CONTINUOUS FIBER CERAMIC COMPOSITE PROGRAM

Technical Progress Report for Phase I

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**INDUSTRY ENERGY EFFICIENCY DIVISION
THE OFFICE OF INDUSTRIAL TECHNOLOGIES
DEPARTMENT OF ENERGY**

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TECHNICAL PROGRESS DURING PHASE I OF THE CONTINUOUS FIBER CERAMIC COMPOSITES PROGRAM

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EXECUTIVE SUMMARY

United States industry has a critical need for materials that are lightweight, strong, tough, corrosion resistant and capable of performing at high temperatures. The availability of such materials will enable substantial increase in energy efficiency and reduction in emissions of pollutants. Continuous fiber ceramic composites (CFCCs) are an emerging class of materials which have the potential for the desired combination of properties to meet the industrial needs. A \$10 billion annual market has been estimated for CFCC products by the year 2010, which equates to over 100,000 industrial sector jobs.¹

The Department of Energy's Office of Industrial Technologies completed in 1990 a comprehensive program plan for the development of CFCC materials.² The resulting CFCC program began in the spring of 1992 as a three-phase 10-year effort to (1) assess potential applications of CFCC materials, (2) develop the necessary supporting technologies to design, analyze and test CFCC materials, (3) conduct materials and process development guided by the applications assessment input, (4) fabricate test samples and representative components to evaluate CFCC material capabilities under application conditions and (5) analyze scaleability and manufacturability plus demonstrate pilot-scale production engineering. The program is a model partnership between industry, government, academia and national laboratories to provide energy savings and emission reductions for industry and a contribution to the economic prosperity of the nation.

DOE awarded 10 Phase I cooperative agreements to industry-lead teams plus identified generic supporting technology projects to benefit all of these contracts. This document highlights the broad progress and accomplishments on these contracts and support technology projects during Phase I:

- * Effective teams have been established to identify applications with high payoff, to conduct design studies to define material property and configuration goals, to conduct the necessary CFCC materials development, to establish a property database, to evaluate representative components in a realistic use environment, and to later scale up to commercialization. Each team includes a CFCC fabricator and one or more end user, plus several support team members such as a fiber supplier, a fiber coater, a property test laboratory and a composite design specialist.

- * Each team has identified one or more industrial applications that could benefit from use of CFCC components and has conducted sufficient design study to define the temperature, stress and configurational requirements for the CFCC material. These requirements have guided CFCC development during Phase I and have provided a basis for assessing feasibility to proceed to Phase II. The applications and benefits are described in the document "Continuous Fiber Ceramic Composites (CFCCs) for Low Cost Energy and a Cleaner Environment."¹

- * CFCC contractors have achieved substantial technical progress during Phase I as summarized in Table 1. Key challenges that have been focused on are achieving high temperature stability in an oxidizing or corrosive environment, retaining high strain-to-failure composite fracture behavior at high temperature, increasing the matrix cracking yield stress and establishing low cost fabrication processes. The matrix cracking yield stress is the stress at which cracks form in the matrix. Prior CFCC materials have not survived for long time when stressed at high temperature above the matrix cracking yield stress.

TABLE 1 SUMMARY OF PHASE 1 ACCOMPLISHMENTS

Team	Status of Technology Before CFCC Program	Status of Technology After Phase I
AlliedSignal	<ul style="list-style-type: none"> * Concept for diesel application * No existing CFCC or prior development 	<ul style="list-style-type: none"> * OEM Caterpillar identified two concepts and 11 options * OEM conducted finite element analysis * Viable design concept defined * Critical material property requirements defined * 60 compositions fabricated and tested * CFCC successfully developed * CFCC judged feasible by OEM
Alzeta	<ul style="list-style-type: none"> * Concept for burner application * No existing CFCC or prior development effort 	<ul style="list-style-type: none"> * High payoff applications defined * Two radiant burner concepts designed, fabricated and tested * Radiant output <u>doubled</u> compared to prior burner technology * 4500 hours, 12,000 cycles demonstrated with no material or performance degradation * Increase in temperature capability demonstrated * Commercialization in three years
Amercom	<ul style="list-style-type: none"> * Existing baseline material * Inadequate for oxidation, corrosion conditions of high temperature applications * Pitting and >0.1 mil/h recession at 950°C in sodium sulfate saturated air * Expensive non-reusable tooling * Inadequate controlled porosity for hot gas filtration application 	<ul style="list-style-type: none"> * High-payoff applications identified * Improved corrosion resistant CFCC developed * No visible degradation after 950°C in sodium sulfate saturated air * Process demonstrated with >50% reduction in tooling cost * Controlled porosity CFCC demonstrated

TABLE 1 SUMMARY OF PHASE 1 ACCOMPLISHMENTS (cont'd)

Babcock and Wilcox	<ul style="list-style-type: none"> * Existing baseline material * 24 ksi tensile strength * Low strain-to-failure (0.09%) * Fabrication required over 30 infiltration cycles * Batch fabrication * No effective interface coating 	<ul style="list-style-type: none"> * Improved properties, shapes * Doubled strength to 44 ksi * Improved strain-to-failure (.26%) * Fabrication achieved with <15 infiltration cycles; major cost reduction * Semi-automated fabrication demonstrated; more cost reduction * Interface coating demonstrated * Property database established * Modeling capabilities established * Applications identified, assessed * Representative components designed, fabricated and submitted to OEMs for testing
Dow Chemical Company	<ul style="list-style-type: none"> * No existing CFCC; concept only * No CFCC fabrication technology 	<ul style="list-style-type: none"> * Matrix slurries successfully formulated and coated onto fibers * Flat plate CFCC samples successfully fabricated with toughness eight times higher than monolithic matrix material * Major progress in tube fabrication; limit in initial trials to 26" radius of curvature; achieved 1" by end of Phase I * Application identified and rig built to assess material stability under application conditions
Dow Corning	<ul style="list-style-type: none"> * Existing baseline CFCC * Not stable in oxidizing atmosphere above about 1000°C * 6" by 6" plates demonstrated * Expensive CVD interface layer 	<ul style="list-style-type: none"> * Improved CFCC (40 ksi strength) with no strength decrease to 1200°C * 12" by 12" plates demonstrated * Decreased cost interface layer from liquid precursor * 75% strength retention after thermal shock from 1000°C to water * Equivalent strength with 50% less infiltration cycles * High payoff applications identified

TABLE 1 SUMMARY OF PHASE 1 ACCOMPLISHMENTS (cont'd)

DuPont Lanxide Composites CVI	<ul style="list-style-type: none"> * Existing baseline CFCC * High temperature durability limited; failed in less than 100 hours at 1200°C at 12 ksi * Composition options defined, but no database * No testing in application environments 	<ul style="list-style-type: none"> * Six options successfully fabricated * One improved CFCC did not fail after 4700 hours at 1200°C at 12 ksi * No CFCC strength loss after 500 hours exposure to simulated steam reformer gas stream at 1040°C * Survived 1500 hours at 1000°C in flowing coal gas with alkali sulfate additions
DuPont Lanxide CompositesTM DIMOX	<ul style="list-style-type: none"> * Existing baseline CFCC * Limited database * Unsafe interface coating process 	<ul style="list-style-type: none"> * Four modified CFCCs evaluated * Baseline still best * Safe interface coating process developed; viable for production scale * Improved uniformity of interface coating * Strength constant to 1200°C and only decreases to 33 ksi at 1370°C * Strength decrease of only 16% for thermal shock from 1200°C into water * Baseline material survived 1000 hours of stress rupture exposure at 11.6 ksi and 1200°C in air

