Continuous Fiber Ceramic Composites
CFCC Program for DMO Materials

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Honeywell Advanced Composites, Inc.
(formerly AlliedSignal Composites, Inc.)
(formerly DuPont Lanxide Composites, Inc.)

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Patent Status

In October 1997, a patent was filed with the US Patent Office that covered oxidation protection mechanisms for composite bodies. The patent was issued on May 8, 2001 as Patent Number 6,228,453 to Lanxide Technology Company and AlliedSignal Composites Inc. This patent was a “continuation-in-part” to Patent No. 5,682,594. The first page of this patent is included as Appendix 1.

A separate filing was submitted in 2001 that covered the method for making materials with this type of oxidation protection.

Technical Status

All discussion in this final report is provided as non-proprietary data.

Identity of Contracted Party

Contract # DE-FC02-92CE40994 was awarded to DuPont Lanxide Composites Inc. (DLC) in September 1994. In August 1998, DuPont Lanxide Composites Inc. was acquired by AlliedSignal Inc., and renamed AlliedSignal Composites Inc. (ACI). In December 1999, AlliedSignal Inc. merged with the Honeywell Company to form
Honeywell International. Because of this merger, AlliedSignal Composites Inc. was renamed Honeywell Advanced Composites Inc. (HACI). Novations and “change of name agreements” were performed by DCMC.

Throughout this report, the name “HACI” is generally used despite the actual name at the time the work was performed.

Shortly after the end of the contract period, Honeywell Advanced Composites Inc. was acquired by the Power Systems division of the General Electric Company and is currently known as Power Systems Composites, LLC.
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Table 1. Acronyms and abbreviations used in this report

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<th>Acronym or Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>alumina or aluminum oxide</td>
</tr>
<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
</tr>
<tr>
<td>BN</td>
<td>boron nitride</td>
</tr>
<tr>
<td>CFCC and CFCCs</td>
<td>continuous fiber ceramic composites</td>
</tr>
<tr>
<td></td>
<td>This abbreviation was used as the title of this DOE program. It was also used to describe a type of material system. In the industry, CFCC refers to a ceramic composite reinforced by long, essentially continuous fibers of any arrangement. These include fibers woven into fabrics, other weaves and knits (which may be 2-D or 3-D reinforcement), braids, or tapes of parallel filaments (such as those produced by drum winding or filament winding).</td>
</tr>
<tr>
<td>CG</td>
<td>ceramic grade</td>
</tr>
<tr>
<td>CMC and CMCs</td>
<td>ceramic matrix composite</td>
</tr>
<tr>
<td></td>
<td>This term refers to the material system, or it refers to a particular part. In the industry, CMC refers to a ceramic composite that is reinforced by any means (e.g., particulate, whisker, chopped fiber, continuous fiber, 2-D or 3-D reinforcement).</td>
</tr>
<tr>
<td>CVI</td>
<td>chemical vapor infiltration</td>
</tr>
<tr>
<td></td>
<td>Similar to CVD (chemical vapor deposition).</td>
</tr>
<tr>
<td>DIMOX</td>
<td>DIMOX™ directed metal oxidation process by Lanxide</td>
</tr>
<tr>
<td></td>
<td>The process is licensed by HACI and also by others. Licensing is differentiated by end-use market segment.</td>
</tr>
<tr>
<td>DOE</td>
<td>(United States) Department of Energy</td>
</tr>
<tr>
<td>DMO</td>
<td>directed metal oxidation</td>
</tr>
<tr>
<td>GE</td>
<td>General Electric</td>
</tr>
<tr>
<td>HACI</td>
<td>Honeywell Advanced Composites, Inc.</td>
</tr>
<tr>
<td>MR&amp;D</td>
<td>Materials Research &amp; Design, Inc. Business that provides research and design services to the advanced materials community.</td>
</tr>
<tr>
<td>OEM</td>
<td>original equipment manufacturer</td>
</tr>
<tr>
<td>OIT</td>
<td>Office of Industrial Technologies Used in conjunction with DOE.</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory (located in Oak Ridge, Tennessee) In this report, work specified as taking place at ORNL usually refers to work performed at HTML (High Temperature Materials Laboratory at ORNL).</td>
</tr>
<tr>
<td>SIC</td>
<td>silicon carbide</td>
</tr>
<tr>
<td>UTRC</td>
<td>United Technologies Research Center</td>
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</table>
1 Executive Summary

This project, the CFCC program for DMO materials, focused on developing fiber-reinforced alumina matrix composites via the DIMOX™ directed metal oxidation process\(^1\) for use in various industrial heat management and industrial gas turbine applications. The acronym DMO was used for directed metal oxidation, which was represented by the Lanxide patented process DIMOX™ and other variations that were explored during the term of the project. The acronym CFCC (continuous fiber-reinforced ceramic composites) was used as the title of the DOE program and was used to describe a type of material system. The project was performed as a United States Department of Energy, Office of Industrial Technologies materials research project via a cooperative agreement with 25 percent cost sharing by the industrial partners with DOE.

Successful development of CFCCs by Honeywell Advanced Composites would save energy, reduce pollution, and lead to better competitiveness for US industries. Various applications for CFCC materials were investigated, and they continue to be investigated by Foster Wheeler Development Corporation, Solar Turbines, GE Power Generation, Teledyne Engines, and other companies. The composite materials that were studied in this project are expected to have utility and economic advantage over metals in the temperature ranges of 800°C to 1350°C (roughly 1500°F to 2500°F). Higher operating temperatures, longer service life, and new designs not possible with existing materials would enable the greater efficiencies. Planned activities included material development, process development, expansion of the current database, application-specific testing, representative component fabrication and testing, process economics, and joining.

Through an organized, systematic approach using a work breakdown structure, tasks were proposed by HACI, discussed with the DOE Technical Project Manager, Mr. Joseph Mavec, and approved prior to the commencement of work. The major task headings are listed below.
Task 1: Applications assessment  
Task 2: Scientific assessment  
Task 3: Materials and process development  
Task 4: Characterization  
Task 5: Program management and reporting

The bulk of the efforts were performed under Task Three, which had the following major subtask headings:

- Process feasibility
- Process engineering
- Component fabrication and testing
- Component evaluation
- Joining

A significant, meaningful contribution to this project was made through the Task 2 efforts. Universities and laboratories provided scientific support to multiple CFCC projects besides this project. These efforts were coordinated and funded via Oak Ridge National Laboratory. Oak Ridge National Labs' High Temperature Materials Laboratory (HTML), University of Cincinnati, Ames National Laboratory, BIRL (Basic Industries Research Laboratory) at Northwestern University, and Sandia Livermore National Laboratory provided significant effort to this project.

The project began with focused work on the silicon-carbide-fiber-reinforced alumina CFCC material system (SiC/Alumina). SiC/Alumina can be described as a typical CFCC that is produced as a laminate of many plies. During the project, these laminates were produced in a flat plate form and into complex-shaped articles. The flat plates were used
for process optimization and initial data for material system. The net shape components were used for rig testing to simulate environment and stress of the industrial application. Steps were taken to ensure that properties of the net shape components were similar to the flat plate database, using co-processed witness plates and test bars cut from net shape components. Many of the net shape parts were fabricated to allow sufficient material for test bars to be cut from the edge stock of the shape. This allowed higher confidence in detailed component design, such as for turbine engine tip shrouds for GE.

At the beginning of the CFCC program, the SiC/Alumina material system and DMO process were defined in an initial manner. Most process steps were performed by a procedure that worked but had never been studied for optimization. The CFCC program provided a means for process optimization, development of a database based on standardized physical testing, and application-specific testing. Process tasks optimized in this project include graphite tooling, fiber selection, fabric weave style, preforming methods, selection of prepreg resins, burnout process for prepreg resins, BN interface coatings, SiC interface coatings, DIMOX™ barrier materials, DIMOX™ bedding materials, metal removal processes, NDE and machining steps.

Modifications to material recipe and process steps were also studied. The original reinforcing fiber was ceramic-grade (CG) Nicalon™, produced by Nippon Carbon, Japan. An improved version Hi-Nicalon™ and other silicon carbide fibers were studied. Hi-Nicalon™ reinforced composites were found to be superior in every physical property to the baseline CG Nicalon™, but with a higher raw material price. Use of oxide composition fibers resulted in a different material system, called Oxide/Oxide CFCC material, which was also studied. The most studied case of the oxide/oxides was Nextel 610™/Alumina (Nextel Fibers, 3M Corporation). Oxide/Oxide CFCCs were found to have inferior mechanical properties at high temperatures, and no end-use applications were found.

In the late years of the program, the statement of work was modified to add the optimization of a new DIMOX™ material system, called thin sheet alumina, as a low-cost route for high temperature sheet metal type materials. These materials used
chopped alumina fibers combined in a continuous paper machine process to produce preform stock. The preforms were fired into a ceramic composite through in-situ DIMOX™ process. Similar tasks of process optimization, testing, components, and application-specific testing were conducted. Industrial applications for tube shields for Foster Wheeler Development Corporation and high-temperature air-to-air recuperators with Teledyne Ryan Engines were assessed.

Standardized physical testing went beyond data collection for the material systems to include procedural improvements. Tensile and fatigue data were collected primarily in air environments at room temperature up to 1300°C (2400°F [±/±]). Significant amounts of data were collected at 1200°C (2200°F [±/±]). Most data collection focused on determining the direction of change in properties of the material, versus the research premise prior to process or material modifications. The ultimate data obtained are creep data through 1500 hours on four CFCC materials, which helps to identify stress and temperature utility of the CFCCs. Procedural improvements included work on ASTM standards for composite testing.

Application-specific testing was performed to simulate exposure conditions found in industry. The testing was performed in a laboratory environment. For example, highly alkaline coal ash exposure testing was conducted for study of power plant component applications. High pressure steam atmosphere testing was performed for study of behavior in a turbine engine environment. Several of the specialized physical tests and application-specific tests were performed at Oak Ridge National Laboratory. In addition to testing, highly specialized materials characterization, microscopy, failure analysis, and theoretical work at ORNL supported these tasks to a level of scientific detail that HACI could not have performed. The High Temperature Materials Laboratory (HTML) at ORNL remains a valuable asset in the study of CFCC materials.

Another CFCC program conducted by Honeywell Advanced Composites is “CFCC for CVI Materials” which focuses on similar types of tasks with a silicon-carbide-reinforced silicon carbide matrix by CVI (chemical vapor infiltration) process. The program is still underway during the preparation of this final report. At times, these programs
coordinated activities and testing. This coordination allowed head-to-head comparison of properties and efficient use of testing resources. These coordination points will be discussed as they occurred throughout the program.

In conclusion, the CFCC program allowed determination of the life-limiting characteristics of the SiC/Alumina material system. One conclusion of this CFCC program is that the SiC/Alumina has good short-term performance in many environments, but it is too highly micro-cracked in its as-fabricated condition for utility beyond about 1500 hours in industrial environments. The life of the composite in static stress states can be impressive. However, in cyclic stress conditions, the alumina matrix material suffers from multiple cracking, which allows rapid oxidation and embrittlement of the composite. Attempts were made to understand and provide solutions using improved-stability silicon carbide fibers, oxidation coatings, and improved processing. CFCC allowed the resources to consider combinations of material systems.

The result today is that other ceramic composite matrix systems, such as enhanced CVI and SiC/Si MI (melt infiltration) matrices, have shown superiority over the DIMOX™ alumina for many long life properties sought for industrial applications. The CFCC program remains of very high value to HACI, due to the many composite-fabrication steps that were optimized and are practiced today with the technical knowledge gained from this program. Specific examples include the dual layer interface coating of BN/SiC, which is used in every silicon-carbide-fiber-reinforced CMC (ceramic matrix composite) that we produce.

Regarding the thin sheet material, processing was optimized to the extent necessary to prove the novel-manufacturing route, which results in its low cost. Testing and evaluation for applications such as high-temperature recuperators are not a priority today with microturbine manufacturers. Therefore, that work was stopped. The testing and evaluation continues today on private funding by Foster Wheeler for industrial applications.
2 Introduction

2.1 HACI's CFCC Project for DMO Materials

The CFCC project began with focused work on the silicon carbide fiber-reinforced alumina CFCC material system (SiC/Alumina). Through an organized, systematic approach using a work breakdown structure, tasks were proposed by HACI, discussed with the DOE Technical Project Manager, Mr. Joseph Mavec, and approved prior to the commencement of work. The major task headings are listed below.

- **Task 1**: Applications assessment
- **Task 2**: Scientific assessment
- **Task 3**: Materials and process development
- **Task 4**: Characterization
- **Task 5**: Program management and reporting

The bulk of the efforts were performed under Task 3, Materials and Process Development. The following subtasks fell under Task 3:

- Process Feasibility
- Process Engineering
- Component Fabrication and Testing
- Component Evaluation
- Joining

To improve the material system, significant numbers of iterations and trials were performed in Task 3. Several applications for SiC/Alumina were studied through database, design, and testing. In response to one of the applications, thin sheet alumina material was studied in the later years of the project.
SiC/Alumina can be described as a typical CFCC that has the following characteristics:

- Produced as a laminate of many plies of ceramic fabrics
- Held together with BN and SiC dual layer interface
- Densified with an alumina DIMOX™ ceramic matrix

The alumina matrix in this material is formed by the DIMOX™ directed metal oxidation process. The process was invented by Lanxide and was practiced by Honeywell Advanced Composites, Inc. (HACI) under license for the market segments of turbine engines, aerospace, rockets and missiles, heat exchangers, and friction materials.

The goal of the CFCC program was to encourage and accelerate development of the material system—for industrial applications—by engaging end users as program partners to guide the material development with application and environmental definition. Development for industrial applications was important to HACI because early projects with SiC/Alumina were focused almost exclusively on military components for turbine engines and aerospace hardware. CFCC was an avenue to overcome high-cost hurdles that had discouraged industrial applications.

End users performed application assessment for CFCC components in CFCC Phase I. The applications studied in Phase I were continued in Phase II, with implementation of the recommendations made in Phase I. The economic assessments performed in Phase I were not reworked as Phase II continued with materials work, design, prototyping, and testing of components.

In Phase II, commercial components were not produced. The final goal of the program was to create prototypes sufficiently shaped and sized to allow for limited testing in end user systems. To achieve this goal, application-specific testing was conducted using promising materials. Shaped components were built to further explore fabrication, and these components were then tested in more complex stress states.

In addition to assessment of existing applications, a minimal level of effort for new application assessment was included in Phase II, to allow for evaluation of any new
applications that were identified. For example, in response to evolving technology of
DIMOX™ and to the requests by Foster Wheeler and Teledyne, thin sheet DIMOX™
materials work was included in Phase II. The inclusion of the Teledyne recuperator
testing represents an example of new application-specific testing that was incorporated
into the CFCC program.

Successful development of CFCCs (via directed metal oxidation) by Honeywell
Advanced Composites in various applications being investigated by Foster Wheeler
Development Corporation, Solar Turbines, and GE Power Generation would save energy,
reduce pollution, and lead to better competitiveness for US industries. Other benefits of
successful CFCC development would include higher operating temperatures, longer
service life, and new designs not possible with existing materials. With these ends in
mind, planned activities included material development, process development, database
expansion, component fabrication and testing, process economics, and joining.
2.2 Introduction to Fiber-Reinforced Ceramic Composite Materials

Fiber-reinforced ceramic composites demonstrate the high-temperature stability of ceramics—with an increased fracture toughness resulting from the fiber reinforcement of the composite. Fiber-reinforced CMCs possess a unique failure mechanism; they exhibit a graceful type of failure. The fibers, along with the debond layer, cause the fibers to slide out of the composite during overload and crack propagation, as shown in Figure 1. This “pull-out” allows a transfer of load from the matrix to the fibers. A ceramic composite with many cracks often still can carry a significant load for many hours before breakage occurs. The “factor of safety” from ultimate strength to a typical design load is about 3:1, implying that the material can handle three-times the maximum stress of the operating conditions. A 3:1 ratio is encouraging to designers of turbine engine and industrial process components.

Figure 1. Fiber ends sticking out of a fracture surface. This demonstrates how the fiber ends transfer load to each other and to the matrix—to provide graceful failure.
Ceramic composites represent a relatively new class of materials. Because of low fabrication volume, the prototyping cost of these composites is high. Improvements in processing and detailed cost modeling have shown that, in volume, ceramic composites are favorably priced when compared to high-performance metals such as cobalt- and nickel-based super alloys. Solar Turbine Engines’ turbine engine combustor liner provides an example of a cost-driven use of CMCs. Uncooled CMCs replace complex, louvered and cooled metal liners in their Centaur power generation engine. The CMC combustors liners have been field tested at customer sites for over 40,000 hours and are being optimized for low cost on an approved commercialization plan.

