossil Energy AR&TD Materials programs during FY 1993. The focus alloy of the Fossil Energy Materials program is the Fe₃Al/FA-129 alloy. This alloy has been scaled-up to large commercially-produced heats because it is weldable, and has good room-temperature ductility in the wrought condition. However, the FA-129 alloy was also found to be quite weak at higher temperatures (>600°C) and to have only 1.5-2% ductility in the as-cast condition. Therefore, during FY 1993, part of the AIC Material program effort on iron-aluminides included exploring a modified Fe₃Al/FA-129 type alloy with improved high-temperature strength. Ten new small heats of modified Fe₃Al/FA-129 alloys (FAMM-1 through -10) were melted and processed into thin sheet stock and tested during FY 1992-93. Relative weldability data (SIGMAJIG threshold cracking stress (σ_0)), showed generally good weldability, with three of the FAMM series alloys being as good as or better than FA-129 (σ_0 >25 ksi; FAMM-1, -3 and -7), and three other alloys being only slightly less weldable (σ_0 - 20-25 ksi; FAMM-6, -9 and -10), as reported last year. The best room-temperature ductility was found in the FAMM-1 (7%) and -3 (2.6%) alloys after they were hot-rolled (HR) at 850°C and solution-annealed (SA) at 1000-1050°C. The best tensile yield strength (56-65 ksi) at 650°C was found in the FAMM-2 and -3 alloys (HR at 850°C plus 1h at 750°C). During FY 1993, these alloys were creep-rupture tested at 600-650°C/20-30 ksi, and the data is given in Table 4. The FAMM-10 alloy had the best creep-rupture resistance at 650°C/20 ksi (280-300 h), after a SA treatment at 1200-1250°C (Table 4). At 600°C/30 ksi, FAMM-10 a rupture life of 1141 h, more than 45 times better than FA-129 (Table 4). Thus far, a SA-treatment of 1000-1250°C appears to improve the combination of room-

Table 4. Creep-rupture properties of new, modified FA-129 alloys

Alloy	Processing/Heat-Treatment Condition	Creep Conditions		Rupture		Minimum Creep-rate (%/h)
		Temp. (°C)	Stress (ksi)	Time (h)	Elongation (%)	
FA-129	HR-600°C/1h-750°C	593	30	20-25	70-80	1.0
FAMM1	HR-850°C	650	20	13	60	3.2
	HR-850°C/1h-1050°C	600	30	46.3	41.9	0.34
	HR-850°C/1h-1050°C	650	20	29	59	0.31
	HR-750°C/1h-1250°C	650	20	48	49.5	0.42
FAMM2	HR-850°C	650	20	17	52	1.6
	HR-850°C/1h-1050°C	600	30	71.7	21.1	0.24
	HR-850°C/1h-1050°C	650	20	40	33.3	0.16
	HR-750°C/1h-1250°C	650	20	52.8	9.9	0.07
FAMM3	HR-850°C	650	20	43.8	48	0.6
	HR-850°C/1h-1000°C	600	30	63.4	24.5	0.2
	HR-850°C/1h-1000°C	650	20	66.3	38.6	0.18
	HR-750°C/1h-1250°C	650	20	74.5	39.5	0.17
FAMM4	HR-850°C	650	20	19.5	42	1.24
	HR-850°C/1h-1050°C	650	20	22.8	36.5	0.9
FAMM5	HR-850°C	650	20	4.9	10.2	(no secondary creep regime)
FAMM6	HR-750°C/1h-1000°C	650	20	22.9	38.9	0.7
	HR-750°C/1h-1250°C	650	20	specimen broke during loading		
FAMM7	HR-750°C/1h-1000°C	650	20	34.6	30.9	0.3
	HR-750°C/1h-1250°C	650	20	27.3	47.3	0.6
FAMM8	HR-750°C/1h-1000°C	650	20	96.8	28.4	0.2
	HR-750°C/1h-1250°C	650	20	78.2	14.5	0.13
FAMM9	HR-750°C/1h-1000°C	650	20	34.9	53	0.44
	HR-750°C/1h-1250°C	650	20	26.4	57.8	0.94
FAMM-10	HR-750°C	650	20	92.9	19.3	0.08
	HR-750°C	650	20	56.9	23.5	0.17
	HR-750°C/1h-1000°C	650	20	172.7	27.6	0.02
	HR-750°C/1h-1250°C	650	20	specimen broke during loading		
	HR-750°C/1h-1250°C	650	20	299.4	32	0.01
	HR-750°C/1h-1200°C	650	20	288.7	24	0.01
	HR-750°C/1h-1200°C	650	20	281.1	43.3	0.01
	HR-750°C/1h-1250°C	600	30	1141.5	16.1	0.002

temperature ductility and high-temperature strength compared to as-rolled material. While joint program work on a modified Fe₃Al/FA-129 alloy is finished, the effects of the combination of minor alloying additions used in the FAMM-10 alloy will be tested on FeAl/Fe-30Al alloys during FY 1994.

3. Phase/Structure, Microstructure and Physical Properties Studies:

Room-temperature X-ray diffraction (XRD) and high-temperature XRD (HTXRD) studies of the ordered-phase transition temperatures of Fe₃Al and FeAl type alloys were completed and reported at the end of FY 1992. Scanning electron microscopy (SEM) studies of fracture modes and transmission electron microscopy (TEM) studies of precipitate, dislocation and ordered-phase structures in tensile- or creep-tested wrought Fe₃Al and FeAl alloys continued during FY 1993 while new microstructural studies of as-cast Fe₃Al began. One significant result for welding of wrought alloy FA-129 sheet materials was that the fusion-zone (FZ) was almost entirely D0₃-phase (the lower temperature ordered phase, with inherently lower ductility and higher susceptibility to environmental embrittlement), while the heat-affected-zone (HAZ) and base-metal (BM) remained mainly B2-phase (the higher temperature partially ordered phase with often better ductility and inherently better environmental embrittlement resistance). Similarly, a large commercial casting of FA-129 with almost zero room-temperature ductility was also found to consist of entirely the D0₃ phase, with relatively dislocation-free grains. The as-cast microstructures of the binary Fe-28Al (at.%) and ternary Fe-28Al-5Cr alloys corresponding to the FA-129 alloy were similar, but with coarser grain sizes. These microstructural results motivated the exploration of new FeAl/Fe-30 Al alloys mentioned above, in an attempt to avoid the fully-ordered D0₃ phase regime and obtain alloys that have a B2 phase structure in the as-cast condition.

Systematic physical properties data measurement began at ORNL in FY 1992 because such data has generally been lacking for aluminides and other ordered intermetallics, and continued in FY

1993. Preliminary thermal expansion data was reported last year. The thermal expansion of iron-aluminides was somewhat higher than that found in type 316 austenitic stainless steel, with FeAl alloys showing slightly more expansion than Fe₃Al alloys above 600-800°C. The thermal expansion of a typical Ni₃Al alloy (IC-221M) was found to be the same as a typical nickel-based superalloy, alloy-713C. During FY 1993, specific heat measurements were made on a typical Ni₃Al alloy (IC-221M) on the Fe₃Al/FA-129 alloy using differential scanning calorimetry (DSC) (Fig. 2). The thermal conductivity of the Ni₃Al alloy is close to that of the nickel-based superalloy 713C, and somewhat below the thermal conductivity of type 304 stainless steel at <800°C. By contrast, the thermal conductivity of the Fe₃Al/FA-129 alloy is significantly lower than that of type 304 austenitic stainless steel. There are also clear inflection points in the thermal conductivity curve for the Fe₃Al/FA-129 alloy that correlate with the temperatures of the D0₃→B2 and B2→α phase transitions. Work will continue during FY 1994 on various physical properties measurements for other related aluminide alloys.

MILESTONES DURING FY 1993

AIC Supplemental Milestone 93CC-51: Determine physical properties of Ni₃Al, Fe₃Al, and FeAl and prepare draft publication or report (due March 31, 1993).

This milestone was completed and satisfied by the paper entitled "Thermal Expansion Data on Several Iron- and Nickel-Aluminide Alloys," (Porter and Maziasz), which was prepared, submitted to and published in *Scripta Metallurgica et Materialia*, as indicated in the publications below.

PUBLICATIONS

Journals

1. P.J. Maziasz and C.G. McKamey, "Microstructural Characterization of Precipitates Formed During High-Temperature Testing and Processing of Iron-Aluminide Alloys," *Materials Science and Engineering*, A152 (1992) 322-334.

Fig.2 - A plot of thermal conductivity data versus temperature for Ni_3Al and Fe_3Al type alloys (IC 221M and FA-129, respectively), with similar data for a nickel-based superalloy (IN 713C) and an austenitic stainless steel (type 304) from the literature included for comparison.

2. C.G. McKamey, P.J. Maziasz, and J.W. Jones, "Effects of Addition of Molybdenum or Niobium on Creep Rupture Properties of Fe₃Al," *Journal of Materials Research*, 7 (Aug., 1992) 2089-2106.
3. C.G. McKamey, P.J. Maziasz, G.M. Goodwin and T. Zacharia, "Effects of Alloying Additions on the Microstructures, Mechanical Properties and Weldability of Fe₃Al-Based Alloys," accepted for publication in *Materials Science and Engineering A* Journal in 1993/94.
4. W.D. Porter and P.J. Maziasz, "Thermal Expansion Data on Several Iron- and Nickel-Aluminide Alloys," *Scripta Metallurgica et Materialia* 29 (1993) 1043-1048.
5. S. Viswanathan, C.G. McKamey, P.J. Maziasz and V. Sikka, "Tensile Properties of As-Cast Fe₃Al-Based Alloys," submitted to *Materials Science and Engineering A* in 1993.

Other Publications

1. P.J. Maziasz, C.G. McKamey and C.R. Hubbard, "Designing Precipitate-Strengthened Iron-Aluminides For High-Temperature Applications," Alloy Phase Stability and Design, eds. G.M. Stocks, D.P. Pope and A.F. Giamei, Mat. Res. Soc. Symp. Proc. Vol. 186, Materials Research Society, Pittsburg PA (1991) pp. 349-355.
2. P.J. Maziasz, C.G. McKamey, O.B. Cavin, C.R. Hubbard and T. Zacharia, "Some Effects of Composition and Microstructure on the B2 $\leftrightarrow$ D0₃ Ordered Phase Transition in Fe₃Al Alloys," in High-Temperature Ordered Intermetallic Alloys-V, eds. I. Baker, R. Darolia, J.D. Whittenberger, and M.H. Yoo, Mat. Res. Soc. Symp. Proc. Vol. 288, Materials Research Society, Pittsburg, PA (1993) p. 209.

PRESENTATIONS

Oral Presentations

1. P.J. Maziasz, "Designing Precipitate-Strengthened Iron-Aluminides For High-Temperature Applications," Symposium on Alloy Phase Stability and Design, Spring 1990 MRS Meeting, San Francisco, CA, April 16-20, 1990.
2. C.R. Hubbard, "Phase Equilibria of Fe-28Al Alloys by High Temperature XRD," 39th Annual Denver X-ray Conference, Steamboat Springs, CO, July 30 - August 3, 1990.
3. P.J. Maziasz and C.G. McKamey, "Microstructural Characterization of Precipitates Formed During High-Temperature Testing and Processing of Iron-Aluminide Alloys," presented at the International Conference on High-Temperature Aluminides and Intermetallics, sponsored by ASM-International, held in San Diego, CA, Sept. 16-19, 1991.
4. O.B. Cavin, C.R. Hubbard and P.J. Maziasz, "High Temperature X-ray Diffraction Determination of Phase Transitions in Large Grain Alloys," presented at Accuracy of Powder Diffraction II, held at NIST in Gaithersburg, MD, May 25-29, 1992.

5. W.D. Porter, P.J. Maziasz and J.A. Cook, "Physical Properties Measurements of Iron and Nickel Aluminide Alloys," presented at the Technology Transfer Conference and Workshop on Nickel and Iron Aluminides, held in Oak Ridge, TN, August 4-5, 1992.
6. P.J. Maziasz and W.D. Porter, "Physical Properties Measurements of Ni₃Al Alloys," oral presentation at the GM-Saginaw/ORNL CRADA (ORNL 92-0076) Meeting on Ni₃Al for Heat-Treating Assemblies, held at ORNL, Oak Ridge, TN, Nov. 9-10, 1992.
7. P.J. Maziasz, C.G. McKamey, O.B. Cavin, C.R. Hubbard and T. Zacharia, "Some Effects of Composition and Microstructure on the B2 $\leftrightarrow$ D0₃ Ordered Phase Transition in Fe₃Al Alloys," poster presented at Symposium L - High-Temperature Ordered Intermetallic Alloys-V, Fall 1992 MRS Meeting, held in Boston, MA, Nov. 30 - Dec. 4, 1992.
8. C.G. McKamey, P.J. Maziasz and S. Viswanathan, "Microstructure and Fracture Behavior of As-Cast Fe₃Al-Based Ordered Intermetallic Alloys," poster presented at the International Metallographic Society Meeting in Charleston, SC, July 18-21, 1993.

HONORS AND AWARDS

First Place - Scanning Electron Microscopy Catagory for the poster "Microstructure and Fracture Behavior of As-Cast Fe₃Al-Based Ordered Intermetallic Alloys," (C.G. McKamey, P.J. Maziasz and S. Viswanathan) presented at the International Metallographic Society Meeting in Charleston, SC, July 18-21, 1993.

PATENTS/DISCLOSURES

An invention disclosure was filed with Martin Marietta Energy Systems, Inc. on "High-Temperature, Corrosion Resistant Iron-Aluminides Exhibiting Improved Weldability," (P.J. Maziasz, G.M. Goodwin and C.T. Liu) on August 27, 1993. In addition, the data obtained on improved high-temperature mechanical properties of weldable FeAl-type B2-phase alloys should be the basis for another invention disclosure next quarter.

LICENSES

None

INDUSTRIAL INPUT and TECHNOLOGY TRANSFER

This work is directly relevant to work on Fe₃Al alloys being done on other programs and to industrial interfacing/technology transfer efforts for iron-aluminides in general by ORNL/MMES. The physical properties data on iron- and nickel-aluminides is important input to industries interested in or involved in CRADA's concerning those materials (ie, GM-Saginaw CRADA on Ni₃Al). These alloys may also be applicable for various metals processing applications (hot dies, rolls, furnace furniture, etc.) or for pulp and paper industry applications. Furthermore, these alloys are environmentally beneficial because heat-resistant iron-aluminide alloys would be more recyclable and less of a waste hazard than heat-resistant Fe-Cr-Ni alloys (Cr and Ni are RCRA waste, whereas Fe and Al are not).

COST SHARING

None

ESTIMATED ENERGY SAVINGS

An increase in the high-temperature tensile- and creep-strength limits by as much as 100-150°C will enable applications that require iron-aluminides for better oxidation resistance to also operate more efficiently and cost effectively. Improved high-temperature strength, with good fabricability, weldability and sufficient room-temperature ductility should also enable these new iron-aluminides to better compete with conventional stainless steels and alloys for structural applications. The lower density and higher recycleability of FeAl alloys may have benefits for advanced automotive applications. Good weldability in particular can also enable use of these alloys in weld-overlay cladding applications on conventional structural steels and alloys.

HIGHLIGHTS

NEW FEAL ALLOYS HAVE SIGNIFICANTLY IMPROVED WELDABILITY AND HIGH-TEMPERATURE CREEP-RUPTURE STRENGTH: New modified FeAl/Fe-36 at.%Al alloys have been developed with significantly improved weldability that is now comparable to that of type 316 austenitic stainless steel, and with creep-rupture strength at 600°C/30 ksi that is now comparable to type 304 stainless steel, relative to the base aluminide alloy. These new alloys also retain the outstanding oxidation/corrosion resistance to >1100°C that is common to this class of iron-aluminide alloys.

NEW WELDABLE IRON-ALUMINIDES HAVE SIGNIFICANTLY IMPROVED CREEP-STRENGTH AT 600°C

Problem:

FeAl type iron-aluminide alloys have outstanding oxidation at $>1000^{\circ}\text{C}$, but lack strength at 600°C and above, and many lack weldability. The challenge was to modified the alloys to improve weldability while also improving the high-temperature creep-strength.

Results:

New modified FeAl type alloys (FA-385-M1 and -M2) have been developed which have much better weldability and creep-rupture strength than the base alloys. The modified FeAl alloys have weldability similar to that of type 316 austenitic stainless steel, and creep-resistance similar to that of type 304 stainless steel.

Threshold Hot-Cracking Stress
for Welded Iron-Aluminide Alloys

ORNL DWG 94-5663

Creep-Strain/Time Curves
For FeAl Alloys

ORNL DWG 94-5664

Significance - For Energy Conservation:

Better weldability and high-temperature strength will enable FeAl alloys to be used in structural applications that require oxidation/corrosion resistance in systems that are more efficient and save energy at higher service or process temperatures.

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

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

WORK ELEMENT: Metallic and Intermetallic Alloys/Composites

PROJECT TITLE: High-Temperature Precipitation-Strengthened Iron Aluminides and Other Intermetallic Alloys

PHASE: FY 1993

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPLE INVESTIGATORS: P.J. Maziasz (615) 574-5082

PHASE OBJECTIVE: Improve the high-temperature strength of weldable FeAl alloys by precipitate-strengthening effects. Also determine and improve the mechanical behavior of wrought, cast and weld-deposited FeAl material. Also measure physical properties of iron- and nickel-aluminides.

ULTIMATE OBJECTIVE: To provide oxidation-resistant FeAl alloys with sufficient high-temperature mechanical properties to compete with 300 series austenitic stainless steels for structural applications in advanced energy conversion or industrial processing systems. Furthermore, to provide iron-aluminides suitable for use as weld-overlay cladding on conventional structural steels and alloys.

TECHNICAL APPROACH: Microalloying of combinations of minor elements to produce fine dispersions of precipitates that are stable at high-temperatures. Combine with effects of alloying elements and impurities on weldability. Optimize processing parameters to produce the best combination of room-temperature ductility and high-temperature strength.

PROGRESS: Modified FeAl/FA-385 alloys were found with significantly improved weldability and high-temperature creep-rupture resistance at 600°C and 207 MPa. This weldability is comparable to that of type 316 austenitic stainless steel, while the creep resistance is similar to that of type 304 stainless steel. The effects of processing/heat-treatment parameters on improvements in room-temperature ductility and further improvements in high-temperature strength are currently being explored for these alloys. As-cast properties are also being explored. Physical properties studies show thermal expansion and conductivity of Ni₃Al alloys to be similar to that of nickel-based superalloys like 713C, whereas FeAl alloys have more thermal expansion lower thermal conductivity than comparable steels.

Patents: ____
Books: ____

Publications: 5
Presentations: 8

Proceedings: 2

ACCOMPLISHMENTS:

Licenses: none

(However, this work is directly relevant to all the other technology-transfer efforts on iron-aluminides that are ongoing at ORNL)

PROJECT TITLE: High-Temperature Precipitation-Strengthened Iron Aluminides and Other Intermetallic Alloys

CRITICAL ISSUES: To find solutes which produce fine precipitates that effectively strengthen the alloy at high-temperatures without impairing ductility at room-temperature, and which provide or enable good weldability. Other critical issues involve finding processing/heat-treatments that provide the best combination of good room-temperature and high-temperature properties, and finding FeAl alloy compositions that also have good mechanical properties in the as-cast or in the as-welded (ie., weld-overlay cladding) conditions.

POTENTIAL PAYOFF: Iron-aluminides, particularly FeAl type, have lower density and vastly superior high-temperature oxidation/corrosion resistance compared to most heat-resistant steels or Fe-Cr-Ni alloys. Improved weldability and high-temperature strength will enhance the opportunities for these materials to be used in structural or processing applications. Improve weldability will also facilitate near-term applications of FeAl as an alumina-forming protective cladding on conventional structural steels and alloys. FeAl alloys are made from cheap and abundant constituents that are the major components of metals recycling waste-streams today, and should themselves also be recyclable. FeAl are environmentally beneficial in that they provide outstanding oxidation/corrosion resistance without the use of Ni and Cr, which are classified as hazardous RCRA waste.

MODELING FRACTURE OF ADVANCED CERAMIC MATERIALS

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DE-AI05-900R21941

INTRODUCTION

The objective of this program is to develop two micro-mechanics computer simulations which can elucidate important microstructural and stochastic aspects of the strength and fracture toughness of advanced ceramic materials. Such understanding, combined with experimental observations, will enhance microstructural design of improved, advanced ceramic-based materials for use in a myriad of energy-related applications. Mimicking physical phenomena with simplistic algorithms, these simulations will explore the stochastic influence of complex microstructural phenomena, such as thermal-expansion-anisotropy, microcracking, crack deflection and crack bridging, on strength and fracture toughness.

Ceramic materials can have significant positive impact on innumerable heat-resisting applications where higher operating temperatures equate to more energy-efficient operation. Brittleness, however, is a major concern in designing with these materials. A general stratagem has been to improve the fracture toughness, and indeed, much progress has been achieved in the last few years in developing ceramic microstructures, including ceramic composite systems, which lead to improved fracture resistance.

Understanding of the mechanisms that influence fracture resistance in these materials is typically formulated in terms of idealized micro-mechanics models. Statistical aspects of

these mechanisms, related to the stochastic nature of a ceramic microstructure, are rarely considered. Such considerations are crucial to the development of new and improved materials and to structural design with these materials. Knowledge about these stochastic aspects is most readily attained from statistically generated microstructures and micro-mechanical descriptions of the toughening mechanisms, thereby relating grain-boundary properties and their distributions to processing variables and structural performance.

Accordingly, two microstructural, micro-mechanics models were developed: one to study the propagation of a "straight-through" crack in a random, two-dimensional ceramic microstructure; and another to elucidate microstructural aspects of a three-dimensional crack front on crack-bridging phenomena. Both models are based upon spring-network approaches.

TECHNICAL PROGRESS

Summary

Two microstructural, micro-mechanics fracture models were formulated and computer coded, and several simulations were performed. The first model, developed in collaboration with N. Sridhar and Prof. David Srolovitz at the University of Michigan, is a two-dimensional, triangular network of springs upon which a polycrystalline microstructure is mapped. Thermal anisotropy effects are introduced into the simulation by initially contracting the network spring in a randomly selected, high-expansion direction in each grain. Initial studies have examined the influence of the size of the resulting misfit strain, the grain size and Poisson's ratio on microcrack density. The second model simulates a planar crack propagating in a "quasi-three-dimensional" polycrystalline ceramic microstructure, meandering

through the microstructure with a three-dimensional crack front as local stresses and fracture criteria dictate. It consists of two two-dimensional rectangular networks of springs which are joined across the fracture plane by a network of cohesive springs. Thus far, no polycrystalline microstructure has been superposed on this model, but rather each cohesive bond has been assumed to represent a grain boundary. Initial studies examined the fracture resistance as a function of crack length (i.e., R-curves behavior) for different dispersion in the distribution of grain-boundary strengths.

Milestone

1. Complete development of two micro-mechanics computer simulations models and related computer code. End 07/93.

The research involved the development of two micro-mechanics models and the use of these models in computer simulation studies to elucidate the influence of various microstructural aspects on the strength and fracture toughness behavior of advanced ceramic materials. Both models are based upon a spring-network approach in which simple springs are interconnected at nodes to form an network. The spring elements can have either linear-elastic properties to model elastic effects, or other constitutive properties to model various micro-mechanical processes (e.g., the frictional pull-out of a microstructural "reinforcement"). Similar spring-network models, except for the "microstructural" constitutive elements, have been successfully used to simulate fracture at the atomistic level and to study elastic properties of random media.

Polycrystalline aspects of the ceramic microstructure are introduced into the spring network models by "overlaying" a random, "digitized" ceramic microstructure on the spring

network. Accordingly, different spring elements with different constitutive properties and breaking strengths are used to represent various microstructural features, e.g., transgranular versus and intergranular properties. Thermal-expansion-anisotropy (TEA) effects are introduced into the models by using springs of different initial lengths. Such effects can also be correlated with digitized microstructures of actual advanced ceramics. Microcracking is simulated by discrete spring failures, as influenced by breaking strength distributions and TEA effects. Crack bridging is simulated by surviving springs, or clusters of springs, in the wake of the crack tip. As mentioned above, the constitutive properties of these "bridging" elements can be modified to simulate frictional "pull-out."

The two random-microstructure, spring-network models were: (1) A two-dimensional model in which a "straight-through," but non-planar crack propagates through a random, two-dimensional microstructure with TEA-induced strains to elucidate the influence of residual thermal stresses and interface properties on microcracking and crack propagation behavior; and (2) A quasi-three-dimensional model in which a planar crack interacts with a random microstructure in the third dimension (the crack front is not constrained to remain straight) to elucidate bridge-formation processes in the crack wake and their influence on the fracture toughness. The models were formulated, computer code was developed, and several simulations were performed. Progress in each is discussed below.

Non-Planar, Two-Dimensional Fracture Model. This model, developed in collaboration with N. Sridhar and Prof. David Srolovitz at the University of Michigan, simulates TEA-induced microcracking and TEA-influenced crack propagation in a microstructural simulation of a polycrystalline advanced ceramic. It consists of a two-dimensional, triangular network of

springs upon which a polycrystalline microstructure is mapped. The energy of each spring (or bond) has both a bond-stretching and a bond-bending component. The total energy of the system is a sum over all the bonds.

The simulation is periodic in a direction parallel to the tensile axis and has free surfaces in the transverse directions. It thus simulates a sample with an effectively infinite gage length. The network is stressed by applying a fixed strain over the gage length and relaxing the node positions with a double-precision conjugate gradient algorithm to minimize the total energy. Bond rupture is affected via a critical bond-strain-energy criterion, and thus mimics a critical strain-energy-release-rate or fracture surface energy criterion for failure. (The bulk bonds and grain-boundary bonds are assumed to have different critical strain energies.) When a bond fractures, the system is re-equilibrated at the existing applied strain, and additional bonds are allowed to fracture, if required, before applying a further strain increment.

Thermal expansion anisotropy effects are introduced into the simulation by randomly selecting a high-expansion direction in each grain and initially contracting the network spring in this direction. This contraction was applied gradually, testing for localized fracture (microcracks) at each (misfit) strain step. Initial studies have examined the influence of the size of this misfit strain, the grain size and Poisson's ratio on microcrack density.

Planar, Three-Dimensional Crack-Front Model. This model simulates a planar crack propagating in a "quasi-three-dimensional" polycrystalline ceramic microstructure. The (planar) crack front is able to meander through the microstructure as local stresses and fracture criteria dictate, thereby developing a three-dimensional crack front. The model consists of two two-dimensional rectangular networks of springs which are joined across the

fracture plane by a network of cohesive springs. A planar crack is initially introduced into the fracture plane by "cutting" the appropriate cohesive bonds. Stress are applied normal to the fracture plane, and as before the node positions are relaxed via a conjugate gradient algorithm to minimize the total energy. Bond fracture, which give rise to crack advance, is determined by a critical cohesive bond-strain.

Thus far, no polycrystalline microstructures have superposed on this simulation, but rather each cohesive bond has been assumed to represent a grain boundary. Accordingly, the cohesive strength of each bond represents a grain-boundary strength, which is then selected from a equal-probability distribution. Preliminary studies for this simulation have examined the fracture resistance as a function of crack length (i.e., R-curves behavior) for different dispersion in the distribution of grain-boundary strengths.

Acknowledgment

This research is sponsored by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Concepts Division, Advanced Industrial Concepts Materials Program, under Interagency Agreement No. DE-AI05-900R21941, and under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

PUBLICATIONS

1. Narayanaswamy Sridhar, David J. Srolovitz, and Edwin R. Fuller, Jr., "Computer Simulations of Thermal Expansion Anisotropy Induced Microcracking in Brittle

Ceramics," submitted to proceedings of JFCC International Workshop on Fine Ceramics '94.

PRESENTATIONS

1. (Invited) E. R. Fuller, Jr.* and W. C. Carter, "Stochastic Aspects of Brittle Fracture: Computer Simulations of Fracture Processes," Symposium on Design of Ceramic Microstructures, 1993 PAC RIM Meeting, The American Ceramic Society, Honolulu, Hawaii, November 7-10, 1993, November 8, 1993.
2. (Invited) E. R. Fuller, Jr., "Computer Simulations of Thermal Expansion Anisotropy-Induced Microcracking," Northwestern Graduate Student Seminar, Department of Materials Science and Engineering, Northwestern University, Evanston, IL, November 18, 1993.
3. (Invited) Edwin R. Fuller, Jr.*, N. Sridhar, and David J. Srolovitz, "Computer Simulations of Thermal-Expansion-Anisotropy-Induced Microcracking in Brittle Ceramics," JFCC International Workshop on Fine Ceramics '94, "Materials Processing and Design: Grain Boundary Controlled Properties of Fine Ceramics," March 17-19, Mikawa Heights, Koda-cho, Nukata-gun, Aichi-ken, JAPAN, 1994, March 18, 1994.
4. N. Sridhar*, W. H. Wang, D. J. Srolovitz, and E. R. Fuller, Jr., "Microstructural Mechanics Model of Anisotropic Thermal Expansion Induced Microcracking," ACerS Symposium on Computational Methods & Molecular Dynamics and Computational Materials Theory, 96th Annual Meeting and Exposition of the American Ceramic Society, Indiana Convention Center, Indianapolis, IN, April 23-24, 1994, April 27, 1994; Am. Ceram. Soc. Bull. 73 [3], 223 (March 1994).

5. H. Cai, E. R. Fuller, Jr.*, and W. C. Carter, "Computer Simulations of Fracture Resistance Curves," ACerS Symposium on Computational Methods & Molecular Dynamics and Computational Materials Theory, 96th Annual Meeting and Exposition of the American Ceramic Society, Indiana Convention Center, Indianapolis, IN, April 23-24, 1994, April 27, 1994; Am. Ceram. Soc. Bull. **73** [3], 223 (March 1994).

HONORS AND AWARDS

none

PATENTS/DISCLOSURES

none

LICENSES

none

INDUSTRIAL INPUT AND TECHNOLOGICAL TRANSFER

Even though micro-mechanics computer simulations are in their primal stages, they have already generated substantial industrial interest because of the potential for rapid materials development and reliability assessment. Perhaps the most significant industrial effort in advanced ceramics is that of Dr. Liza Monette, Dr. Shiun Ling and Dr. Michael P. Anderson at the Exxon Research and Engineering Company in Annandale, NJ. They have developed models similar to our two-dimensional, non-planar fracture model. A similar effort was recently initiated at the Du Pont Central Research and Development Laboratory in

Wilmington, DE, by Dr. Anand Jagota and Dr. Stephen J. Bennison. In addition, Dr. William A. Curtin of Virginia Polytechnical Institute and State University, has developed a model similar to our quasi-three-dimensional, planar crack model. We have ongoing dialogue with each of these groups, and are currently planning a workshop, in collaboration with the NIST Distributed Center for Computational Materials Science and the National Institute of Mechanics and Materials at the University of California at San Diego, to establish a national research agenda in these areas..

Additionally, a workshop on *Statistics and Materials Science: Microstructure-Property-Performance Relations* was held at NIST on July 26-28, 1993. The workshop was jointly sponsored by the National Institute of Statistical Sciences (NISS) and NIST to identify the important scientific and technological challenges in materials computer simulations and to stimulate cross-disciplinary research between materials scientists and statisticians. The principal findings of the fifty-two workshop participants from industry, academia, and government were that: (1) crucial problems in materials science are inherently statistical, so that statistics is an enabling technology for advances in materials science; and (2) fulfilling industrial needs and goals demands cross-disciplinary collaboration between statisticians and materials scientists. The workshop was sponsored by the Advanced Technology Program at NIST and a detailed report, which describes the scientific program, and presents the technical findings and recommendations, is available from the National Institute of Statistical Sciences (NISS) as Technical Report #14.

COST SHARING

NIST's internal R&D funds provide support for research in the general area of materials computer simulations of fracture properties of advanced ceramics at a level of approximately 80% of the AIC Materials Program support.

HIGHLIGHTS

Two microstructural, micro-mechanics fracture models were formulated algebraically, computer code was developed, and several preliminary simulations were performed. In one model, residual, anisotropy, thermal strains were introduced into a random, two-dimensional microstructure to elucidate the influence of the size of the resulting misfit thermal strain, the grain size and Poisson's ratio on microcrack density. In the other model the evolution of a three-dimensional crack front by a planar crack propagating in a microstructure with random-strength grain boundaries resulted, under some conditions, in the development of a rising fracture resistance with initial crack extension, i.e., a short-crack R-curve.

COMPUTER SIMULATION MODEL OF THERMAL-EXPANSION-ANISOTROPIC INDUCED MICROCRACKING AND FRACTURE RESISTANCE CURVES

Problem:

Ceramic materials can have significant positive impact on innumerable energy-related applications at elevated temperatures. Brittleness, however, is a major concern in designing with these materials. A general stratagem has been to improve the fracture toughness, and indeed, much progress has been achieved in developing ceramic microstructures, including ceramic composite systems, which lead to improved fracture resistance. Understanding of toughening mechanisms is typically formulated in terms of idealized micro-mechanics models. Statistical aspects of these mechanisms, related to the stochastic nature of a ceramic microstructure, are rarely considered. The challenge was to develop micro-mechanics computer simulations which could elucidate important microstructural and stochastic aspects of the strength and fracture toughness of advanced ceramic materials.

Results:

Two microstructural, micro-mechanics fracture models were formulated algebraically and computer code was developed. Several preliminary simulations were performed. In one model, residual, anisotropy, thermal strains were introduced into a random, two-dimensional microstructure to elucidate the influence of the size of the resulting misfit thermal strain, the grain size and Poisson's ratio on microcrack density. In the other model the evolution of a three-dimensional crack front by a planar crack propagating in a microstructure with random-strength grain boundaries resulted, under some conditions, in the development of a rising fracture resistance with initial crack extension, i.e., a short-crack R-curve.

Significance - For Energy Conservation:

Better understanding of important microstructural and stochastic aspects of the strength and fracture toughness of advanced ceramic materials will enable the microstructural design of improved, advanced ceramic-based materials for use in a myriad of heat-resisting applications where higher operating temperature equates to more energy-efficient operation.

Significance - for Materials Technology

The future of materials science will be driven, in large part, by the ability to tailor microstructures to obtain desired physical properties. The simulation techniques developed here are an effective tool for determining processing-property relations which were heretofore unobtainable, and for designing new technologically important ceramic-based materials.

microstructures have not been superposed on this model, but rather each cohesive bond was assumed to represent a grain boundary. Preliminary studies examined the fracture resistance as a function of crack length (i.e., R-curves behavior) for different dispersion in the distribution of grain-boundary strengths.

Patents: none

Publications: one submitted

Proceedings: none

Presentations: three invited and two contributed

ACCOMPLISHMENTS: Two microstructural, micro-mechanics fracture models were formulated and computer coded, and several simulations were performed. Concepts intrinsic in this research are essential for designing new technologically important ceramic-based materials for use in a myriad of energy-related applications.

Licenses: none

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: **MODELING FRACTURE
 OF ADVANCED CERAMIC MATERIALS**

FISCAL YEAR: FY 1993

COMPLETION DATE: July 31, 1993

PERFORMING ORGANIZATION:

Ceramics Division
National Institute of Standards and Technology (NIST)
Gaithersburg, MD 20899

PRINCIPAL INVESTIGATOR: Dr. Tze-Jer Chuang
Telephone: (301) 975-5773
Facsimile: (301) 990-8729

PHASE OBJECTIVE: The objective of this project was to develop two micro-mechanics computer simulations which can elucidate important microstructural and stochastic aspects of the strength and fracture toughness of advanced ceramic materials.

ULTIMATE OBJECTIVE: The overall objective of this project is to provide increased understanding of the stochastic influence of complex microstructural phenomena on the structural reliability of advanced ceramic-based materials to enhance their microstructural design for use in a myriad of energy-related applications.

TECHNICAL APPROACH: Micro-mechanics materials models are used in computer simulation studies to elucidate the influence of microstructural phenomena on the strength and fracture toughness of advanced ceramic materials. The models are based on a spring-network which is "overlaid" with a random, "digitized" ceramic microstructure. Aspects of the constitutive properties of each network element are used to model various micro-mechanical processes.

PROGRESS: Two microstructural, micro-mechanics fracture models were formulated and computer coded. Several simulations were performed. The first model, developed in collaboration with N. Sridhar and Prof. David Srolovitz at the University of Michigan, is a two-dimensional, triangular network of springs upon which a polycrystalline microstructure is mapped. Thermal anisotropy effects are introduced into the simulation by initially contracting the network spring in a randomly selected, high-expansion direction in each grain. Initial studies have examined the influence of the size of the resulting misfit strain, the grain size and Poisson's ratio on microcrack density. The second model simulates a planar crack propagating in a "quasi-three-dimensional" polycrystalline ceramic microstructure, meandering through the microstructure with a three-dimensional crack front as local stresses and fracture criteria dictate. It consists of two two-dimensional rectangular networks of springs which are joined across the fracture plane by a network of cohesive springs. Thus far, polycrystalline

PROJECT TITLE: Modeling Fracture of Advanced Ceramic Materials

CRITICAL ISSUES: Critical issues in computer simulations of microstructural and micro-mechanical materials properties are related to trade-offs between computational speed, algorithm efficiency, and complexity of the physical processes which can be modelled.

FUTURE PLANS: Research efforts in the current project concentrated on the development of two microstructural, micro-mechanics models and on verification of the models with initial computer simulation studies. Future plans would involve more extensive simulation studies and the introduction of more complex aspects of materials behavior. For example, high-temperature creep deformation and creep rupture processes should be possible. An important aspect of computer simulation studies is to maintain a close collaboration with on-going experimental research activities. In this regard, as the simulations are developed, we would hope to interact synergically with both industrial projects and other DOE AIC materials projects which consider microstructural aspects of the structural behavior of advanced ceramic materials.

POTENTIAL PAYOFF: The future of materials science will be driven, in large part, by the ability to tailor microstructures to obtain desired physical properties. Results from this project will be an effective tool for determining processing-property relations which were heretofore unobtainable by linking them to the tailored microstructures. We expect that the concepts developed from it will be essential for designing new technologically important ceramic-based materials for use in a myriad of energy-related applications. Such techniques will become more important throughout the materials science community and will be invaluable in time. The power of such techniques can only increase with time as computer speed and memory continue to grow rapidly.

**SUPERIOR METALLIC ALLOYS THROUGH RAPID
SOLIDIFICATION PROCESSING (RSP) BY DESIGN**

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ABSTRACT

Project Objective: To collaborate with U.S. industries in applying rapid solidification processing in combination with composition adjustments to produce metallic alloys with superior properties and performance.

The industrial sector requires metallic alloys whose properties, performance, and reliability extend beyond those obtained from current processing practices. These needs can be fulfilled by metallic alloys that have fine and stable (to high temperatures) microstructures. Rapid solidification processing (RSP) by design can fulfill these needs through control of alloy chemistry and powder processing parameters. The fine and stable microstructures are being realized from the RSP research, and application of the principles to metallic alloys of interest to industry is underway. Significant improvements have been observed for RSP 304 SS, A286, and 718 alloys compared to their ingot metallurgy (IM) counterparts. A nickel-base alloy has been designed for the RSP approach using the knowledge from the research findings and input from the industrial sector. The base composition is Ni-25Cr-15Fe-0.06C (in wt%) with other additions to promote effective use of nitrogen and oxygen as well as carbon.

Contacts with domestic industries have produced considerable interest in the RSP technology. Four Cooperative Research and Development Agreements (CRADAs) have been signed to compare in a "look-see" manner, the microstructure, properties and performance limits of selected alloys/materials currently being used with those obtained by RSP. These materials are for high temperature electrical, corrosion and wear, and photovoltaic applications. Significant improvements in the properties and performance for these materials from RSP will produce energy savings and lead to more efficient energy systems.

INTRODUCTION

Rapid solidification processing (RSP) using powder atomization methods and the control of minor elements such as oxygen, nitrogen, and carbon can provide metallic alloys with superior properties and performance compared to conventionally processed alloys. Previous studies on nickel- and iron-base superalloys have provided the baseline information to properly couple RSP with alloy composition, and, therefore, enable alloys to be designed for performance improvements.

TECHNICAL PROGRESS

Summary

Previous studies on RSP A286, Ni-20Fe-20Cr, and 718 superalloys have shown fine and stable grain sizes compared to their conventionally processed counterpart (e.g., 0.01 versus 0.10 mm grain size after a 1 h-1100°C heat treatment). The origin of the fine grain size for the RSP alloys has been traced to the solidification microstructure obtained during powder processing. The small grain size appears to be a feature of RSP and can be effectively used for improving the properties of metallic alloys.

The fundamental information from the previous RSP studies on superalloys is currently being applied to the design of a series of nickel-base alloys for high temperature, energy efficient applications. The powders have been processed by gas atomization of a fine melt stream and consolidated into bars by hot extrusion. For comparison, extrusion fabrication of conventionally melted and cooled ingots of the alloys was included.

A substantial effort has been devoted to four Cooperative Research and Development Agreements (CRADAs). These studies have focused on "look-see" type evaluations for using RSP on alloys related to current product lines of the industrial partners. Three of the studies have been completed and the fourth is near completion. A second phase study has been initiated with one of the industrial partners. This study should provide more in-depth information and enable the industrial partner to decide on the commercial adoption of the RSP technology.

Milestones

The milestones for this project are associated with completion of the RSP studies on superalloys; design of some nickel-base alloys and verification of properties and performance improvements; and technology transfer activities (i.e., information dissemination and CRADA participation).

1. **RSP Applications to Superalloys:** The research findings for the Ni-20Fe-20Cr alloy series, A286, and 718 have provided valuable insight towards establishing the potential opportunities for using the RSP technology in the design of improved alloys for structural applications. A common feature observed for the RSP alloys is small and stable (to high temperatures) grain sizes, e.g., 0.01 mm after a 1100°C-1 h heat treatment compared to ~0.10 mm for conventionally processed counterparts. The origin of the fine grain sizes was traced to the primary dendrite boundaries observed in the solidified powders. The RSP study on the superalloys also revealed the following: (1) the development and control of the γ' and γ'' phases for precipitation strengthening were not affected by RSP; (2) powder particle size did not influence the microstructure and mechanical properties; and (3) more effective use of the interstitial elements (O, N, and C) can be obtained by restricting the Al and Ti levels in the alloys.

The results from the RSP studies on the superalloys provided the basis for the design of a series of nickel-base alloys with a base composition of Ni-25Cr-15Fe-0.06C. Additions to the base alloy included Mo, V, Nb and/or Si. Twenty batches of powder (~5 kg/batch) were processed using gas atomization. A processing variable included in the powder atomization stage was the gas used for melt stream break-up and subsequent cooling of the molten droplets. Both helium and nitrogen were used, and it appears that the powder solidification rates were not affected by the choice of atomization gas. Also, the nitrogen that was entrained during atomization appears to have gone into solution, whereas entrained helium produced some porosity as indicated in Figs. 1a and 1b. The chromium level for the nickel-base alloy series is high enough to promote some nitrogen solubility. Porosity from insoluble gases in the powders is retained after consolidation and is a concern for high temperature applications where bubble growth/coalescence can occur.

(a) helium atomization

(b) nitrogen atomization

Fig. 1. Influence of atomization gas on porosity of RSP Ni-25Cr-15Fe with Mo, V, and Nb additions.

Powder characterization has been completed and the powder batches (fifteen) shipped to ORNL for consolidation by hot extrusion. Five batches of powder representing three alloys have been held in reserve for evaluation by industry. Characterization of the extruded powders should be initiated in December 1993. The emphasis will be on microstructural features, fineness, and stability after various heat treatments.

Mechanical property testing with an emphasis on high temperatures will be performed on the RSP nickel-base alloy series.

2. **Technology Transfer:** The primary activity for this task has been the interaction with U.S. industries interested in utilizing the RSP technology. The effort has involved joint studies via four CRADAs, to improve the properties and performance of metallic alloys. The areas of application include high temperature electrical, corrosion and wear, and photovoltaic devices, all of which have very significant implications for improving energy efficiency and conservation.

Three of the four studies have been completed and the remaining study is nearly finished. The studies have provided valuable insight towards effective use of the RSP technology for improving the properties and performance of current specialty alloy products associated with the industrial partners. One of the partners has requested a Phase 2 evaluation of the RSP technology. This phase will constitute a more detailed, joint evaluation, and will provide the company with sufficient information for commercial utilization of the technology. The existing CRADA was amended to include the Phase 2 effort, and the study was initiated in July 1993.

PUBLICATIONS (1992-1993)

Journals

W. Kim, J. E. Flinn, and J. G. Byrne, "Parametric Studies of the Hot Isostatic Pressing of Rapidly Solidified 304 Stainless Steel Powder, *Acta Metall. Mater.*, 41 (1993), 49-57.

J. E. Flinn, Book Review (Invited) on *Powder Technology Handbook, Matls. Sci. and Eng., A160* (1993), 155.

J. E. Flinn Book Review (Invited) on *Particle Size Measurements, Matls. Sci. and Eng., A161* (1993), 309.

Other Publications

J. E. Flinn, D. V. Miley, C. H. Sellers, and G. L. Fletcher, "Microstructure Solidification and Homogenization of Inert Gas Processed Superalloy Powders," *Microstructural Science*, eds. W. R. Kanne, Jr., G. W. E. Johnson, J. D. Braun, M. R. Louthan, Jr. (IMS-ASM International, Materials Park, OH), Vol. 20 (1993), 333-349.

J. E. Flinn and T. F. Kelly, "Advanced High-Temperature Alloys by Design Using Rapid Solidification Processing," *Critical Issues in the Development of High Temperature Structural Materials*, eds. N. Stoloff, D. J. Duquette, and A. F. Giamei (TMS, Warrendale, PA), in press.

PRESENTATIONS (1992-1993)

ASM/TMS Joint Meeting (Chicago, IL):

- J. E. Flinn, "National Lab/Industry Research Partnerships — The Role of the Researchers (Invited)
- J. E. Flinn, "RSP Stainless Steels for Improved Properties" (Invited).

Engineering Foundation Conference on Critical Issues in the Development of High Temperature Structural Materials (Kona, HA): J. E. Flinn and T. F. Kelly, "Advanced High-Temperature Alloys by Design Using Rapid Solidification Processing."

1993 ASM/TMS Metals Show (Pittsburgh, PA): J. E. Flinn, J. C. Bae, and T. F. Kelly, "Rapid Solidification Processing of Austenitic Stainless Steels: Origin and Stabilization of Fine Grain Sizes" (Invited).

Overviews of the RSP technology given to Allied Signal, Teledyne, Teledyne Allvac, General Motors, and National Center for Manufacturing Sciences.

PATENTS/DISCLOSURE (1992-1993)

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER (1992-1993)

1. CRADA studies involving RSP technology with four industrial partners are nearly completed.
2. A Phase 2 investigation with one of the CRADA partners was initiated.
3. Industry provided input for the design of several nickel-base alloys using RSP, and expressed an interest in providing some evaluation.

COST SHARING (1992-1993)

1. CRADA activities involving cost-in-kind contributions were ~\$150,000 from industrial partners.
2. Cost share from the Bureau of Mines for the Idaho National Engineering Laboratory CRADA participation was ~\$100,000.

HIGHLIGHTS (1992-1993)

1. Four CRADA studies are nearly completed with one of the industrial partners requesting a "more-in-depth" Phase 2 modification to the existing CRADA. The Phase 2 study was approved and the work initiated in July 1993.
2. RSP powders were prepared for a nickel-base alloy series by design.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Superior Metallic Alloys Through Rapid Solidification Processing by Design

FISCAL YEAR: FY 1993

COMPLETION DATE: September 30, 1994

PERFORMING ORGANIZATION: Idaho National Engineering Laboratory, EG&G Idaho, Inc., Idaho Falls, ID.

PRINCIPAL INVESTIGATOR: John E. Flinn (208) 526-8127.

PHASE OBJECTIVE: Dissemination of the RSP research findings to industry and completion of the Cooperative Research and Development Agreements (CRADAs) (four) experimental efforts.

ULTIMATE OBJECTIVE: To transfer the RSP technology to the U.S. industrial sector.

TECHNICAL APPROACH: Rapid solidification processing of metallic alloy powders by a gas atomizer with a 7 kg melt capacity. The approach combines RSP with melt composition control, particularly the minor elements O, N, and C, to produce fine and stable (to high temperatures) microstructures. These provide significant improvements in properties and performance of the alloys after powder consolidation. The alloys involve commercial compositions, alloys of immediate interest to industry and alloys by design.

PROGRESS: RSP of superalloys has produced fine and stable grain sizes that provide significant improvements in mechanical properties. The origin of the fine grain size has been traced to the primary dendrites produced during the RSP of powder. Control of the primary dendrite size will control the grain size. Dissemination of the research findings to U.S. industries has attracted their interest in the RSP technology, resulting in four CRADAs. Collaborative research with the four industrial partners is underway.

Patents: --

Publications: 8

Proceedings: 10

ACCOMPLISHMENTS

Licenses: --

Technology Transfer or Industrial Interaction: (1) Visits and discussions with 20 companies. (2) Dissemination of research findings to 50 companies. (3) Award of Excellence for Technology Transfer. (4) Four CRADAs involving eight potential applications for the RSP technology.

CRITICAL ISSUES

Research: (1) Obtain grain sizes of $\sim 1 \mu\text{m}$ during powder solidification and (2) effective utilization of interstitial elements (O, N, and C) for control and stabilization of submicron microstructural features for performance benefits.

Technology Transfer: (1) Utilization of RSP technology by industry; (2) pilot scale gas atomizer (~ 200 kg capacity) to provide sufficient quantities of RSP powder for field tests; (3) simplification of the CRADA approval process; (4) nondisclosure protection for CRADA partners; (5) funding accessibility for CRADA participation.

PROJECT TITLE: Superior Metallic Alloys Through Rapid Solidification Processing by Design

FUTURE PLANS: Assist U.S. industries, within available capabilities and resources, in adopting the RSP technology for commercial production of powder metallurgy products.

POTENTIAL PAYOFF: Good probability that at least \$150,000,000 in sales will be realized from the RSP technology within five to seven years. This will provide 300 to 1000 new jobs and tax revenues that will exceed (first year) the Federal investment in the research and CRADA activities.

ESTIMATED ENERGY SAVINGS: The commercial applications of the RSP technology from the CRADA investigations will yield significant energy savings. Several applications involve high temperature electrical properties requiring extended lifetimes of components for more energy efficient systems. Significant improvements in wear, corrosion, and structural

performance from RSP will produce significant energy savings. Also, improvement in the efficiency from RSP for photovoltaic applications is anticipated.

OTHER SOURCES: (1) Cost-in-kind from CRADA partners - \$375K. (2) Bureau of Mines contribution to RSP research - \$7,450K; Bureau cost share on CRADA activities - \$300K.

SUPERIOR STRUCTURAL ALLOYS DESIGNED BY RAPID SOLIDIFICATION PROCESSING

PROBLEM: The industrial sector requires metallic alloys whose performance and reliability extend beyond those available from ingot and current powder metallurgy (P/M) processing.

RESULT: Research from this project shows that rapid solidification processing (RSP) of metallic alloys provides very fine and stable microstructures (to high temperatures), which produce significant to substantial improvements in properties and performance. Information on these findings has been disseminated to U.S. industries and their response to the technology has been favorable. CRADAs with industrial partners are addressing alloy improvements for very high temperature stability, corrosion and wear, fatigue, load bearing reduction in mass, electrical, magnetic, and photovoltaic applications.

SYNTHESIS AND DESIGN OF INTERMETALLIC MATERIALS

A. D. Rollett, J. J. Petrovic, R. G. Castro, D. Butt and S.-P. Chen

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INTRODUCTION

The development of new and advanced materials based on silicides has been supported by the Office of Industrial Technologies for several years. During this period, silicide-based materials have advanced from being of interest to the research community, to being actively considered for a number of industrial applications. The inherent high temperature capability of the silicides allow for a wide range of potential applications, e.g. in gas turbine engines; the particular application set under investigation by this program, however, is that of gas burner nozzles. One of the highlights of this year's effort has been the preparation of net-shape burner nozzles by plasma spraying of MoSi₂ powders for testing by one of our industrial collaborators, Air Products [see the highlights for a picture of the nozzles]. Another vital aspect of the year's effort has been the initiation of a collaboration with Advanced Refractory Products on the development of manufacturing processes for MoSi₂-SiC composites [see highlights for signing of the CRADA].

As implied by the highlights noted above, the most useful silicide is MoSi₂ because of its optimal combination of oxidation resistance, high temperature plasticity etc. The major impediment to application of any silicide is the quasi-ceramic brittleness at room temperature, and alloying has failed to lower the brittle-to-ductile transition from around 1000°C. The approach taken by this program, therefore, has been to synthesize composites in order to maximize the fracture resistance at room temperature, and also to improve the high temperature creep strength. By adding ZrO₂ and SiC, the fracture toughness has been enhanced by a factor of three and the creep resistance has been improved. Such an approach to the synthesis of new materials demands a sound understanding of the microstructure-property relationships. Therefore we have had an active program in micro-mechanical modeling as a complement to the experimental materials synthesis effort. Use of the spring lattice model, for example, has

confirmed our understanding of many of the features of transformation toughening by ZrO_2 and has provided several important insights into how to optimize materials [see highlights for model description]. Lastly, a tangent to the development of structural MoSi_2 -based composites has been the synthesis of Si_3N_4 - MoSi_2 composites, where the silicide acts both as a ductile reinforcement (at high temperatures) for the silicon nitride, and as a conductive phase (above a minimum volume fraction) that permits electro-discharge machining (EDM). This patented approach yields a novel form of a standard high temperature material that can be machined by EDM, which is a much more cost-effective process than the conventional method of grinding [see highlights].

TECHNICAL PROGRESS

Summary with Milestones

1. **Deliver a MoSi_2 based component to industry for test and evaluation. The component will be a MoSi_2 -based composite burner component.**

Status: This milestone has been met. Prototypical components have been fabricated by thermal spray (low pressure plasma spray) build-up on a graphite mandrel. These prototypes have been delivered to a burner manufacturer for evaluation and test.

2. **Demonstrate the feasibility of a machinable, oxidation resistant MoSi_2 + Si_3N_4 composite.**

Status: This milestone has been met. A Si_3N_4 matrix composite containing 30 vol.% MoSi_2 particulate phase has been shown to have an electrical resistivity suitable for electro-discharge (EDM) machining.

3. **Complete the first stage of transfer of MoSi_2 + SiC whisker composite technology to Advanced Refractory Technologies.**

Status: This milestone has been met. ART has processed initial SiC whisker- MoSi_2 powder blends and supplied them to LANL. LANL has begun the consolidation of these blends, and the evaluation of the consolidated composite properties.

4. **Parametric study of effect of particle size, morphology etc. on composite properties, with feedback to experimental materials synthesis.**

Status: This milestone has been met. Studies of the contribution of micro-cracking to the toughness of composites with transformation toughening particle reinforcement (ZrO_2) indicate that microcracking only makes a minor contribution to overall toughness.

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Progress on the first and third milestones is reported in the sections below on industrial input and technology transfer activities. Progress on the second milestone is reported on in the experimental section. Progress on the fourth milestone, which has to do with the design of advanced composites, is addressed in the section below on micromechanical modeling.

As a background to the development of new MoSi₂-based composites, it is worth noting that MoSi₂ is a potentially important reinforcement material for ceramic matrix composites based on non-oxides, such as Si₃N₄ and SiC, and on oxides, such as ZrO₂, Al₂O₃, Y₂O₃, YAG (yttrium aluminum garnet), and mullite (3Al₂O₃.2SiO₂). This being the case, we have initiated an investigation of the MoSi₂-Si₃N₄ composite system, since Si₃N₄ is currently the most important structural ceramic material for industrial applications. Above its brittle-to-ductile transition, MoSi₂ represents an oxidation-resistant, ductile particulate phase material. Since MoSi₂ exhibits the same high temperature oxidation mechanism as Si₃N₄, namely formation of an adherent and coherent SiO₂ layer, its presence as a particulate phase in a Si₃N₄ matrix should not degrade the composite oxidation resistance. Furthermore, MoSi₂ and Si₃N₄ are thermodynamically stable and do not react with each other at the elevated temperatures of composite fabrication and use. It is also possible that MoSi₂ particles in a Si₃N₄ matrix may improve elevated temperature mechanical properties such as strength, high temperature fracture toughness, creep, and slow crack growth resistance. If so, this would be a potential reliability benefit for such composites. At suitable volume fraction, it is also possible that MoSi₂ particles may improve the machinability of Si₃N₄ matrix composites, by allowing for the use of electro-discharge machining (EDM) as compared to the currently employed diamond machining. This is a potential cost benefit because of the lower cost of EDM compared to diamond machining.

Micromechanical Modeling

We used a "spring-network" (SN) model to include the effects of microstructure, second-phase particle toughening and micro-cracking phenomena. We treat the system as a two-dimensional triangular lattice of 50x50 nodes, each of which is connected to its six nearest neighbors by elastic springs. The microstructure is generated with a Potts model. Transformation of a second-phase particle is modeled by irreversibly increasing the equilibrium spring length when the mean stress on the second-phase particle exceeds a prescribed critical stress, σ_c . Cracking of a bond is modeled by irreversibly turn off the

interaction between the nodes that was connected originally when the corresponding breaking length is reached. We assigned a 1% increase in the length of the springs ($e^T=0.01$) connected to second phase particles upon transformation. Also the second phase particles are randomly distributed in the matrix with a particle size of 1 node (labeled as S_j in the figures, where j representing composites with a transformation stress of σ_{cj}) or cluster of 7 nodes (labeled as L_j) to study the microstructural effects on the fracture toughness.

We calculate fracture toughness increase, ΔK , as a function of the dilatational strain, e^T , volume fraction of particles, f , and the critical transformation stress, σ_c . We then compared these results with available experimental measurements in $\text{MoSi}_2/\text{ZrO}_2$ (ZTM), $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (ZTA) and the continuum theory. The composites with finite volume fraction of small and large second-phase particles do not fracture along grain boundaries as compared to the pure polycrystals. The change of the fracture path is accompanied by a decrease in local stress as the transforming second-phase particles expand and shield the crack by exerting compressive stresses on the original crack.

The local stress, σ_L , for composites with second phase particles is linearly related to the local stress intensity, K_L . The same relation exists between the far-field stress, K_∞ and stress intensity, K_∞ . The reduction of the stress (or ΔK) over the block of nodes can be monitored as a function of the number of particles transformed as the strain is applied. The increase of the fracture toughness is described by

$$\Delta K = K_\infty - K_L = \alpha(\sigma_\infty - \sigma_L) = \alpha(-\Delta\sigma_{xx}) \quad (1),$$

where α is a constant that depends on the simulation cell. All results in fracture toughness are calculated as a ratio to the fracture toughness of the matrix, K_{1c} . It has been shown by continuum theory [1, 8, 9] that the increase of the fracture toughness due to the transformation is proportional to the modulus of the materials, E , the dilatational strain, e^T , the volume fraction of the transforming particles, f , and is inversely proportional to the critical stress of the transformation, σ_c as

$$\Delta K = \alpha_1 E e^T f (\sigma_c)^{-1} / (1-\nu) \quad (2),$$

where ν is the Poisson's ratio, α_1 is a constant.

The first way to change the fracture toughness is to change the dilatational strain, e^T , of the particles. As shown in Fig. 1, ΔK is linear in e^T for values from -0.0025 to

Transformation Toughening

Fig. 1: The linear dependence of ΔK vs. dilatational transformation strain, e^T .

+0.025. But this linear dependence is consistent with the continuum results as expressed in eq. (2). We found that for $\epsilon^T > 0$ the composite is tougher than the single phase material so it is good for dilatational transformation strain to be large and positive if massive micro-cracking (shattering of the sample) can be avoided.