TABLE 1 SUMMARY OF PHASE 1 ACCOMPLISHMENTS (cont'd)

<p>GE Corporate R&D</p>	<ul style="list-style-type: none"> * Existing baseline material * Small coupons fabricated in laboratory by hand layup * Baseline fiber/matrix interface coating not oxidation resistant 	<ul style="list-style-type: none"> * Tensile strength of unidirectional architecture <u>doubled</u> to 100 ksi * Tensile strength of cross ply architecture nearly doubled to 50 ksi * Matrix cracking yield stress increased over 20% * Oxidation resistant interface coating developed with cross ply strength of 51 ksi and 1204°C strength of 30 ksi * No property degradation after 100 hours in air at 1200°C * Semi-automated preform process demonstrated for substantial cost reduction versus pre-CFCC * Continuous fiber coating process demonstrated for further cost reduction and improved reproducibility * Application feasibility projected by OEM assessment
<p>Textron Specialty Materials</p>	<ul style="list-style-type: none"> * No existing CFCC; concept only 	<ul style="list-style-type: none"> * All steps in fabrication process successfully developed * CFCC with high strength and toughness demonstrated * Tensile strength of 60-65 ksi achieved * Drum wrapping and filament winding, both production-viable processes, demonstrated * Tube 24" long by 4" diameter successfully fabricated; suitable for initial testing by OEM * Joining of CFCC to monolithic material demonstrated * Surface densification process demonstrated to seal surface porosity and improve oxidation resistance by factor of 10 * Team of CFCC fabricator, OEM and end user formed to aggressively pursue testing in application environment

Technical Progress Highlights

AlliedSignal Ceramic Components and Caterpillar Inc. teamed in Phase I to explore the feasibility of achieving a self-lubricating CFCC material for exhaust valve guides in a low heat rejection diesel engine. Caterpillar conducted 2D finite element analysis to explore three design options and to identify material requirements and performance targets. One design appears feasible. AlliedSignal Ceramic Components evaluated four matrix compositions of silicon nitride and 10 grades of carbon fibers. The optimum fiber type, fiber loading and silicon nitride matrix were experimentally determined. A test sample was fabricated and shown to provide solid lubrication running against A.I.S.I. 4140 mild steel at 300°C, thus demonstrating technical feasibility of the material for the valve guide application.

The **Alzeta** program has demonstrated potential for near-term commercial production. The program is directed towards development of a new generation of radiant burners with greater durability, longer life and higher temperature capability. 10% market penetration of these burners would save 50 billion cubic feet of natural gas and reduce nitrogen oxide emissions by 35,000 tons per year. A burner incorporating a CFCC outer shell operated with minimal material degradation for 3000 hours at 250°F higher temperature than a conventional burner. A CVD SiC infiltrated porous mat was tested for 1500 hours with no degradation. A concept to utilize a CFCC "reverberatory screen" was explored and demonstrated to increase radiant output up to 100%.

Amercom teamed with OEMs from four industry sectors and identified applications ranging from hot gas candle filters to industrial furnace components to turbine and diesel components that would have high payoff from the use of CFCC materials. Amercom also conducted materials development focused on improvement in high temperature stability, on cost reduction and on achieving a controlled pore structure for hot gas filters. A graded matrix CFCC was developed with a silicon carbide interior and a mullite oxide surface that exhibits improvement in corrosion resistance. A process modification was demonstrated that eliminates costly hot tooling and is projected to reduce fabrication cost by 50%. A filter concept was demonstrated that meets flow and pressure drop requirements of the candle filter application.

Babcock and Wilcox achieved broad progress during Phase I. They increased the tensile strength of their baseline oxide-oxide CFCC material from 24 ksi to 44 ksi and the strain-to-failure from 0.09 to 0.26. They improved their matrix precursor materials to eliminate 50% of the infiltration cycles, thus substantially reducing fabrication cost. They fabricated representative components for several applications and worked with end-users to begin exploratory testing of these components. They substantially increased the property database and began developing design methodology and life prediction codes.

Dow Chemical began Phase I with a concept and a few exploratory trials rather than an existing CFCC material. Their concept was to incorporate SiC fibers into their self-reinforced silicon nitride (SRSN) material. They had to start from zero in establishing key composite technologies such as preform fabrication, interface layer composition and deposition, and composite densification. They have made good progress in preform fabrication, but are still early in the tasks to demonstrate an effective interface layer and densification process. Key preform fabrication accomplishments include development of successful matrix slurries, demonstration of techniques and apparatus to

infiltrate these slurries into candidate fiber architectures, and fabrication of an infiltrated tubular preform two inches in diameter and 11 inches long. Dow has demonstrated some progress with interface layers. One resulted in composite strength greater than the matrix material strength and with a factor of 8 increase in work of fracture (a measure of toughness).

Dow Corning demonstrated improved high temperature stability of their polymer infiltration pyrolysis (PIP) CFCC material. Specifically, their improved material retained a tensile strength of over 40 ksi from room temperature to at least 1200°C and fractured in a non-catastrophic mode with high strain-to-failure (0.7%). This material survived 500 hours stress rupture testing in air at 1100°C at a stress of 20 ksi. This is particularly encouraging because the test stress was above the matrix cracking yield stress (10 ksi) for the material. Prior CFCC materials exhibited severe oxidation and embrittlement degradation when tested in air above the matrix cracking yield stress. Dow Corning also achieved improvement in fabrication capability. They scaled up to panels 12 inches by 12 inches. They also demonstrated modifications in their fabrication process that have the potential to significantly reduce cost.

DuPont Lanxide Composites (DLC) accomplished improvements to processing of their baseline 2D NicalonTM SiC-based fiber/alumina matrix CFCC. The primary improvement was to establish a production-viable process for CVD of their fiber interface coating without a reduction in properties. DLC also fabricated four alternate CFCC materials to explore the potential of SiC particulate filler, alumina fibers, higher temperature SiC-based fibers and chopped fibers. Useful information was gained from these studies, but none of the materials exhibited properties comparable to the baseline material. DLC teamed with Foster Wheeler Development Corporation, GE Industrial and Power Generation Division, Solar Turbines Inc. and Westinghouse Electric to evaluate a broad range of applications. Heat exchanger tubes and gas turbine components were identified as viable applications.

A second program at **DuPont Lanxide Composites** focused on SiC-based fibers in a SiC matrix produced by chemical vapor infiltration (CVI). Potential applications were assessed with Foster Wheeler Development Corporation and GE Industrial and Power Generation Division. Oxidation and corrosion resistance were identified as key properties for most of the applications. Six variants of CVI SiC-SiC composites were fabricated and evaluated under coal flue gas, steam reformer and stressed oxidation conditions. Variants included two fibers, a standard plus an enhanced oxidation resistant matrix and two external oxidation protection coatings. Substantial improvements in high temperature stability were demonstrated for a couple of the variants compared to baseline material. For example, the enhanced matrix material with standard fiber and no surface coating did not fail after >4500 hours exposure in air at 1200°C under a tensile stress of 12 ksi.

General Electric Corporate Research and Development achieved excellent success during Phase I. Tensile strength was nearly doubled to 100 ksi for uniaxial and to 50 ksi for cross-ply fiber architectures. Matrix cracking yield point was increased to over 25 ksi for uniaxial and over 20 ksi for cross ply. An oxidation resistant interface coating was developed which resulted in increased material stability at high temperature. Low cost fabrication procedures were demonstrated with an increase in reproducibility and strength. Application studies were completed, and the CFCC material properties were shown to provide a reasonable margin over design stresses.