The next several sections provide a description of ceramic composite materials. The CMCs consist of three primary material phases: the reinforcing fibers, the thin interface coating around the fiber, and the matrix that fills in and completes the shape of the component. Description begins with the matrix, which helps define the overall composite.

The material optimization performed under CFCC entailed a series of systematic optimizations. The goals of material optimization were to define the processing window, to increase the robustness of the process, to increase process yields (while reducing cost), and to define the complexity of parts that could be fabricated. All of these goals were applied to work in all of the three primary material phases—the fiber, the interface, and the matrix.

### 2.2.1 Matrix Processes

The matrix of the ceramic composite serves the functions of filling in the porosity around the fibers, completing the shape of the component, and providing environmental protection for the material. Common ceramic matrix materials are alumina, carbon, silicon carbide, silicon nitride, and silicon refractory metal in combination with silicon carbide. Matrix materials have extremely high melting points and are generally very hard. Due to their high melting-point temperatures, these matrix materials provide the composite with extreme temperature capability. The key benefit that CMCs provide,
however, is that they generally weigh one third of the metals they replace (because of the low density of matrix materials).

There are four basic techniques used to infiltrate the interface-coated preform with the matrix:

- DIMOX™ directed metal oxidation process
- Chemical vapor infiltration process (CVI)
- Pre-ceramic polymer infiltration process (PIP)
- Melt infiltration

In this CFCC program, DIMOX™ was the principal matrix process used. CVI process was used for the application of interface coatings, and PIP was used for joining and sealing processes. Melt infiltration with silicon metal was not practiced in this project.

In each of these techniques, the matrix serves to densify the preform, which provides a solid phase by which load can be carried from fiber to fiber. The matrix, which is the external surface of the material, determines final density and porosity characteristics. The matrix also helps determine use temperature, corrosion, erosion, and wear properties of the composite. These properties affect not only the use in application; they also affect manufacturing processes such as furnace processing temperature and machineability.

Sections 2.2.1.1 through 2.2.1.4 provide descriptions of the four basic matrix-processing techniques.
2.2.1.1 DIMOX™ directed metal oxidation process

The DIMOX™ directed metal oxidation process was invented by Marc Newkirk of Lanxide Corporation through his investigations of slags that formed in molten aluminum in casting foundries. This nuisance slag to the casting industry was found to be a ceramic material, harder than and having a higher melting temperature than the base aluminum alloy. After several years of study, a reproducible process was patented including means for reinforcing the ceramic with particulates or fibers.

The companies that predated HACI were originally formed as joint ventures with Lanxide. The purpose of the joint ventures was to bring the ceramic composites to commercial use in turbine engine, heat exchanger, and high-temperature processing applications. The CFCC program became one vehicle for material processes and applications to be investigated.

In the CFCC program, all DIMOX™ composites were reinforced with continuous fibers. The following steps outline DIMOX™ directed metal oxidation process. Figure 2 provides a pictorial description of the process.
1. The process to produce a composite starts with the preform. The reinforcing fibers are typically woven into fabrics, which are cut, stacked in layers, and shaped into the desired article.

2. Graphite tooling is used to hold the preform in the shape of the article. The graphite tooling is designed with many holes to perforate the tooling, to allow gases to pass through the preform in the CVI interface coating processes.

3. The interface-coated preform is removed from the tooling and is placed on a surface of a metal ingot. The fabrication layup is assembled at room temperature and then placed into a furnace.

4. At high temperature, the molten metal wicks into the preform and reacts with an oxidant to form a ceramic matrix.

5. The molten metal reaction front progresses through the preform via wicking and capillary action. A characteristic of this growth front is that it fills very small channels in the preform, and the direction of the growth front can be engineered and controlled.

6. If required, parts may undergo an additional operation, the metal removal process, to remove any residual metal.
The DIMOX™ directed metal oxidation process provides a manufacturing advantage—although the required furnace operating temperature is less than 1000°C, the use temperature of the composite exceeds 1300°C.

2.2.1.2 Chemical vapor infiltration process (CVI)

This process can be used for deposition of thin interface coatings or for infiltration of porous bodies for matrix densification. Reactant gases are introduced into a reactor at appropriate processing conditions to obtain a reaction and the deposition of the product onto and into the substrate. For example, introduction of MTCS (methyltrichlorosilane) and hydrogen at 1000°C under full vacuum will result in a reaction and deposition of silicon carbide (SiC) onto and into the preform. Different reaction gases are chosen depending on the matrix or interface desired, and many process variations exist.

One reactor can be used for several processes, based on similar chemistry, with time differences for both infiltration or deposition results. Another attractive characteristic of the process is that it is relatively insensitive to part geometry. As long as the reactor chamber is large enough for the part and tool, the part can be processed with few or no process changes. There are limitations and concerns about the number of parts and the volume they occupy in the chamber; coating and deposition non-uniformity is often a quality and engineering issue to be dealt with. Initially, the porous body (e.g., fiber preform) is placed into the reactor in a near-net-shape tool of machined graphite. A characteristic of this process is that most composite parts will require several CVI furnace cycles, and some machining steps. The last infiltration step ideally yields a part with the desired final dimensions with a chemically resistant seal coat.

2.2.1.3 Pre-ceramic polymer infiltration process (PIP)

During this process, the composite preform is dipped in a preceramic polymer solution, cured, and pyrolyzed to develop the matrix. This sequence of process steps is repeated until the desired part density is achieved.
The following steps outline one example of this process.

1. PCS (polycarbosilane) preceramic polymer is infiltrated into the preform at room temperature and possibly with vacuum assist.

2. The resin cures to a semi-solid state quickly at a low temperature (e.g., 150°C).

3. The resin is then placed into a furnace in a nitrogen atmosphere. The temperature is raised to at least 1000°C for pyrolysis.

4. The ceramic conversion of the resin occurs with volume shrinkage. The shrinkage causes channels to remain in the preform, which allows for further resin infiltration.

This process is extremely versatile, and many types of resins are available. The Ceraset™ family of resins (which HACI owns a license to use, sell, and produce) can be used for matrix formation, joining, and coatings. Ceraset™ is a polyureasilazane, which can be converted to several ceramic compounds, including SiC and Si₃N₄ (silicon nitride).

This process has to be matched with the end-use application. To bring the resin to a stable composition, the composite must be processed from the initial stages to a temperature above the maximum-use temperature of the article.

2.2.1.4 Melt infiltration

The objective of this matrix formation process is to infiltrate the preform with silicon metal. The preform is infiltrated in such a way that excess carbon is available for a high-temperature reaction in which silicon carbide is formed with a residual phase of silicon metal.

This process is similar to DIMOX™. The metal phase is part of the matrix. In addition, the phase can remain, or it can be processed to remove it or to alloy it.
While the silicon metal typically fills very small voids in the preform well, the metal does not fill large voids well. To fill large voids, a family of pre-processes that use either preceramic resin or ceramic particulates may be employed. Such pre-processes result in a very dense matrix.

Advantages of this process include a higher thermal conductivity of the matrix phase and composite, due to very low porosity and high thermal properties of silicon metal. A disadvantage of the process is that the processing temperature must be around 1400°C, the melting point of silicon. This high temperature excludes the use of many inexpensive reinforcing fibers, which makes this a premium-price composite.

### 2.2.2 Reinforcing Fibers

There are three primary steps to create the reinforcement phase of a composite material:

1. Selection of the reinforcement fiber.

   Fiber selection involves choosing the composition, the purity, the price, and the brand of the fiber. Typical composition choices include silicon carbide, carbon, and oxides such as mullite or alumina. (See Figure 3.)

2. Selection of the form in which the fiber will be used (e.g., fabrics, braids). (See Figure 4.)

3. Selection and procurement of tooling or mandrel used for compaction and shape of the fibers (e.g., plate, cylinder, complex near-net shape). Once fibers and fabrics are compacted and they take the shape of a component (or a flat plate), the article is referred to as a preform.
Figure 3. Spools of Hi-Nicalon™ fiber. The black multi-filament fiber looks identical to ceramic-grade Nicalon™, Tyranno fiber, and Sylramic fibers referred to in this report.

Figure 4. Nicalon™ fiber and fabric used in CFCCs.
2.2.2.1 Reinforcement fiber selection

Fiber selection involves choosing the composition, the purity, the price, and the brand of the fiber. Typical composition choices include silicon carbide, carbon, and oxides such as mullite or alumina.

Because there are few uses for ceramic fibers besides CFCCs, the market for ceramic fibers is small. Therefore, the costs are high. Silicon carbide fibers used with the DIMOX™ alumina matrix cost from $1,000/Kg (+/- $450/lb) to $6,900/Kg (+/- $3100/lb).

With any fiber selection at these costs, the total CFCC component price will be higher than the price of most metals, except for high-performance super alloys. When analyzing the economics of replacing metal parts, therefore, the performance of the CMC and its value in use must be considered. Performance and value in use create rationale for selecting fibers for long-term stability of the composite instead of selecting fibers because of the initial price. Analysis during CFCC found that composites with Hi-Nicalon™ fibers ($6,900/Kg) had higher operating temperature capability and longer life at similar temperatures than composites with ceramic-grade Nicalon™ fibers ($1,200/Kg).

2.2.2.2 Fiber form selection

Typically, ceramic fibers are woven into fabrics that are either two-dimensional (2-D) or three-dimensional (3-D). Plain weaves or harness satin weaves (HSWs) are considered 2-D because the thickness of the fabric results solely from the thickness of the fiber. Braids, angle-interlock weaves, and some filament windings are considered 3-D because the structures have a woven or knitted thickness. The vast majority of the composites studied in CFCC were composed of 2-D fabrics.

The material properties of the composite vary significantly based on the direction of the reinforcement fibers (in reference to the test direction) and the volume fraction of fibers found in the composite. Most CMCs are found to have 25% to 50% fibers. In addition, the direction of reinforcement is described with reference to the angles at which the majority of the fibers lie. For example, a balanced 0° to 90° fabric has the same number
of filaments in each direction, and the filaments are at right angles to each other, as shown in Figure 5. Angle interlocks and braids can align fibers in specific angle directions, such as having a +/- 30° fiber angle in reference to the axial direction of a part.

Figure 5. A cross section of 2-D fabric-reinforced SiC/Alumina via DIMOX™ process
The section shows bundles of filaments coming out of the page and, at right angles, bundles of filaments weaving across the page.

An important feature to consider when designing a CMC is that the tensile strength of the composite comes mostly from the fiber. The compressive strength of the composite is derived mainly from the matrix. Therefore, composite reinforcement and fiber direction are designed for a specific component and its strength requirement. In addition, a cost tradeoff has to be considered; 3-D reinforcement and special angle reinforcement can be much more expensive than 2-D fabric layups.
Another variable to consider when selecting fabric is the unit cell size. To say that a fabric contains 26 ends per inch means that, in one inch of cloth width, 26 filaments are aligned in one direction. Such a fabric is very tight. Most fabrics fall in the range of 15 to 22 ends per inch.

The interest in the open area of a fabric is due to an effect called *canning*. This effect occurs when the outside of the composite seals off and consequently leaves voids in the interior. Generally, canning is undesirable in CFCC materials.

Fabric end counts and unit cell sizes are usually chosen by the composite fabricator. They do not represent design criteria for the end user. Composites made in CFCC with 26 ends per inch were found too tight. Fabrics more open than 15 ends per inch were found loose, and fibers were often bent and damaged. Fabrics with 18 to 20 ends per inch were found most desirable.

### 2.2.2.3 Tooling selection and preforms

The preforms fabricated in this CFCC program were predominantly two-dimensional (2-D) structures of fabric layup. To create preforms, the fabrics were shaped on an aluminum mandrel. To obtain desired fiber volume fractions in the composite, the fabrics had to be compressed, or consolidated, tighter than they naturally lie. Vacuum bagging, autoclaving, and pressing were the primary consolidation techniques. After all fabric layers were assembled and consolidated, the preform was placed in a graphite tool to hold its shape during interface coating.

### 2.2.3 Interface Coatings

The second phase in the material system is the interface coating, which is a very thin layer coating approximately 0.5-micron thick. Interfaces can be applied to a preform through CVI, preceramic polymer, or solution based processes. Interfaces are typically carbon or boron nitride (BN). Ideally, this coating is applied to each filament of the fiber, and the coating controls the bonding strength between the fibers and the matrix.

This layer provides a “slip-plane”, which allows the fibers to slide in the matrix, absorbing energy and stopping minor cracks. Because of the physical slippage, the
interface layer also controls the maximum tensile properties of the composite. Ultimate tensile strength provides an example of this control. While the fiber provides most of the tensile strength, the slippage of the interface may allow only 30% of the total available fiber strength to be apparent. This strength translation represents a tradeoff in properties of the composite. It is possible to achieve full fiber strength with a tight bond to the matrix. In such a case, however, the composite would have brittle properties.

The interface also performs the engineering function of holding the preform together. Therefore, the preform is self-standing without tooling and fixtures. For example, graphite tooling is often used to hold the preform together prior to the application of BN interface. After BN interface is applied, no tooling and fixtures are necessary—the coating is strong enough to hold the preform together prior to the SiC CVI process step.

2.2.4 Design and Prototyping Iterations in Development

One hurdle to the commercialization of ceramic composites is a lack of design methods. Three distinct issues were addressed in CFCC to help eliminate this hurdle:

- A database was created. Many different types of test data were obtained, and a database was assembled in which the data is easily retrieved and used.
- Design constraints of the processes were tested and understood. HACI therefore had a definition of the process window of conditions that delivered consistent properties within a specific band of tolerance. To help customers with appropriate designs for ceramic composite components, the process window of operating conditions was combined with geometry-specific rules.
- CFCC tasks addressed the method of design and the issue of design methodologies, or design codes.

In the CFCC program, design limitations for SiC/Alumina primarily involved limitations in fabrication processes rather than limitations in design practices. Prior to CFCC, early design rules (e.g., a rule for component size) existed in part due to equipment limitation. In CFCC, design rules were further studied. Because these rules are based on processing
limitations, they are still valid for composites with the BN/SiC dual interface system.

Design rules for SiC/Alumina are listed below in Table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Design Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component wall thickness</td>
<td>.080&quot; to .30&quot; thick; but ratio of maximum-to-minimum thickness can not exceed 2.0</td>
</tr>
<tr>
<td>Cylinders</td>
<td>Length to diameter ratio should not exceed ten.</td>
</tr>
<tr>
<td>Bends and Radii</td>
<td>Minimum .125&quot; inside radii.</td>
</tr>
</tbody>
</table>

Two principal design conclusions were reached in CFCC. First, it was concluded that ceramic composites have very little life when used at stresses above the proportional limit. The proportional limit stress is only about 8Ksi to 10 Ksi, while most steels have a proportional limit of 25Ksi to 30 Ksi. Most components considered in CFCC had average operating stresses below the 8-Ksi limit, but higher stresses were found in attachment areas and holes. This made the design of each component an exercise to reduce stress and resulted in many clever attachment methods.

Through micro cracking, the material has some ability to redistribute stress in a high-stress concentration, but a reduction in elastic modulus occurs. Therefore, design for components with high levels of stress, or complex stress states, have to be approached very carefully and with application-specific testing.

Second, it was concluded that, especially for initial prototyping of industrial components, the design could be accomplished with standard CAD-type design software, using the linear elastic properties of the material (i.e., the portion of the stress-strain curve below the proportional limit).

Additionally, discussions were held with the program partner OEMs regarding their design needs and the preliminary test data required to evaluate the composite system. FWDC initiated the design code acceptance process through ASME Section 8 committee.
The ASME design rules are established for pressure vessels, reactor vessels, heat exchangers, and piping. The rules are used widely for industrial equipment design. GE CR&D found it necessary to perform special testing for thermal cycling and thermal shock at turbine engine temperatures because design predictions were not available. Some of that data was then used in GE proprietary design codes to design turbine engine components.