The second quantity in eq. (2) that can be easily changed is the volume fraction of the transformable particles, f . The volume fraction dependence of ΔK has been calculated and found that the increase in the fracture toughness associated with the transformation is linear in f , for small and large particles (Fig. 2a). There are about 10 to 15% variations in the calculated values of ΔK . The measurement of ΔK in ZTM indicates a linear dependence of f (of ZrO_2) as shown in Fig. 2b is a direct confirmation of the simulation results. This calculated linear dependence is also consistent with eq. (2). While results on ZTA show nonlinear dependence that have been attributed to both transformation and micro-cracking.

The third way in changing the composite fracture toughness is to modify the critical transformation stress of the particles, σ_c . The change in σ_c can be achieved by adding stabilizers like CaO, MgO, or Y_2O_3 in ZrO_2 particles. The alloying of stabilizers in ZrO_2 stabilizes the tetragonal and cubic ZrO_2 and thus increases the critical transformation stress. The simulation results (Fig. 3a) are in good agreement with experiments of the $\text{MoSi}_2/\text{ZrO}_2$ (+ x% of Y_2O_3) composites (Fig.3b). The similarity between the measurements and the simulation results are striking. A direct comparison with continuum theory (eq. (2)) reveals some new features. If we exclude the portion that does not transform because σ_c is too high, we found that for different stress levels the ΔK vs. σ_c curve can be broken into two regions that have their own power law dependence $\Delta K = \beta \sigma_c^n$ (Fig. 4):

$$(a) \text{ for large } \sigma_c (> 0.0003), \Delta K = \beta_1 \sigma_c^{-1.3},$$

$$(b) \text{ for small } \sigma_c (< 0.0003), \Delta K = \beta_2 \sigma_c^{-0.05} = \sim \beta_2 \quad (3)$$

where β_1 and β_2 are constants.

We have also studied particle's modulus, particle-matrix interfacial cohesion and the effect of the particle distributions on the fracture toughness. We found that choosing particles with characteristics like (1) large dilatational transformation strain (ϵ^T), (2) large volume fraction (f), (3) small transformation stress (σ_c), (4) strong particle-matrix

Simulation, Chen et al (1993)

Fig. 2: (a) The linear dependence of ΔK vs. f for (a) small and large particles.

Petrovic, et al, Mat. Sci. & Eng. A155, 259 (1992)
Lange, J. Mater. Sci., 17, 247 (1982)

Fig. 2: (b) The experimental results of ΔK as a function of f for MoSi₂/ZrO₂ (ZTM) [7] and Al₂O₃/ZrO₂ (ZTA) [8].

Fig. 3: (a) The ΔK dependence on the critical transformation stress, σ_c .

Fig. 3: (b) The experimental ΔK of the ZTM as a function of x Mole % of Y_2O_3 stabilizer in ZrO_2 particles. These two curves of simulation and ZTM (both fitted to a 3rd order polynomial) are strikingly similar.

Fig. 4: The log-log plot of ΔK vs. σ_c .

cohesion (r^b_{pm}), (5) large particle modulus (E_p), and (6) uniform distributions of transformable particles are beneficial in making tougher composites.

CRADA effort:

S. P. Chen has discussed future collaborations with Dr. M. P. Anderson, Shing Ling, Liza Monette of the Exxon research center in the summer on discrete micromechanical modeling. S. P. Chen will visit Exxon in the Fall to start the collaborations.

MoSi₂ Reinforced-Si₃N₄ Matrix Composites

MoSi₂ may be an important reinforcing species for Si₃N₄ matrix composites. Above its brittle-to-ductile transition, MoSi₂ represents an oxidation-resistant, ductile particulate phase material. Since MoSi₂ exhibits the same high temperature oxidation mechanism as Si₃N₄, namely formation of an adherent and coherent SiO₂ layer, its presence as a particulate phase in a Si₃N₄ matrix should not degrade the composite oxidation resistance. Furthermore, MoSi₂ and Si₃N₄ are thermodynamically stable and do not react with each other at the elevated temperatures of composite fabrication and use.

It is possible that MoSi₂ particles in a Si₃N₄ matrix may improve elevated temperature mechanical properties such as strength, high temperature fracture toughness, creep, and slow crack growth resistance. If so, this would be a potential reliability benefit for such composites. At suitable volume fraction, it is also possible that MoSi₂ particles may improve the machinability of Si₃N₄ matrix composites, by allowing for the use of electro-discharge machining (EDM) as compared to the currently employed diamond machining. This is a potential cost benefit. It is important to recognize that the major element of cost of a Si₃N₄ component is the cost associated with the diamond machining of that component.

We have examined the electrical resistivity of two MoSi₂ particle-Si₃N₄ matrix composites. The first composite contained 20 vol.% MoSi₂ particulate phase and was hot pressed at 1750°C using a 5 wt.% MgO densification aid, so that a hot pressed density of 96% was achieved. The second composite contained 30 vol.% MoSi₂ particulate phase and was hot pressed at 1750°C without any densification aid, achieving a hot pressed density of 59%. We attempted to further densify this specimen by canning in an evacuated Ta can and then HIPing at 1850°C, but little further densification occurred.

This result makes it clear that a MoSi_2 particulate phase will not act as a densification aid for Si_3N_4 , and that densification aids such as MgO will be required.

The results of electrical resistivity measurements on these two specimens using a DC voltage drop technique are shown below:

Vol. % MoSi_2 Phase	Electrical Resistivity (ohm-cm)
20	Greater than 10^6
30	44

These electrical resistivity results are very important, since they make it clear that electrically conductive MoSi_2 particle- Si_3N_4 matrix composites can be obtained if the volume fraction of the MoSi_2 phase is at least 30 vol.%, since sufficient interconnected MoSi_2 phase paths exist at this volume fraction to produce electrical conduction pathways in the composite material. Such composites should have sufficient electrical conductivity to allow for electro-discharge machining.

X-ray diffraction and SEM analyses have shown no evidence of any reactions between MoSi_2 and Si_3N_4 under the processing conditions employed. Thus, this system is a thermodynamically stable one. Additionally, detailed SEM analyses of the region in the vicinity of the MoSi_2 - Si_3N_4 phase interfaces have indicated that, if an MgO densification aid is employed, the MgO is present only in the Si_3N_4 phase, with no MgO detected in the MoSi_2 phase. This result is important, since our results have shown that an MgO densification aid must be used to obtain dense MoSi_2 - Si_3N_4 composites.

We are now in the process of hot pressing a series of MoSi_2 particle- Si_3N_4 matrix composites containing 0, 10, 20, 30, 40, and 50 vol.% MoSi_2 phase, and using a 5 wt.% MgO densification aid addition to the Si_3N_4 matrix in order to obtain dense composites. Once this series of composites is fabricated, we will measure electrical resistivity as a function of vol.% MoSi_2 phase. We will also begin evaluating the electro-discharge machining characteristics of the composites containing 30 vol.% MoSi_2 phase or greater. Fracture toughness and strength of these composites will be determined as a function of temperature, with particular emphasis on determining if the MoSi_2 phase improves the mechanical properties of the Si_3N_4 matrix, especially at elevated temperatures.

Based on the present results, in FY-1994 we will initiate efforts targeted at the technology transfer of the MoSi_2 - Si_3N_4 composite technology. The appeal to industry of

these composites is the fact that industrial components will be cheaper to fabricate than monolithic Si_3N_4 , since they can be electro-discharge machined (EDM), rather than machined by expensive diamond machining. In addition, these composites may have improved mechanical properties in comparison to monolithic Si_3N_4 . With regard to technology transfer, it is important to note that we have a U.S. Patent on these materials (U.S. Patent No. 5,064,789, Silicon Nitride Reinforced With Molybdenum Disilicide, John J. Petrovic and Richard E. Honnell). Target industries will be producers and users of advanced ceramics.

Plasma Spray Fabrication of MoSi_2 Composites

Highlights of this years activities on plasma-spraying of MoSi_2 have focused on two research areas:

plasma spray-forming of prototype MoSi_2 components for potential use in industrial gas fuel burner applications and

reactive plasma-spraying as a technique for gettering SiO_2 in MoSi_2 .

A meeting with Air Products and Chemicals, Inc.(APCI) was held on 26 May 1993. At that time a Bilateral Proprietary Information Agreement was executed between APCI and LANL to investigate potential industrial applications of MoSi_2 for the industrial gas fuel burner industry. The purpose of this agreement is to evaluate MoSi_2 and MoSi_2 fuel burner components in three major application fields: (1) submerged injection of inert or oxidizing and reducing gases into molten metals, ferrous and non-ferrous, (2) lancing pure oxygen inside shaft furnaces processing iron, and (3) combustion heating that would include hot gas recirculation burners and high-enthalpy waste combustors. Initial prototype fabrication at LANL has focused on spray-forming converging-diverging MoSi_2 nozzles for lancing compressed O_2 into foundry shaft furnaces. Figure 5 shows 5 prototype converging-diverging nozzles which have been spray-formed on sacrificial graphite mandrels. The graphite mandrels are subsequently burned out leaving a near-net shape nozzle. These nozzles will be delivered to APCI during the first quarter of FY-1994 for in-house lab screening tests.

Tubular components of MoSi_2 and MoSi_2 containing discrete layers of Al_2O_3 were fabricated during the last two quarters of FY-1993. Figure 6 shows tubular components approximately 4"-9" long which were fabricated using the plasma spray-forming process. Tube fabrication was also done on sacrificial graphite mandrels which

Fig. 5. Prototype converging/diverging nozzles produced by plasma spray-forming. Nozzles will be delivered to APCI for in-house testing.

Fig. 6. Various sizes of plasma spray-formed MoSi₂ and MoSi₂/Al₂O₃ composite tubes.

were subsequently drilled-out after the spray process. Preliminary investigations to characterize the tube strength of MoSi₂ in the as-sprayed condition and after heat-treatment at 1500°C for 2 hours has been done by Dr. John Hellmann et. al., at Pennsylvania State University, Center for Advanced Materials. The strength of plasma-sprayed MoSi₂ tubes were measured via diametral compression of O-ring and C-ring sections in air at room temperature. Weibull analysis of the strength distributions indicated that the as-sprayed material possessed a smaller flaw distribution (i.e., higher Weibull moduli of 13.0 for C-rings and 13.6 for O-rings) than material which was heat treated (Weibull moduli of 10.9 for C-rings and 8.0 for O-rings). The heat-treated material exhibited higher strengths (i.e., 54% for the c-rings and 40% for O-rings). Fractography revealed that critical flaws were associated with residual porosity which initiated failures at the surface of the tube sections (inner surface for O-ring and outer surface of c-ring). Table I summarizes the specimen dimensions and average strengths. The heat-treatment resulted in an increase in relative density from 91% to 95% which exhibited significantly higher strengths than the as-sprayed MoSi₂.

Investigations have been completed on the reactive plasma-spraying of MoSi₂ using a Ar/10%CH₄ powder carrier gas. Results of this investigation have shown that carbon and SiC particles could be incorporated into spray deposits of MoSi₂ as a result of in-flight reactions with the Ar/10%CH₄ gas precursor. These particles were subsequently used to getter the SiO₂ present in MoSi₂. HIPing of the sprayed deposits at 1800°C/206MPa for 2 hours, showed substantial decreases in the level of oxygen in the sprayed deposits. A factor of three increase in the elevated temperature yield strength was observed in 4-point bend tests at temperatures between 1100°C and 1400°C, Figure 7. Increases in the elevated temperature yield strength were attributed to a decrease in SiO₂ which can cause grain boundary slide in MoSi₂ at elevated temperatures. Formation of SiC particles in the HIPed samples resulted from the gettering of SiO₂ with carbon that was present in the MoSi₂ deposits.

Indentation Creep of MoSi₂

As reported in previous quarterly reports, specimens of both hot pressed and hot isostatically pressed MoSi₂-SiC composites were prepared for indentation creep experiments. The specimens contain 0, 5, 10, 20, 30, and 40 volume percent SiC. Five or six specimens of each were cut from pressed disks for testing at 1000-1200°C and 258.4-361.7 MPa. The objective of this work is to determine the effects that additions of SiC have on the creep behavior of MoSi₂; in particular, to determine whether such

TABLE I: Specimen Dimensions and Average Strengths for Plasma Sprayed and Heat Treated MoSi₂

MATERIAL	SPECIMEN GEOMETRY	OUTER RADIUS (mm)	INNER RADIUS (mm)	WIDTH (mm)	AVERAGE STRENGTH (MPa)
AS-SPRAYED	C-RINGS	8.128	6.350	9.449	135.6 (12.7) ^a
	O-RINGS	8.128	6.350	9.550	131.6 (11.1)
H.T. 1500°C 2HR.	C-RINGS	8.077	6.261	9.449	288.7 (37.5)
	O-RINGS	8.077	6.261	9.449	213.3 (30.1)

a - Number in parentheses represents one standard deviation.

Fig. 7. Elevated temperature yield strength of reactivity plasma-sprayed MoSi₂ deposits at temperatures between 1100°C and 1400°C.

additions improve the creep resistance of MoSi₂. A secondary objective of this work is establishing or developing indentation creep as useful method for characterizing the creep behavior of materials largely through efforts to correlate the complex stress state experienced during indentation creep with the simpler stress state of compressive creep.

As reported previously, the rate of creep of the MoSi₂-SiC materials increases with increasing SiC content from 0 to 20 volume %, and then decreases from 20 to 40 volume %. It was demonstrated that the complex dependence of creep on SiC content was associated with grain size and the amount of reinforcing phase (i.e., SiC). The addition of SiC decreased the grain size of the MoSi₂ by almost an order of magnitude. This lead to the significant increase in the creep rate between 0 and 20% SiC. However, the effect of SiC in obstructing grain boundary sliding dominated creep between 20 and 40% SiC leading to the observed decrease in creep rate.

Evaluation of the stress and grain size exponent and activation energies for creep gave no direct indication of the specific mechanism(s) controlling the creep rate. The grain size exponent was found to be greater than zero. Therefore, the rate controlling mechanism must be a boundary mechanism since lattice mechanisms are independent of grain size.

In order to more fully assess the rate controlling mechanism(s), microstructural studies were performed. Optical and SEM studies of polished cross sections through the indented regions combined with TEM studies indicated that the predominant mechanism for creep in these materials is grain boundary sliding. At SiC contents below 10-20 volume % there was severe cavitation indicating creep occurred by unaccommodated grain boundary sliding. At higher SiC contents the grain boundary sliding appeared to be completely accommodated apparently due to the smaller grain size of the MoSi₂. TEM studies showed that the SiC phase was primarily located at grain junctions and thus inhibits creep at higher concentrations by obstructing grain boundary sliding. The results suggest that the creep behavior of MoSi₂-SiC composites could be improved further by using a larger grain size MoSi₂ starting powder. Since the grain boundary surface area would be decreased by using a larger grain size material, it should be possible to get significant improvements in the creep behavior using smaller additions of SiC.

Efforts to correlate indentation with compressive creep behavior have worked relatively well. Preliminary finite element modeling of the axisymmetric indentation creep geometry have lead us to use a stress correction factory of 2.75 (i.e., the effective

stress on the specimen equals the stress on the indenter divided by 2.75). Using this correction factor it was found that the creep rates observed during indentation and compressive creep are statistically equivalent as are the stress exponents. However, the activation energies for creep are not in good agreement.

PUBLICATIONS

1. D. P. Butt, J. J. Petrovic, and H. H. Kung, "Indentation Creep of MoSi₂-SiC Composites," presented at Materials Week '93, Sponsored by the Minerals, Metals & Materials Society and ASM International, Pittsburgh, PA, October 1993.
2. D. P. Butt, J. J. Petrovic, D. A. Korzekwa, and H. H. Kung, "Creep Behavior of MoSi₂-SiC Composites," to be presented at the *Fall Meeting of the Materials Research Society*, December 1993.
3. D. P. Butt, J. J. Petrovic, D. A. Korzekwa, and H. H. Kung, "Creep Behavior of MoSi₂-SiC Composites," to be published in *High Temperature Silicides and Refractory Alloys*, Proceedings of the Fall Meeting of the Materials Research Society, 1993.
4. J. J. Petrovic, "MoSi₂-Based High-Temperature Structural Silicides," MRS Bulletin, XVIII (July 1993), 35-40.
5. J. J. Petrovic and A. K. Vasudevan, "Overview of High Temperature Structural Silicides," Proceedings, Symposium F: High Temperature Silicides and Refractory Alloys, Fall 1993 Materials Research Society Meeting, November 1993, Boston.
6. D. J. Bray, R. L. Hexemer Jr., K. A. Blakely, and J. J. Petrovic, "The Effects of Raw Material Preparation on Densification and Mechanical Properties of MoSi₂ Based Composites," Proceedings, Symposium F: High Temperature Silicides and Refractory Alloys, Fall 1993 Materials Research Society Meeting, November 1993, Boston.
7. J. D. Rigney, R. G. Castro and J. J. Lewandowski, "Insitu Fracture Monitoring of Plasma-Sprayed MoSi₂-Ta Composites" J. Mater. Sci. 28 (1983) 4023-4027.
8. R. G. Castro, H. Kung and P. W. Stanek, "Reactive Plasma-Spraying of MoSi₂ Using a Ar/10%CH₄ Carrier Gas" accepted for publication in Mater. Sci. Eng. A, October 1993.

9. S. P. Chen, R. Lesar and A. D. Rollett, " Modeling of Transformation toughening in composite materials", *Scripta Metallurgica et Materiali*, 28, 1393-1398 (1993).
10. S. P. Chen, "Modeling Mechanical Properties of Brittle Composites: The Separation of Transformation Toughening and Micro-cracking," in preparation.

PRESENTATIONS

1. J. J. Petrovic is a Co-Organizer of Symposium F: "High Temperature Silicides and Refractory Alloys" at the Fall 1993 Materials Research Society Meeting in November 1993 in Boston. This Symposium contains 51 presentations on structural silicide materials. There will also be a refereed Proceedings of the Symposium. J. J. Petrovic will present the first talk at this Symposium entitled "Overview of High Temperature Structural Silicides". Charles A. Sorrell will be a Session Chairman in the Session on Silicide Synthesis and Processing.
2. J. J. Petrovic and A. K. Vasudevan, "Overview of High Temperature Structural Silicides," Symposium F: High Temperature Silicides and Refractory Alloys, Fall 1993 Materials Research Society Meeting, November 1993, Boston.
3. D. J. Bray, R. L. Hexemer Jr., K. A. Blakely, and J. J. Petrovic, "The Effects of Raw Material Preparation on Densification and Mechanical Properties of MoSi₂ Based Composites," Symposium F: High Temperature Silicides and Refractory Alloys, Fall 1993 Materials Research Society Meeting, November 1993, Boston.
4. R. G. Castro, H. Kung and P. W. Stanek, "Reactive Plasma of MoSi₂ Using a Ar/10%CH₄ Powder Carrier Gas", presented at TMS/ASM Materials Week, Chicago IL (1992).
5. R. G. Castro, J. R. Hellman, A. E. Segall, and D. L. Shelleman, "Fabrication and Testing of Plasma Spray-Formed MoSi₂ and MoSi₂ Composite Tubes" to be presented at 1993 MRS Fall Meeting, Boston, MA (1993).

HONORS AND AWARDS

None.

PATENTS, LICENSES AND DISCLOSURES

1. Patent Pending: "Molybdenum Disilicide Composites Reinforced With Zirconia and Silicon Carbide," Inventor: John J. Petrovic, submitted to the U.S. Patent Office in June 1992.
2. Patent Pending: "Improved Molybdenum Disilicide Composites Reinforced With Zirconia and Silicon Carbide," Inventor: John J. Petrovic, submitted to the U.S. Patent Office in June 1992.
3. Patent Pending: "Reactive Plasma Spray of MoSi_2 and MoSi_2 Composites," Inventor: Richard G. Castro, submitted to the U.S. Patent Office in August 1993.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER ACTIVITIES

A CRADA entitled "Technology for Commercial Whisker-Reinforced Molybdenum Disilicide Composites" was signed in February 1993 with Advanced Refractory Technologies (ART) in Buffalo, New York. ART is an advanced ceramics company, and the only U.S. supplier of SiC whiskers. Under this CRADA, ART is establishing processing conditions and formulating blends of their SiC whiskers with MoSi_2 powders, and supplying these blends to Los Alamos. Los Alamos is consolidating these supplied ART SiC whisker- MoSi_2 powder blends by hot pressing/hot isostatic pressing, and evaluating the properties of the consolidated composites. Properties of interest are the composite microstructures, strength, fracture toughness, and creep resistance. ART and Los Alamos are working jointly to identify and exploit commercial applications for these materials.

The first SiC- MoSi_2 blends were received from ART in late June 1993. A second shipment of blends was received from ART in late September 1993. The following blends containing different volume fraction amounts of SiC reinforcement have been received. Each blend is a 500 gm batch.

Blend Conc. MoSi ₂ /SiC (vol/vol %)	M-Grade SiC(w) (Lot No.)	R-Grade SiC(w) (Lot No.)	Starck A-10 SiC(p) (Lot No.)
100/0	ARSEM-0	ARSER-0	ARSEA10-0
90/10	ARSEM-10	ARSER-10	ARSEA10-10
80/20	ARSEM-20	ARSER-20	ARSEA10-20
70/30	ARSEM-30	ARSER-30	ARSEA10-30
60/40	ARSEM-40	ARSER-40	ARSEA10-40
50/50	ARSEM-50	ARSER-50	ARSEA10-50

ART manufactures two grades of SiC whiskers, an M-Grade and an R-Grade. The M-Grade material is stoichiometric SiC, with primarily a beta phase structure. The whisker diameter is approximately 1.5 microns, with a whisker aspect ratio of approximately 12. Whisker surface morphology is uniform and relatively smooth. The R-Grade material is similar to the M-Grade material, but is primarily alpha phase and contains more particulate content. The M-Grade SiC whiskers are slightly more expensive than the R-Grade SiC whiskers. The H.C. Starck A-10 SiC powders are submicron in size, and are included in the study for comparison purposes to the SiC whiskers.

Initial consolidation work of the ART blends has focused on establishing the optimum consolidation temperature for these composites, optimizing the consolidated microstructures obtained from the blends, and consolidating an initial series of Grade M SiC whisker composites for initial property evaluations. The following hot pressings have been made to date:

Hot Pressing Run #	ART Blend Type	Consolidation Temp. (°C)	Hot Pressed Density	Comments
558	ARSEM-30	1600	93.4%	Used as-received blend. The SiC whisker distribution in the composite was inhomogeneous.
560	ARSEM-30	1700	93.0%	Used as-received blend. The SiC whisker distribution in the composite was inhomogeneous.
561	ARSEM-30	1800	95.9%	Used as-received blend. The SiC whisker distribution in the composite was inhomogeneous.
562	ARSEM-30	1800	94.7%	Roll-blended as-received blend before hot pressing. Homogeneous whisker distribution observed in the composite.

563	ARSEM-30	1600	94.4%	Roll-blended as-received blend before hot pressing. Homogeneous whisker distribution observed in the composite.
564	ARSEM-0	1600	94.9%	Roll-blended.
565	ARSEM-10	1600	94.5%	Roll-blended.
566	ARSEM-20	1600	94.9%	Roll-blended.
567	ARSEM-30	1600	95.6%	Roll-blended.

Our initial pressings of as-received blends from ART showed the presence of relatively large regions of SiC whisker inhomogeneity, which were of approximate dimensions 0.7 mm length by 0.1 mm width. Such regions were regions of higher than average whisker volume fraction, and would have an adverse effect on the composite mechanical properties. These inhomogeneity regions resulted from clumps of whiskers which were present in the as-received ART blends. We determined that a simple roll-blending operation on the as-received ART blends was sufficient to disperse the SiC whisker clumps in the blends which led to these inhomogeneities. Consolidated microstructures of these roll-blended materials did not exhibit any SiC whisker inhomogeneities in the consolidated microstructure. This information was communicated to ART, so that they could modify their blend processing accordingly.

The effect of hot pressing consolidation temperature was assessed. Hot pressed densities obtained at 1600°C were similar to those obtained at 1800°C. In addition, microstructural observations suggested that some coarsening and alteration of the SiC whisker morphology may occur at 1800°C. For these reasons, the 1600°C consolidation temperature is currently considered to be best. Additionally, a lower consolidation temperature is desirable from an industrial viewpoint.

Having established some of the optimization aspects of the consolidation of the SiC whisker-MoSi₂ matrix composites, we are now in the process of microstructural and mechanical property evaluations as a function of consolidation temperature and volume fraction of SiC whiskers. A series of Grade M SiC whisker composites with 0, 10, 20, and 30 vol.% whiskers has been fabricated by hot pressing at 1600°C. Now that we have received the blends, we will also fabricate 40 and 50 vol.% composites. We are now in the process of evaluating microstructures, indentation fracture toughness, and strength of these materials, as a function of temperature. We will also attempt indentation creep

studies as a function of volume fraction of SiC whiskers. In parallel with these characterization studies on the Grade M SiC whisker composites, we will fabricate a series of Grade R SiC whisker and A-10 SiC powder composites as a function of volume fraction, for comparison to the Grade M materials.

The following blends from ART containing carbon additions were received from ART in September 1993:

Blend Conc. MoSi ₂ /SiC (vol/vol %)	Blend Designation (Lot. No.)	Type SiC(w) Reinforcement	Wt. % Carbon
100/0	PRBCSE-0-1.0	None	1.0
100/0	PRBCSE-0-2.0	None	2.0
70/30	PRBCSEM-30-1.0	Grade M	1.0
70/30	PRBCSEM-30-2.0	Grade M	2.0
70/30	PRBCSER-30-1.0	Grade R	1.0
70/30	PRBCSER-30-2.0	Grade R	2.0

The purpose of the carbon additions in these blends is two-fold. First, the carbon can react with silica present on the surfaces of the MoSi₂ powder to remove this silica and also form in-situ SiC. Previous work has shown that removal of the silica improves the composite high temperature mechanical properties. Secondly, the carbon may also act to weaken the interface between the SiC whiskers and the MoSi₂ matrix. This interfacial modification may lead to higher fracture toughness values of the composites. We will begin the fabrication of these carbon-containing composites in the near future.

COST SHARING

A formal agreement for cost sharing has been concluded with ART, as described above. Tests by Liquid Air and Air Products on the applicability of silicide composites for burner applications will be conducted by the companies and represents an (informal) cost sharing with the intermetallics program at LANL.

Interactions with Air Products and other companies have been described elsewhere in this report.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Synthesis and Design of Intermetallic Materials

PHASE: FY94

COMPLETION DATE: Open

Performing Organization: Los Alamos National Laboratory (LANL)

Principal Investigators: Anthony. D. Rollett, J. J. Petrovic, R. G. Castro and S.-P. Chen
(505 667 4366)

PHASE OBJECTIVE: Develop and deliver prototypical MoSi_2 -based components to industry for testing in high-temperature applications, e.g. advanced gas burner nozzles.

ULTIMATE OBJECTIVE: Develop MoSi_2 -based composites that will combine good room temperature fracture toughness with excellent oxidation resistance and high-temperature strength for industrial applications.

TECHNICAL APPROACH: Apply composite synthesis principles from advanced ceramic composites, such as the addition of SiC particles or whiskers and phase transformation toughening additions such as partially-stabilized zirconia. Test the composite materials for toughness and strength. Develop an integrated set of modeling tools that cover length scales from atomistic, through continuum mechanics to discrete mechanics models that model microstructural effects. Develop new compositions with other high temperature materials such as Si_3N_4 .

PROGRESS: Plasma spray has proved to be very successful for fabricating MoSi_2 -based gas burner nozzles. Five such tubular components have been delivered to Air Products for industrial testing. Development of laminated composites of MoSi_2 with Al_2O_3 interlayers has shown promising results for advanced versions of nozzles. A new development has been the synthesis of Si_3N_4 - MoSi_2 composites, where the minority silicide phase provides conductivity for electro-discharge machining and ductile reinforcement at high temperatures; a patent has been obtained for this development. Good progress has been made on the CRADA-based work with Advanced Refractory Technologies (ART) on the development of MoSi_2 - SiC composites. Indentation Creep has been demonstrated to be an efficient method for screening the high temperature deformation properties of MoSi_2 -based materials. Micromechanical modeling of composites with brittle matrices, such as those being synthesized, has guided the experimental effort, as well as producing scientifically novel results.

Accomplishments: Los Alamos now has significant industrial interactions aimed at developing industrial applications for silicides, e.g. a CRADA with ART on MoSi_2 - SiC composites; collaboration with Air Products on gas burner nozzles.

Licenses: -

Awards: -

PROJECT TITLE: Synthesis and Design of Intermetallic Materials, continued.

Products: LANL-Advanced Refractory Technologies (ART) development of MoSi₂-SiC composites.

Industrial Activities: CRADA ongoing with ART (Buffalo, NY). Collaboration with Air Products on advanced gas burner nozzles.

Patents: Five issued; new patent obtained for MoSi₂-Si₃N₄ composites.

CRITICAL ISSUES:

- MoSi₂ undergoes a brittle-to-plastic transition at about 1100°C and is too soft above that temperature for structural applications. Therefore it must be strengthened to raise its creep resistance. SiC reinforcement has been shown to accomplish this.
- MoSi₂ is also too brittle at room temperature and current work on phase transformation toughening additions and ductile metal additions are addressing this issue.
- Thermal shock and thermal fatigue are important material properties for high temperature applications, such as natural gas burners.
- Any additions made to MoSi₂ should not significantly diminish its inherent oxidation resistance. This issue is being addressed by other programs.
- Microstructural effects are very important for control of toughening: modeling of MoSi₂ now includes both continuum and discrete micromechanics approaches.

FUTURE PLANS:

- *Technical:* Develop microstructurally realistic models of toughening for materials with combined reinforcements, such as ZrO₂ and SiC. Fabricate novel composites with silicides, e.g. Si₃N₄-MoSi₂ composites.
- *Technology Transfer:* Collaborate with manufacturers of industrial burners on development of advanced burners based on MoSi₂ composites. Collaborate with Advanced Refractory Technologies on the development of commercial source for MoSi₂ with SiC reinforcement composites. Continue to work with Exxon on modeling fracture in composites.

POTENTIAL PAYOFF:

For Energy Conservation: Anticipated energy savings from operating devices at higher temperatures and higher thermal efficiencies, e.g. burners, heat exchangers, gas turbines.

For Materials Technology: Anticipated benefits include improved materials for high temperature structural components, such as gas turbine components, heating elements in furnaces and waste heat regeneration components.

PROJECT TITLE: Synthesis and Design of Intermetallic Materials, continued.

Figure compares the high temperature strength of various composites of MoSi₂: a) MoSi₂-10%ZrO₂-10%SiC; b) MoSi₂-10%ZrO₂-10%SiC with 2% carbon; MoSi₂-20%SiC (w); d) plasma sprayed MoSi₂ with reactive gas (CH₄). Note that there are several alternate processing routes available for this material that combine toughness with high temperature strength.

Synthesis and Design of Intermetallic Materials

FY93 Significant Accomplishments

- Prototypical net shape Gas Burner Nozzles have been fabricated by the Plasma Spray technique for test by an industrial collaborator, Air Products.
- Collaborative development of MoSi₂-SiC(w) composites with Advanced Refractory Technologies (Buffalo, NY) is making excellent progress. Results have already suggested that an expensive processing step (hot isostatic pressing) can be eliminated.
- A composite of MoSi₂ and Si₃N₄ has been fabricated that has low enough resistivity to be machinable by the electro-discharge technique (EDM).
- A parametric study of the effect of microstructural design on composite toughness has been completed with the aid of a computer model that incorporates the micro-mechanics of transformation toughening. The results show, for example, that the contribution of micro-cracking to the overall toughness of composites (e.g. MoSi₂-ZrO₂) is small.

Ni₃Al TECHNOLOGY TRANSFER

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INTRODUCTION

Ductile Ni₃Al and Ni₃Al-based alloys have been identified for a range of applications. These applications require the use of material in a variety of product forms such as sheet, plate, bar, tubing, piping, and castings. Although significant progress has been made in the melting, casting, and near-net-shape forming of nickel aluminides, some issues still remain. These include the need for (1) high-strength castable composition for turbochargers, furnace furniture, and hot-die applications; (2) castability (fluidity, hot-shortness, porosity, etc.); (3) weld reparability of castings; and (4) hot fabricability of cast ingots. All of the issues listed above can be "show stoppers" for the commercial application of nickel aluminides. This report describes work completed to address some of these issues during the fourth quarter of FY 1993.

TECHNICAL PROGRESS

Summary

The casting of test bars and turbochargers continued at PCC Airfoils, Inc. (Douglas, Georgia). Among the several approaches attempted to eliminate the reaction of zirconium in the castable nickel-aluminide composition with the investment shell material, the addition of a stronger oxidizing element to the alloy other than zirconium has been identified to be the most practical one. Several test-bar trials at PCC Airfoils followed by tensile, fatigue, and metallography at the Oak Ridge National Laboratory (ORNL) have helped optimize the amount of the strong oxidizer. A batch of turbochargers of the new composition has confirmed the complete elimination of the surface reaction. A larger batch of the new composition is currently being procured from a commercial source and will be used to cast a large batch of turbochargers for engine testing.

As part of a General Motors-Saginaw Division (GM-Saginaw) [Saginaw, Michigan] Cooperative Research and Development Agreement (CRADA), ten 1-in. by 2-in. test coupons were cut from trays cast at two different times. One tray contained low silicon, and the other tray contained a slightly higher amount. One surface of each coupon was machined and a hole drilled for its attachment to a box used in the heat-treating furnace. A weld bead each of IC-221W composition and a newly developed low-aluminum weld wire (IC-221LA) were also placed on the machined surface of the coupons. The coupons have been in the furnace test since July 1993. A similar set of coupons from the currently used HU material was also installed in the furnace for comparative testing. The HU coupons were supplied by Alloy Engineering & Casting Company (Champaign, Illinois).

The weld-wire-composition optimization continued. Two sets of weld-wire compositions have been identified. The first one is known as IC-221W and is suitable for weld-overlay deposits on a range of base materials. The second weld-wire composition is

known as IC-221LA. This composition contains lower aluminum and high chromium and is suitable for weld repair of castings and fabrication of components. Work was initiated with The Pennsylvania State University on evaluation of hydrogen embrittlement during laser welding of nickel-aluminide alloys.

Many interactions occurred with industry. The most significant interactions were with Cummins Engine Company, Inc. (Columbus, Indiana); PCC Airfoils; GM-Saginaw; Alloy Engineering; Texas Instruments (TI) [Attleboro, Massachusetts]; Rapid Technologies, Inc. (Newnan, Georgia); Metallamics, Inc. (Traverse City, Michigan); and Sandusky International (Sandusky, Ohio). All of these companies have contributed significantly to the commercialization effort on nickel aluminides. PCC Airfoils has made the most technical and financial contributions to this program during this quarter.

Milestones

1. Optimize alloy composition/casting parameters to reduce casting defects. Start 10/92. End 9/93.

The IC-221M alloy is the high-strength, castable alloy optimized for its castability through a joint program between ORNL, PCC Airfoils, and Cummins. One of the nagging problems in the use of IC-221M alloy for production-quantity turbochargers has been the surface reaction between the alloy and the ceramic shell material. A closely coordinated joint program between ORNL, PCC Airfoils, and Cummins has made significant progress to eliminate the surface reaction during the last quarter. Detailed metallography and microprobe analysis have confirmed that the reaction is from the oxidation of zirconium in the alloy to ZrO_2 . The extent of reaction is dependent on the zirconium content of the alloy. No reaction is observed for zirconium content of ≤ 0.85 wt %. However, the lower zirconium content also introduces porosity in the casting. A further examination revealed that the reaction can be reduced by:

- (1) eliminating the grain refiner, (2) minimizing the contact time at $\geq 1000^\circ\text{C}$ between the

casting and the shell, and (3) controlling the zirconium content of the alloy. All three approaches are currently being investigated. For each approach, ORNL supplies the melt stock. The test bars are cast at PCC Airfoils, and PCC Airfoils conducts the initial metallography with follow-up metallography and fatigue testing performed at ORNL. The metallography and fatigue data are used to make decisions for the follow-up experimental condition.

The IC-221M alloy composition was modified by the addition of a stronger oxidizer than zirconium to eliminate the surface reaction. After several casting trials, metallography, and mechanical properties testing, a composition designated as IC-221HP has been identified to be free of reaction with the mold shell material. This composition not only eliminates the reaction with the shell material but also gives optimum mechanical properties, with fatigue properties still significantly better than the currently used alloy IN-713C.

A set of turbochargers have also been cast from the IC-221HP composition. The turbochargers showed no surface reaction and an acceptable level of microporosity. However, some shrinkage of porosity was observed in the hub section of the turbocharger. The shrinkage of porosity in the hub section can be eliminated by a slight modification of the mold and pouring temperatures. A large batch of alloy IC-221HP has been ordered from Cannon Muskegon Corporation (Muskegon, Michigan). The alloy cast will be paid for by Cummins. At the availability of the alloy, both the test bar and turbocharger castings will be carried out with three objectives in mind which include: (1) cast test bars to confirm the performance of a commercially melted larger batch of IC-221HP, (2) cast test bars to further optimize casting conditions to minimize porosity, and (3) cast sufficient turbochargers for engine testing at Holset Engineering Company, Inc. (Madison, Indiana). Most of this work is expected to be completed by the end of the third quarter of FY 1994.

2. Castability of nickel aluminides. Start 10/92. End 9/93.

A computer software was procured to model the mold design for proper mold filling with minimum shrinkage areas. The software will be applied to the sand castings of nickel-aluminide alloys and, especially, to the heat-treating trays for GM-Saginaw. The software was installed on the computer. A preliminary computer analysis of a sand-cast test block of nickel aluminide was completed. The computed results were confirmed by the actual measurements of the test block. These results are now being extended to a tray casting.

3. Weld reparability of castings. Start 10/92. End 9/93.

Efforts continued in several areas which include: (a) optimization of filler-wire composition for weld repair of sand castings and the fabrication of components, (b) obtaining commercial quantities of weld wire of selected compositions, (c) preparation of weld overlays, (d) preparation of simulated welds and training, and (e) weld metal mechanical properties. Significant progress has been made in all of these areas, and a brief highlight for each activity is listed below:

A. Optimization of Filler-Wire Composition for Weld Repair of Sand Castings and the Fabrication of Components. The previously developed filler-wire composition (IC-221W) was found to produce cracks during the weld repair of castings, especially under severe restraint conditions. At this point, it was identified that limited high-temperature ductility of IC-221W was the primary cause for such cracking. In order to improve the ductility, a filler wire of lower aluminum content was identified. This composition is known as IC-221LA and contains sufficient aluminum to provide the desired oxidation and carburization resistance needed for many applications. This composition has sufficient ductility to not only prevent weld cracking but also to allow its wire fabrication through normal ingot metallurgy route. A patent disclosure is currently being planned on the new composition.

B. Obtaining Commercial Quantities of Weld Wire of Selected Compositions. The encapsulating of prealloyed powder in a nickel strip has been identified as the most economical method for the fabrication of nickel-aluminide weld wire of both IC-221W and IC-221LA compositions. The powder compositions are properly compensated for in the nickel content of the strip. Using this method, spools of 1/8- and 1/16-in.-diam wire of IC-221W weighing 25 lb each were procured from Ametek Specialty Metal Products Division (Eighty Four, Pennsylvania). The performance of the wire produced by this method was so good that an additional 50 lb of the 1/16-in.-diam wire in two 25-lb spools are currently on order. Since the performance and the price of the IC-221W were so good by the prealloyed encapsulation method, orders are currently in place with Ametek to supply 100 lb of the IC-221LA wire.

C. Preparation of Weld Overlays. The availability of 1/16-in.-diam wire has made possible the automated, high-deposition-rate weld deposits of IC-221W and IC-221LA compositions. The initial trials have shown that up to 1/4-in.-thick layers of IC-221W composition can be successfully weld-overlay deposited on base materials such as mild steel, 2-1/4Cr-1Mo, 9Cr-1Mo, steel, and type 304 stainless steel. The weld overlays are now being extended to alloys such as HU and Inconel 800H. The success of weld overlays opens up an opportunity of using nickel aluminides as high-quality and inexpensive coatings on other materials to take advantage of their oxidation and carburization resistance. Metallography and hardness testing of the weld overlays are currently under way.

D. Preparation of Simulated Welds and Training. The roller assemblies currently being manufactured as part of Metallamics' CRADA at Sandusky required a great deal of welding. In order to avoid any problems during commercial fabrication, several steps were taken at ORNL. The first step was to obtain a 4-in.-long ring from each of the centrifugally cast pipe from Sandusky. Sections were cut from one of the rings to

machine-weld configurations that simulated the actual assembly design. The welding of the sections from the ring was carried out to finalize the weld-wire composition and the welding parameters. The IC-221LA composition was identified as the best filler-wire composition and gas tungsten arc as the best welding method. Since the commercial wire of IC-221LA was not available, it was prepared at ORNL through the making of the ingot, extrusion, and cold-swaging process combinations. The wire was produced in 3/32- and 1/8-in.-diam sizes. Sufficient wire was produced for the welding of two roller assemblies.

The welding technology including the process parameter and weld-wire requirements were transferred to Sandusky through a visit by the welder experienced in welding nickel aluminide at ORNL. The major step in transferring the welding technology was to train Sandusky in the use of the gas tungsten arc process as opposed to the stick electrode process that is used frequently in industry. The welder at Sandusky was sufficiently trained to weld repair some defects that were observed in the trunnion shaft during machining.

E. Weld Metal Mechanical Properties. During the filler-wire optimization, sheets were fabricated from four different compositions. Tensile tests were conducted on specimens from the sheets at temperatures ranging from room temperature to 1000°C. The composition with the best combination of strength was chosen for the fabrication of weld wire and the welding trials. Weldment tests are planned on selected welds fabricated from the chosen weld composition.

4. Hot workability of IC-218LZr, Start 10/92, End 9/93.

The IC-218LZr alloy is selected for use as aerospace fasteners and for other applications where cast components cannot be used. It is essential that a commercial source be developed for the production of wrought product from this alloy. One possible route for commercial rod can consist of casting 3- to 4-in.-diam ingots, encapsulating the

ingots in a mild steel can, and hot extruding to a ratio exceeding 16:1. The hot-extrusion temperature for the alloy is 1100°C. The extrusion ratio of 16:1 results in a complete breakdown of cast structure into an equiaxed, fine-grain structure. The bar produced is machined or acid cleaned to remove the can. The procedure just described has been used commercially for a 100-lb batch of IC-218LZr. The bar produced could be cold swaged to different sizes. The hot-extruded and cold-swaged bars have been successfully fabricated into aircraft fasteners by Valley Todeco (Sylmar, California).

Although the procedure described above has been used only once, a source for bar needs to be established. This source needs to coordinate the activities of an ingot producer, extruder, machining, and cold working. Efforts will continue to establish such a source.

5. Hydrogen embrittlement during laser welding of nickel-aluminide alloys. Start 10/92. End 9/93.

The progress made during the first year of study of hydrogen embrittlement during laser welding of nickel aluminide is outlined below:

Examination of the base IC-221M, IC-221W, IC-396M, and IC-396W alloys confirmed that the Ni₅Zr eutectic constituent was presented in all of the castings. Microhardness testing showed that the centers of the 25- × 25- × 75-mm castings were significantly softer than the outer edges. This variation in hardness was attributed to a transition from columnar to equiaxed grains found near the centers of the castings.

Welds produced by ORNL with metal-powder-cored wire of the IC-221W composition were analyzed in some detail. Weld deposits were made with as-fabricated wire, and with wire which had been vacuum heat treated in an effort to reduce possible contamination from undesirable trace elements such as hydrogen. Weld beads made with both wires cracked in a similar manner, and both exhibited similar microstructures. The appearance of the cracks was consistent with a solidification cracking mechanism, and all

were associated with zirconium enrichment, as found in previous studies. Indications about a possible influence of hydrogen on the cracking were inconclusive. Initial laser-beam welding indicated that there was no evidence of hydrogen-assisted cracking under ambient conditions.

A final testing matrix and procedures were established to examine the relative importance of hydrogen-assisted cracking and solidification cracking. A method of precharging specimens will be used to produce a range of hydrogen concentrations in the alloys prior to welding. Also, a device for preloading specimens to a controlled stress level was designed and fabricated.

6. Fracture-toughness properties of nickel-aluminide alloys. Start 10/92. End 9/93.

Several papers dealing with the fracture toughness of nickel aluminides have been published. Work is currently under way to determine the environmental effects on fracture toughness in the temperature range of 600 to 800°C.

7. Technology transfer activities. Start 10/92. End 9/93.

The purpose of this milestone is to undertake activities that will promote the transfer of nickel-aluminide technology to industry. These activities include visiting potential producers and users of materials and describing the technology in detail, training industry personnel either at ORNL or at the industrial facilities, and holding technology transfer meetings at ORNL. As a result of these activities, several additional applications have been identified for these materials.

Strong interaction continued with TI in support of their activity to develop the nickel-aluminide alloy IC-50 for automotive, catalytic-converter application. At the request of TI, ORNL supplied the physical property data on the alloy. TI is developing a plan to produce a large quantity of 2-mil foil from IC-50. ORNL is working closely with TI to maximize the chance of success. Toward this goal, ORNL supplied a long piece of as-cast IC-50 to produce a larger quantity of 2-mil-thick foil for catalytic-converter applications.

A new collaboration was started with Rapid Technologies (a furnace company) for the use of alloy IC-396M and, potentially, NiAl. The specific application is for rails in a walking-beam furnace. Rapid Technologies will use Cast Masters (Bowling Green, Ohio) [ORNL's licensee] to fabricate the parts. ORNL will make sure that Cast Masters selects the correct composition and Rapid Technologies receives the data needed in support of the proposed application. Rapid Technologies will share the operating experience on the rails with ORNL. The investment-cast parts of the Ni₃Al alloy were cast by Cast Masters and have been operating in furnaces at Rapid Technologies for several weeks.

Based on the successful experience, Rapid Technologies has decided to procure a license from ORNL. As part of the licensing agreement, Rapid Technologies will not only use nickel-aluminide components in their furnaces but will market it to others. The licensing agreement is currently being negotiated and is expected to be signed during the next quarter.

A CRADA is also being negotiated with Rapid Technologies to address some of the special issues related to the application of nickel aluminides in walking-beam furnaces. The CRADA is expected to be approved during the next quarter.

It has been decided to hold the technology transfer meetings every second year. Therefore, the next meeting will be scheduled in 1994.

PUBLICATIONS

1. K. H. Wu and C. T. Liu, "Reactive Sintering of Ni₃Al Intermetallic Alloys Under Compressive Stress," pp. 841-46 in *High-Temperature Ordered Intermetallic Alloys V*, Vol. 288, ed. Ian Baker, Ram Darolia, J. Daniel Whittenberger, and Man H. Yoo, Materials Research Society, Pittsburgh, PA, 1993.
2. David J. Alexander, "High Temperature Fracture Toughness of Ni₃Al Alloy IC-396M," pp. 1185-90 in *High-Temperature Ordered Intermetallic Alloys V*, Vol. 288, ed. Ian Baker, Ram Darolia, J. Daniel Whittenberger, and Man H. Yoo, Materials Research Society, Pittsburgh, PA, 1993.

3. C. T. Liu, "Recent Advances in Ordered Intermetallics," pp. 3-19 in *High-Temperature Ordered Intermetallic Alloys V*, Vol. 288, ed. Ian Baker, Ram Darolia, J. Daniel Whittenberger, and Man H. Yoo, Materials Research Society, Pittsburgh, PA, 1993.

PRESENTATIONS

1. Vinod K. Sikka, "Properties of P/M Processed $\text{Ni}_3(\text{Al},\text{Si})$ with Chromium Additions," 1993 International Conference & Exhibition on Powder Metallurgy and Particulate Materials, Nashville, TN, May 16-19, 1993.
2. Vinod K. Sikka, "Nickel and Iron Aluminides for High-Temperature Aggressive Environments," symp. High Temperature Intermetallics, Materials Week '93, Materials Research Society, Pittsburgh, PA, October 20, 1993.
3. Vinod K. Sikka, "Casting and Properties of Nickel-Aluminide Alloys," symp. High Temperature Intermetallics, Materials Week '93, Materials Research Society, Pittsburgh, PA, October 18, 1993.
4. David J. Alexander, "High-Temperature Fracture of Ni_3Al Alloy IC-218LZr," symp. High Temperature Intermetallics, Materials Week '93, Materials Research Society, Pittsburgh, PA, October 20, 1993.
5. K. H. Wu and C. T. Liu, "Reactive Sintering of Ni_3Al Intermetallic Alloys Under Compressive Stress," symp. High-Temperature Ordered Intermetallic Alloys V, Materials Research Society, Boston, Massachusetts, November 30-December 3, 1992.
6. David J. Alexander, "High Temperature Fracture Toughness of Ni_3Al Alloy IC-396M," symp. High-Temperature Ordered Intermetallic Alloys V, Materials Research Society, Boston, Massachusetts, November 30-December 3, 1992.
7. C. T. Liu, "Recent Advances in Ordered Intermetallics," symp. High-Temperature Ordered Intermetallic Alloys V, Materials Research Society, Boston, Massachusetts, November 30-December 3, 1992.

8. Vinod K. Sikka, "Advanced Intermetallic Alloys: Nickel and Iron Aluminides," WATtec '93, Knoxville, Tennessee, February 19, 1993.

HONORS AND AWARDS

V. K. Sikka was chosen as a 1993 Fellow of ASM International and was honored at the ceremonies during the annual ASM meeting at Pittsburgh, Pennsylvania, during October 1993.

PATENTS/DISCLOSURES

A patent application by M. L. Santella and V. K. Sikka, entitled "Improved Method of Fabricating Wires of Intermetallic Alloys for Welding," ESID No. 1174-X was filed in July 1993.

LICENSES

Negotiations were started for a licensing agreement with Rapid Technologies.

COST INFORMATION

PERSONNEL INFORMATION

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

CRADA with GM-Saginaw on Use of Nickel Aluminides in Heat-Treating Furnace:

The optical and scanning electron microscopy of selected pieces of the destructively tested trays was also presented at the review meeting held on April 19, 1993.

One of the weld-repaired tray was supplied to GM-Saginaw for furnace testing. In addition to the tray, ten test coupons each of low and high silicon trays with two welds each and a mounting hole were also supplied. The tray with test coupons is expected to go into the batch furnace for testing during the third week of September. The test coupons will be taken out at 1, 2, 3, 4, 6, 12, 18, 24, 30, and 36-months duration from the starting date. The exposed samples will be metallographically evaluated at ORNL.

Test coupons of nickel aluminide and HU materials after one month of exposure in the batch furnace were metallographically examined at ORNL. Metallography and hardness data on the furnace-exposed samples were compared with the data on the coupons tested under simulated conditions at ORNL. The results on the coupons after the one-month exposure were presented at the meeting held at GM-Saginaw on September 24, 1993.

CRADA with Metallamics. The objective of the CRADA with Metallamics is to centrifugally cast the nickel aluminide for roller applications. Under this CRADA, two rollers are being cast by Sandusky and four trunnions are being cast by Alloy Engineering & Casting. The centrifugally cast rollers and trunnions will be machined and welded by Sandusky. The assembled rollers will be tested at Bethlehem Steel. ORNL is playing a very significant role in this effort which includes: (1) helping in the melting procedure, (2) developing chemical analysis standards, (3) providing weld wire, (4) training Sandusky welders in the welding of nickel aluminide, (5) mechanical properties of cast pipe, and (6) mechanical properties of weldments made in the cast pipe.

Two 14-1/2-in.-OD by 1-in.-wall-thick pipes were centrifugally cast at Sandusky. No problems were encountered in either melting or casting of the pipes. Sandusky also prepared sufficient master alloy for casting four trunnions at Alloy Engineering & Casting. All four trunnions of acceptable quality were cast and shipped to Sandusky. It was decided, with Bethlehem Steel's agreement, to install two of the rollers, one with the as-cast surface and the other with the machined surface. The pipe that needed to have the machined surface was machined even though successful machining was considered to be an extremely slow process by Sandusky. The machining of the trunnions has also been completed. The welding of the trunnions to the rollers and shipping of the completed assemblies are expected during the next quarter. The roller assemblies are expected to go into service in Bethlehem Steel's furnace during the first week of January 1994.

COST SHARING

A very significant cost sharing has been made by Rapid Technologies in developing the walking-beam furnace applications (approximately \$70 K). A similar cost share has been made by TI in the catalytic converter application of IC-50. Both GM-Saginaw's and Metallamics' CRADAs are fifty-fifty cost-share programs.

APPLICATION OF Ni₃Al-BASED ALLOYS FOR WALKING-BEAM FURNACES

Problem:

The walking-beam furnaces are used for progressively heating the work piece from room temperature to a temperature where it is formed into a final shape by a step known as closed-die fabrication. The work piece travels on a set of beams. The travel distance is typically 15 ft from the entrance to the exit. The walking beams are nominally 24 in. long × 8 in. high × 1 in. thick with the top edge being of a saw-tooth configuration. The work piece travels by moving from saw tooth to saw tooth. The beam's life, especially on the exit end of the furnace, with the current materials was only 200 h. The failures were related to a combination of oxidation, reaction of the oxidation product with the oxide scale on the work piece, and melting.

Results:

The nickel-aluminide alloys have been identified to extend the beam life by factors of four to five and at a cost of approximately one-fourth of that of the currently used material. The Ni₃Al-based alloy parts can be sand cast into shapes and even welded as opposed to the current material, which could only be formed into beams by machining and is unweldable. The prototype parts of Ni₃Al-based alloy have been cast and field tested for their significantly improved performance.

Cast Prototype Beam of Nickel Aluminide for Use in Walking-Beam Furnace

Significance - For Energy Conservation:

The walking-beam furnaces designed by Rapid Technologies, Inc. (Newnan, Georgia) is the most energy efficient method of heating work pieces world wide. The use of nickel aluminide for the beam allows the implementation of such energy efficient technology in manufacturing.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

WORK ELEMENT: High-Temperature Materials

PROJECT TITLE: Ni₃Al Technology Transfer

PHASE: FY 1993

PHASE COMPLETION DATE:

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

PRINCIPAL INVESTIGATOR(S): V. K. Sikka (615) 574-5112; M. L. Santella (615) 574-4805; C. T. Liu (615) 574-4459; J. R. Weir, Jr. (615) 574-4064; and D. J. Alexander (615) 574-4467

PHASE OBJECTIVE: To conduct additional research needed to mature the Ni₃Al and Ni₃Al-based alloy technology for industrial applications and commercial manufacturing.

ULTIMATE OBJECTIVE: (1) To commercialize the Ni₃Al and Ni₃Al-based alloys, and (2) to help U.S. materials industries to take the lead in the world market on intermetallic alloys.

TECHNICAL APPROACH: Conduct activities in support of: (1) optimize compositions for high-strength castable compositions for turbochargers and hot-die applications; (2) castability studies including fluidity, hot-shortness, and porosity; (3) weld reparability of castings and weld procedure development; (4) hot fabricability of IC-218LZr composition; (5) develop fracture toughness data on cast and wrought compositions; and (6) conduct technology transfer activities.

PROGRESS: A significant progress was made in the maturation of nickel-aluminide technology and applications. A close collaboration between ORNL, Cummins Engine Company (Columbus, Indiana), and PCC Airfoils, Inc. (Douglas, Georgia) has helped eliminate the nagging problem of near-surface reaction between zirconium in the alloy and the investment-casting shell material. The problem has been fixed by the addition of a strong oxidizer in the alloy, and the new alloy composition has been identified as IC-221HP. A large size heat of this composition is currently being melted by a commercial vendor in order to cast a large batch of turbochargers for engine testing. Two trays and 20 test coupons have been in furnace test at General Motors-Saginaw (GM-Saginaw) [Saginaw, Michigan] since July 1993. The results of coupon tests will be reviewed at the forthcoming meeting in February 1994 to plan the next set of castings at Alloy Engineering & Casting Company (Champaign, Illinois). The roller casting and fabrication in support of furnace-roll installation at Bethlehem Steel Corporation - Burns Harbor Plant Chesterton, Indiana) continued as planned. The roller assembly will be shipped to Bethlehem Steel in December 1993.

Significant progress has been made in the identification of wire compositions for weld repair of castings and for weld overlays. Sources were established for the procurement of commercial-quantity weld wire of both compositions. Welding technology was transferred to Sandusky International (Sandusky, Ohio) through training of their welder.

Patents: 1 Disclosure
Books: 0

Publications: 4
Presentations: 8

Proceedings: 1

PROJECT TITLE: Ni₃Al Technology Transfer

ACCOMPLISHMENTS:

Licenses: Supported the activities of eight of the current licensees.

CRADAs: Actively participated in CRADAs with both GM-Saginaw and Metallamics. Both CRADAs are on schedule.

Other Successful Technology Transfer Activities as Evidence of Industry Interest: In addition to licensees, worked closely with Texas Instruments, Alloy Engineering & Casting, RibTech (Gahanna, Ohio), Devasco International Inc. (Houston, Texas), PCC Airfoils, and Rapid Technologies, Inc. (Newnan, Georgia). The AIC Program was leveraged to a total of \$275 K by industry in-kind support.

CRITICAL ISSUES: (1) Casting process optimization for sand and investment castings in support of licensees and the CRADAs signed during FY 1992, (2) weld repair of castings with special emphasis on methods for the fabrication of weld wire and the development of weld procedures, and (3) mechanical properties and microstructural data on prototype components.

FUTURE PLANS: (1) Continue optimizing alloy composition and process parameters for sand and investment castings of Ni₃Al-based alloys, (2) continue developing methods for the fabrication of weld wire and developing procedures for the welding of components, (3) continue optimizing parameters for hot working the IC-218LZr composition, (4) develop fracture toughness and other mechanical properties data on prototype components, and (5) continue technology transfer activities.

POTENTIAL PAYOFF: Nickel-aluminide components for a range of applications with major benefit of U.S. industry taking the lead position in the world. Industries benefiting from nickel-aluminide technology are: automotive, steel, and manufacturing.

ADVANCED CERAMICS AND COMPOSITES

ADVANCED METHODS FOR PROCESSING CERAMICS

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Contract 19X-SM063C

INTRODUCTION

Advanced methods of processing ceramic materials are providing unique solutions to difficult industrial problems. In this case, Georgia Tech is developing two advanced process which have the potential for improved thermal insulation and thermal barrier coatings. These two separate processing techniques are (1) Rapid Polymerization of Aqueous Slurries (RPAS) directed by Joe Cochran and (2) Combustion Chemical Vapor Deposition (CCVD) directed by Brent Carter. The first topic, RPAS, draws heavily on technology developed in a long term DOE project "Thin Wall Hollow Spheres from Slurries" in that the main thrusts are to form fibers from rapid setting slurry techniques which was also critical to hollow sphere technology and then to reduce the fiber conductivity with radiation scattering opacifiers, also initiated in the earlier project. CCVD is a newly developed technique for containerless coating of a wide variety of compositions and crystalline textures ranging from polycrystalline to single crystal. This project was initiated in October, 1992. Therefore, this FY93 annual progress report covers the first year of the project and will be presented as two separate reports covering RPAS and CCVD.

RAPID POLYMERIZATION OF AQUEOUS SLURRIES FOR FIBERS

TECHNICAL PROGRESS

Summary

The object of this effort is to develop an economical processing method for producing ceramic fibers which could have application as high temperature thermal insulation. Fibers developed in this program will be large enough (above 10 μm) to be environmentally safe and will require opacification with infrared scattering phases to provide a low thermal conductivity. Thus, the effort is broken into two tasks, (1) Radiation Initiated Polymerization of Aqueous Slurries and (2) Reduction of Thermal Conductivity Using IR Opacification.