Textron Specialty Materials achieved remarkable progress during Phase I. They started with a concept and progressed all the way to establishing high strength and component fabrication capability. The concept consisted of incorporating silicon carbide or carbon fibers in a nitride-bonded silicon carbide matrix. They successfully developed the procedures to fabricate a CFCC material and demonstrated a strength of over 60 ksi and strain-to-failure of over 0.6%. They identified viable radiant and immersion heater tube applications for the aluminum remelt industry, formed an industry team to design and test a specific component and fabricated a full size component suitable for testing.

Eighteen **Supporting Technology** projects were established in Phase I to address key issues in composite design, material characterization, test methods and performance-related phenomena. The objective of these projects was to provide broad expertise from academia, government laboratories and technology companies to help understand and solve problems basic or generic to all the industrial CFCC contracts. Examples include fiber-matrix-interface interactions, failure mechanisms and allowable operation limits, design database generation and use, time-dependent behavior (creep, stress rupture, fatigue) and composite modeling. Excellent progress was achieved in establishing the supporting technology projects and in integrating them with the industrial programs through informal linkages and partnerships, joint meetings and technical highlights reports.

The remainder of this document highlights the progress and accomplishments of each contract. **Phase I Material and Scope** identifies the nature of the CFCC material selected for development, the state of the technology at the start of the CFCC program and the key goals of Phase I for that specific contract. The baseline technology varied broadly for the different contracts. In some cases the CFCC already existed and the program focused on applications assessment, fabrication and extension of database. In other cases the program began with a concept and focused on material development to demonstrate feasibility for a selected application or applications. **Partnerships Established** identifies the teams that were formed during Phase I. **Property Improvements** highlights the improvements in strength and high temperature stability achieved in Phase I. **Fabrication Improvement/Cost Reduction** describes progress towards cost-effective fabrication of the types of shapes required for the selected application(s). **Applications/CFCC Viability Assessment** discusses the final status at the end of Phase I of the material capabilities versus the projected application design requirements.

The document concludes with a brief description of the **Supporting Technologies** scope and projects and a review of some of the Phase I highlights.

The AlliedSignal Ceramic Components Team

Phase I Material and Scope

The AlliedSignal Ceramic Components (CC) program began with a concept rather than a pre-existing CFCC material. The concept was to develop a self-lubricating CFCC material for exhaust valve guides and other similar components in a low heat rejection diesel engine. The proposed CFCC material was carbon fibers in a silicon nitride matrix. The silicon nitride would provide strength and corrosion resistance and the carbon would provide self-lubrication.

The objectives of Phase I were (1) to conduct fabrication screening trials to determine if a carbon fiber/silicon nitride composite could be fabricated with favorable properties, (2) to define valve guide design concepts and evaluate their feasibility by finite element analysis and (3) to conduct friction and wear measurements of CFCC development iterations to estimate whether a coefficient of friction of 0.2 and an average wear coefficient of 1×10^{-8} mm/N-m without external lubrication were feasible.

Partnerships Established

A partnership was established during Phase I between CC and Caterpillar. CC conducted the CFCC material development and some property screening tests. Caterpillar conducted design studies, benefits/economics analysis, friction and wear tests and material exposure tests in simulated diesel exhaust.

Design Studies

Caterpillar identified two exhaust valve concepts and eleven installation options. These were narrowed to three design options for 2-D finite element analysis. Analysis determined that one of these designs was

clearly viable both from material and engine perspectives.

Fabrication/Property Evaluation

- * Four silicon nitride matrix materials were evaluated: reaction bonded, sintered reaction bonded, and hot isostatically pressed GS-44 and GN-10 compositions. The best matrix-only friction results were obtained with GS-44.

- * 16 carbon fiber grades were evaluated. These were first screened for stability in flowing air at 600°C. Four grades were selected for composite development trials.

- * Composite fabrication was explored with both continuous and chopped fibers. Test samples were successfully fabricated with chopped fibers but not with continuous fibers.

Typical Microstructure of Dense Silicon Nitride Reinforced with Chopped Carbon Fibers

- * Over 60 CFCC compositions were fabricated and tested for friction and wear using a pin-on-plate type of test. This test is

considered more severe than the application, but suitable for material screening. Two grades of carbon resulted in coefficient of friction of 0.2 or lower. However, the coefficient of friction increased with time due to wear debris from the CFCC imbedding in the A.I.S.I. 4140 mild steel.

* CFCC variations were exposed to a simulated diesel exhaust atmosphere at 650°C for 250 hours. All exhibited reduction in strength. The typical sample of the preferred composition decreased from 55.8 ksi to 43.5 ksi. Strength decrease was not judged to be a concern because the ceramic is in compression in the application. Further study is needed to determine effects on friction and wear.

Applications/CFCC Viability Assessment

Caterpillar studies determined that CFCC materials would provide a benefit for diesel exhaust valve guides and that allowable component cost is in the range of feasibility for candidate CFCC materials. They also identified a viable component design. CFCC materials were developed in Phase I that were close to the unlubricated frictional requirements. Longer term testing is necessary under conditions closer to the application requirements to demonstrate material feasibility.

The Alzeta Team

Phase I Material and Scope

The Alzeta program differed from the other programs. Alzeta is a manufacturer rather than a CFCC material developer. Alzeta manufactures a ceramic fiber radiant burner for residential, commercial and industrial applications. The Alzeta program focused on assessment of a broad range of radiant burner applications, design of burners with CFCC components, and laboratory testing of CFCC materials and first generation burner components.

Partnerships Established

The Alzeta team includes Southern California Gas Company (SCG) as a funding partner and a number of CFCC manufacturers as material suppliers. The role of SCG in the program is to promote the development of low-NO_x high performance radiant burners that will benefit end users across a broad spectrum of applications. Material suppliers include DuPont Lanxide Composites as a supplier of porous mats and ceramic composite screens, and 3M Corporation, Amercom, Dow Corning and Textron as suppliers of ceramic composite screens and tensile samples.

Design Concepts Identified

Two design concepts were identified. One consists of refractory ceramic fibers bonded together by a low volume fraction of chemically vapor deposited silicon carbide. This is intended for use as a more durable radiant surface that will perform in a manner that is similar to current generation burners. The second concept consists of a strong lathwork or screen of CFCC that can be used as a protective sheath over a conventional ceramic fiber burner. This screen alternatively

can be used as a reverberatory screen supported above the burner surface as illustrated:

CFCC Radiant Burner Design Concept

The purpose of the reverberatory screen is to increase radiant output. If strong and tough, the screen could also protect other burner parts.

Concepts Testing

* Burners have been constructed using high porosity mats of a SiC-based fiber bonded with a CVD SiC matrix, and several iterations on this basic design have been tested in a thermal cycling test fixture. The best performing mat to date was supplied by DuPont Lanxide Composites and has experienced minimal performance degradation after 4500 hours of testing and 12,000 thermal cycles.

* Reverberatory screens and screen tensile samples were fabricated by 3M, Amercom, Dow Corning, DuPont Lanxide Composites and Textron Specialty Materials. Tests of burners with reverberatory screens have shown that radiant output from the burner surface can be nearly doubled when compared to conventional radiant burners. Life testing of screen materials was also performed on 1-D tensile samples to aid in the material selection process. Tensile strength of samples was measured before and after 1200 hours of exposure to a combustion environment to quantify loss of strength and toughness over time. The best performing sample group showed a 13 percent decrease in strength as a result of combustion environment exposure, and this level of degradation has been determined to be acceptable.

* A radiant burner was constructed with a durable CFCC outer shell over a conventional ceramic fiber burner surface. The shell was 3M SiconexTM material which consists of 3M NextelTM fibers and a SiC matrix. The outer shell increased the durability of the ceramic fiber surface and was shown to slow material aging in a high temperature environment. The burner was operated for 3000 hours at a burner surface temperature of 1120°C radiating to a 800°C load.