New component design evolved into a process of more than simply reviewing engineering drawings. For HACI to state that something was a feasible part to fabricate came to mean that we had a proposal outline and a suggested approach to use all of our experience and learning to fabricate a component. The following list outlines a typical design and fabrication process.
Step 1—Applications Assessment
- CAD design and stress analysis of the segment
- Initial check of part geometry to HACI fabrication rules
- Prototyping price estimates
- Designing a task for plate segments of sub-elements to simulate a portion of the component or to obtain required data for the design and analysis

Step 2—Material Performance Assessment
- Plate or sub-element fabrication of 2-D SiCf/Al2O3
- Testing at HACI and customer site (application-specific tests)
- Microscopy and analysis of the material performance

Step 3—Component and Process Development
- With new data, design analysis and stress analysis
- Fabrication of tooling
- Fabrication of initial 2-D hand layup reinforced component
- Analysis of process—perhaps cutting initial component into test bars for additional data collection
- Testing of component-to-application stress magnitude in a simple environment

Step 4—Component
- Analysis of information learned to date
- Adjustment of tooling, preform, or process
- Fabrication of components
- Rig or Engine testing by OEM in final-application environment
- Redesigning or path forward
- Manufacturing price estimates

Step 5—Path to Commercialize
- Field testing of single and then multiple numbers of parts
HACI maintains every customer’s projects under strict and consistent proprietary information rules. In all cases, projects are maintained as proprietary information, unless HACI knows that it is allowable for specific data to be shared with others—as was the case with the CFCC program. For commercial projects however, the knowledge of existence of a program was the property of the customer. HACI held that the customer owned the engine, the system, and the component design. HACI in turn held the material system, all materials data, and all processing information, including aspects such as tooling design. Therefore, data from each program was entered into our database, but there was no direct identification back to the specific customer design. HACI worked on several programs for turbine engine combustors at the same time, but, because each design was customer owned, the programs all remained as proprietary information.

The CFCC program contributed to our base of experience more than other commercial design and prototyping programs. Through the OEM partnerships in CFCC, the combination of application engineering and materials processing became a significant learning ground upon which to explore process and materials occurrences in testing that were otherwise unexplained. Whether data related to a tensile bar or to a component, it was relatively common in a commercial program to have one piece of data perform outside the average of the others. Whether the number represented by the data was high or low, HACI exhibited a high degree of curiosity to study the situation. Commercial or internal resources often did not allow study of the situation. CFCC provided the financial resources and the time to understand why a component performed differently than expected.

2.3 Specific CFCC Task Descriptions

2.3.1 SiC/Alumina Material System

The material optimization performed under CFCC included a series of systematic optimizations. The overall goals were to define the processing window, to increase the robustness of the process, to increase process yields while reducing cost, and to define the complexity of parts that could be fabricated.
All of these goals applied to work in all three material phases—fiber, interface, and matrix.

Table 3 identifies the materials work performed with SiC/Alumina.

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Process Feasibility</td>
<td></td>
</tr>
<tr>
<td>3.1.3.1</td>
<td>Matrix Densification improvements</td>
<td>Addition of oxygen getters</td>
</tr>
<tr>
<td>3.1.4.1</td>
<td>Multiple debond layers</td>
<td>Concepts to improve oxidation resistance of the material through multiple layers.</td>
</tr>
<tr>
<td>3.1.4.2</td>
<td>Modified BN Interfaces</td>
<td>Modifications of the BN interface and scale-up process consistency.</td>
</tr>
<tr>
<td>3.2</td>
<td>Process Engineering</td>
<td></td>
</tr>
<tr>
<td>3.2.1.1</td>
<td>Study of Process Engineering Variables</td>
<td>A study to look at fabric weave, preform layers, interface coatings, matrix growth and metal removal steps; all to investigate the process windows and robustness of the steps.</td>
</tr>
<tr>
<td>3.2.2.1</td>
<td>Modeling of the CVI Interface</td>
<td>Work by HACI and also with Sandia National Labs for BN process modeling.</td>
</tr>
<tr>
<td>3.2.3.1</td>
<td>Evaluation of 2-D Braided Composites and U-shaped bends.</td>
<td>Evaluation and demonstration of potential means for low cost CMC tubes and headers.</td>
</tr>
<tr>
<td>3.2.4.1</td>
<td>Materials Database Extensions</td>
<td>Tasks that sought to expand the types of physical testing performed on SiC/Alumina, and perform tests for each specific customer important to their design tasks.</td>
</tr>
<tr>
<td>3.2.4.4</td>
<td>SiC Alumina with Hi-Nicalon™ fibers</td>
<td>Work with a more stoichiometric fiber and the affects on long life properties.</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Process Economics</td>
<td></td>
</tr>
<tr>
<td>3.2.5.1</td>
<td>Commercialization Economics</td>
<td>Work to reduce the costs of CFCC materials and components.</td>
</tr>
</tbody>
</table>
To study the optimization of SiC/alumina ceramic composite processing, several hundred flat plates were fabricated. In this study, many plates were not fully densified, but they were destructively analyzed in mid-process. A typical flat plate measures 6" x 9" x ¼". The CMCs were also produced into complex near-net-shape articles, including many sizes of tubes, heat exchanger headers, combustor liners, and shrouds.

2.3.2 Thin Sheet Alumina Composites

During the course of this program, both Foster Wheeler Development Corporation and Teledyne Engines approached HACI seeking a ceramic composite replacement for sheet metal. Although the two companies’ end uses were totally different, both customers required a material that was formable, thin, capable of holding its own weight and maintaining its shape, and very resistant to hot temperatures. A thin, fiber-reinforced alumina matrix composite was demonstrated, which was created via the DIMOX™ directed metal oxidation process.

The fiber-reinforced thin sheet ceramics require a low-cost preforming approach, and they use ceramic fiber sheets produced on a high-speed paper-forming process. These CFCCs are designed for use temperatures up to 1300°C (2300°F).

Table 4 identifies CFCC work with thin sheet alumina.
Table 4. Thin sheet alumina tasks

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task title and hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Process Feasibility</td>
<td></td>
</tr>
<tr>
<td>3.1.2</td>
<td>Preform Development</td>
<td></td>
</tr>
<tr>
<td>3.1.2.1</td>
<td>Formable Ceramic Fiber Paper</td>
<td>Initial work with Hercules and Lanxide licensed technology for ceramic papers</td>
</tr>
<tr>
<td>3.1.2.2</td>
<td>Ceramic Fiber Paper with Improved Toughness</td>
<td>Work on fiber and interface selection.</td>
</tr>
<tr>
<td>3.2</td>
<td>Process Engineering</td>
<td></td>
</tr>
<tr>
<td>3.2.1.1</td>
<td>Study of process variables and affects on materials.</td>
<td>Work with IPST and Western Michigan University for scale-up processing.</td>
</tr>
<tr>
<td>3.3</td>
<td>Component Fabrication and Testing</td>
<td></td>
</tr>
<tr>
<td>3.3.1.4a</td>
<td>Thin Sheet Recuperator</td>
<td>Work with Teledyne Ryan Aeronautical and RPI (Rensselaer Polytechnic Institute) for application testing of a turbine engine recuperator.</td>
</tr>
<tr>
<td>3.3.1.4b</td>
<td>Thin Sheet Erosion Testing for Tube Shields</td>
<td>Work with Foster Wheeler for application testing of an industrial tube shield.</td>
</tr>
</tbody>
</table>

The paper-making technology is used to produce a highly loaded ceramic sheet, and the DIMOX™ directed metal oxidation process is used to densify the formed sheet into a rigid, thin-walled ceramic tube or sheet structure. Sheetmaking trials at Western Michigan University consisted of forming sheets on the Fourdrinier paper machine. Materials technology included scale-up of the oxide interface coating process to a 50-gallon reactor. Composition work improved an important characteristic—low percentage of firing shrinkage. Joining and lamination technology was improved so that the shrinkage of joining compounds matches the material.

Test parts for industrial alkali environments were considered with Foster Wheeler Development Corporation. Development of tube shields represents an interesting application of CFCCs because tube shields represent an immediate opportunity for
CFCCs to replace sheet metal. In the application, shields are used to protect heat exchanger tubes and process piping from erosion and further corrosion in particulate-laden gas streams. Laboratory testing of baseline particulate-reinforced thin sheet materials has shown encouraging erosion performance to the application temperature of 1800°F. Multi-layered thin sheet was tested for erosion resistance and corrosion resistance of a bonded joint for potential attachments. Shape trials to look at curvature limits for tube shields were performed. Representative component tube shields were considered, and plans for joining and attachment were discussed.

A suitable pilot plant to test tube shields was not found, and the CFCC program ended prior to completion of a risk assessment of placing thin sheet tube shields directly into an operating, coal-fired power plant. The application interest continues beyond the CFCC program, and we plan to keep working with FWDC in development of this application.

The application of recuperators for automotive gas turbine engines is of high interest to Teledyne Ryan Aeronautical. The thin sheet replaces metals in the thin-walled elements, which enables temperature operations higher than those available with metals. Prototype, parallel-plate cross-flow recuperators up to 20 layers thick were made and tested. Fabrication challenges were overcome by laminating a multi-layered structure. Dimensional control, warpage, and shrinkage in the high-temperature firing process were studied.

Complex curvature designs with high surface area for laminar-type counter-flow recuperators were made. Several designs of curved elements were fabricated. Through the iteration of curved elements, many design changes were implemented, and many improvements in assembly and fabrication were demonstrated. One large, laminar flow recuperator assembly was tested at Rensselaer, and it produced heat transfer that matched predictive modeling to 1000°C.

In the future, consistency and scale-up of the paper-making preform fabrication needs to be improved. Trials for bonding thin sheet ceramics to metals will need to be performed for erosion applications. Fabrication techniques such as sheet embossing were considered for the exploration of increased heat transfer.
2.3.3 Materials Testing

In order to assess material iterations, physical property measurements from different tests were taken. Prior to CFCC, 4-point flex testing was the standard test for material properties. As the materials and applications became more complex, properties specific to the end user became the standard benchmark of performance. In other programs, low-cycle fatigue strength in air or stress rupture at high temperature in a steam environment became important tests for customers. Table 5 identifies SiC/Alumina testing tasks, which were performed to expand the types of physical testing.

Table 5. SiC/Alumina testing tasks

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
</table>
| 3.2.4.1           | Materials Database Extensions | • Tensile testing
|                   |                            | • Compression testing
|                   |                            | • Flex testing
|                   |                            | • Isopescu shear testing
|                   |                            | • Stress rupture testing
|                   |                            | • Creep testing
|                   |                            | • Low-cycle fatigue
|                   |                            | • High-cycle fatigue |
| 3.2.4.1           | Specialty Tests Performed | • Tow composites testing
|                   |                            | • Joining tests
|                   |                            | • Thermal cycling tests
|                   |                            | • Fatigue and hold cycles
|                   |                            | • C-ring tensile tests
|                   |                            | • C-ring compression tests |
| 3.2.4.1           | Physical Property Measurements | • Density
|                   |                            | • Coefficient of thermal expansion (CTE)
|                   |                            | • Fiber volume fraction
|                   |                            | • Residual metal concentration |
In the CFCC program, test procedures and data collection methods were improved. Physical testing was performed at many sites, including Oak Ridge National Laboratory, University of Cincinnati, University of Dayton Research Institute, HACI's own test laboratory, and others.

Composite testing is not straightforward because the materials usually exhibit a non-linear behavior. For SiC/Alumina, a typical tensile stress-strain curve shows two distinct regions—the regions below and above the proportional limit of the material. (See Figure 6.) For ceramic composites, the proportional limit occurs at the stress where matrix micro cracking becomes excessive, and load is transferred to the fibers. It is indicated by a bend in the stress-strain curve. Flex-test photographs illustrate many visible cracks in the exterior matrix material while the composite continues to carry load. Therefore, typical testing consisted of flexural and tensile tests to composite failure and tensile stress rupture tests below and above the proportional limit of the material. Material iterations in processing sought to increase the proportional limit, as this increases the usable stress for long lifetimes. Process changes sought to decrease the initial modulus of the material, which provides more tolerance to strain within the design stress. In addition, iterations sought to increase total area under the stress strain curve, which is a measure of total fracture toughness.

Figure 6. Typical tensile stress-strain curve of SiC/Alumina.
HACI has expert composite-testing capability, both in personnel and in equipment. HACI is a charter member of Mil-Handbook 17 committee for ceramic composites and of ISO and ASTM test standards committees for ceramic composite materials. HACI has been nationally recognized as possessing both the best ceramic composite materials database and the best electronic-record retention and search capability. HACI corresponds regularly with other test experts at Oak Ridge National Laboratory, University of Washington, U.S. Air Force Wright Materials Laboratory, and U.S. Army Aberdeen Materials Laboratory. HACI is represented on the ASME committee for ceramic composite materials for pressure-containing equipment for heat exchangers. HACI's test laboratory equipment has been used in ASTM, ISO, and Mil-Handbook round-robin testing and has been validated via inter-laboratory testing with General Electric, Pratt & Whitney, NASA Glenn Material Laboratory, and other customer sources.

Material scientists often relied on microscopy to define the material improvements by optical, SEM, or TEM microscopes. HACI owns optical microscopes and had ready access to SEM. Oak Ridge National Laboratory provided TEM microscopy services. Beyond testing, highly specialized characterization, microscopy, and theoretical work at ORNL supported these tasks to a level of scientific detail that HACI could not have performed. By using physical and microscopy analysis, a product-to-process correlation was determined. Throughout the end-use task descriptions, the behavior of the material and the microscopy results are described.

2.3.4 Application-Specific Testing

Once the material properties were tested and found appropriate for the design of the end-use component, application-specific testing was conducted. In this step, the end user assists the material producer significantly to determine a means to test the material in a controlled laboratory situation, which simulates the environment to which the part will be exposed.

Although testing was performed in a laboratory environment, application-specific testing was used to simulate exposure conditions found in industry. For example, highly alkaline coal ash exposure testing was performed to study power-plant-component applications.
High-pressure steam atmosphere testing was performed to study behavior in a turbine engine environment. Several of the specialized physical tests and application-specific tests were performed at Oak Ridge National Laboratory. Table 6 identifies application-specific tests.

**Table 6. Examples of application-specific tests**

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Customer or Task</th>
<th>Example of application-specific test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various</td>
<td>Materials Development</td>
<td>• Tow composites tests</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Long duration steam exposures for various fibers and interface coatings</td>
</tr>
<tr>
<td>Various</td>
<td>Foster Wheeler Development Corporation</td>
<td>• Exposure testing in coal ash</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Exposure testing in flue gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Exposure testing in power plant heat exchanger</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High pressure tube testing</td>
</tr>
<tr>
<td>Various</td>
<td>Solar Turbines</td>
<td>• Cylinder combustion tests</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Specific creep cycle tests</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Steam environment tensile tests</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Steam and high pressure exposure tests</td>
</tr>
<tr>
<td>Various</td>
<td>General Electric Power Systems</td>
<td>• Thermal cycling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Thermal Shock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Long duration creep tests</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Steam and high pressure exposure tests</td>
</tr>
<tr>
<td>Various</td>
<td>Teledyne Engines</td>
<td>• Joined Parallel plate sections</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Thermal cycling tests</td>
</tr>
</tbody>
</table>
2.3.5 CFCC Applications Work with Foster Wheeler Development Corporation

Foster Wheeler Development Corporation (FWDC) is located in Livingston, New Jersey, which is only a 2-hour drive from HACI's site in Newark, Delaware. Therefore, many meetings were held. Such close interaction has resulted in a positive relationship. FWDC's commercial interests are design, construction, modification, and operation of power plants—from individual modules within a power plant to complete site operation. Their research interests in ceramic composites were directed to understanding the capability of materials that could be used for higher temperature and components that are more corrosion-resistant. Reduction in maintenance costs would provide value in use for the CMCs to replace metal alloys. Their specific interests included high-temperature heat exchangers, steam reformers, particle separators, and tube shields.

FWDC exerted considerable effort in the design of a high-temperature heat exchanger built with CFCC materials. A summary of this design effort was published in an ASME paper. The HITAF (High-temperature Advanced Furnace) work was also partially sponsored via a DOE HIPPS project. They also prepared for HACI an extensive Phase I applications assessment report. During their Phase I CFCC program efforts (and early in Phase II), they used subcontracts from the CFCC program for DIMOX™ materials and the CFCC program for CVI materials. Both types of materials underwent database review and initial design of the HITAF work.