Efforts to rapidly polymerize aqueous slurries have concentrated on formulation of slurry compositions with maximum cure rates. The efforts were carried out by investigating the effects of varying monomer, photoinitiators, and coinitiator concentrations. The development of a calculation which allows conversion of temperature vs time data to rate of polymerization allows a meaningful comparison between the kinetics of different solution compositions. This approach allowed demonstration that millimeter sized drops of slurry could be polymerized in free fall through a 10 inch long UV light source and that 3 millimeter thickness of slurry could be polymerized in 9 seconds which permits numerous applications for the technology.

Considerable progress has been made on IR opacification of alumina and mullite compositions to reduce thermal conductivity. We have successfully replicated an isolated pore structure in the 1-10 μm diameter range in the walls of hollow spheres using rice starch as a fugitive burn-out material. This was made possible by adding

a small amount of glass phase to provide liquid phase sintering. This resulted in thermal conductivity competitive with insulating castables and fire brick.

Milestones

1. Radiation Initiated Polymerization of Aqueous Slurries

Aqueous slurries are prepared which contain water soluble monomers, crosslinking monomers, initiators, and coinitiators. Initiators and coinitiators absorb radiation, are elevated to excited stages, react with monomers, and form propagation radicals. Crosslinking agents, on the other hand, branch the polymer network and provide the final polymer-ceramic green bodies with rigidity. To date, acrylamide and methylene bisacrylamide have been used as the monomer and crosslinking agent, respectively, and three initiators (one ketone and two benzophenone derivatives) and one coinitor have been investigated.

The first step of the study was to investigate kinetics of the polymerization of the acrylamide. This was achieved with a UV radiation source equipped with high speed, computer controlled data collection. Results show that polymerization rate increases considerably with monomer content and a coinitor is absolutely necessary when benzophenone initiators are used. Results also show that among the three initiators investigated, 4-(2-hydroxyethoxy)phenyl-(2-propyl) ketone, referred as K, is the most effective initiator. This initiator provided consistently higher polymerization rates in all experimental conditions than did the other two benzophenone initiators. It has been found that the optimal composition consisted of 7M of acrylamide, 0.111M of initiator K and 0.210M of coinitor in aqueous solution. With this

composition, 1 cc of the solution can be cured in under 2 seconds with the 300 watt/inch UV source. This composition was used as the liquid vehicle to form a UV curable ceramic slurry. In order to fabricate a slurry, the acrylamide concentration must be decreased due to the volume contributed by the ceramic powder. The decrease in monomer concentration along with the fact that ceramic powder blocks UV radiation would predict a slower polymerization rate. Experiments verified that the reaction rate of the slurry was four times slower than that of the reference solution (without ceramic powder). Despite the slower reaction, a 2 to 3 mm cure thickness was achieved in 9 second UV exposure in ceramic slurry with 4M of monomer. This result can be further improved if monomer concentration can be increased. Ceramic spheres (1 mm diameter) were actually cured from a slurry with 8.38M of monomer (which is close to solubility of acrylamide at room temperature) when the slurry was dripped through the UV irradiator (residence time ~ 200 msec). This suggested that UV polymerization is a practical method to cure thin layer of ceramic slurry in a short time.

2. Reduction of Thermal Conductivity Using IR Opacifiers

Thermal conductivity of alumina and mullite hollow spheres was successfully reduced with rice starch additions to be competitive with commercial insulating materials (castables and IFB's). The effect of rice starch additions can be seen in Figure 1 where conductivity of alumina hollow spheres consistently decreases with increasing additions of rice starch up to 60 v/o (25 w/o). Conductivity values were calibrated against commercial materials and a comparison of the conductivity of hollow sphere beds with these commercial materials, shows a significantly reduced

Figure 1. Thermal Conductivity of Alumina Hollow Sphere Beds With Opacifying Pores From Rice Starch Burnout.

conduction using rice starch additions, Figure 2. The radiation scattering porosity produced by the rice starch was twice as large as theoretically optimal. Thus, significant conductivity reductions are still possible by reducing pore size to the optimum scattering diameter.

PUBLICATIONS

1. R.P. Gonzales, "Hollow Sphere Radiant Thermal Conductivity Reduction Using Infrared Pore Opacification," M.S. Thesis, Georgia Institute of Technology, Atlanta, GA, September, 1993.

Figure 2. Conductivity of Loose Beds of Pore Opacified Hollow Spheres Compared to IFB's and Insulating Castables.

2. P.R. Chu, J.K. Cochran, "Kinetics Optimization of UV Curable Aqueous Slurries for Application in Ceramic Processing," Proceedings of the 18th Annual Cocoa Beach Conference on Composites and Advanced Materials, American Ceramic Society, Westerville, Ohio, January 1994. Accepted for publication.
3. P.R. Chu and J.K. Cochran, "Coaxial Nozzle Formation of Hollow Spheres from Liquids I: Model," Manuscript No. 199543P, Journal of American Ceramic Society, Submitted, July, 1993.
4. P.R. Chu, J.K. Cochran, "Coaxial Nozzle Formation of Hollow Spheres from Liquids II: Confirmation," Journal of American Ceramic Society, submitted March, 1994.

PRESENTATIONS

1. R.P. Gonzales and J.K. Cochran, "Hollow Sphere Radiant Thermal Conductivity Reduction Using Infrared Pore Opacification," Annual Meeting of American Ceramic Society, Cincinnati, OH, April 26, 1993.
2. P.R. Chu, J.K. Cochran, and T.J. Hwang, "Ceramic Processing by Radiation Initiated Polymerization of Aqueous Slurries," Annual Meeting of American Ceramic Society, Cincinnati, OH, April 26, 1993.
3. P.R. Chu and J.K. Cochran, "Kinetics Optimization of UV Curable Agnears Slurries for Application in Ceramic Processing," 18th Annual Conference on Composites and Advanced Materials, American Ceramic Society, Cocoa Beach, FL, Jan. 11, 1994.
4. R.P. Gonzalez and J.K. Cochran, "Infrared Pore Opacification and Thermal Conductivity in Alumina Hollow Spheres," Annual Meeting of American Ceramic Society, Indianapolis, IN, April, 1994.
5. P.R. Chu and J.K. Cochran, "UV Polymerization of Aqueous Slurries for Application in Ceramic Processing," Annual Meeting of American Ceramic Society, April, 1994.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

A white paper on use of hollow spheres in refractory was submitted to DOE in December, 1993 in a teaming effort with Carborundum, Georgia Tech, Ceramic Fillers, and ORNL. The purpose of the effort was to demonstrate use of hollow sphere refractories in industrial applications. A plan was presented to commercialize the products if successful.

COST SHARING

Georgia Tech has provided \$34K of cost sharing funds for graduate student support. Microcel Technology purchased a \$3K mixing system for handling polymerization safely.

HIGHLIGHTS - UV Curing Times for Aqueous Ceramic Slurries of 200 msec Achieved

Processing times for hardening ceramic slurries to solid shapes often limit production rates for ceramic products. By optimizing the composition of aqueous ceramic slurries containing water soluble monomers, UV curing times of under 200 msec have been achieved for millimeter size droplets and under 9 sec for hollow cylinders 3mm thick. Thus, UV curing rates are sufficient for high volume fiber production and many coating applications.

RAPID UV POLYMERIZATION FOR CERAMIC PROCESSING FROM WATER BASED CERAMIC SLURRIES

PROBLEM - Ceramic processing from organic based ceramic slurries have problems such as environmental pollution and high cost of the organic solvent. Both problems can be solved by replacing organic based slurries with water based slurries.

RESULT - Water based slurries can be cured by polymerizing water soluble monomers, which were incorporated into the slurries, with UV radiation. The curing rate of the ceramic slurries depends on the polymerization rate of the liquid phase vehicle, i.e. the monomer and UV activated initiator aqueous solution. The polymerization rate of the liquid vehicle can be optimized by manipulating the composition of monomer, initiator and/or coinitiator. It has been demonstrated that the 2 ~ 3 mm of cure thickness can be achieved from slurry in 9 seconds of UV exposure.

SIGNIFICANCE - for energy conservation - Improved production rate and therefore reduced average energy consumption per part.

SIGNIFICANCE - for industrial application - UV polymerization is a generic hardening method for thin ceramic parts from slurries and provides alternative curing mechanism for ceramic fibers, fiber coatings, spray drying powders, ceramic substrate by tapecasting.

(Research at Georgia Institute of Technology under DOE-AIC support)

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Rapid Polymerization of Aqueous Slurries for Fibers

FISCAL YEAR: FY 1993

COMPLETION DATE: June, 1994

PERFORMING ORGANIZATION(S): Materials Science and Engineering, Georgia Tech

PRINCIPAL INVESTIGATOR(S): Joe Cochran, (404) 894-6104

PHASE OBJECTIVE: Phase I

1. Rapid Polymerization of Aqueous slurries with Radiation Initiated Reactions
2. Reduce High Temperature Conduction with a Closed Pore System

ULTIMATE OBJECTIVE: Develop an economical processing method for producing ceramic fibers which could have application as high temperature thermal insulation.

TECHNICAL APPROACH: Form polycrystalline fibers from polymerized aqueous slurries which will be large enough to be non-respirable ($>10\ \mu\text{m}$) and which will produce a radiation scattering pore system on firing.

PROGRESS: An isolated 1-10 μm diameter pore system has been produced in liquid phase sintered alumina by burn-out of rice starch. This pore system has been demonstrated to reduce conductivity of hollow spheres 40% at 1200°C. The pore system technology should be transferable to fiber fabrication. UV polymerization of aqueous slurries has been accomplished in free flight showing that reaction rates are fast enough for economical fiber formations.

Patents:0 **Publications:**3 **Proceedings:**1 **Presentations:**5

ACCOMPLISHMENTS:

Licenses:-

Known Follow-on Product(s): High Temperature Thermal Insulation

Industry Workshop:-

Technology Transfer and Industry Interest: Fiber formation utilizing rapid polymerization is not developed sufficiently to access industrial potential. However, reduced conductivity of hollow ceramic spheres with pore opacification is of considerable interest to both one-electronics firm and a refractories manufacturer.

PROJECT TITLE: Rapid Polymerization of Aqueous Slurries for Fibers

CRITICAL ISSUES: Advances in pore opacification utilizing rice starch has rapidly reduced thermal conductivity and smaller pore size should produce further reductions. Actual fiber formation should be attempted in further work.

FUTURE PLANS: New, safer, water soluble monomers need to be investigated.

ESTIMATED ENERGY SAVINGS: Insulation now used for applications above F are estimated to save approximately 0.1 quads.

THERMAL CONDUCTIVITY REDUCTION WITH SCATTERING PORES PRODUCED WITH BURN OUT OF RICE STARCH PARTICLES

COMBUSTION CHEMICAL VAPOR DEPOSITION

TECHNICAL PROGRESS

Summary

The deposition of several materials via CCVD was demonstrated including YSZ, SiO_2 , BaTiO_3 , and yttrium iron garnet. A series of experiments was performed for the liquid fuel CCVD deposition of YSZ to study the effects of the systematic variation of coating parameters. They include: i) a Y composition study, ii) substrate angular orientation study, iii) substrate location, iv) deposition rate, v) oxygen content of atomizing gas, vi) gravity effect, vii) a first attempt to deposit thick coatings, and viii) an increased area coating. With the exception of i), all studies were performed using 2.5 weight percent Y_2O_3 YSZ coatings.

Milestones

1. Demonstration of compositional control of YSZ.

Six depositions of YSZ on a-axis sapphire were made using different ratios of yttrium 2-ethylhexanoate (Y-2EH) to zirconium 2-ethylhexanoate (Zr-2EH) dissolved in toluene. The ratios were chosen so that (assuming coating stoichiometry same as solution stoichiometry) the Y_2O_3 contents of the coatings would be 0, 1, 2, 3, 4, and 5 weight percent. The total moles of Y + Zr used for each deposition was held constant at 6.6×10^{-4} .

All six films produced were, clear, dense, and shiny with nodular microstructures and thicknesses of about $0.25 \mu\text{m}$. Each 1.4 cm^2 substrate gained $0.13 \text{ mg} \pm 0.02 \text{ mg}$ during deposition. All coatings were adherent with the exception of the pure zirconia coating which cracked and delaminated near its edges where it was thickest.

X-ray diffraction (XRD) results indicate that the crystal structure of the coatings changed from predominantly monoclinic to tetragonal to predominantly cubic as the Y content of the coatings increased. Several coatings with 8 weight percent Y_2O_3 were deposited. As expected, these displayed entirely cubic crystal structures.

2. Demonstration of texture dependence on angular orientation.

Substrates were coated by varying the angle between their normals and the flame direction. Angles of 0° , 30° , 60° , and 90° were used. The major effect of orientation variation is on the coating texture. Coatings produced at 30° and 60° were denser and smoother than those deposited at 0° and 90° .

3. Demonstration of deposition rate dependence on reagent concentration.

This study tested the effect of varying the deposition rate by adjusting the coating precursor concentration. The amount of Y + Zr in solution was held constant at 7×10^{-4} moles. The volumes of the toluene solution used were 22, 36, 60, 100, 140, and 200 ml. These correspond to Y + Zr concentrations of 0.032, 0.019, 0.012, 0.007, 0.005, and 0.0035 M, respectively. All other process parameters were held as constant as possible for this series of experiments.

The major result of this study was a marked dependence of coating morphology on reagent concentration. Low reagent concentration resulted in coatings that were predominantly particulate, whereas high concentrations produced coatings with dense and nodular morphologies. Moderate concentrations resulted in intermediate coating morphologies involving a dense base of coating material, holes, and hillocks.

PUBLICATIONS

1. A.T. Hunt, W.B. Carter, and J.K. Cochran, "Combustion Chemical Vapor Deposition: A Novel Thin Film Deposition Technique," Applied Physics Letters, vol. 63, no. 2, pp. 266-268, 1993.
2. J.M. Hampikian, A.T. Hunt, and W.B. Carter, "CCVD of Silica Coatings on Ni-20 Cr," to be published in the Proceedings of the TMS-ASM Fall Meeting, held in Pittsburgh, PA, Oct. 17-21, 1993.
3. A.T. Hunt, "Combustion Chemical Vapor Deposition from Liquid Organic Solutions," Ph.D. thesis, Georgia Institute of Technology, November 1993.

PRESENTATIONS

1. A.T. Hunt, W.B. Carter, and G.W. Book, "Combustion Chemical Vapor Deposition - A Novel CVD Method," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, OH, 19 April, 1993.
2. J.M. Hampikian, A.T. Hunt, and W.B. Carter, "CCVD of Silica Coatings on Ni-20 Cr," presented at the TMS-ASM Fall Meeting, held in Pittsburgh, PA, Oct. 17-21, 1993.

HONORS AND AWARDS

1. Andrew T. Hunt was a winner in the Science Applications International Corporation Georgia Tech Student Technical Paper Competition for his paper entitled "Combustion Chemical Vapor Deposition: A Novel Thin Film Deposition Technique," coauthored with W.B. Carter and J.K. Cochran.
2. Andrew T. Hunt awarded Finalist in the 1993 B.F. Goodrich Collegiate Inventors Program for his invention of CCVD.

PATENTS/DISCLOSURES

1. Andrew T. Hunt, Joe K. Cochran, and William Brent Carter, "Method and Apparatus for the Combustion Chemical Vapor Deposition of Films and Coatings," U.S. patent application #08/036,54 filed 24 March 1993.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

A proposal has been written with General Electric Power Generation to explore possible uses of CCVD coatings for applications in advanced gas turbine thermal barrier coatings.

United Technologies Research Corporation has expressed interest in CCVD for applying oxidation resistant coatings. Several trial coatings have been deposited on UTRC supplied substrates and returned for evaluation.

COST SHARING

None.

HIGHLIGHTS

Compositional control of yttria stoichiometry in yttria stabilized zirconia has been demonstrated by varying the precursor solution concentration.

DEVELOPMENT OF CONTAINERLESS PROCESS FOR CHEMICAL VAPOR DEPOSITION OF TOUGH YTTRIA STABILIZED ZIRCONIA

Problem:

Current chemical vapor deposition processes require the use of coating chambers which are often also vacuum vessels. This dramatically effects the economics of the coating process and limits the size of parts that can be coated to those that will fit inside the coating vessel. Often equipment must be disassembled in order to be coated.

Results:

The development of CCVD can potentially avoid the limitations of size and economics imposed by the necessity of using a coating chamber with conventional CVD methods. A U.S. patent application has been filed to provide protection for the process.

**2 Micron Thick 2.5% YSZ
Coating on Sapphire
Displaying Toughness**

**XRD Composite Showing
YSZ Structure Variation
with Solution Concentration**

Significance - For Energy Conservation:

The replacement of some conventional CVD processing with CCVD, which does not use energy intensive vacuum furnaces, may result in energy savings.

Significance - For Materials Technology:

(R&D performed at Georgia Tech under DOE-CE-AIM Program)

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: COMBUSTION CHEMICAL VAPOR DEPOSITION

PHASE: FY 1993

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATOR: W.B. Carter 404/894-6762

PHASE OBJECTIVE: Develop an understanding of the CCVD process for the deposition of YSZ coatings.

ULTIMATE OBJECTIVE: Develop an alternative deposition technology for applying inorganic coatings that is economically superior to existing processes.

TECHNICAL APPROACH: A new CVD process, combustion CVD (CCVD), is being developed. CCVD is a flame assisted deposition process performed in the open atmosphere without a furnace or vacuum vessel.

PROGRESS: Progress has been made in understanding the CCVD process for the deposition of yttria stabilized zirconia. Several other oxides have been deposited.

Patents: 1 Filed **Publications:** 2* **Proceedings:** 1**

Presentations: 2

* 1 peer reviewed journal publication, 1 thesis

** Accepted for publication

ACCOMPLISHMENTS:

Licenses: None

Known Follow on Products:

Industry Workshop: None

Technology Transfer of Industrial Interaction: Interest in CCVD has been expressed by Alcoa, United Technologies Research Center (UTRC), and General Electric Power Generation (GEPG). Trial coatings have been deposited on UTRC supplied substrates. A joint proposal has been written with GEPG.

PROJECT TITLE: Combustion Chemical Vapor Deposition of Zirconia and Yttrium Stabilized Zirconia

CRITICAL ISSUES: Control of deposition process.

FUTURE PLANS: Deposit YSZ coatings over large areas, begin modeling of CCVD process, and attempt deposition of SiC using a Smithell separator.

**CCVD PROCESS PARAMETERS HAVE BEEN STUDIED EXPERIMENTALLY
COATING THICKNESS VS. SUBSTRATE DISTANCE FROM BURNER NOZZLE**

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

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ORNL Subcontract #19X-SL260C

INTRODUCTION

Ceramic matrix composites promise higher operating temperature and better thermodynamic efficiency in many energy conversion systems. Ceramic composites fabricated by the chemical vapor infiltration (CVI) process have demonstrated excellent mechanical properties and good processing economies in small scale demonstrations. Preserving these attributes in scale-up, however, requires improved understanding of gas flow through the fiber preform and of the relationship between fiber architecture and densification behavior. This understanding is needed for design of preforms for optimum infiltration.

The objective of the research is to observe the deposition of matrix material in a ceramic fiber preform at various stages of CVI, to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to apply these observations to improved modeling of the relationship between gas transport and fiber architecture in CVI preforms. Matrix deposition is observed using x-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory by repeatedly imaging a small preform sample after various processing times. Analysis focuses on the geometry and dimensions of the channels between and the holes through layers in cloth lay-up preforms and the incorporation of this data into a transport model.

TECHNICAL PROGRESS

A set of several samples was prepared and partially infiltrated; these samples were sent to Kinney's group for tomographic imaging. Included were samples with $0^\circ/45^\circ$ and $0^\circ/30^\circ/60^\circ$ lay-ups. The cloths were of Tyranno and Nicalon fibers. Infiltration and imaging was partially completed on some of the samples, but limited beam time prevented completion of the experiments.

Analysis centered on a $0^\circ/90^\circ$ cloth lay-up SiC/Nicalon composite that was densified under isothermal/forced-flow condition by methyltrichlorosilane (MTS) and imaged by high resolution XTM at four times during densification, i.e., before infiltration and after three, six, and nine hours of infiltration. The volume fraction of SiC deposited within the tows of the cloth layers was studied as a function of infiltration time and position relative to the gas inlet; this was used as a comparison with the work going on in Kinney's group. The widths of the channels and holes in the composite were studied in detail: these are particularly important because they are the main route of gas flow during the final stages of densification. From the measurement of channel width as a function of position, several other quantities were obtained as a function of time and distance from the gas inlet: total channel volume, preform channel structure, average channel width, the relationship between channel width and displacement between holes in the cloths on either side of the channel, and the thickness of SiC deposited on the wall of the channels. The number of moles of SiC deposited within the sampling volume (i.e., the channel and the tows on either side of the channel) and surface area per unit volume are also quantified.

Perhaps the most important observation made on the $0^\circ/90^\circ$ layup sample was the first observation of the dependence of channel structure on the relative displacements of the bordering cloths: patterns of channel widths were found for the nineteen different channels of the sample. Figure 1 maps channel width across the cross-section of the sample for three channels; darker pixels represent positions where the channel is wider. Figures 1(a), (b), and (c) (channels 1, 10, and 11, respectively) show the three patterns of channel openings observed: two-dimensional networks of "pipes," one-dimensional arrays of "pipes," and relatively structure-free channels. As shown in Figs. 2(a), (b), and (c), these patterns correspond to situations where the holes in the cloths on either side of the channel are

Fig. 1. Channel width as a function of position.

(A) CHANNEL 1

(B) CHANNEL 10

(C) CHANNEL 11

★ Top Cloth
■ Bottom Cloth

1 mm

Fig. 2. Hole positions on either side of the channels shown in Fig. 1.

well-aligned, displaced along the axis of a tow or displaced along a direction bisecting the two orthogonal tows, respectively.

The periodicity would be expected to be manifest in the densification of the sample. The data showed that densification of SiC strongly depends on the distance from the gas inlet, i.e., on the concentration of MTS and HCl, both inside microporosity (tows) and on the walls of macroporosity (channel and holes) but does not seem to relate significantly to cloth lay-up geometry. The rate of SiC deposition on the surface of tows is most rapid on the walls of channel near the gas inlet, and particularly at the tips of tows (i.e., the boundaries of the holes). Holes in the cloth layers near the gas inlet are almost clogged after three hours of infiltration, and after three hours, the MTS gas flowed around these cloths, mostly along the wall of the reaction chamber. Loose fibers or small bundles of fibers within open sections of channels may also play significant role in limiting the final density which the composite can reach.

Hole alignment or the direction of displacement of the holes does not, however, *appear* to have an effect on the local deposition rates. In other words, the macroscopic gradients seem to render insignificant any local variations. Use of the displacement of the holes as a measure of local structure is, however, an oversimplification of the actual three-dimensional nature of the cloths. As is indicated in the two-dimensional section perpendicular to two cloths (Fig. 3), well-aligned holes can correspond to two very different channel structures. The two structures can be termed anti-coincident and coincident for the situation where the parallel tows on either side of the channel are the nearest-neighbors across the channel and where the orthogonal tows are nearest-neighbors, respectively. The channels formed by anti-coincident and coincident well-aligned cloth layers would have very different channel volumes, etc. It may be that looking for differences in local deposition based on only hole position is inaccurate and that the weave structure must be taken into account. This is currently under investigation.

PUBLICATIONS

J. H. Kinney, T. M. Breunig, T. L. Starr, D. Haupt, M. C. Nichols, S. R. Stock, M. D. Butts, and R. A. Saroyan, "X-ray Tomographic Study of Chemical Vapor Infiltration Processing of Ceramic Composites," *Science*, **260**, pp. 789-92, 1993.

Coincident Cloth Alignment

Anti-Coincident Cloth Alignment

Fig. 3. Cross-section schematically showing the arrangement of cloths on either side of a channel in the coincident (top) and anti-coincident (bottom) alignments. This shows that well-aligned holes can have one of two very different structures.

M. D. Butts, "Nondestructive Examination of Nicalon Fiber Composite Preforms Using X-ray Tomographic Microscopy," MS Thesis, Georgia Institute of Technology, June 1993 (supervised by S. R. Stock).

S. B. Lee, "Nondestructive Examination of Chemical Vapor Infiltration of 0°/90° SiC/Nicalon Composites," PhD Thesis, Georgia Institute of Technology, December 1993 (supervised by S. R. Stock).

PRESENTATIONS

S. B. Lee, S. R. Stock, T. L. Starr, M. D. Butts, T. M. Breunig, M. C. Nichols, and J. H. Kinney, "Influence of Tow Geometry on Microstructure Evolution of CVI Composites," 17th Annual Conference and Exposition on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, Florida, January 14, 1993.

T. L. Starr, S. R. Stock, M. D. Butts, and S. B. Lee, "Constriction of Flow Paths During Forced Flow CVI," Ninety-fifth Annual Meeting, American Ceramic Society, Cincinnati, Ohio, April 20, 1994.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

None.

COST SHARING

None.

HIGHLIGHTS

An illustration from publication 1 above, which was produced by our collaborators on the joint work described in this report appeared on the cover of Science.

CHEMICAL VAPOR INFILTRATION AND THE ROLE OF THE WIDTH OF CHANNELS BETWEEN CLOTH LAYERS

Problem: The densification of ceramic composites using chemical infiltration (CVI) is a complex process that is critically dependent on gas transport through the network of fibers that reinforce the composite. Previous methods of investigating the relationship between fiber architecture and the densification process have been limited to destructive, post-process sectioning. Nondestructive observation at several stages from preform to dense composite would produce better understanding of CVI.

Results: Channel width as a function of position in a 0°/90° sample was found to belong to one of three types of patterns: two-dimensional networks of pipes, arrays of parallel pipes or relatively pattern-free (upper row of the Figure). These patterns correspond to channels with holes on either side of the channel being well-aligned, being displaced along fiber tow directions or being unaligned, respectively (lower row of the Figure).

Significance - For Energy Conservation: Ceramic matrix composites allow higher operating temperatures and better thermodynamic efficiency for many energy conversion systems.

Significance - For Materials Technology: Better understanding of the CVI process will improve the properties and lower the cost of ceramic composite materials fabricated using this process. Improving knowledge of structure-transport relationships will benefit other composite fabrication processes, leading to more widespread application of composites.

(R&D performed at Georgia Institute of Technology under subcontract #19-SL260C with Martin Marietta Energy Systems under their contract #DEAC05-84OR21400).

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

PHASE: FY 1993

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATORS: T. L. Starr 404/853-0579 and S. R. Stock 404/894-6882

PHASE OBJECTIVE: Relate geometry and dimensions of channel between and of holes through layers in cloth lay-up preforms during CVI densification and relate to transport model.

ULTIMATE OBJECTIVE: Develop understanding of relationship between preform fiber architecture and densification behavior, and use to design preform for optimum infiltration.

TECHNICAL APPROACH: In collaboration with Dr. J. H. Kinney at Lawrence Livermore National Laboratory, we will use very high resolution X-ray computed tomography to repeatedly image small preform samples after various processing times. Different cloth lay-ups will be examined. The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical infiltration (CVI) process. These observations will allow us to relate local deposition rates in various regions of the composite to the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms.

PROGRESS: A second imaging run was begun during Spring 1993. The influence of cloth positioning on channel geometry and the spatial variation of channel widths was studied in detail for a 0°/90° Nicalon/SiC composite as a function of infiltration time. Two-dimensional arrays of pipes were found when the holes in adjacent cloths were well-aligned, a single set of parallel pipes were found when the holes were shifted along one of the tow directions and little structure was seen when the translation was not along between the tow directions. The change in surface area of macroporosity per unit volume was found to be in good agreement with model predictions.

Patents: None Publications: Three Proceedings: None Presentations: Two

ACCOMPLISHMENTS:

Licenses: None

Known Follow-on Product: None

Industry Workshop: None

Technology Transfer or Industrial Interaction: None

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

CRITICAL ISSUES: Continuation of the second set of densification experiments is key to determining the effect of such variables as lay-up geometry and fiber type.

FUTURE PLANS: Analysis of image data for a 0°/45° sample will continue. Experiments with different layup variations will be continued.

POTENTIAL PAYOFFS:

ESTIMATED ENERGY SAVINGS:

CHARACTERIZATION OF THREE-WAY AUTOMOTIVE CATALYSTS

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INTRODUCTION

A CRADA between General Motors - AC Rochester Division (GM-ACRD) and Martin Marietta Energy Systems (MMES) is aimed at improved performance and lifetime of platinum-rhodium based three-way-catalysts (TWC), which are the primary catalytic system for automotive emission control systems. While these TWC can meet the currently required emission standards, higher than optimum Pt-Rh loadings are often required to meet lifetime requirements. In addition, more stringent emission standards will be imposed in the near future, demanding improved performance and service life from these catalysts. Understanding the changes of TWC conversion efficiency with ageing is a critical need in improving these catalysts. Fresh specimens of different TWC formulations can have very different catalytic performance even for similar levels of noble metal (Pt, Rh) loading. In addition, their relative ranking can change with even mild ageing. The efficiency, selectivity, and robustness of a catalyst system reflects the state of the chemically active material; including morphology, structure, elemental and chemical form. The ageing behavior and lifetime of the catalyst are determined by the evolving state of the catalyst, which in turn is a function of the chemical environment (both reactants and poisons) and exposure time and temperature. Reactivation of a catalyst requires at least partial reversal of the microstructural evolution responsible for the degradation in catalytic performance. Initially in a fresh catalyst, the active material is often distributed on a very fine scale, approaching single atoms or small atomic clusters. As such, a wide range of analytical techniques have been employed to provide high spatial resolution characterization of the evolving state of the catalytic material.

TECHNICAL PROGRESS

Summary

Initial technical meetings between GM-ACRD and MMES were held on October 26 and November 16/17, 1992 to formulate the research program required to answer some of the basic questions concerning the evolution/degradation of platinum-rhodium TWC. As-produced and test stand-aged catalyst monoliths were received at ORNL in the second and third quarters of FY1993, respectively. As-produced monoliths as well as monoliths rapidly aged on an engine test stand or thermally aged in air have been characterized by a variety of both surface analytical techniques and optical and electron optical techniques. Though no noble metal clusters have been observed in the as-produced catalysts, a number of techniques have indicated a strong association of platinum with specific oxides in the washcoat. This association and the details of the process for loading the noble metals result in inhomogeneous distribution of platinum at both macroscopic and microscopic scales. Coarse platinum particles have been observed both in specimens aged in air at high temperatures (~20 nm) and in specimens test stand aged (20-50 nm depending on ageing schedule). The level of rhodium incorporated in these particles was minimal for the air aged material and varied with test stand ageing schedule.

Milestones

1. Characterization of as-prepared catalysts.

Basic characterization of the freshly-prepared TWC monolith utilizing both surface analytical techniques (AES, SIMS, XPS, etc.) and light and electron optical techniques (light macro/microscopy, SEM, EMPA, AEM, and HREM) have been completed. The washcoat is a fine-grained multi-component layer with both large pores and cracking, especially in the thicker regions of the washcoat. A dark stripe was observed on all washcoat faces parallel to the channels in the monolith. Mercury porosimetry was used to measure pore sizes of blank and washcoated monoliths. Washcoated specimens exhibited significant pore volume below 0.2 μm diameter with pores being indicated down to calculated diameters of ~3 nm. This fine scale porosity is associated with the washcoat.

Though bulk surface analytical techniques (AES, SIMS, XPS) were applied to the characterization of the fresh catalyst, a variety of problems resulted in poor sensitivity for platinum or rhodium (overlap of Al and Pt peaks in XPS, use of nitrogen beam in SIMS, etc.). The inability of these normally sensitive surface analytical techniques to detect platinum may indicate that 1) platinum is distributed more-or-less uniformly throughout the washcoat and as such is below the detection limit for these techniques or that 2) platinum is not present in the near surface regions analyzed by these techniques.

Light and electron microscopy indicate that the washcoat is comprised of at least two phases (alumina and ceria) and significant porosity. Energy dispersive X-ray spectroscopy (EDS) indicated that some regions were predominantly aluminum oxide with some cerium present, whereas other regions contained significantly larger amounts of cerium relative to aluminum. Many of the Ce-enriched particles exhibited a fibrous structure in the SEM. Analyses both on and off the dark stripe indicated the presence of platinum. However, both EMPA and the X-ray fluorescence microprobe indicated an association of platinum, and possibly rhodium, with the dark stripe. Both high resolution SEM and transmission electron microscopy (TEM) indicated that the alumina regions of the washcoat were agglomerates of fine-grained particles ~10 nm in diameter. High resolution and analytical electron microscopy indicated that the alumina particles were crystalline and that there was no indication of resolvable noble metals clusters (>0.7 nm diameter) in the fresh catalyst. High-angle annular dark field ("Z-contrast") imaging in the scanning transmission electron microscope (STEM) failed to resolve any noble metal clusters, even though it was able to image 1-2 nm diameter gold particles on a test specimen.

Analytical electron microscopy (AEM) was performed on dispersed particulates abraded from the catalyst. For the fresh catalyst, the alumina exhibited significant levels of cerium ranging from 15-40 wt% (for elements with atomic number $Z > 11$) and trace amounts of chlorine (<0.5 wt%). The form which this distributed cerium takes in the alumina has not been identified to date. Platinum was observed in both alumina and ceria regions via EDS in the SEM and in the AEM. As no evidence for noble metal clusters could be found, it is possible that the platinum might be in a noncrystalline or distributed form. An attempt to identify the chemical state of the platinum via extended electron loss fine structure (EXELFS) was not successful as a result of low platinum signals in EELS.

Several levels of elemental inhomogeneity were identified by EDS on washcoat specimens in the SEM, EMPA, and AEM. Higher levels of distributed cerium were detected in the alumina at the top (entrance) side of the convertor than at the bottom (exit) side. Similarly, higher platinum levels were observed at the convertor top side. An association of high platinum levels with specific oxides in the washcoat was noted. Currently the mechanism responsible for this association has not been identified. The level of platinum measured decreased as the distance from the internal free surface of the washcoat increased. The rhodium detected in the washcoat by EDS in the AEM were near the detection limit of the technique (0.1-0.2 wt %) and were consistently less than expected based on the loading ratio of platinum/rhodium. This observation indicates that either rhodium is not being deposited at the desired level or that rhodium is not being distributed uniformly with platinum.

2. Characterization of catalysts thermally aged in air.

As a first approximation to vehicle ageing of the catalyst, some short term (1h) ageing of catalyst material was performed in air at high temperatures (750-850°C). After ageing up to 800°C, no obvious changes in washcoat microstructure or noble metal distribution were observed. No chlorine was detected in any of the materials aged in air. After ageing at 850°C, lower platinum levels were measured in the washcoat matrix. A more striking difference evident in the 850°C aged catalyst was the presence of relatively coarse (~20 nm diameter) metallic particles enriched in platinum. The measured rhodium levels were much less than would be expected from the measured platinum levels (Pt/Rh ~100). As high platinum areas were observed in the "as formed" washcoat, it is expected that preferential formation of platinum particles would occur in such regions.

3. Characterization of catalysts test stand aged.

Rapid ageing tests (RAT) of automotive catalysts on engine test stands have been developed to simulate the effect of prolonged exposure to exhaust gas/temperatures. Specifically, RAT-B(75) and RAT-A(50) are designed to simulate 50,000 and 100,000 miles of normal vehicle exposure, respectively. RAT-H(10) Special is designed to simulate 20,000 miles with a badly tuned engine which results in high operating temperatures for the catalyst.

In the mildly aged RAT-B(75) material platinum enriched, crystalline particles ~20 nm in diameter were observed [Fig. 1(a, c)]. The EDS spectra typical of the matrix (M) and the

Fig. 1. (a) Pointer indicating platinum particle in RAT-B(75) test stand aged material, (b) EDS spectra from platinum particle (P) and from adjacent matrix (M), and (c) "Z-contrast" STEM image of platinum (circled) and ceria (C) particles along with analyzed areas P and M for spectra in (b).

platinum particles (P) are shown in Fig. 1(b). The measured Pt/Rh ratio was ~20/1, approaching the loading ratio. Extended ageing produced larger (~50 nm diameter) platinum rich particles in the RAT-A(50) material [Fig. 2(a)]. Fig. 2(b) gives typical EDS spectra for the platinum particles (P) and the adjacent ceria (C) crystallites. The platinum-rich particles were crystalline with an fcc structure and lattice parameter that matches pure platinum [Fig. 2(c)]. The measured Pt/Rh ratio was ~30/1. In addition, there were apparently crystalline regions high in phosphorus (up to 20 wt%); one of the chief impurities in gasoline. Large (500 nm diameter) Al₂O₃ crystals were observed in some regions, indicating the possibility of grain growth of the original fine-grain alumina during test stand ageing. Analysis of the microstructure and elemental distribution for the RAT-H(10) Special test stand aged material is currently in progress.

PUBLICATIONS

None for CRADA at this time.

PRESENTATIONS

Four presentations have been made at periodic progress report meetings between GM-ACRD and MMES personnel working on this CRADA.

HONORS AND AWARDS

None for CRADA at this time.

PATENT/DISCLOSURES

Discussion between CRADA partners of possible patent application on GM-ACRD process for preparing catalyst monoliths.

LICENSES

None for CRADA at this time.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Joint work proceeding under CRADA No. ORNL92-0115 on "Improved Catalyst Materials and Emission Control Systems" between General Motors Corporation, AC Rochester Division and Martin Marietta Energy Systems.

COST SHARING

CRADA specifies matching levels of effort and support between GM-ACRD and MMES.

HIGHLIGHTS

1. Signing of CRADA between General Motors Corporation, AC Rochester Division and Martin Marietta Energy Systems on "Improved Catalyst Materials and Emission Control Systems", CRADA No. ORNL92-0115.
2. Initial microstructural characterization of as-produced and thermally aged catalyst materials completed and presented to GM-ACRD. Though a number of high spatial resolution analytical techniques were utilized, no noble metal clusters were observed in the as-prepared material. The distribution of platinum was found to be inhomogeneous on the scale of both millimeters and nanometers. One factor contributing to the fine-scale inhomogeneity was a strong association of platinum with specific oxides in the washcoat. The levels of rhodium observed were very low, near the experimental detection limit, and less relative to measured platinum levels than would be expected from the loaded Pt/Rh ratio. In the material aged in air for one hour at 850°, the levels of platinum distributed in the washcoat matrix were reduced and coarse (20 nm diameter) platinum-enriched particles were observed.
3. Initial microstructural characterization of RAT-A and RAT-B test stand aged catalyst materials completed and presented to GM-ACRD. Coarse (20-50 nm diameter), single crystal platinum-enriched particles were observed in both materials. The platinum/rhodium levels measured in these particles were less than that loaded in the washcoat.

Fig. 2. (a) Aggregate of ceria particles (C) and platinum particle (P) in RAT-A(50) test stand aged material, (b) EDS spectra from platinum particle (P) and from ceria (C), and (c) convergent beam electron diffraction pattern from platinum particle indexed consistently as 110_{Pt}.

DEVELOPMENT OF IMPROVED AUTOMOTIVE CATALYST SYSTEMS

Problem

Platinum-rhodium based three-way-catalysts (TWC) can meet the currently required emission standards. However, higher than optimum Pt-Rh loadings are often required to meet lifetime requirements. In addition, more stringent emission standards will be imposed in the near future, demanding improved performance and service life from these catalysts. Optimized processing of the catalyst is required to maximize the performance, lifetime, and utilization of platinum and rhodium for these catalytic convertors.

Results

Coarse, metallic particles enriched in platinum have been identified in rapidly aged catalysts. The conversion performance of the catalyst decreases as the size of these particles increases, which results in decreased surface area of the catalyst. Methods to maintain a high surface area for the catalytic material are being investigated.

Coarse (~50 nm), metallic platinum (P) and ceria (C) particles identified by energy dispersive X-ray spectrometry (EDS) and convergent beam electron diffraction (CBED).

Significance - For Energy Conservation

More efficient utilization of platinum/rhodium in catalytic convertors would reduce demand for expensive and strategic materials while meeting low emissions standards. Higher convertor performance and lifetime will permit newer standards to be meet and reduce platinum/rhodium consumption and recycle costs.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

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

PHASE: FY 1993**COMPLETION DATE:** FY 1996

PERFORMING ORGANIZATIONS: Martin Marietta Energy Systems (MMES) and
General Motors - AC Rochester Division (GM-ACRD)

PRINCIPAL INVESTIGATORS: E.A. Kenik (615) 574-5066 and W. LaBarge
(313) 257-0875

PHASE OBJECTIVE: Evaluate spectroscopy and analysis techniques for characterization of microstructural and chemical state of noble metals (Pt, Rh, Pd) and their interactions with catalyst support materials. Correlate catalyst structure with manufacturing processes and identify optimum techniques for further evaluation.

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

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

PROGRESS: Two basic formulations for catalytic convertors have been prepared at GM-ACRD. Initial characterization of first as-prepared material has been completed and that of second material underway. Though no noble metal clusters have been observed in the as-produced catalysts, a number of techniques have indicated an inhomogeneous distribution of platinum in the washcoat. Test stand ageing to several different conditions has been completed by GM-ACRD for both formulations. Coarse (~20-50 nm diameter) platinum particles form both in material aged in air and in materials rapidly aged on engine test stands.

Patents: - Publications: - Proceedings: - Presentations: 4

ACCOMPLISHMENTS:

Licenses: -

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

Industry Workshop: -

Technology Transfer or Industrial Interaction: Joint research between GM-ACRD 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.

CHEMICAL VAPOR INFILTRATION OF TiB₂ COMPOSITES

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INTRODUCTION

This program is designed to develop a Hall-Heroult aluminum smelting cathode with substantially improved properties. The carbon cathodes in current use require significant anode-to-cathode spacing in order to prevent shorting, causing significant electrical inefficiencies. This is due to the nonwettability of carbon by aluminum which causes instability in the cathodic aluminum pad. 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 program is designed to evaluate potential fiber reinforcements, fabricate test specimens, and test the materials in a static bath and lab-scale Hall cell.

TECHNICAL PROGRESS

Summary

Efforts this period were devoted to preparing specimens for the licensee, Advanced Innovative Technologies, Inc., and for testing at the Alcoa Technical Center. Significant work was required to properly design and fixture specimen preforms for producing the shape required by Alcoa. Two sets of two samples each were provided to Alcoa and were tested in their bench-scale Hall cell. The results were promising in that aluminum was produced and did flow, albeit not uniformly.

Milestone

1. Complete preparation and testing of TiB₂ composites with candidate fibers in static soak tests in aluminum and cryolite. End 9/90

Samples of TiB₂ matrix composites were prepared for evaluation by industrial companies. A disk specimen was prepared and provided to Advanced Innovative Technologies, Inc. They will be evaluating the material with regard to its potential as a Hall cell cathode.

Interactions with the Alcoa Research Center in Pennsylvania has resulted in a geometric shape that can be tested in the bench-scale cells at Alcoa. A specific geometry for use in their bench-scale cells requires a half-inch hole in the center with the sides sloping toward the hole. This will allow the reduced aluminum to drain from the cathode during the test. Significant efforts were required to develop appropriate fixturing to produce such a shape, and the first specimens have been produced. T. L. Starr at GTRI has provided results from his chemical infiltration model that will guide optimization of the densification process for this geometry.

Attempts to prepare the relatively small (3-cm) TiB₂ matrix-carbon fiber samples with a 1-cm hole by chemical vapor infiltration were problematic. The use of carbon cloth resulted in disassembly of the cloth due to the minimal number of weaves that remain after cutting the specimen to dimensions. The problem was solved by replacing the carbon cloth with carbon felt, which retained its integrity after cutting to shape.

Several specimens of the required geometry (3 cm diameter, 6 mm in thickness, with a 1-cm hole with sloping sides) were prepared. A number of runs were required to both find the correct preform configuration and infiltration conditions.

Two sets of two specimens each were provided to R. A. Christini of the Alcoa Technical Center, Alcoa, PA. He has proceeded to test the samples in a bench-scale Hall-Heroult cell. Initial indications are that the material behaved well, producing aluminum and allowing it to properly drain from the cell. Destructive examination of the material and cell indicate that the specimen survived the short duration tests. Christini reports, however, that not all areas of the material were wetted or allowed flow of aluminum. It is likely that some greater control over the deposited TiB₂ is necessary to prevent codeposition of boron and to provide more uniform surfaces.

PUBLICATIONS

1. "Chemical Vapor Infiltration of TiB_2 Composites," T. M. Besmann, J. H. Miller, K. M. Cooley, R. A. Lowden, and T. L. Starr, ORNL/TM-12214.
2. "Chemical Vapor Infiltration of TiB_2 Composites," T. M. Besmann, J. H. Miller, K. M. Cooley, R. A. Lowden, and T. L. Starr, submitted to the J. Am. Ceram. Soc.

PRESENTATIONS

1. T. M. Besmann, K. M. Cooley, and T. L. Starr, Chemical Vapor Infiltration of TiB_2 Fibrous Composites, Advanced Industrial Concepts Materials Program Annual Information and Review Meeting, June 7-9, 1993, Oak Ridge, Tennessee.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None this period.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

The Alcoa Technical Center provided specifications for test specimens which were fabricated at ORNL. Two test specimens have been evaluated in a bench-scale Hall cell at Alcoa.

COST SHARING

None.

HIGHLIGHTS

TiB₂-matrix composites were tested at the Alcoa Technical Center and the results indicate that the material does result in the reduction of aluminum and allows flow of aluminum from the cell.

DEVELOPMENT OF TiB_2 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. TiB_2 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.

Results: Specimens of TiB_2 -matrix composite were provided to the licensee, Advanced Innovative Technologies, Inc. for evaluation. Candidate TiB_2 cathodes were produced for testing at the Alcoa Technical Center. The carbon fiber reinforcement is expected to overcome both the inherent brittleness of monolithic TiB_2 and yet remain unaffected by molten aluminum. Alcoa has tested the material in their bench-scale Hall cells and determined that it reduces aluminum, is wet by the aluminum, and allows flow of aluminum from the cell. These are all prerequisites for commercial use as a replacement cathode in the reduction of aluminum.

Significance For Energy Conservation:

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

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: CHEMICAL VAPOR INFILTRATION OF TiB₂ COMPOSITES

PHASE: FY 1993

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR: Theodore M. Besmann, 615/574-6852

PHASE OBJECTIVE: Efforts this period were devoted to preparing specimens for the licensee, Advanced Innovative Technologies, Inc., and for testing at the Alcoa Technical Center.

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

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.

PROGRESS: Efforts this period were devoted to preparing specimens for the licensee, Advanced Innovative Technologies, Inc., and for testing at the Alcoa Technical Center. Significant work was required to properly design and fixture specimen preforms for producing the shape required by Alcoa. Two sets of two samples each were provided to Alcoa and were tested in their bench-scale Hall cell.

Patents: none Publications: one Proceedings: none Presentations: one

ACCOMPLISHMENTS: Specimens were prepared for the licensee, Advanced Innovative Technologies, Inc., and for testing at the Alcoa Technical Center. The results were promising in that aluminum was produced and did flow, albeit not uniformly.

Licenses: one

DEVELOPMENT OF CHEMICAL VAPOR COMPOSITE (CVC) MATERIALS

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INTRODUCTION

The objective of this program is to develop the Chemical Vapor Composite, (CVC) process in order to economically fabricate strong, fracture tough ceramic composites. The CVC process fabricates composite material by simply mixing particles (powders and/or fibers) with vapor reactants which are transported and co-deposited on a hot machined substrate. A key feature of the CVC process is control of the density, geometry and composition of the entrained particles in the matrix material during deposition. The CVC process can fabricate ceramic composites materials to net shape (± 0.0005 inches) on one side in a single step by deposition on a negative mold. The process does not require a woven preform and can deposit composite material over 100 times faster than Chemical Vapor Infiltration (CVI) process. The reduced cost of CVC ceramic composites materials permits many new potential applications that are not possible using conventionally-made ceramic materials.

The program is designed to determine to relationships between material properties, process parameters and microstructure. This understanding of the CVC process will be used to fabricate strong, fracture-tough, ceramic composite material that is stable at high temperatures. The ultimate goals of the program are to produce in a single step, net shape ceramic composites that are:

- Stable in air and combustion atmospheres (>2000 h at 1200°C)
- Fracture tough ($K_{Ic} > 15 \text{ MPam}^{1/2}$)
- Strong at high temperatures (80 Ksi at 1200°C)

TECHNICAL PROGRESS

Summary

Considerable progress was made this year, with major accomplishments in equipment modifications, material characterization and optimization and technology transfer. A shower head type inlet manifold for reactant gasses and powder was used to deposit SiC/SiCp composite without bands of microporosity. Material strength of SiC/SiCp increased from 350 MPa to 470 MPa by using higher purity SiC powder. The Weibull modulus of the as-deposited SiC/SiCp improved from 9.2 to 22.4. No loss of strength was measured after exposure of SiC/SiCp in air at 1200°C for 2000 h. Also ceramic to metal transition joints were fabricated with the CVC process by gradually varying the composition and volume percentage of powder in the matrix material. Transition joints (1 in. × 1 in. × 1/8 in.) of SiC to Mo were fabricated and remained in tact after thermally cycling from 1200°C to room temperature.

Milestones

1. The inlet manifold which mixes reactant gas and particulates (powder and/or fibers) was redesigned and installed in the 30 Kw horizontal CVC reactor. The inlet manifold has separate nozzles for powder and reactant gas. The substrate for CVC depositions is a 24 in. long, 4.5 in. diam graphite tube. The redesigned manifold introduces the reactant gases via a shower head geometry of eight 1/16 in. diam holes evenly spaced at one end of the tube substrate. The powder and by flow gases were introduced with one 1/4 in. diam hole in the center of the shower head. During CVC deposition the inlet manifold remained stationary while the graphite tube is rotated. CVC SiC/SiCp deposits with the shower head mounted revealed no porous layered microstructure. This layered microstructure is distinguished by bands of microporosity which can limit the strength of the CVC SiC/SiCp material. Eliminating the microporosity also stops the pathway for the atmosphere to enter the bulk material during high temperature operation.
2. No loss in strength was observed after exposure of SiC/SiCp to 1200°C air for 500 and 2000 h. A Weibull plot of the as-deposited and 2000 hour exposed CVC SiC is shown in Fig. 1.

Fig. 1. Comparison of as-deposited CVC SiC to 2000 h at 1200°C.

3. Examination of the baseline fracture surface of CVC SiC/SiCp bend bars reveals that the SiC powder deflects the crack during fracture. This crack deflections appears to occur primarily at the interface between the columnar grains which grow from the particulates and the rest of the matrix instead of at the particulate matrix interface. The layered microstructure of the CVC deposit also appears to contribute to the deflection of the crack which will lead to increased toughness. EDX analysis of the fraction origins reveals a narrow ring of impurities in the matrix around the particulates. The impurities have been identified as Iron (Fe), Nickel (Ni), Titanium (Ti), and Vanadium (V). A higher purity powder was used to deposit CVC SiC/SiCp which increased the strength from 350 MPa to 470 MPa and the Wiebull Modulus to 22. A Weibull plot for the as-deposited CVC material is shown in Fig. 2.

Fig. 2. CVC SiC/SiCp with Higher Purity Powder.

4. Ceramic-to-metal transition joints were fabricated by gradually varying the volume percent of metal powder in the ceramic matrix material during deposition. Transition joints to SiC to Mo and SiC to W were fabricated and thermal cycled four times from 1200°C to room temperature and remained intact. A cross section of a thermal cycled Mo to SiC transition joint is shown in Fig. 3.
5. CVC SiC/SiCp material was fabricated with four different powder sizes (10, 30, 40, and 65 microns) and five different powder feed rates (5, 10, 15, 20, and 30 grams/h). The material was cross-sectioned polished and characterized for porosity and powder volume percent. A plot of powder volume percent versus powder feed rate for two different powder sizes (20 and 65) was linear as shown in Figs. 4 and 5.

AIM

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Fig. 3. Cross-Section of CVC Mo to SiC Transition Joint.

Fig. 4. Plot of Volume Percent of 30 Micron SiC Powder in SiC Matrix vs Powder Feed Rate.

Fig. 5. Plot of Volume Percent of 65 Micron SiC Powder in SiC Matrix vs Powder Feed Rate.

PUBLICATIONS

Journals

S. Johnson, "SiC Coatings on RB SiC Mirrors for Ultra-Smooth Surfaces," *SPIE*, (July 1993).

P. Reagan, M. Allendorf, "Model Helping Make Dream of Low-Cost Ceramic Composites Come True," *Sandia Technology Bulletin* (August 1993).

P. Reagan, "Cheap Ceramics," *Aviation Weekly and Space Technology* (November 1993).

P. Reagan, Chemical Vapor Composites," *Journal De Physique IV* (1993).

PRESENTATIONS

P. Reagan, "Chemical Vapor Composite CVC Transition Joints," MRS Spring Meeting, April 1993 San Francisco, CA.

P. Reagan, L. M. Ewart, and S. C. Stowells, 95th Annual American Ceramic Society Meeting (Cincinnati, OH): "The Microstructure and Mechanical Properties of SiC/SiCp formed by Chemical Vapor Composites (CVC) Process," April 1993.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

The following companies and organizations are perusing the technology transfer of specific CVC components:

Atlanta Research:	Re Rocket Thrusters
NASA:	Re Rocket Thrusters
Holcroft:	SiC fans
Ametek:	Optical SiC Probe
S.S.G.:	SiC Mirrors
M.R.S.:	SiC Mirrors
WPAFB-NSAP:	SiC to Mo Transition Joints
Knolls Atomic Power Lab:	SiC to Mo Transition Joints
MAGNETEK	W & Mo MMC Dies
KOHLER	W & Mo MMC Dies
CANMET	W & Mo MMC Dies
INTERNATIONAL COPPER ASSOC.	W & Mo MMC Dies
SCHLAGE LOCK	W & Mo MMC Dies
UCLA (PISCES)	W Panels
U.S. ARMY	W Antiarmor

COST SHARING

TTC has funded \$150 K in 1993 to commercialize Chemical Vapor Composite manufacturing. TTC intends to develop a business plan to market CVC components based on joint evaluation of prototypes by end users and TTC.

DEVELOPMENT OF CHEMICAL VAPOR COMPOSITE CVC MATERIALS

PROBLEM: A reliable and flexible process is needed to produce, in a single step, ceramic composites to final shape. Current technology is limited by problems of unreliability, multiple production steps, scale-up to large size and cost.

RESULTS: A novel flexible process has been developed and patented, that mixes powder and/or fibers in a chemical vapor deposition (CVD) gas stream to produce in a single step, reliable, non-brittle composites to final shape. Production rates are up to 100 times faster than CVD. It allows tailoring of density, composition, and toughening phase during deposition, and is scalable to large components.

SIGNIFICANCE

APPLICABLE TO ENERGY CONSERVATION: Process can produce low cost heat exchangers, radiant tubes, burners and refractories for high temperature applications. Components can be made for low-NO_x combustors, waste incinerators, chemical and particle clean-up equipment.

INDUSTRIAL COMPETITIVENESS: Process is adaptable for fabricating low cost metal matrix components, carbon carbon-composites and ceramic-to-metal transition joints. Production cost estimates for end products are in the \$100 per pound range for Chemical Vapor Composite.

(R&D PERFORMED AT THERMOTREX CORPORATION UNDER DOE-CE SUPPORT)

PROJECT SUMMARY

PROJECT TITLE: Development of Chemical Vapor Composite (CVC) Materials

FISCAL YEAR: FY 1992

COMPLETION DATE: 1995

PERFORMING ORGANIZATION: ThermoTrex Corporation, 85 First Avenue,
P.O. Box 8995, Waltham, MA 02254-8995

PRINCIPAL INVESTIGATOR: Peter Reagan (617) 622-1347

PHASE OBJECTIVE: Understand the relationship between the Chemical Vapor Composite (CVC) deposition process parameters and microstructure in order to improve key material properties (strength and toughness).

ULTIMATE OBJECTIVE: Develop a reliable, flexible, and economical process to fabricate strong, fracture tough ceramic composites to net shape in a single step.

TECHNICAL APPROACH: The objective of the program is to develop a baseline relationship between the CVC process parameters and the microstructure of the deposited material. The next objective is to relate the microstructure of the deposited materials with the measured material properties. An experimental program will be carried out in order to determine the effect of powder flux and size on the microstructure of the deposited material.

PROGRESS: Designed and fabricated shower head inlet gas and powder manifold in CVC Reactor that reduces bands of microporosity in deposited CVC SiC/SiCp material.

CVC SiC/SiCp material thermally tested at the 1200°C in air for 2000 h showed no loss of strength. CVC SiC/SiCp after thermal testing had an average strength of 370 Mpa with Weibull Modulus of 14.

Increased deposition strength of CVC SiC/SiCp by 110 Mpa was achieved by using higher purity powder. As-deposited strength was 470 Mpa with a Weibull Modulus of 24.

Fabricated CVC transition joints from metal to ceramic by gradually varying powder composition and volume percent during deposition. CVC Mo to SiC joint was intact after cycling to 1200°C in vacuum four times.

Identified a wide variety of industrial uses of CVC materials.

Patents: 1, Publications: 2, Proceedings: 0, Presentations: 2

ACCOMPLISHMENTS

TECHNOLOGY: The following companies are evaluating supplied CVC components.

Atlantic Research:	Re Rocket Thrusters
Holcroft:	SiC fans
Ametek:	Optical SiC Probe
S.S.G.:	SiC Mirrors
M.R.S.:	SiC Mirrors
WPAFB-NSAP:	SiC to Mo Transition Joints
Knolls Atomic Power Lab:	SiC to Mo Transition Joints

CRITICAL ISSUES

Proprietary information prevents disclosure.

FUTURE PLANS

Improved accuracy and reliability of CVC fiber feeders. Understand relationship between microstructure of material and CVC process parameters. Identify a variety of industrial users of CVC material. Fabricate and test prototypes and estimate their impact on energy conservation.

POTENTIAL PAYOFF

Low cost ceramic composite components would be available to industrial users. The reduced cost of CVC materials would lead to many new applications that were closed to currently available advanced materials. Cost estimates for production of ceramic composites by CVC are in the \$100 per pound range.

DEVELOPMENT OF NEW COMPOSITE AEROGEL MATERIALS

A. J. Hunt and W. Cao

Energy and Environment Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

INTRODUCTION

Aerogel materials are porous, low density, nanostructured solids with many unique properties including low thermal conductivity, high transparency, high surface area, catalytic activity, and low sound velocity. This research is directed toward developing new nanocomposite aerogel materials for a number of applications. An important focus of the work in the past two years has been to substantially improve the thermal resistance of silica aerogel by adding nanophase carbon. The resulting aerogel composites open up a number of new industrial applications for aerogel based thermal insulation. Three primary benefits accrue from composite aerogel thermal insulation; extending the range of applications to higher temperatures, providing a more compact insulation for space sensitive-applications, and lowering the cost of the aerogel by as much as 30%. Superinsulating aerogel can replace existing CFC-containing polyurethane insulation and significantly improve the thermal efficiency of refrigerators and freezers, reduce heat losses in hot and cold piping, insulate batteries in electric vehicles, and reduce energy losses in a variety of industrial applications. Industry has been very interested in improved aerogel insulation and several CRADAS for the commercialization of aerogel-based materials are under discussion. Recently, we have generalized the aerogel insulation research to the wider area of nanostructured aerogel composites. A number of new materials have been prepared with unusual properties attributable to their very fine dimensions such as quantum size effects. These materials may be useful for magnetic cooling cycles, electroluminescent displays, and optical devices. Work on both these areas advanced significantly in FY 1993.