Comparison of Radiant Output from CFCC Reverberatory Screen Burners Versus Conventional Surface Combustors at Constant Surface Firing Rate

Applications/CFCC Viability Assessment

Applications assessment indicated that CFCC materials could provide a high payoff in radiant surface burners by improving efficiency and reducing NO_x emissions. A 10% market penetration was predicted to save 50 billion cubic feet of natural gas and reduce NO_x emissions by 35,000 tons per year. Successful Phase I testing suggests that flat plate radiant surface burners could be a near-term commercialization success for CFCC materials. Field tests are projected in one to two years and commercialization for initial applications in three years.

The Amercom, Inc. Team

Phase I Material and Scope

Amercom had a relatively mature family of CFCC materials prior to the CFCC program. These materials consisted of aluminum borosilicate fibers or SiC fibers in a matrix produced *in situ* by chemical vapor infiltration/deposition (CVI). These baseline materials had been successfully demonstrated for thousands of hours in low stress applications, but were not adequate for the high payoff industrial applications targeted by the CFCC program. The objectives of the Amercom Phase I program were (1) to further study potential high payoff applications and better define the material requirements, (2) to modify their SiC-SiC material and fiber-matrix interface to increase high temperature stability, (3) to develop a controlled porosity material for candle filters and (4) to explore options for fabrication cost reduction, especially by reducing the cost of tooling.

Partnerships Established

Amercom established partnerships with ABB-Combustion Engineering, Surface Combustion Inc., Solar Turbines and Detroit Diesel to explore options for CFCC applications, to select viable applications for detailed study and to conduct benefits assessments. MSNW was added to the team to conduct micromechanical analysis to estimate the viability of composite architectures under estimated application stresses. University of Virginia participated in electron microscopy and auger analysis of the fiber-matrix interface and in fracture analysis in an effort to understand (and find solutions to) high temperature degradation mechanisms. Materials Sciences Corp. also participated in Phase I. They used micromechanics computer models to predict a full set of design properties from the limited property data

available.

Property Improvements

Three tasks were directed towards improvement in properties in a high temperature oxidizing atmosphere: (1) evaluate the stability of alternate fibers to the Amercom CFCC fabrication conditions and to oxidation, (2) develop a non-oxidizing interface to replace the pyrolytic carbon fiber-matrix interface in the baseline material and (3) develop a graded matrix with SiC in the interior and mullite (an oxide) at the surface.

* Nine alternate fibers were studied. All were determined to be compatible with the CVI process, but none provided strength improvement over the baseline material.

* A graded matrix was successfully demonstrated. This material had ultimate tensile strength of 27.6 ksi and strain-to-failure of 0.64% compared to 29.8 ksi and 0.56% for a SiC-SiC control. Corrosion testing was very promising. 20 hours exposure to sodium sulfate saturated air at 950°C resulted in no visible attack to the graded matrix CFCC. Standard SiC-SiC CFCC exhibited >0.1 mil per hour surface recession and severe pitting.

* Many variants were evaluated in an effort to achieve a non-oxidizing interface between the fibers and matrix. All resulted in decreased strength and strain-to-failure. However, improved understanding was gained of the interface and the factors influencing strength and toughness. Some promising options were identified for study in Phase II.

Fabrication Improvement/Cost Reduction

* Major effort was focused on reduction in tooling cost. The baseline CVI process requires a rigid graphite tool to support each CFCC fiber preform in the CVI furnace. These support tools are expensive, consume valuable space in the furnace and can only be used once. A technique was developed in Phase I to rigidize the fiber preform at a low temperature using metal tooling and subsequently position the preform in the CVI furnace without requiring support tooling. A cost savings of 50% is projected. Strength of the resulting product is lower than for baseline material, but still above 20 ksi.

* Amercom conducted development on three concepts for achieving controlled porosity in a candle filter tube. Tubular test samples were fabricated and evaluated for face velocity and pressure drop at Industrial Filter and Pump Mfg. Co. One concept performed close to the application requirements and was selected for refinement in Phase II. This concept consists of a filament wound structure supporting a filter membrane. The filter membrane contains straight smooth-surfaced flow channels with a tailorable diameter (4-10 microns) and flow path length (1-3 mm).

Test Sample to Evaluate the Porous Candle Filter Concept

Cross Section Showing the Controlled Porosity Flow Channels

Applications/CFCC Viability Assessment

Many applications were evaluated. The following were selected as having high payoff and being the most viable for near-term development: candle filter tubes, hot furnace fans, radiant burner tubes, diesel piston rings and a heat exchanger manifold.

The Babcock and Wilcox Corporation Team

Phase I Material and Scope

Babcock and Wilcox (B&W) demonstrated a baseline CFCC material prior to the CFCC program. They proposed to continue development of their CFCCs using aluminum oxide fibers in matrices of aluminum oxide, zirconium oxide and yttrium aluminum garnet (YAG). An all-oxide CFCC was selected to provide high stability and corrosion resistance in the high temperature oxidizing environments of the intended applications. The general fabrication process selected by B&W involves a series of liquid infiltrations into a fiber preform, alternated with a series of drying cycles and heat treatments to convert the liquid precursors to the desired oxide. The objectives during the Phase I program were (1) to establish an effective team, (2) to improve properties, (3) to reduce cost by decreasing infiltration cycles and developing filament winding, (4) to generate a property database suitable for design modeling, (5) to evaluate and select viable applications and fabricate/ test initial representative components.

Partnerships Established

B&W established during Phase I an interdisciplinary team consisting of end users (B&W industrial divisions and General Electric Company), a fiber coater and matrix precursor developer (Basic Industrial Research Laboratory at Northwestern University), composite characterization laboratories that are also participating in developing design methodology and life prediction codes (Cleveland State University and VPI and State University) and a braider/weaver of fiber preforms (Fiber Materials, Inc.). B&W also established an agreement with Solar Turbines to test under a separate program combustor liners fabricated

under the CFCC program.

Property Improvements

Baseline B&W alumina-alumina CFCC with 23.3% porosity had a tensile strength of 24 ksi and strain-to-failure of 0.09%. Efforts to increase strength and composite fracture behavior in Phase I focused on development of an interface layer between the fibers and matrix to minimize bonding of the matrix to the fiber. A tin oxide fiber coating was developed that resulted in strength increase to 44 ksi and strain-to-failure improvement to 0.26% for an alumina-alumina CFCC with 23.2% porosity.

Improvements in Strength and Composite Fracture Behavior

Test bars of the improved CFCC material were fabricated and submitted to the test laboratory team members to generate a mechanical property database. Poisson's ratio, shear strength, shear modulus, and tensile and compressive strength in both the longitudinal and transverse directions were measured for flat plates and tubes. Thermal

conductivity was also measured. These data permitted for the first time for the B&W team to analytically predict whether the CFCC material would survive in candidate applications.

Fabrication Improvement/Cost Reduction

Major cost reduction and improvement in the quality of fabricated parts were achieved in Phase I.

- * New sols for alumina, zirconia and YAG with increased solids yield were developed and refined to allow successful infiltration into fiber preforms. This resulted in a reduction of infiltration cycles from over 30 for the baseline CFCC to less than 15 for the improved CFCC, equating to a labor cost reduction of over 50%.

Reduction in Infiltration Cycles Needed to Achieve Acceptable Density

- * A technique was developed to deposit the tin oxide fiber coating from a liquid precursor as an in-line step in the filament winding process. This makes possible a rapid automated preform fabrication process which will further reduce cost.
- * Four commercially available alumina fiber materials were evaluated for (1) ability to be preformed by filament winding, braiding and weaving, (2) compatibility with interface

coatings and (3) stability in the candidate matrix materials.