Table 7 identifies the DMO CFCC work with FWDC.
Table 7. Foster Wheeler application tasks

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Process Engineering</td>
<td>Process Modeling— Materials Screening for FWDC</td>
<td>Materials Screening – Coal ash exposure tests, and analysis of basic corrosion mechanisms.</td>
</tr>
<tr>
<td>3.2.3.1 Fiber Architecture— Evaluation and Demonstration of 2-D Braiding</td>
<td></td>
<td>Fabrication of composites with preform architectures of 2-D braiding and tri-axial weaves, for tubes and headers</td>
</tr>
<tr>
<td>3.2.3.2 Fiber Architecture— Development and Demonstration of U-Bends</td>
<td></td>
<td>Fabrication of composites with preform architectures for U bends</td>
</tr>
<tr>
<td>3.2.4.2 Materials Screening— Database for material performance in FWDC Application-Specific Testing</td>
<td></td>
<td>Erosion Tests, Corrosion tests. Screening of Oxide-Oxide CFCC materials</td>
</tr>
<tr>
<td>3.2.5.1 Process Economics</td>
<td></td>
<td>Commercialization Economics for cost determination.</td>
</tr>
<tr>
<td>3.3 Component Fabrication and Testing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.2 Representative Parts— The prototyping of components in different ways.</td>
<td></td>
<td>Component Evaluation for Tube Evaluation, and Development of a Ceramic Air Heater</td>
</tr>
<tr>
<td>3.3.2.2 Simulation Tests— Testing of typical use environments without the risk of a field installation.</td>
<td></td>
<td>Mechanical Testing of Tubular Subelements, FWDC and Penn State tube testing.</td>
</tr>
<tr>
<td>3.3.3.2 Field Exposure Tests of coupons and parts.</td>
<td></td>
<td>Field Exposure testing inside power plants for actual corrosion and environmental affects.</td>
</tr>
<tr>
<td>3.3.4.1 Reliability and Life determination.</td>
<td></td>
<td>Work towards ASME Code Acceptance of CMCs, common design standards and other engineering tools.</td>
</tr>
<tr>
<td>3.5 Joining</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5.1 Composite to composite joining</td>
<td></td>
<td>Composite to itself and composite to other ceramic joining methods, with a goal of pressurized joint design.</td>
</tr>
</tbody>
</table>
Application-specific testing was performed for representative atmospheres in FWDC labs, and field exposure testing was performed at several power plants. Subelement fabrication, joining experiments, and further design work were performed in the tasks with FWDC.

At the beginning of the project, the hurdles to commercialization were thought to be lack of design data, a general concern of low fracture toughness of ceramics, and experience in fabrication of complex components. Influential persons such as the chief metallurgist at FWDC supported the project and showed interest in ceramic composites. However, such persons were not convinced that ceramic composites belong in commercial power plants.

At the end of the project, however, FWDC believed that database data was sufficient to support design and construction for their parts, but they clarified that this was only the case because of their experience with the CFCC program. They had supporting data, which included data on the corrosion resistance of CMCs. Data showed that CMCs were 20 times more resistant than metals at temperatures exceeding the metal’s utility. This type of positive data excited the engineers at FWDC. They worked on the ASME Pressure Vessel Code and public databases such as Mil Handbook 17 to provide widespread confidence in the utility of ceramic materials. They maintained a desire for more field-testing data, especially longer-term test data for strength retention and corrosion resistance.

Despite the desire for more field-testing data, barriers arose that stalled momentum. First, samples that were exposed for 9000 hours inside the “Robbins Plant particle separator” could not be recovered after a major system failure. There was no opportunity to repeat the test. Second, the cost of the materials was still too high to seriously design and purchase ceramic components. For several years at the end of CFCC, FWDC resisted using more stoichiometric fibers such as Hi-Nicalon™ because they found the price premium versus standard ceramic-grade Nicalon™ to be prohibitive. Third, part of the resistance to move away from ceramic-grade Nicalon™ fibers was FWDC’s desire to learn more about one particular alloy rather than to introduce new materials.
Fourth, FWDC was concerned about manufacturing consistency. Occasionally, in the course of testing, one sample of a group would perform poorly. This caused one to question whether question CMCs were mature enough for use in pressurized equipment.

2.3.6 CFCC Applications Work with Solar Turbines Corporation

Solar Turbines Corporation is a division of the Caterpillar Corporation. Solar develops, manufactures, operates, and maintains turbine engines primarily for small electrical generation sites and for the oil and gas industry. One of Solar’s most successful products is a gas pipeline compressor station in which the turbine engine draws its fuel from the pipeline. This makes it a freestanding unit that is ideal for remote locations. Solar’s design emphasis is on long-term durability rather than highly detailed or sophisticated designs that might tend to require more maintenance. Prior to CFCC, Solar was aware of ceramic composite research in military engines, but they did not have resources to study the long-term applications of CMC in industrial turbine engines.

Solar’s turbine engine combustor liner provides an example of a cost-driven use of CMCs. Uncooled CMCs replace complex, louvered and cooled metal liners in their Centaur power generation engine. The goal of CFCC was to test several CMC materials in test rigs and laboratory engines to determine durability of the rigs and engines.

Combustors are a good fit for CFCC materials. Combustors see high surface temperatures and require high tolerance to thermal stress, both of which are strong attributes of ceramic composites.

The combustors for Solar’s test rig were straight, 8-inch diameter cylinders, and they saw uniform stresses in operation. Due to the uniform design, the test rig combustors were also used by Argonne National Laboratory in studying non-destructive testing (NDE) of ceramic composites. With the material producers and Argonne, Solar established a program for combustors to be NDE-examined before and after each round of testing. For all parties involved, this provided valuable feedback on the behavior of CMC materials.
At the end of this CFCC program, Solar had chosen CVI SiC/SiC and MI SiC/SiC materials as the best CMCs for their application. On the CSGT (ceramic stationary gas turbine) program, the CMC combustors have been field tested at customer sites for over 40,000 hours, and they are being optimized for low cost on an approved commercialization plan. The DIMOX™ materials performed well in initial rig tests, but over time they became brittle and suffered cracks due to steam and oxygen ingress into the composite. Several improvements were promising. For example, Hi-Nicalon™ fibers were found to be significantly better than ceramic-grade Nicalon™. However, no improvement was found to seal the microcracked DIMOX™ matrix.

Table 8 identifies the applications work performed with Solar.

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Process Engineering</td>
<td>Plate NDE testing, and NDE density-to-strength correlations.</td>
</tr>
<tr>
<td>3.2.3.1</td>
<td>Evaluation of 2-D Braiding</td>
<td>Part of the cost and process variables considered for combustors.</td>
</tr>
<tr>
<td>3.2.4.3</td>
<td>Database Extension for Solar Turbines</td>
<td>Long term creep testing was important to Solar.</td>
</tr>
<tr>
<td>3.2.5.1</td>
<td>Commercialization Economics</td>
<td>Large volume cost modeling was performed to look at the source of costs.</td>
</tr>
<tr>
<td>3.3</td>
<td>Component Fabrication and Testing</td>
<td>Non destructive testing by Argonne National Laboratory.</td>
</tr>
<tr>
<td>3.3.1.3</td>
<td>Representative combustor liners for Solar test rig.</td>
<td>8&quot; dia x 8&quot; long cylinders for NDE and initial testing</td>
</tr>
<tr>
<td>3.3.2.3</td>
<td>Two hour test in combusor rig.</td>
<td>Screening test for thermal shock and thermal stresses.</td>
</tr>
<tr>
<td>3.3.3.3</td>
<td>One hundred hour test in combusor rig</td>
<td>Initial endurance test for combustors.</td>
</tr>
</tbody>
</table>
2.3.7 Applications Work with General Electric Corporate Research and Development and General Electric Power Systems

General Electric Power Systems (GEPS) develops, manufactures, operates, and maintains the world's largest and most powerful power-generation turbine engines. These engines are used by utility companies for primary electricity generation. In contrast to Solar's interest in combustors, GE's Phase I analysis focused on fuel efficiency and cost savings to their customers and found their turbine tip shroud as the primary application. GE Corporate Research and Development (CR&D) works with GEPS for materials testing, component design, and rig testing. In Phase II, GE CR&D lead the program under the design and application guidance of GEPS. As the overall success of the shroud development progressed, GEPS took a more active role.

Results of GE's Phase I CFCC tasks were that application assessments were performed for value of ceramic composites in large power generation turbine engines. In this assessment, turbine tip shrouds were identified as the component with the highest value payoff, and combustor liners were identified as second. A number of other components including vanes and blades have high payoffs. However, such components are much more difficult to fabricate, they may require properties beyond the SiC/Alumina material system, and they represent a higher risk in testing.

Shrouds are a good fit for CFCC materials. They see high surface temperatures and require high tolerance to thermal shock and thermal stress, both of which are strong attributes of ceramic composites. Shrouds are stationary (versus rotating) components so they have a more static and predictable stress level, and they have definable attachment requirements.

Table 9 identifies the applications work performed with GE.
Table 9. GE Power Systems application tasks

<table>
<thead>
<tr>
<th>CFCC Program Task</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Process Engineering</td>
<td>Various process methods and preforming methods to fabricate shrouds.</td>
</tr>
<tr>
<td>3.2.4.1</td>
<td>Materials Database Extension for GEPS</td>
<td>Database including creep and high cycle fatigue.</td>
</tr>
<tr>
<td>3.2.5.1</td>
<td>Commercialization Economics</td>
<td>Price models for future shrouds.</td>
</tr>
<tr>
<td>3.3</td>
<td>Component Fabrication and Testing</td>
<td>Design iterations of shrouds to reduce stress and reduce cost.</td>
</tr>
<tr>
<td>3.3.1.1</td>
<td>Shrouds for General Electric Power Generation</td>
<td>Fabrication of representative shroud components.</td>
</tr>
<tr>
<td>3.3.2.1</td>
<td>Application-Specific Environmental Tests at GEPS</td>
<td>Rig and special tests to simulate engine conditions with specimens.</td>
</tr>
<tr>
<td>3.3.3.1</td>
<td>Shroud Mechanical and Rig Tests at GEPS</td>
<td>As a shroud test rig is available, testing of shroud attachment and thermal performance.</td>
</tr>
<tr>
<td>3.5.2.</td>
<td>Composite to Ceramic Joining</td>
<td>Design and process investigations for ceramic barrier layers, and also ceramic sealing methods between shroud components.</td>
</tr>
</tbody>
</table>

GE evaluated the existing database on Nicalon™/alumina for completeness and relevance to the turbine engine shroud application. Plates were fabricated, and specimens were prepared and tested by HACI and GEPS to complete the required database.

In CFCC, many application-specific tests were performed. They included mechanical and thermal tests on plate materials (including temperature gradients across the thickness), thermal cycling, high-cycle fatigue tests, and static load tests. Data from the tests was used for design optimization of the shrouds.
Results were documented and data was used for shroud design. The design of the CFCC shroud actually tested combines functionality of the metal part it replaces and design-for-manufacturing attributes for three CMC processes (DIMOX™, CVI, and MI).

After application-specific testing and several design reviews with GEPS for acceptance, HACI fabricated ten representative shrouds for GEPS testing. Via the CFCC program for CVI Materials, SiC/SiC shrouds were also provided, and shrouds were fabricated of GE’s MI composite materials. Representative shrouds were run under simulated engine-operating conditions in a rig test for approximately 200 hours. The test rig in Schenectady, New York, performed well and closely simulated gas turbine conditions.

Price of the CFCC component is extremely important to GE. The value in use of the shroud provides payoff to the engine owner, but the competitive selling price of the engines puts the initial component cost at GE’s level. Information generated in the program on the costs of fabricating CFCCs was used to assess the impact of process improvements made in the program and to update projections of CFCC component prices.

It was originally planned in CFCC that HACI would develop a ceramic, abradable, thermal barrier coating for Nicalon™/alumina composites. HACI’s work in this area is represented by technology from existing knowledge of alumina titanate coatings, and/or coatings derived from our preceramic polymers. However, as the CFCC program evolved and as component testing was successful, development of thermal barrier coatings did not become a more active pursuit at HACI, but rather at the OEM engine companies. This occurred because of the experience that the OEMs had in coatings for metal components and because of the proprietary information issues that arose at the OEM engine companies. This situation was not anticipated in the original statement of work. In retrospect, HACI can see that the advanced application of super-alloy components in turbine engines is practiced with commercially available metals. The thermal barrier coatings and cooling mechanisms, however, are highly specialized and proprietary to each company.
Therefore, the tasks on thermal barrier coatings ended up being coupon preparation for GE, including bare ceramic coupons and coated ceramic coupons with options HACI could produce internally. There was very little feedback from the OEMs, except to state that their coatings modified for use on a ceramic substrate were superior to HACI’s options. Late in the CFCC program, some surface conditions were thought to be superior to others to facilitate OEM-applied coatings, but no new thermal-barrier technology or external-coatings technology was applied to this CFCC program.

2.3.8 Applications Work with Teledyne Engines Corporation

Teledyne Engines Corporation develops and manufactures small turbine engines for commercial and military applications. Their engines are of an appropriate size to be considered for turbine-powered cars and trucks. Teledyne is very interested in CMCs and has a good history of application development and testing with HACI for military turbine engines, such as those used for missiles.

Prior to CFCC, Teledyne expressed interest in high-temperature material applications for future, automotive gas turbine engines. To meet fuel efficiency requirements of cars and trucks, recuperators are used to recover exhaust heat and heat-incoming combustion air. Thin sheet DIMOX™ materials were being considered for the hot elements inside a recuperator assembly.

Recuporator designs were started under a cost-shared DOE-OTT program with a team of Ford, Teledyne, RPI (Rensselaer Polytechnic Institute), and HACI. This project was focused on application of a recuperator to an automobile. Due to early termination of the OTT program, the recuperator designs and ideas could not be implemented or tested in that program.

Tasks in the CFCC program were added to use the existing design and to optimize the material processes for fabrication of recuperator elements. Material improvements made in CFCC included demonstration of fiber-reinforced thin sheet materials. Because fabrication was successful, CFCC tasks were used to bring sub-element recuperator sections and a turbine engine recuperator to rig testing at RPI.
Table 10 identifies work performed with Teledyne. No other rig testing or engine testing was available for recuperator elements.

**Table 10. Teledyne Engines application tasks**

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Task Title and Hierarchy.</th>
<th>Example of work performed in this task</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Component Fabrication and Testing</td>
<td></td>
</tr>
<tr>
<td>3.3.1.4</td>
<td>Thin Sheet Recuperator and Heat Exchanger</td>
<td>Work with Teledyne Ryan Aeronautical and RPI (Rensselaer Polytechnic Institute) for application testing of a turbine engine recuperator.</td>
</tr>
</tbody>
</table>
3 Technical Results and Discussion

3.1 Materials and Processing of SiC/Alumina

In this program, all DIMOX™ composites were reinforced with continuous fibers. The process to produce a composite is outlined in the following steps.

1. The process to produce a composite starts with the preform. The reinforcing fibers are typically woven into fabrics, which are cut, stacked in layers, and shaped into the desired article. Graphite tooling is used to hold the preform in the shape of the article.

2. Any applied binder and the normal finish on the fiber are burned off in a short furnace cycle.

3. The graphite tooling is designed with many holes that perforate the tooling, thus allowing gases to pass through the preform in the CVI interface coating processes. The interface coating, typically BN and SiC, is applied to the preform to tailor the interface and engineer the fiber-matrix debonding. The coating is applied via chemical vapor infiltration.

4. After the coating process, the preforms are rigid, and they are removed from the tooling.

5. The interface-coated preform is placed on the surface of an aluminum alloy ingot.

6. The fabrication layup is assembled at room temperature and then is placed into a furnace. At high temperature, the molten metal wicks into the preform and reacts with an oxidant to form a ceramic matrix. The molten-metal reaction front progresses through the preform via wicking and capillary action. A characteristic of this growth front is that it fills very small channels in the preform, and the direction of the growth front can be engineered and controlled. The grown matrix has some residual aluminum alloy present in the form of inter-connected microchannels.
7. If required, parts may undergo an additional operation, the metal removal process, to remove any residual metal.

8. The parts are then ready for machining and non-destructive examination.

This manufacturing cycle is normally practiced in about 30 days. However, the cycle can be as short as 17 days.

For materials and processing study, the desired article is a flat plate, approximately 6”x9”x¼” thick. The typical plate has eight to 12 layers of fabrics providing a 35% fiber volume fraction. The standard interface is 0.5 micron of boron nitride with a 1.0-micron layer of silicon carbide over the BN. As is the nature of research and development, prior to CFCC little work had been performed to measure consistency of process and properties. The first task in the materials processing was to establish a baseline of properties with the best-known recipe at the time.

3.1.1 Baseline Properties

Of great importance and value to HACI was the opportunity on the CFCC program to produce large numbers of plates strictly for gathering data. In these early years of HACI, there were two general tendencies. There was a tendency for selling and shipping whatever was produced. In addition, there was a tendency for making changes to accommodate more-complex shapes and for impromptu problem solving, without a robust understanding of the process and property relationships.

In CFCC, first, baseline properties were obtained on the Nicalon™/alumina composite. Second, a process/properties engineering study was conducted. One hundred or more plates were used in every step.