TECHNICAL PROGRESS FY 1993

Summary

This year we continued the development of silica/carbon composite aerogels for thermal insulation applications and extended our exploration into new aerogel composites based on alternative doping materials. The thermal insulation work concentrated on developing composites with smaller pore size to improve the pressure versus thermal resistance performance, determining optimum carbon doping levels for various applications, modeling the thermal conductivity in aerogels and designing and building a new instrument to measure the pressure and temperature dependence of aerogel's thermal conductivity. New composite silica aerogels containing iron, iron oxide, iron/carbon, and silicon were prepared and tested. The photoluminescent response of silicon/silica composites was characterized. The magnetic and optical properties of the iron- and iron oxide- silica aerogels were characterized. Transmission electron microscopy was used extensively to characterize the nanostructure and crystallinity of the new composites.

Milestones

1. Develop opacified aerogels for higher temperature applications.

In evacuated silica aerogel at ambient temperatures, infrared radiation is responsible for up to half or more of its thermal conductivity; therefore reducing the radiation substantially improves the thermal performance of aerogel insulation. At elevated temperatures (200° to 500°C), the radiative component of heat transfer in aerogel becomes dominant and must be suppressed. In the 3-8 micron region of the infrared, silica has low intrinsic absorption that allows significant leakage of radiation through the aerogel. This radiation can be blocked by adding a finely dispersed material with a high absorption coefficient. Carbon was found to be the best additive for applications not requiring visual transparency. In earlier work, carbon particles were added to the aerogel at the sol or liquid stage and subsequently processed and dried. Thermal resistance measurements showed an increase of more than 50% in thermal resistance at ambient temperatures and

much larger percentage increases at higher temperatures.

However, the addition of carbon at the formulative stage of the gel reduced the strength of the gel and at the increased doping levels required to opacify the aerogel for higher temperature applications, the strength deteriorated considerably. To overcome these limitations we discovered and are developing a new method to add carbon that has many advantages over the particle addition method. A true nanocomposite aerogel is created by the process of chemical vapor infiltration (CVI). A silica or other composition aerogel is infiltrated with a gas that is catalytically decomposed by the aerogel. The decomposition product is left inside the aerogel as a solid deposit at a nanometer scale. Using this method increases the strength of the aerogel composite and allows for doping levels several times the original mass of silica. We have explored a variety of gases for CVI deposition of carbon. Infrared and surface area measurements along with high resolution transmission electron microscopy were used to characterize the composites. Patent applications covering the CVI-aerogel nanocomposite production process are being filed.

In order to assess the thermal performance of composite aerogel insulation we designed and built an instrument to measure the thermal conductivity of aerogel as a function of pressure and temperature. A thin film heater thermal conductivity apparatus with variable pressure capabilities was nearing completion at the end of the fiscal year. To analyze and predict the thermal performance of aerogel the heat transfer due to the radiation, conduction, and gas conductivity and their interaction inside aerogel is being modeled. The objective is to predict the thermal conductivity as a function of temperature, and gas pressure. The predicted effects of carbon doping on the thermal performance of aerogel are quite dramatic at temperatures from 200° to 500° C and if borne out, opacified aerogel will be an outstanding insulating material for temperatures up to 500° C.

2. Carry out development of magnetic nanocomposite material and explore new nanocomposite materials.

We have developed techniques for the preparation of a whole new family of unique nanoporous composite materials based on CVI-aerogel and other preparation techniques. In addition to achieving high densities of carbon in the silica aerogel, nanophase composites were prepared using elemental silicon and iron. Composites of silica aerogels and the oxides of iron, nickel, and copper were also synthesized. Using these methods we believe that a wide variety of new composite materials can be produced. Such nanophase materials have potential applications in magnetic cooling cycles, electroluminescent displays, and for transparent magnetic materials. Silicon-silica composites exhibit photoluminescence that our measurements confirm is due to quantum well confinement effects. These materials may well be useful for electroluminescent display devices. The iron and iron oxide composites exhibit magnetic properties that appear useful for magnetic cooling cycles.

PUBLICATIONS

Journals

W. Cao and A.J. Hunt, "Thermal Annealing of Photoluminescent Si on Silica Aerogels," submitted to Applied Physics Letters, September 1993.

S.Q. Zeng, A.J. Hunt, W.Q. Cao, and R. Greif, Pore size distribution and gas phase thermal conductivity of silica aerogel, submitted to the Journal of Heat Transfer, September 1993.

Other Publications

1. Hunt A.J. "Optical and Thermal Properties of Silica Aerogels," Chemical Processing of Advanced Materials, L. H. Hench and J. K. West eds., John Wiley & Sons, Inc. New York, 1992.

2. A.J. Hunt, "Aerogel - A Transparent, Porous Superinsulator" Proc. of the ASCE, Atlanta, August 10-12, 1992.

3. A.J. Hunt, C.A. Jantzen, and W. Cao, "Aerogel - A High Performance Insulating Material at 0.1 Bar," Insulation Materials: Testing and Applications, Vol 2 ASTM STP 1116, R.S. Graves and D.C. Wysocki, Eds., American Society for Testing and Materials, Philadelphia 1991.

4. K.D. Lofftus, K.V.S. Sastry, and A.J. Hunt, "Colloidal and Kinetic Principles of Sol-Gel Processing" Advanced Materials Proc.

PRESENTATIONS (by Arlon Hunt)

"Aerogel, an Unusual Low Density Material," Varian Corp. Palo Alto CA, July 13, 1992

“Aerogel Insulation for Cold Weather,” Cold Regions Research Engineering Laboratory, Hanover, NH August 19, 1992.

“Development of Improved Aerogel Superinsulation,” Advanced Industrial Concepts Materials Program, Annual Information and Review Meeting, ORNL, Oak Ridge, TN June 7-9, 1993.

HONORS AND AWARDS

Federal Laboratory Consortium Award for Technology Transfer (1990)

Lawrence Berkeley Laboratory Excellence Award for Technology Transfer (1991)

PATENTS/DISCLOSURES

“Process for Forming Transparent Aerogel Insulating Arrays,” Canadian Patent No. 1,288,313, Sept. 3, 1991, A. J. Hunt and P. H. Tewari.

“Aerogel Composites and Method of Manufacture,” Wanqing Cao and Arlon Hunt Disclosure IB 929 LBL in preparation.

LICENSES

A CRADA is under discussion with Aerojet Corporation for the commercialization of aerogel manufacturing. A CRADA is also being discussed with an Alabama company and LBL to license patentable results from the opacification work.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Meetings were carried out with staff members from various industries to explore the use of aerogels in autos, acoustic and visual display devices, windows, and other applications.

COST SHARING

None

HIGHLIGHTS

The process discovered last year was further developed to produce a variety of new nanocomposite materials. Materials were prepared to explore applications for higher performance thermal insulation with greater heat resistance at ambient and higher temperatures, new display devices, and electrode materials.

Chemical Vapor Infiltration of Aerogels

Problem:

While aerogel is the best solid insulating material at ambient temperatures, at higher temperatures infrared radiant energy transfer rapidly decreases its performance. To improve the thermal resistivity at temperatures up to 500°C the radiant transfer must be blocked. Earlier work based on very small carbon particles (from carbon slurries and inks) blocked the radiation, but the disrupted the gel structure and produced a weaker material so that a higher density must be used to compensate for loss of strength causing increased solid conductivity and lower thermal performance.

Results:

Using aerogel catalyzed chemical vapor infiltration (ACCVI) we added carbon to the finished aerogel network and produced a uniformly doped aerogel with improved strength and temperature capabilities. The higher doping achievable in this way decreases the infrared transmission and improves the thermal resistivity at higher temperatures.

INFRARED TRANSMISSION OF VARIOUS SILICA AEROGEL

Infrared transmission of pure silica aerogel, particle doped aerogel (ink) and chemical vapor infiltrated aerogel.

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-CE-AIC Materials Program support)

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Development New Composite Aerogel Materials

PHASE: FY 1993

PERFORMING ORGANIZATION: Lawrence Berkeley Laboratory

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

PHASE OBJECTIVE: Develop new aerogel composite material thermal insulation

ULTIMATE OBJECTIVE: Develop new aerogel-based nanocomposite materials

TECHNICAL APPROACH: Develop processes to make new aerogel-based composite materials with sol-gel chemistry, supercritical drying, and chemical vapor infiltration. Improve the thermal performance of aerogel by reducing radiative heat transfer using carbon nanocomposites to absorb the infrared radiation. Develop new aerogel-based nanocomposite materials.

PROGRESS: Infrared opacified silica aerogel was produced using chemical vapor infiltration methods that displayed improved thermal and physical properties. This provides higher temperature and stronger aerogel thermal insulation. The process was generalized to produce a wide variety of new composite materials. Some of these composites display unusual characteristics (e.g. photo-luminescence in silicon silica composites) due to quantum confinement effects.

Patents: (Canadian Patent 1,288,313) **Publications:** 2 **Proceedings:** none
Presentations: 1

ACCOMPLISHMENTS: The ambient temperature thermal resistance of aerogel has been increased by more than 50%. A new method was discovered that improves the thermal and physical performance of aerogel at ambient and higher temperatures while reducing the cost.

Licenses: none

PROJECT TITLE: Development New Composite Aerogel Materials

CRITICAL ISSUES: Improve the performance and lower the cost of aerogel insulation for ambient and higher temperature applications and develop new nanocomposite materials based on aerogel.

FUTURE PLANS: 1) Improve methods to produce opacified aerogel for use at elevated temperatures ($< 500^{\circ}\text{C}$), 2) increase the compressive strength of and decrease the vacuum requirements for opacified aerogel, 3) develop new nanocomposite materials based chemical vapor infiltration of aerogel.

POTENTIAL PAYOFF: New high performance thermal insulation for ambient and intermediate temperature applications in hot and cold pipe insulation, refrigerators, automobile battery insulation, and new composites with unusual optical, magnetic and electrical properties.

ESTIMATED ENERGY SAVINGS: Opacified aerogel in refrigerators and freezers (over current technology): 3 Quads in 20 years.

HIGH DEPOSITION RATE CERAMICS SYNTHESIS

M. D. Allendorf, T. H. Osterheld, and D. R. Hardesty

Combustion Research Facility
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Livermore, California 94551-0969

INTRODUCTION

The purpose of this work is to develop a quantitative understanding of the chemical and physical mechanisms that result in high deposition rates and fully dense ceramic materials from innovative high-temperature ceramic synthesis processes. Such processes include the chemical vapor infiltration (CVI), particle-enhanced chemical vapor deposition (PECVD), and flame synthesis or spraying of materials. Experimental investigations use the unique laser and other diagnostic capabilities available at the Combustion Research Facility to characterize novel processes for achieving rapid and efficient deposition of ceramic materials. Chemical-kinetic experiments and modeling of gas-phase and surface chemistry are being performed to determine decomposition mechanisms. A long-term goal is the development of computational models of ceramic synthesis processes for use in designing, optimizing, and operating industrial reactors. Three tasks are defined, as follows:

1. Experimental Studies of Gas Flows with Entrained Solids (with ThermoTrex Corp.)
2. Chemical and Physical Mechanisms of Deposit Formation
3. Process Modeling of Flame Spray Technologies (with General Magnaplate Corp.)

TECHNICAL PROGRESS FY93

Summary

In Task 1, work completed in FY92 was published in two articles. In Task 2, a new mass spectrometer system was designed, installed, and tested to provide sensitive detection of stable reaction products. This system was used to investigate the high-temperature decomposition kinetics of methyltrichlorosilane (MTS), an important precursor used to deposit silicon carbide during chemical vapor infiltration. Results of these studies indicate that methane and hydrogen chloride are important products of MTS decomposition and that significant

decomposition commences at temperatures at about 1200 K for reactor pressures of 25 torr. In addition to the experimental results, calculations were performed that provide quantitative estimates of the temperature and pressure dependence of the MTS decomposition rate. Finally, a new computational model of silicon carbide deposition was developed that couples detailed gas-phase chemistry with elementary surface reactions. In Task 3, a new modeling effort, directed toward the simulation of turbulent flames used to deposit wear-resistant coatings, was initiated. This work, which is continuing, is being performed in collaboration with the General Magnaplate Corporation, which is developing a portable flame-spray process.

Milestones and Progress

Task 1

An ongoing collaboration with research staff at the ThermoTrex Corporation continued this year with the publication in *Journal of Materials Research* of a paper entitled "Deposition of Silicon Carbide Using the Chemical Vapor Composites Process: Process Characterization and Comparison with RASSPVDN Model Predictions." This article describes experiments and modeling of the CVC process, which is under development by ThermoTrex for the rapid production of ceramic composites. In addition, a brief article describing the CVC process and the Sandia modeling effort was published in the Sandia newsletter *Manufacturing Technology*. The purpose of *Manufacturing Technology* is to bring new Sandia developments in this field to the attention of industry; Sandia distributes this newsletter free of charge to over 17,000 industrial, government, and academic subscribers. Inquiries regarding the CVC technology and Sandia's modeling effort were coordinated through Sandia. In the first month following publication of the article, inquiries were received from several manufacturers with potential applications for the CVC technology. In addition, requests for further information were received from technical news organizations, which plan to run their own articles on the topic. This increased visibility for CVC technology will hopefully lead to the identification of industrial customers for this AIM-sponsored technology. Sandia's interaction with ThermoTrex will continue in 1994, with the goal of developing strategies for scaling the CVC process for the production of larger parts.

Task 2

1. Experimental studies of silicon carbide precursor decomposition

In this subtask we use a high-temperature flow reactor (HTFR) completed in FY92 coupled with laser diagnostics and mass spectrometry to measure the high-temperature kinetics of ceramic precursor decomposition. The focus of our current investigations is the compound methyltrichlorosilane (MTS), which is commonly used to form silicon carbide composites via chemical vapor infiltration (CVI). Results of these studies provide input to ceramic deposition models (see below) by measuring rate constants and identifying reaction pathways.

A major achievement this year was the design, purchase, installation, and testing of a quadrupole mass spectrometer system for the HTFR. This versatile piece of equipment provides sensitive detection of stable molecular species resulting from the decomposition of precursor compounds. Tests showed that compounds present in amounts as small as 5 ppm can be detected and distinguished from background molecules in the chamber. The spectrometer uses a quartz sampling probe to remove small amounts of gas from the HTFR during an experiment. The probe operates at a low pressure relative to the reactor to minimize any further reaction that could occur in the probe itself. Once the sample enters the spectrometer, it is formed into a molecular beam via expansion through a sonic orifice. Modulation of this beam by a tuning fork chopper allows lock-in amplification to be employed, effectively removing interference from background gases that build up in the chamber. This equipment represents a major increase in sensitivity over laser Raman spectroscopy that had been employed previously.

A second important achievement in 1993 was the successful application of mass spectrometry to the study of MTS decomposition. In a relatively short time we have obtained data that provide significant new insight into the high-temperature reactions of this SiC precursor. Our accomplishments to date are as follows:

1. MTS has been detected and its cracking pattern in the spectrometer identified.
2. An appropriate temperature range for kinetics experiments was identified by monitoring the decomposition of MTS at 25 torr over a range of temperatures. In experiments of this type, we learned that it is best to obtain data at relatively low precursor decomposition rates in order to avoid interference from secondary reactions. We have found that over the 940 - 1020 °C range, MTS decomposition in the reactor can be held to 10% or less.

3. Methane and hydrogen chloride were identified as major MTS decomposition products (see Figure 2). This result is consistent with predictions of a detailed mechanism describing MTS pyrolysis (see discussion below). To date, no silicon-containing products have been detected. This may be the result of efficient trapping of these species by the walls of the reactor and is being investigated further.
4. The effect of using hydrogen versus helium as the carrier gas was examined. Preliminary results indicate that exchanging helium for hydrogen does not have a major effect on the MTS decomposition rate, but does increase the amount of CH_4 product observed (probably through the reaction $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$). These observations are also consistent with theoretical predictions.
5. We attempted to trap the silicon-containing radical SiCl_2 by adding ethylene to the reaction mixture. SiCl_2 is expected to be a secondary product of MTS decomposition via the reaction $\text{CH}_3\text{SiCl}_3 \rightarrow \text{CH}_3 + \text{SiCl}_3$ followed by $\text{SiCl}_3 \rightarrow \text{SiCl}_2 + \text{Cl}$. No evidence of a trapped product was obtained, which may be due to a relatively slow reaction between SiCl_2 and ethylene. This chemistry will be pursued further in FY94.

Figure 1: Mass spectrum of 1% MTS in helium, sampled from the HTFR (25 torr, 673 K). The solid line indicates the spectrum in the presence of MTS, while the dashed line shows the background signal. Compounds identified are fragments of the parent compound which form inside the spectrometer following ionization.

Theoretical estimates of the MTS decomposition rate under typical ceramic synthesis conditions were also completed this year. These calculations are used to guide experiments, interpret the data, and allow the experimental results to be extrapolated outside the range of conditions in which they were collected. Statistical methods (RRKM theory) were employed to obtain the temperature and pressure dependence of several MTS unimolecular decomposition reactions. These results are summarized in a two papers, one presented at the Twelfth *International Conference on Chemical Vapor Deposition* and the other submitted to *Journal of Physical Chemistry*. The key results are:

1. Three possible chemical pathways for MTS decomposition were identified. The products of these different pathways have widely differing surface reactivities and thus their relative concentrations in the gas-phase will affect the SiC deposition rate.
2. The rate of the most efficient decomposition pathway ($\text{CH}_3\text{SiCl}_3 \rightarrow \text{CH}_3 + \text{SiCl}_3$) is very pressure-dependent, decreasing rapidly with decreasing pressure. This is important since, in CVI, lower pressures (5-75 torr) are sometimes used to increase the rate of precursor diffusion into the pores of the preform. Thus, there may be counteracting affects at work in which slower gas-phase chemistry is offset by faster diffusion.
3. The temperature-dependence of the rates of each decomposition pathway was determined.

Figure 2: MTS decomposition at 1273 K and 25 torr. The MTS concentration is monitored at masses 148 and 133 (corresponding to $\text{CH}_3\text{SiCl}_3^+$ and SiCl_3^+). Signals corresponding to HCl and CH_4 appear in the spectrum, identifying these species as decomposition products. Introduction of H_2 causes the CH_4 concentration to increase, probably due to $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ (the MTS decrease is caused by dilution). The figure also shows that residence time is easily adjusted in the HTFR, allowing the extent of pyrolysis to be controlled.

The results of these studies were published recently as a Sandia Technical Report and have also been forwarded to investigators in the Ceramics Working Group of the AIM Program (a major focus of this group is the development of new chemical vapor infiltration processes).

2. Modeling the deposition of silicon carbide

Considerable progress was made in FY93 toward developing a generic model for the deposition of SiC. First, the estimated MTS decomposition rates discussed above were combined with our previously developed knowledge of organosilicon chemistry to obtain a comprehensive mechanism describing the gas-phase reactions occurring in high-temperature reactors. This detailed mechanism contains nearly one hundred reactions, including twenty-three for species containing both silicon and carbon. Its development represents a major step forward in understanding SiC CVD. Previous efforts to describe this chemistry typically use a single, global reaction to describe the gas-phase. In addition, they usually assume that the gas-phase is at equilibrium, an assumption that we now know is incorrect. Our mechanism suggests that the primary source of silicon in SiC deposition is SiCl_2 , while the carbon source is CH_4 .

Second, we developed a mechanism that converts the products of gas-phase MTS decomposition to silicon carbide on the deposition surface. This mechanism assumes that CH_4 and SiCl_2 are the principal gas-phase species reacting with the surface. Using a total of six reactions in each case, mechanisms were developed for deposition on several different crystalline faces, including the (100), (220), and (111) edge. The reactions are reversible; thermochemistry for each reaction was estimated, consistent with the overall thermochemistry of SiC formation.

Coupling the surface mechanism with the gas-phase MTS decomposition mechanism enables use to simulate recent experiments at Oak Ridge National Laboratory in which SiC was deposited on a weave of fibers stretched perpendicular to the flow of an MTS/ H_2 mixture. Deposition rates similar to those observed in the experiments could be obtained by adjusting rates of the reactions in the surface mechanism (which are not well understood). However, the experimental activation energy (24 kcal mol^{-1}) is lower than that predicted by the model (35 kcal mol^{-1}). The simulations also suggest that the principal carbon source changes from CH_4 to C_2H_4 as the temperature reaches 1450 K. It is thus necessary to include additional reactions in the surface mechanism. Development of the mechanism will continue in FY94 as additional experimental results from the HTFR become available for comparison.

Task 3

The General Magnaplate Corporation (GMC) is developing a flame-spray process for the production of wear-resistant coatings. These coatings find applications in many manufacturing sectors, including the paper, food processing, pharmaceutical, and petrochemical industries. Sandia expertise in the field of flame modeling was employed this year with the aim of developing a computational model that can assist GMC with process optimization. Efforts this year were directed toward the following goals:

1. Assembly of appropriate thermodynamic information for materials used in the spray process. This work is complete; an extensive data base was compiled that includes thermodynamic information for metals, ceramics, and polymers of interest to GMC.
2. Measurement of unknown spray parameters. Experiments were conducted at GMC to measure powder feed rates, gas flow rates, and deposition surface temperatures, data that are required before simulations can begin. Discussions with the torch manufacturer (Alamo Supply Company of Houston, Texas) provided accurate dimensions of the complex spray nozzles in use by GMC (see Figure 3). Results obtained from these simulations will be made available to Alamo Supply Company as well as GMC.
3. Modification of an existing code to simulate the turbulent flame produced by the spray torch. We are modifying a turbulent flame code originally developed to simulate pulverized coal combustion in utility boilers to predict particle melting in flame-spray torches. This work is in progress; we hope to complete these modifications during the first quarter of FY94 so that we can begin simulating the actual spray process.

Figure 3: This figure shows a cross-section of the flame-spray torch used in the GMC process. The coordinate system used in the calculations is also shown. Light shading in the flame region indicates the hottest gases, while darker shading indicates cooler gases and/or particles.

PUBLICATIONS

1. M. D. Allendorf, C. F. Melius, and T. H. Osterheld "Thermodynamics and Kinetics of Methyltrichlorosilane Decomposition," *Proc. Twelfth International Symp. Chem. Vapor Deposition*, Electrochemical Society Proceedings Series, Pennington, 1993, Vol. 93-2, p. 20 (released prior to publication as *Sandia National Laboratories Report* SAND93-8464).
2. T. H. Osterheld, M. D. Allendorf, and C. F. Melius "Unimolecular Decomposition of Methyltrichlorosilane: RRKM Calculations," submitted to *J. Physical Chemistry*, 1993 (released prior to publication as *Sandia National Laboratories Report* SAND93-8576).
3. M. D. Allendorf, C. F. Melius "Theoretical Study of the Thermochemistry of Compounds in the Si-C-Cl-H System," *J. Phys. Chem.*, **97** (1992), 720 (released prior to publication as *Sandia National Laboratories Report* SAND92-8623).

4. M. D. Allendorf "Equilibrium Predictions of the Role of Organosilicon Compounds in the CVD of Silicon Carbide," *J. Electrochem. Soc.*, **140** (1992), 747 (released prior to publication as *Sandia National Laboratories Report SAND92-8526*).
5. M. D. Allendorf, R. H. Hurt "Deposition of Silicon Carbide using the Chemical Vapor Composites Process: Process characterization and comparison with RASSPVDN Model Predictions," *J. Materials Res*, **8** (1993), 1651 (released prior to publication as *Sandia National Laboratories Report SAND92-8228*).

PRESENTATIONS

1. M. D. Allendorf, C. F. Melius, and T. H. Osterheld "Thermodynamics and Kinetics of Methyltrichlorosilane Decomposition," presented at the meeting of the Electrochemical Society, Honolulu, May 1993.
2. M. D. Allendorf, C. F. Melius, T. H. Osterheld "Kinetics of Methyltrichlorosilane Decomposition," presented at the Amer. Ceramic Society Annual Meeting, Cincinnati, April 1993.
3. M. D. Allendorf, R. H. Hurt, N. Yang, P. Reagan, M. Robbins "Experimental Study of the Chemical Vapor Composites (CVC) Process," presented at the Annual Meeting of the Amer. Assoc. for Aerosol Res., San Francisco, October 1992.
4. M. D. Allendorf, D. A. Outka "The Reactivity of HCl and Methyltrichlorosilane with Silicon Carbide Surfaces," presented at the Materials Research Society, Boston, December 1992.
5. D. A. Outka, M. D. Allendorf "Fundamental Studies of Silicon Carbide Surface Chemistry," presented at the meeting of the Electrochemical Society, Toronto, October 1992.
6. M. D. Allendorf "High Deposition Rate Chemical Vapor Deposition," presented at the Advanced Industrial Concepts Materials Program Review Meeting, Oak Ridge, June 1993.

HONORS AND AWARDS: None during this reporting period.

PATENTS/DISCLOSURES: None during this reporting period.

LICENSES: None during this reporting period.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER: Sandia obtained detailed information from Alamo Supply Company (Houston, Texas) concerning the design of flame-spray torches. General Magnaplate Corporation (Newark, New Jersey) also provided Sandia with details of their flame-spray coatings processes currently under development. Ultramet Corporation (Pacoima, California) was given descriptions of software packages available from

Sandia for use in simulating high-temperature chemically reacting flows. Ultramet is reviewing them to determine their utility for optimizing and scaling proprietary ceramic synthesis processes.

COST SHARING: None.

NEW INSIGHT INTO SILICON CARBIDE DEPOSITION PROCESSES OBTAINED FROM HIGH-TEMPERATURE MEASUREMENTS

Problem: To develop and optimize new processes for manufacturing silicon carbide ceramics, an improved understanding of high-temperature reactions occurring during deposition is required.

Results: A high-temperature flow reactor (HTFR) coupled with a new mass spectrometer (MS) were used to monitor the decomposition of methyltrichlorosilane (MTS), a commonly used silicon carbide precursor. The HTFR allows precursor decomposition to be studied at temperatures as high as 1500 K, while mass spectrometry provides a sensitive diagnostic for the detection of MTS and its decomposition products. The experiments identified methane and hydrogen chloride as major reaction products. They also indicate that changing the process carrier gas from helium to hydrogen increases the amount of methane formed but has little effect on the MTS decomposition rate. These investigations provide the first experimental confirmation of computational models simulating gas-phase reactions in chemical vapor infiltration and other ceramic manufacturing process. In addition, they demonstrate the flexibility of the HTFR-MS for the study of high-temperature ceramic synthesis processes.

Left: Mass spectrum of MTS. **Right:** MTS decomposition at 1273 K and 25 torr. MTS is monitored at masses 148 and 133 (corresponding to $\text{CH}_3\text{SiCl}_3^+$ and SiCl_3^+). Signals due to HCl and CH_4 appear in the spectrum, identifying these species as decomposition products. Introduction of H_2 causes the CH_4 concentration to increase, probably due to $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ (the MTS decrease is caused by dilution). The figure also shows that residence time is easily adjusted in the HTFR, allowing the extent of pyrolysis to be controlled.

Significance - For Energy Conservation: The energy efficiency of many industrial processes is limited by the materials exposed to heat and corrosive environments. Silicon carbide ceramics 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 to operate in more efficient regimes.

Significance - For Materials Technology: Research to date has shown that to achieve high-quality silicon carbide at practical deposition rates requires a thorough understanding of the interrelated gas-phase and surface chemistries. These experiments provide quantitative data that can be used to validate computational process models, whose use will expedite process development and lead to improved control over deposition rates and deposit composition.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: High Deposition Rate Ceramic Synthesis

PHASE: Technology Proof-of-Concept

PERFORMING ORGANIZATION: Sandia National Laboratories, Livermore,
California

Combustion Research Facility

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

PHASE OBJECTIVE: To develop a quantitative understanding of the chemical and physical mechanisms that result in high deposition rates and controlled materials properties from new high-temperature routes to ceramics and other refractory materials.

ULTIMATE OBJECTIVE: To develop predictive computational models and other tools for designing, optimizing, and operating new ceramics processing technologies.

TECHNICAL APPROACH: Novel techniques for rapid deposition of ceramics 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 laser diagnostics and on-line gas and particle sampling 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. Such data 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:

- Completed installation of a mass spectrometer system for the detection of stable product species produced in high-temperature flow reactor (HTFR) experiments.
- Conducted HTFR investigations of methyltrichlorosilane (MTS) pyrolysis, a silicon carbide precursor. Identified reaction products and temperature/pressure regime for future work.
- Completed calculations predicting the temperature and pressure dependence of MTS pyrolysis.
- Developed a mechanism for predicting silicon carbide chemical vapor deposition, including coupled gas-phase and surface reaction chemistry.
- Conducted experiments at General Magnaplate Corporation of Linden, New Jersey, to characterize a new process for flame-sprayed metal-ceramic coatings under development there.

Patents: none

Publications: 5

Presentations: 6

ACCOMPLISHMENTS

- **Technology Transfer:** Process development research was conducted in collaboration with three companies: ThermoTrex Corporation, General Magnaplate Corporation, and Alamo Supply Company.
- **Licenses:** none.

PROJECT TITLE: High Deposition Rate Ceramic Synthesis

CRITICAL ISSUES: There is a critical need 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 composites is silicon carbide. Research during FY93 provided data of both an experimental and theoretical nature necessary for developing a model to simulate silicon carbide deposition.

FUTURE PLANS: Research efforts in the immediate future (FY94) will continue to focus on SiC deposition from chlorinated organosilanes. This research will be correlated where possible with complementary efforts to understand chemical vapor infiltration within the AIM program, specifically at ThermoTrex Corporation, Oak Ridge, Los Alamos, and the Lawrence Livermore National Laboratories. We will also continue the effort begun last year to develop a generic model of flame-spray processes for depositing wear-resistant coatings.

POTENTIAL PAYOFF: Results of this research should permit rapid and efficient development of new materials synthesis reactors. Use of the computational models developed here is expected to shorten the time required to design, optimize, and scale-up new synthesis processes and to facilitate extension of existing technology to new materials. By shortening process development times, this research will bring the desirable properties of ceramics into industries such as paper processing, automotive manufacturing, and chemicals faster and more economically than is currently feasible.

OTHER SOURCES: none.

ESTIMATED ENERGY SAVINGS: In addition to improved energy utilization obtained through better process design, estimated energy savings derived from widespread application of techniques such as TTC's Chemical Vapor Composites process are: gas turbine power generators, 0.4 quad/yr in 2010; high pressure heat exchanger systems, 0.6 quad/yr; radiant fire tubes, 0.06 quad/yr; aluminum industry, 0.03 quad/yr.

METALLIC AND INTERMETALLIC-BONDED CERAMIC COMPOSITES

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INTRODUCTION

The purpose of this task is to establish a framework for the development and fabrication of metallic-phase-reinforced ceramic matrix composites with improved fracture toughness and fatigue resistance. The incorporation of metallic phases which plastically deform in the crack tip region, and thus dissipate strain energy will result in an increase in the fracture toughness of the composite as compared to the monolithic ceramic. It is intended that these reinforced ceramic matrix composites would be capable of operating over a temperature range from 20°C to 800-1200°C for advanced applications in the industrial sector. In order to systematically develop these composites, a combination of experimental and theoretical studies must be undertaken.

TECHNICAL PROGRESS

Summary

Intermetallic-Bonded Oxide Ceramic Composites

Although nickel-aluminide reinforced alumina composites yielded significant increases in toughness compared to the fine-grained alumina matrix (7.8 v. 2.5 MPa√m), the hot-pressed composite microstructures providing the maximum toughness increases are anisotropic. In these composites, the interface between the nickel aluminide and the alumina debonds readily and substantial toughening is only achieved with highly oriented and elongated particles. An alternate means to achieve similar toughening would be to distribute the nickel aluminide in an interconnected and meandering manner, thus minimizing the ability of cracks to bypass the Ni₃Al reinforcements. The ability to fabricate more isotropic and meandering microstructures depends for a large part on the wetting behavior of the nickel aluminide on the alumina. Approaches relying on alloying the nickel aluminide to achieve better wetting have been pursued and are described in

detail later in the report. Composites which utilized a combination of a wetting phase addition (TiC), Ni₃Al, and alumina to achieve the desired microstructural features were investigated. Composites were fabricated at temperatures above the nickel aluminide liquidus at a variety of pressures, as shown in Table I. The measured densities of the composites may not reflect the true density, since some of the Ni₃Al can exude during hot-pressing. The microstructures of composites fabricated with 65 vol.% alumina, 10 vol.% Ni₃Al, and 25 vol.% coarse (Fig. 1a) and fine (Fig. 1b) TiC are shown in Figure 1. Also shown in Figure 1 are typical microstructures of alumina containing 10 vol.% Ni₃Al reinforcements. The Al₂O₃/TiC/Ni₃Al composites exhibit a much finer, more isotropic microstructure. It is clear that the presence of TiC allows the nickel aluminide to spread uniformly throughout the composite and form a very fine meandering distribution of nickel aluminide (Fig. 1c). The measured hardness, fracture toughness, and flexural strengths of selected composites is also shown in Table I. The TiC additions not only aid in the nickel aluminide redistribution, but also increase the hardness of the composite. The addition of 10 vol. % nickel aluminide to the Al₂O₃/TiC composite significantly increases the toughness relative to unreinforced Al₂O₃/TiC materials, which typically have a toughness of 3.5 to 4.5 MPa√m. In fact, the mechanical properties of these three-phase composites compare very favorably with Al₂O₃/SiC_w (10 vol.%) composites, however, the raw material costs of these new three-phase composites are significantly lower (Table II). In addition, the Al₂O₃/TiC/Ni₃Al composites are hot-pressed at much lower temperatures and pressures than Al₂O₃/SiC_w(10 vol.%) composites, offering further cost advantages. A draft of a possible patent disclosure for these materials is currently being reviewed by the ORNL Patents Office. Further work is underway to optimize the relative fraction of the constituent phases and to pursue the possibilities of pressureless-sintering these composites.

Wetting experiments were carried out in vacuum (appr. 10⁻⁴ Pa) at a temperature of 1723K for a period of 15 minutes. A range of different nickel aluminide compositions

Table I - Fabrication Conditions and Mechanical Properties of Al₂O₃/TiC/Ni₃Al Composites.

Al ₂ O ₃ [#]	TiC ^{**}	Ni ₃ Al	Temp. (K)	Pressure (MPa)	Density % T.D.	Hardness ⁺ (GPa)	Toughness MPa √m	Strength (MPa)
65	25*	10	1823	14	92	18	7.14 ± 0.2	345 ± 23
65	25	10	1773	14	92.5			
65	25	10	1823	14	95			
65	25	10	1973	14	96			
65	25	10	1823	28	97	18.3	8.06 ± 1.1	580 ± 47
65	25*	10	1823	28	100			
65	25	10	1823	28	96			
65	25	10	1823	28	95			
90**	--	10	1623	35	100	14	7.6	556
90 ++	10 vol.%SiC _w		2023	35	100	< 19	6.2 - 7.0	450 - 575

All compositions given in volume-percent. Alumina - 3 micron powder.

**TiC - 1.3 micron or 3 micron (*) powder.

+ Hardness is measured with a 5kg Vickers indent (VPH). Toughness is measured by indent-and-fracture four-point bend test using a 20 kg Vickers indent.

** Anisotropic microstructure, toughness reported is for the most favorable orientation of the composite exhibiting the highest flexural strength.

++ Typical range of values is given for Al₂O₃/SiC_w.

Table II - Cost comparison of various alumina-based ceramics.*

Material	Toughness (KJ)	Cost (\$/kg)
Alumina	3	45
Alumina 10 vol.% SiC whiskers	4 - 7	74
Alumina 20 vol.% SiC whiskers	6 - 8.5	105
Alumina 10 vol.% Ni ₃ Al	4.5 - 7.8	61
Alumina 20 vol.% Ni ₃ Al	-	78
Alumina/25 TiC/10 Ni ₃ Al	7 - 8	56

*Prices calculated for raw materials only - purchased in approx. 45 kg quantities.

Figure 1: (a) -- 65 Al_2O_3 /25 TiC/10 Ni_3Al composite fabricated with 3.0 μm TiC powder. Specimen hot-pressed at 1823K with 14 MPa applied pressure. (b) -- 65 Al_2O_3 /25 TiC/10 Ni_3Al composite fabricated with 1.3 μm TiC powder. Specimen hot-pressed at 1823K with 28 MPa applied pressure. (c) -- Higher magnification view of composite shown in (a). The lightest phase is the Ni_3Al and the darkest phase is the Al_2O_3 . (d) and (e) -- Composites of 90 Al_2O_3 /10 Ni_3Al shown for comparison. Starting Ni_3Al powder size shown for each composite. All compositions given in volume-fraction.

and substrate materials was examined in order to determine whether the wetting angles can be reduced by appropriate choices of alloy and substrate. The results are listed in Table I. When Zr, C, and B additions are included in the Ni_3Al alloy, the wetting angles on alumina ranged from 75 to 80°, as opposed to >90°. Furthermore, wetting angles on TiC and TiB_2 are below 20°, suggesting a means of tailoring the wetting in oxide-based composites.

In order to explore the toughening potential of different Ni_3Al alloys in an Al_2O_3 ceramic matrix, many $\text{Ni}_3\text{Al}/\text{Al}_2\text{O}_3$ laminates were fabricated. Specimens with a cross section of approximately 5 x 6 mm and a length of 25 mm were cut and chevron-notched with a slow-speed diamond saw. These specimens were then tested in a 4501 Instron testing machine at room temperature in three-point bending, with a span of 20 mm. The plane of the Ni_3Al film was oriented parallel to the direction of the cross-head movement and perpendicular to the crack, i.e. in a crack-splitting mode. This allows the crack to propagate through the matrix, leaving the Ni_3Al film to span the crack plane. Using this geometry, interfacial debonding and plastic flow behavior in the constrained Ni_3Al film can be examined. Preliminary analysis indicates that the energy dissipated during fracture of these laminates is a function of the nickel aluminide alloying content. One major problem in the work with $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}$ laminates is reproducibility. Future laminates will be processed in a high vacuum (10^{-4} Pa) at negligible applied loads. The information obtained from such tests will provide feedback for selecting optimized alloys for the powder-processing work.

Intermetallic-Bonded Non-oxide Ceramic Composites

A summary of the hot-pressing conditions and densification behavior for composites fabricated from nonoxide ceramic powders with Ni_3Al additions is given in Table IV. In addition, composites were also fabricated by pressureless sintering in 1 atm argon at 1823K and 1873K, as shown in Table V. This method is amenable to fabrication

Table III - Wetting Behavior of different nickel aluminide-substrate combinations. The alumina substrates were AD995 or AD998 grades.

Composition, at. %	Substrate Material	Wetting Angle, Degrees
Ni-22Al-1Zr-0.1B	Alumina	>90
Ni-16Al-8Cr-1Zr-0.1B	Alumina	>90
Ni-23Al-1C-0.1B	Alumina	76
Ni-22Al-1Zr-1C-0.1B	Alumina	77
Ni-22Al-1Zr-.1C-.1B	Alumina	77
Ni-22Al-1Y-0.1B	Alumina	>90
Ni-16Al-8Cr-1Zr-.1C-.1B	Alumina	80
Ni-22Al-1Ti-.1B-.1C	Alumina	80
Ni-18Al-5Ti-.1B-.1C	Alumina	79
Ni-22Al-1Zr-0.1C-0.1B	TZ 2.5Y	76
Ni-22Al-1Zr-0.1C-0.1B	Al ₂ O ₃ -2w/oCr	76
Ni-22Al-1Zr-0.1C-0.1B	Al ₂ O ₃ -10w/oCr	82
Ni-22Al-1Zr-0.1C-0.1B	Al ₂ O ₃ -TiC	72
Ni-22Al-1Zr-0.1C-0.1B	Mullite	90
Ni-22Al-1Zr-0.1C-0.1B	TiC	10-20
Ni-22Al-1Zr-0.1C-0.1B	TiB ₂	20
Ni-22Al-1Zr-0.1C-0.1B	TiB ₂ on Graphite	spreading
Ni-17Al-5Si-1Zr-0.1C-0.1B	AD998	80
Ni-22Al-1Zr-0.1C-0.1B	AD998,	80
	PVD C- Coating	
Ni-22Al-1Zr-0.1C-0.1B	Alpha-SiC	64

Table IV - Summary of results on processing conditions and densification behavior of hot-pressed nickel aluminide bonded non-oxide ceramic composites. All composites were hot-pressed at 1723K, 34 MPa for 60 min.

Alloy Comp	Alloy Content (wt. %)	Particulate Type and Size (μm)	Bulk Density (g/cm ³)	Density (% T.D.)
IC-50	20	TiC (1 μm)	4.9	96
IC-15	20	TiC (1 μm)	5.1	100
IC-50	20	TiC (2-6 μm)	4.6	86
IC-15	20	TiC (2-6 μm)	4.9	96
IC-50	20	WC (2 μm)	14.2	92
IC-50	20	WC (0.8 μm)	14.4	99
IC-50	20	WC (5-8 μm)	14.9	99

Table V - Results on pressureless sintering of Ni₃Al-WC and Ni₃Al-TiC composites. Pellets were pressed at 69 MPa and heated in argon to either 1823K or 1873K for 2 h.

Particle Type and Size (μm)	Ni ₃ Al Alloy	Alloy Content (wt. %)	Density- 1823K (g/cm ³ , %T.D.)	Density- 1873K (g/cm ³ , %T.D.)
WC, 0.8	IC-136M	10	12.6, 85	12.4, 84
WC, 2.3	IC-136M	10	12.3, 83	12.1, 82
WC, 5-8	IC-136M	10	11.3, 76	11.4, 77
WC, 0.8	IC-136M	20	10.8, 77	10.9, 78
WC, 2.3	IC-136M	20	10.0, 71	10.9, 78
WC, 0.8	IC-50	20	11.9, 84	11.2, 79
WC, 2.3	IC-50	20	10.7, 76	10.8, 77
WC, 5-8	IC-50	20	10.5, 74	10.4, 74
TiC, 1	IC-136M	10	4.6, 88	3.4, 65
TiC, 1-3	IC-136M	10	3.8, 73	3.9, 74
TiC, 2-6	IC-136M	10	3.7, 71	3.8, 73
TiC, 1	IC-136M	20	4.6, 87	--
TiC, 1-3	IC-136M	20	4.6, 87	4.5, 85
TiC, 2-6	IC-136M	20	4.5, 85	4.5, 85
TiC, 1	IC-50	20	4.6, 87	4.6, 87
TiC, 1-3	IC-50	20	3.9, 74	4.2, 79
TiC, 2-6	IC-50	20	4.0, 75	4.0, 75

of complex-shaped parts. As shown, the densities of the pressureless sintered composites were generally low compared to those achieved by hot-pressing, however, this could be improved by the use of higher gas pressures during sintering.

Milestones

None.

PUBLICATIONS

None.

PRESENTATIONS

K. B. Alexander, J. H. Schneibel, H. T. Lin and P. F. Becher, "Fabrication and Properties of Alumina Matrix Composites Containing Nickel Aluminide Reinforcements", TMS/ASM Materials Week Annual Meeting, Pittsburgh, PA, October 18, 1993.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

Disclosure Draft being examined by Patents Office for applicability.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Discussed possibilities of cooperative work with Rich Palicka of Cercom. They are trying to see if these composites have a market where abrasive-corrosion resistance is important. Also discussed areas of mutual interest and cooperative work with Jim Stephan and Terry Brog of Golden Technologies (Coors). Sent them pre-prints of recent paper.

COST SHARING

None.

HIGHLIGHTS

None.

DEVELOPMENT OF ISOTROPIC, HIGH-TOUGHNESS, ALUMINA-BASED COMPOSITES CONTAINING NICKEL ALUMINIDE

Problem:

Nickel aluminide does not wet oxide ceramics sufficiently to allow liquid phase sintering. In alumina-based composites containing nickel aluminide, interfacial debonding occurs readily, therefore, the intermetallic phase must be physically constrained within the matrix or little toughening is observed. To obtain high toughness, with an isotropic microstructure, a meandering or interconnected distribution of nickel aluminide in the alumina matrix must be obtained.

Results:

Three-phase composites of alumina, TiC, and nickel aluminide have been shown to result in high toughness, strength, and hardness. The TiC additions (1) aid in the formation of a meandering, interconnected, and isotropic nickel aluminide distribution by altering the wetting behavior, and (2) contribute to the hardness. The nickel aluminide ligaments deform in the crack tip wake and increase the toughness. The mechanical properties of these materials are comparable to SiC-whisker reinforced alumina composites, at lower raw material costs.

Significance - For Energy Conservation:

Low cost, low density ceramic composites with high toughness could significantly reduce the costs associated with moving components. The enhanced reliability due to the high toughness will result in longer-life components.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

WORK ELEMENT: Ceramic Composites

PROJECT TITLE: Reinforced Ceramic Composites

PHASE: FY 1994

PHASE COMPLETION DATE: October 1994

PERFORMING ORGANIZATION(S): Oak Ridge National Laboratory and Lawrence Berkeley Laboratory

PRINCIPAL INVESTIGATOR(S): K. B. Alexander (624-0631), P. F. Becher (624-5157), H. T. Lin (626-8857), J. H. Schneibel (626-4644), T. N. Tiegs, and R. O. Ritchie, LBL (415-642-0417)

PHASE OBJECTIVE: FY 93 - Optimize microstructural features to maximize toughness in ceramic composites reinforced with nickel aluminide and other phases while maintaining strength and hardness.

ULTIMATE OBJECTIVE: To develop ceramic composites with high fracture toughness for intermediate temperature use in wear, tribological and engine applications. To commercialize the use of these composites through technology transfer to industry.

TECHNICAL APPROACH: Use a variety of processing procedures to vary the microstructure so as to design the composite for optimal mechanical properties. Since the wettability of the phases during fabrication is crucial, this work is supplemented by wetting studies of nickel aluminide alloys on ceramic substrates.

PROGRESS: FY 93 - Microstructurally anisotropic $\text{Ni}_3\text{Al}/\text{Al}_2\text{O}_3$ composites and isotropic $\text{Ni}_3\text{Al}/\text{TiC}/\text{Al}_2\text{O}_3$ composites, both of which resulted in strengths and toughnesses comparable to SiC-whisker reinforced alumina with the same reinforcement content, at lower raw material costs, were fabricated and tested.

Patents: -

Publications: -

Proceedings -

Presentations: 3

ACCOMPLISHMENTS: Nickel aluminide additions have been shown to be an effective toughening agent in ceramic matrices if the microstructural distribution is carefully controlled. The microstructural features yielding optimal toughening have been identified and composites have been fabricated with properties comparable to, or better than, commercial ceramic composites.

Technology Transfer Activities as Evidence of Industry Interest:

Ongoing discussions with Cercom, Golden Technologies, and 3M to establish basis for collaborative efforts on metallic- and intermetallic-phase-reinforced ceramics. Joint R&D efforts between Golden Technologies and ORNL are currently being discussed; Golden Technologies currently manufactures reinforced ceramic composites and wants to explore ways to improve the high temperature properties.

PROJECT TITLE: Reinforced Ceramic Composites

CRITICAL ISSUES: Issues that must be addressed include the role of various microstructural parameters (matrix grain size and second-phase size, distribution, and aspect ratio), interfacial characteristics, and intermetallic alloy properties (yield strength, ductility) on the toughness of the composites. The goal is to develop a sound basis for the design of these composites such that the desired properties (toughness, strength, and elevated temperature stability) can be attained.

FUTURE PLANS: Interactions with industry will be pursued. Specimens will be fabricated from the composites developed on this program and tested by industrial participants. The collaborative effort with LBL to evaluate the fatigue crack growth behavior of the intermetallic phase reinforced composites generated through this program will be continued.

POTENTIAL PAYOFFS: The development of these tough, ceramic-based composites will yield a new class of advanced, low-cost materials for intermediate temperature use in industrial applications requiring high hardness, toughness, and strength.

FUNDING HISTORY:

ESTIMATED ENERGY SAVINGS: The use of ceramic-based composites, with their lower density, has considerable potential for energy savings due to the reduction in weight of moving components.

MICROWAVE ASSISTED CHEMICAL VAPOR INFILTRATION

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INTRODUCTION

The purpose of this program is to develop a new process for the fabrication of ceramic matrix composites by chemical vapor infiltration. CMC's have been identified as candidate materials for applications ranging from hot gas filtration to automotive engine components capable of higher operating temperatures, reduced wear, and improved energy efficiency. These materials have seen little commercial application largely because of the expense associated with processing. The need for lower cost processing is apparent. The present commercial process developed by SEP and licensed to DuPont employs an isothermal diffusion limited infiltration. Processing times are on the order of weeks to months with interruptions for regrinding and opening of closed pores. Batch processing with large furnaces intended for economy of scale are employed. However, costs are still prohibitively high for most application. Significantly reduced processing times have been demonstrated using forced CVI methods developed at ORNL. However, this approach is not suitable to large scale batch processing and is limited to simple shapes. The microwave assisted CVI approach intends to incorporate the advantages of forced CVI (thermal gradient processing) with its reduced processing times, while maintaining the possibility of large scale reactors without limitations on part geometry.

The approach centers on the use of microwave heating of ceramic materials with several distinct advantages resulting. The prime advantage lies in the ability of microwave heating to produce inverted thermal gradients. This may be accomplished by direct volumetric heating of the preform with gradients established by convective and radiative losses near the surface. Alternatively, the unique ability of microwaves to selectively heat one phase or component may be exploited. For example, seeding of a preform with an appropriate material to generate a hot region where preferential deposition can occur is possible.

TECHNICAL PROGRESS

Summary

This period has been devoted in part to the exploration of material systems suitable for MACVI processing. A number of potential processing schemes are possible using combinations of absorbing and transparent material as composite components. This includes the use of an absorbing preform (nicalon fiber) combined with a transparent matrix (silicon nitride). Composites 5 cm in diam by 1 cm. thick have been fabricated to densities of 65% theoretical. Processing times for these materials are under 20 h. Higher densities will require additional microwave power now possible with the new reactor. The most effective MACVI scheme will involve the use of a transparent fiber with an absorbing matrix. The hot spot will be initiated by appropriate treatment of the central region of the preform. To this end alumina fibers with pretreatments to control thermal gradients has been explored. Nextel 610 fibers have been effectively pretreated carbon coating resulting in preferential heating in the interior of the preform. Possible matrix materials include siliconized silicon carbide, doped silicon carbide, alumina, and zirconia. A patent for MACVI was issued on October 19, 1993.

Milestone

Fabrication of dense ceramic matrix composite by microwave CVI with mechanical properties testing. End September 1993.

A new reactor has been designed, constructed, and installed. The system is expected to eliminate the previous years difficulties due to limitations in power. Experiments to deposit Si_3N_4 in NicalonTM (SiC) cloth substrates were conducted in a water cooled bell jar inserted into a modified Microwave Materials Technologies model 10-1300 multimode microwave furnace. This 1300 watt furnace, which operates at 2.45 GHz, was modified so that additional convective (air) cooling could be supplied within the cavity. The samples were mounted on a 5 cm diam quartz tube centered over the thermocouple and exhaust orifices. The quartz tube was fixed to the base plate with silicon cement. The reactant gas inlet line was attached to a hole drilled through the base plate at a position where gases entered the bell jar on the exterior of the quartz tube supporting the sample. This allows reactant gases to pass through the sample as they are exhausted to vacuum.

The chemicals used for deposition of Si_3N_4 were silane and ammonia, reacting in excess hydrogen according to: $3 \text{SiH}_4 + 4 \text{NH}_3 = \text{Si}_3\text{N}_4 + 12 \text{H}_2$. Flow rates were 50 sccm silane, 500 sccm ammonia, and 2000 sccm hydrogen. System pressure was 300 Torr. Power levels typically were in the range of 800-900 watts with an internal substrate temperature of approximately 950°C. Substrates were 10 stacked circular (5 cm diam) NicalonTM cloth layers. Figure 1 shows a cloth stack before and after the infiltration run. For the densified cloth shown in Fig. 1, the initial weight was 6.46 gm while the final weight following 29.5 h of infiltration was 26.78 gm. Figure 2 shows a cross-section of the Si_3N_4 infiltrated cloth stack, which had a height of approximately 1 cm.

These experiments highlight two process development issues requiring additional attention. The first is associated with non-uniform Si_3N_4 deposition occurring within the cloths. The infiltrated stacks had regions of high porosity. The darker areas seen in the infiltrated stack shown in Fig. 1 are indications of this. Since the CVI was done under forced flow conditions with relatively high flow rates, this effect was thought to be the result of cooling of certain cloth regions by the (cool) flowing gases. Additional experiments are needed to optimize the flow rate, inlet gas temperature, and microwave power input level in order to avoid this cooling phenomenon. The second issue is related to initial porosity and packing density of the cloth layers. The stacks used in these experiments were loosely held in a microwave transparent ceramic receptacle. The initial porosity was high, on the order of 89%. While a significant amount of Si_3N_4 was deposited, the final porosity of the disc was still on the order of 60%. Although this density is far too low for most applications, it must be noted that if the initial porosity were in the range more commonly used for CVI (i.e. ~40-45%), final densities in the range of 80-85% would have been attained with the amount of Si_3N_4 deposited during the run. Densities in this range are competitive with existing conventional CVI processes for infiltrating disc shaped cloth lay-ups and are high enough for many applications. Furthermore, the required weight gains can apparently be obtained in approximately 30 h of CVI time, using microwave assisted CVI. Again, these times are competitive with existing forced flow technologies. Methods to hold the cloth layers in a compressed state are under investigation. While compressing the preform may be required in infiltrating cloth lay-ups, the ultimate use of 3-dimensional woven structures should remove the need for preform compression. Mechanical testing of these materials was not undertaken due to the relatively low density.

Fig. 1. Cloth before and after infiltration.

Fig. 2. Cross-section of Si_3N_4 infiltrated cloth.

A new six kilowatt microwave CVI reactor has been designed in conjunction with Cober electronics. The system constructed by Cober has been shipped and installed at LANL. The complete reactor is shown in Fig. 3. The essential features of the system are listed below:

Cylindrical Cavity/Vacuum Can (approximately 18 in. diam, 33 in. length).

- stainless steel construction, mode stirrer, and vacuum seals rated for corrosive gas duty
- interior Teflon coated (including mode stirrer)
- removable interior base tray (stainless steel)
- external water cooled jacket, 6 kW duty
- viewports: 2 four-in. diam viewports on cavity side (one/side)
1 four-in. diam viewport on hinged door (end of cavity)
- fittings: 2 KF 50 ports on top of cavity
8 KF 25 ports on bottom (2 of the 8 possibly KF 50)
2 KF 25 ports on load cell compartment (for purge gases)
- Microwave Generator
 - 6 kilowatts, 2.45 GHz, with low ripple filter
 - forward and reflected power meters
 - closed loop feedback controller, configured for both thermocouple and fiber optic inputs
- In-situ Balance Assembly
 - monitor sample weight in-situ (1 kg capability with 0.1 g readability)
- Data Acquisition System
 - interfaces for Macintosh computer (computer supplied by LANL)
 - record/display temperature, forward & reflected power, weight change, pressure.

An Accufiber eight channel, fiber optic, high temperature measurement and control system has been purchased. This system will be used for monitoring temperature gradients within the preform and potentially incorporated within the process control system of the new reactor. Investigations using Nextel 610 high purity fibers have been undertaken. Recent results from the AIC program "Microwave Processing of Ceramic oxide Filaments," have demonstrated microwave heating of alumina fibers by applying a carbon coating. Using this

Fig. 3. Six kilowatt microwave CVD reactor.

approach woven cloths nextel have been treated in the center regions of a lay up resulting in preferential heating in the interior of the preform. This approach does not rely on convective or radiative losses to produce a thermal gradient. The use of an absorbing matrix material will be required for this process and is under investigation.

PRESENTATIONS

D. J. Devlin and R. P. Currier, "Ceramic Matrix Composites by Microwave Assisted CVI" (Invited Paper) Microwaves: Theory and Applications in Materials Processing II Symposium, 95th American Ceramic Society Annual Meeting, Cincinnati, Ohio 1993.

D. J. Devlin, R. P. Currier, R. S. Barbero, B. F. Espinoza, "Chemical Vapor Infiltration with Microwave Heating" 17th Annual Conference and Exposition on Composites and Advanced Ceramics, Cocoa Beach, Florida, January 1993.

D. J. Devlin, "Microwave Assisted Chemical Vapor Infiltration" presented at the Materials Research Society December 1991 Meeting, Symposium R, Boston, Massachusetts.

D. J. Devlin, R. P. Currier, R. S. Barbero, B. F. Espinoza, "Microwave Assisted Chemical Vapor Infiltration," Advanced Industrial Concepts Annual Review Meeting, Oak Ridge, Tennessee, June 7-9, 1993.

PUBLICATIONS

D. J. Devlin, R. P. Currier, R. S. Barbero, B. F. Espinoza, and N. Elliot, "Microwave Assisted Chemical Vapor Infiltration," Mat. Res. Soc. Symp. Proc. **250**: 245 (1992).

D. J. Devlin, R. P. Currier, R. S. Barbero, B. F. Espinoza, "Chemical Vapor Infiltration with Microwave Heating," Ceramic Engineering & Science Proceedings, Vol 14, No. 9-10 p 761-67, 1993.

D. J. Devlin and R. P. Currier, "Ceramic Matrix Composites by Microwave Assisted CVI" (Invited Paper) Microwaves: Theory and Applications in Materials Processing II, to be published in Ceramic Transactions.

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

U.S. Patent No. 5254374 "Chemical Vapor Infiltration using Microwave Energy," Issued October 19, 1993.

LICENSES

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

None

COST SHARING

None

HIGHLIGHTS

Silicon carbide reinforced composites have been fabricated using existing MMT microwave reactor. A new 6 kilowatt microwave reactor has been designed, constructed, and installed. A patent for MACVI has been issued.

MICROWAVE ASSISTED CHEMICAL VAPOR INFILTRATION

Problem

Currently, continuously reinforced ceramic matrix composites are fabricated by an isothermal chemical vapor infiltration approach typified by the SEP process. The fabrication of silicon carbide composites by this method requires weeks to months of processing time. Materials can cost up to \$5000/lb, prohibitively expensive for most intended applications. The need for lower cost processing is apparent.

Results

The use of microwave heating of ceramic fiber preforms is being explored as a means of developing an improved rapid process for the fabrication of composites by chemical vapor infiltration. The volumetric and preferential heating of certain materials by microwaves provides a means of establishing inverted thermal gradients in a preform. The result is the ability to rapidly infiltrate the preform developing the matrix from the inside-out. Using this technique, silicon carbide reinforced silicon nitride composites have been fabricated. Furthermore, the feasibility of pretreating regions of a preform resulting in preferential heating has been demonstrated. A patent for the method has been issued.

Significance-For Energy Conservation

The development of a cost-effective process for the fabrication of ceramic matrix composites will enable the introduction of these materials into areas of technology directly related to energy conservation. These include heat engine and automotive applications where increased efficiency is the objective. In addition, the method itself will conserve energy by drastically reducing processing times.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS MATERIALS (AICM) PROGRAM

PROJECT TITLE: MICROWAVE ASSISTED CHEMICAL VAPOR INFILTRATION

PHASE: FY93

COMPLETION DATE: FY95

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATORS: David J. Devlin, (505) 667-9914

Materials Science and Technology Division

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PHASE OBJECTIVE: Fabricate dense ceramic matrix composites using inverted thermal gradients produced by microwave heating. Design, construct, and install a new reactor capable of achieving the desired goal of high density ceramic composites with reduced processing time. Explore key processing issues, including absorption of microwave energy in matrix and reinforcement materials of practical interest.

ULTIMATE OBJECTIVES: A more energy efficient and economically competitive process for producing reinforced ceramic matrix composites. A process capable of uniform density composites without shape limitations. Demonstrate the benefits microwave heating brings to ceramic composite processing using chemical vapor infiltration techniques.