- * The filament winding process was refined to achieve larger tubes and to reduce interlaminar debond defects. NDE techniques were identified at B&W and in collaboration with Argonne National Laboratory to detect fabrication defects and were used to help guide fabrication development.

CFCC Heat Exchanger Tube Preform Being Fabricated on B&W Filament Winder

- * Representative components were fabricated for a gas turbine combustor, a heat exchanger tube, a soot blower tube and tube shields for a boiler.

Applications/CFCC Viability Assessment

A number of applications, especially for boiler components, were identified where an oxide-oxide CFCC would decrease maintenance, conserve energy and reduce emissions. The Phase I database and modeling capabilities were used to assess feasibility of the material for specific applications. Representative components were fabricated and delivered to the end users for a first evaluation under the application conditions.

The Dow Chemical Company Team

Phase I Material and Scope

Dow Chemical began Phase I with a concept and a few exploratory laboratory trials rather than an existing CFCC material. Their concept involved incorporation of SiC fibers into their self-reinforced silicon nitride (SRSN) material. The advantage of the SRSN material is its high strength and toughness and corrosion resistance. The high strength and toughness were projected to lead to a CFCC with unusually high interlaminar shear and interlaminar tensile strengths.

The objectives of Phase I included (1) develop low cost processing routes based on tape casting of SRSN, (2) develop formulations, procedures and equipment to infiltrate slurries into fiber tows, (3) develop lamination procedures to form infiltrated fiber into shaped preforms, (4) demonstrate the capability to densify a CFCC with reasonable strength and toughness, (5) select and screen interface coatings to maximize toughness, (6) evaluate the potential of an application of The Dow Chemical Company and, (7) conduct material stability tests in a simulated application environment.

Partnerships Established

Dow Chemical corporate research teamed with an operating division of Dow Chemical to select and evaluate a chemical processing application. Dow obtained fibers from 3M, Dow Corning and Textron Specialty Materials and interface coatings from 3M and General Atomics.

Property Improvements

Property testing is at an early stage.

Results with one CFCC material have been

encouraging. The material fractured in a non-catastrophic mode as shown below. The work of fracture was eight times higher than for the monolithic matrix material. High temperature testing has not yet been conducted.

Fracture Behavior at Room Temperature of an Early SRSN matrix/SiC Fiber CFCC

* Testing the stability of the material under the application conditions is critical. A testing facility to evaluate potential CFCCs under simulated operating conditions has been constructed under Dow Chemical funding.

Fabrication Improvement/Cost Reduction

* Matrix slurries were developed that successfully infiltrated fiber yarns.

* Equipment and procedures were developed to apply the slurry to aligned fiber using a tape caster to form a flexible tape. This has reduced layup time by a factor of three and has increased reproducibility.

* Techniques were developed to laminate cut strips of the tape into flat plates and into

tubes. Initial tapes were nonflexible and could not be bent to a diameter smaller than 52 inches. The application required four inches. Modifications in the slurry binder and plasticizer increased the flexibility to allow bending to a 16 inch diameter. A damp forming method was developed to successfully yield a two inch diameter tube.

*Two Inch Diameter 11 Inch Long Tube
Fabricated By Damp Drum Wrapping*

isostatic pressing (HIP) are required to achieve densification of the present composition. Over 97% of theoretical density has been achieved by HIP. However, it is encouraging to note that some cost reductions in the densification process have already been incorporated into the process, and further improvements are expected once coated fibers become available for use. Additional work is also ongoing to examine other densification techniques.

Applications/CFCC Viability Assessment

A proprietary Dow Chemical chemical processing application was identified that would provide economic benefits and possibly increase U.S. international competitiveness.

* A fiber/matrix interlayer is needed to prevent fiber interaction with the matrix during fabrication and to allow slip between the fiber and matrix during mechanical loading. This portion of the program was delayed awaiting receipt at Dow of acceptable coated fibers.

* Densifying fiber/matrix preforms has been a major challenge. Initially a temperature of 1825°C was required. This resulted in severe degradation of fibers. Matrix composition modifications have reduced the densification temperature to 1600°C. Even at this temperature, glass encapsulation and hot

The Dow Corning Corporation Team

Phase I Material and Scope

Dow Corning developed a baseline CFCC material prior to the CFCC program using a polymer infiltration and pyrolysis (PIP) technique analogous to that used for carbon-carbon composites. The polymer is infiltrated into the fiber preform, cured at low temperature and then pyrolyzed above 1000°C to yield porous ceramic. The procedure is repeated until most of the porosity has been filled with ceramic matrix. The Phase I objectives included (1) to identify industrial applications with high payoff for use of a CFCC material, (2) to compare the properties of the baseline PIP material and projected improvements to the application needs, (3) to improve the properties of the PIP CFCC, especially the stability at high temperature, (4) explore process improvements that will decrease cost and increase reproducibility, (5) demonstrate scaleup in size of 2D CFCCs and (6) improve the understanding of composite failure mechanisms.

Partnerships Established

Dow Corning assembled a team that included Kaiser Aerotech, Solar Turbines, Sundstrand Fluid Handling, MSNW, Techniweave, MSC and Argonne National Laboratory. Dow Corning and Kaiser Aerotech carried out material and process development and established the Kaiser Ceramic Composites joint venture to manufacture and market CFCC components. Solar Turbines and Sundstrand conducted application assessments. MSNW identified a suitable interface coating and developed a perceramic polymer coating process. Techniweave designed 3D architectures for improved interlaminar properties and fabricated 3D preforms for processing and evaluation.

MSC conducted micromechanical modeling and data verification. Argonne National Laboratory performed NDE, mechanical testing and microstructural evaluations. NDE techniques were demonstrated for verifying fiber architecture, locating delamination flaws and identifying the residual stress in the CFCC.

Property Improvements

* Tensile strengths over 40 ksi at room temperature and 1200°C have been demonstrated. The composite fractures in a non-catastrophic mode with strain-to-failure of up to 0.7%.

Composite Fracture Behavior of PIP 2D CFCC

* PIP 2D CFCC retained 75% of its strength after thermal shock from 1000°C into water, compared to retention of only 20% strength for monolithic silicon carbide and silicon nitride.

Thermal Shock Behavior of PIP CFCC

Fabrication Improvement/Cost Reduction

* A liquid precursor technique was developed to coat fiber tows and woven fabric with the improved interface coating. Cost is projected to be substantially lower than for the CVD coating process used previously. Flexural strength of the resulting CFCC is over 50 ksi.

* 3D fiber architectures were explored to increase interlaminar properties. 3D fiber preforms are more rigid than 2D preforms and thus more difficult to infiltrate, especially with polymers containing high level of fillers. Dow Corning succeeded in infiltrating 3D preforms with resins containing up to 45% SiC filler particles, which is comparable to the prior 2D capabilities.

* PIP technology was transferred to Kaiser Aerotech. Fabrication of 12" by 12" panels

was demonstrated, at Kaiser Aerotech in a production environment, compared to the prior fabrication of 6" by 6" panels at Dow Corning in a laboratory environment.

* Studies during Phase I indicate that the number of infiltration cycles can be reduced from 12 to 8 without reduction in CFCC strength by control of polymer, filler and fiber coating characteristics. This reduces fabrication cost.