HACI fabricated approximately 100 plates, nominally 15 cm X 23 cm X 0.25 cm (6” X 9” X 0.10”) for microstructural and mechanical testing. The plate size was derived from cutting plans to obtain many different sized test bars including 8-inch long, high-temperature tensile test coupons. The following baseline and new properties were determined:
- Baseline compressive strength
- Baseline shear strength
- Baseline flexural strength
- Baseline tensile strength

Table 11 provides data on the baseline properties of the 8/12/8 harness-satin fabric-based composites.

<table>
<thead>
<tr>
<th><strong>Table 11. Data on baseline properties of the 8/12/8 harness-satin fabric-based composites</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ambient Test Conditions</strong></td>
</tr>
<tr>
<td><strong>MEAN</strong></td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
</tr>
<tr>
<td>Shear strength (MPa)</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Tensile properties</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Tensile Strength (MPa)</td>
</tr>
<tr>
<td>• Strain (%)</td>
</tr>
<tr>
<td>• Modulus (GPa)</td>
</tr>
<tr>
<td>• Linear Elastic Limit (MPa)</td>
</tr>
</tbody>
</table>

Throughout the course of the material’s development, the ultimate tensile strength of the SiC-fiber/Alumina material was measured. Figure 7 illustrates the range of values obtained during that time.
Changes in tensile strength over the years are attributed to three factors:

- Actual changes to the product recipe
- Slight process changes as the scale of fabrication moved from one plate at a time by a research technician to batch processing by plant operators
- Changes in reinforcing fiber as the manufacturers went through the same types of time and batch scale transitions

### 3.1.2 Process Quality Control Levels

From the customers’ perspective, these changes were not a good sign of manufacturing maturity of the process and material. Some customers enjoyed hearing progress reviews of the materials research and development. Other customers sought improvements in complex shape making and in stabilization of the database. To meet both research needs and manufacturing needs, the following two actions were taken:

- A set of guaranteed minimum property values were put into a material specification for use with deliverable parts and customer design.
Manufacturing quality plans were instituted, and three quality control levels were adopted within our plant. Table 12 identifies the three quality control levels, and each was assigned its own paper color. Using this “visual factory” approach, paper documentation accompanied each part through its fabrication. This unique “traveler” was used for conveying process instructions and data recording.

This method allowed research in CFCC to proceed in harmony with commercial customer projects. The same technicians and plant equipment were used for research, prototyping, and commercial projects.

Table 12. Quality control levels

<table>
<thead>
<tr>
<th>Quality Control Level</th>
<th>3—Research</th>
<th>2—Standard</th>
<th>1—Customer Specified</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color of paper traveler</strong></td>
<td>Pink</td>
<td>White</td>
<td>Blue</td>
</tr>
<tr>
<td><strong>Instructions for process steps</strong></td>
<td>Specific—typed on the traveler</td>
<td>By standard operating procedure (SOP) at each work center</td>
<td>By customer’s quality-plan-approved SOP</td>
</tr>
<tr>
<td><strong>Data recording</strong></td>
<td>Written notes, photographs, and measurements of all visual indications, weight gains, and process records</td>
<td>As established in SOP. Typically one data point—and manufacturing approval of batch process to SOP</td>
<td>As required in customer quality plan—and manufacturing approval of batch process to quality plan</td>
</tr>
<tr>
<td><strong>Changes and decision making</strong></td>
<td>By research scientist or engineer—with his signature</td>
<td>Only as allowed in SOP—signatures by project engineer and manufacturing supervisor</td>
<td>Only as allowed in customer quality plan—usually involves customer notification and their approval</td>
</tr>
</tbody>
</table>
3.1.3 Process Engineering Approach

The objective of this subtask was to establish an understanding of the current process window for the various DiMOX™ directed metal oxidation process steps. The following variables were included in the study:

- Fabric weave
- Preforming technique
- Interface coatings
- Matrix growth process
- Metal removal

The work in process engineering was conducted to understand how variations impacted the microstructure and properties of CFCCs. Table 13 provides details of the variables that were studied.

HACI performed process and material development work in this subtask to meet application needs, to reduce manufacturing costs, and to improve part-to-part uniformity. The following specific technical objectives were included:

- Demonstrating improved process yields and efficiencies by optimizing key process steps
- Demonstrating better yields, efficiency, and economics for CVI interface coating of fiber preforms by development and application of a process model
- Improving long term high-temperature oxidative stability of existing CFCCs by optimizing interface coatings
- Increasing the maximum service temperature of CFCCs by use of Hi-Nicalon™ high-performance, high-temperature fibers
- Completing remaining material data requirements as identified by OEM partners
Table 13. Process engineering variables studied

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Variables</th>
<th>Potential Benefits to CFCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Weaving</td>
<td>• Ends per inch</td>
<td>Improve understanding of weaving variables and basis for selecting fiber architecture for future applications</td>
</tr>
<tr>
<td></td>
<td>• Filaments per bundle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Sizing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Architecture</td>
<td></td>
</tr>
<tr>
<td>Preforming</td>
<td>Fiber volume fraction</td>
<td>• Meet end-user property requirements</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Improve part economics, repeatability, and preform quality</td>
</tr>
<tr>
<td>Interface Coating</td>
<td>• Modified compositions</td>
<td>• Improve properties</td>
</tr>
<tr>
<td></td>
<td>• Coating thickness</td>
<td>• Improve properties and uniformity</td>
</tr>
<tr>
<td></td>
<td>• Process window</td>
<td>• Reduce cycle time and cost</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Improve reproducibility</td>
</tr>
<tr>
<td>Matrix Growth</td>
<td>• Barriers</td>
<td>• Increase productivity. Reduce cost</td>
</tr>
<tr>
<td></td>
<td>• Initiators</td>
<td>• Improve product quality, yields, properties, microstructural uniformity, surface finish, net shape capability, reproducibility</td>
</tr>
<tr>
<td>Metal Removal</td>
<td>• Bedding type</td>
<td>• Reduce disposal costs</td>
</tr>
<tr>
<td></td>
<td>• Temperature</td>
<td>• Improve microstructure</td>
</tr>
<tr>
<td></td>
<td>• Time</td>
<td>• Reduce fabrication costs, Enhance oxidation protection, and Improve surface finish and net shape</td>
</tr>
</tbody>
</table>

Each test variable was be characterized by metallographic mounts and 4-point flex tests at room temperature and elevated temperature (up to 1200°C). Plates with the highest flexural properties were machined into tensile coupons. Room-temperature and high-temperature tensile tests were performed on each of these plates.
Of the total 100 plates, approximately ten with process variables of particular interest were fully machined, cut into coupons, and tested. Tensile tests were performed on specimens from each lot; half were tested at room temperature, and half were tested at 1200°C. Values for the following measures were obtained:

- Room-temperature tensile strength
- Elevated-temperature tensile strength
- Young's modulus
- Strain-to-failure
- Poisson's ratio
- Thermal expansion coefficients (CTE) in the range from room temperature to 1200°C
- Thermal conductivity
- Composite density

Table 14 provides test result data.

In addition, long-term thermal aging tests were performed. Retained flexural strength after long-term thermal aging at 1200°C was measured on coupons from various plates. Typically, prior to testing, coupons were aged at temperatures ranging from 1000°C to 1200°C. Aging times ranged from 500 hours to several thousand hours.

All data was captured in HACI's database. When similar plates and data allowed, HACI statistically analyzed data from the 100 plates described above. In addition, edge coupons were analyzed, which were created from plates fabricated as a part of HACI's ongoing Nicalon™/alumina fabrication operations. Quantifying the variance components within panels was an objective of this work—from panel-to-panel, from batch-to-batch, and over time. This objective was achieved through data reduction, data organization, engineering analysis, and statistical analysis.
Table 14. Test matrix for Nicalon™/alumina composites

<table>
<thead>
<tr>
<th>Material Test Datapoints Obtained.</th>
<th>Each Process Variable</th>
<th>6 Highest-Strength Plates</th>
<th>Ten Chosen Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallographic Mounts</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>RT Flex Tests</td>
<td>5</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Elevated Temperature Flex (to 1200° C)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>RT Tensile Tests</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Elevated Temperature Tensile (to 1200° C)</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Failure Strain</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>CTE</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Strength after HT Aging</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Flex Stress Rupture</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Tensile Fatigue</td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
3.1.3.1 Matrix processing

To prepare DIMOX™ composites for matrix processing, the interface-coated preform is placed adjacent to molten aluminum alloy. Matrix processing preparation is discussed in terms of the layup method used to place the preform and alloy. The following three types of layup methods characterize placement of the preform and the alloy:

- Cold layup
- Hot pour
- Alloy drop

In the cold layup, a flat plate preform can be placed at room temperature onto a flat ingot of aluminum. The flat plate preform and the flat ingot of aluminum are placed in a refractory container covered with wollastenite, which is a refractory sand. The container is then placed into an electric box furnace for heat-up and processing. In the furnace at 1000° C, the wollastenite serves to keep the molten alloy from flowing away from the preform.

In a hot pour layup, the preform and wollastenite are placed into a cold furnace and heated to a temperature above the melting point of aluminum (i.e., to about 750° C). A technician then opens the furnace door and pours a ladle of molten aluminum onto the hot preform.

In the alloy drop method, alloy is held above the preform in a refractory container having a fusible plug in the bottom. At the designed temperature, the plug melts allowing the alloy to pour onto the preform.

In CFCC, all three methods were used and examined. Differences in the execution of these three methods exist. The differences are based on the shape of the composite part, the quantity of parts in one furnace run, and the economics and safety inherent in each method. There are also composite differences found from each layup method.
Another potentially robust method is discussed at the end of this section. In this method, particles are incorporated into the matrix.

Table 15 details the process attributes of the cold layup method, the hot pour method, and the alloy drop method.

<table>
<thead>
<tr>
<th>Layup method</th>
<th>Process Attribute</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reliability of matrix growth</td>
</tr>
<tr>
<td>Cold Layup</td>
<td>Good only with use of initiators</td>
</tr>
<tr>
<td>Hot Pour</td>
<td>Highest composite quality</td>
</tr>
<tr>
<td>Alloy Drop</td>
<td>High—if no issues with fusible plugs, etc.</td>
</tr>
</tbody>
</table>

3.1.3.1.1 **Cold layup method**

The cold layup method had the lowest cost, and it was the safest method. However, initial experiments found wide variation in depth of composite matrix produced in a specific period and variation of surface finish on the composite. These issues were traced to the initiation of the matrix growth. During heat-up at intermediate temperatures, an oxide layer frequently formed on the alloy ingot, in small gaps between the preform and the alloy. This oxide layer presented a barrier to uniform matrix initiation into the preform, which resulted in non-uniform growth rate.
In the composite article, non-uniform growth rate was indicated by one of two effects: areas in which matrix growth never started or areas in which matrix growth apparently started late and never reached the back surface of the preform. In either case, these effects were not found until the composite article was removed from the furnace and cleaned through grit blasting. Areas of the preform not fully densified by matrix were removed by the grit blasting, and the article became scrap.

The problem of non-uniform growth rate was solved using initiator chemicals. Materials such as nickel alloys defeated the oxide layers and promoted uniform matrix initiation. Recipes of the initiators were tested and optimized in the CFCC program.

3.1.3.1.2 Hot pour method

The hot pour method was commonly used in the early materials research of the DIMOX™ process. For small plates (about 3" x 3"), the preform and alloy could be heated in the same small box furnace. By using small crucibles for the aluminum alloy, various metals could easily be added to the alloy when it was cold. The effect of the additions could then be studied.

Early complex shapes presented two challenges: shaping alloy ingot into the shape of the preform and ensuring that the ingot shape and the preform shape consistently matched each other.

Therefore, prototyping required a scale up of hot pour techniques. In the hot-pour method, up to about four small shapes such as the GE shrouds or tubes for FWDC could be laid up in one furnace. The alloy was heated in the adjacent furnace and poured by two technicians who wore full (aluminized) heat suits, gloves, hoods, and spats (shoe and foot covers). This method was scaled up to accommodate crucibles containing 10 pounds of alloy before concerns of safety forced the invention of alloy drop methods.

3.1.3.1.3 Alloy drop methods

In the alloy drop methods, custom crucibles with fusible plugs were fabricated. The layup consisted of two levels in the furnace; the alloy was positioned over the preform to pour correctly onto the preform when the plug melted. For simple shapes, this method
worked. Nevertheless, a challenge arose. Because calculation of growth end time was necessary, instrumentation to determine the exact time of alloy drop was necessary. Thermocouples and other temperature devices were constantly attacked by the molten aluminum atmosphere and therefore proved unreliable. For complex shapes, the modification to rigid refractory layups made with wollastonite became necessary to maintain part shape and alloy control.

3.1.3.1.4 Modification to hot pour and alloy drop methods

A technique was developed to manually release plugs for the hot pour method and the alloy drop method. For both methods, the refractory containers holding the alloy were made with thin, recessed areas that could easily be punched. These areas were well labeled, or they were situated at a hole in the furnace cover. A technician with a steel rod could easily punch the alloy container while it was hot, even if he or she was fully suited up. This technique resulted in a much faster and safer operation than traditional alloy handling.

In the scale up of sizes for Solar combustors and for FWDC heat exchanger headers, an extension of this idea was created. At the end of the growth time, the alloy had to be drained away from the composite to stop the DIMOX™ reactions. Punch areas were designed and fabricated in the growth-layup refractory containers and the drain containers. These layups were tested in large parts including scale ups of GE shrouds and Solar combustors, and they were found to represent a reasonable scale-up method.

HACI used these ideas to construct an eight-furnace production area. As product development reached the point of commercial-scale manufacturing of parts, a commercial project for turbine tip shrouds became the catalyst for scale-up. (The customer was not involved in CFCC.) The design of the scale-up also was built to handle Solar Centaur engine combustors (30-inch diameter) and multiple-part GE shroud components from CFCC. The facility used top-opening furnaces and hot pours of alloy for multiple parts. This required use of a remote-controlled large crucible and a crane adjacent to HACI's alloy foundry. In addition, the facility employed hot drain using reusable, repairable,
punch-out growth-layup containers. The facility produced several batches of manufacturing-scale, production-rate shrouds.

3.1.3.1.5 Particle additions to the matrix

A potentially robust method for improving the high-temperature stability of CFCCs was evaluated. The method involves incorporating particulates that effectively getter oxygen entering the composite at high temperature through matrix microcracks or through diffusion. These getters would significantly reduce the oxidation of the fiber-matrix interface, thus enhancing composite life at elevated temperatures. AlN and Si₃N₄ are examples of particulates that are compatible with the Nicalon™/alumina composite at high temperature and that are able to getter oxygen.

HACI fabricated 3” x 3” and 6” x 3” 2-D Nicalon™ preforms incorporating AlN, Si₃N₄, or other oxygen-getter particles. Alumina matrices were grown through the fiber preforms. The resulting plates were characterized by preparing metallographic mounts and by performing room-temperature flexural tests, high-temperature (1200°C) flexural tests, and high-temperature (1100°C) tensile-tensile fatigue tests.

The result of this work was not positive, and it had unexpected conclusions. The particulates in all cases showed reaction with the process, which was attributed to reactivity of the high-temperature molten aluminum growth alloys. The particulates showed occasional ability to getter oxygen as the result of long-term thermal aging tests. This ability was not consistent; attack of the BN interfaces was still discovered.

In the case of Si₃N₄ and SiC particulates, an additional problem was found. Attack of the CVI SiC coatings near the particulates was seen. This phenomenon was not understood. It was only hypothesized to be the result of slight impurities in the particles. Several purities of particles, however, consistently showed the same problem. The conclusion of this work was that the strength of the composite suffered as the particles displaced additional reinforcing fibers.

This method was abandoned and was not being revisited for several years until work in the melt infiltration process yielded occasional particulate attack at interface coatings.
3.1.3.2 Interface coatings

Prior to Phase I of CFCC, a limited database existed on the baseline properties of SiC/Alumina. In addition, SiC/Alumina was being produced with an unsafe interface coating process. At that time, the SiC process for the dual-layer interface coating process was performed in a process condition that left pyrophoric by-products in the CVI reactor and exhaust piping. Although no major accidents or incidents occurred, a number of minor incidents showed that the process was not scaleable. Prior to CFCC, the materials work to expand the database stopped. Instead, resources, money, and manpower were used to find SiC process conditions that permitted safe application of the thin, uniform dual-layer interface coating. By the end of Phase I, and with the help of CVI scientists at Oak Ridge National Laboratory, a process was found that met the needs of the SiC/Alumina material.