TECHNICAL APPROACH: Exploit microwave induced inverted thermal gradients to promote inside-out densification of composites by chemical vapor infiltration. Use multimode microwave cavities as infiltration reactors. Establish inverted thermal gradients in substrates using microwave driven volumetric heating together with heat losses at surfaces through radiation and convection. Establish inverted gradients using selective microwave heating by seeding preforms or coating specific regions of the preform with an absorbing material. Use vapor infiltration to introduce gases which react in the hot region to densify the composite. Explore various processing strategies, such as diffusion limited, forced, and pulsed reactant flows. Examine the effects of various microwave heating schedules and power level modulation schemes. Explore alternative process chemistries. Use basic results in process optimization and projections on commercial viability and scale-up.

PROGRESS: Silicon carbide reinforced silicon nitride composites were fabricated using microwave heating and inverted thermal gradients. While high densities were not achieved, the results do suggest significantly reduced processing times are possible. Methods for selectively heating interior regions of fiber preforms by coating with a microwave absorbing material have been developed. A large six kilowatt microwave reactor capable of producing high density material has been designed, constructed, and installed LANL.

Patents: 1 Publications: 3 Proceedings: 3 Presentations: 4

ACCOMPLISHMENTS: Proof-of-concept phase is complete. Have shown microwave heating can be combined with vapor infiltration to densify composites. Silicon carbide reinforced silicon nitride composites have been fabricated. New and more promising approaches to the development and control of inverted thermal gradients for MACVI have been developed. A more robust and powerful reactor has been installed.

Licenses: 0

Follow-on Products:

Industry Workshops:

Technology Transfer: Pursuing the possibility of industrial collaborations with a number of interested companies.

PROJECT TITLE: MICROWAVE ASSISTED CHEMICAL VAPOR INFILTRATION

CRITICAL ISSUES: With the new reactor in place and sufficient power the critical issue, the silicon nitride composite will be increasing the initial preform density. Present cloth layups are at most 20 volume percent fiber. A higher initial density will allow a further reduction in processing time while achieving higher final densities. This may be accomplished with a microwave transparent fixture for use during the early stages of infiltration. Once the cloths are effectively stuck together, the fixture can be removed. Control of the thermal gradients can be difficult because of problems associated with thermal run away and the reliance of convective and radiative loss at the surface. An alternative scheme is to use a transparent preform (alumina fiber), treated in the center of the preform with an absorbing coating. Heating will occur initially in the treated area, not relying on losses at the surface resulting in a tightly controlled hot spot. Infiltration with a microwave absorbing matrix will then lead to rapid inside-out densification. A fiber and treatment scheme has been

successfully developed. A critical issue will be the development and control of a suitable matrix chemistry.

FUTURE PLANS: Further optimize the silicon carbide reinforced silicon nitride using the new reactor. The objective is to achieve sufficient density to warrant mechanical testing of the composite. Develop a processing scheme for treated alumina fibers with an absorbing matrix.

POTENTIAL PAYOFF: A successful microwave assisted infiltration process has the potential to eliminate many limitations encountered with conventional approaches to composite fabrication by chemical vapor infiltration. First, constraints on substrate geometry could be removed. Second, more spatially uniform, high density composites should be attainable. Third, relatively short processing times should be possible when pulsed reactant flows are employed. Fourth, machining operations to reopen closed pores should not be necessary since densification would occur from the inside-out. Finally, use of a cold wall reactor will minimize unwanted reaction on the walls and fixtures thereby saving on reactant costs and minimizing waste production.

SYNTHESIS AND PROCESSING OF COMPOSITES **BY REACTIVE METAL INFILTRATION**

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INTRODUCTION

Ceramic-metal composites have advantages as engineering materials because of their high stiffness-to-weight ratios, good fracture toughness, and because their electrical and thermal properties can be varied through control of their composition and microstructure. However, broader commercial application of these materials requires improvements in synthesis and processing so that high-performance parts can be produced more economically. Reactive metal infiltration is a promising new route to synthesize and process a wide range of ceramic and metal-matrix composites to near-net-shape with control of both composition and microstructure. Reactive metal infiltration offers significant potential for manufacturing a broad range of advanced ceramic composites that are needed for light-weight structural and wear applications for transportation and energy conversion devices. In applications such as heat engines, power generation equipment, and automotive and aerospace components, use of refractory, light-weight ceramic composites could reduce energy consumption by as much as 1×10^{15} BTU/yr, with a reduction in NO_x emissions of 600,000 tons/yr.¹ Near-net-shape fabrication of parts should lead to additional savings because costly and energy intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.

The goals of this research program are to; 1) identify feasible compositional systems to fabricate composites by reactive metal infiltration, 2) understand the mechanism(s) of composite formation by reactive metal infiltration, and 3) control and optimize the reactive metal infiltration process to economically produce composites and composite coatings.

1. S. Richlen, *Ceramic Science and Engineering Proceedings*, 11 [7-8], 576-577 (1990).

TECHNICAL PROGRESS

Summary

We are developing a reactive metal infiltration process that converts brittle ceramic preforms to tough metal-ceramic composites by direct redox reaction with molten metal. Generally, reactions between Al and oxides are of the form;

where MO_y can be either a simple binary or complex oxide, and the residual metal phase can take a variety of forms as determined by the phase equilibrium relations of the given system. Evidence is accumulating that reactive infiltration is applicable generally to oxide-metal combinations for which there is both favorable wetting of the oxide by the molten metal (i.e., contact angle $\theta < 90^\circ$) and a negative Gibbs energy for reaction.

In the Al/mullite system, molten aluminum metal reduces mullite to produce alumina and elemental silicon according to the reaction;

With excess aluminum present (i.e., $x > 0$), a composite of alumina, silicon, and aluminum is formed. Metal-ceramic composites have been produced by infiltrating dense ceramic preforms with molten metal, and by sintering mixtures of ceramic and metal powders. Experimental results on variable composition metal-ceramic powder reaction couples indicate that reactive metal infiltration can be a general route to composite synthesis.

Composite formation by reactive metal infiltration appears to be a diffusion controlled process with parabolic reaction kinetics at short times; consequently, metal-ceramic composite coatings can and have been fabricated by controlling the infiltration time. Additionally, in select systems, reactive metal infiltration affords near-net-shape forming capability.

Fabricating composites with physical properties optimized for particular applications is one of the potential benefits of the reactive metal infiltration process. For composites in the Al/Si/ Al_2O_3 system, improvements in Young's modulus, fracture strength, density, hardness, fracture toughness, and specific modulus are apparent relative to the pure mullite preform. Reactive-formed metal-ceramic composite fracture toughness increases with increasing Al concentration, while modulus and density remain relatively constant, making it possible to fabricate novel tough, high specific modulus (i.e., modulus + density) materials. Mechanical property data are consistent with microstructural evidence and coefficient of thermal expansion data that indicate a three-dimensional, alumina skeletal structure is formed during reactive

infiltration, as many of the physical properties of the composite are controlled by that rigid alumina skeleton. Results also indicate that, relative to the ceramic preform, the composites are more flaw tolerant; that is, the strength degradation from crack formation and propagation appears to be less severe in the metal-ceramic composite relative to the mullite preform.

Milestones:

1. Evaluate Reactions and Mechanisms of Composite Formation in the Al/Mullite System

Explanation: Commercial development of the reactive metal infiltration technique to manufacture ceramic composites hinges on understanding and controlling the infiltration process. This is being accomplished by determining the chemistry, thermodynamics, and reaction kinetics of metal-ceramic reactions, and learning how the reactions are affected by experimental process variables such as time, temperature, and atmosphere.

Status: Understanding the wetting behavior of molten metals on ceramics under different conditions is important because wetting is a necessary condition for reactive metal infiltration. To assess infiltration in the absence of reaction, sessile drop experiments were conducted on dense Al/Si/Al₂O₃ composite discs produced by vacuum hot pressing at 1450°C and 41 MPa for 1/2 hr. Contact angles for 99.99% Al on dense, reactively-formed Al/Si/Al₂O₃ composites containing 0, 2, or 12 excess moles of aluminum were measured as a function of time at 1100°C. Average steady-state contact angles of 96°, 97°, and 98° (i.e., non wetting) were found. In general, there is little wetting or infiltration of Al into the reactively-formed Al/Si/Al₂O₃ composites at 1100°C in oxygen-gettered argon. One possible explanation for this behavior is that the composites are thermodynamically stable, and there is little or no driving force for further Al wetting. Another possibility is that wetting is strongly P_{O2} dependent and our experiments were in an unfavorable range for wetting. We are intensively studying this issue.

As illustrated in Figure 1, there are significant differences in the wetting behavior of Al on mullite in vacuum and argon. A vacuum atmosphere favors greater variation in wetting angle with time at temperature, and ultimately, a lower wetting angle. However, there also are substantial weight losses in vacuum experiments from evaporation of aluminum. Based on these results, further Al wetting and penetration studies were conducted on the doped mullite samples in oxygen-gettered argon only.

To determine the effects of ceramic composition on Al wetting and penetration, wetting studies were conducted on mullite and mullite doped with 5 wt% NiO, SiO₂, TiO₂, or ZrO₂ at 1100°C in oxygen-gettered argon. Similar to pure mullite, the wetting angle of Al on SiO₂- and TiO₂-doped mullite decreases rapidly at first, and then more gradually at longer times. By contrast, the rate of decrease in the wetting angle of Al on NiO- and ZrO₂-doped mullite is relatively constant over the course of the experiment. As compared with pure mullite, the

Fig. 1. A lower wetting angle and greater changes with time are observed for Al on mullite at 1100°C in vacuum versus oxygen gettered argon.

wetting angle of 99.99% Al is slightly higher ($\sim 10^\circ$) on 5 wt% NiO-, SiO₂-, and TiO₂-doped mullite, and slightly lower on 5 wt% ZrO₂-doped mullite. These results show that minor compositional variations in the mullite preform have only minor effects on the Al wetting behavior.

Kinetic information on Al infiltration of phase-pure and doped mullite was obtained by sectioning the metal-ceramic reaction couples formed during wetting experiments, and measuring the depth of composite formation using optical microscopy. The depth of Al/Si/Al₂O₃ composite formation in phase-pure mullite after 75 minutes at 1100°C was approximately 2.7 mm. Comparable results were obtained for the 5 wt% NiO- and TiO₂- doped mullite, while greater penetrations of 3.1 and 3.3 mm were obtained for 5 wt% SiO₂- and ZrO₂-doped mullite. Additional experiments are being conducted to verify that the differences observed are significant, and to determine why the kinetics of composite formation are faster in SiO₂- and ZrO₂-doped mullite

To more quantitatively determine the kinetics of metal-ceramic composite formation in the Al/mullite system, an apparatus was designed and constructed to fabricate metal-ceramic composites by controlled dipping of ceramic preforms in molten aluminum. Reaction times were accurately controlled by dipping a ceramic preform into molten aluminum at 1100-1200°C for a

prescribed time, and then removing it. The reacted samples were sectioned, and the thickness of the composite layer formed was measured by optical microscopy. The results presented in Figures 2 and 3 show that there is a 5-10 min. incubation time for Al penetration and reaction with mullite. The rate of metal-ceramic composite formation in the Al/mullite system is proportional to the square root of time for short reaction times (<1 hr) and increases with longer reaction times. As expected, composite formation rate also increases with temperature. Based on the measured infiltration distances at given times for different temperatures, an activation energy for composite formation of ~200 kJ/mole was calculated (Figure 4). This activation energy is consistent with a diffusion controlled process.

Scanning electron microscopy of Al/mullite reaction couples reveals that silicon diffuses out of the mullite ceramic during reactive metal infiltration. This is also supported by X-ray diffraction analysis and scanning electron microscopy with electron dispersive spectroscopy, which indicate that composites produced by reacting aluminum with mullite are silicon deficient.

Transmission electron microscopy indicates that, in the Al/mullite reaction, aluminum diffuses into the mullite preform along grain boundaries, reduces individual mullite grains to produce alumina and silicon metal, and then the elemental silicon diffuses out of the body. The diffusion of Si out of the mullite preform may be the rate limiting step for Al/Si/Al₂O₃ composite formation from Al and mullite by reactive metal infiltration.

Fig. 2. The kinetics of Al/Si/Al₂O₃ composite formation during reactive metal infiltration is proportional to the square root of time for short reaction times.

Fig. 3. The kinetics of Al/Si/Al₂O₃ composite formation during reactive metal infiltration is proportional to time for long reaction times.

Fig. 4. Consistent with a diffusion controlled process, an activation energy of ~200 kJ/mole is calculated for Al/Si/Al₂O₃ composite formation during reactive metal infiltration.

2. Evaluate Other Metal-Ceramic Systems

Explanation: Process flexibility is critical to economic competitiveness and a commercially viable manufacturing process. To determine if reactive metal infiltration can be a general route to composite synthesis, we are evaluating metal-ceramic reactions in compositional systems other than Al/mullite.

Status: Reactions other than Al/mullite that may produce metal-ceramic composites by reactive metal infiltration include;

As written, these reactions indicate that a variety of metal and intermetallic/ceramic composites can be produced by reactive metal infiltration. X-ray diffraction analysis of reacted metal-ceramic combinations in several of these new systems indicate the reactions proceed as written. For example, the X-ray diffraction spectra of powder reaction couples for reactions 3 and 4 presented in Figures 5 and 6 reveal the presence of the expected reaction products when the ceramic is reacted with $x = 0, 1/3$, and 1 excess moles of aluminum at 1400°C for 2 hr in gettered argon. The desirable intermetallic phase, NiAl, is formed when $x = 1$.

In the Al/Mo/mullite reaction, excess aluminum concentration, x , was varied from 0 to 12. After reacting for 2 hr at 1200°C in argon, Reaction 5 proceeds as written for $x = 0$ (Figure 7). With excess aluminum, $\text{Mo}(\text{Al},\text{Si})_2$ is formed in preference to MoSi_2 .

Excess aluminum compositions of $x = 0, 1$, and 3 were evaluated in both the Al/TiO₂ and Al/Al₂TiO₅ systems, and in both cases, after reacting at 1400°C for 2 hr in argon, the reactions proceed as written in Reactions 6 and 7 above.

3. Assess Near Net-Shape Fabrication by Reactive Metal Infiltration

Explanation: The difficulty and expense of grinding and machining ceramics to final shape frequently are major limitations to commercial application, regardless of property advantages. One significant advantage of reactive metal infiltration is the potential it offers for near-net-shape processing. Final shape fabrication without machining will save energy, lower costs, and should give the reactive metal infiltration process a competitive advantage over traditional composite synthesis techniques.

Fig. 5. XRD spectra of NiO reacted with $x = 0, 1/3$, and 1 excess moles of Al at 1400°C for 2 Hr in argon (Reaction 3).

Fig. 6. XRD spectra of NiAl₂O₄ reacted with $x = 0, 1/3$, and 1 excess moles of Al at 1400°C for 2 Hr in argon (Reaction 4).

Fig. 7. XRD spectra of mullite reacted with $x = 12$ excess moles of Al, and $x = 0$ and 12 excess moles of Al with Mo at 1200°C for 2 Hr in argon (Reaction 5).

Status: Making parts to near-net-shape by reactive metal infiltration requires balancing the densities of the products and reactants. As discussed in previous reports, for the stoichiometric Al/mullite reaction, the molar volumes of reaction products differ from that of dense mullite by less than one per cent. Consequently, composite formation in the Al/mullite system is expected to be a near-net-shape process.

To demonstrate the validity of the theoretical calculations, dense, commercial MV-30 mullite-glass tubes (Vesuvius McDanel, Beaver Falls, PA) were infiltrated with molten aluminum for 12 hr at 1200°C in argon, and completely converted to an Al/Si/Al₂O₃ composite.

A comparison of mullite-glass ceramic preforms with composites produced by reacting the tubes with aluminum demonstrates the feasibility of fabricating net-shape parts by reactive metal infiltration (Figure 8). Within the measurement error of ± 0.05 mm, the linear dimensions of the tubes are identical before and after reactive infiltration (Table 1). Additionally, the fine surface texture on the (extruded) ceramic tube is maintained throughout the reaction.

Subsequent, more carefully controlled experiments were conducted to measure the volume of samples before and after reaction using a liquid displacement technique that has an accuracy of better than ± 0.1 percent. On average, metal-ceramic composites formed by reacting phase-pure mullite with aluminum show a 0.32 percent expansion, with a standard deviation of 0.97. Composites formed by reacting mullite-glass ceramic preforms with aluminum show a 1.42 percent volume contraction with a standard deviation of 0.42.

The crystalline mullite ceramic preform, and the formation of a crystalline alumina skeletal structure on reaction with aluminum may be key to the dimensional stability of the

Fig. 8. Aluminum infiltrated mullite composite tubes in comparison to the commercial mullite preforms. Infiltration was conducted at 1200°C for 2 Hr in argon.

Table 1. Dimensions of Mullite-Glass Tube Preforms Relative to Mullite-Glass Tubes Infiltrated with Aluminum at 1200°C for 12 hr in Argon Demonstrate the Feasibility of Near-Net-Shape Processing By Reactive Metal Infiltration.

Sample	Outside Diameter (mm)		Inside Diameter (mm)		Height (mm)	
	Preform	Infiltrated	Preform	Infiltrated	Preform	Infiltrated
1	17.68	17.65	11.4	11.41	15.15	15.13
2	17.68	17.68	11.4	11.36	14.76	14.75
3	17.68	17.65	11.4	11.39	15.28	15.25

Al/mullite system during reactive metal infiltration. It is believed that, when aluminum reacts with crystalline mullite, a rigid alumina skeletal structure rapidly forms within the dense mullite preform to preserve sample size and shape during the reaction.

4. Fabricate Composite Coatings by Reactive Metal Infiltration

Explanation: Reactive metal infiltration is one of a few techniques with the potential to make coatings on ceramics that are thick enough for appreciable toughening. Tough composite coatings could improve the performance and broaden the commercial applications of otherwise brittle ceramics as engineering materials.

Status: By applying reaction kinetics information obtained from controlled infiltration experiments, it was possible to define reaction times to fabricate composite coatings on dense ceramic preforms by reactive metal infiltration. Controlled thicknesses Al/Si/Al₂O₃ composite coatings were fabricated on dense mullite preforms using the dipping technique described earlier in this report, and reaction times of 15 - 60 min. (Figure 9). In previous work, we also determined that specific additives to the ceramic preform can be used to modify the rate of infiltration and the thickness of the composite coating. For example, mullite doped with ZrO₂ exhibits a self-limiting infiltration that can be used to make composite coatings on monolithic ceramic parts.

Fig. 9. Uniform Al infiltration and composite formation is observed with time at 1100°C.

5. Evaluate Metal-Ceramic Composite Microstructure and Properties.

Explanation: Composite properties are being measured and correlated with microstructure to determine the ranges of properties that are achievable in metal-ceramic composites produced by reactive metal infiltration. By developing specific process-microstructure-property models, it will be possible to tailor reactively-formed metal-ceramic composite properties to desired applications.

Status: To characterize the properties of reactively-formed Al/Si/Al₂O₃ composites as a function of excess aluminum concentration, high-purity mullite powder (MULCR, Baikowski International Corp, Charlotte, NC, and Chichibu MP40, SCIMAREC Co., Ltd, Tokyo, Japan) was reactively hot pressed with x = 0, 2, and 12 excess moles of reagent grade aluminum powder (>99% Al, Fisher Scientific, Pittsburgh, PA) at 1450°C and 70 MPa for 1/2 hr.

The physical properties of the dense ceramic precursors and the dense reactively-formed metal-ceramic composites were determined using conventional analytical techniques. Young's

modulus (E) was determined using a pulse-echo technique. Fracture strength (σ_f) was measured on standard size B (3 mm x 4 mm x 45 mm) bars using a standard 4-point bend technique with a test cross head speed of 0.02 in/min. at room temp. Density (ρ) was determined by dimensions and mass and by the Archimedes' method. Hardness (H_v) and fracture toughness (K_{IC}) were determined by Vickers indentation, and indentation crack length using a Zwick diamond indenter at room temperature with indentation loads of 3-10 kg. Specific modulus was determined by dividing Young's modulus by density.

Physical properties of the metal-ceramic composites formed with Baikowski and Chichiba mullite precursors are presented in Tables 2a and 2b, respectively. Relative to the measured properties of dense, high-purity mullite (Ceraten, SA, Getafe, Spain) presented in Table 3, reactively-formed Al/Si/Al₂O₃ composites have improved properties. Consistent with the formation of an alumina skeletal structure during reactive forming, modulus, hardness, and density all initially increase for $x = 0$, and then decrease as x increases to 2 and 12. The alumina skeletal structure also dominates the thermal expansion of the reactively formed composite. The presence of the metal in the microstructure increases the fracture toughness of the composites, and fracture toughness increases with increasing aluminum concentration, x .

Table 2a: Properties Composites Formed by Reacting Baikowski High-Purity Mullite with $x = 0$ and 2 Excess Moles of Al at 1450°C and 70 MPa for 1/2 hr.

	E	H_v	K_{IC}	σ_f	CTE	ρ	$E_{specific}$
$x = 0$	365	15.73	4.63	302	6.93	3.79	96.3
$x = 2$	302	15.89	4.08	302	7.23	3.59	84.1

E = Young's modulus (GPa)

H = Vickers Hardness (GPa)

K_{IC} = Fracture toughness (MPa·m^{1/2})

σ_f = 4-point bend strength (MPa)

CTE = Thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$)

$E_{specific}$ = Specific Modulus (GPa·cm³/g)

Table 2b: Properties of Composites Formed by Reacting Chichiba High-Purity Mullite with $x = 0, 2$ and 12 Excess Moles of Al at 1450°C and 70 MPa for 1/2 hr.

	E	H_v	K_{IC}	σ_f	CTE	ρ	$E_{specific}$
$x = 0$	343	15.34	3.55	113	6.50	3.69	93.0
$x = 2$	345	15.53	3.91	260	6.74	3.69	93.5
$x = 12$	281	8.83	5.59	280	7.58	3.46	81.2

Table 3: Properties of High-Purity Ceraten mullite.

	E	H _v	K _{IC}	σ _f	CTE	ρ	E _{specific}
Mullite	198	11.21	1.72	182	3.92	3.00	66.0

A summary of the physical properties of reactively-formed Al/Si/Al₂O₃ composites in comparison to pure mullite is presented in Tables 4a and 4b. Relative to pure mullite, significant property improvements are evident in strength, toughness, and specific modulus.

Table 4a: Properties of Al/Si/Al₂O₃ Composites Formed By Reacting Baikowski High-Purity Mullite with x = 0, 2 and 12 Excess Moles of Al at 1450°C and 70 MPa for 1/2 hr in Argon. Values Are Relative to Pure Ceraten Mullite (i.e., all values for mullite in this table would be 1.00).

	E	H _v	K _{IC}	σ _f	CTE	ρ	E _{specific}
x = 0	1.84	1.40	2.69	1.66	1.770	1.26	1.46
x = 2	1.53	1.42	2.37	1.66	1.844	1.20	1.27

Table 4b: Properties of Al/Si/Al₂O₃ Composites Formed by Reacting Chachiba MP40 High-Purity Mullite with x = 0, 2 and 12 Excess Moles of Al at 1450°C and 70 MPa for 1/2 hr in Argon. Values are Relative to Pure Ceraten Mullite (i.e., all values for mullite in this table would be 1.00).

	E	H _v	K _{IC}	σ _f	CTE	ρ	E _{specific}
x = 0	1.73	1.37	2.06	0.62	1.658	1.23	1.41
x = 2	1.74	1.38	2.27	1.43	1.719	1.23	1.42
x = 12	1.42	0.79	3.2	1.54	1.934	1.15	1.23

Hardness and fracture toughness values were also obtained for composites made by reactively infiltrating Al into MV30 mullite-glass preforms at 1200°C for 8 hr in oxygen-gettered argon. Hardness increased from 7.1 GPa in the preform to 8.2 in the Al/Si/Al₂O₃ composite, whereas fracture toughness increased from 2.2 to 6.4 MPa·m^{1/2}. Indentation results also indicate

that strength degradation from crack formation and propagation may be less severe in reactively-formed composites. Along with the expected radial crack damage, Vickers indents in reactively-formed metal-ceramic composites show evidence of lateral and/or Palmquist cracks. Additionally, the length of the radial cracks formed Vickers diamond indents at comparable loads decreases with increasing metal content in the composite.

6. Patent and Literature Review

Explanation: A comprehensive search of prior art was conducted to determine the novelty of the reactive metal infiltration process, and to establish a strong position to patent the process and its products. Reactions between molten aluminum and oxides have been known for many years, as for example, in aluminum smelting,^{2,3} but they have not generally been studied as a technique for synthesizing composites. There appears to be no prior art on fabricating net-shape metal-ceramic composites by direct molten metal reaction with crystalline ceramic preforms.

Status: A patent application on Composite Synthesis and Processing by Reactive Metal Infiltration was filed in June, 1993. The patent application has 34 claims including those for near-net-shape fabrication, fabricating unique property metal-ceramic composites, and making composite coatings by reactive metal infiltration. We continue to monitor current patents and literature for art relevant to the reactive metal infiltration process.

PUBLICATIONS

- 1) R. E. Loehman, "Metal-Mullite Reactions," to be published in the Proceedings of the 3rd International Conference on Advanced Materials held in Tokyo, Japan, September 4, 1993.
- 2) R.E. Loehman, "Ceramic-Metal Reactions and Bonding Mechanisms in Composites, Ceramic Joining, and Electronic Packaging," to be published in *Scripta Metallurgica*, the proceedings of the Second International Workshop on Interfaces held in Santiago de Compostela, Spain, September 27, 1993.

PRESENTATIONS

- 1) R. E. Loehman, K. G. Ewsuk, A. P. Tomsia, J. Ortega, and W. Fahrenholtz, "Near-Net-Shape Fabrication of Metal-Ceramic Composites by Reactive Metal Infiltration," presented at the 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, (April 18-22, 1993).

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2. A. E. Standage and M. S. Gani, "Reaction Between Vitreous Silica and Molten Aluminum," *J. Amer. Ceram. Soc.*, **50** [2], 101-105 (1967).
 3. K. Prabirputaloong and M. R. Piggott, "Reduction of SiO₂ by molten Al", *J. Amer. Ceram. Soc.*, **56**, 184-88 (1973).

- 2) K. G. Ewsuk, R. E. Loehman, S. J. Glass, A. P. Tomsia, W. Fahrenholtz, and J. Ortega, "Microstructure and Properties of Reactive Formed Metal-Ceramic Composites," presented at the 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, (April 18-22, 1993).
- 3) R. E. Loehman, K. G. Ewsuk, A. P. Tomsia, W. Fahrenholtz, and J. Ortega, "Composites through Reactive Metal Infiltration," presented at the DOE/Advanced Materials Concepts Annual Review, Oak Ridge, TN (June 7-9, 1993).
- 4) K. G. Ewsuk, (invited) "Processing and Properties of Composites Formed by Reactive Metal Infiltration," presented at the University of New Mexico Engineering Class Seminar, Albuquerque, NM (July 21, 1993).
- 5) K. G. Ewsuk, (invited) "Processing and Properties of Composites Formed by Reactive Metal Infiltration," presented at the University of New Mexico Engineering Class Seminar, Albuquerque, NM (September 3, 1993)
- 6) R. E. Loehman, (invited) "Metal-Mullite Reactions," presented at the 3rd International Conference on Advanced Materials, Tokyo, Japan (September 4, 1993)
- 7) R.E. Loehman, (invited) "Ceramic-Metal Reactions and Bonding Mechanisms in Composites, Ceramic Joining, and Electronic Packaging," presented at the Second International Workshop on Interfaces, Santiago de Compostela, Spain (September 27, 1993)
- 8) K. G. Ewsuk, S. J. Glass, R. E. Loehman, A. P. Tomsia, J. Ortega, and W. Fahrenholtz, (invited) "Advanced Metal-Ceramic Composites Fabricated by a Novel Reactive Metal Infiltration Process," presented at the Annual New Mexico ACerS/MRS Section Meeting, Albuquerque, NM (October 25-26, 1994).
- 9) J. Ortega, W. Fahrenholtz, R. E. Loehman, K. G. Ewsuk, and A. P. Tomsia, "Microstructure and Properties of Reactive Metal Formed Al_2O_3 -Al-Si Composites," presented at the Annual New Mexico ACerS/MRS Section Meeting, Albuquerque, NM (October 25-26, 1994).
- 10) W. Fahrenholtz, J. Ortega, R. E. Loehman, K. G. Ewsuk, and A. P. Tomsia, "Near-Net-Shape Formation of Metal-Ceramic Composites by Reactive Metal Infiltration," presented at the Annual New Mexico ACerS/MRS Section Meeting, Albuquerque, NM (October 25-26, 1994).
- 11) K. G. Ewsuk, R. E. Loehman, A. P. Tomsia, W. Fahrenholtz, and J. Ortega, "Metal-Ceramic Composite Formation by Reactive Metal Infiltration," presented at the 1993 PAC RIM Meeting, Honolulu, HI, (November 7-10, 1993).

HONORS AND AWARDS

None this reporting period

PATENTS/DISCLOSURES

United States Patent Application "Composite Synthesis and Processing by Reactive Metal Infiltration", filed in June, 1993

LICENSES

None this reporting period

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

We have had discussions on applications of reactively-formed metal-ceramic composites with Motorola and Ceradyne, Inc., and samples have been provided to Motorola for evaluation.

COST SHARING

None this reporting period

HIGHLIGHTS

Metal-ceramic composites can be made to near-net shape by reactive infiltration of Al into mullite preforms. The composites have superior properties to the mullite preform. The process is controlled well-enough to produce reproducible composition and property composites. Properties measurements show that modulus and hardness of reactively-formed metal-ceramic composites are controlled by a rigid ceramic skeletal structure that forms during the reaction, whereas fracture toughness is controlled by the ductile metal phase present. Through compositional variations, reactively-formed metal-ceramic composite properties can be varied to achieve desirable combinations for specific applications.

CE/AIC Materials Program Annual Progress Report for FY93 (CEW - 2359)

NEAR-NET SHAPE PROCESSING OF CERAMIC-METAL COMPOSITES MAY PROMOTE THEIR COMMERCIAL APPLICATION

Problem: Use of advanced materials and composites is generally restricted by high processing costs.

Results: Metal-ceramic composites can be made to near-net shape by reactive infiltration of Al into mullite preforms. The composites have superior properties to the ceramics they are made from. The process can be controlled to give reproducible compositions and properties that fit a wide spectrum of commercial needs. Properties measurements show that modulus and hardness of reactively-formed metal-ceramic composites are determined by a rigid ceramic skeletal structure that forms during the reaction, whereas fracture toughness is controlled by the ductile metal phase present. Through compositional variations, reactively-formed metal-ceramic composite properties can be engineered to achieve desirable combinations for specific applications.

← Mullite Preforms

← Metal-Ceramic Composites Formed
After Reacting with Aluminum

Near-Net-Shape Processing is Possible with Reactive Metal Infiltration

Significance - for Energy Conservation: It is generally recognized that one of the main costs associated in making components of advanced materials and composites is the cost of materials removal to get the part to its final shape. Grinding, cutting and finishing operations are very energy intensive, particularly for hard materials that may require diamond tooling. Making parts to net shape eliminates grinding and saves energy.

Significance - For Materials Technology: Developing methods for net-shape processing is a major R&D effort in materials science. Use of infiltration reactions to make complex parts to net shape will be a major advance of the field.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

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

PHASE: Technology Development

PERFORMING ORGANIZATION: Sandia National Laboratories
Albuquerque, NM
Advanced Materials Laboratory

PRINCIPAL INVESTIGATOR: Ronald E. Loehman (505) 272-7601

PHASE OBJECTIVE: To research and develop synthesis and processing of ceramic-metal composites by reactive infiltration; to develop a fundamental understanding of infiltration reactions mechanisms and kinetics so that the process can be controlled and made commercially useful.

ULTIMATE OBJECTIVE: To develop an economical process for making ceramic-metal composites with commercially-valuable properties.

TECHNICAL APPROACH: We are developing a reactive metal infiltration process that converts brittle ceramic preforms to tough metal-ceramic composites by direct redox reaction with molten metal. Generally, reactions between Al and oxides are of the form;

where MO_y can be either a simple binary or complex oxide, and the residual metal phase can take a variety of forms as determined by the phase equilibrium relations of the given system. Evidence is accumulating that reactive infiltration is applicable generally to oxide-metal combinations for which there is both favorable wetting of the oxide by the molten metal (i.e., contact angle $\theta < 90^\circ$) and a negative Gibbs energy for reaction.

In the Al/mullite system, molten aluminum metal reduces mullite to produce alumina and elemental silicon according to the reaction;

With excess aluminum present (i.e., $x > 0$), a composite of alumina, silicon, and aluminum is formed. Metal-ceramic composites have been produced by infiltrating dense ceramic preforms with molten metal, and by sintering mixtures of ceramic and metal powders. Experimental results on variable composition metal-ceramic powder reaction couples indicate that reactive metal infiltration can be a general route to composite synthesis. Composite formation by reactive metal infiltration appears to be a diffusion controlled process with parabolic reaction kinetics at short times; consequently, metal-ceramic composite coatings can and have been fabricated by controlling the infiltration time. Additionally, in select systems, reactive metal infiltration affords near-net-shape forming capability.

Fabricating composites with physical properties optimized for particular applications is one of the potential benefits of the reactive metal infiltration process. For composites in the Al/Si/Al₂O₃ system, improvements in Young's modulus, fracture strength, density, hardness, fracture toughness, and specific modulus are apparent relative to the pure mullite preform. Reactive-formed metal-ceramic composite fracture toughness increases with increasing Al

concentration, while modulus and density remain relatively constant, making it possible to fabricate novel tough, high specific modulus (i.e., modulus + density) materials. Mechanical property data are consistent with microstructural evidence and coefficient of thermal expansion data that indicate a three-dimensional, alumina skeletal structure is formed during reactive infiltration, as many of the physical properties of the composite are controlled by that rigid alumina skeleton. Results also indicate that, relative to the ceramic preform, the composites are more flaw tolerant; that is, the strength degradation from crack formation and propagation appears to be less severe in the metal-ceramic composite relative to the mullite preform.

PROGRESS;

- Determined the kinetics of infiltration of Al into dense mullite. Kinetics are parabolic at short times but become linear at longer times.
- Determined from TEM studies that infiltration initiates down ceramic grain boundaries, thus giving insight into the mechanism
- Studied other metal-ceramic systems for potential for reactive infiltration processing. Verified that $\text{Mo}(\text{Si},\text{Al})_2\text{-Al}_2\text{O}_3$ composites can be made by reaction and identified other promising systems.
- Measured properties of composites and found significantly improved toughness with little loss in stiffness compared with the ceramic preform. Properties variations have been modeled to give predictive capability.

Patents: 1 application **Publications:** 2 **Presentations:** 11

ACCOMPLISHMENTS:

Technology Transfer: Have visited, provided samples, and held discussions with Motorola, Pask Research and Engineering, Ceradyne, and Allied Signal.

Licenses: none

PROJECT TITLE: Synthesis and Processing of Composites by Reactive Metal Infiltration.

CRITICAL ISSUES: Ceramic-metal composites have advantages as engineering materials because of their high stiffness-to-weight ratios, good fracture toughness, and because their electrical and thermal properties can be varied through control of their composition and microstructure. However, broader commercial application of these materials requires improvements in synthesis and processing so that high-performance parts can be produced more economically. Reactive metal infiltration is a promising new route to synthesize and process a wide range of ceramic and metal-matrix composites to near-net-shape with control of both composition and microstructure. Reactive metal infiltration offers significant potential for manufacturing a broad range of advanced ceramic composites that are needed for light-weight structural and wear applications for transportation and energy conversion devices.

FUTURE PLANS: The goals of this research program are to; 1) identify feasible compositional systems to fabricate composites by reactive metal infiltration, 2) understand the mechanism(s) of composite formation by reactive metal infiltration, and 3) control and optimize the reactive metal infiltration process to economically produce composites and composite coatings.

POTENTIAL PAYOFF: In applications such as heat engines, power generation equipment, and automotive and aerospace components, use of refractory, light-weight ceramic composites could reduce energy consumption by as much as 1×10^{15} BTU/yr, with a reduction in NO_x emissions of 600,000 tons/yr. Near-net-shape fabrication of parts should lead to additional savings because costly and energy intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.

ESTIMATED ENERGY SAVINGS: Use of refractory, light-weight ceramic composites could reduce energy consumption by as much as 1×10^{15} BTU/yr, with a reduction in NO_x emissions of 600,000 tons/yr, according to S. Richlen (Ceram. Sci. and Eng. Proc. **11**[7-8], 576-7 (1990))

THREE-DIMENSIONAL X-RAY TOMOGRAPHY OF CRACK-RESISTANT COMPOSITES

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INTRODUCTION

The goal of this research is to apply noninvasive, volumetric imaging technology (the x-ray tomographic microscope) to the characterization and process-modeling of ceramic matrix composites. Specifically, we propose to follow the evolution of a composite's microstructure during chemical vapor infiltration processing, and relate the microstructure to processing parameters and fiber architecture. The results will be used to validate process models and provide the fundamental and practical understanding necessary for cost-effective "intelligent" processing of ceramic matrix composites.

Chemical vapor infiltration (CVI) is an important technology for fabricating SiC ceramic matrix composites. In CVI, a vapor precursor of the SiC matrix material—methyltrichlorosilane (MTS)—is passed through a network of reinforcing fibers at elevated temperature. The MTS dissociates, and the SiC matrix phase deposits on the fibers. As matrix growth progresses, avenues for gas transport become more tortuous and begin to close off, eventually stopping the infiltration process. Pore closure, which determines the final density of the composite, is affected by the fiber architecture in ways which are not well understood.

The x-ray tomographic microscope (XTM) has been developed for imaging composite microstructures during CVI. The XTM is ideally suited for this task, as it is both noninvasive and volumetric; hence, the XTM can be used to quantify in three-dimensions the microstructural changes that occur in a composite during infiltration. Our current research is focused on quantifying matrix deposition in a Nicalon fiber (amorphous SiC)/SiC matrix composite structure, and in determining the effects of fiber architecture (e.g., cloth orientation, weave, and number of fibers in a tow) on consolidation. Specifically, we use the XTM to follow the time evolution of V_v (the volume fraction of microporosity in a tow), S_v (the surface area available for deposition), and N_v (the number and location of isolated pores within the composite). These measured values can be used to validate the predictions of process models.

In a previous study, we reported the results of the first XTM experiments where matrix growth was measured *in situ* during CVI.¹ Two square-weave Nicalon fiber preform architectures (0/45 and 0/90) were volumetrically imaged during isothermal forced infiltration with MTS at 975C. The filling of the micropores within the fiber tows was followed as a function of both position within the preform and infiltration time. Measurements of surface area and local density were also obtained as a function of the processing time. The observations did not show any differences in the infiltration behavior between the two architectures.

TECHNICAL PROGRESS IN 1993

Summary

The analysis of the pore structures of chemically vapor infiltrated composites was extended to measurements of topological properties. Two new analytical approaches have been developed and tested. First, the number of isolated pores has been measured. Second, the connectivity density of the percolating pores has been measured for different architectures. It was observed that the connectivity density of the macroporosity in a ceramic matrix composite exhibits critical behavior.

Milestones:

1. Percolation Analysis of Pore Networks

With three-dimensional data, it is possible to count all isolated (non-connected) particles in a sample. Identifying isolated particles and correctly enumerating them in a large (>100 million voxels) volume set is a computationally intensive task. Thanks to an efficient cluster labeling algorithm developed by Hoshen and Kopelman², however, it is possible to label and count all of the isolated features in a large volume set quite rapidly on a standard workstation. In this method of counting, particles of type A are composed entirely of voxels containing attenuation coefficients unique to the type-A particle. The algorithm performs a single pass through the data, giving each cluster of type A voxels a unique label. In those cases where two or more previously isolated clusters merge together, the higher numbered clusters are relabeled as belonging to the lowest number in the newly-merged cluster. A cluster may be considered as being face-connected only, or edge and corner connections may also be included.

We have used the HK algorithm to count the number of pores which become isolated (closed-off from the infiltration) during consolidation of a ceramic matrix

composite. Prior to infiltration, there are no isolated pores, as they are all interconnected. As infiltration proceeds, pores close off and become isolated from the infiltrating vapor mixture, and their number increases gradually with composite density. Near the completion of infiltration, however, the number of isolated pores avalanches. Soon afterwards, there are no longer any percolating (continuous) clusters and infiltration ceases.

2. Topological Properties of Pore Networks

We are interested in knowing if the topological properties of the pore network can be used to explain the onset of pore avalanche. A similar study of sintering showed a strong correlation between decreased interconnectedness and increased isolated porosity.³ However, in that study, the method for measuring the connectedness (the number of connections or pathways between pores) was developed for serial sectioning, and did not lend itself to computer methods. Feldkamp described a method for calculating the connectedness of three-dimensional structures which is straightforward to implement on a computer.⁴ The algorithm computes the Euler-Poincare' characteristic, X , for a network. X is a topological number describing the number of connections, or branches, minus the number of nodes. For the volume sets from the CVI data, we calculated $\beta_1 = 1 - X$, where β_1 is the first Betti number. β_1 is the number of branches that must be cut to form a disconnected, or isolated, structure. For example, a simply connected pore network, or Caley tree, has $\beta_1 = 0$. Closure of any pathway or branch in a simply connected pore network will produce an isolated pore. A multiply connected structure will have $\beta_1 > 0$, indicating that many pathways must seal off before an isolated pore is formed.

Figure 1 shows preliminary results from a combined cluster/connectivity analysis. The number of pores is represented by the left abscissa, and the connectivity (β_1) is represented by the right abscissa. There is a sharp break in both curves at about 70% fractional density. A sudden decrease in the number of connections towards a more simply connected network is associated with a simultaneous increase in the number of isolated pores. This correlation between connectivity and porosity may lead to new techniques of optimizing fiber architectures for chemical vapor infiltration processing.

Figure 1: The connectivity density and the number of pores in a 0/45 ceramic matrix composite at different stages in its consolidation. Initially, there is only one interconnected pore permeating the entire sample. As infiltration proceeds, and the fractional density of the composite increases, pores gradually become isolated. The connectivity density only gradually decreases during the early stages of consolidation. However, at a critical density, the connectivity density rapidly decreases as vapor pathways close off. This is accompanied by an avalanche in isolated pores. Infiltration ceases shortly thereafter.

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4. L.A. Feldkamp, S.A. Goldstein, A.M. Parfitt, et al., *J. Bone and Min Res* 4:3–11 (1989).

PUBLICATIONS

Journals

J.H. Kinney, T.N. Breunig, T.L. Starr, et al., "X-ray Tomographic Study of Chemical Vapor Infiltration Processing of Ceramic Composites", *Science*, 260:789–792 (1993)

Conference Proceedings

J.H. Kinney, D.L. Haupt, T.M. Breunig, M.C. Nichols, T.L. Starr, and S.R. Stock, "Time Evolution of Microstructure during Forced Flow chemical Vapor Infiltration of a Continuous Fiber Ceramic Matrix Composite", Ceramic Engineering and Science Proc., volume 14, pages 1028–1037 (1993).

T.M. Breunig, M.C. Nichols, J.H. Kinney, and D.L. Haupt, "Quantitative Microstructural Changes in a Composite Material Using Destructive and Noninvasive Techniques", Ceramic Engineering and Science Proc., volume 14, pages 500–509 (1993).

Presentations without Proceedings

Quantitative Microstructural Characterization using Three-Dimensional X-ray Tomographic Microscopy Data, International Conference on Quantitative Microscopy and Image Analysis, Charleston, SC, July, 1993

Influence of Fiber Architecture on CVI of SiC Composites, 95th Annual Meeting of the American Ceramic Society, Cincinnati, OH, April, 1993.

Quantitative Microstructural Characterization of Composite Materials Using Destructive and Noninvasive Techniques, NDE for Process Understanding, Sensing and Control, American Society for Nondestructive Testing, Spring Conference, Nashville, TN, March 1993 (invited).

HONORS AND RECOGNITION

Cover Photograph, May 7, 1993, *Science*.

PATENTS/DISCLOSURES

"A Two Stage Asymmetric X-ray Magnifier for X-ray Tomographic Microscopy", patent received #5,245,861 (1993).

"Total Reflection X-ray Imaging Detector", patent disclosure filed. Patent application is in process.

LICENSES

A CRADA has been signed with General Electric Corporation to transfer XTM technology and for joint development of advanced reconstruction software.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

COST SHARING

The technology transfer of the XTM to General Electric is being supported by a grant from Defense Programs through a technology transfer initiative. The maturation of this technology directly benefits from the AIC Materials Program efforts in ceramic matrix composites. Labor costs for maintaining the hardware and software are shared among grants from the National Institutes of Health and internal Laboratory Director's Research and Development money. A new Vax workstation for data analysis was procured by the Chemistry and Materials Science Department at Lawrence Livermore National Laboratory. A large area CCD array is on loan from Sandia National Laboratories, CA.

HIGHLIGHTS

We have demonstrated that high-resolution x-ray tomographic microscopy can be used to analyze matrix growth quantitatively during chemical vapor infiltration. The measured parameters, such as the surface area evolution, number of pores, and pore volume, are of great importance for validating process models. The availability of x-ray tomography systems with microscopic resolution, coupled with efficient analysis software, will aid our understanding of the generic class of problems in which microstructure changes with time. Important examples include materials synthesis and processing, crack nucleation and growth, and materials compatibility.

Three-Dimensional X-ray Tomography of Crack Resistant Composites

Problem:

Before continuous filament ceramic matrix composites can be used with confidence, it will be necessary to reduce and control the porosity which remains after processing. Such "intelligent" processing will require an understanding of how process variables and fiber geometry determine the microstructure of the composite. Efforts to understand densification mechanisms in ceramic matrix composites have been frustrated by the lack of direct experimental observation of the evolving microstructure during processing. Can noninvasive, three-dimensional tomography provide the necessary microstructural information to validate process models and improve our understanding of these technologically important materials?

Results:

A high resolution, three-dimensional tomography system has been used to quantify microstructural evolution in continuous filament composites **during** chemical vapor infiltration processing. Microstructural parameters such as the amount of fiber tow consolidation and changes in surface area provide information which is essential for validating process models.

Figure 1: A three-dimensional XTM visualization of the interconnected porosity in a continuous filament ceramic matrix composite after three hours of chemical vapor infiltration.

Figure 2: The connectivity density and the number of pores in a 0/45 ceramic matrix composite at different stages in its consolidation. The connectivity density only gradually decreases during the early stages of consolidation. However, at a critical density, the connectivity density rapidly decreases as vapor pathways close off. This is accompanied by an avalanche in isolated pores. Infiltration ceases shortly thereafter.

Significance for Materials Technology

High-resolution x-ray tomography can quantitatively analyze matrix growth during chemical vapor infiltration. The measured parameters are of great importance for validating process models. The availability of x-ray tomography systems with microscopic resolution will revolutionize our understanding of the generic class of problems in which microstructure changes with time.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: THREE-DIMENSIONAL X-RAY TOMOGRAPHY OF CRACK RESISTANT COMPOSITES

PHASE: FY 1993

PERFORMING ORGANIZATION: Lawrence Livermore National Laboratory

PRINCIPAL INVESTIGATOR: J.H. Kinney (510)–422–6669

PHASE OBJECTIVE: This period was devoted to investigating the topological properties of the pore networks in chemically vapor infiltrated composites.

ULTIMATE OBJECTIVE: This program seeks to establish design rules and criteria for optimizing the processing of continuous filament ceramic matrix composites.

TECHNICAL APPROACH: The approach is to apply noninvasive, volumetric imaging technology (the x-ray tomographic microscope) to the characterization and process-modeling of ceramic matrix composites. Specifically, we follow the evolution of a composite's microstructure during chemical vapor infiltration processing, and relate the microstructure to processing parameters and fiber architecture. The results will be used to validate process models and provide the fundamental and practical understanding necessary for cost-effective "intelligent" processing of ceramic matrix composites.

PROGRESS: The analysis of the pore structures of chemically vapor infiltrated composites was extended to measurements of topological properties. Two new analytical approaches have been developed and tested. First, the number of isolated pores has been measured. Second, the connectivity density of the percolating pores has been measured for different architectures. It was observed that the connectivity density of the macroporosity in a ceramic matrix composite exhibits critical behavior.

Patents: one

Publications: one

Proceedings: two

Presentations: four

ACCOMPLISHMENTS: Patent number 5,245,861 was awarded for the x-ray tomographic microscope.

POLYMER AND BIOBASED MATERIALS

CHEMICAL RECYCLING OF MIXED WASTE PLASTICS

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INTRODUCTION

The goal of this work is the production of high-value chemicals from mixtures of waste plastics by using selective pyrolysis, which is achieved by taking advantage of differences in reaction rates, catalysis, and coreactants. Target wastes are mixtures at the molecular level, such as blends or composites, mixtures from manufactured products, such as carpets, and post-consumer mixed-plastic wastes.

The experimental approach begins with small-scale experiments that use molecular beam mass spectrometry (MBMS) to analyze the reaction products in a rapid fashion so that the effects of process parameters can be rapidly screened. This information is used to screen and optimize promising applications of selective pyrolysis for specific waste streams. Small-scale, fixed-bed and fluidized-bed reactors are used to provide products for conventional chemical analysis, to determine material balances, and to test the concept under conditions that will be used at a larger scale. An important element of this project uses technoeconomic assessments and market analyses of durables and other waste availability and end-product utilization to identify target applications that have the potential for economic success.

TECHNICAL PROGRESS

Summary

The most promising application is for recovering caprolactam from waste nylon 6 carpet. Extensive tests have been performed this past year under conditions similar to those envisioned for the pilot plant. More than 250 catalysts were screened using the MBMS and analyzed by multivariate statistical techniques. A 10 cm fluidized-bed reactor was constructed this year and used for runs at the 200-1000 g/hr level. This reactor was used to optimize the engineering parameters for producing caprolactam and demonstrate adequate product purity and yield. We have successfully converted the nylon

component in waste carpet to caprolactam, while the polypropylene and styrene/butadiene latex components of the backing remain unreacted and are used in a subsequent step as a fuel for process energy. These results convinced AlliedSignal to enter into a cooperative research and development agreement (CRADA). AlliedSignal is the major North American producer of caprolactam and nylon-6 fiber. The technical statement of work for the CRADA was written at the end of 1993, and it will be signed in early 1994. Work conducted under the auspices of the Advanced Industrial Concepts Materials Program since 1990 led to a patent that was issued in June 1993 and is the basis for this CRADA. A complimentary project with the Waste Materials Management Division (WMM) began in 1993 as a result of the AIC work, to develop the engineering-scale of this process. This will include the construction of a 25-50 kg/h circulating fluidized bed reactor. The WMM project is the major DOE contributor to the CRADA. This new NREL/DOE facility will be available for subsequent applications of the AIC recycling technology. About 2 million tons of carpet waste is generated annually in the U.S. About one-fourth of the total waste carpet is made of nylon-6. When successfully implemented through the year 2010, the selective pyrolysis of waste carpet could result in reducing electricity consumption by approximately 1,650 billion BTU's and reducing petroleum consumption by 340,000 billion BTU's because up to 500 million pounds of caprolactam will not have to be produced from imported oil. New plants are estimated to create 37,500 person-years of new jobs.

Progress was made in FY 1993 in the other major areas: recovering diamines from the isocyanates and high-value oxygenates from the polyols in waste polyurethane (PU), and recovering of dimethylterephthalate from wastes containing polyethylene terephthalate (PET). In the PU example bench scale testing has begun so that conventional chemical analysis and material balances can be performed. There are significant safety considerations in this process because one of the products is toxic. Thorough testing for exposure was performed and procedures were developed to eliminate possible chemical exposure. In the PET application, experiments were performed in recycling polyester fibers of interest to the textile industry.

Work continued this year to develop the Intelligent Chemical Processing System that will allow the prediction of conversion products for a wide range of plastics. A data set of 200 experiments has been added to the data base to demonstrate quantitative analysis of carpet mixtures (nylon 6, nylon 6/6, PET, styrene/butadiene latex and polypropylene) and to compare catalysts for converting nylon 6 to caprolactam. Methods of dealing with the day-to-day variabilities in MBMS data are being investigated to correlate data collected at different times.

Milestones

1. Assess Batch Engineering Data for Continuous Scale Experimentation, April 1993.

This milestone assessed the data from batch engineering experiments that were transferred from the MBMS experiments on converting waste polyethylene terephthalate (PET) to either terephthalic acid or the ester, dimethylterephthalate (DMT). The latter is the desired product because it is easily purified by two methods as required for food applications of recycled PET. It is produced in approximately 75% yield under current operating conditions. Technoeconomic assessment of this process has shown that PET conversion is not as economically favorable as nylon-6 carpet, because of lower yields and the lower value of the product. Although other competing technologies exist, they require pre-sorted PET waste. The selective pyrolysis process can use cheaper, mixed feedstocks. Therefore, work will continue on process development because PET is an important commodity plastic.

2. Identify Process Conditions for Producing High Value Chemicals from Waste Plastics, May 1993.

This milestone assessed the MBMS data to identify the best conditions for producing caprolactam from waste nylon-6 carpet. Two viable combinations of catalysts, supports and coreactants emerged for producing the purest caprolactam. However, one of these systems had significantly faster kinetics than the other and hence was chosen for further development. The findings from this study are now being used in the ongoing fluidized-bed reactor experiments.

3. Demonstration of a Model Intelligent Chemical Processing System for Optimizing Waste Utilization - Multivariate Calibration, June 1993.

FY93 studies were directed at qualitative and quantitative analysis of process streams using MBMS. The application of multivariate statistical analysis to mass spectral data on complex plastics mixtures showed that it is possible to accurately identify individual mixture components. Multivariate techniques were used to obtain quantitative estimates of the mixture components. Calibration/prediction experiments on real plastic mixtures of known composition resulted in root-mean-square prediction errors of less than 10%. This represents a key component in developing a method for monitoring input streams, the central feature of process control.

4. Update Technoeconomic Assessment of Waste Nylon-6 Carpet Stream, September 1993.

A revised technoeconomic assessment, carried out by A. J. Power and Associates under subcontract, suggested that this process will be cost effective and energy efficient. These preliminary estimates indicate that a 100 million pounds/year of caprolactam plant (270 million pounds/year of carpet waste) would require a \$40 million investment, and could produce caprolactam for \$0.39/lb including a collection cost of \$0.10/lb. For comparison, A. J. Power and Associates estimated that the cost of producing caprolactam from petroleum/natural gas is approximately \$0.74/lb (including capital charges). Thus, the simple payback of the technology appears very appealing to industry (1.3 years for the difference in amortized production cost between the two processes). In addition, selective pyrolysis technology allows companies to build smaller increments of production capacity than the 300-500 million pounds of typical capacity increments for current technology plants, which require significantly higher capital investments. Caprolactam's list market price ranges from \$0.89/lb to \$0.95/lb depending on purity. Large contracts are negotiated at a lower prices.

PUBLICATIONS

None - emphasis has been on having the intellectual property collected before issuing the publication. Technical briefs were issued on this work by OIT and NREL.

PRESENTATIONS

Presentations were made at: the American Chemical Society Meeting, Denver, CO, April 1993;

the AICD Materials Program Review Meeting, Oak Ridge, TN, June 1993; the Techview 93 Second Annual NREL Industry Open House, Golden, CO, September 1993; the American Textile Bobbin Show, Atlanta, GA, October 1993; and the Advanced Composites Conference and Exposition, Dearborn, MI, November 1993.

PATENTS/DISCLOSURES

Patent applications have been filed directed to the following embodiments:

"Controlled catalytic and thermal sequential pyrolysis and hydrolysis of polymer waste comprising...

- I. A process of producing caprolactam from nylon 6.
- II. A process for producing caprolactam and hydrocarbons from mixtures of nylon 6 and polyolefins.
- III. A process for producing terephthalic acid or its esters along with by-products from PET and PE.
- IV. A process for producing amines, isocyanates, etc. from polyurethanes.
- V. A process for producing terephthalic acid, styrene or mixtures of these two from PVC, PET, polystyrene and polyethylene.
- VI. A process for producing amines, isocyanates, HCl or mixtures of the same from PVC and PU.
- VII. A process for producing styrene, phenols, etc., from polystyrene and polyphenylene oxide.
- VIII. A process for producing phenols, hydrocarbons, etc. from polycarbonates and acrylonitrile butadiene-styrene polymers.

Patents had issued for I (U.S. Patent 5,216,149) and VII (U. S. Patent 5,300,704). The rest are pending.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

The CRADA negotiations with AlliedSignal have been the major technology transfer activity this year, and these have helped to better define the goals of this work sponsored by the AIC Materials Program, the complimentary work sponsored by WMM, and the work that will be performed by AlliedSignal when the CRADA begins. Other technology transfer activities have come from the meetings listed above. These have generated interest from industry, and discussions are ongoing on other potential applications, in particular for PU recycling. Additionally, NREL researchers have discussed this

technology with representatives of the American Plastics Council.

COST SHARING

The CRADA will last three years and the \$6.4 million cost will be shared 51% by AlliedSignal. The majority of the DOE funding (86%) is from the Waste Materials Management Division, which is focused on scale-up of the fluidized bed reactor. The AIC Materials Program funding that will be used for this CRADA will support efforts aimed at understanding the chemical processes and optimizing conditions, with emphasis on catalyst development.

HIGHLIGHTS

In FY 1993, four major accomplishments were achieved: 1) a new, larger (10cm), fluidized-bed reactor system, complete with a solids feeder and electrostatic precipitators, was constructed with cofunding from a complementary WMM project for the engineering development of the waste nylon 6 carpet example; 2) the CRADA negotiations were completed with AlliedSignal for the waste nylon 6 carpet example that will be signed in early 1994; 3) the demonstration of quantitative and qualitative analysis using the Intelligent Chemical Processing System for a set of the nylon-6 carpet conversion data; 4) the demonstration of the ability to recycle polyester from cotton/polyester fiber fabrics. This project continues to attract a high level of interest from industry. Future collaborations between WMM, or other DOE Offices, and relevant industrial partners, such as the American Plastics Council, will likely be based on this work for the Advanced Industrial Concepts Materials Program.

INNOVATIVE CHEMICAL RECYCLING OF PLASTICS

Problem:

Increased use of plastics in many industries and by consumers requires cost-effective and environmentally-safe recycling or disposal methods. Specially important is the treatment of mixed plastics streams for both minimizing waste and recovering intrinsic value.

Results:

This is a process for recovering the maximum chemical value from mixed-plastic waste streams by using selective, catalytic pyrolysis to convert one component of a mixture to its monomer or other high value-product, while other components of the mixture are left unreacted. Subsequent reaction conditions can then be used and the residual materials are either converted to high-value 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 caprolactam from post-consumer nylon 6 waste carpet, toluenediamine and allyl alcohol from waste polyurethane, and dimethylterephthalate from post-consumer, mixed plastics containing polyethyleneterephthalate.

N6 = nylon; PP = polypropylene; MDI & TDI polyurethane (PU) components;
PET = polyethyleneterephthalate; PE = polyethylene; PVC = polyvinylchloride; PS = polystyrene

Significance - For Energy Conservation:

A new technology for chemical recycling of 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.

Significance - 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.

Research by the National Renewable Energy Laboratory,
under support from the Materials Program,
Office of Industrial Technologies, the U. S. DOE.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: CHEMICAL RECYCLING OF MIXED WASTE PLASTICS

PHASE: FY 1993

PERFORMING ORGANIZATION: National Renewable Energy Laboratory

PRINCIPAL INVESTIGATOR: Robert J. Evans, (303) 384-6284

PHASE OBJECTIVE: This period was devoted to process optimization of nylon 6 waste carpet recycling for a pending cooperative research and development agreement (CRADA) and further development of polyethylene terephthalate and polyurethane conversion to valuable chemicals.

ULTIMATE OBJECTIVE: This project is developing selective pyrolysis processes to convert waste plastic mixtures into monomers or other high-value, chemical products. The goal is to develop processes that can be transferred to industry to minimize waste and recover the highest possible value.