Applications/CFCC Viability Assessment

The team identified a gas turbine combustor liner, a containment shell for a sealless chemical pump and bladed and unbladed turbine rotor disk as high payoff applications for the PIP CFCC material. Critical stresses for the combustor liner were predicted to be 7.2 ksi hoop and 0.8 ksi interlaminar shear. The PIP 2D CFCC has interlaminar shear strength of 3-3.5 ksi and matrix cracking yield stress of about 10 ksi and thus is a viable candidate for the combustor liner. Stresses for the turbine disk are higher, but the use temperature is lower. The use temperature for chemical pumps is also relatively low, but the fluids can be very corrosive. Further assessment is underway to determine viability of the PIP CFCC for the turbine disk and the chemical pump containment shell.

The DuPont Lanxide Composites CVI Team

Phase I Material and Scope

DuPont Lanxide Composites (DLC) developed commercial scale capabilities prior to the CFCC program for fabrication of composites by chemical vapor infiltration (CVI) of SiC matrix into SiC-based fiber preforms. They determined that their baseline material had limitations in oxidation and corrosion resistance and thus developed several modified materials projected to have improved stability. The objectives of the Phase I CFCC program were (1) to study potential applications and identify test conditions to validate CFCC materials for selected applications, (2) to fabricate test coupons of the baseline material and modified materials, (3) to measure key mechanical and thermal properties needed for component design analysis and (4) to compare the modified materials with baseline material after exposure to simulated coal gas, steam reformer and stressed oxidation conditions.

Partnerships Established

DLC teamed with Foster Wheeler Development Corporation (FWDC). Foster Wheeler is a leading producer of technology for coal-fired utilities and for steam generation. The team compared the CVI CFCC fabrication capability and properties with industry needs and selected viable applications. FWDC defined and conducted key tests to experimentally determine the stability of candidate materials in simulated application environments. DLC also provided property database to the GE CFCC program to include in the GE Industrial and Power Generation Division turbine evaluation studies.

Property Improvements

Six material variants were evaluated: two fibers, baseline versus enhanced oxidation resistance matrix and two external oxidation protection coatings. Pre-test measurements included room temperature and high temperature tensile strength, thermal diffusivity, specific heat, coefficient of thermal expansion and room temperature compressive strength, shear strength and toughness.

- * Enhanced oxidation resistance matrix CFCC did not fail during 4700 hours exposure to 12 ksi tensile stress at 1200°C. Baseline material fractured in less than 100 hours at the same stress and temperature.

- * Enhanced matrix CFCC prestressed to 20 ksi (above the matrix cracking yield stress) did not fail after >1000 hours at 12 ksi and 1200°C.

- * All six CVI CFCC materials survived 500 hours under simulated steam reformer conditions with no visual degradation or change in tensile strength. Exposure consisted of 1040°C in a flowing CH₄, H₂O, CO gas stream. 1000 hour and 1500 hour tests are completed and property measurements are in progress.

- * Testing in a simulated coal flue gas environment was conducted for 500, 1000 and 1500 hours at temperatures up to 1260°C. The sample test surfaces were intermittently coated with ash and exposed to flowing flue gas. Samples tested at 1260°C exhibited 0-30% strength reduction, depending on the material. The CFCC with protective surface coatings performed best. Some coal flue gas tests were conducted at 1000°C with extra alkali sulfate added to

assess resistance to hot corrosion. One contained 7% alkali sulfate, the other 44%. All materials survived the low alkali exposures with no degradation. Some degradation was observed for the high alkali testing.

Fabrication Improvement/Cost Reduction

Phase I included no fabrication improvement tasks.

DLC Commercial Scale CVI Fabrication Facility

Examples of CVI CFCC Parts Fabricated by DuPont Lanxide Composites

Applications/CFCC Viability Assessment

FWDC identified property requirement targets for selected applications and compared them to the material properties. Tubes for a high temperature air heater for a coal-fired power generation application were identified as viable. The steam reformer was identified as another application, but requires further material development to achieve hydrogen-impermeable tubes. Hot gas transfer pipes are also a candidate, but also require nonpermeable material. Westinghouse recommended hot gas filtration as an important application. Trials at DLC and Westinghouse determined that the desired porosity and corrosion resistance could be achieved with the CVI material.

The CFCC material tests in simulated application environments were very promising. These tests, plus comparisons of material strength versus application design stress, indicate that the DLC CVI materials are technically viable for the candidate applications.

DuPont Lanxide Composites DIMOXTM Team

Phase I Material and Scope

DuPont Lanxide Composites established a CFCC material prior to the CFCC program. This baseline material consisted of 2D fabric of a SiC-based fiber in an aluminum oxide matrix. The matrix was grown into a fabric preform by the Lanxide DIMOXTM directed metal oxidation process. This process involves growth of a ceramic-metal composite material at the surface of a molten metal through controlled oxidation. If a fiber preform is placed adjacent to the molten metal, the ceramic-metal material will grow through the fiber preform to form a non-porous matrix. The residual metal is then extracted to leave a CFCC.

The objectives of Phase I were (1) to assess applications for potential use of the DLC CFCC, (2) to fabricate and evaluate four alternate alumina matrix CFCC materials, (3) to establish an interface coating process that is safe and can be scaled to production levels and (4) to increase the matrix cracking yield stress.

Partnerships Established

DLC formed applications evaluation partnerships with Foster Wheeler Development Corporation, GE Industrial and Power Generation Division, Solar Turbines Inc., and Westinghouse Electric.

Property Improvement

The four alternate materials were fabricated and evaluated.

- * SiC particles were added to the matrix. This increased thermal conductivity by 20% and decreased matrix microcracks. However, it did not increase the microcracking yield

stress or the strength. Microcrack yield stress remained at 6-9 ksi. Strength decreased from 36 ksi to 26 ksi.

- * CFCC samples were successfully fabricated with alumina fibers. The strength was low (19 ksi) and degraded further as the temperature was increased above 700°C.

- * CFCC samples were fabricated with an alternate fiber. All had low strength and fractured in a brittle mode.

- * CFCC samples were fabricated with chopped fibers. These fractured in a non-catastrophic mode, but had decreased strength compared to baseline material due to the decreased fiber volume fraction.

- * Tested under a parallel program the baseline CFCC: Retained room temperature strength to 1200°C and only decreased to 33 ksi at 1370°C. Water quench thermal shock testing from 1200°C resulted in a strength decrease of only 16%.

- * Survived over 1000 hours of stress rupture exposure at 11.6 ksi and 1200°C in air.

- * Survived over two million cycles without failure at 1000°C with an applied tensile stress between 8 and 83 MPa at a frequency of 5 Hz.

- * A property database was provided to all OEM partners for the baseline CFCC material.

Fabrication Improvement/Cost Reduction

Effort focused on establishing a production-viable process for coating the fiber fabric with a SiC layer to protect the fibers during the

fabrication process. A process was successfully developed which was safe and also improved the uniformity of coating deposition within the fiber preform. Mechanical properties of the CFCC fabricated with the modified coating process were identical to mechanical properties of the CFCC with the original process.

Improvement in Coating Thickness Uniformity with the New Process

Applications/CFCC Viability Assessment

FWDC identified heat exchanger tubes for coal-fired combined-cycle utility generation as a prime candidate for the DLC CFCC material. They also identified steam reformers as a potential application. This application requires high reliability containment of high pressure hydrogen gas. The current CFCC material contains open porosity, so further material development is needed before the reformer application can be considered. Westinghouse identified hot gas filtration as an area with high payoff. Trials determined that the required levels of porosity could not be achieved readily in the alumina matrix CFCC, but could in a CVI SiC/SiC material. Phase II effort was recommended to be transferred to the DLC CVI program. GE and Solar identified gas turbine combustor and shroud components as viable for the DLC CFCC alumina matrix material. Further high temperature durability testing in air under cyclic stress loading is required to verify material feasibility for these long life applications.