A number of published and unpublished articles about SiC CVI (as well as side conversations in the Interface Working Group sponsored by Wright Materials Laboratory and others) have shown that a number of companies were addressing the same pyrophoric problem with SiC CVI. Some of these companies chose not to change the process but instead established procedures for opening and cleaning the CVI reactors. Others changed their CVI process in a number of ways. The maturity of SiC CVI now is very high. In 1994, it was not very high. In one of the Cocoa Beach Ceramics Sessions, Oak Ridge Scientists stated that they believed that there should be no companies with SiC CVI process problems and that this process was completely understood. HACI was clearly a benefactor of the resources of this research.

In Phase II of CFCC, the technical tasks focused on improving the BN interface layer and on improving interface-layer oxidation protection. The second phase in the material system is the interface coating, which is a very thin-layered BN coating that is approximately 0.5 micron thick, as shown in Figure 8.
Figure 8. Polished sample for microscopy, showing the fibers, the interface coatings, and the matrix. Note the 10-micron scale bar. The fibers are about 15 microns in diameter. They contain dark rings which are the BN debond coatings. The white layers outside the dark rings are the SiC CVI interface coatings. Note that every fiber has the BN coating, and that the SiC coating penetrates very small spaces. The dark phase is the DIMOX™ alumina matrix, which fills the very small voids around the SiC coatings.

In the SiC/Alumina material system, HACI used CVI interfaces only. In the case of BN, a precursor such as boron-triflouride or boron-trichloride was introduced with ammonia into a CVI reactor at about 1000°C at full vacuum, to deposit BN. HACI has always followed the BN step with a deposition of SiC to provide a protection layer for BN. In the DIMOX™ system, the SiC protection layer was required to prevent reaction with the molten aluminum during matrix processing.

The BN coating is applied, ideally, to each filament of the reinforcing phase. The coating controls the bonding strength between the fibers and the matrix. The interface presents technical, scientific, and economic challenges.
The CVI process is short and difficult to control accurately. The fibers and preform may be very expensive, and poor yields through the interface process add significantly to the final, delivered part cost.

The interface also performs the engineering function of holding the preform together. Therefore, the preform is self-standing without tooling and fixtures. For example, graphite tooling is often used to hold the preform together prior to the application of BN interface. After BN interface is applied, no tooling and fixtures are necessary—the coating is strong enough to hold the preform together prior to the SiC CVI process.

In contrast, after a carbon-type interface is applied, tooling and fixtures are necessary—the coating is not strong enough to hold the preform together prior to the SiC CVI process. This poses a problem because the CVI SiC bonds strongly with the graphite tool. Separating the tool from the preform might require destructive machining.

In multiple layers, the applied CVI coating is frequently considered non-repairable. However, a process advantage of CVI-produced BN exists. In many cases, when a process upset occurs prior to complete coating application, the preform can be recovered, and additional interface can be applied. This was not well understood at the beginning of this program. Therefore, part of the CFCC program work was a process study on BN, with the goal to understand the affect to the composite with various types of process upsets.

Research and investigation of debond layers included a literature review and peer reviews with other scientists in the CMC community. HACI’s chief scientist, Dr. Ali Fareed, led most of the work. The interest in multiple debond layers came from a conclusion that BN and SiC, as fiber interface coatings, were good materials of choice. While they had faults, they had the principle advantage of being understood to enable repeatable experiments and scale-up for manufacturing size components. Many other coatings were investigated, including oxide interfaces. In the DIMOX™ matrix, oxide interfaces might have an advantage over BN and SiC in being matched in CTE. Also, oxide interfaces in the DIMOX™ matrix might have the advantage of being stable with air and oxygen ingress through matrix microcracks. Dual layer and multiple applications of dual layer
interfaces were believed strategies to use the existing BN and SiC compounds, and they allow mechanisms for cracking and oxidation. The DIMOX™ process required stability of the interface in the presence of molten aluminum for matrix formation, and SiC was the only interface known that met this unique requirement.

Some of the best scientific interchanges regarding fiber-matrix interfaces were the meetings of the Interface Working Group, typically held in Dayton, OH. The meeting had the following goals

- Obtain a clear view of the state of technology
- Establish tasks to be completed
- Avoid redundant work
- Facilitate collaboration

After the meetings, HACI discussed topics to decide if there was a research direction we should consider or if a novel interface had any advantage over the BN/SiC system for the DIMOX™ SiC/Alumina materials. The most significant interface studies that directly impacted HACI's interface development are indicated below:

a) **Oxygen content in the BN.** Most BN chemistry is designed to produce low retained oxygen levels. BN with increased oxygen level (10 wt.%) was shown by ORNL to have increased reaction with Nicalon™ during high temperature exposure, leading to increased SiO₂ formation at the BN-fiber interface. HACI's BN contains about 10% oxygen, which was believed to be too much. The sources of the oxygen are numerous, including partial content in the precursor gases, entrained moisture in the graphite liner of the reactor, and air and moisture captured in gas feed lines during maintenance. Overall, specific programs to eliminate air and moisture would only result in oxygen reductions of a few percent and resulted in longer processing times, more excruciating maintenance, and were not amenable to production operations. Therefore, to minimize the negative affects of oxygen in the BN, most work centered on high quality in the result of the composite.
b) **Nitrogen:Boron ratio.** N:B ratio should be 1:1 or slightly higher. Boron-rich BN is not stable, particularly in terms of allowing diffusion of glass matrix species through it, as observed by UTRC.

c) **Carbon content in the BN.** Many BN coatings contain carbon. C in BN appears to be non-detrimental and may be beneficial. 3M’s BN has intentional C. Higher-C-containing BN was found to inhibit diffusion of glass matrix species better than BN with lower C contents. HACI cannot allow a high carbon content due to potential reactions with aluminum, which forms aluminum carbide—a very weak ceramic phase.

d) **Multi-layer interfaces.** UTRC evaluated multilayers of BN/C-rich BN as a means of promoting crack deflection prior to the innermost BN debond layer. Five layers of BN/C-rich BN each ~0.05μm were used to demonstrate crack deflection in the C-rich BN layer. HACI performed experiments on multiple layers of BN and SiC. The technical approach was to achieve matrix crack deflection from fabrication cool-down at a BN/SiC interface other than the innermost BN layer. Hence, the fiber and innermost debond layer were to be preserved and protected from exposure to the external environment. Several plate preforms were coated but obtained mixed results of the benefits. In addition, the multiple layers proved to be a processing problem regarding SiC coating building on the graphite tools, which created preform-to-tool sticking, and tool-to-tool sticking, which resulted in premature tool failure.

e) **Resistance to moisture.** Results at NASA Lewis showed that BN deposited at high temperatures (1400°C and 1800°C) as well as high-temperature BN doped with Si exhibited dramatically improved resistance to humidity exposure at ~800°C. Mini-composites with high-temperature BN were presented with demonstrated long-term properties (14,000 hours at 20 Ksi, 1100°C in air with a residual tensile strength of 36 Ksi by UTRC). However, high-temperature BN deposition results in highly non-uniform coatings within a single fabric. It was not possible to obtain uniform interface coatings in multiple layer preforms.
HACI’s BN interface is applied at low temperature, versus the high-temperature BNs applied at 1400°C.

f) **Oxide interface coating.** Specifically from CFCC and from these research sessions, HACI became interested in oxide interface coatings. Lanxide’s prior attempts at mullite and alumina interface coatings were partially successful, but dropped due to the reactions with molten aluminum during the DIMOX™ process. New work that improved the SiC overlayer and new material processes such as thin sheet maintained the interest in oxide interface coatings. Dr. Sankar Sambasvasian at Northwestern University’s Basic Industrial Research Laboratory (BIRL) was funded partially by CFCC to apply oxide interface coatings. He wanted to have HACI evaluate his interfaces in the DIMOX™ process. His laboratory’s capacity was about 2” x 2”. If the evaluation were successful, a scale-up effort would have to be completed prior to application-specific testing of the composites. HACI worked with BIRL and provided 30 single plies of ceramic-grade Nicalon™ and Nextel 720 fabric for coating. Microscopy of the monazite-coated fabrics proved difficult, and the coatings could not be made uniform and continuous. A different process was used by BIRL to apply alumina interfaces on Nextel 610 and 720 fabrics but it did not work on SiC fabrics.

HACI often identified themselves as a future-parts-manufacturing company and therefore aimed for large-scale production of interface coatings. As a result, the work on single tow or mini-composites was interesting as research, but held very little scalability for HACI. The focus remained on improving what HACI could do for net-shape composites.

### 3.1.3.2.1 Analysis of interface coatings

The interface also presents the challenge of scientific analysis. For daily characterization, an optical microscope of 500x to 1000x only shows a line where the interface exists. Bulk chemical analysis requires a scanning electron microscope (SEM). Detailed elemental analysis requires a transmission electron microscope (TEM).
Throughout this CFCC project, Dr. Karren More at Oak Ridge National Laboratory performed the TEM work. The primary reason for TEM-type characterization on an as-fabricated interface is to establish chemical content and purity for the initial nucleation of the interface on the fiber, through the total thickness of the interface, providing a product-to-process correlation to deposition conditions and time. For example, in an exposed sample from a 1000-hour, application-specific steam-exposure test, the TEM provides chemical reaction data for the interface to the adjoining materials, the fiber, and the matrix layer outside it. Ceramists and chemists gather information about the stability and compatibility of the composite, which are important for long-life application in service.

3.1.3.2.2 Interface coatings scale-up

During CFCC, CVI reactors of several sizes were used, and process scale-up in amount of fiber-coated per batch was performed to permit fabrication of large, representative components. The initial work on BN was performed in small, horizontal tube reactors, which were 9 inches and 11 inches in diameter. A 16-inch, horizontal tube reactor with features for daily operation was built. A 30-inch, horizontal production reactor was built, which was later expanded to a 36-inch (inside diameter) reactor. (See Figure 9.) All construction costs of reactors were paid with HACI capital funds. Operating costs were charged to the specific component in each run, whether they were commercial or CFCC related.
Figure 9. HACI’s bottom-loading, 36-inch (ID) CVI reactor for BN interface coatings.

Interface coatings in the early reactors were applied in highly supervised runs of an individual plate at a time. Oxygen and other contaminants to BN were highly controlled through long leak tests and through individual attention.

The 16-inch reactor was designed to change as little of the physical layout as possible. It was designed to make upgrades to pumps, gas feed systems, and exhaust scrubbers. Such upgrades were made to enable the reactor to run daily, to meet the prototyping demand of parts, and to prove process robustness.
The 16-inch reactor scale-up was highly successful, but over time, impurities were seen to increase compared to the 9-inch and 11-inch reactors. The levels were stable, but higher oxygen was found in the BN composition, compared to the smaller reactors, as shown in Table 16. Conditions of the reaction were optimized to maintain uniformity for all parts in the reactor and to maintain the nitrogen to boron ratio (N:B).

Table 16. CVI-BN reactors versus BN composition and furnace capacity

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>N:B ratio</th>
<th>Capacity of flat plates per run</th>
</tr>
</thead>
<tbody>
<tr>
<td>9&quot; reactor</td>
<td>12%</td>
<td>6%</td>
<td>1.06</td>
<td>1 to 2</td>
</tr>
<tr>
<td>16&quot; reactor</td>
<td>4%</td>
<td>10%</td>
<td>1.15</td>
<td>2 to 8</td>
</tr>
<tr>
<td>(initial)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16&quot; reactor</td>
<td>3%</td>
<td>8%</td>
<td>1.12</td>
<td>4 to 8</td>
</tr>
<tr>
<td>(optimized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30&quot; reactor</td>
<td>2%</td>
<td>9%</td>
<td>1.12</td>
<td>20 to 30</td>
</tr>
</tbody>
</table>

CFCC program funding helped with the scale-up to the 30-inch reactor. For example, design iterations and start-up runs for process optimization were funded in part by CFCC programs.

The building process of the 30-inch reactor was similar to that of the 16-inch reactor. However, the 30-inch reactor was built in a vertical orientation instead of the horizontal tube orientation of the 16-inch reactor. The 30-inch reactor was a bottom-loading reactor with dual bottom heads and a trolley system to enable rapid unloading and loading of parts.
The startup of the reactor was very successful, yielding equivalent amounts of BN deposited on all CMC plates, regardless of their vertical position within the reactor or their radial position on the tray.

3.1.3.2.3 BN/SiC process engineering study

The program plan for the BN/SiC process engineering was to explore the Process/Product/Property correlation for SiC/Alumina by exploring the process windows for BN and SiC coatings.

The method was to operate outside current conditions and therefore to establish a process window for the 16-inch reactor. Such a process window would allow for easy scale-up to a robust process window for manufacturing.

The approach was to design experiments for mapping the process window using the other factors in the overall process study. These factors included the three preform architectures of 8- and 12-harness satin weave fabrics. Test data was obtained on basic properties and time-dependent properties. For further use in quality control, the acceptable process window was to be described from the property data. About 90 panels of data were used in this study.

Background

Balancing the advantages and disadvantages of the CVI process step represented one of the goals of this study. As an individual fabrication step, the CVI process was attractive because it appeared insensitive to part geometry. Besides the tooling that was required to hold the preform, there were few special preparations required of the part. The inside of the reactor contained graphite shelving on which to place parts for the coating step. The individual steps are outlined below.

1. Place the parts of variable shape on the tray
2. Run the process
3. Unload the reactor
Despite the advantages of this process as an object of study, the CVI process for thin debond-layer coatings was a relatively short process that was difficult to control. The CVI reactor operated in vacuum conditions, at temperatures near 1000°C, and many operational steps existed for feed gas introduction. Disadvantages included that the BN and SiC coatings were considered non-repairable. Poor yields through the interface process occurred due to coating thicknesses that were out of specification; the coatings were either too thick or too thin.

Because of the disadvantages, HACI sought to understand more about the CVI processes through this study. Other tasks were performed including CVI process modeling, in partnership with Sandia-Livermore National Laboratory.

Details of the study

As a starting point for the study, a preferred target of process results obtained from experience was used as a premise to be proved or disproved. Table 17 provides the initial interface coating specification.

<table>
<thead>
<tr>
<th>Coating Parameter</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN—Coating thickness</td>
<td>0.3 microns</td>
<td>0.6 microns</td>
</tr>
<tr>
<td>SiC—Weight gain percent from coating application</td>
<td>50%</td>
<td>90%</td>
</tr>
</tbody>
</table>

One of the difficulties of the initial process window was that the determinations in each category were subject to measurement variability, and they were not strictly repeatable. In the BN thickness determination, a scientist with a polished mount from the sample (similar to Figure 8, page 59) had to estimate a nominal coating thickness, which was not on the very exterior, on the very interior layers of the part, or inside a tow where adjacent filaments would affect the coating thickness.
In the "% SiC weight gain" determination, the starting weights were also subject to measurement variation. It is well known that bare BN coatings are hygroscopic. That is, they absorb water. Therefore, storage conditions influenced the actual weight prior to SiC-CVI. Although the amount of the weight of the variability was small compared to the total preform weight, the repeatability of the measurement was frequently in question. Generally, the final SiC coated weight was a consistent data point.

Quality control of the BN and SiC interface coatings was realized to be most effectively obtained by process control rather than by individual part control. It was hoped that these experiments in process window would provide confirmation of the initial target windows or would define them further.
Fourteen variable conditions in the BN process were explored. Conditions included variations in process conditions and facility-caused process upsets such as power failures in mid-cycle. The fourteen variables are listed below.

- Short cycle in time
- Long cycle in time
- Low temperature
- High temperature
- High reactant flow
- Low reactant flow
- High reactant ratio
- Low reactant ratio
- Extra-high reactant ratio
- Extra-high reactant ratio and long cycle
- High pressure
- Addition of nitrogen to reactants
- Start, interrupt, and restart interruption
- Start, interrupt, cool, and restart interruption

In the SiC CVI process, reactor-to-reactor uniformity was tested for the 1.0-meter-diameter reactor coatings versus the 1.4-meter-diameter reactor coatings.
The following steps represent the test setup:

1. **Preforming**—fourteen sets of six panels split by three preform architectures

2. **BN cycle runs**—fourteen cycle runs with six panels per run

3. **SiC cycle runs**—two cycle runs—one cycle in each size of reactor with three panels per BN cycle in each SiC cycle. All three architectures were represented in each cycle.

The experimental strategy accounted for the small size of the 16-inch BN reactor and the previous determination of a “sweet spot” in the center of the reactor. Six panels in each BN run were arranged—two in the center “sweet spot”, two just ahead of the “sweet spot”, and two just behind the “sweet spot”. Architectures were separated, and panel locations were recorded.