TECHNICAL APPROACH: The experimental approach begins with small-scale experiments that use molecular beam mass spectrometry (MBMS) to analyze the reaction products in a rapid fashion so that the effects of process parameters can be rapidly screened. This information is used to screen and optimize promising applications of selective pyrolysis for specific waste streams. Small-scale, fixed-bed and fluidized-bed reactors are used to provide products for conventional chemical analysis, to determine material balances, and to test the concept under conditions that will be used at a larger scale. An important element of this project uses technoeconomic assessments and market analyses of durables and other waste availability and end-product utilization to identify target applications that have the potential for economic success.

PROGRESS: The waste nylon 6 carpet is the most advanced application and extensive tests were performed this year. A new 10 cm fluidized-bed reactor was constructed this year to optimize the process. The yields and purity of the monomer, caprolactam, from nylon 6 carpet has increased and parameter optimization was made easier due to this new reactor. In other applications, the conversion of poly(ethylene terephthalate) (PET) to its monomer, dimethyl terephthalate has expanded from mixed plastic bottle wastes to polyester fiber textile blends. Also, the intelligent chemical processing system has demonstrated quantitative and quantitative ability to analyze carpet mixtures. The data base is now being expanded to include a wider range of plastics.

Patents: 2 Issued, 6 Pending

Proceedings: None

Publications: None

Presentations: five

Licenses: None

ACCOMPLISHMENTS: In FY 1993, four major accomplishments were achieved: 1) a new, larger (10cm), fluidized-bed reactor system, complete with a solids feeder and electrostatic precipitators, was constructed, 2) the completion of the CRADA negotiations with AlliedSignal for the waste nylon 6 carpet example that will be signed in early 1994, 3) the demonstration of quantitative and qualitative analysis using the Intelligent Chemical Processing System for a set of the nylon-6 carpet conversion data, 4) the demonstration of the ability to recycle polyester from cotton/polyester fiber fabrics.

PROJECT TITLE: CHEMICAL RECYCLING OF MIXED WASTE PLASTICS

CRITICAL ISSUES: The CRADA with AlliedSignal will require rapid development of the technology over the next three years if successful commercialization is to be achieved. Other applications will hence develop at a slower rate. Safety considerations exist for the polyurethane recycling process that will need attention over the next year as bench-scale testing progresses.

FUTURE PLANS: The plan for next two years is to expand the development of applications that are relevant to the automotive industry. Technology transfer activities have been focused in this area and negotiations are in progress with General Motors on possible collaborative work .

POTENTIAL PAYOFF: This chemical recycling of mixed plastics technology was designed to be cost-effective, less energy consuming, reduce fossil fuel dependence, environmentally safe, and reduce disposal. About 2 million tons of carpet waste is generated annually in the U.S. About one-fourth of the total waste carpet is made of nylon-6. When successfully implemented through the year 2010, the selective pyrolysis of waste carpet could result in reducing electricity consumption by approximately 1,650 billion BTU's and reducing petroleum consumption by 340,000 billion BTU's because up to 500 million pounds of caprolactam will not have to be produced from imported oil. New plants are estimated to create 37,500 person-years of new jobs.

COMPOSITES AND BLENDS FROM BIOBASED MATERIALS

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INTRODUCTION

The program is focused on the development of composites and blends from biobased materials for use as membranes, high value plastics, and lightweight composites. Biobased materials include novel cellulose derivatives, wood modified with synthetic monomers, and wood fiber/synthetic plastic composites. Recent research efforts have focused on two areas: (1) composites and blends from cellulose derivatives, and (2) wood reinforced with synthetic monomers. The program is designed to evaluate the thermal, mechanical and permselective properties of these materials and relate their performance to the chemical structure and morphology of the composites or blends.

TECHNICAL PROGRESS

1. Composites and Blends from Cellulose Derivatives

Research efforts in the preparation and characterization of novel cellulose esters have focused on two approaches. The first approach is the preparation and characterization of organic/inorganic hybrid (OIH) composites using cellulose esters as the organic component. The second approach is the preparation and evaluation of cellulose mixed esters (CME), e.g., cellulose acetate propionate and cellulose acetate butyrate, copolymers and their blends. To initiate discussions with potential industrial collaborators NREL has joined the NSF Industry/University Cooperative Research Center for Separations Using Thin Films at the University of Colorado at Boulder.

a. Cellulose Ester OIH Materials

Cellulose acetate (CA) and tetraethyl orthosilicate (TEOS) were used to prepare OIH materials using sol-gel chemistry. Triethoxysilane groups were grafted onto the CA backbone

to promote the formation of covalent linkages between the organic and inorganic components. The grafting reaction is shown schematically in Figure 1. The grafted CA can be crosslinked directly or used as one component of the OIH material. The effects of the sol-gel reactions conditions, e.g., level of grafting, TEOS concentration, catalyst concentration, and film formation conditions on the mechanical and morphological properties of the OIH materials were determined.

Fig. 1. The grafting reaction used to modify cellulose acetate.

The presence of grafted triethoxysilane groups on the CA and the addition of TEOS both had a substantial impact on the properties of the OIH materials. The presence of grafted triethoxysilane groups with and without additional TEOS led to the formation of an insoluble, crosslinked CA network. The addition of TEOS increased the apparent crosslink density, limited swelling and increased the modulus of the material above its glass transition temperature. The TEOS that was added to form the OIH material was not completely converted to SiO_2 and formed a discrete second phase as determined by small angle X-ray scattering (SAXS) and silicon nuclear magnetic resonance (^{29}Si -NMR) measurements. All of these results indicate that the chemical resistance and the thermal and mechanical properties of cellulose esters could be improved by the formation of OIH materials.

These studies also demonstrated that the phase behavior of the CA/TEOS system is very complex and can be varied over a wide range. These OIH materials can be prepared as dense films with nanometer sized inorganic domains and as highly porous materials with micrometer sized voids. This wide range of structures should allow for the development of new applications for these materials.

b. CME Copolymers and Blends

The addition of bulky propionyl and butyryl groups to CA has a substantial impact on the thermal, mechanical and permselective properties of cellulose esters. Cellulose mixed

esters are an attractive alternative to CA for gas separation applications, where CA blends are currently used. The addition of bulky propionate and butyrate groups to the CA, Figure 2, increase the gas permeability of the cellulose esters. These copolymers and blends were evaluated as materials for membrane and plastics applications.

Fig. 2. Schematic of cellulose acetate propionate and cellulose acetate butyrate.

A series of cellulose mixed esters were prepared and extensively characterized. The type and location of the acyl group, i.e., acetate, propionate and butyrate, was determined using carbon nuclear magnetic resonance (^{13}C -NMR) spectroscopy. This analysis demonstrated that these CME copolymers are completely substituted, with the acyl groups randomly positioned around the cellulose ring.

The thermal and permselective properties of the cellulose mixed esters and their blends were also evaluated. Thermal and permselective properties of these semicrystalline CME copolymers are sensitive to the copolymer composition. The melting point of all the copolymers decreases with the addition of a second type of ester group, indicating that each of the three cellulose ester homopolymers pack into a unique crystalline unit cell, as confirmed by X-ray scattering results. Permselective properties of the CME were also influenced by the ester composition. Addition of either propionate or butyrate groups to the CME led to an increase in the pure gas permeability and a decrease in selectivity.

Blends of CME's were studied to determine the effects of ester type and loading on the mixing behavior. Cellulose triacetate was used as one component in all of the blends and various amounts of several CMEs were added by solvent blending. Thermal analysis was used to study the mixing behavior of the CME blends. The mixing behavior of these semicrystalline CMEs is very complex. In all cases, the CME is excluded from the cellulose triacetate crystallite. Even with a very low degree of substitution on the mixed ester (e.g., an average of

only one propionate or butyrate group on four anhydroglucose repeat units) the CME was excluded from the cellulose triacetate crystallite. Both homogeneous or heterogeneous amorphous components were formed depending on the CME type and the amount of CME in the blend. Permselective properties of these blends are being evaluated.

2. Wood Modified with Synthetic Monomers

The dimensional stability and mechanical properties of wood can be improved by the addition and *in situ* polymerization of synthetic monomers. Polymer modified wood has potential uses in lightweight composite applications. Researchers at the University of Southern Mississippi and a specialty veneer manufacturing company, in cooperation with NREL, have been working on routes for improving the efficiency of the impregnation and polymerization steps. The effects of mixed monomer systems are being evaluated. Improvements in the impregnation and polymerization steps will decrease monomer usage and improve the process economics. Use of a monomer mixture allows for control over the degree of swelling and the penetration of monomers into the wood cell wall. Controlled swelling and penetration are necessary to maximize the effectiveness of the monomers and improve the mechanical properties of the composite.

PRESENTATIONS

Preparation and Characterization of New Cellulosic-Based Organic/Inorganic Hybrid Materials via the Sol Gel Process, Saeed S. Shojaie and Stephen S. Kelley, National Renewable Energy Laboratory, Golden, CO, and Timothy G. Rials, Southern Forestry Experiment Station, Pineville, LA; presented at the National Meeting of the American Chemical Society, San Diego, CA, March 16, 1994.

Mixing Behavior of Cellulose Esters, Stephen S. Kelley, National Renewable Energy Laboratory, Golden, CO, and Timothy G. Rials, Southern Forestry Experiment Station, Pineville, LA; presented at the National Meeting of the American Chemical Society, San Diego, CA, March 15, 1994.

Treatment of Cellulose Esters as Copolymers, Stephen S. Kelley; presented at the Southeastern Regional Meeting of the American Chemical Society, Johnson City, TN, October 20, 1993.

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Thermal and Mechanical Properties of Cellulose Mixed Esters, Stephen S. Kelley and Timothy G. Rials; presented at the National Meeting of the American Chemical Society, Chicago, IL, August 23, 1993.

Starch Esters as Biodegradable Plastics: Effects of Ester Group Chain Length and Degree of Substitution on Anaerobic Biodegradation, Chris Rivard, Luc Moens, Kim Roberts, John Brigham and Stephen S. Kelley; presented at the National Meeting of the American Chemical Society, Chicago, IL, August 26, 1993.

Mixing Behavior of Cellulose Esters, Stephen S. Kelley; invited seminar at Oregon State University, Corvallis, OR, March 1993

Mixing Behavior of Cellulose Esters, Stephen S. Kelley; invited seminar at the University of Wisconsin, Madison, WI, February 1993.

PUBLICATIONS

None.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Discussions with cellulose ester membrane manufacturers, W.R. Grace and Dow Chemical Co., have been conducted to evaluate the potential applications for novel cellulose

based materials. NREL has joined the NSF Industry/University Cooperative Research Center for Separations Using Thin Films at the University of Colorado at Boulder.

COST SHARING

None.

HIGHLIGHTS

NREL is working with membrane manufacturers to identify the best approach to improved compaction resistance, higher flux and higher selectivity that can be obtained from these novel cellulose esters.

COMPOSITES AND BLENDS FROM BIOBASED MATERIALS

Problem: Naturally occurring polymers are an underutilized raw material that show potential for commercial development. The goals of this project are to develop polymeric composites and blends from biobased materials for use as membranes, plastics and composites. Recent research efforts have focused on two areas: (1) composites and blends from cellulose derivatives, and (2) wood modified with synthetic monomers. Industrial collaborations and graduate student education is being supported through membership in the NSF Industry/University Cooperative Research Center for Separations Using Thin Films at the University of Colorado at Boulder.

Results: Composites and blends are being developed from cellulose derivatives for potential applications as membranes and plastics. Cellulose ester based organic/inorganic hybrid (OIH) materials have been prepared and evaluated. Cellulose ester OIH materials show an increase in chemical resistance, mechanical properties and thermal stability 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.

Cellulose mixed esters (CME) with bulky substituents, propionate and butyrate groups, have also been evaluated as copolymers and blends. Cellulose acetate blends are currently used for

gas separation applications and the use of CME may overcome some of the limitations of the current materials. Addition of bulky substituents increases the permeability and decreases the processing temperatures of the CME. The mixing behavior of the CME blends is very complex. However, it is clear that the addition of even a few propionate or butyrate groups is sufficient to exclude the CME from crystallizing into the cellulose triacetate unit cell. The amorphous component of the CME blends was single phase or two phase, depending on the type and amount of CME.

Significance for Energy Conservation: Gas Research Institute estimates that there are 24 trillion cubic feet of known gas reserves that are substandard due to high levels of CO₂. Improved cellulose ester membranes are a promising route to upgrade these reserves.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: Composites and Blends from Biobased Materials

PHASE: FY 1993

PERFORMING ORGANIZATION: National Renewable Energy Laboratory

PRINCIPAL INVESTIGATOR: Stephen S. Kelley (303) 384 -6123

PHASE OBJECTIVE: Develop initial information of permselective and compaction properties of novel cellulose esters for gas separation membranes.

ULTIMATE OBJECTIVE: Develop composites and blends from biobased materials for use as membranes, plastics and lightweight composites. Gas separation membranes are one initial target for novel cellulose esters.

TECHNICAL APPROACH: Research efforts in the preparation and characterization of novel cellulose esters have focused on two approaches. The first approach is the preparation and characterization of organic/inorganic hybrid (OIH) composites using cellulose esters as the organic component. The second approach is preparation and evaluation of cellulose mixed esters (CME), e.g., cellulose acetate propionate and cellulose acetate butyrate, copolymers and their blends. To initiate discussions with potential industrial collaborators NREL has joined the NSF Industry/University Cooperative Research Center for Separations Using Thin Films at the University of Colorado at Boulder. Researchers at the University of Southern Mississippi and a specialty veneer manufacturing company, in cooperation with NREL, have been working on routes to modify the properties of wood by impregnation with synthetic monomers.

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

Patents: None Publications: None Proceedings: One Presentations: Seven

ACCOMPLISHMENTS: Results obtained to date have allow for initial discussions between NREL and two cellulose ester membrane manufacturers, W.R. Grace and Dow Chemicals.

Licenses: None

CRITICAL ISSUES: To optimize the permselective and mechanical properties of these novel cellulose esters for commercially important gas separation applications: CO_2/CH_4 and O_2/N_2 . To develop more information on the performance of these novel cellulose ester materials under realistic field conditions.

FUTURE PLANS Continue to improve the chemical routes used to prepare these novel cellulose esters and develop a better understanding of the factors that control performance. Prepare membranes using commercial processes to develop more data on the performance of these materials. Work with membrane manufacturers to establish a CRADA and evaluate the strengths and limitations of these membranes

POTENTIAL PAYOFFS: Gas Research Institute estimates that there are 24 trillion cubic feet of known gas reserves that are substandard due to high levels of CO_2 . Improved cellulose ester membranes are a promising route to upgrade these reserves. According to a recent SRI report separation of O_2/N_2 for improved combustion efficiency and low grade N_2 are both rapidly growing markets.

CONDUCTING POLYMERS: SYNTHESIS AND INDUSTRIAL APPLICATIONS

S. Gottesfeld, Principal Investigator

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The Conducting Polymer project funded by the AIC Materials Program is developing new methods for the synthesis of electronically conducting polymers and is evaluating new industrial applications for these materials which will result in significant reductions in energy usage or industrial waste. The applications specifically addressed during FY 1993 are electrochemical capacitors, gas separation and metalization of insulators. As an active material in electrochemical capacitors, conducting polymers have the potential of storing large amounts of electrical energy at low cost. Such devices are needed in electronics for power failure back-up, in power supplies for filtering, and in electric vehicles for peak power and load leveling. As a gas separation membrane, conducting polymers offer very high selectivity and the potential to electrically adapt the membrane for specific gas combinations. Potential energy savings in the U.S. for this application are estimated at 1 to 3 quads/yr. As an initial conductive coating for insulators, conducting polymers can reduce both the cost and the pollution associated with conventional electroless plating. The industrial applications include metalizing printed circuit boards, coating structural components in automobiles, and coating plastics to improve appearance and function.

MILESTONES:

I. Electrochemical Capacitors Based on Conducting Polymer (CP) Films

During the last two years we focused on developing new conducting polymer (CP) materials tailored for electrochemical capacitor applications. Electrochemical capacitors are a new family of high power, energy storage devices with a range of applications from electronics to transportation. Electrochemical capacitors using CP materials have the potential to meet both the energy and power requirements for several applications, while reducing the cost of the devices to commercially viable levels.

A. Demonstration of conducting polymer materials with reversible p- and n-dopability

In our work on this part of the conducting polymer project, we attempted to identify and synthesize a monomer that could be electrochemically polymerized to provide the highest possible energy and power densities. An ideal conducting polymer for electrochemical capacitors would allow high-levels of both p-type and n-type doping. As a capacitor built with such material is charged, one plate is p-doped (electrons are withdrawn) while the other is n-doped (electrons are inserted). To compensate these charges anions must penetrate the p-doped side and cations must penetrate the n-doped side. The advantages of such an ideal conducting polymer would be a larger voltage window and highly conducting active material on both plates at full charge.

By focusing on various derivatives of polythiophene a year ago, we demonstrated a new polymer, poly-3-(4-fluorophenyl)-thiophene (PFPT), which approaches this ideal behavior. This polymer uses the fluorophenyl side groups on the polymer chain to

improve the n-type doping and the access of ions to the spaces between the polymer chains. The measured energy density for the new polymer is over 40 W-hr/kg of active material.

During this year, we have continued to evaluate the fundamental charging properties of conducting polymer materials that exhibit both n- and p-reversible doping. In comparing polythiophene (PT), poly-3-phenylthiophene (P3PT) and poly-3-(4-fluorophenyl)-thiophene (PFPT), we found successively higher degrees of n-type doping and better reversibility. This is shown clearly in the cyclic voltammograms in Fig. 1 below.

Fig. 1. Comparison of the cyclic voltammograms of polythiophene (PT), poly-3-phenylthiophene (P3PT) and poly-3-(4-fluorophenyl)-thiophene (PFPT). Of these polymers, PFPT allows the greatest n-type doping.

The PFPT (heavy solid line) has an n-type doping approximately 10 times better than PT (thin solid line).

B. Demonstration of Potential for High Power In Capacitors Based on the New Conducting Polymer Material (PFPT)

The dual, reversible doping characteristics of PFPT enables an increase of the voltage window to more than 3-volts (Fig 1), and thus significantly increases the energy density--an important requirement for most applications. Yet another crucial requirement for electrochemical capacitors which we addressed this year is high power density. This requires the porous structure of the active material to have high rates of both electronic and ionic transport. We have run impedance measurements on capacitor electrodes made by the electrodeposition of our new active conducting polymer (PFPT) on carbon paper. The results show that the impedance associated with penetration of electronic and ionic charge into the film of the conducting polymer is low. The values obtained are close to 1 ohm cm²

for both the p- and the n-doped states of PFPT. This corresponds to an intrinsic time constant for discharge of the order of 3 seconds for capacitors with an areal charge density of 1F/cm^2 , translating to a power density of about 40 kW/kg of active material. This is to be compared with a requirement for transportation applications of the order of 2 kW/kg of the complete device, and therefore leaves ample room for the other elements of the complete PFPT capacitor.

C. Further New Materials Development

As figure 1 demonstrates, PFPT shows a significantly higher degree of n-dopability while maintaining a high degree of charge/discharge reversibility. However, one question still remains: What is the origin of the improvement and is it a steric, electronic or morphological effect? Clarification of this aspect is very important, because it affects prospects for improving further the charge capacity and because of the need to minimize charge-trapping effects encountered with the PFPT material. We consequently continued this year to synthesize and evaluate new monomers which should provide improved n-dopability in dual, n- and p-dopable polymers.

To specifically address the problem of charge trapping, we have recently synthesized a range of monomers to further optimize the electronic properties of the side group. We believe that optimization of side group electronic properties will result in minimized charge trapping effects. We have also synthesized a monomer that we believe will enable both p and n-doping based on shuttling of anions only through the active film. This would be achieved through a positive charge on the special, $-S^+(\text{CH}_3)_2$ side group of the monomer. By establishing a purely anionic shuttling process during both p- and n-doping, the reversibility of the doping process should be significantly improved. Electropolymerization and testing of conducting polymers based on such optimized monomers is underway.

II. Conducting Polymer Membranes For Gas Separation

This year we have pursued strongly our newest activity in development and optimization of conducting polymer films for gas separation. This application of conducting polymers is particularly exciting because of its potential for large energy savings in industry. Of special interest are membrane separations of oxygen and of nitrogen from air, as well as separation of methane from CO_2 . Potential energy savings in the US are estimated at 1-3 quads/yr.

Our FY-93 goals for this research activity have been:

- (a) develop techniques for the reproducible fabrication of polyaniline membranes, aiming at a combination of good selectivity and high throughput,
- (b) fabrication and assembly of a new system for accurate automated measurements of gas permeabilities through polymeric membranes, and
- (c) analysis of fundamental gas transport properties of membranes of polyaniline (PANI), aiming at the effect of doping level on selectivity.

A. Conducting Polymer Membrane Fabrication

Our central research objective is to fabricate reproducibly effective membranes made of polyaniline and demonstrate the commercial utility of such membranes for gas separation applications. A first prerequisite has been to develop thermodynamically stable polymer solutions (dopes). Such solutions have been formulated this year, yielding substantially improved polyaniline membranes. These dopes remain stable for periods of weeks without precipitation or gellation -- a very important property for manufacturability. Thick films (50 μm) were cast from such dopes on glass plates by means of a Gardener blade, thermally annealed, separated from the plate and immersed in methanol for 48 hours to extract residual casting solvent. The films were then subjected to a particular acid doping treatment for optimization of gas transport properties. Having developed such thermodynamically stable dopes, two approaches are being pursued at this time to significantly reduce the polyaniline membrane thickness, and hence increase gas flux. Both approaches involve forming an asymmetric membrane in which a thin compact layer of polyaniline (<1 μm) provides the gas separating layer while being physically supported by a thicker (50-80 μm) porous polymer backing. In the first method, the polyaniline dope is spun or dip coated onto an ultra porous polymer film whereas the second approach involves preparing a graded porosity membrane all made of polyaniline.

B. New Gas Permeator System

During this year, we completed the fabrication and assembly of a new automated Membrane Gas Permeator System. The new system will be extremely valuable in our work on gas separations through conducting polymer membranes. Our Membrane Gas Permeator System represents a significant advancement in instrumentation for measurements of gas transport through membranes. Its design and data acquisition features places it beyond the best present day standards. The new system is under full computer automation and control. Data acquisition and test valve sequencing is enabled by a LabView program and a Gateway computer. The system can measure in the temperature range -100°C to 500°C and with input gas pressures ranging between atmospheric and 300 psig. The first measurements conducted on the new system were devoted to gas permeability through standard membrane samples provided by NIST. The high accuracy obtained with our new gas-permeability system was demonstrated by the good agreement with NIST-documented permeabilities.

Start-up capital equipment funds for this system (\$35K) were allocated in FY-93 by the AIM program. However, our system now includes an additional component -- a new Balzers Quadrupole Mass Spectrometer (\$80K) -- acquired from the tritium facility at LANL. Researchers from that group expressed interest in our new gas separation project and facilitated the transfer of this valuable piece of equipment, which is to be used as part of the new system. The mass spectrometer will, in the near future, enable measurements of gas permeability from gas mixtures, rather than from a pure gas input alone.

We believe that, because of its advanced and automated nature, the new system could also serve US industries with interest in testing membrane samples for gas permeability/separation. In fact, interest in use of the new system has already been expressed by one US industry active in this field.

First results for gas permeability through *as-cast* PANi membranes (non-optimized doping), obtained on our new Gas Permeator system, are shown in Table 1. We have

initially measured the permeabilities through 50 μm thick, *as-cast* polyaniline membranes, to provide baseline data for comparison with gas permeabilities about to be measured through PANI membranes of different doping levels and different thicknesses. Additionally, from time-lag analysis performed with the on-line computer controlling the permeation experiment, we have generated a base set of values for diffusion and solubility coefficients of various gases in the *as-cast* PANI membranes. Table 1 presents these data, demonstrating the capability of the system to resolve the diffusivity and solubility components of the measured permeability.

Table 1. Gas Transport Properties of an As-Cast Polyaniline Membrane Measured on our New Gas Permeator System

Gas	Permeability (Barrer) ¹	Diffusion Coefficient ²	Solubility Coefficient ³
Hydrogen	6.36	6.02	0.827
Helium	5.56	1.88	2.18
Oxygen	0.354	0.545	0.451
Nitrogen	0.131	0.858	0.170
Argon	0.111	0.738	0.150
Carbon Dioxide	1.82	0.177	7.74
Methane	0.119	1.53	0.0075

(1) 1 Barrer = $10^{-10} \text{ cm}^3(\text{STP})\text{cm} / \text{cm}^2 \text{ s cmHg}$

(2) $\times 10^{-8} \text{ cm}^2 / \text{s}$

(3) $\times 10^{-5} \text{ cm}^3 (\text{STP})/\text{cm}^3 \text{ Pa}$

C. Insight Into Key Parameters Controlling Selectivity in PANI Membranes

Important insight has been obtained this year into a key property which apparently contributes very significantly to the high selectivity of doped PANI membranes in the separation of oxygen from nitrogen. Fully HCl doped and undoped polyaniline membrane samples were analyzed in a collaborative effort with NIST in Boulder, CO. The adsorption experiment performed on a system at NIST enables determination of the mass of gas absorbed by an ordinary sample of the polymeric membrane. The small volume of such membrane samples makes the gas absorption measurement difficult and requires a special system with high sensitivity and accuracy in the measurement of gas volumes. The results obtained, in terms of solubility coefficients of oxygen and nitrogen, are given in the first two rows of Table 2.

Table 2 also compiles, for comparison, some of the highest reported¹ oxygen solubility coefficients in polymer membrane materials.

The solubility of oxygen in undoped PANI is seen from our determination (Table 2) to be twice as high as any documented solubility of oxygen in a polymeric material. The N_2 solubility coefficient for undoped PANI has been determined by us to be about one third that of oxygen (Table 2). The most profound effect takes place on doping. Significant increase ($\times 4$) in the solubility coefficient for oxygen gas in PANI is recorded as the PANI membrane is doped. At the same time, the solubility of nitrogen increases by less than a factor of two. *Fully doped PANI thus shows an order of magnitude larger oxygen solubility as compared with any other polymer.* The ratio of solubilities O_2/N_2 in doped PANI approaches a full order of magnitude.

Table 2. Solubility of Oxygen and Nitrogen in Undoped and Fully Doped Polyaniline and in some other Representative Polymers
 $[S(298) = 10^{-5} \text{ cm}^3 (\text{STP}) / (\text{cm}^3 \text{ Pa})]^1$

Polymer	Oxygen	Nitrogen
undoped polyaniline	0.515	0.172
HCl fully doped polyaniline	2.04	0.294
silicone rubber	0.126	0.081
trans-1,4-polyisoprene (Gutta-percha)	0.102	0.056
poly (bisphenol A- carbonate)	0.095	0.028
Polytrifluoroethylene (Teflon)	0.210	0.120

¹ Van Amerongen (1950, 1964) and Polymer Handbook

The results of these experiments indicate that the very high O₂/N₂ separation factors achieved with optimally doped PANI membranes are enabled to large extent by enhanced oxygen solubility effects. The larger solubilities in the fully doped PANI membranes may be allowed, in turn, by paramagnetic interaction between triplet O₂ and free spins in the doped form of PANI. Electron Spin Resonance experiments are being performed to further test this hypothesis.

D. Other Membrane Characterization Efforts

Information at the molecular level is required to clarify effects of molecular structure on gas permeability through PANI membranes. Such information is provided by experiments we started this year in collaboration with a group from the department of physics at University of Wisconsin. Effects of free volume on mass transport characteristics are studied with X-ray scattering techniques. Analysis of such experiments gives highly accurate atomic bond distances within a chain of the polymer, as well as interchain distances. Such measurements were taken during this year on the Brookhaven National Lab synchrotron light source, targeting PANI samples prepared by us at Los Alamos. These measurements have already provided the following important insights: As-cast PANI films are found to exhibit extremely poor interchain ordering. HCl or HBr doping of the films produces pronounced changes in both the intramolecular and intermolecular ordering of the polymer chains. Changes in the intramolecular order are found to be highly reversible on undoping, whereas intermolecular changes display considerable irreversibility. Such permanent changes in the local structure of PANI identify a unique mechanism by which subsequent exposure to halogenic acids during doping cycles effects a highly site-specific redoping of the polymer host. This type of information reveals molecular level reasons for the observed effects of doping cycles on gas permeability through PANI.

Additional efforts devoted to molecular level characterization of PANI membranes are in progress at the Los Alamos Neutron Scattering center (LANSCE). Radial distribution functions for scattered neutrons allow for the precise determination of inter- and intra-molecular distance in the amorphous polymer. ESR measurements are also being

performed in collaboration with a group at UCSB. Polyaniline samples, with and without oxygen gas, are being studied for elucidation of oxygen triplet-PANI free spin interaction. Differential Thermal Mechanical Analysis (DMTA) has been used to examine the glass transition temperature of PANI. Measurements of as-cast and cycled, undoped PANI membranes show T_g values of about 210° C and 250 C°, respectively. This shift to higher values of T_g following acid doping and undoping probably indicates that the cycling process removes residual casting solvent which acts as film plasticizer.

III. Conducting Polymer Coatings on Insulators.

Experimental activity during this year focused on maximizing the conductivity of conducting polymer (CP) precoats employed in the metallization process we developed previously in this project. We were approached by Milliken Research of South Carolina to collaborate with them in a project on the improvement of the long-term stability of films of polypyrrole. Milliken, a large textile manufacturer, has developed a new product based on conducting polymer coating of textiles. The conductive textile product suffers from long-term losses of the electronic conductivity. Our metallization process, developed previously in this program, employs similar conducting polymer (polypyrrole) precoats. We have thus been interested in the same long-term stability questions. We have run a series of XPS measurements and elemental analyses on films of polypyrrole prepared according to protocols used in the Milliken process and in our own metallization process. The targets were correlations between conductivity and nature/degree of doping in films of polypyrrole (PPy), trying first to establish the real compositions of PPy films formed in aqueous surface polymerization processes. One important finding established this year was a high, rather unexpected, oxygen content in the PPy films. (No oxygen is expected from the formula of the polymer.) XPS spectra from Ta -supported PPy samples, which enabled complete desorption of water at higher temperatures, showed the same high content (16-17%) of oxygen observed by us for PPy coatings on textile fiber. These results seem to suggest that the high oxygen content is intrinsic to the real structure of PPy formed in polymerization baths of the type employed in both the Milliken process and in our own metallization process. Complete elemental analysis performed outside our lab (Galbraith) suggests that this high oxygen content in PPy is, in fact, a bulk property. This high content of oxygen apparently results from -OH or -CO groups at polymer chain termini which may be an important factor in the determination of both the conductivity and the long-term stability of these PPy films.

PUBLICATIONS

1. E. Sabatani, A. Redondo, J. Rishpon, A. Rudge, I. Rubinstein and S. Gottesfeld
" Morphology Control in Electrochemically Grown Conducting Polymer Films
2. Effects of Cathodic Bias on Anodically Grown Films Studied by Spectroscopic Ellipsometry and QCM, *J. Chem. Soc. Faraday Trans.*, **89**(2), 287-294 (1993).
2. F. Uribe, J. Valerio and S. Gottesfeld, "Application of Conducting Polymer Precoats for the Metallization of Insulators", *Synth. Metals*, **55-57**, 3760-3765 (1993).
3. E. Sabatani, E. Ticianelli, A. Redondo, I. Rubinstein, J. Rishpon and S. Gottesfeld, "Morphology Effects in Conducting Polymer Films Studied by Combined QCM and Spectroscopic Ellipsometry, *Synth. Metals* (1993).

4. S. Gottesfeld, F. Uribe and S.P. Armes, "The Application of a Polypyrrole Precoat For The Metallization of Printed Circuit Boards" in **Metalized Plastics 3**, K.L.Mittal ed., Plenum Press, 1992, pp.3-9.
5. A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld and J.P. Ferraris, "Conducting Polymers as Active Materials in Electrochemical Capacitors":
 (i) Proceedings of the International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, S.P. Wolsky and N. Marincic, Editors, Florida, Dec. 1992;
 (ii) *J. Power Sources*, **47**, 89 (1994)
6. A. Rudge, I. Raistrick, S. Gottesfeld and J.P. Ferraris, "A Study of the Electrochemical Properties of Conducting Polymers for Application in Electrochemical Capacitors", *Electrochim Acta*, in press
7. Mattes, B. R., Anderson, M. A., Reiss, H. and Kaner, R. B. "The Separation of Gases Through Thin Films of Conducting Polymers." in *Applications for Conducting Polymers*. Aldissi, M. ed., Kluwe Academic Publishers, The Netherlands, (1993).
8. Winnokur, M. D., Maron, J., and Mattes, B.R. "Processing-induced Changes in the Local Structure of Amorphous Polyaniline using RDF Analysis" (submitted to *Macromolecules*).

PRESENTATIONS

1. Mattes, B. R. "A Materials Science Case Study of New Polymeric Materials for Gas Separations: Correlation of Physical and Morphological Characteristics of Conducting Polymers with Pure Gas Permeabilities." ICOM 93, Heidelberg, Germany, Sept. 1-5, 1993.
2. Mattes, B.R., Radebaugh, R., and Pellegrino, J. "Oxygen and Nitrogen Separations through Polyaniline Membranes." ICOM 93, Heidelberg, Germany, Sept. 1-5, 1993.
3. Mattes, B. R. "Conducting Polymer Membranes for Gas Separations." Gordon Conference on Membranes, Plymouth, NH, August 1-5, 1993.
4. J. P. Ferraris, A. Rudge, and S. Gottesfeld, "Electrochemical and Optical Characterization of Lowered Bandgap Polymers", presented at the Electrochemical Society Meeting in Toronto, Canada, Oct 1992 (Abstract No. 644).
5. F. A. Uribe T. E. Springer and S. Gottesfeld, "Metal Electroplating on Insulators Precoated with Conducting Polymer Films: Experimental and Theoretical Aspects," Extended Abstract No. 380, The Electrochemical Society Meeting in Toronto, Ont., October 1992.
6. A. Rudge, J. Davey, S. Gottesfeld and J. Ferraris, Schemes for Use of Conducting Polymers as Active Materials in Electrochemical Supercapacitors, presented at the Electrochemical Society Meeting in Hawaii, May 1993 (Abstract No. 42).
7. E. Sabatani, E. Ticianelli, A. Redondo, I. Rubinstein, J. Rishpon and S. Gottesfeld "Film Growth and Film Conversion Processes Studied by

Combined Ellipsometry and QCM", presented at the Electrochemical Society Meeting in Hawaii, May 1993 (Abstract No. 1930).

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Electrochemical Capacitors

- (1) A CRADA agreement between LANL and Evans Co., Rhode Island, on the development of electrochemical capacitors based on the conducting polymer active material development at LANL has been implemented in December of 1992. Interactions with Evens Co during this year have been aimed at an effective transfer from electrode and cell development (LANL) to model sealed device fabrication (Evans). Sealed devices are being developed now at Evans based on the carbon paper electrode and non-aqueous solution technology developed at LANL.

Conducting Polymer Coatings on Insulators

- (2) Analysis of polypyrrole coatings on insulator substrates has been performed this year as a joint project with Milliken Research, a major textile industry in South Carolina.

Conducting Polymer Membranes for Gas Separation

- (3) An agreement has been worked out between LANL and Henis Technologies, St. Louis, MO. This agreement will enable donation of \$500K worth of hollow fiber spinning equipment from Monsanto to LANL. Such equipment will give us capabilities of hollow fiber spinning, hollow fiber module fabrication and gas-separation process design and development. and equipment design. In our immediate work on conducting polymers for gas separation, this equipment will be used for spinning hollow fibers of optimized polyaniline membrane material for industrial module application. Such equipment will enable the smooth transfer at LANL from the laboratory development and testing of advanced conducting polymer membranes to the fabrication of modules for gas separation enabling effective testing under conditions relevant to industrial applications.
- (4) A non-disclosure agreement is implemented between LANL and Praxair. Praxair is a subsidiary of Linde involved with commercial scale production of nitrogen. Praxair will be evaluating conducting polymer membranes provided by LANL for evaluation in applications to air separations.
- (5) A non-disclosure agreement is implemented between LANL and the Uniax Corporation , Santa Barbara, CA. Uniax has a polyaniline membrane technology. We evaluate on our new Gas Permeator system the gas transport properties of some of their proprietary materials.

PATENTS:

Electrochemical Supercapacitors - A. J. Rudge, J. P. Ferraris and S. Gottesfeld, application submitted to US Patent Office, Nov. 25, 1992

HIGHLIGHTS

1. We have demonstrated this year a new conducting polymer material for use as active material in electrochemical capacitors, that can be both p- and n-doped effectively and reversibly. This provides a very good basis for the further development of this type of conducting polymer materials for supercapacitor applications, achieving energy densities significantly higher than those of supercapacitors based on high surface area carbon, at a comparable cost. Because of the combined p and n-doping, the voltage of the capacitor in the charged state can be increased to 3V. We have developed electrodes with this active material where the loading is sufficient to reach an energy density of 40 W-hr per kg of active material, and, at the same time, the charging process is reversible.
2. This year, we began a new activity to develop and optimize conducting polymer films for gas separation. This new application of conducting polymers has a tremendous potential for energy savings in industry. Of particular interest are membrane separations of oxygen and nitrogen from air, and separation of methane from CO₂. Potential energy savings in the US are estimated at 1-3 quads/yr.

ENGINEERED POROUS MATERIALS: THE APPLICATION OF CONDUCTING POLYMER MEMBRANES FOR GAS SEPARATIONS

PROBLEM:

The process of separating pure components out of a mixture of gases is of great industrial importance. Current gas separation technologies have major shortcomings, including poor energy efficiency and the generation of secondary pollution. Improvements in membrane separation technology are highly desirable and could lead to very significant gains in performance, saving large amounts of energy (1-3 quads/Yr) and reducing pollution. A new efficient membrane separation system should combine high gas selectivity with high permeability, be environmentally stable, be easy to manufacture and maintain, and must be low in cost.

RESULTS:

A new family of membrane materials -- electronically conducting polymers -- is used to achieve significant improvements over present membrane separation technologies. The unique advantage of these membrane materials is the tunability of the transport properties by controlled doping. This year, we initiated a project devoted to the development and characterization of such membranes, with the eventual goal of demonstrating this new technology at a semi-industrial level. In FY-93, we completed fabrication and assembly of a new automated system for pure and mixed gas permeability measurements which is already in use in the study of gas separation through polyaniline (PANI) membranes. In another effort this year, we measured, for the first time, the exceptionally high solubility of oxygen in the PANI membrane (see Table) and identified it as an important element of the exceptionally high O₂/N₂ separation factors achieved with PANI membranes.

Solubility^a of Oxygen and Nitrogen in Undoped and Fully Doped Polyaniline
and in Some Other Representative Polymers

Polymer	Oxygen	Nitrogen
undoped polyaniline	0.515	0.172
fully HCl doped polyaniline	2.04	0.294
cis-1,4-polyisoprene (natural rubber)	0.112	0.055
poly (dimethylbutadiene)	0.114	0.046
silicone rubber	0.126	0.081
trans-1,4-polyisoprene (Gutta-percha)	0.102	0.056
poly (bisphenol A-carbonate)	0.095	0.028
Polytrifluoroethylene (Teflon)	0.210	0.120

^a[S(298) = 10⁻⁵ cm³ (STP) / (cm³ Pa)]

SIGNIFICANCE:

A membrane technology which would be the basis for several industrial gas separations could mean energy savings of the order of 1-3 quads/Yr, achieved by replacing cryogenic separation processes and by enabling economic approaches to the separation of methane from CO₂ in the natural gas industry. Other advantages are in reduction of secondary pollution generated by present day processes.

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

PROJECT SUMMARY
ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: SYNTHESIS AND INDUSTRIAL APPLICATIONS OF CONDUCTING POLYMERS

PHASE: FY 1993

PERFORMING INVESTIGATOR: SHIMSHON GOTTESFELD (505) 667-0853

PHASE OBJECTIVES:

- (1) Demonstrate new conducting polymer materials for electrochemical capacitors
- (2) Establish new activity on conducting polymer membranes for gas separation

TECHNICAL APPROACH: (1) New conducting polymer materials for electrochemical capacitors are developed by: (a) identifying and synthesizing appropriate monomers according to electronic and steric factors, (b) oxidative polymerization of such monomers, usually performed electrochemically, and (c) testing of electrodes with such active materials in appropriate non-aqueous electrolytes for charge/discharge reversibility and for longevity under multicycling conditions. (2) Free standing conducting polymer membranes are synthesized by oxidative chemical processes and then undergo undoping-redoping cycles to achieve optimized gas separation characteristics. The gas separations targeted primarily are oxygen from air and methane from methane/CO₂ mixtures. Appropriate substrates are investigated to achieve ultra thin, pinhole free membrane that would allow high fluxes. Gas permeability and fundamental parameters which determine separation factors are investigated with a variety of characterization techniques.

PROGRESS: Important steps made towards reproducible fabrication of conducting polymer membranes. New advanced system completed for automated gas permeability measurements. Fundamental membrane properties characterized, revealing uniqueness of conducting polymer membranes for gas separation.

Patents: One Application in FY93

Publications: 8

Proceedings: 7

ACCOMPLISHMENTS:

- (1) Joint work on a CRADA agreement between LANL and Evans Co., Rhode Island, on the development of electrochemical capacitors based on conducting polymer active materials started December 1992.
- (2) New activity on gas separation by membranes of conducting polymers advanced significantly during FY 93. New permeability testing system completed and several interactions with industry established.

PROJECT TITLE: SYNTHESIS AND INDUSTRIAL APPLICATIONS OF CONDUCTING POLYMERS

CRITICAL ISSUES: (1) The stability of conducting polymer materials under multi charge/discharge cycling conditions is a critical issue in their complete demonstration for electrochemical capacitor applications. (2) The development of thinner, pinhole free membranes of conducting polymers is critical for their demonstration as real candidates for industrial gas separation processes.

FUTURE PLANS: (1) Work on further development/optimization of active conducting polymer materials for electrochemical capacitor applications together with Evans, Co., according to the CRADA agreement signed this year: (2) Develop free standing thinner conducting polymer membranes for industrial gas separation and study the structure/selectivity relationships.

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

MAGNETIC FIELD PROCESSING OF INORGANIC POLYMERS

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INTRODUCTION

The purpose of this project is to investigate, understand, and demonstrate the use of magnetic field processing to modify the properties of inorganic-based polymers and to develop the basic technical knowledge required for industrial implementation. Polyphosphazene membranes for chemical separation applications are being emphasized by this project. Polyphosphazenes have an alternating nitrogen and phosphorus backbone structure. In general, polyphosphazene materials have superior high temperature and chemical resistance properties to carbon-based (organic) polymers.

TECHNICAL PROGRESS

Summary

FY-1993 efforts have demonstrated that a variety of electromagnetic field processing techniques can be used to modify the morphology of polyphosphazene membranes. The techniques demonstrated include AC and DC magnetic fields as well as microwave fields. The significance of this result is that

processing techniques based on DC magnetic fields developed by permanent magnets, which require no external process energy input, or microwave fields, which can be generated in large chambers, can be used. This provides a high degree of process flexibility. However, there is limited knowledge of the effect of process variables on final membrane characteristics.

A CRADA has been signed between the INEL and ChromatoChem, Inc., Missoula MT, to jointly develop a chemical separation system having extended capabilities. Chromatochem's current system shows high efficiency for separating metal ions from process streams but cannot separate trace organics. Mating magnetically processed (MFP) membranes (having improved flux capabilities) with Chromatochem's current technology will extend its capability to the extraction of trace organics. The intended approach is to use a tube-in-shell membrane module in which MFP membranes are fabricated on the inside of tubular ceramic substrates surrounded by an external shell. The permeate migrates through the membrane and porous ceramic supporting substrate to the interior of the shell, where it travels to a collection point.

Milestones

1) DC Electromagnetic Experiments

Liquid crystal and linear polyphosphazene membranes will be cast in pure DC fields generated by high-strength permanent magnets. The sample membranes will be characterized to determine the contribution of pure DC fields to morphology.

The purpose of this work is to demonstrate that pure DC magnetic fields interact with polyphosphazene. Permanent neodymium-iron-boron magnets, along with an adjustable yoke, were used to study the morphology of small, cast membranes. A working magnetic field strength of 0.25 to 0.75 Tesla could be achieved by adjusting pole gap distance. Some nonuniformity of the field occurred as a result of the gap adjustment, but was not considered critical to the study. The results obtained from this study showed that the pure DC magnet had essentially the same effect as a previously used DC electromagnet, which contained small amount of AC ripple. The general trend is an increase in the membrane asymmetry with increasing field strength. Figure 1 illustrates the change in morphologies between unprocessed, 0.25, 0.5, and 0.75 Tesla MFP membranes.

2) AC Electromagnetic Field Experiments

Liquid crystal and linear polyphosphazene membranes will be cast in AC electromagnetic fields. The sample membranes will be characterized to determine the contribution of AC fields to morphology. The AC frequencies to be emphasized during experimentation will be in the kilohertz to low gigahertz range.

The purpose of this work is to demonstrate that a variety of AC electromagnetic fields interact with polyphosphazene. Membranes were cast in AC magnetic fields at 60 Hz and 450 kHz, as well as in a 1.5 GHz microwave electromagnetic field. The field strengths of the AC study were limited to much lower values as a

0.0 Tesla

0.25 Tesla

0.5 Tesla

0.75 Tesla

Figure 1.
Magnetic Field Processing of Polyphosphazene Membranes

result of the increased AC inductive loading on the electromagnet power supply. The results obtained are similar to the DC results in that a distinct change in membrane morphology could be observed. Figures 2 through 4 illustrate the typical morphologies obtained during testing. These morphologies are similar, but not the same as, those obtained using the DC fields. Additional AC samples will be cast and their membrane properties characterized to determine if there is a significant difference between the resulting membranes.

3) Combine/Test Ion Exchange-Membrane Technologies

As part of the effort to develop industrial applications for magnetic field processed membranes, membrane technology will be integrated with an industrial ion exchange technology that will yield a system that can extract both heavy metal ions and trace organics from process streams.

This work is being performed in collaboration with ChromatoChem, Missoula, MT. ChromatoChem has fabricated and sent to the INEL an ion exchange column for characterization and integration with a magnetically-processed membrane. This column is currently being characterized. The intended approach is to integrate a tube-in-shell membrane module with the ion exchange column as previously described. Efforts are underway to develop and fabricate the hardware that will be used to magnetically process membranes cast on the interior of a 250 mm porous ceramic tube having controlled porosity ($0.2 \mu\text{m}$). Figure 5 is a

a.

b.

Figure 3.

- a. Polyphosphazene Membrane; 60 Hz, 0.11 Tesla
- b. Polyphosphazene Membrane; 450 kHz, <0.1 Tesla

a.

b.

Figure 4.

a. Polyphosphazene Membrane; 1.5 GHz, 18 mW/cm²

b. Polyphosphazene Membrane; 1.5 GHz, 162 mW/cm²

Figure 5
Tube in Shell Membrane Module

photomicrograph of an MFP membrane cast on the inside of a short section of a tubular ceramic substrate and a tube in shell test module.

PUBLICATIONS

R.C. Boehm, "A Computational Investigation of the Structure of Poly(bisphenoxy)phosphazene: Its Relation to Magnetic Coprocessing of Polymeric Membrane Filters," Accepted by the *Journal of Chemical Physics*, to be published.

PRESENTATIONS

AIC Annual Program Review, June 1993

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

None

LICENSES

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

ATOCHEM NA supplied the polyphosphazene materials used in the experiments. A CRADA has been initiated between the INEL and ChromatoChem, Missoula, MT.

COST SHARING

The ChromatoChem CRADA involves a \$50K work-in-kind cost share.

HIGHLIGHTS

Based on the results of the FY-1993 effort, it was determined that a permanent magnet system will be emphasized for MFP of membranes on the interior of ceramic tubes. The use of permanent magnets is attractive due to the minimization of process energy required to change membrane morphology.

MAGNETIC FIELD PROCESSING OF INORGANIC POLYMERS

PROBLEM:

Application of electromagnetic fields to polyphosphazene-based chemical separation membranes during fabrication has demonstrated improved transport properties in test samples. The use of magnetic field processing to fabricate practical membrane geometries typical of an industrial application has not been demonstrated.

RESULTS:

Efforts are underway to make a tube-in-shell membrane module in which magnetically processed membranes are fabricated on the inside of tubular ceramic substrates surrounded by an external shell. In this design, the permeate migrates through the membrane and porous ceramic substrate to the interior of the shell, it then travels to a collection point. Figure 1 contain photos of a magnetically-processed membrane on the inside of a tubular ceramic substrate and a tube-in-shell test module.

Figure 1

Significance - For Energy Conservation:

Improvement of polymer properties through magnetic processing has potential to achieve significant energy savings. For example, if membranes having superior properties could be fabricated, their industrial implementation would become feasible, and energy would be saved. 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-AIC Materials Program under DOE Idaho Field Office contract DE-AC07-76ID01570.)

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Magnetic Processing Of Inorganic Polymers

PHASE: FY 1993

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 improved capability of magnetic field processed (MFP) polyphosphazene membranes in industrial applications.

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

TECHNICAL APPROACH: Compare the chemical separation properties of polyphosphazene membranes fabricated with and without magnetic field processing in geometries typical of industrial applications.

PROGRESS: FY-1993 efforts have demonstrated that a variety of electromagnetic field processing techniques can be used to modify the morphology of polyphosphazene membranes. The techniques demonstrated include AC and DC magnetic fields as well as microwave fields. The significance of this result is that processing techniques as simple as DC magnetic fields developed by permanent magnets, which require no external process energy input, or microwave fields, which can be generated in large chambers, can be used. This provides a high degree of process flexibility. However, there is limited knowledge of the effects of processing variables on final membrane characteristics.

A CRADA has been initiated between the INEL and ChromatoChem, Inc., Missoula MT, to jointly develop a chemical separation system having extended capabilities. 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 capabilities) with Chromatochem's current technology will extend its capability to the extraction of trace organics. The intended approach is to make a tube-in-shell membrane module in which MFP membranes are fabricated on the inside of tubular ceramic substrates surrounded by an external shell. The permeate migrates through the membrane and porous ceramic substrate to the interior of the shell, where it travels to a collection point. Figure 1 is a photomicrograph of a MFP membrane on the inside of a tubular ceramic substrate and a tube in shell test module.

Patents: - Publications: 1 Proceedings: - Presentations: 1

ACCOMPLISHMENTS:

Licenses: -

Technology Transfer or Industrial Interaction:

ATOCHEM NA supplied the polyphosphazene materials used in the experiments. A CRADA has been signed between ChromatoChem, Inc., Missoula MT, and the INEL.

PROJECT TITLE: Magnetic Processing Of Inorganic Polymers

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

FUTURE PLANS: Develop the knowledge and techniques required to fabricate and implement MFP membranes in an industrial application.

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 demonstrate 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 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.

POLYMERIZATION AND PROCESSING OF ORGANIC POLYMERS IN A MAGNETIC FIELD

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INTRODUCTION

Purpose. The purpose of this program is to demonstrate the utility of magnetic fields, to beneficially modify or control the physical, optical, magnetic, and electrical properties of materials through the application of magnetic fields during polymerization, processing and solidification steps and to develop magnetic-field processing parameters to achieve the sought improvements. This objective has been expanded now to include composite processing and, specifically, fiber orientation in a composite.

Background. Our previous work had demonstrated beneficial effect of magnetic field upon the electrical properties¹⁻⁴ and physical properties^{5,6} of polymers when processed in a magnetic field. The electrical conductivity of polyacetylene was increased by more than an order of magnitude and the tensile strength of a liquid crystalline polymer by more than 100%.

A brief survey of the literature on diamagnetic materials response to magnetic fields as a function of the field strength is summarized in Table 1. Large organized structures such as liquid crystals, membranes, filamentous aggregates and stiff polymer chains, in general, achieve orientation already in 1T field. Macromolecular assemblies of micron sized rodlike particles orient substantially better than individual macromolecules.

From studies of rodlike microcrystals of cellulose as models of colloidal suspensions, in which the particle interactions were adjusted at will, it was observed that fields around 10T were sufficient for saturation of orientation perpendicular to field.

We have made a major jump in the scale of macromolecular assemblies from rodlike microcrystals of cellulose, described in the literature, to 1-2 mm long graphite filaments (~10 μ m diameter) for orientation in air in a magnetic field. The results are positive.

Since the intent of this work was to demonstrate the feasibility of generating 3-D reinforced composites, using magnetic field, the prospects look good.

TECHNICAL PROGRESS

SUMMARY

A general microhardness - yield stress - morphological changes relationship as a result of magnetic field processing of hydroxypropyl cellulose (HPC) and polyphenylquinoxaline (PPQ) was conducted. When the data was compared to Tabor's straight line relationship of microhardness three times the yield stress it fell below the line indicative of low "stiff - compliant ratio" materials. A more detailed nanoindenter and atomic force microscope examination of HPC films revealed microscopic areas in the film that possessed microhardness that was 77% higher vs. 21% for the rest of the film and tensile modulus that was 27% higher vs. 0% for the rest of the film. Such higher microhardness and modulus values become understandable if the spots sampled represent a crystalline component of the film.

TABLE 1.
Field Strength vs Structural Orientability

1T	→	Liquid Crystalline Systems Large Biological Systems (Viruses, sickle red blood cells, retinal rods, Chloroplasts, etc.)
4T	→	Rhodopsin Biological Membranes
10T	→	Colloidal Suspensions
20T	→	Can Unwind a Helix
30T	→	All Thermal Effects Damped Out
40T	→	Any Molecule Oriented
50T	→	?
60T	→	?
100T	→	?
200T	→	?

The presence of a uniform magnetic field may reduce the convection in a melt or solution, damp out any instabilities in addition to any orientation effects and, therefore, improve the quality of the solidified structure. We observe this improvement in a matrix material LUDOX AS-40 when the film is prepared in a magnetic field.

Evaluation of carbon fiber and silicon carbide whisker response to a 1.2T magnetic field on a water surface showed that carbon fibers orient parallel to the field, but the response of different batches of silicon carbide whiskers is complex and not similar.

We have now been successful in orienting 1-2 mm long graphite fibrils ($\sim 10 \mu\text{m}$ diameter) in air and immobilizing them perpendicular to a plastic surface.

MILESTONES

1.0 Processing of Liquid Crystalline Polymer Films.

The year before we had demonstrated that processing a liquid crystalline polymer in a magnetic field can more than double its tensile strength and increase its microhardness by more than 20%. To get a better insight for these changes we undertook a more detailed examination of the films.

Microhardness. Microhardness tests provide a rapid evaluation of variations in mechanical properties affected by changes in chemical or processing conditions, heat treatment, microstructure and aging. In polymeric materials microstructural/morphological changes upon processing will have a significant effect upon microhardness.

The basic relationship between indentation hardness and bulk properties of materials, as demonstrated by Tabor, is approximately three times the yield stress, $H \approx 3Y$. It is, however, true with ideally plastic solids only showing no elastic strain. We have plotted the HPC and PPQ data on the basic Tabor's straight line graph, Figure 1.

Figure 1. Correlation between microhardness and yield stress of HPC and PPQ

The data fall below the line. This appears to be related to lower "stiff-compliant ratio" for these two polymers and is typical of low crystallinity content materials in general.

Our WAXD data on the polymers agrees with this assessment. Polymers with high crystallinity content (high stiff-compliant ratio) approach Tabor's relationship, and those with low deviate from classical plasticity theory.

The other information that can be extracted from the relationship of the data points to the Tabor's line is:

- 1) that the PPQ possesses a very low crystallinity content, certainly below that of HPC (10-15% crystalline);
- 2) that the processing conditions per se did not increase crystallinity content in either of the two polymers; and
- 3) it is a quick and easy test to sort out crystallinity content contributions, if any, to mechanical properties enhancements.

A further detailed microhardness evaluation of the HPC films using a nanoindenter showed some spots of unusually higher (77% vs. 21% for the rest of the film) microhardness and increased (27% vs. 0% for the rest of the film) elastic modulus, Figure 2.

The sample evaluation protocol consisted of taking 9 or 12 data points per area in the shape of "S" as follows:

Figure 2. Microhardness Evaluation Procedure

In the $200 \times 200 \mu\text{m}$ (12 data points) areas sampled occasionally one or two data points (sample spots) had a significantly higher microhardness (77% vs. 21%) and elastic modulus (27% vs. 0%) as compared to the rest of the film. These higher value data points were not included in the averages calculated for the film. Such higher microhardness and modulus values become understandable if the spots sampled represented a crystalline component of the film. The fact that the higher microhardness spots were so few would at least qualitatively agree with the very low (10-15%) crystallinity content in HPC found before.

It was our intention then to shed more light on the surface structure of the films by using Atomic Force Microscopy (AFM). AFM produces images that are accurate topographs of the sample surface. It can image nonconducting surfaces and, thus, metal coating deposition before imaging is not required. Furthermore, AFM as well as scanning tunneling microscopy are capable of resolving surface details down to the atomic level. Both characterization techniques will become very important for our composites work as we will correlate processing parameter effects e.g., magnetic fields on the morphology of the composite and, hence, its physical properties.

We have used AFM on the control, shear only and magnetic field/shear processed samples to shed light on the nature of the surface (morphology) of the films. Representative findings are illustrated in Figure 3. The shear and magnetic field directions are from the lower left corner to the upper right corner.

Figure 3.

MORPHOLOGY vs PROPERTIES

MST-7

The most intriguing aspect of the AFM topographs is that the magnetic field has a certain topological uniformity inducing effect on the processed films if the shear only and magnetic field/shear samples are compared. The distinct edge on lamellae that are seen in the shear only sample have been reoriented by the magnetic field to give a more uniform planar surface appearance. The WAXD data on the shear only sample confirms the distinct lamellar texture and on the magnetic field/shear sample high chain orientation, which is due to the magnetic field acting in combination with the shear.

The highest modulus reported for a shear formed 2-hydroxypropylcellulose film has been 0.25 GPa.⁷ The modulus for our magnetic field/shear processed films is 1.00 GPa and for a few sample spots 1.28 GPa, a five times higher value. The higher moduli values are consistent with higher degrees of chain orientation. Considerable literature exists on how unusual properties may be obtained from semicrystalline polymers through control of hierarchical structure.⁸⁻¹¹

A hierarchical model of flattened spherulite has been proposed showing the breakup of lamellae into oriented crystalline blocks that form networks of oriented fibrous crystals (fibrils), which may be also bridged by transverse lamellae. At large elongations, a highly oriented structure is formed that consists of microfibrils and fibrils and the polymer exhibits significant strength in the direction of orientation. This is what we observe.

Shearing produced a rough surface with structural features characteristic of lamellae and crystalline blocks all oriented in the direction of shearing. Application of a 1.2T field on top of the shearing action and perpendicular to its direction produced highly dichroic film indicative of high chain orientation. WAXD indicated a structural unit with a d spacing of 52 Å. Samples oriented in a 4.2T field showed this same structural unit size without the shearing action. Increased degree of orientation with increasing field would be expected and has been observed before.

Finally, the fact that the rate of orientation depends on the inverse square of the molecular weight emphasizes the need to use high fields for commercial polymer processing if magnetic fields are to show their beneficial effects.

POLYSILANES

We are collaborating with a small private company SILCHEMY in Albuquerque, New Mexico in evaluating polysilane processing in magnetic field. Polysilanes are a comparatively new and unique class of materials with high potential in such areas as positive photoresists for dry development, imaginable etch barriers and contrast enhancers among others, Magnetic field induced ordering of these materials would enhance their unique properties and perhaps generate new ones.

SILCHEMY Proprietary Information.

Magnetic Field Processing of Polysilanes. The chemical structures of five novel high molecular weight polysilanes are illustrated in Table 2.