GE Corporate R & D Team

Phase I Material and Scope

GE demonstrated a baseline CFCC material prior to the CFCC program. This baseline material consisted of SCS-6TM monofilament SiC fibers in a SilcompTM matrix. The baseline material was prepared by casting a slurry of SiC plus carbon particles over hand aligned fibers to form a thin tape, laminating tapes to form a flat panel, and infiltrating with molten silicon to react the carbon to SiC and fill the remaining pores with silicon. The advantages of this process are high strength and toughness, near-zero porosity, short fabrication time and no dimensional change during densification.

The objectives of Phase I were (1) to apply the baseline interface coating to fibers in a continuous rather than batch process, (2) to develop an interface coating with improved high temperature stability, (3) to increase strength and matrix cracking yield point by use of a smaller diameter fiber, (4) to achieve automated fiber alignment and tape fabrication by drum winding, (5) to fabricate tubes, (6) to determine the properties needed for component design and assemble a database of these properties for the GE material and other CFCC materials and (7) to transfer the GE CFCC fabrication technology to a CFCC manufacturer (Textron Specialty Materials).

Partnerships Established

A team was established headed by GE Corporate Research and Development (GE CR&D) and including GE Industrial and Power Generation (GE IPG) and Textron Specialty Materials. The role of GE IPG was to identify candidate gas turbine components, define and gather a design database for candidate CFCC program materials and assess the viability of the materials for

selected turbine components. This linked the GE program to CFCC programs at Babcock and Wilcox, Amercom and DuPont Lanxide Composites. These programs included tasks to gather or generate property data for compilation into the GE IPG database. The Textron role was to provide fiber, continuous fiber coatings and to establish and demonstrate inhouse capability to fabricate the GE CFCC material.

Property Improvements

High strengths (approaching the theoretical potential based on fiber strength) and toughness were demonstrated. Of special importance is the high matrix cracking yield stress in the 26-29 ksi range. This is well above the predicted application stress. Studies have shown that most CFCC materials are susceptible to fatigue and oxidation damage if stressed above the matrix cracking yield stress.

* Use of 3 mil versus 5.5 mil diameter fibers increased the tensile strength from 55 ksi to 100 ksi and the matrix cracking yield stress from about 22-24 ksi to 26-29 ksi. Strain-to-failure was increased slightly from about 0.8% to 0.9%. These results were for samples with 20 volume% uniaxially oriented fibers. Increase to 30 volume % should further increase the properties.

Stress Strain Curves for the Improved CFCC with 3 mil Diameter Fibers

* A new oxidation resistant fiber coating was developed and demonstrated to improve room temperature and high temperature properties. For cross-ply fiber architecture using the baseline 5.5 mil fibers, the room temperature strength was increased from 35 ksi to 51 ksi. Matrix cracking yield stress was increased from about 15 ksi to over 20 ksi. The new material retained a strength of 30 ksi at 1204°C with the matrix cracking yield stress still near 20 ksi. The strength reduction versus temperature matches the strength reduction of the fiber versus temperature, so is not due to composite degradation. 100 hours exposure in air at 1200°C resulted in no property degradation..

Stress Strain Curves at Various Temperatures for CFCC with Improved Interface Layer

Fabrication Improvement/Cost Reduction

* Continuous coating of the SiC fibers was demonstrated for the baseline interface coating. The coating was more uniform than batch coatings and resulted in strength improvements up to 50%, as well as in substantial cost reduction.

* A computer-controlled drum winding apparatus was constructed which dramatically reduced fabrication time and improved reproducibility.

Near-Net Shape Tube 4" Diameter and 4" Long with 0.1 inch Wall Thickness Reinforced with 5.5 mil Diameter Fibers

* Fabrication technology was transferred to Textron and fabrication trials initiated.

Applications/CFCC Viability Assessment

GE IPG completed the property database compilation for the various CFCC materials and conducted analysis to predict the viability of the materials for gas turbine components. A combustor liner and a turbine shroud were identified as viable applications. The GE CR&D CFCC had the highest probability of survival due to its high values of thermal conductivity, matrix cracking yield stress and interlaminar shear strength compared to other CFCC materials.

Textron Specialty Materials Team

Phase I Material and Scope

Textron Specialty Materials (TSM) proposed a new CFCC concept that would combine the fiber and composite fabrication capabilities at TSM with the nitride-bonded silicon carbide (NB SiC) capabilities of Nova Industrial Ceramics. The NB SiC is a low cost material in large scale commercial production. The objectives of the Phase I program were (1) to develop slurry formulations for the NB SiC precursors, (2) to use drum wrapping to apply these slurries to candidate fibers to form tape containing a single layer of fiber, (3) to stack the tape layers to form a multilayer laminate, (4) to establish the time/temperature parameters to densify the matrix in a nitrogen atmosphere, (5) to measure the strength for each iteration to guide subsequent iterations, (6) to demonstrate the TSM Rapid DensificationTM process to seal surface-connected porosity with silicon carbide, (7) to demonstrate fabrication by lowcost filament winding, (8) to establish a team of end users and OEMs to study applications and prepare a preliminary commercialization plan.

Partnerships Established

TSM established during Phase I a vertically integrated team consisting of the matrix material manufacturer (Nova Industrial Ceramics), original equipment manufacturers (Hauck Burners Corp. and Williams International), a plant design and construction company (Stone and Webster), a specialty industrial furnace manufacturer (Schaefer), an end user (Doehler-Jarvis) and a composites property and architecture analyzer (Materials Sciences Corp.).

Property Improvements

During Phase I, TSM fabricated NB SiC

composites with monofilament SiC fiber, graphite yarn and SiC-based yarn. Over 80 uniaxial tensile strength tests were conducted with bars cut from these composites.

* NB SiC matrix with 18 volume % SCS-6 monofilament SiC fibers exhibited tensile strength of 60-65 ksi and strain-to-failure of 0.8-1.0%. CFCCs with only 6% fiber had tensile strength of 23-30 ksi and strain-to-failure of 0.5-0.6%. CFCCs with 8 and 16% fiber had intermediate strength. These are excellent properties, especially for such low volume fractions of fibers. Since fibers currently dominate cost, low fiber content is beneficial.

Typical Stress-Strain Curves for NB SiC with Monofilament SiC Fibers

* NB SiC matrix with 8-10% carbon yarn reinforcement exhibited tensile strength of 15-25 ksi and strain-to-failure of 0.2-0.6%.

* NB SiC matrix with Tyranno SiC-based yarn had low strength (5-7 ksi) and fractured in a brittle mode. The fibers were not thermochemically stable under the fabrication conditions.

Fabrication Improvement/Cost Reduction

Extensive process development was conducted in Phase I, and component fabrication feasibility was clearly demonstrated.

- * 15 slurry formulations were explored, and three were selected that adequately coated fibers and produced homogeneous matrices.
- * Monolayer tapes were prepared using drum wrapping. These tapes were then laminated to form flat plates for property testing and small tubes. Tube fabrication time was one day, which was later reduced to two hours using filament winding. Filament winding can be automated and be very low cost.
- * Nitridation time/temperature/gas flow cycles were successfully developed to achieve maximum conversion of silicon to silicon nitride at minimum time and temperature to avoid degradation of fibers. This major milestone was necessary to demonstrate feasibility of the NB SiC concept.
- * The TSM Rapid Densification™ process was successfully demonstrated to fill near-surface porosity of the NB SiC. This process deposits SiC at approximately 100 times the rate achieved by CVD processes, so has good potential for low cost manufacturing. The resulting CFCC exhibited a factor of 10 reduction in oxidation at 1100°C compared to baseline material.
- * A tubular configuration for a radiant heater was successfully fabricated. The fabrication included the demonstration of capability to join the CFCC material to a monolithic NB SiC flange.