Yields for the BN and SiC coating runs were recorded with respect to the initial target windows. Table 18 provides the results.
Table 18. Yields for the BN and SiC coating runs

<table>
<thead>
<tr>
<th></th>
<th>Below Target</th>
<th>Initial Target</th>
<th>Above Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN Coating Thickness</td>
<td>&lt;0.3 micron</td>
<td>0.3 to 0.6 microns</td>
<td>&gt;0.6 microns</td>
</tr>
<tr>
<td>90 Panels</td>
<td>39%</td>
<td>59%</td>
<td>2%</td>
</tr>
<tr>
<td>SIC Weight Gain</td>
<td>&lt;50%</td>
<td>50% to 90%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>87 Panels</td>
<td>0</td>
<td>89%</td>
<td>11%</td>
</tr>
<tr>
<td>DIMOX™ Growth</td>
<td>Incomplete matrix</td>
<td>Complete growth</td>
<td></td>
</tr>
<tr>
<td>87 panels</td>
<td>0</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>Metal Removal</td>
<td>Incomplete</td>
<td>Successful</td>
<td></td>
</tr>
<tr>
<td>87 panels</td>
<td>0</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions of processing study

Testing was performed to obtain data for comparison to the baseline properties, and relationships were sought to show preferred process windows. The conclusions of the testing and analysis are provided below.

- BN thickness has little effect on . . .
  - Room-temperature tensile strengths
  - High-temperature (1100°C) tensile strengths
  - High-temperature (1100°C) proportional limit strengths
  - Room-temperature compressive strength
  - Room-temperature shear strength
  - Room-temperature flexural strength
  - High-temperature (1200°C) flexural strength
• SiC weight gain has little effect on . . .
  – Room-temperature tensile strengths
  – High-temperature (1100°C) tensile strengths
  – Room-temperature proportional limit strengths
  – High-temperature (1100°C) proportional limit strengths
  – Room-temperature shear strength
  – Room-temperature flexural strength
  – High-temperature (1200°C) flexural strength
• SiC weight gain increases provide increased room-temperature compressive strength.

Two more findings are provided below.

• BN process condition had little effect on flexural stress rupture to 500 hours except when BN coatings were very thick.

• BN process condition had little effect on tensile fatigue durations at 120 Mpa stress except for samples in the interrupt and cool condition.

Data from the processing study

The first sets of 43 plates were fabricated under various operating conditions and with three different fabric architectures (8-harness satin weave, 12-harness satin weave, and a hybrid layup). The reinforcing fiber in all cases was ceramic-grade Nicalon™ SiC.

a) **Tensile Properties.** Tensile coupons were machined and tested at room temperature in air. Seventy-six coupons were tested for tensile properties. The average properties of tensile strength of 256 MPa (36.8 Ksi), strain to failure of 0.60%, and modulus of 150 GPa (21.6Msi) were recorded. About 42 coupons were then tested for tensile strength at 1,100°C (2,012°F) in air. The average ultimate tensile strength was 190 MPa (27.3 Ksi) and strain to failure of 0.6%. The tensile and linear-elastic-limit values generally fell within the one standard deviation limit with the exception being the extreme coating thicknesses of < 0.30 and > 0.60 microns. A similar observation also applied to the SiC coating.
b) **Compression Properties.** Twenty compression coupons were machined from ten plates and tested at room temperature. The average compressive strength was 639 MPa (92.5 Ksi) with a compressive strain to failure of 0.79% and a modulus of 84 GPa (12.2 Msi). The compressive-strength property at ambient conditions was measured as a function of BN and SiC coating thicknesses. No discernable trends towards increase or decrease in compressive strength were noted when BN thickness increased from 0.2 microns to 0.5 microns. There was a slight increase in compressive strength when SiC coating increased from 65% to 88% (weight gain).

c) **Shear Properties.** Nineteen coupons from ten different plates were machined for testing of interlaminar shear using the double notch shear method. The average interlaminar shear strength was 31 MPa (4.5 Ksi). Shear strength was evaluated at ambient conditions as a function of BN and SiC coating thicknesses. No discernible trends towards increase or decrease in shear strength were noted when BN thickness increased from 0.2 microns to 0.5 microns. Also, there was no increase in shear strength when SiC coating increased from 65% to 88% (weight gain).

Conclusions from the process experiments showed the robustness of the initial targets for interface coatings. Process interruptions where coatings were fully cooled created a two-layer coating, which is not desired for BN coatings. SiC is not affected by this process interruption. BN coatings should not be allowed to get very thick, and only very thick SiC coatings produce structural results to overcome and increase fiber properties in compression. No experiment showed a more favorable dual-layer interface. Therefore, the original target values for interface coatings were verified.
3.1.3.2.4 Process modeling of CVI interface deposition

A process model of CVI interface deposition proved helpful in the following tasks:

- Optimizing the coating conditions in the BN interface reactor
- Understanding part loading factors and process economics
- Providing a set of operating guidelines and equations for larger interface reactors

To verify the models developed for the 16-inch reactor, HACI conducted experiments using the 30-diameter interface reactor.

HACI funded a program with Sandia National Laboratory in which Sandia developed an analytical process model for the CVI deposition of BN and SiC interfaces. The process model predicted the coating thickness for BN and SiC as a function of time, temperature, reactant concentration, feed rate, and stoichiometry. Model predictions were confirmed by comparing the predictions with the microstructures and properties of plates coated and evaluated in other subtasks and in ongoing Nicalon™/alumina fabrication operations.

Dr. Mark Allendorf was the principle investigator at Sandia National Laboratory. The following steps outline the interaction between HACI and Sandia:

1. HACI provided Sandia with processing and plate results data.
2. Sandia provided an initial model, which replicated HACI’s results. In addition, Sandia fine-tuned their model to be more accurate in terms of uniformity for various fabric architectures.
3. HACI performed specific BN runs requested by Sandia and ensured the requested set-up parameters. HACI provided run data to Sandia, including all data from the BN study results.
4. Sandia in turn provided a downstream depletion model for runs with higher fiber loadings.
The modeling effort with Sandia yielded the following results:

- Explanation of the relationships between the following elements of the process for a fixed ratio of gas feeds:
  - Number of plates or preforms (i.e., the total fiber loading in the reactor)
  - Location in the gas stream
  - Time
  - Temperature
- Explanation of coating uniformity through a number of plies (i.e., edge-to-center coating ratios)
- Sandia’s continued work on the model for HACI (although the DIMOX\textsuperscript{TM} CFCC program was ending).

### 3.1.3.3 Reinforcing fibers

The purpose of the matrix-processing task section of the program was to study the DIMOX\textsuperscript{TM} process variables, to optimize them, and then to explore improved fibers (see Figure 10). This course of action assumed that the fiber type explored would not require re-optimization of the DIMOX\textsuperscript{TM} process. Processing at this time was considered relatively insensitive to the fiber, due to the coatings of BN and SiC on the fiber. It was known that fiber type would affect the physical properties and time-dependent strength of the composite. The original reinforcing fiber for the DIMOX\textsuperscript{TM} processing tasks was silicon-carbide-based ceramic-grade Nicalon\textsuperscript{TM}, produced by Nippon Carbon in Japan.
Figure 10. This graph shows how many different sets of composite properties are the result of fiber selection.

Silicon carbide fibers are produced from preceramic polymer resins, which are melt-spun into fibers. Common impurities in the fibers are excess carbon, oxygen, and trace metals such as iron and calcium. The methods to make more stoichiometric fibers are exotic, with process descriptions well beyond the scope of this paper. A common example is the conversion of ceramic-grade Nicalon™ fiber (priced at $1250/Kg today and containing 12% oxygen) to Hi-Nicalon™ fiber (priced at $6,900/Kg today and containing 0.5% oxygen). Tasks in this program sought to quantify the benefit of such expensive fibers.

Compatibility to DIMOX™ processing requires the fiber be evenly distributed in the preform. Microstructures of the composite must show the filaments of Nicalon™ within the tow and with space around each filament. The filaments must not be smashed together into a tight bundle. This provides space for interface coatings for each filament and space for alumina matrix to grow into the fiber tow. These two characteristics allow excellent load transfer from matrix to fiber and reduce matrix microcracking. Therefore,
most preforms of Nicalon™ fiber are 500 filaments per tow with low tension on wound
tows, at 35% overall fiber volume fraction.

Not all fibers can be placed into all weave forms. Two basic types of silicon carbide
fibers exist: monofilaments and multi-filament tows. In general, the term
"monofilaments" refers to large-diameter fibers produced by CVD deposition onto
small-diameter core fibers. The process creates a strong but very thick fiber. Examples
of monofilaments include the family of Textron SCS-6 fibers that use a carbon core
overcoated with CVD SiC to a total of 80- to 200-micron diameter. These fibers cannot
be woven into fabrics. Consequently, they are used as unidirectional tapes, or they are
used in filament winding.

Multi-filament tows are produced by forcing a solution through a die with many holes in
it. This creates small ropes, called tows, of 500 to 1000 filaments. Examples of
multi-filament tows include Nippon Carbon's 12- to 15-micron-diameter ceramic-grade
Nicalon™ fiber. This program focused on the use of multi-filament tow fibers.

Fiber selection involves choosing the composition, the purity, the price, and the brand of
the fiber. Typical composition choices include silicon carbide, carbon, and oxides such
as mullite or alumina. Because there are few uses for ceramic fibers besides CFCCs, the
market for ceramic fibers is small. Therefore, the costs are high. Table 19 provides the
approximate costs of ceramic fibers.

<table>
<thead>
<tr>
<th>Year</th>
<th>Fiber</th>
<th>Composition</th>
<th>Price $/Kg</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>Ceramic-grade</td>
<td>SiC, 12% oxygen</td>
<td>$1,250</td>
<td>Produced by Nipon Carbon, Japan</td>
</tr>
<tr>
<td></td>
<td>Nicalon™</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 1989 | Nextel 312/610   | Alumina silica fibers | $350       | High creep rate at high
|      |                  |                    |            | temperatures.                   |
| 1993 | Hi-Nicalon™      | SiC, 0.5% oxygen   | $6,900     |                                 |
| 1998 | Sylramic         | SiC, 0.5% oxygen   | $13,000    |                                 |
With any fiber selection at these costs, the total CFCC component price will be higher than the price of most metals, except for high-performance super alloys. When analyzing the economics of replacing metal parts, therefore, the performance of the CMC and its value in use must be considered. Performance and value-in-use create rationale for selecting fibers for long-term stability of the composite instead of selecting fibers because of the initial price.

3.1.3.3.1 SiCf/Al₂O₃ properties with Hi-Nicalon™

A new low-oxygen-content, high-temperature version of Nicalon™ silicon carbide fiber, Hi-Nicalon™, has the potential to yield CFCCs with longer lives at higher temperatures. Hi-Nicalon™ by Nippon Carbon is recommended for long lifetimes at high temperatures.

Hi-Nicalon™ is a heat-resistant silicon carbide fiber that retains high mechanical properties after 1,500°C exposure in inert atmosphere, and it has flexible form even after 2,000°C exposure. Hi-Nicalon™ features 0.5 weight percentage oxygen, while standard-grade Nicalon™ features 12 weight percentage oxygen. It also has higher density and higher thermal conductivity. The thermal conductivity increase translates well to increased composite thermal conductivity, which contributes to lower thermal stresses.

HACI prepared an initial database for Hi-Nicalon™/alumina composites. HACI purchased Hi-Nicalon™ fiber and contracted weavers for 2-D woven fabric in 8-harness satin weave cloth. Ten 6” x 9” Hi-Nicalon™/Alumina composite plates were fabricated using directed metal oxidation. The plates were cut into coupons, and the physical, mechanical, and thermal properties were measured. The following tests were conducted:

- Flexural strength at room temperature, 1,000°C, and 1,200°C
- Fracture toughness at room temperature, 1,000°C, and 1,200°C
- Tensile strength at room temperature, 1,000°C, and 1,200°C.
- Tensile-tensile low-cycle fatigue tests (LCF) at room temperature and 1,100°C were also performed.
Five samples were tested for each property at each temperature. Properties that were expected to vary as functions of orientation were tested in the x and y directions.

In addition, the following tests were conducted:

- Tensile stress rupture tests at 1,000°C, 1,100°C, and 1,200°C (3 tests per temperature)
- Thermal expansion coefficients (CTE) in the range from room temperature to 1,200°C
- Thermal conductivity
- Composite density

The room-temperature tensile property showed an average value of 330 MPa (48 Ksi) for Hi-Nicalon™ and 250 MPa (36 Ksi) for the ceramic-grade Nicalon™. The proportional limit for the Hi-Nicalon™ was slightly higher than the limit for the ceramic-grade fiber.

The high-temperature tensile properties were measured through multiple tests in the range of 1,100°C to 1,300°C (2,000°F to 2,370°F) in air. For the Hi-Nicalon™ fibers, the ultimate tensile strength showed a drop of about 20% at 1,300°C and about 15% loss in ultimate strain. The ceramic-grade fibers rapidly degraded.

Tension-tension LCF fatigue data was measured at approximately 1,100°C (2,012°F) using a trapezoidal waveform, R = 0.10 and a frequency of 0.25 Hz. Initial analysis indicated that the Hi-Nicalon™ composite performance is improved over standard-grade Nicalon™ fiber.

In a tensile stress rupture test at 1,100°C in air, with applied stresses of 80, 100, or 150 Mpa (14.5 Ksi), the Hi-Nicalon composites had superior short-term and long-term durability, as indicated in Table 20.
Table 20. Tensile stress rupture test data of Hi-Nicalon™ and ceramic-grade Nicalon™ composites at 1093°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Time to failure at 80 MPa</th>
<th>Time to failure at 100 MPa</th>
<th>Time to failure at 150 MPa</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic-grade Nicalon™</td>
<td>1,000 hours</td>
<td>&lt; 60 hours</td>
<td>43 hours</td>
<td></td>
</tr>
<tr>
<td>Hi-Nicalon™</td>
<td>&gt; 1,000 hours</td>
<td>&gt; 1,000 hours</td>
<td>&gt; 500 hours</td>
<td>Survived 500.5 hours with 259 MPa residual strength</td>
</tr>
</tbody>
</table>

3.1.3.3.2 Sylramic alumina

Sylramic-reinforced alumina composites were fabricated. Fiber was obtained from batches of fiber released in early batch production by Dow Corning. The material had very low strain to failure, 0.2% ultimate strain, versus the typical 1.0% ultimate strain of Hi-Nicalon™. Because of this low measure, Sylramic alumina tests were not pursued further in this CFCC program. Figure 11 provides room-temperature tensile testing results of Sylramic alumina.

Later data from the EPM program showed specific material data from specific fiber and fabric lots. The data indicated that good properties could be obtained, but some fabric lots produced low strain data. Because none of the CFCC customers had a need for the higher-purity fiber, further understanding of the strain results of specific fiber lots was not pursued in this program.
Figure 11. The results of room-temperature tensile testing of Syrlamic-reinforced alumina composites show low ultimate-strain percentage values.

3.1.3.3 Ideal fiber properties

Mr. Kent Buesking of Materials Research & Design, Inc. (MR&D), who has property-modeling experience, helped HACI determine which fiber would match best with the DIMOX™ alumina matrix. It was known that fiber selection makes a difference in initial microcracking because shrinkage leading to microcracks is affected by fiber CTE and modulus.

Fiber properties might be able to help control the amount of CTE mismatch on cool-down. Because MR&D had performed prior analysis on particulate- and fiber-reinforced DIMOX™ composites, they had a strength model that isolated the matrix
properties from the fiber properties. The set of matrix properties was combined with fiber properties of ceramic-grade Nicalon™, Hi-Nicalon™, Sylramic, Nextel 720, and a definition of an ideal fiber.

The following steps outline MR&D’s analysis.

1. Comparison of the coefficient of thermal expansion of the matrix versus CMC tow bundles

2. Comparison of mechanical shrinkage—from process fabrication down to room temperature

3. Comparison of compositions—with tensile-stress loading up to 100 MPa, a presumed proportional limit or design strength for many applications

The results of the study showed that to achieve CTEs that matched the DIMOX™ matrix, the ideal fiber would have properties similar to carbon fibers. Prior to CFCC, Lanxide experimented with carbon-fiber-reinforced alumina. The interface coatings of BN and SiC were not able to prevent reactions between the fiber and the molten aluminum. The metal removal process caused further reactions. It was concluded, therefore, that Hi-Nicalon™ fiber provided the best balance of properties from available materials.

3.1.3.4 Fabric and preform architectures

The preforms fabricated in this CFCC program were predominantly two-dimensional (2-D) structures of fabric layup. In preparation, fabric was coated with an acrylic resin, which was thermoplastic and solvent sensitive. The resin-coated of fabric was dried and cut to the desired shape for each ply.