Table 2. Polysilanes

$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{Si})\text{---} \\ \\ \text{R}' \end{array} \text{---} \begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{Si})\text{---} \\ \\ \text{R}'' \end{array} \right]_n$	
R'	R''
1.	$(\text{CH}_3)_2\text{CH--}$
2. $(\text{CH}_3)_2\text{CH--}$	$\text{CH}_2\text{CH}_2\text{CH}_2\text{--}$
3.	CH_3
4.	None
5. $\text{H}_{25}\text{C}_{12}$	None

Films of the polysilanes have been cast and processed by the magnetic field/shear technique on a polysiloxane substrate. Some of the polysilanes have also been cast on a Teflon substrate in a magnetic field without the shearing effect. Polarized IR data showed all of the films to be dichroic, indicating a significant degree of chain orientation. These observations were corroborated by the WAXD data. Molecular weight differences of two No. 3 samples were also reflected in their orientability by the magnetic field/shear technique. Sample No. 5 is an elastomer that showed an unusual response in the polarized IR beam.

SILCHEMY Proprietary Information

2.0 Processing of composites

Practically all of the world's magnetic processing work on polymer composites has been done in Latvia, Russia and Uzbekistan since the early 1970's.^{13,14} This work, in addition to, structural composites has been conducted also on neat epoxy resins, coatings, and adhesives. Improvements have been claimed in thermal properties (higher T_g), tensile strength, tensile modulus, reduced water absorption, density, and optical properties. This work has translated into the production of lighter, stronger, tougher, and more durable epoxy structural composites, adhesives, coatings, and printed circuit boards, and has been of interest to the Soviet military.

In a recent workshop, by leading Country's composites users, suppliers, and fabricators barriers to polymer composites growth were identified. The most important technical barrier identified for the next 5 - 15 years was the industry's inability to control resin flow and fiber orientation.¹² We have thus redirected the emphasis in our magnetic field processing efforts to composites, as a result of the interest expressed by one of our industrial collaborators.

There are two phases in our composites processing work: 1) an early one on magnetic field effects on preregs cured in a magnetic field, and 2) the current work on developing techniques for 3-D reinforced composite fabrication using a magnetic field.

Prepregs.

Our initial work involved using prepregs that were available at the Lab and had been stored in a freezer. We chose several different Nylon and Kevlar fiber reinforced epoxy prepregs for curing studies in 1.2T and 4.2T fields. The cured samples were evaluated for tensile strength and microhardness and compared with samples cured outside the magnetic field.

Although some increases in the tensile strength and microhardness were observed in the samples cured in a magnetic field, especially at 4.2T, there was a lot of scatter in the data when samples from different batches of prepregs were tested. Discussions with the people who were the custodians of the prepregs indicated that different batches of prepregs almost surely had different room temperature exposure histories. This would partly explain the scatter in the data. The largest observed increases were in the 9 - 28% range for the tensile strength, and up to 30% for the microhardness. Because of the prepreg quality problems, no firm conclusions are warranted at this time on the magnetic field effects on the cured prepreg properties.

3-D Reinforced Composites

After Pratt and Whitney had learned about the results of our magnetic processing work of polymers, they inquired about the possibility of composite reinforcing material orientation by a magnetic field. They also had some specific reinforcing materials (carbon, graphite fibers) and a substrate material (Ludox AS-40) in mind for the exploratory work. Since this was an inquiry about the possibility of orienting large objects (mm-sized fibrils) compared to molecules/crystallites, by necessity, it had to be a proof of principle demonstration first. Also, a non-disclosure agreement between the Laboratory and the Pratt and Whitney Co. was signed.

Reinforcing Materials

In addition to the graphite and carbon fibrils several different batches of silicon carbide whiskers were also evaluated for their response to the magnetic field.

Graphite Fibers The graphite and carbon fibers were cut into two size ranges: 1-2 mm and ~ 1 cm (filament diameter range 7-9 μm). They were then treated with fuming nitric acid ($\text{HNO}_3 > 90\%$) at room temperature for 3 days to remove the sizing, about 1% of the weight of the fiber. The bundles were then washed with a water until neutral, dried and manually separated into essentially individual fibrils before use.

Silicon Carbide Whiskers Several different batches of beta silicone carbide whiskers were obtained from MST-4 and were used as received. Some typical whisker physical data¹⁵ are: length 3 to 21 mm, diameter 6-16 μm , conductivity 40 - 300 ($\Omega \text{ cm}$)⁻¹. The whiskers that we used included also the catalyst ball.

Magnetic Field Response A typical response of graphite fibrils to magnetic field is illustrated in Figure 4B. Initially, the fibrils are floated on water in a glass dish, then the dish is placed in the magnetic field and the water is allowed to evaporate to dryness. The corresponding sample evaporated outside the magnetic field is illustrated in Figure 4A.

Figure 4. Graphite fibrils after evaporation of water. A-no magnetic field, B-magnetic field on.

The field used was 1.2T and a higher field would be expected to give an even better alignment.

The silicon carbide whisker response to 1.2T field was complex and varied from batch to batch. For example, there were whiskers that oriented parallel or perpendicular to the field or migrated to the one or the other pole faces. All this may indicate a large diversity in the composition of the whiskers that we have looked at. This in turn may indicate variations in whisker growth processes. A further complicating factor may have been the presence of the catalyst balls, which contained certain metal impurities. Thus, in any future activity with whiskers, they should be used without the catalyst balls.

Matrix Material The solidified structures in many materials can be strongly influenced by convection, which itself depends on the magnetic field. Convection in a solution or melt may be either reduced or amplified by the magnetic field depending upon the material in question. Experiments concerning the effect of a magnetic field on solidification of melts of semiconductors and alloys have already been reported demonstrating the relevance of this technique to technological developments.¹⁶ The presence of a uniform magnetic field may reduce the convection in a melt or solution, damp out the instabilities and, therefore, improve the quality of the solidified structure. We have observed this in cellulose films reported last quarter and we observe this now in the matrix material LUDOX AS-40. The samples dried in a magnetic field gave coherent (strong) films with fine striations in the film following the field lines. The samples dried outside the field broke up into small "curved" crystals as the materials dried. This difference persisted also when the films were dried at 60° C/vacuum oven. The WAXD analysis of the magnetic field and control samples also showed differences including sharper peaks for the magnetic field samples.

Proof of Principle Demonstration The demonstration was conducted in a 4.2T field. The schematic of the basic process is illustrated in Figure 5. The fibrils fall 20 in. through space in a magnetic field (parallel to the fall line) to reach the Petrie dish. The bottom of the Petrie

The interest of our industrial collaborator is in the formation of a 3-D composite using magnetic fields. A schematic for a 3-D reinforced composite is illustrated in Figure 7.

For a higher yield of orientation fields in excess of 4T are indicated. used for the cure. Vertical orientation of practically all of the fibrils was achieved, Figure 6. light is introduced in the cavity by means of a fiber optics cable. An exposure of 20 secs was blend cures almost instantly in a UV light. After the fibrils have reached the Petrie dish a UV dish is covered with a thin coating of polyurethane oligomer/methacrylate monomer blend. This

Figure 5. Schematic of the Basic Process

Figure 6. Vertical Orientation of Fibrils in a Magnetic Field

Figure 7. Schematic of a 3-D reinforced composite.

REFERENCES

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PUBLICATIONS

1. Raimond Liepins, Randy K. Jahn, Norman Elliott, and Kevin Hubbard, Polymer Preprints, **34**(1), 751 (1993)
2. Raimond Liepins, Randy K. Jahn, Norman Elliott, and Kevin Hubbard, J. Appl. Poly. Sci., **49**, xxx (1993)

PRESENTATIONS

1. Raimond Liepins, Randy K. Jahn, Norman Elliott, and Kevin Hubbard, "Magnetic Field Processing of Polymers", American Chemical Society Meeting, Denver, CO, April, 1993

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

None

LICENSES

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

1. Pratt and Whitney of the United Technologies Corp., non-disclosure agreement, composite processing.
2. Silcherry, joint development of polysilanes as non-linear optical materials.
3. Initial discussions with Dow Chemical USA on investigating magnetic processing of new Dow thermoset material.

COST-SHARING

Silcherry - supply of materials

Los Alamos National Laboratory - magnetic field processing

HIGHLIGHTS

The use of a 4.2 T magnetic field is the minimum required to orient graphite fibrils in space. Proof of principle demonstration for the formation of a 3-D composite was concluded with encouraging results.

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. It is not clear at this time how magnetic fields will interact with more complex molecules and systems and what are the minimum fields for noticeable interactions.

Results:

We have demonstrated the orientation of graphite fibrils in a 4.2 T magnetic field. This has significant implications for the generation of 3-D composites using magnetic fields.

Significance for Energy Conservation:

Currently, one approach to 3-D composites is to introduce the reinforcement in the third dimension manually. If this can be accomplished using magnetic fields the cost of processing 3-D composites would be one tenth of what it is today.

Project Summary
Advanced Industrial Concepts (AIC) Materials Program

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

Phase: 1993

Performing Organization: Los Alamos National Laboratory

Principal Investigator: Raimond Liepins, 505-667-2656

Phase Objective: This period was devoted to processing of unique non-linearly optically active polysilanes and the demonstration of the proof of principle of 3-D composite formation.

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

Approach: Increasing the orientation of the polysilane molecules increases both the mechanical properties and the non-linear optical properties. The generation of 3-D reinforced composites should also be possible with sufficiently strong magnetic fields.

Progress: Of the five novel high molecular weight polysilanes processed by the magnetic field/shear technique on a polysiloxane substrate, samples with unusual infrared and mechanical properties were generated. For the formation of composites, the use of a 4.2 T field was sufficient to orient graphite fibrils in space. With this knowledge at hand the proof of principle for 3-D composite formation was demonstrated.

Patents: None

Publications: Raimond Liepins, Randy K. Jahn, Norman Elliott, and Kevin Hubbard, Polymer Preprints, 34(1), 751 (1993)

Raimond Liepins, Randy K. Jahn, Norman Elliott, and Kevin Hubbard, J. Appl. Poly. Sci., 49, xxx, (1993)

Proceedings: None

Accomplishments: The use of a 4.2 T field was sufficient to orient graphite fibrils in space opening the door for 3-D composite formation by means of magnetic fields.

Licenses: None

Critical Issues: To demonstrate magnetic field interaction with more complex molecules and molecular assemblies and establish minimum fields for noticeable material interaction with magnetic fields.

Future Plans: As a result of previous years' work under this program, Dow Chemical USA has expressed interest in a collaboration to investigate the potential of magnetic field processing of a new liquid crystal thermoset developed by them. A CRADA with Dow will be signed within the first few months of 1994, at which time we will investigate the effect of magnetic fields on orientation and mechanical properties of this Dow material.

Potential Payoff: Dow is a major supplier of materials to the U.S. automotive industry. The use of magnetic fields in the processing of their material has the potential to result in the development of high strength, lightweight structural components to be used in place of metal components in automobile bodies. This would lead to significant fuel and energy savings due to the lighter weight of these new materials.

NEW MATERIALS AND PROCESSES

ADVANCED MICROWAVE PROCESSING CONCEPTS

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INTRODUCTION

The purpose of this work is to explore the feasibility of several advanced microwave processing concepts to develop new energy-efficient materials and processes as well as to reduce consumption of strategic metals. The project includes three tasks: (1) microwave sintering of multilayer ceramic capacitors; (2) commercialization of the variable-frequency microwave furnace; and (3) microwave curing of polymer composites.

Multilayer capacitors are an interesting candidate for microwave processing for several reasons. First, a reduction of sintering temperature (the so-called "microwave effect") might make the barium titanate dielectric compatible with silver electrodes, reducing the uses of palladium and sharply reducing costs. Second, we can study the effect of internal metallic phases on the behavior of the parts during microwave processing. Third, they are a high-value product normally processed in relatively small batches compared to traditional ceramics.

The variable frequency microwave furnace, whose initial conception and design was funded by the AIC Materials Program, will allow us, for the first time, to conduct microwave processing studies over a wide frequency range. This novel design uses a high-power traveling wave tube (TWT) originally developed for electronic warfare.

Microwave curing of thermoset resins will be studied because it holds the potential of in-situ curing of continuous-fiber composites for strong, lightweight components.

TECHNICAL PROGRESS

Microwave Furnace Development

In collaboration with our industrial partner, Microwave Laboratories, Inc., (MLI), we have begun several types of experiments in the variable frequency furnace. At MLI, thermal paper was used to map the power density at various frequencies. It was found, as expected, that frequency sweeping dramatically improves the time-averaged power density within the furnace cavity, as shown in Figure 1. These results are supported by

model calculations performed at MLI for various frequency ranges using their "benchtop" furnace cavity dimensions.

Figure 1. Illustration of enhanced power uniformity over large areas in the Variable Frequency Microwave Furnace. The darkened areas represent heating of the sample to a temperature of 100 to 125°C.

At ORNL, reflected power was measured over the frequency range from 4 to 8 GHz with a SiC load at various locations within the cavity. As expected, the characteristics of the cavity change with sample location and temperature. For any given setup, there are many frequencies within the 4-8 GHz range for which reflected power is quite low and the sample can be heated efficiently.

The Variable Frequency Microwave Furnace was used to sinter Al_2O_3 and $\text{Al}_2\text{O}_3\text{-ZrO}_2$. The specimens were casketed with ZrO_2 bubbles in a BN crucible. Based on low-power frequency scans, several individual frequencies were selected for which reflected power was low. The samples were easily heated to a nominal 1200°C and sintered for 1 h. During sintering the frequency was modulated ± 0.1 GHz to better distribute the microwave power. Samples sintered at 4.84, 6.05, and 7.22 GHz are presently being analyzed.

MLI has now commercialized the VFMF and has received orders for several units, to begin shipment during FY 1994.

Polymer Curing

A sample of epoxy resin was obtained from Engineering Technology Division for preliminary curing studies. The material is a two-part system consisting of ERL-2258 resin and M-phenylenediamine hardener.

Polymer curing studies began with the curing of neat resin samples. The specimens were prepared by mixing 50 g ERL-2258 resin with 12.5 g MPDA with gentle heating until the MPDA was completely dissolved. Air bubbles were removed in a vacuum dessicator and the resin was poured into a 4-inch Petri dish.

Samples cured at a fixed frequency of 6 GHz, using 50 W power for 30 minutes, were completely charred. It appeared that thermal runaway was initiated at a local hot spot and then propagated to cover most of the specimen. In contrast, a sample cured for 30 minutes at 50 W while sweeping the frequency from 4.5 to 7.5 GHz, 5000 times per second was uniformly cured and showed no evidence of overheating.

In parallel experiments at MLI, epoxy disks up to 6 inches diameter were uniformly cured at various frequencies and sweep rates. MLI began collaborative work with a major chemical company to explore curing of other polymer systems, and results are very encouraging.

MII ESTONES

The milestone in July 1993 calling for a report on the polymer curing progress was satisfied by the paper, "Polymer Curing in a Variable Frequency Microwave Oven", presented in Montreal, Canada, July 12-14, 1993 (see publications list).

PUBLICATIONS

Journals

N/A

Other Publications

1. R. J. Lauf, F. L. Paulauskas, and A. C. Johnson, "Polymer Curing in a Variable Frequency Microwave Oven", 28th Microwave Symposium Proceedings, pp. 150-155, Internal Microwave Power Institute.
2. R. J. Lauf, et. al., "Materials Processing Using a Variable Frequency Microwave Furnace," Ceramic. Trans. 36, 571-579, American Ceramic Society (1993).

PRESENTATIONS

1. R. J. Lauf, F. L. Paulauskas, and A. C. Johnson, "Polymer Curing in a Variable Frequency Microwave Oven," presented at International Microwave Power Institute, Montreal, Canada, July 11-14, 1993.
2. R. J. Lauf, et. al., "Materials Processing Using a Variable Frequency Microwave Furnace", presented at the American Ceramic Society Annual Meeting, Cincinnati, Ohio, April 1993.

HONORS AND AWARDS

1. Advanced Technology Award, International Hall of Fame (sponsored by the Inventors Clubs of America) for "Variable Frequency Microwave Furnace." Atlanta, GA. November 7, 1992.
2. D. W. Bible and R. J. Lauf, Federal Laboratory Consortium Award for Excellence in Technology Transfer, for the invention, development, and commercialization of the Variable Frequency Microwave Furnace.

PATENTS/DISCLOSURES

1. R. J. Lauf, D. W. Bible, and F. L. Paulauskas, "Method for Curing Polymers", ESID 137B-X, disclosed August 25, 1993. This invention has been elected for filing by Martin Marietta Energy Systems, Inc.
2. We have received a Notice of Allowance from the U.S. Patent Office for "Variable Frequency Microwave Furnace System," in August 1993.
3. We have received a Notice of Allowance from the U.S. Patent Office for "Process for Manufacturing Multilayer Capacitors" by R. J. Lauf, C. E. Holcombe, and N. L. Dykes.

LICENSES

1. Microwave Laboratories, Inc., has licensed the original Variable Frequency Microwave Furnace (patent pending) and is currently negotiating to add later disclosures and expand the terms of the license.

DEVELOPMENT OF THE VARIABLE FREQUENCY MICROWAVE FURNACE

Problems:

In a fixed frequency microwave furnace, standing waves create a nonuniform distribution of power within the applicator cavity, making it difficult to achieve uniform, reproducible heating over the entire working volume.

Results:

Sweeping the frequency over a wide range excites many different microwave modes within the applicator cavity.

Significance - For Energy Conservation:

By changing the microwave frequency, one can maximize the efficiency of coupling to whatever load is placed in the furnace cavity.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: ADVANCED MICROWAVE PROCESSING CONCEPTS

PHASE: FY 1993

PERFORMING ORGANIZATION: Oak Ridge National Laboratory

PRINCIPAL INVESTIGATOR: R. J. Lauf
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6087
615-574-5176

PHASE OBJECTIVE: Polymers and polymer-matrix composites are important engineering materials whose widespread use could be more economical if processing times were shorter. Microwave heating can speed the curing process, provided that issues of uniformity and scale-up can be resolved.

ULTIMATE OBJECTIVE: The ultimate objective is to develop an understanding of microwave curing for continuous or semicontinuous processing in a manufacturing environment.

TECHNICAL APPROACH: We are studying the curing behavior of epoxy resins (both neat resins and fiber reinforced prepreg systems) using frequency sweeping to heat the samples uniformly. Cured samples are characterized by micro hardness, glass transition temperature, and mechanical testing. The influence of additives such as inorganic pigments on microwave absorption is also being determined.

PROGRESS:

Patents: 2 (pending)
Proceedings: 2

Publications: none
Presentations: 2

ACCOMPLISHMENTS:

Licenses: Microwave Laboratories, Inc., has licensed the Variable Frequency Microwave Furnace.

Known Follow-On Products: The Microwave Laboratories T-4000 series microwave furnaces are in production and available for order. The first unit was shipped in September.

Industry Workshops:

Technical Transfer or Industrial Interaction: We have been working collaboratively with Microwave Laboratories under a CRADA.

BIOMIMETIC THIN FILM SYNTHESIS

G. L. Graff, A. A. Campbell, P. C. Rieke, N. R. Gordon, and B. C. Bunker
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INTRODUCTION

The purpose for this program is to develop a new process for forming thin film coatings and to demonstrate that the biomimetic thin film technology developed at PNL is useful for industrial applications. In the biomimetics process, mineral deposition from aqueous solution is controlled by organic functional groups attached to the underlying substrate surface. Several novel aspects of biomimetic processing are appealing to industrial clients including: (1) low temperature, low cost processing, (2) processing conditions which are benign and environmentally conscious, (3) formation of dense, crystalline films without subsequent thermal treatments, (4) ability to coat a wide range of substrates including polymers, metals, and ceramics, (5) the ability to coat complex-shaped and microporous substrates, (6) control over film deposition location on a micron length scale, allowing for deposition of complex patterns, (7) ability to control crystal orientation in the films, and (8) formation of dense films containing nanometer-sized crystallites (nanophase materials). All of the properties cannot be achieved with conventional thin film processing technologies such as sol-gel and vapor deposition. Therefore, biomimetic coatings provide potential solutions to many current coatings problems.

TECHNICAL PROGRESS

Summary

I. Iron Oxide Films

In previous years, the biomimetic methods was used to prepare dense, highly ordered films of FeOOH on both Si and polystyrene substrates. This year, solution conditions were established to allow for the in-situ conversion of FeOOH films into magnetic Fe₃O₄ films. The conversion occurs in a solution held at 70°C, as does the initial deposition. The

resulting magnetite films retain the same morphology as the parent FeOOH film, with a high degree of perpendicular orientation, a high crystallite density, and a needle-like acicular crystallite geometry. Direct growth of Fe₃O₄ on the same substrates via a one step process is possible. However, the oriented needle-like morphology thought to be critical for maximizing the magnetic performance of the films is not achieved in the one step process. Oriented films prepared by the two step process have been sent to Sandia National Laboratories for measurement of magnetic properties.

II. Tin Oxide Films

Tin oxide coatings are desired by the automotive industry to form hard, scratch resistant, or impermeable coatings on plastics. While tin oxide coatings were prepared in previous years, the coatings are typically applied in acidic solutions (pH 0-1) and deposition kinetics have been too slow for large-scale commercialization. Work this year has involved the use of water-soluble tin complexes to increase the pH of deposition and to increase deposition kinetics. Fluoride, sulfate, and oxalate complexes were investigated. The best results to date have been obtained with oxalate complexes, which allow films to be deposited above pH 5 at a deposition rate exceeding 2 $\mu\text{m}/\text{day}$. While film formation is still relatively slow, the results are a dramatic improvement over earlier efforts, which produced films less than 1 μm thick even when processing times exceeded one week.

III. Calcium Phosphate Films

Calcium phosphate films are desired for producing bioactive coating on porous Ti materials used in bone and dental implants. This year, quality calcium phosphate coatings were produced on porous Ti using the biomimetic process. The coated implant materials were compared to implants having calcium phosphate coatings prepared using commercial plasma spray techniques. Preliminary results on coated porous Ti implanted in rabbits show that bone grows faster within the implant when the biomimetic coating is present and that the interfacial bonding between the implant and the growing bone is much stronger. Several implant companies, including Americal Medical Electronics, Health Tech. Development, and Astromet, Inc. have visited PNL or discussed possible commercialization of the technology with PNL employees.

Milestones

I. Focus Coatings Research

PNL personnel met with Carl Miller and Larry Carol from General Motors and decided to focus the biomimetics coatings effort on chemically resistant tin oxide coatings on acetal and nylon parts for fuel delivery systems. It was also decided that the need for impermeable fuel tanks might be more readily solved using a PNL-developed (but non-biomimetic) composite of Al foil sandwiched between layers of high density polyethylene (HDPE). The goal was to make a small-scale replica of a fuel tank with a complex saddle geometry.

II. Demonstrate Vacuum Forming

Initial studies demonstrated that vacuum forming could not supply sufficient force to adequately deform the HDPE/Al composite to make an impermeable fuel tank. An alternate cup drawing process was developed to make the fuel tank shape. The technique was demonstrated by making one half of a "soda-can" geometry. The shaped laminate material retained its integrity at greater than 20% strain, indicating the viability of the process.

III. Coatings on Complex Shapes

Injection molded polystyrene parts with a variety of complex shapes were coated with both tin oxide and iron oxide. Scanning electron micrographs showed that uniform coatings were produced on all areas exposed to the deposition solution including corners, cracks, and holes. Fracture surfaces show excellent film adhesion.

IV. Mechanical Testing

The adhesive tape test and a pull-off test were adapted to investigate the adhesion of biomimetic coatings to various substrates. The films never fail the adhesive tape test, which is a standard in the microelectronics industry. The pull off test (using an Instron test bench) did not provide reliable quantitative values concerning adhesion. However, the Instron tests did indicate that film adhesion is comparable to the strength of the underlying polymer. Failure of the substrate always accompanies film delamination.

V. Surface Modification of HDPE

HDPE is the standard fuel tank material. HDPE functionalization is a prerequisite for application of biomimetic coatings to fuel tanks. None of the standard methods of functionalization, including sulfonation or use of plasmas or reactive plasmas, were successful in producing surface groups that stimulate biomimetic film formation. Due to the concurrent success of the HDPE/Al alternative for making impermeable fuel tanks, the HDPE surface modification project was abandoned.

VI. Optimization of Tin Oxide Deposition

A detailed kinetics study using Raman, particle size analysis, film thickness measurements, and transmission electron microscopy was used to determine the mechanisms for tin oxide formation and to see if the rate of film formation could be accelerated. The results showed that tin oxide rapidly nucleates within a thick (up to 2 μm) sulfonated layer on the surface of polystyrene. However, tin oxide does not grow on top of the substrate once the sulfonated polystyrene is completely filled, resulting in a stop to film formation. Work with water soluble tin complexes, including fluorides, sulfates, and oxalates suggests that deposition conditions can be tailored to more benign pH conditions (above pH 5), to suppress undesired solution nucleation, and to enhance growth of tin oxide particles on the substrate surface. Growth rates (above the polystyrene layer) as high as 2 $\mu\text{m/day}$ have been achieved. While the results look promising, even the enhanced growth rates are too slow for many potential commercial applications.

PUBLICATIONS

Journals

1. B. C. Bunker, et al., "Ceramic Thin-Film Formation on Functionalized Interfaces Through Biomimetic Processing," *Science*, 264, 48 (1994)
2. A. A. Campbell, et al., "The Nucleation and Growth of Calcium Oxalate Monohydrate on Self-Assembled Monolayers (SAMS)," *Scanning Microscopy*, 7, 423 (1993)

3. P. C. Rieke and S. B. Bentjen, "Deposition of Cadmium Sulfide Films by Decomposition of Thiourea in Basic Solutions," *Chemistry of Materials*, 5, 43 (1993)
4. B. C. Bunker and G. L. Graff, "Aqueous Biomimetic Synthesis of Ceramic Thin Films," *Materials Technology*, Feb. 1994
5. P. C. Rieke, et al., "Spatially Resolved Mineral Deposition on Patterned Self-Assembled Monolayers," *Langmuir*, (accepted for publication)
6. P. C. Rieke, et al., "Aqueous Solution Deposition Kinetics of Iron Oxyhydroxide on Sulfonic Acid Terminated Self-Assembled Monolayers," submitted to *Langmuir*
7. G. E. Fryxell, J. C. Linehan, P. C. Rieke, and G. Coffey, "Utilization of Solid State CP-MAS NMR to Characterize Self-Assembled Monolayers," submitted to *J. Am. Chem. Soc.*
8. P. C. Rieke, et al., "Beam Damage of Self-Assembled Monolayers," *J. Vac. Sci. Tech.*, 11, 2292 (1993)

Other Publications

1. G. L. Graff, "Precipitation Puts Dense Films on Complex Substrates," brief report in "Chementator", *Chemical Engineering*, March 1994, p. 25
2. P. C. Rieke, et al., "Biomimetic Lithography and Deposition Kinetics of Iron Hydroxide Thin Films," in *Biomolecular Materials by Design*, Materials Research Society Proceedings, Nov. 1993 (submitted)
3. L. Song, A. A. Campbell, and B. C. Bunker, "The Role of Interfacial Chemistry in Surface Nucleation and Growth of Calcium Oxalate Monohydrate," *Mat. Res. Soc. Symp. Proc.*, Spring 1993 MRS Meeting, Symposium V. Hydroxyapatite and Related Materials.

PRESENTATIONS

1. B. C. Bunker, "Biomimetic Synthesis of Ceramic Thin Films," invited talk at the International Symposium on Artificially Structured Materials and Biomimetics," Tagernsee, Germany, March 14-16, 1994
2. A. A. Campbell, G. E. Fryxell, G. L. Graff, and P. C. Rieke, "The Nucleation and Growth of Calcium Oxalate Monohydrate on Self-Assembled Monolayers (SAMS)," invited seminar at the Department of Pathology, University of Florida, January, 1993
3. G. E. Fryxell, P. C. Rieke, J. C. Linehan, A. A. Campbell, G. L. Graff, and L. Woods, "Synthetic Elaboration of Functionalized Self-Assembled Monolayers," invited presentation at the "Symposium on Chemistry in Self-Assembled and Organized Media" at the Northwest Regional Meeting of the American Chemical Society, Laramie, Wyoming, June 1993.
4. P. C. Rieke, "Control of Heterogeneous Nucleation by Functionalized Self-Assembled Monolayers," invited seminar at Naval Research Laboratory, December, 1993

HONORS AND AWARDS

Biomimetic research at PNL received the 1992 DOE/BES Award for Outstanding Scientific Accomplishment in Materials Chemistry and has been nominated for Pacific Northwest Laboratory's Directors Award for Scientific and Engineering Excellence.

PATENTS/DISCLOSURES none

LICENSES none

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Interactions have continued between PNL researchers and General Motors (AC Rochester Division) on the CRADA established last year. Both partners are committed to continuing the CRADA for at least two more years. Currently, coatings applications are being investigated pertaining to

automobile fuel delivery systems, although work could expand into other areas such as coatings for plastic windows, and coatings for parts in the exhaust system. The coating system of greatest current interest involves tin oxide coatings on acetal fuel delivery parts. PNL has successfully functionalized acetal with gaseous HCl followed by gaseous SO₃. Tin oxide coatings have been deposited on the functionalized surfaces. However, the functionalization methods damages the acetal, so more benign functionalization routes are under investigation. Another GM priority is for impermeable fuel tanks. PNL has developed the non-biomimetic HDPE/Al/HDPE laminate structure to solve the fuel permeation problem and has demonstrated that cup drawing techniques can allow the laminates to form structures analogous to fuel tanks.

More companies are becoming aware of biomimetic processing and are approaching PNL concerning potential interactions. Lexalite, a company that fabricates optical components, has exchanged visits with PNL and is interested in establishing a CRADA on coatings technologies. Representatives from American Medical Electronics, who are involved in several bone implant technologies, have visited PNL and have expressed interest in commercializing PNL's calcium phosphate coatings. PNL has been contacted by many firms as a result of the recent Science article, but it has not yet been determined which of the many potential applications are most appropriate for joint PNL-industrial interactions.

ORIENTED MAGNETITE FILMS FOR MAGNETIC STORAGE DEVICES VIA BIOMIMETIC PROCESSING TECHNIQUES

Problem: Magnetic media are typically prepared by making a slurry of suspended particles such as magnetite and tape casting on an appropriate substrate. Problems with the tape casting method include a low solids loading for the desired particulates (20-50 vol%), the use of toxic organic binders, and the fact that the acicular needles of the magnetic particles end up being oriented parallel to the substrate instead of assuming a perpendicular orientation that would maximize storage densities. Films deposited via vacuum technologies exhibit superior film qualities. However, such films can only be prepared in limited geometries and sizes and are expensive to fabricate.

Results: Films of the magnetic phase magnetite (Fe_3O_4) have been deposited on sulfonated polystyrene substrates and Si wafers coated with functionalized self-assembled monolayers. Processing involves two steps. First, dense, highly oriented crystallites of goethite (FeOOH) are deposited on the substrate (see Figure) via exposure to iron nitrate solutions at 70°C . Coated substrates are placed in a second solution to convert them to magnetite. The conversion process retains the perpendicular orientation, the acicular grain shape, and the high density of the original film.

Significance for Energy Conservation: Over 50% of the costs involved in producing sputtered films are energy costs (pumps, heating, cooling, high-bias sources, etc.). The slurry process involves many processing steps and the use of toxic solvents that must be removed and disposed of. The new biomimetic process involves much lower energy consumption and involves use of water rather than the toxic organic solvents.

Significance for Materials Technology: The denser, more oriented films are expected to provide higher magnetic storage densities than conventional films. In addition, the magnetite films demonstrate that ordered polycrystalline films can in principle be made for a wide range of future applications in opticals, electronics, and optoelectronics.

(Research performed at Pacific Northwest Laboratory (PNL) under DOE-CE-AIC support.)

PROJECT SUMMARY
ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Biomimetic Thin Film Synthesis

FISCAL YEAR: FY 1993

COMPLETION DATE: open

PERFORMING ORGANIZATION: Pacific Northwest Laboratory

PRINCIPAL INVESTIGATORS: Gordon L. Graff (509-375-6786), Allison A. Campbell (509-375-2180), and Norman R. Gordon (509-375-2613)

PHASE OBJECTIVE: Develop biocompatible calcium phosphate coatings for use in bone and dental implant materials. Develop low temperature solution process for converting as-deposited FeOOH into the desired magnetic phase Fe_3O_4 . Develop methods for accelerating the kinetics of tin oxide film formation. Establish optimum methods for forming impermeable fuel tanks using layered polyethylene/Al composites.

ULTIMATE OBJECTIVE: Adapt features of mineralization processes used by bioorganisms to the development of materials with improved properties over conventionally processed materials. Demonstrate industrial relevance of the biomimetics thin film process by directly solving industrial coatings needs.

TECHNICAL APPROACH: The approach is to attach functional groups known to promote biomineralization to substrate surfaces. The organic molecules used in functionalization are often bifunctional, with one end serving to covalently attach the molecule to the substrate and the other end serving to promote nucleation of desired phases onto the substrate surface. The functionalized surface then controls the phase, orientation, and microstructure of crystalline films grown on the substrate from aqueous solutions at low temperatures.

PROGRESS: Calcium phosphate films have been deposited on Ti metal bone implants coated with self-assembled monolayers. Use of solution techniques to develop oriented, fully dense films of magnetite has been successful. Solution complexation methods have been used to grow thick tin oxide coatings on plastics under mild pH conditions. Impermeable HDPE/Al/HDPE sandwich composite has been produced using cup drawing techniques.

Patents/Disclosures: 0

Publications: 8

Proceedings: 3

ACCOMPLISHMENTS:

Licenses: -

Known Follow-On Products: -

Industry Workshop: -

Technology Transfer of Industrial Interaction: "Industrial

Applications of

PROJECT TITLE: Biomimetic Thin Film Synthesis

Biomimetic Thin Films," CRADA (AC Rochester); potential CRADAS with Lexalite and Americal Medical Electronics; interactions with General Motors Research - Polymers Div., Ford, Chrysler, Hoechst-Celanese Corp.

CRITICAL ISSUES: The slow deposition kinetics is still the factor most frequently mentioned by potential customers as the key limitation to biomimetic processing. While PNL can fabricate many types of films, it needs better capabilities for characterizing film properties.

FUTURE PLANS: Explore the potential for biomimetic processing in biomedical applications and in high-value-added products for industries such as microelectronics where the patterning advantage of biomimetics can be exploited. Expand the number and variety of industrial partners.

POTENTIAL PAYOFF: The biomimetics process is showing promise for fabrication of thin films on polymers and ceramic-polymer composites, allowing use of lower strength, lower cost materials for numerous manufactured parts. For thin films, advantages include elimination of toxic organics associated with sol-gel and conventional slurry processing, and the corrosive and toxic species currently used to etch patterns into ceramic thin films. The ability to coat complex shapes is already being exploited by industrial partners in the automotive industry, in optical components, and in biomedical applications such as coating of implant materials.

MATERIALS R&D — STUDENT INTERNSHIPS

R. B. Thompson

Ames Laboratory
108 Office and Laboratory
Iowa State University
Ames, Iowa 50011

INTRODUCTION

This program has as an objective the conduct of programmatic research for the Advanced Industrial Concepts Materials Program while training minority graduate students in the process.

Well-known demographics indicate that minorities will constitute an increasing fraction of our future work force. Consequently, efforts have been initiated to increase the fraction of minorities and women who choose technical career paths. Included are a wide ranging set of programs beginning with pre-school education, progressing through efforts to retain students in technical paths in grades K-12 and undergraduate education, and ending with encouraging graduate education. The Materials R&D — Student Internships is a unique approach in the latter category. Here, we have focused on a particular area of applied materials research, the Advanced Industrial Concepts Materials Program. Our goal, then, is to educate minority graduate students in the context of this program. The Ames Laboratory was selected as a site for this pilot project since it is a DOE national laboratory, located on the campus of a major research university, which includes in its research interests programs with a strong technological flavor.

More specifically, the pattern through which a student will pass involves a sequence of steps progressing through recruitment, project selection, research, mentoring, and graduation. Recruiting is being accomplished by nationally advertising "AICD Materials Technology Fellowships for Minorities." We feel that it is essential to offer at least one such fellowship each year to maintain continued visibility on minority campuses and to establish effective working relationships with appropriate personnel. Other factors which we believe to be essential to the success of the project include offering each student a variety of project opportunities — active

choice in project selection will greatly increase the student's motivation and likelihood of success — and continued mentoring throughout the program.

The projects offered to the students are consistent with the guidelines of the AIM program. The Ames Laboratory is located on the campus of a major land grant institution, Iowa State University, which takes its charter of technology transfer quite seriously, and many of the Laboratory staff hold shared faculty appointments. The receipt of three R&D 100 awards in 1991 and one in 1992 by Ames Laboratory scientists is one example of this commitment to technology transfer.

TECHNICAL PROGRESS

Summary

During FY 1992, the first minority fellow, Ms. Patricia Pulvirenti, continued with her second year of course work and research. She has now completed about 75% of the courses required for the Ph.D. degree and has presented early research results at a conference. Her work is concerned with the dynamic magnetostrictive response of Terfenol-D, a highly magnetostrictive material. The second student, Ms. LaVonne Carson, completed her first full year of studies. Each student is enrolled in the Materials Science and Engineering Department of Iowa State University.

Milestones

1. Continue research of first student in program.

One of the factors limiting the high frequency response of magnetostrictive materials is the resistive loss associated with the eddy currents induced in the material by the time varying magnetic field. Ms. Pulvirenti has continued her studies of the time dependent magnetostrictive response of $\text{Tb}_{0.27}\text{DY}_{0.73}\text{Fe}_{1.9}$ (Terfenol-D). The energy conversion in this material is less than 50% and her objective is to investigate possible improvements which could improve this efficiency and also extend the range of frequencies over which the material can be used.

Studies of the response of the material to periodic waveforms of different shapes (square, triangular, sinusoidal) showed some unusual effects which are still under investigation, particularly for the case of square wave excitation. Experiments were initiated to decrease the

resistivity by diffusing aluminum into the material. This would be expected to lower losses, increase frequency response and decrease the unusual transient phenomena. The first set of experiments yielded a less than desired concentration of aluminum within the bulk and a modified set of diffusion conditions are now being investigated. The aluminum profiles are being determined in Ames using EDS (energy dispersive spectroscopy). Collaborations are planned with the University of Hull (U.K.) for studies of the frequency dependent properties of the surface modified material.

2. Continue research of second student of the program.

Ms. LaVonne Carson, who joined the program in August 1992, has selected a project concerned with the production of nanocrystalline materials in large quantities, thereby moving this class of materials from the research to industrial arena. The techniques being investigated employ the heat generated by an Ar plasma to vaporize material. During this year, Ms. Carson has fulfilled safety training requirements, has learned to operate an existent RF plasma system and begun experiments to determine the parameters and most promising elemental systems which result in the production of nanocrystalline material. It is planned that Ms. Carson will assume the lead in the use of a new DC plasma system that will shortly come on line.

PUBLICATIONS

None.

PRESENTATIONS

1. P. Pulvirenti and D. C. Jiles, "Time-Dependent Magnetostriction of Terfenol-D," Advanced Industrial Concepts Annual Review Meeting, Oak Ridge, Tennessee, June 7-9, 1993.

HONORS AND AWARDS, PATENTS/DISCLOSURES, LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

The direction of the materials development efforts of Ms. Pulvirenti has benefited from significant input from the ETREMA Division of Edge Technology, a producer of these highly

magnetostrictive materials. Among the applications of interest are efficient sonar projectors and active devices for vibration control.

COST SHARING

No industrial cost sharing has occurred to date. However, the Ames Laboratory has provided important program support through the efforts in minority education of its senior management. R. B. Thompson, Associate Director for Science and Technology, has developed and coordinated the program at no direct cost. Ms. Connie Hargrave, who is now serving as Ames Laboratory Education Coordinator, continues her efforts in recruitment and mentoring as part of her broader responsibilities.

HIGHLIGHTS

Measurements of the magnetostrictive strain of Terfenol-D under square wave excitation showed the magnetostriction continuing to change after the field had been stabilized and, in some cases, apparently showing an overshoot when the field was applied. The origin of these unusual phenomena, which have important implications in dynamic magnetostrictive application, are presently under study.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: MATERIALS R&D — STUDENT INTERNSHIPS

PHASE: FY 1993

PERFORMING ORGANIZATION: Ames Laboratory

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

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 directed towards the development of magnetostrictive materials with enhanced dynamic energy transfer efficiencies for transducers and activators and development of plasma torch techniques for production of nanocrystalline materials in large quantities.

PROGRESS: Dynamic magnetostriction measurements were made on Terfenol-D as a function of excitation waveform and frequency. Some unusual transient effects were observed, particularly under square wave drives. Studies of the effects of diffusing aluminum into the material to decrease resistivity to lower loss and improve transient response were initiated. Experiments were also initiated to determine the parameters and most promising elements in the large scale production of nanocrystalline materials via plasma techniques.

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

ACCOMPLISHMENTS:

Licenses: none **Known Follow-on Product(s):** none **Industry Workshop:** none

Technology Transfer or Industrial Interaction: Close contact is being maintained with the ETREMA Division of Edge Technologies regarding application driven improvements needed in the dynamic response of magnetostrictive materials.

PROJECT TITLE: Materials R&D — Student Internships

CRITICAL ISSUES: Attracting high quality minority students to technical areas.

FUTURE PLANS: It is planned to add one student a year until a level of five is reached. Each project will be selected in accordance with the guidelines of the AIC Materials Program and will involve technology transfer. The initial project is coupling closely with the ETREMA Division of Edge Technologies, a supplier of highly magnetostrictive materials.

POTENTIAL PAYOFF: Payoffs include improving the technical labor pool of the country plus project specific results.

MICROWAVE PROCESSING OF CERAMIC OXIDE FILAMENTS

G. J. Vogt, J.D. Katz, W.P. Unruh, B. Rusnak, and J.R. Thomas, Jr.

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INTRODUCTION

The objective of the microwave filament processing project is to develop microwave techniques at 2.45 GHz to manufacture continuous ceramic oxide filaments. Microwave processing uses the volumetric absorption of microwave power in oxide filament tows to drive off process solvents, to burn out organic binders, and to sinter the dried fibers to produce a flexible, high-strength ceramic filament. The technical goal is to advance filament processing technology by microwave heating more rapidly with less energy and at a lower cost than conventional processing, but with the same quality as conventional processing. The manufacturing goal is to collaborate with a US manufacturer of ceramic oxide filaments to evaluate the technology using a prototype filament system and to transfer the microwave technology to the industrial partner.

TECHNICAL PROGRESS

Summary

Significant progress was made toward controllable microwave sintering of ceramic oxide filament tows. Hybrid heating with lossy carbon coatings has successfully produced controlled sintering temperatures for low-loss aluminosilicate fibers with low microwave power. Process temperature of a moving tow can be regulated by pulse-modulated microwave heating with an active feedback control circuit through a photodiode sensor or an optical fiber thermometry (OFT) sensor. To aid process control, tow temperatures are now directly measured with a commercial optical fiber thermometry (OFT) system, sensing the emitted light at two different wavelengths. Microwave sintering experiments of aluminosilicate tows have demonstrated that

changing dielectric properties within the filaments can effectively regulate the tow heating. Numerical modeling of the heat transfer in filament sintering has provided insight into general microwave heating and into understanding the heating-burst behavior of aluminosilicate filaments.

A Cooperative Research and Development Agreement (CRADA), entitled "Microwave Processing of Continuous Oxide Ceramic Filaments," was negotiated with the 3M Company, a manufacturer of continuous ceramic oxide fibers. The CRADA has received approval from the DOE Albuquerque Area Office. We anticipate that the CRADA will be signed in October, 1993, by the Los Alamos Laboratory Director and by 3M management.

Milestones

1. Assess and demonstrate controlled microwave sintering of ceramic oxide filaments. The task in FY 1993 is to address the most challenging aspect in filament tow processing, microwave heating the fibers in a controllable manner to achieve sintering and to retain the submicron-sized microstructure without overheating. Microwave heating was studied by the heating experiments with commercial aluminosilicate, alumina, and silicon carbide filament tows.

Active Temperature Control. Alumina and other low-loss oxide ceramic fibers are difficult to sinter in a controlled manner because their dielectric loss rises rapidly with temperature above 500°C. High microwave power must be used initially to produce even modest heating of the fibers, since small-diameter fibers have large surface-area-to-volume ratios and thus dissipate the volumetrically deposited thermal energy to the surroundings very rapidly. After heating to ~600°C, the dielectric loss rises rapidly, requiring much less microwave power to heat the fiber. This leads to a runaway condition that must be managed by fast feedback control of the microwave source to avoid fiber melting or excessive grain growth in the fiber.

We have fabricated and tested an active feedback control circuit that successfully provides the rapid response and control required to sinter low-loss fibers in a single mode cavity.

Feedback is accomplished by using either an infrared photodiode or optical fiber thermometry (OFT) to monitor the fiber tow in the cavity. The feedback signal is used to simultaneously set the pulse frequency and width of a pulsed magnetron, thereby providing rapid adjustment of the average power applied to the fiber tow. Because magnetron microwave sources exhibit a significant frequency shift with changing power level, heating control is best effected by pulse modulating the magnetron source, which is tuned to the resonant frequency of the filament processing cavity.

The feedback control circuit is capable of maintaining a constant tow temperature that can be set at any value over the range of interest. Its response time is less than one millisecond, providing the rapid control needed to compensate for rapidly varying fiber properties. Nicalon tows are readily heated to a stable temperature using this feedback control. With constant power heating, the mean filament temperature fluctuated strongly as the filament is pulled through the TE₁₀₂ cavity at 3.3 cm/min. In Figure 1a, temperature fluctuations ranged from 1100° to 1550° C while attempting to control the filament temperature at 1400°C. With pulsed heating control through feedback from a two-color OFT sensor, the temperature fluctuations are greatly reduced, as seen in Figure 1b, for controlled heating at 1400°±50°C.

Passive Heating Control by Hybrid Heating. Alumina and other oxide ceramics are typically transparent to 2.45 GHz microwaves at temperatures below 500°C due to their low dielectric loss. Although the oxide ceramics will absorb microwaves sufficiently at higher temperatures to produce direct microwave heating, the problem is how to heat the ceramic to >500°C to begin microwave heating. We have investigated the use of hybrid heating as an alternate approach to using excessive microwave power to initiate heating. Hybrid filament heating is carried out by heating a lossy coating applied to the low-loss filaments, which in turn heats the low-loss filaments to a critical temperature at which the filaments begin to absorb microwaves. An excellent candidate for the lossy coating is submicron-sized carbon. Carbon has the advantages of low cost and easy removal by oxidation.

Figure 1a. Temperature fluctuations observed with constant power heating for a Nicalon filament pulled at 3.3 cm/min.

Figure 1b. Temperature fluctuations observed with pulse controlled microwave heating for a Nicalon filament pulled at 3.3 cm/min.

Figure 2. Temperature-vs-time trace for a Nextel 550 filament tow heated in a TE_{102} cavity. The heating bursts are indicated by the rapid rise and fall in temperature with an increase in microwave power. The new power level is labeled at the beginning of each heating burst.

Hybrid heating has experimentally provided controlled heating of aluminosilicate tows in a TE₁₀₂ cavity. Aluminosilicate filaments will not heat to sintering temperatures (>900°C) in a TE₁₀₂ cavity with power levels up to 1 kW. However, heating to temperatures near 1000°C was readily achieved by hybrid heating. The optimum sintering temperature for green filament tows is expected to be between 1000° and 1100°C, to produce densification with a submicron average grain size for optimal mechanical properties.

Heating Behavior of Aluminosilicate Filaments. Nextel™ aluminosilicate filaments have exhibited an unexpected burst-heating behavior at sintering temperatures. After initially heating to 600°-700°C by hybrid heating, an abrupt increase of 50-100 W in microwave power produces a heating burst in the filament tow. In Figure 2, the temperature of a stationary tow rapidly rises from 900°-1000°C to 1100°-1400°C over several seconds, and then rapidly cools to 900°-1000°C under constant microwave power. Stationary samples continue to undergo burst heating with further increases in microwave power (see Figure 2), while requiring greater power levels to maintain the steady temperature near 900°-1000°C. Aluminosilicate fibers undergo a characteristic phase transition to mullite over the temperature range of 1100°-1200°C. Heating experiments with stationary samples indicate that each burst of microwave heating produces only a partial phase transformation to mullite. XRD analysis shows that only a fraction, typically ~ 10% by weight, of the filaments has transformed to mullite with each burst. Similar behavior is observed while heating moving tows.

A probable explanation for the burst-heating behavior is that the dielectric loss of the filament decreases abruptly with the mullite phase transition, causing the tow temperature to fall rapidly as radiative heat loss dominates the diminished rate of microwave heating. This phenomenon offers a mechanism for self-regulated heating that cannot be duplicated by conventional electrical heating. Selective microwave heating of one phase over others has been observed in other microwave applications.

Numerical Modeling of Microwave Heating. To test our explanation of the burst-heating in aluminosilicates, a finite-difference model of microwave heating was developed for qualitative comparison with experiments. The model assumed a continuous decrease in the

dielectric loss factor for the filament tow while being heated to temperatures above the mullite phase transition temperature. The heat burst behavior was readily reproduced in the qualitative model using an exponential temperature-dependence for the dielectric loss of the amorphous filament tow. A numerical simulation depicting a hot spot moving along the tow length is presented in Figure 3. This hot spot behavior has been observed in microwave heating experiments.

Tow Temperature Measurements. Routine temperature measurements of a moving filament tow are not easily made in a microwave cavity due to the presence of the electromagnetic field and to the small diameter of the heated tow. However, temperature measurements are surely needed for monitoring the effective microwave heating during process development and later for process control. The Accufiber optical fiber thermometry (OFT) system has provided the reliable temperature measurements needed to control filament heating. A sapphire OFT sensor can be precisely positioned to view the filament tow within the microwave cavity, perpendicular to the applied microwave electric field without significantly affecting the cavity resonance. The OFT system can measure temperatures over a 200°-2000°C range with a single-wavelength determination and over 500°-2000°C range with a dual-wavelength determination.

Video Recording of Microwave Filament Heating. A color video system was adapted for use with the microwave filament apparatus to record microwave experiments. Filament heating patterns can now be conveniently viewed on a color monitor during processing experiments and stored for valuable post-analysis of microwave heating experiments. Video images of microwave heating experiments, for example, can conveniently document transient heating patterns with moving hot spots.

New Microwave Laboratory. The microwave filament processing program will move during FY-1994 into a new laboratory in the Materials Science Laboratory at Los Alamos. During the past year, project time was spent in the final preparation and in the procurement of state-of-the-art microwave equipment, purchased with funding outside this program. The

Figure 3. One-dimensional time-dependent numerical simulation for microwave heating of an aluminosilicate tow with a dielectric loss defect near $x=1.6$ cm in the tow. The simulation is for a tow 5-cm long with heating of the center 3-cm length. Modeling with an exponential temperature-dependence for the dielectric loss and a phase change at 1250°C to a new phase with a lower dielectric loss yields a local hot spot (at $x=1.6$ cm) which splits and spreads toward the ends of the tow. This hot spot mobility has been observed experimentally with NextelTM 550 tows. The time labels in seconds are given relative to the initial hot spot arbitrarily labeled at 0 seconds.

filament processing program will benefit greatly from this new state-of-the-art facility, which presents a significant enhancement of our microwave processing capabilities. Briefly, the new facility includes a 2-18 GHz variable frequency microwave source, new network analyzer with dielectric measurement capability, an industrial CO₂ laser for preheating, state-of-the-art microwave power meters for computer data acquisition, and an additional optical fiber thermometry unit for temperature distribution measurements.

2. Establish a CRADA, or equivalent agreement, with a collaborating U.S. company for the development of microwave technology for processing continuous oxide ceramic filaments. This agreement will be the direct means of transferring this microwave technology to industry. The U.S. company will play a critical role in the technology development by supplying the needed expertise in sol-gel filament preparation and characterization.

A joint research and development program in "Microwave Processing of Continuous Ceramic Oxide Filaments" was proposed with the 3M Company, a manufacturer of continuous fibers, based on collaborative research completed in FY-1992. A CRADA has been successfully negotiated with 3M to perform the proposed work. The CRADA has received approval from the DOE Albuquerque Area Office. The agreement will be signed by Los Alamos and the 3M Company during October, 1993. The three-year program will develop microwave techniques for the drying, burnout, and sintering of a proprietary prototype filament. The potential energy and economic advantages of microwave processing will be evaluated through direct comparison with conventional thermal processing.

PUBLICATIONS

Proceedings

1. G.J. Vogt and W.P. Unruh, "Microwave Hybrid Heating of Alumina Filaments," to be published in *Microwaves: Theory and Application in Materials Processing II*, Ceramic Transactions, The American Ceramic Society, Westerville, Ohio.

PRESENTATIONS

1. G.J. Vogt and W.P. Unruh, "Microwave Hybrid Heating of Alumina Filaments," presented at Symposium XII, Microwaves: Theory and Applications in Materials Processing II, 95th Annual Meeting of The American Ceramic Society, Cincinnati, Ohio, April 18-22, 1993.
2. G.J. Vogt, F.D. Gac, J.D. Katz, B. Rusnak, and W.P. Unruh, "Microwave Processing of Ceramic Oxide Filaments," presented at the DOE/Advanced Industrial Concepts Materials Program, Annual Information and Review Meeting, Oak Ridge, Tennessee, June 7-9, 1993.
3. G.J. Vogt, F.D. Gac, J.D. Katz, B. Rusnak, and W.P. Unruh, "Microwave Processing of Ceramic Oxide Filaments," presented to the Industrial Research Institute, Los Alamos, New Mexico, September 23, 1993.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

We have successfully negotiated a CRADA with the 3M Company for the microwave processing of continuous ceramic oxide filaments. The CRADA will be signed by Los Alamos and the 3M Company in October, 1993. The project is sponsored by the Advanced Industrial Materials Program, DOE-EERE.

COST SHARING

None

HIGHLIGHTS

The project has produced several microwave highlights in FY 1993.

1. A CRADA on microwave filament processing was successfully negotiated with the 3M Company. This three-year program will begin in FY 1994.
2. Microwave heating of filament tows can be successfully controlled by pulse modulating the magnetron source and by feedback controlling the pulse rate and frequency through an optical feedback sensor.
3. Amorphous aluminosilicate filament tows under microwave heating have exhibited an unexpected self-regulating behavior that prevents over heating by means of a phase transition to mullite. Because the new mullite phase appears to absorb 2.45 GHz microwaves less effectively than the amorphous phase, microwave heating abruptly decreases as the filament temperature exceeds the transition temperature.

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 and to remove organic residue by combustion. The energy is delivered directly to the filament tows without the need to heat an external furnace. Oxide filaments can be heated controllably to sintering temperatures by pulse-modulated microwave power with active feedback control and by the use of low-cost hybrid heating with carbon dip-coatings. Alumina/silica filament tows can be readily heated to sintering temperatures in a simple single-mode cavity.

Aluminosilicate Nextel™ 550 filament tow can be heated in a TE_{102} cavity to radiant temperatures through hybrid heating with a lossy carbon coating.

Significance - For Energy Conservation: Microwave sintering for specific filament compositions can save more than 90% of the energy currently used in conventional processing.

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. Potential benefits from microwave processing include consistent production of filaments with circular cross sections and the manufacture of larger diameter filaments.

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

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: MICROWAVE PROCESSING OF CONTINUOUS CERAMIC OXIDE FILAMENTS

PHASE: FY 1993

COMPLETION DATE:

PERFORMING ORGANIZATION: Los Alamos National Laboratory

PRINCIPAL INVESTIGATORS: Gerald J. Vogt, 505/667-5813, Joel D. Katz, 505/665-1424

PHASE OBJECTIVE: Develop microwave sintering processes for commercial 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 gels with greater energy efficiency than conventional thermal processing.

TECHNICAL APPROACH: Use volumetric microwave absorption to heat ceramic oxide filament tows in order to drive the process drying, prefiring, and sintering in the preparation of continuous tows from solution-based gels. 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: Microwave heating of filament tows was successfully controlled by pulse modulation of a magnetron source and by active feedback control of the pulse rate and frequency through an optical feedback sensor. Materials properties can be used to control microwave processing by inherent self regulation. Amorphous aluminosilicate filament tows under microwave heating have exhibited an unexpected self-regulating behavior that prevents excessive heating by means of a phase transition to mullite.

Patents: none **Publications:** none **Proceedings:** 1

Presentations: 3

ACCOMPLISHMENTS:

Licenses: none

Known follow-on Products: none

Industry Workshops: none

Technology Transfer or Industrial Interaction: CRADA with the 3M Company was successfully negotiated on microwave processing of continuous ceramic oxide filaments. Work will begin in FY 1994.

PROJECT TITLE: MICROWAVE PROCESSING OF CONTINUOUS CERAMIC OXIDE FILAMENTS

CRITICAL ISSUES: To controllably sinter the green filament tows while retaining the submicron grain size necessary for the desired flexibility and mechanical strength.

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 sol-gel filament tows. The energy efficiency and economics of microwave processing will be directly compared to those of conventional thermal 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. Microwave filament processing offers significant improvements over conventional processing in faster processing, lower manufacturing and capital costs, and energy savings with direct volumetric heating. Also, very rapid volumetric heating could produce new fiber microstructures with enhanced mechanical properties. Microwave processing could significantly reduce the processing time required in the manufacturing of large diameter filaments by sol-gel precursors.

ESTIMATED ENERGY SAVINGS: Microwave sintering for specific filament tows can be carried out with an estimated energy savings of >90% over conventional processing. Conventional filament processing utilizes 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 will require only seconds-to-minutes to complete a processing step, compared to hours by conventional processing.

MICROWAVE JOINING OF SiC

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INTRODUCTION

The purpose of this work is to optimize the properties of SiC-SiC joints made using microwave energy. The current focus is on production of SiC from chemical precursors, design of new applicators for joining of long tubes, and joining of tube assemblies.

TECHNICAL PROGRESS FY 1993

Summary

SiC was produced through microwave-assisted decomposition of two different types of chemical precursors—a commercial polycarbosilane precursor purchased from Dow Corning and a precursor prepared in-house via sodium reduction of trichloromethylsilane. Both precursors were decomposed inside a quartz crucible in a single mode microwave applicator. X-ray analysis demonstrated that the product was SiC.

A single mode mitered bend cavity applicator was designed, fabricated and operated. 3-D computer simulations predicted an extended area of maximum electric field near the center of the cavity, in the vicinity of the bend. SiC rods were heated in this cavity, demonstrating excellent

coupling (2-3% reflected power), as well as increased heating rate and higher sample temperature for the same input power compared to a conventional rectangular cavity applicator.

A small scale reaction bonded SiC (RBSC)-sintered SiC (SSiC) tube assembly was joined in a 900 watt multimode applicator. The tube diameters ranged from 2.54 cm (1") to 3.81 cm (1.5"), and the length of the tube assembly was 6.35 cm (2.5"). The tube assembly was leak-tight before and after cycling between ambient temperature and 1100°C and SEMs of joints sectioned from it were identical to those made in small samples that had mechanical strength of 190 MPa.