Radiant Heater Tube 24 Inches Long by 4 Inches Diameter Fabricated from NB SiC with SCS-6™

Applications/CFCC Viability Assessment

The team identified radiant and immersion heaters for aluminum melting and a combustor liner for a small industrial turbine as the first applications to evaluate, to be followed with pyrolysis tubes for petrochemical processing. The material strength appears more than adequate for these applications. Exposure of the matrix material to molten aluminum for 80 hours resulted in no sign of wetting or reaction.

Supporting Technology Projects

Scope

The Supporting Technologies Task was established to provide basic or generic support to the CFCC program in four categories: (1) composite design, (2) materials characterization, (3) test methods and (4) performance-related phenomena. 18 projects were initiated in Phase I involving six universities, four government laboratories and two companies.

Composite Design Subtask Progress

Widespread success with polymer matrix composites has been partially due to a capability to analytically design the architecture of the composite to meet the needs of the application. This requires a basic understanding of the behavior of constituent materials plus their interactions when fabricated into a composite, as well as the behavior of the overall composite when a stress field is applied. The objective of the Phase I composite design subtask was to begin to establish micromechanics and macromechanics models for CFCC materials, with the long range objective of achieving experimentally-verified capabilities comparable to those for polymer matrix composites.

Phase I efforts focused on micromechanical modeling, assembly of measured properties to support the modeling, and experimental study of crack propagation.

* The micromechanics modeling was conducted at UCLA and included three aspects:

(1) fiber/matrix interphase modeling for optimizing toughness and strength, (2) fabric architecture modeling and (3) laminate modeling. Finite element and closed-form models were developed and demonstrated to correlate well with existing data for cross-ply architecture CFCCs. Specific data requirements were defined to provide better verification and model refinement and will be generated in Phase II. User-friendly menus and user manuals will be prepared for these models and will be made available to the CFCC industrial teams to support their material development and component design efforts.

* Macromechanics modeling was conducted at Materials Sciences Corporation. The objective is to demonstrate a structural analysis capability that integrates micromechanics materials effects models into macro models for CFCC thermomechanical response. Initial models were defined and integrated into a finite element code. These account for fiber, matrix, interphase, porosity, fiber architecture, fiber/matrix debonding and matrix microcracks. Data requirements for verification and refinement were submitted to the Test Methods Subtask.

* Bulk thermal conductivity measurements for several CFCC materials were performed at Oak Ridge National Laboratory (ORNL) and added to the database for modeling. A scanning thermal conductivity microprobe apparatus was developed and demonstrated to allow study of thermal conductivity effects in CFCC materials on a micromechanics level.

* Techniques were developed at NIST to investigate the initiation and propagation of matrix cracks in CFCC materials. These techniques were applied at room temperature to initial CFCC samples and were demonstrated to provide very useful information relative to composite design, crack-fiber

interactions, and basic understanding of toughening mechanisms and failure mechanisms. The test techniques will be extended to elevated temperature and simulated environments in Phase II and will be applied to CFCC samples supplied from the industrial contracts.

Materials Characterization Subtask Progress

Phase I plans were to address characterization of the individual composite constituents (fibers, matrix, interface) and the complete composites. However, after discussions with the industry teams and review of other programs (such as at DOD and NASA), the plans were modified. The clear need was for increased focus on interface characteristics.

- * An interface test capability was established and demonstrated at ORNL. It allows direct observation of movement of a fiber in the matrix under an applied stress, plus measurement of debond stress, coefficient of friction, sliding shear stress and residual stress. These data help provide improved understanding of the material and design factors which control composites toughness and strength. Samples of SiC/SiC CFCCs were fabricated and tested for mechanical properties and fiber-matrix interface characteristics. Preliminary models were prepared to relate the mechanical behavior to the micromechanics acting at the fiber-matrix interface.

- * A program was initiated at Pennsylvania State University in July 1993 to focus on determination of optimum interface or interphase characteristics for oxide-oxide CFCC systems. This project will also interact with the UCLA micromechanics modeling effort by providing samples and data for verification of the evolving models.

Test Methods Subtask Progress

CFCC materials have highly directional structures and properties. They require a different test methodology than monolithic ceramics. Test methodologies are well established for polymer matrix composites, but not for the high temperature regimes of interest for CFCCs. The test methods subtask is defining the test requirements, establishing thermomechanical test facilities and developing reproducible test procedures. The subtask also is addressing NDE for characterization as well as for final quality assurance.

- * University of Washington and ORNL collaborated in Phase I to assess the test methods needed for CFCC materials. They defined tests for tensile strength, compressive strength, in-plane shear, interlaminar shear, flexure strength, strain, tension-tension cyclic fatigue and creep/stress rupture. They published a technical highlights report April 1993 "Thermochemical Test Methods for CFCCs". Equipment are being established for these tests, and a sample test matrix has been drafted to obtain an initial database with SiC/SiC CFCC material.

- * Non-destructive characterization (NDC) studies were initiated at Argonne National Laboratory (ANL) and at ORNL. ANL focused on infrared imaging and ORNL on ultrasonic techniques. Both showed good potential for detecting delaminations and density variation. Other NDC techniques were also screened including x-ray radiography, computed tomography, eddy current and electrical resistivity. NDC techniques appear capable of providing useful data on density uniformity, voids, delaminations, matrix material distribution and fiber geometry.

* ORNL conducted an effort to determine if fibrous debris generated during fabrication posed health problems for workers. Sampling was conducted at a CFCC company that used small diameter SiC yarn. Airborn fibers and particles were detected, but not in dangerous levels or fiber size.

Performance-Related Phenomena Progress

Most of the CFCC applications require long life with the components exposed to mechanical and/or thermal stress at high temperature, often in a chemically-aggressive atmosphere. The life will likely be determined by time-dependent degradation of the CFCCs or accumulation of damage.

* Performance simulation modeling was initiated at VPI. The objective is to combine pertinent data, basic understanding and models together to predict the remaining strength and life of CFCC components. Effort began in October 1993 and focused on data and supporting experiment needs to prepare simulation models.

* An environmental effects project began at ORNL July 1991. This project seeks to understand the interactions of the CFCC materials with representative application environments. Key issues are composite stability, failure mode and damage tolerance. Efforts so far have focused on careful thermogravimetric characterization of the oxidation kinetics of SiC/SiC composites fabricated by CVI. Emphasis is shifting to evaluation of the combined effects of stress and oxidation.

* A separate project was spun off the environmental project in October 1993 to focus on time-dependent behavior. The objective is to evaluate the creep and fatigue behavior. This is a particularly important task because most of the industrial teams do not have equipment or experience in creep, creep rupture and fatigue testing. Creep tests were initiated at 1100-1400°C for a SiC/SiC CFCC fabricated by CVI. Creep was low, but the exposure resulted in embrittlement.

* A project has been in progress at Idaho National Engineering Laboratory since September 1991 to understand failure mechanisms of CFCC materials and to apply this to prediction of structural integrity for applications. A draft report describing failure conditions for structures was distributed for comment. Fracture toughness testing has begun.

* A project to evaluate the thermal shock behavior of CFCC materials was begun in December 1992 at the University of Cincinnati. Effort so far has focused on evaluation of various tests for thermal shock behavior and on selection of one or more tests appropriate for CFCC materials. The objective is to select tests that will identify the critical composite parameters that control thermal shock resistance/damage.

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