Milestones

1. Demonstrate the production of SiC from chemical precursors using microwave heating.

SiC has been produced from polycarbosilane precursors using both conventional and microwave heating, so that comparisons could be made between the two processes. First, commercial Dow Corning polycarbosilane (PC X9-6348) was cured in a Lindberg muffle furnace at several different temperatures from 500°C to 1200°C in a N₂ environment. In each case, the precursor was heated from 25°C to the desired curing temperature in approximately 1 hour, and then held at that temperature for 24 hours. The cured precursor was then weighed and analyzed via infrared (IR) spectrometry and X-ray diffraction. The IR spectra of the cured precursors indicated that extensive degradation of the precursor occurred between 500 and 900°C. Weight loss data provided further support for this observation, i.e., at temperatures above 900°C, the change in percent weight loss was insignificant. The IR spectrum of the precursor cured at 1200°C showed just one absorption peak, centered at 800 cm⁻¹, which corresponds to the Si-C bond stretching mode. In addition, a shoulder centered at 1100 cm⁻¹ may correspond to the Si-O bond stretching mode. The X-ray spectrum of the conventionally cured precursor showed the 3 major diffraction angles ($2\theta \cong 35, 59$ and 70°) that correspond to the 3 most abundant peaks in the standard SiC spectrum. However, these peaks were relatively broad, from which it was concluded that the polycarbosilane was transformed at 1200°C to partially crystallized SiC. It is anticipated that further heating to higher temperatures would enhance the crystalline structure.

The same commercial precursor was cured using the single mode microwave applicator, together with a 1.0 kW 2.45 GHz microwave source. This was accomplished by inserting a quartz crucible containing the pre-weighed polycarbosilane precursor inside a block of Al₂O₃ insulation, which was inserted into the applicator. The temperature of the precursor was

monitored through a small hole in the insulation using an infrared pyrometer. Within about 10 minutes, a temperature of 1500°C was reached, which was held for about 30 minutes. The cured precursor was then analyzed in the same manner as described above for the precursors cured using conventional heating. Elemental analysis of the microwave-cured precursor showed only a trace amount ($< 0.06\%$) of impurities other than Si and C. The corresponding IR spectrum was similar to that of the furnace-cured precursor, showing the Si-C absorption at 800 cm^{-1} , together with a small shoulder centered at about 1100 cm^{-1} , which appeared to increase with time. This may imply that there is excess elemental Si present, which reacts over time with oxygen in the atmosphere to form SiO_2 .

The X-ray spectrum of the microwave-cured precursor showed the three SiC peaks, which were much sharper than those of the conventionally-cured precursor, suggesting that microwave heating provides a higher level of crystalline SiC. The microwave curing also required much less time to obtain an improved product. However, microwave curing in these investigations was performed at 1500°C, versus 1200°C for the conventional curing (the highest achievable temperature in the muffle furnace).

2. Design, fabricate and operate a single mode mitered bend cavity applicator.

We have designed and fabricated a single mode mitered bend cavity operating in the TE_{103} mode. The cavity, which was constructed from WR-284 waveguide sections, is shown in Figure 1. As indicated in the figure, choking structures were extended from the cavity walls to allow heating of long ceramic tubes without microwave leakage. Figure 2 shows a 3-D computer simulation of the electric field pattern in the mitered bend cavity. The simulation shows an extended area of maximum electric field near the center of the cavity and in the vicinity of the bend.

Heating experiments using a 0.9 cm (3/8") diameter SSiC rod 7.2 cm in length inserted along the axis of the bend verified the advantages of the mitered bend cavity, as compared to a rectangular single mode cavity applicator. Using the 0-1 kW, 2.45 GHz microwave source, a temperature of 1660°C was achieved within 4-5 minutes with 550 watts of input power in the mitered bend cavity. For the rectangular single mode cavity with the sample oriented parallel to the electric field, using the same source, it was possible to attain a maximum temperature of only 1550°C. For the perpendicular configuration in the rectangular cavity, it was possible to reach

FIGURE 1 MITERED BEND CAVITY APPLICATOR

FIGURE 2 ELECTRIC FIELD DISTRIBUTION IN MITERED BEND APPLICATOR

approximately the same temperature as with the mitered bend, but the input power was 800 watts and the time required was approximately 20 minutes. These data are summarized in Figure 3.

3. Fabricate a RBSC-SSiC tube assembly.

In certain designs of high temperature heat exchangers, a RBSC-SSiC joint would be advantageous so that the SSiC could be used only in the highest temperature sections, while the low-cost, more easily fabricable RBSC could provide the transition to the metal sections. During the previous year, we made small SSiC-RBSC joints using the single mode apparatus. The specimens were 0.95 cm in diameter, and the joining temperature was 1450-1500°C, which took 5-8 minutes to reach with 400-600 watts of power. The specimens were held in this temperature range for 10-15 minutes. The joints obtained had a 5 μm interlayer that was very similar in appearance to that of the small RBSC-RBSC joints.

In order to establish the feasibility of joining tube assemblies, a SSiC tube of 2.54 cm (1") outer diameter was joined to a RBSC socket of 2.54 cm (1") inner diameter and 3.81 cm (1.5") outer diameter. In addition, a butt joint was provided along the gas flow direction by adding a RBSC end cap of 1.23 cm (0.5") inner diameter. This was done to ensure leak-tight behavior. The tube assembly was joined in a 900 watt multimode applicator using an insulated enclosure lined on the inside with a thin coating of SiC to provide hybrid (microwave plus radiant) heating. This joined tube assembly passed the same vacuum test (12×10^{-3} torr) as RBSC-RBSC tube sections joined earlier. In addition, the joined tube assembly was cycled several times between ambient temperature and the anticipated service temperature of 1100°C, and it remained leak-tight after the temperature cycling. Joining temperatures in the range of 1410-1550°C and joining times in the range of 10-55 minutes were investigated. The minimum time and temperature to ensure a leak-tight joint was determined to be 1450°C for 20 minutes. SEM evaluation of sections cut from this tube assembly showed that the butt joints were all identical in appearance to those made with small specimens, and to those cut from a RBSC-RBSC tube section, for which Coors Ceramics Analytical Laboratory measured the average mechanical strength to be 190 MPa. This mechanical strength is adequate for radiant burner and heat exchanger applications.

FIGURE 3 SiC HEATING DATA FOR ALTERNATIVE CAVITY APPLICATORS

PUBLICATIONS

1. R. Silbergliitt, I. Ahmad, W.M. Black and J.D. Katz, "Recent Developments in Microwave Joining," *MRS Bulletin*, **XVIII (11)**, 47-50 (November 1993).
2. I. Ahmad and R. Silbergliitt, "Joining of Ceramics Using Microwave Energy," *MRS Symposium Proceedings, Joining and Adhesion of Advanced Inorganic Materials*, **314**, 119-130 (1993).
3. I. Ahmad, R. Silbergliitt, W.M. Black, H.S. Sa'adaldin, Y-L. Tian and Katz, J.D., "Microwave Joining of Dissimilar SiC Ceramics," *Ceramic Transactions, Microwaves: Theory and Application in Materials Processing II*, **36**, 409-415 (1993).
4. H.S. Sa'adaldin, W.M. Black, Y-L. Tian, I. Ahmad and R. Silbergliitt, "Heating of SiC in a Single Mode Mitered Bend Cavity," *Ceramic Transactions, Microwaves: Theory and Application in Materials Processing II*, **36**, 359-364 (1993).

PRESENTATIONS

1. R. Silbergliitt, "Microwave Joining of Silicon Carbide," presented at the Advanced Industrial Materials (AIM) Review Meeting, Oak Ridge, TN, June 9, 1993.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Golden Technologies, Inc., the Coors company responsible for ceramics R&D, has provided materials and joining requirements for radiant burner tube assemblies. Technology transfer plans include fabrication and scale-up of tube assemblies, and testing by the user industry under simulated service conditions.

COST SHARING

The Virginia Center for Innovative Technology has co-funded this project through a grant of \$100K to George Mason University. An additional \$61K in CIT funding is anticipated for FY 1993. GMU has absorbed \$50K in overhead charges and anticipates absorbing an additional \$30K on the new CIT grant. This will bring the total state and university contribution to \$241K.

HIGHLIGHTS

Microwave joining of SiC tube assemblies demonstrated to provide leak-tight joints identical in appearance to those in small specimens and survivable under temperature cycling.

FABRICATION OF SILICON CARBIDE TUBE ASSEMBLY

Problem:

Fabrication of silicon carbide tube assemblies is required for power generation, heat exchanger and process systems that could save up to 5 quads per year of industrial energy consumption. Silicon carbide is generally difficult to fabricate in the required lengths and the material with the highest strength and service temperature, sintered silicon carbide, is extremely difficult to join, making fabrication of large tube assemblies prohibitively expensive.

Results:

A tube assembly composed partly of sintered silicon carbide and partly of reaction bonded silicon carbide (RBSC), a more easily fabricable and less expensive material which is formed by infiltrating a C/SiC preform with molten silicon, was fabricated using microwave joining. The joined tube assembly was leak-tight under a vacuum of 12×10^{-3} torr, after repeated cycling between ambient temperature and the anticipated service temperature of 1100°C . Scanning electron micrographs of RBSC-sintered SiC butt joints sectioned from the joined tube assembly were identical in appearance to RBSC-RBSC joints made in small specimens that had strength equal to that of the parent material.

RBSC Tube Assembly Fabricated With Microwave Joining and SEM of Sectioned Joint

Significance:

This fabrication of a leak-tight RBSC-sintered silicon carbide tube assembly that can survive service temperatures demonstrates the feasibility of using microwave joining to fabricate high temperature heat exchangers in which sintered silicon carbide is used only in the highest temperature sections, and RBSC provides the transition to the metal sections.

*[Research performed by Technology Assessment and Transfer, Inc. *-George Mason University-Los Alamos National Laboratory, sponsored by DOE-AIM and SBIR Programs and Virginia Center for Innovative Technology (CIT)]*

**Research team currently based at FM Technologies, Inc., Fairfax, VA.*

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

PROJECT TITLE: Microwave Joining of SiC

PHASE: FY 1994

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

PHASE OBJECTIVE: Optimize joining methods, including forming interlayers in situ, and develop applicators and techniques for joining of longer and larger tubes.

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: A small scale tube assembly of RBSC-sintered SiC has been fabricated using microwave joining. This tube assembly was demonstrated to be leak-tight before and after cycling between ambient temperature and 1100°C. RBSC-RBSC and RBSC-sintered SiC butt joints sectioned from the tube assembly were identical in appearance to those sectioned from joined RBSC-RBSC tube sections that had average mechanical strength of 190 MPa, more than adequate for radiant burner and heat exchanger applications.

Patents: none

Publications: 7

Proceedings: 6

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.

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 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 for which a demonstration of this method is planned in FY 1995.

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.

AIM

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5 of 5

Microwave Processing of Materials: Glass-Ceramics

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INTRODUCTION

Glass-ceramics are important commercial materials that are used extensively in severe thermal environments such as heat exchangers, regenerators, missile nose cones, high-temperature windows, and cookware. Processing glass-ceramics with microwaves presents an excellent opportunity to apply the principles already learned from studies of sintering and grain growth in ceramics. Nucleation and growth of ceramic crystals from a glass matrix is a diffusion-limited process. Therefore, it is likely that nucleation and growth will be accelerated by microwave heating. It is also likely that the microstructures produced by microwave processing will be different from those produced by conventional processing.

A major concern in conducting microwave furnace experiments is to ascertain that temperature is properly measured. Because the sample is heated directly by the microwave energy (and not by indirect methods such as radiation or convection), temperature measurement must be made directly within the sample, and not simply in the vicinity of the sample as is often done in conventional furnaces. This investigation made simultaneous measurements of temperature in ceramic samples (alumina and zirconia) using a thermocouple, an optical fiber probe, and a 2-color infrared pyrometer. Agreement among the three types of measurement ($\pm 20^{\circ}\text{C}$) was well within the range typically achieved for conventional furnaces.

TECHNICAL PROGRESS

Glass-ceramic processing

Experiments have been performed on the heat treatment of commercially-available glass-ceramic compositions. Side-by-side studies of heat treatments to effect the glass to glass-ceramic

conversion were made to determine what advantages are provided by microwave processing as compared with conventional thermal processing. Standard nucleation and growth studies are being conducted. Techniques being used in these studies include x-ray diffraction and microstructural evaluation.

The initial study of glass-ceramic processing is being conducted using a commercial glass-ceramic produced by Corning, Inc. called FotoForm®. It is based on the $\text{Li}_2\text{O} \cdot \text{SiO}_2$ (lithium metasilicate) and $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (lithium disilicate) systems. Normal processing of this material involves UV exposure to form pre-nuclei, followed by a heat treatment schedule consisting of nucleation at 515°C and crystallization at either 615°C (to form the metasilicate) or at 815°C (to form the disilicate). The metasilicate is relatively soluble in HF (compared to the parent glass) and can be etched away to form intricate shapes, if desired.

The glass was supplied in rectangular sheets, $\approx 20 \times 25$ cm (8 x 10 in), that had received a standard UV flood at Corning to form the pre-nuclei. The sheets were cut into coupons, 2.5 x 2.5 cm (1 x 1 in) for heat treatment. All of the coupons were heat treated conventionally at 515 °C for 1 h to nucleate the glass. After nucleation, heat treatments were performed in both conventional and 2.45 GHz microwave furnaces. Figure 1 shows the experimental setup being used to study glass-ceramic thermal processing in the microwave furnace. The heat-treated glass samples were analyzed using both x-ray diffraction and microstructural analysis.

The formation of both the metasilicate ($\text{Li}_2\text{O} \cdot \text{SiO}_2$) and the disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) phases from the parent glass was accelerated by microwave heating as compared with conventional heating, Figure 2. In the as-nucleated state only a broad diffraction hump was observed; no change was observed after heat-treatment at 515°C conventionally, Figure 2d. In contrast, microwave heat treatment at 515°C or conventional heat treatment at 615°C produced a fully developed metasilicate pattern, as shown in Figure 2c. Microwave heat-treatment at 575°C showed the development of the disilicate phase, as well as remnants of the metasilicate phase. Heat-treatment at 815°C conventionally showed the fully developed disilicate phase.

Figure 1. Schematic of arrangement for processing glass-ceramic parts in the microwave furnace.

Figure 2. The phases present in the heat-treated FotoForm® glass depended on the processing temperature and the method of heating: (a) The disilicate phase was formed at 815°C in a conventional furnace. (b) A mixture of meta- and disilicate phases was formed at 575°C in the microwave furnace. (c) The metasilicate phase was formed at 515°C in the microwave furnace and at 615°C in the conventional furnace. (d) No crystalline phases were present in the glass conventionally heat treated at 515 °C.

The results of this investigation so far indicate that microwave processing lowers the processing temperature for this particular glass ceramic by ~100 to 150°C. This is in agreement with previous results obtained in this and other programs on the processing of ceramics and glasses using microwave heating.

Temperature measurement

Introduction

The importance of accurate temperature measurement inside a microwave furnace is manifested in the reliance on temperature to describe system behavior. Whether it be the sintering of a green powder compact, or a description of microstructural evolution, temperature has become a defining measurement in the field of ceramic processing. Furthermore, temperature measurements have also become important in describing the comparison between microwave and conventional furnaces—and more importantly the advantages of one over the other.^{1,2} Therefore, it is necessary to ensure that temperature is measured correctly in a microwave furnace.

Typical methods of measuring temperature in both a conventional and microwave furnace include the use of thermocouples, radiation pyrometers, and optical fiber probes. Thermocouples used in this study were made of reference grade wire with an accompanying Certificate of Compliance. Likewise, the optical fiber probe and radiation pyrometer were calibrated by the manufacturer. In high temperature (>800°C) ceramic processing, all three instruments have suitable measurement ranges in both furnaces. In any of these cases, the accurate measurement of temperature inside a microwave furnace is a non-trivial problem.

Materials and methods

In this study, conditions were optimized for the temperature measurement of ceramic parts in a 2.45 GHz microwave furnace. Measurements were also made in a conventional furnace under similar conditions to facilitate a direct comparison of measured temperature in the two different environments. In addition, two different materials (dense alumina and dense zirconia) were

studied to examine the effect of material properties and heating behavior on temperature measurement.

Conventional Furnace Approach

The temperature measurement comparison in an electrically-heated conventional furnace served as a reference to establish a reasonable temperature measurement variation. For this comparison we used a NEYTECH 85P furnace* to heat an 85g sample of dense alumina. This sample was cylindrical in shape with a diameter of 3 cm and a height of 5 cm. The alumina part was also machined to allow for the insertion of two type-S thermocouples (one sheathed in platinum and the other in inconel) and an Accufiber® lightpipe# directly into the sample. The lightpipe was covered with a stainless steel tube to prevent light emitted from the heating elements from affecting the measurement. To further reduce the “shine-through” from the heating elements, the entire sample was covered with a 0.5 cm thick sintered SiC optical shield. A diagram of the conventional furnace system appears in Figure 3. The conventional furnace was programmed to follow a temperature profile that provided temperature measurements from all three devices at several temperatures between 600-1000°C. A steady-state temperature was maintained at each set point for at least thirty minutes. The tips of all three temperature measurement devices were no more than 2 cm apart.

Microwave Furnace Approach

For processing in the microwave furnace, ceramic samples were prepared from die-pressed alumina (Baikowski CR30)† and zirconia (TOSOH TZ-8Y)‡ powder. For both materials, using a stack of three parts allowed the machining necessary to fully embed the thermocouple and lightpipe within the middle part of the sample stack. A similar hole was machined in the top part of the sample stack to produce a blackbody cavity necessary for accurate pyrometer measurements. The sample stack was cylindrical in shape with a diameter of 5 cm and a height of 6 cm. The ceramic samples of both materials were sintered in a conventional furnace to full density prior to temperature measurement experiments.

* Neytech , Yucaipa, CA

LUXTRON, Accufiber Division, Beaverton, OR

† GTE Products Corporation, Exeter, NH

‡ TOSOH Corporation, Japan

Figure 3. Conventional furnace temperature measurement system.

Each sample stack was enclosed in an insulation system composed of refractory fiberboard to prevent heat loss from the sample. The fiberboard of the insulation system was of the same material as the sample stack to ensure similar heating characteristics and to eliminate unwanted temperature gradients. In addition, in both the alumina and zirconia systems a “picket fence” of 0.6 cm diameter SiC rods was used to provide indirect heating of the sample stack at lower temperatures (<500°C).³

The microwave furnace used a 6 kW, continuously variable, 2.45 GHz microwave generator. The microwave cavity consisted of a water-cooled aluminum vessel 70 cm in diameter by 120 cm long. The cavity had ports for both the thermocouple and lightpipe as well as an optical window for an IRcon® 2-color infrared pyrometer.^Δ A diagram of the microwave furnace system appears in Figure 4.

To prevent arcing and false temperature measurements the thermocouple had a platinum sheath to shield the thermocouple wires from the microwave field. In addition, an alumina tube covered the thermocouple, as well as the lightpipe, to reduce material discontinuities inside the sample stack. Additionally, for the thermocouple, the alumina tube also helped to prevent arcing and subsequent temperature misrepresentations.

^Δ IRcon Inc., Niles, IL

Figure 4. Microwave furnace temperature measurement system.

Results and discussion

Comparisons between the temperature measurement devices in both the conventional and the microwave furnaces were reasonably close. In the dense alumina sample that was heated in the conventional furnace, both of the thermocouples and the lightpipe gave readings within 12°C of one another (see Figure 5, Table 1). Over the entire temperature range, the two thermocouples were in very good agreement—within 2°C. The lightpipe, inserted into a different hole in the ceramic sample, deviated slightly from that of the thermocouple as the temperature of the furnace increased. Precautions taken to prevent “shine-through” from the heating elements were effective in eliminating disturbances in the measurement of the lightpipe. The temperature range of the conventional furnace limited measurements to 1000°C.

In the microwave furnace, temperature measurements were made with a comparable degree of variation. Temperature measurement variation among the three devices in the microwave furnace was generally within $\pm 20^\circ\text{C}$ (see Figure 6 & 7, Table 2). The pyrometer showed the largest variation from the other two devices probably due to the emissivity properties of alumina and zirconia. More importantly, the thermocouple and lightpipe measurements were in accordance with the 12°C maximum temperature differential observed in the conventional furnace.

Figure 5. Temperature measurement of an alumina sample stack in a conventional furnace.

Table 1. Comparison of Steady-State Temperatures (30 min hold) Measured in an Alumina Block Heated in a Conventional Furnace.

Type S T/C Pt sheath (°C)	Type S T/C Inconel sheath (°C)	Accufiber® Lightpipe (°C)
978	979	967
882	882	873
784	783	777
683	683	678
587	586	582

Figure 6. Temperature measurement in an alumina sample stack in a microwave furnace.

Figure 7. Temperature measurement in a zirconia sample stack in a microwave furnace.

Table 2. Comparison of Steady-State Temperature Measurements in a Microwave Furnace.

	Zirconia		Alumina	
Type S Thermocouple (°C)	Accufiber® Lightpipe (°C)	Infrared Pyrometer (°C)	Accufiber® Lightpipe (°C)	Infrared Pyrometer (°C)
1400	****	****	1409	1384
1300	1280	1312	1303	1285
1200	1187	1219	1200	1187
1100	1093	1126	1102	1091
1000	990	1038	1003	996
900	913	940	****	****

In the microwave furnace, systematic differences were noted between the alumina and zirconia samples. As in the conventional furnace, temperature measurement differences in the alumina sample increased with increasing temperature. The opposite behavior was observed in the zirconia stack where the difference in temperature measurements decreased with increasing temperature.

The difference in behavior between the alumina and zirconia samples can be seen by considering the readings from both the lightpipe and the pyrometer with respect to the thermocouple in Table 2. For the alumina stack, the lightpipe reading increased from 3°C to 9°C above the thermocouple's reading as the furnace temperature increased from 1000°C to 1400°C. The pyrometer reading increased from 4°C to 16°C below the thermocouple's reading over the same temperature range. The opposite behavior occurred for the zirconia samples. In the zirconia samples, temperature deviation from the thermocouple reading decreased with increasing furnace temperature with the pyrometer reading above and the lightpipe reading below the thermocouple reading. Generally, the thermocouple reading was between that of the lightpipe and the pyrometer indicating that the thermocouple is not grossly inaccurate.

In all cases, the heating behavior of the alumina and zirconia systems was consistent in all microwave heating experiments. Furthermore, the relationship between temperature difference and furnace temperature was independent of the staircase direction of the programmed temperature profile. However, measurement agreement generally improved during the steady state plateau and the ramp-down as compared with the ramp-up to temperature.

Summary

It has been demonstrated in this study that with careful planning good agreement between temperature measurement devices is possible inside a microwave furnace. This includes the use of thermocouples, radiation pyrometers, and optical fiber probes. It should be emphasized that careful attention must be paid to the proper shielding of temperature probes such as thermocouples and lightpipes to prevent inaccurate measurements caused by arcing and “shine-through”, respectively. In addition, proper positioning of the temperature measurement devices inside of the heated sample is necessary to avoid significantly low measurements.

References

1. T.N. Tiegs, J.O. Kiggans and H.D. Kimery, “Microwave Processing of Silicon Nitride,” in **Microwave Processing of Materials II**, W.B. Snyder, W.H. Sutton, D.L. Johnson, and M.F. Iskander, eds., *MRS Symp. Proc.*, **189**, 267-72 (1991).
2. M.A. Janney, H.D. Kimery, M.A. Schmidt, and J.O. Kiggans, “Alumina Grain Growth in a Microwave Field,” *J. Am. Ceram Soc.*, **74** [7] 1675-81 (1991).
3. M.A. Janney, H.D. Kimery, and J.O. Kiggans, “Microwave Processing of Ceramics: Guidelines Used at the Oak Ridge National Laboratory,” in **Microwave Processing of Materials, III**, R.L. Beatty, W.H. Sutton, and M.F. Iskander, eds., *MRS Symp. Proc.*, **269**, 173-85 (1992).

PUBLICATIONS

Journals

N/A

Other Publications

D.J. Grellinger and M.A. Janney, "Temperature Measurement in a 2.45 GHz Microwave Furnace," to be published in **Microwaves: Theory and Practice in Materials Processing, II**, D.E. Clark, et al, eds., *Ceramic Trans.* (1993).

PRESENTATIONS

D.J. Grellinger and M.A. Janney, "Temperature Measurement in a 2.45 GHz Microwave Furnace," presented at the Annual Meeting of the American Ceramic Society, Cincinnati, OH; April, 1993.

HONORS AND AWARDS

N/A

PATENTS/DISCLOSURES

N/A

LICENSES

N/A

COST INFORMATION

PERSONNEL INFORMATION

N/A

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Corning, Inc. provided samples of glass-ceramic for evaluation.

COST SHARING

None

HIGHLIGHTS

Preliminary indications show that the processing temperature for FotoForm® glass-ceramic can be lowered by ~100°C by microwave processing.

We have demonstrated that excellent agreement among three different temperature measurement devices (thermocouple, optical light-pipe, and two-color pyrometer) in a microwave furnace can be achieved. Thus, we have demonstrated that our claims of microwave processing temperatures as measured by thermocouple are quite reasonable.

Microwave Processing of Materials: Zirconia-Toughened Alumina

Problem:

Microwave heating represents an emerging technology for high temperature processing of materials. Processing glass-ceramics with microwaves presents an excellent opportunity to apply the principles already learned from studies of sintering and grain growth in ceramics. Nucleation and growth of ceramic crystals from a glass matrix is a diffusion-limited process. Therefore, it is likely that nucleation and growth will be accelerated by microwave heating. It is also likely that the microstructures produced by microwave processing will be different from those produced by conventional processing.

Results:

The results of this investigation so far indicate that microwave processing lowers the processing temperature for this particular glass ceramic by ~100 to 150°C. This is in agreement with previous results obtained in this and other programs on the processing of ceramics and glasses using microwave heating.

It has been demonstrated in this study that with careful planning good agreement between temperature measurement devices is possible inside a microwave furnace. This includes the use of thermocouples, radiation pyrometers, and optical fiber probes. It should be emphasized that careful attention must be paid to the proper shielding of temperature probes such as thermocouples and lightpipes to prevent inaccurate measurements caused by arcing and "shine-through", respectively. In addition, proper positioning of the temperature measurement devices inside of the heated sample is necessary to avoid significantly low measurements.

Significance for Energy Conservation:

Energy benefits are expected from the more direct use of energy afforded by microwave heating and the lower processing temperatures.

Significance for Materials Technology:

Microwave heating provides new routes for processing ceramic materials with improved properties and unique microstructures.

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Microwave Processing of Materials:Glass-Ceramics

PHASE: FY1993

COMPLETION DATE: FY1995

PRINCIPAL INVESTIGATOR:

Mark A.Janney

Metals and Ceramics Division, Oak Ridge, TN 37831-6087, (615)574-4281

PHASE OBJECTIVE: Processing glass-ceramics with microwaves presents an excellent opportunity to apply the principles already learned from studies of sintering and grain growth in ceramics. Nucleation and growth of ceramic crystals from a glass matrix is a diffusion-limited process. Therefore, it is likely that nucleation and growth will be accelerated by microwave heating

ULTIMATE OBJECTIVE: The ultimate objective of this project is to provide clear engineering guidelines for using microwave processing in an industrial environment for high temperature applications.

TECHNICAL APPROACH:

At ORNL, the work has focused on two efforts. (1)Experiments have been performed on the heat treatment of commercially-available glass-ceramic compositions. Side-by-side studies of heat treatments to effect the glass to glass-ceramic conversion were made to determine what advantages are provided by microwave processing as compared with conventional thermal processing. Standard nucleation and growth studies are being conducted. (2) Conditions were optimized for the temperature measurement of ceramic parts in a 2.45 GHz microwave furnace. Measurements were also made in a conventional furnace under similar conditions to facilitate a direct comparison of measured temperature in the two different environments. In addition, two different materials (dense alumina and dense zirconia) were studied to examine the effect of material properties and heating behavior on temperature measurement.

PROGRESS:

Patents: 0

Publications: 0

Proceedings: 1

Presentations: 1

ACCOMPLISHMENTS:

Licenses: ----

Known follow-on Products: ---

Industry workshops: ---

Technology Transfer or Industrial Interaction: Corning Inc. provided the glass-ceramic precursor materials for this investigation.

PROJECT TITLE: Microwave Processing of Materials: Glass-Ceramics

CRITICAL ISSUES: Identification of mechanisms responsible for “microwave effect.”

FUTURE PLANS: Continue investigations on processing of glass-ceramics to include compositions that sinter as glasses, then convert to the crystalline state.

POTENTIAL PAYOFF: New manufacturing processes that are more energy efficient may result from the glass and glass ceramic effort. Furthermore, lower temperature processing would allow some glasses to be used in applications that are currently not feasible.

FUNDING HISTORY:

ESTIMATED ENERGY SAVINGS:

POLYMERIC MATERIALS WITH IMPROVED SURFACE PROPERTIES

E. H. Lee
G. R. Rao*
L. K. Mansur

Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6376

INTRODUCTION

The main thrust of this program is to improve surface-sensitive properties of polymers using ion beam treatments. The major objectives of this investigation are: (1) Use single and multiple ion beam treatments to modify surface-related properties of polymers, (2) characterize these modifications by using specific test methods for different properties, (3) understand basic underlying mechanisms for the modification of properties with a view towards tailoring polymer surfaces using ion beams, and (4) transfer technology to industries that can use this technique for specific applications through the DOE Office of Technology Transfer (OTT) end user programs.

TECHNICAL PROGRESS

Summary

The effects of ion implantation on surface sensitive properties of polymers were investigated with two specific goals in mind. One was to understand ion implantation effects from a fundamental standpoint to aid in the tailoring of polymer surfaces, and the second was to conduct in-depth investigations on improvements in wear properties of polymers by ion implantation. Improvements in wear behavior can have significant impact for industrial applications requiring lightweight materials with hard, durable surfaces.

A Monte Carlo computer code TRIM, TRAnsport of Ions in Matter (1992 version), was used to determine and quantify changes caused by ion implantation. Energetic ions impinging on a material lose their energy through (1) electronic stopping or ionization of substrate

*ORNL Post-Doctoral Research Program Administered by ORISE.

atoms, (2) displacements or nuclear stopping that causes recoils, (3) phonons, and (4) plasmons. TRIM calculations, and correlations with hardness data for ion implanted polymers indicated that the linear energy transfer (LET) for ionization was the most important factor for enhancement of hardness due to promotion of cross-linking, whereas LET for recoils caused chain-scission, which is detrimental to hardness improvements. In general, it was observed for various ion implanted polymers that with increasing ionization and decreasing recoils, the improvement in hardness was greater. Plasmons and phonons do not appear to play a significant role in hardness improvements.

The basic mechanisms of LET were demonstrated and confirmed using a series of experiments. TRIM calculations for 200, 1000, and 2000 keV He⁺ implantation in polystyrene and Mylar (Polyethylene Terephthalate) are shown in Fig. 1. The calculations predicted that the near-surface hardness of the 1000 keV He⁺ implanted specimens should be larger than the other two cases since LET for ionization was greater at the surface than for the other two energies. Hardness measurements were performed on the specimens and the results clearly confirmed the predictions for both PS and Mylar as shown in Fig. 1.

Ultra High Molecular Weight Polyethylene (UHMWPE) is an important polymer used in low friction applications. In particular, it is widely used in joint prostheses for human implants, for example in total hip joint replacements where it is typically mated against Co-Cr alloy. One problem is wear of the polymer along with debris formation, which can lead to other internal complications. Using 1 MeV Ar⁺ implantation, it was shown that wear properties of UHMWPE can be significantly improved at fluences above 5×10^{18} ions/m². Wear tests using a 1 N normal load and a reciprocating-sliding wear configuration showed no wear tracks visually after 10,000 cycles and 100 minutes of testing. A major side effect was the formation of implantation induced cracks, which however did not appear to diminish wear improvement. The cracks are believed to be formed due to buildup of residual stresses and contraction of polymer due to loss of species such as hydrogen during implantation. This study shows considerable promise for the use of ion implantation of polymers for biomedical applications.

Ion implantation of Poly(ether ether ketone), a high performance engineering thermoplastic also significantly improved wear properties. Implantation with 1 MeV Ar⁺ to three fluences of 5×10^{18} , 1×10^{19} and 5×10^{19} ions/m² significantly improved wear properties using both nylon and hard Cr-steel counterfaces. While significant improvements were observed for

(a)

(b)

Fig. 1. (a) TRIM calculations for 200, 1000 and 2000 keV He^+ implantation in PS and Mylar showing that LET for ionization is highest at the surface for the 1000 keV implantation. (b) Corresponding hardness measurements showing that the 1000 keV He^+ implanted specimens had the highest hardness values.

all three fluences for the nylon counterface, the best improvement for the steel counterface was obtained for the intermediate fluence indicating the existence of an optimum fluence and optimum implantation conditions.

In a collaborative effort with Lawrence Berkeley Laboratory, polypropylene (PP) was implanted with 100 keV Ti^+ and Ag^+ ions to fluences of 1×10^{19} , 1×10^{20} and 5×10^{20} ions/m² using a Metal Vapor Arc (MEVVA) source. For a nylon counterface, the best improvement in wear properties was obtained for the highest fluence Ti^+ -implanted PP specimen as shown in Fig. 2. The Ag^+ implanted specimen did not show a similar improvement. TRIM calculations showed that the 100 keV Ag^+ implantation had a higher recoil energy loss and lower ionization. In addition it was shown that for low energy implantation, a higher fluence can be used for improved properties.

In a separate study, PEEK, polystyrene and Kapton were implanted separately with 1 MeV He^+ , 1 MeV Ar^+ as well as 1 MeV He^+ and Ar^+ sequentially. Wear tests were performed using a Cr-steel counterface. Tests indicated that the He^+ implanted specimens did not show significant improvements over the wear properties of the unimplanted specimens. The Ar^+ implanted specimens showed good improvement in wear resistance. However, the sequential He^+ + Ar^+ implanted specimens showed the best improvement in wear properties. This was attributed to the formation of a thin, highly crosslinked surface layer formed by the Ar^+ implantations (about 1 μm thick) over a partially crosslinked He^+ implanted layer which was several micrometers deeper. Thus the use of varying ion species with different masses and different energies allows the formation of graded surface layers. This technique has significant potential for tailoring of surface properties of polymers.

RELATED PUBLICATIONS

1. E. H. Lee, Y. Lee, W. C. Oliver, and L. K. Mansur, "Hardness Measurements of Ar^+ -Beam Treated Polyimide by Depth-Sensing Nanoindentation," *J. Mater. Res.*, **8**(2) (1993) 377-87.
2. G. R. Rao, Z. L. Wang, and E. H. Lee, "Microstructural Effects on Surface Mechanical Properties of Ion Implanted polymers," *J. Mater. Res.*, **8**(4) (1993) 927-33.
3. E. H. Lee, G. R. Rao, M. B. Lewis, and L. K. Mansur, "Ion Beam Application for Improved Surface Properties," Invited Paper Presented at the IX International Conference on

Fig. 2. Improvements obtained for wear properties of polypropylene for 100 keV Ti^+ implantation for the fluence of $5 \times 10^{20} \text{ ions/m}^2$.

Ion Implantation Technology, Gainesville, Florida, September 21-24, 1992, *Nucl. Instrum. Meth. B. B74* (1993) 326-30.

4. E. H. Lee, D. M. Hembree, Jr., G. R. Rao, and L. K. Mansur, "Raman Scattering from Ion Implanted Diamond, Graphite and Polymers," Accepted for publication in *Phys. Rev. B*.
5. G. R. Rao, K. Monar, E. H. Lee, and J. R. Treglio, "Metal Ion Implantation Effects on Surface Properties of Polymers," Accepted for publication in *Surface and Coatings Tech.*.
6. E. H. Lee, G. R. Rao, M. B. Lewis, and L. K. Mansur, "Effects of Electronic and Nuclear Processes in Polymers during Ion Implantation," Submitted to *J. Mat. Res.*.
7. G. R. Rao, E. H. Lee, and L. K. Mansur, "Wear Properties of Boron Implanted Poly(ether ether ketone)," Submitted to *Wear*.
8. G. R. Rao and E. H. Lee, "Argon Implantation Effects on Wear Properties of Ultra High Molecular Weight Polyethylene," In preparation; To be submitted to *Wear*.
9. G. R. Rao, E. H. Lee, X. Yao, and I. G. Brown, "Wear property improvements in polypropylene by metal ion implantation," In preparation; To be submitted to *Journal of Materials Science*.
10. G. R. Rao, E. H. Lee, and R. Bhattacharya, "Wear properties of high energy ion implanted polycarbonate," In preparation; To be submitted to *Journal of Materials Research*.

PRESENTATIONS

1/6/93	Visit, Dr. Howard Creveling, Jr., et al., Allison Turbines
1/7/93	Visit, Mr. Garland Cupp et al., American Express
1/19/93	Visit, Dr. Viktor L'vovich Talrose, Director of the Institute of Energy Problem of Chemical Process, Russian Academy of Science
3/3/93	Visit, Dr. Klaus Dahl, Raychem Corporation
4/7/93	Visit, Dr. David Cheng (Corporate Director of Technology Transfer) Hughes Aircraft Company, visit, presentation for ion implantation program
5/13/93	Invited Talk, Gillette Company, Boston, MA.
6/17/93	Visit, Mr. Mikell W. Schultheis, Principal Engineer Corporate Packaging, The Coca Cola Company
6/21/93	Visit, Dr. Eugene D. Schukin, Visiting Prof. North Carolina State Univ., Raleigh, NC (Member Russian Academy and U.S. National Academy of Engineering)

6/22/93	Visit, Mr. Morris A. Johnson (Manager New Development) and Dr. Harrell E. Tweedy (R&D Scientist), UCB Radcure Inc
6/28/93	Visit, Dr. D. V. Sears et. al., Bausch & Lomb, Rochester, New York
6/28/93	Visit, Dr. Mervyn J. Miles, H.H. Wills Physics Laboratory, University of Bristol, England (Field: STM and AFM of polymers)
7/13/93	Invited Talk, Implant Sciences Corporation
7/14/93	Invited Talk, Army Research Laboratory, Watertown, MA.
7/15/93	Invited Talk, Spire Corporation, Bedford, MA.
7/29/93	Presentation to Dr. John A. Midgley, Director, Corporate Technology, Raychem Corporation.
8/20/93	Presentation to Dr. Larry Carol at GM-AC Rochester, Flint, MI.
8/25/93	Presentation to Jack W. Hurd, Office Deputy Chief of Staff for Concurrent Engineering, HQ US Army Materials Command, Alexandria, VA.
9/2/93	Invited Talk, Howmedica, Rutherford, NJ.
10/7/93	Invited Talk, First Annual Symposium of the East Tennessee Section of the Materials Research Society.

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

None

LICENSES

None

COST INFORMATION

None

PERSONNEL INFORMATION

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Awaiting DOE approval of DP CRADA with General Motors.

Over 500 companies have expressed interest and have requested additional information.

COST SHARING

This work is jointly supported by the Division of Materials Sciences, U.S. Department of Energy.

CORRELATION OF LINEAR ENERGY TRANSFER MECHANISMS WITH HARDNESS IMPROVEMENTS FOR ION IMPLANTATION OF POLYMERS

TECHNICAL ACCOMPLISHMENT

- Monte Carlo (TRIM) calculations were used to compute Linear Energy Transfer values for the implantation of energetic ions in polymers
- The greater the Linear Energy Transfer for Ionization, greater is the improvement in hardness
- This correlation was used to correctly predict qualitative hardness improvements in ion implanted polymers

SIGNIFICANCE

- Linear Energy Transfer calculations can be used to determine best implantation conditions for maximum improvement in properties
- Means now available to optimize and tailor polymer surfaces with required properties
- Technological applications feasible because of better understanding of underlying mechanisms

Polystyrene implanted with 1000 keV He⁺ showed best hardness improvement due to highest level of ionization at the surface as compared to 200 and 2000 keV implantations

PROJECT SUMMARY

ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

WORK ELEMENT: Materials Processing Technology

PROJECT TITLE: Polymers with Improved Surface Properties

PHASE FY 1993

PHASE COMPLETION DATE: Continuation

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

PRINCIPAL INVESTIGATOR(S): E. H. Lee (624-5058) and L. K. Mansur (624-4797)

PHASE OBJECTIVE: The objective is to develop innovative technologies for surface modification of polymers.

ULTIMATE OBJECTIVE: To produce smooth, hard, and wear resistant polymers for applications requiring light weight and improved properties.

TECHNICAL APPROACH: Modify surface-sensitive properties of polymers by unique multiple-ion beam treatments and plasma processing and characterize induced changes in microstructure, microcomposition, and properties.

PROGRESS: Investigated effects of ion implantation on mechanical and electrical properties of basic and engineering polymers. Studied effects of shallow depth implantation of metallic ions in the polymers. Also studied correlations between mechanical and electrical properties of the ion implanted polymers to understand underlying mechanisms responsible for the improvements.

Patent Disclosure: 1 **Publications:** 14 **Proceedings:** - **Presentations:** 6

ACCOMPLISHMENTS:

Licenses: To be explored in future

Known Follow-on Product(s): Hard and wear resistant polymers have potential applications for machinery components and barriers for chemical attack.

Industry Workshop: A proposal for Defense Projects CRADA was submitted to work with General Motors.

Other Successful Technology Transfer Activities as Evidence of Industry Interest:
Several invited talks were given to various academic and industrial institutions.
Seventeen presentations also given to visitors to ORNL. Over 500 requests for
information on the new technology were responded to.

PROJECT TITLE: Polymers with Improved Surface Properties

CRITICAL ISSUES: The specific issues are: (1) surface modification by single and multiple-ion beam treatments; (2) structure and properties characterization by AEM, ion scattering/nuclear reaction techniques and mechanical testing; (3) mechanistic analyses to relate the properties measurements to the ion beam processing parameters and to the microstructural and microcompositional results in order to develop principles for improved materials; and (4) transfer the technology developed to industry.

FUTURE PLANS: (1) Produce and characterize polymer alloys which are multiply crosslinked by ion beam technique. (2) Complete mechanical tests on unmodified and ion-beam treated specimens. (3) Carry out a systematic study to identify the effects of ion species, dose, energy, and polymer structure on surface-sensitive mechanical properties. (4) Explore potential collaborative research programs with industries.

POTENTIAL PAYOFF: Improved surface polymers will permit the use of ordinary soft and mechanical-damage-susceptible material in what are normally hard-material applications with the large advantages of their light weight and easy moldability.

SELECTIVE INORGANIC THIN FILMS

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INTRODUCTION

This project is developing inorganic thin films as membranes for gas separation applications, and as discriminating coatings for liquid-phase chemical sensors. Our goal is to synthesize these coatings with tailored porosity and surface chemistry on porous substrates and on acoustic and optical sensors. We are focusing on improving permeability and molecular sieve properties of membranes produced via sol-gel methods by converting them into crystalline zeolitic films. We are also using sol-gel methods to yield thin perovskite films as oxygen-selective membranes. Acoustic plate mode (APM) oscillators and surface plasmon resonance (SPR) sensors are used as substrates for film deposition, both to assist in determining film properties and to improve their sensitivity and selectivity to aqueous chemical species.

TECHNICAL PROGRESS

Summary

A goal of this project is to develop a class of molecular sieve membranes for light gas separation applications. These membranes ideally consist of continuous, highly ordered, polycrystalline thin films of a zeolitic phase deposited on a porous substrate, such as a γ - Al_2O_3 filter. Hydrothermal treatment of silicate substrates in alkaline solutions can lead to a variety of zeolitic phases. We have studied the parameters that control the extent of reaction and product phase, using both glass coupons and supported sol-gel films as nutrient. We have also synthesized a series of perovskite films by crystallizing a sol-gel precursor, and evaluated the performance of these films by calculating oxygen diffusion rates. The project continued to evaluate coated APM oscillators in order to measure the chemical selectivities of sol-gel films, and also developed a

method for using surface plasmon resonance to measure important physical properties of films such as refractive index, porosity, and thickness.

Milestones

1. Complete parametric studies on preparation of porous hydrous titanate coatings:

Control of the process variables that influence the hydrolysis and condensation reactions that occur in solution dictates the development of microstructure in the deposited film. Our understanding and control of thin film hydrous titanate (HTO) processing has allowed deposition of reproducible high surface area films. We found that spin-coating was preferred as the deposition method for developing high surface area HTO films. To optimize the processing of films deposited by spin-coating, we followed the refractive index changes in HTO films as a function of both solution age (1 - 7 days) and spin rate (2000 - 5000 rpm). As expected, film thickness was found to vary inversely with spin rate, regardless of solution age. If the polymeric species in solution are unaffected by deposition conditions, then only a slight variation in the corresponding refractive indices would be expected. We observed considerable variation in refractive index as a function of spin rate at short aging times (1 and 3 days). This effect virtually disappeared by 7 days. At the shorter aging times, the refractive index for the higher spin rates (4-5K rpm) was higher than that measured for 3K rpm samples. This result suggests that the polymeric species collapse to form denser (higher index) structures at the faster deposition rate. The stability of refractive index from center to edge of films deposited on 3 inch diameter silicon wafers appears to partially contradict this suggestion.

Deposition conditions have a great effect on the structure of HTO films. For example, films deposited after short aging times are quite sensitive to deposition conditions but result in a wide range of refractive indices (and perhaps other properties). Films from more aged solutions were unaffected by deposition but showed little variation in refractive index.

2. Synthesize crystalline and composite inorganic films:

Zeolitic membranes that can separate light gases by molecular sieving would benefit a number of industries, particularly natural gas recovery and refining, if they can be used on large scale processes. This will likely require membranes more rugged and permeable than those now available. One strategy for making such membranes is to nucleate zeolite crystals from a thin sol-gel film supported on a porous substrate such as a γ - Al_2O_3 gas filter. Once optimized, this process would enhance permeability by limiting thickness and improving adhesion to the substrate.

We have set up Plackett and Burman-type matrices to identify the synthetic parameters that are most significant in controlling the quality and crystalline phase of the zeolite films. Substrates include borosilicate glass coupons, and Si-Al-O and Ca-Al-Si-O films spin-coated onto Si wafers. The glass substrates are useful for studying the influence of reaction conditions on film growth. The sol-gel films are of interest both as nutrients for zeolitic films, and as hosts for intra-pore growth of zeolite crystals. The high degree of porosity of these films should accelerate nucleation and growth of zeolitic phases, and it is hoped that this growth can occur under conditions mild enough to yield continuous films, and to prevent the nutrient from dissolving in the mother liquors. Reactions are carried out in Teflon bottles containing water, the nutrient (glass or supported film), a source of soluble Al ($\text{Na}_2\text{AlO}_2\text{OH}$ or $\text{Al}(\text{OC}_2\text{H}_5)_3$), a template ion (usually sodium, as NaOH or NaCl), and in some cases a source of reactive Si, such as $\text{Si}(\text{OC}_2\text{H}_5)_4$.

Initial studies used 5- and 6- parameter 8×8 matrices that explored the relative importance of reaction time, Al concentration, Na/Al ratio, water concentration, additional reactive silica, Na source, Al source, and room temperature aging time. These studies indicated that the most significant parameters are reaction time and pH. At long times and high pHs (>12), both films and substrates were heavily etched. A full matrix (16 samples) was used to study the effects of gelation and crystallization times under less alkaline conditions. Gelation times were 0 and 1 hr at pHs of 9 and 11, crystallization times were 1 and 5 hr at pHs of 7 and 9. These conditions yielded partial or complete conversion of the surface to zeolite with little or no etching (Figure 1a). By adjusting starting $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ ratios, films that contained pure sodalite, Linder Type A, and cancrinite phases could be produced.

We also begun to investigate growth of nonaluminosilicate microporous films such as zinc phosphates, using Zn metal as the starting material. A thick film of a porous cesium zinc phosphate phase with a channel structure is shown in Figure 1b.

3. Sol-Gel Preparation of Defect Perovskites for Oxygen Selective Membranes:

Defect perovskite oxides, generally represented by the formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$, are known to exhibit mixed ionic and electrical conductivity when the A sites are partially substituted with cations of lower valence, and the B sites are occupied with transition metal cations. For example in the system, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$, substitution of Sr^{2+} for La^{3+} creates oxygen vacancies ($\delta > 0$), leading to quite high values of oxygen permeation, while the transition metals on the B sites contribute to electrical conductivity. For this reason defect perovskites are attractive candidates for oxygen selective membranes that would require no external electric circuits. Such

*Figure 1a: Zeolite crystals (small grains and cratered cube) nucleated from a sol-gel film.
Scale: 1 cm = 5 μ m*

*Figure 1b: Film consisting of crystals of a microporous cesium zinc phosphate phase.
Scale: 1 cm = 25 μ m.*

membranes would have perfect selectivity for oxygen leading to a number of applications such as oxygen enrichment, controlled oxidative processing and fuel cells. The challenge is to prepare such defect perovskites as ultrathin supported films in order to achieve practical fluxes.

Experiments performed by Arnaud Meunier (Ecole Polytechnique, Palaiseau, France) in collaboration with Phillipe Barboux (Universite de Paris VI) and Jeffrey Brinker (Sandia National Laboratories) utilized sol-gel techniques to prepare stable colloidal precursor sols useful for the fabrication of thin perovskite films. The experiments addressed sol synthesis, thermal conversion to perovskite, characterization of oxygen stoichiometry, and oxygen conductivity.

The objective of the synthetic efforts was to establish conditions required to obtain stable sols of the correct stoichiometry. The composition $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, which is known to exhibit the highest oxygen permeability in this family, was chosen as the target composition. A sol precursor was synthesized by hydrolyzing a mixture of ferric nitrate and cobalt acetate with strontium and ammonium hydroxides. The sols were deposited on fused silica substrates or concentrated and pressed into pellets, and were heated to temperatures ranging from 500-1000 $^{\circ}\text{C}$.

Chemical and structural changes during heating were characterized by thermogravimetric analysis (TGA) and X-ray diffraction (XRD). In some cases comparisons were made with "classic" perovskite powders prepared from mixtures of SrCO_3 , Co_3O_4 , and Fe_3O_4 . XRD results indicate that firing at 1000 °C for two hours in air was required to completely convert the precursors to the target perovskite phase. TGA was used to measure weight changes associated with gain or loss of oxygen during heating and cooling cycles performed in either oxygen or argon atmospheres in order to measure oxygen stoichiometry. We found that cooling perovskite slowly from 1000 °C under oxygen led to the composition $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.75}$. Subsequent heating to 750 °C under argon resulted in a weight loss of 2% corresponding to the composition $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.52}$, which is in agreement with literature values for similar types of heat treatments. Corresponding XRD studies performed on samples heated under identical conditions indicated that the perovskite phase was maintained at different oxygen stoichiometries, but the relative intensities of some peaks changed, suggesting a distortion of the crystalline lattice associated with oxygen vacancy formation.

Resistivity measurements were performed as a function of temperature and atmosphere for both pellets prepared from perovskite powders and films deposited on fused silica substrates. The resistivities of the perovskite samples decreased slightly with heating up to 400 °C in both oxygen and argon (0.0025 to 0.0015 ohm-cm) and then began to increase, presumably due to loss of oxygen above 400 °C. During cooling, samples in oxygen showed more or less reversible behavior while samples cooled under argon exhibited greatly increased resistivities with decreasing temperature (>0.1 ohm-cm), again due to the associated oxygen stoichiometry. Thin films (composed of the low temperature phase) heated and cooled in oxygen showed a decrease in resistivity with increasing temperature that was completely reversible on cooling. Resistivity values ranged from 0.006 to less than 0.001 ohm-cm.

By measuring the rate of change in resistivity associated with changing from an oxygen to an argon atmosphere, we could measure oxygen diffusion coefficients. At 300 °C, we obtained a value of $2 \times 10^{-6} \text{ cm}^2/\text{sec}$ for the perovskite phase. This compares favorably to the $\text{ZrO}_2\text{-CaO}$ solid electrolyte system, which is reported to possess diffusivities of ca. $10^{-7} \text{ cm}^2/\text{s}$ at 1000 °C.¹

4. Measured apparent selectivities of APM device coatings:

Prof. David Ballantine (Northern Illinois University) has measured attenuation and frequency response of film-coated APM devices as functions of solution composition. Studies on several different preparations of $\text{SiO}_2\text{-TiO}_2$ coatings indicate that porosity is the most important factor controlling sensitivity of the frequency shift in the device. These coatings enhance frequency

shift up to 4 orders of magnitude greater than the uncoated device, a sensitivity that is greater than that predicted by theory. This may be due to enhanced ion concentrations within the pores vs. the electric double layer on the bare APM device.

Measurements of the isoelectric points of the coatings have been made. These may allow selective detection of different metal ions in the same matrix by adding chelating agents of known speciation and stability constant, then measuring device response as a function of pH. He has also measured the response of APM devices upon which Ti metal was sputtered prior to film deposition. The films were prepared from four-component ($\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot \text{B}_2\text{O}_3$), sodium titanate, and $\text{SiO}_2 \cdot \text{TiO}_2$ sols by A. A. Russell (SNL). The Ti film "shorts out" acousto-electric coupling, which dominates the frequency shift of unmetallized devices, allowing the relative effects of mass-loading and viscoelasticity to be measured. When the devices are exposed to KNO_3 solution the frequency shift is positive, indicating that viscoelasticity dominates mass loading, which should yield a negative frequency shift. The increased frequency is thought to be due to electrostatic attraction of ions within the pores of the film, which may increase the film's stiffness.

It is expected that zeolitic films will improve sensitivity vs. the sol-gel coatings through increased porosity, and may increase chemical specificity through enhanced selectivity for metal ions of different size and charge.

5. Demonstrated modification of surface plasmon resonance (SPR) response using films:

Using this phenomenon to develop a new class of chemical sensors is a focus of Prof. Sinclair Yee's group at the Electrical Engineering Dept. of the University of Washington.² Surface plasmons, which are periodic variations in the density of charge on the surface of a metal, have characteristic wavevectors that depend on the type and thickness of the metal, and the dielectric constants of the media surrounding the surfaces of the metal (Figure 2a). When a beam of light strikes the metal surface, wavelengths that are of the same wavevector as the surface plasmons are absorbed by the metal, and the intensities of these wavelengths in the reflectance spectrum are attenuated. For a metal film of constant thickness on a given substrate, the absorbed wavelength thus depends on the angle of incidence of the light beam and the dielectric constant of the medium surrounding the film.

A simplified SPR geometry that lends itself to sensor and film characterization applications is shown in Figure 2b. The probe consists of a fiber optic cable terminated in a 1 cm section from which the cladding has been stripped and a silver or gold film has been applied. This section ends in a silver mirror deposited on the cut end of the cable. The probe may now be calibrated to determine the refractive index of a solution by measuring the wavelength of maximum absorbance.

Figure 2a: Traditional SPR configuration (reference no. 2).

Figure 2b: Fiber optic SPR sensor and system.

The sensitivity and specificity of the probe can be improved by depositing a sol-gel derived film onto the metal film. A high-index film improves the sensitivity of the probe to small changes of refractive index in low-index media. A film that is chemically specific to solution species of interest (e.g. metal ions) will change its index reversibly upon sorption and desorption of the species. In this program, we are interested in developing SPR as a technique for simplifying the determination of film properties such as thickness, refractive index, percent porosity, and pore size distribution. In addition, SPR may provide real-time data pertinent to film processing such as monitoring of pore formation during drying, and observation of swelling and solvent loss while soaking in aqueous solutions.

In collaboration with Prof. Yee's group, we have measured refractive indices and percent porosities for a series of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{BaO} \cdot \text{B}_2\text{O}_3$ films for which thickness had already been determined through ellipsometry and profilometry. Hardware and software are now available for simultaneously determining film thickness, refractive index, and percent porosity on a given sample. During the first half of FY94 we will investigate using SPR with BET measurements as a new technique for measuring film pore size and distribution.

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2. R. C. Jorgenson, S. S. Yee, K. S. Johnston, and B. J. Compton, *Proc. SPIE - Int. Soc. Opt. Eng.* **1993**, 1886, 35-48.

PUBLICATIONS

A. A. Russell, D. H. Doughty, D. S. Ballantine Jr., and R. Hart, "Influence of Porous Oxide Films on Acoustic Plate Mode Device Response to Ionic Solutions", *Proc. Electrochem. Soc. - Chemical Sensors II*, **1993**, PV93-7, 732-741.

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K. S. Johnston, R. C. Jorgenson, S. S. Yee, and A. A. Russell, "Characterization of Porous Sol-gel Films on Fiber Optic Surface Plasmon Resonance Sensors", *Proc. SPIE - Int. Soc. Opt. Eng.* **1993**, in press.

PRESENTATIONS

A. A. Russell, D. H. Doughty, D. S. Ballantine Jr., and R. Hart, "Influence of Porous Oxide Films on Acoustic Plate Mode Device Response to Ionic Solutions", Electrochemical Society, Honolulu, HI, June 1993.

M. L. F. Phillips, A. A. Russell, C. S. Ashley, D. H. Doughty, and D. S. Ballantine, "Chemically Selective Coatings", Advanced Industrial Concepts Annual Review Meeting, Oak Ridge, TN, June 1993.

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HONORS AND AWARDS

none.

PATENTS/DISCLOSURES

none.

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none.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

none.

COST SHARING

none.

HIGHLIGHTS

Films consisting of zeolite crystals and zeolite/sol-gel composites have been synthesized from supported sol-gel films. A surface plasmon resonance technique can be used to characterize physical properties of sol-gel films.

NEW ROUTES TO MOLECULAR SIEVE MEMBRANES

PROBLEM: Separating methane from other natural gas constituents (higher alkanes, N_2 , CO_2 , H_2S) using conventional polymer membrane technology is difficult. Molecular sieve membranes consisting of supported zeolitic films are not permeable or durable enough to be used for gas refining on a large scale.

RESULT: Hydrothermal processing of sol-gel films can nucleate zeolite crystals within an amorphous matrix. Phase evolution and degree of film crystallization can be controlled by altering reaction parameters such as pH and temperature.

*Zeolite crystals (small grains and cratered cube)
nucleated from a sol-gel film. Scale: 1 cm = 4 μm .*

SIGNIFICANCE: If membrane permeability and durability allow use on a sufficiently large scale, enhanced recovery at the wellhead and improved efficiency in gas refining could yield multiquad energy savings.

This work was performed at Sandia National Laboratories under DOE-CE-AIC Materials Program support.

PROJECT SUMMARY
ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Selective Inorganic Thin Films

PHASE: Materials Development

COMPLETION DATE: 10/1/96

PERFORMING ORGANIZATIONS: Sandia National Laboratories
Northern Illinois University
University of Washington

PRINCIPAL INVESTIGATOR: Mark L. F. Phillips, Dept. 1846
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PHASE OBJECTIVE: Investigate methods for processing amorphous precursors into crystalline inorganic molecular sieve coatings. Develop techniques for characterizing physical properties and chemical selectivity of films.

ULTIMATE OBJECTIVE: Develop new class of inorganic membranes for light gas separation and possibly catalysis. Use this technology to improve on separation efficiencies currently available with polymer membranes, particularly for light alkanes. Transfer technology base to industry.

TECHNICAL APPROACH: Nucleate and crystallize zeolitic phases from sol-gel derived amorphous coatings, 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.

PROGRESS: Porosity control has been achieved in several oxide film compositions. These films have been deposited on quartz acoustic plate mode (APM) devices. The sensitivities and selectivities of the coated devices were measured with dilute aqueous solutions of metal ions. Zeolite films and composite films of zeolites embedded in amorphous matrices have been synthesized. Surface plasmon resonance has been established as a film characterization method.

Patents: **Publications:** **Proceedings:** **Presentations:**

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1

2

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.

FUTURE PLANS:

1. Continue optimizing conditions for zeolite film synthesis.
2. Explore other sources (e.g. metallic and clay films) of nutrient for zeolitic film crystallization.
3. Use nonaluminosilicate molecular sieves (e.g. zinc phosphates, beryllioarsenates) as membrane phases.
4. Continue to develop surface plasmon resonance as a film characterization technique.

POTENTIAL PAYOFF: If gas membranes capable of enhanced separation of natural gas constituents can be employed economically on a large scale, multiquad energy savings could be achieved annually.

SILICON CARBIDE POWER SYNTHESIS

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[Contribution unavailable due to protected CRADA information.]

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