To create preforms, the fabric plies were stacked between aluminum plates or shaped on an aluminum mandrel. To obtain desired fiber volume fractions in the composite, the fabric plies had to be compressed, or consolidated, tighter than they would naturally lie. Vacuum bagging, autoclaving, and pressing were the primary consolidation techniques. After consolidation, most of the preforms were rigid at room temperature.
After all fabric layers were assembled and consolidated, the preform was placed in a graphite tool to hold its shape during interface coating.

The material properties of the composite vary significantly with respect to the direction of the reinforcement fibers in reference to the test direction and to the volume fraction of fibers found in the composite. Most CMCs are found to have 25% to 50% fibers. In addition, the direction of reinforcement is described with reference to the angles that the majority of the fibers lay. For example, a balanced 0° to 90° fabric has the same number of filaments in each direction, at right angles to each other. Angle interlocks and braids can align fibers in specific angle directions, such as having a +/- 30° fiber angle in reference to the axial direction of a part.

Fiber tows are typically not used directly as reinforcement in a composite. Instead, ceramic fibers are woven into fabrics that are either two-dimensional (2-D) or three-dimensional (3-D). Plain weaves or harness satin weaves are considered 2-D because the thickness of the fabric results solely from the thickness of the fiber. Braids, angle-interlock weaves, and some filament windings are considered 3-D because the structures have a woven or knitted thickness. The vast majority of the composites studied in CFCC were composed of 2-D fabrics.

Very stoichiometric SiC fibers have proved to be very difficult to weave into fabrics. Significant fiber damage has resulted, represented as very low strain to failure in the composite. Creative Weavers are using special fiber coatings and handling techniques to improve the fabric quality of high-purity SiC fibers.

Another variable to consider when selecting fabric is the unit cell size. To say that a fabric contains 26 ends per inch means that, in one inch of cloth width, 26 filaments are aligned in one direction. Such a fabric is very tight. Most fabrics fall in the range of 15 to 22 ends per inch.

The interest in the open area of a fabric is due to an effect called *canning*. This effect occurs when the outside of the composite seals off due to limited open area and
consequently leaves voids inside the composite. Generally, **canning** is undesirable in CFCC materials.

A designed experimental plan for fabric architecture consisted of harness satin weave of 8- and 12-harness count. The composite plates were made from 8-harness satin weave, 12-harness satin weave, and 8/12/8-harness satin weave fabric lay-ups. The all 12-harness-satin reinforcement represented the baseline case. This derived from the initial practice in which HACI sought to maximize the amount of fiber in the composite for highest tensile strength.

Prior to CFCC, scientists noticed that the BN and SiC coatings were not uniform in the composite. Instead, the coatings were heaviest on the outer ply of a component. In the worst cases, the outer plies were so heavily coated that they blocked the DIMOX™ process from proceeding. It was hypothesized that the tight-woven 12-harness satin fabrics were blocking gas infiltration. However, in sufficient numbers of plates, the inner plies of 12-harness satin weave fabrics had good coatings and good tensile behavior. These were signs that, internally in the composite, the coatings were sufficiently thick.

Therefore, the heavily coated outer plies were not the main concern. Rather, the desire was to open the unit cell size to allow oxygen and aluminum flow through the outer plies and into the inner plies. To help the process deliver a composite with uniform coatings, the outer plies were preformed with 8-harness satin-weave fabrics. This preforming yielded less canning on the outer plies. The 8/12/8 layups worked. However, an explanation of the success was merely a hypothesis.

Using the DMO process, HACI later fabricated 8-harness and 5-harness satin weave (HSW) fabrics. These were converted to fully dense plates and coupons for laboratory evaluations. HACI completed 5-harness satin weave fabric evaluation using coupons from four different plates. Tests were conducted at room and at 1,100°C. No significant difference was observed between the 8-and 5-harness-satin-weave-based composites. The only exception was that the room-temperature tensile for 8-harness satin weave was 250 MPa (40KSi), while the 5-harness satin weave gave 212 MPa (31KSi).
Interpreting the results of this study was complicated by the fact that the fibers in the 5-harness satin fabrics were not held straight. The fabrics contained a lot of warping and skewing of the fibers, so that visually the material looked as though the fibers were handled very harshly and were potentially damaged. For this reason, only 8-harness satin fabric was used for all continued work in CFCC.

3.1.3.5 Metal removal process

Two items were targeted in CFCC for improvement of the metal removal process: the cost of the bedding materials and a scale-up in batch size. In the initial period of CFCC, metal removal was an expensive process because the bedding materials were not reusable in this process. The composite plate was covered in a refractory-sand bedding material in a nitrogen atmosphere. The refractory sand contained sufficient initiator metals such as magnesium. At a specific temperature, the aluminum in the composite was drawn by the magnesium vapor, and it was wicked into the refractory sand. This process was practiced one plate at a time in small retort furnaces. As these initiator metals were consumed, other materials in the bedding were nitrided from the furnace cycle, and it was necessary to discard the bedding.

New bedding materials were evaluated. The new bedding only required screening after the process to discard the alloy removed from the plate and the bedding that was reacted into the alloys. The remaining clean bedding was reused, and new bedding was added to achieve the required amount to cover the part.

During scale-up of the metal removal process, about 29 full-sized plates were lost during the metal removal because of suspected furnace failure. The plates were lost in the second operation of a large furnace that was new to this process. Inadequate metal removal was attributed to operating the process at the lower limit of the process window.

To scale up the batch size, a larger furnace was identified. Historically, this furnace had a reproducible temperature profile. A large Inconel retort type box was used to blanket the DIMOX™ plates with nitrogen. The first furnace cycle used similar temperature set points and time cycle as the retort furnace, for two plates in a large Inconel box. Metal
was removed from both plates successfully. The second batch loaded the same size box retort to capacity, 29 plates. After the same temperature settings and time, the plates were found to have only partial metal removal. This was a cause for high concern, as the metal removal process was considered non-repeatable.

Temperature mapping of the bedding material inside the box retort was conducted with old scrap Nicalon™/alumina plates. The temperature in the retort was found at this full capacity to lag significantly from the initial temperature study. It was also found that the thermocouples had been damaged by the process conditions. Putting thermocouples in the bedding material, therefore, was not a viable way to evaluate the thermal profile. Thermocouples outside the bedding were used to develop reliable temperature profiles. A longer ramp-up in time to meet process temperature was found to be necessary with more parts in the furnace. A new furnace temperature profile was fully mapped in coordination with retort temperatures, and a new, rigorous operating procedure was established to prevent process upset.

3.1.3.6 External coatings to inhibit oxygen ingress

The existing database on 2-D Nicalon™/alumina composites was based on tests carried out using as-machined test specimen surfaces with no externally applied coatings. The objective of this subtask was to evaluate the benefits, if any, of applying an external oxidation protection coating. The coating would inhibit oxygen ingress to the fiber/matrix interface at elevated temperatures and under stress. Inhibiting oxygen ingress would result in longer lifetimes at temperature, higher stress capability at temperature, and higher use temperatures. Key tests to evaluate the effectiveness of an external coating included tensile stress rupture and fatigue testing.

An external coating compatible with the DIMOX™ process existed from HACI’s work with heat exchangers. The coating was developed for particulate-reinforced DIMOX composites and was processed at 1400°C to 1500°C. To adapt this coating to Nicalon™-fiber-reinforced composites, the processing temperature had to be reduced. In initial tests with Nicalon™ fiber, the composite was processed at 1200°C (2190°F), and the coatings did not exhibit good adherence to the composite surface.
Hi-Nicalon™-reinforced composites were coated and heated to 1400°C to sinter the coating. The coatings were successfully sintered; they did not flake or scrape off. However, the retained strength of the composite was low after the heat treatment. The material was sintered at 1400°C for 6 hours; either the temperature or time may have degraded the fiber properties.

The composite had a baseline, room-temperature, 4-point flex strength of 480 MPa (70 Ksi). After coating, the room-temperature strength decreased to 92 MPa (13 Ksi). At test temperature of 1,200°C, the average strength of two bars was 134 MPa (19.4 Ksi). At 1400°C, the average strength was 184 MPa (26.7 Ksi). This pattern of higher strength at higher temperature is typical for DIMOX™ material, but the overall strengths indicate composite damage.

The second series of tests included variations to promote wetting and fill-in of residual surface porosity. The coating compositions included oxides and non-oxides in 100% and blend levels. The solutions also had colloidal and submicron particulate blends to reduce the sintering temperature at or below 1,100°C (2,010°F). The blends evaluated exhibited partial success in good coating adherence to the composite surface. Effort was continued toward developing the optimum colloidal and submicron particulate oxide blends to provide robust coating.

These composites were provided to FWDC for testing in coal ash atmospheres. While the coatings survived the application-specific testing, they did not completely protect the composite from ingress of oxygen or other gases in the test atmosphere. In this testing, the CVI SiC outer layers were found most protective to the coal ash. Pure CVI SiC does not adhere to SiC/alumina after thermal cycling due to CTE mismatches. No further work on oxide based external coatings was performed.
3.1.3.6.1 Environmental barrier coatings for hot, moist environments

The Solar Turbines and GE applications introduced steam exposure testing to CMCs. The internal atmosphere of a turbine engine, after combustion, can be generalized as 150 psi, 15% steam at 2,200°F, where the steam is a byproduct of the combustion of natural gas with air. Composite testing was performed at GE, at Solar via test rig, and at Oak Ridge High Temperature Materials Laboratory. Initial hypothesis was confirmed by testing; this atmosphere is detrimental to the BN interface layer. Work on coatings to protect the composite was performed primarily by the engine companies, who were fluent in thermal barrier coatings (TBCs) for metal parts. These steam-resistant coatings became known as environmental barrier coatings (EBCs).

In the discussions with HACI on EBCs for SiC/Alumina, the following four coating-method options were discussed.

1. Coatings that resulted from the NASA EPM Program were considered. This work was dedicated to problems with adhesion to a silicon melt-infiltrated matrix. The work was well funded and highly respected, but HACI was blocked from using their technology for commercial industrial coatings.

2. Engine-company work was considered. Solar and GE had internal experts who were strong in TBCs. The experts were competent at multi-layer coatings for CTE matching for coatings on metals. Engine companies also possessed labs and manufacturing-scale robotic equipment for coatings application. However, those capabilities were proprietary to each engine company.

3. Oak Ridge High Temperature Materials Laboratory initiated small-scale programs to look at EBCs from the ceramics viewpoint, rather than translation of a metal coating. Their approach included CVI-based coatings including high-purity alumina. HACI viewed their program, which had strong testing and analysis, as key to identifying the best coatings. In fact, the testing and analysis by ORNL became the benchmark for later CFCC and CSGT work. However, during the DIMOX™ CFCC program, only coatings from a 5-inch
CVD reactor were available. Therefore, this approach was not available for application-specific testing for Solar or GE components.

4. HACI believed there was an option in using our scientists' knowledge to apply commercially available coatings in multiple layers, and perhaps to use novel methods. This would be an option to perform iterations to find a CTE matched coating for SiC/Alumina, without a large research investment. EBC coatings would be important to industrial customers, who were familiar with plasma spray coatings for corrosion resistance.

Throughout the CFCC program, HACI considered that strength losses in SiC/Alumina materials were due to thermal aging. Because microcracking showed poor thermal aging properties, the drive to develop coatings lessened. Even without coatings, other CFCC materials showed significantly better thermal life. As the GE shroud program strengthened, their philosophy became important; the component has to survive in industrial service at least to the first inspection interval without coatings. The DIMOX™-processed materials were not meeting hot-aging strength tests. Therefore, the EBC strategy remained intact for SiC/SiC materials, but the effort was stopped for SiC/Alumina materials.

3.1.3.7 Mechanical properties

3.1.3.7.1 Database

To design representative components, each original equipment manufacturer (OEM) team member needed material property data. To acquire this data, CFCC coupons were fabricated and tested by HACI and by OEM-specified test labs.

The need for material property data allowed HACI to expand the test capability in our test laboratory and in our database. Capability and experience in creep testing, in stress rupture, and in thermal cycling was expanded. Inter-laboratory correlation of test results was obtained, and a program of regular calibration of test equipment was maintained.

CFCC presented HACI with the opportunities to participate in testing comparisons with ORNL, GE, and University testing to obtain the inter-laboratory correlation. University
data was obtained from University of Washington, University of Dayton Research Institute, University of Cincinnati, University of Michigan, and The Pennsylvania State University.

During material testing, inter-laboratory comments and results led to continuous improvement. This improvement, which allows HACI-generated data to be viewed as credible and unbiased, gave customers confidence in our in-house data. All team members benefited from the creation and maintenance of a database for all materials data. A database with material constituents sorting capability helps materials engineers make decisions about material processing.

The CVI group initially developed a FoxBASE collection of property data. Lanxide collected data material properties in an Excel spreadsheet. HACI took both sets of data and combined them into a FileMaker Pro database. FileMaker Pro allowed sorting by any or all features including fiber, interface, matrix, test type, and temperature. Any customer could rapidly compare all tensile data, for example, at 1200°C to look for differences in carbon versus BN interfaces. Rather than residing on a mainframe or server-type computer, the database could be downloaded to a laptop computer and taken to the customer.

HACI took the database to ORNL for inter-laboratory correlation discussions with Edgar Lara-Cruzio and others. HACI and ORNL worked together on improvements in the database architecture with a future goal to have the HACI and ORNL databases be able to transfer and share data. Sharing of the database was used in adopting industry standards such as those found in ASTM standards, joining technology work, ASME codes, and Mil Handbook for CFCC.

With permission from the OEMs, HACI shared data from CFCC on HACI materials. For example, ORNL shared long-term high-temperature stress rupture data and creep data (8000 hours) on CG Enhanced SiC/SiC. HACI shared GE program data on creep of CG SiC/Alumina, CG-enhanced SiC/SiC and Hi Nicalon™/alumina, and Hi-Nicalon™-enhanced SiC/SiC. (The HACI creep data extends to 1,500 hours for each material type.)
Collaboration with ORNL also extended to furnace design, instrumentation, and test set-ups. HACI used mini-composite tow tensile testing set-ups designed by ORNL, and ORNL considered HACI’s high-temperature furnaces for short tensile bar testing. Modifications of hardware to outfit stress rupture frames to make them creep capable were discussed. Discussions on high-humidity testing in stressed and unstressed conditions have yielded various flex and tensile test configurations.

3.1.3.7.2 Testing and typical data

Before performing application-specific testing, HACI’s testing laboratory determined material performance. HACI would therefore know the general performance to expect. Performance expectation was important for two reasons. First, it was important in working with designers to have an idea of stress levels the material could handle at their condition. Second, it was important in assisting the customer in set-up of application-specific tests, so that they were run at appropriate stress levels.

Figure 12 depicts a data report from initial stress rupture tests performed at HACI’s test laboratory. The GEPS database generation task was for long-term creep data. Because the creep tests at specific temperatures had not been run before, stress rupture tests were run to get an idea of lifetimes at specific stress levels. The initial data points were obtained, and, to adjust the creep test conditions, the data points were reviewed by GEPS and HACI.
3.1.3.7.3 ASTM flex coupon standards

The CFCC program encouraged cooperation and adoption of codes and standards that served to make data uniform for companies producing materials and data and for users performing design and component testing. Testing standards were developed by ASTM committees. HACI regularly participated on ASTM committees and in round robin testing of material tests. The testing standard for 4-point flexural testing affected HACI significantly; the published standard employs specimen geometry different from HACI.

The ASTM standard states that the specimen might fail in tension, compression, shear, or in a mix of different modes depending on which mode reaches the critical stress level for failure to initiate. To obtain a valid flexural strength by this test method, the material must fail in the outer fiber surface in tension or compression rather than by shear failure. The geometry of the specimen must be chosen so that shear stresses are kept low relative

Figure 12. A data report from initial stress rupture tests performed at HACI’s test laboratory.
to the tensile and compressive stresses. This is achieved by maintaining a high ratio between the support span (L) and the thickness/depth (d) of the specimen. In general, this L/d ratio is maintained at values of 16 for 3-point testing and 30 for 4-point testing. If the span-to-depth ratio is too low, the specimen may fail in shear, which invalidates the test.

HACI's internal 3x6x45 mm flex bar L/d ratio for the 4-point specimen was 13. For a year and a half after the proposed ASTM definition became known, HACI continued to use its standard flex bar but reported the type of failure that occurred for each flex specimen. A large portion (nearly 50%) of these tests indicated shear failures, which validated the reasoning in the ASTM standard.

HACI changed the flex specimen size and the dimensions of its testing fixture to maintain the specified L/d ratio of 30. For a specimen thickness of 3 mm, the ASTM recommends a 3x9x98 mm specimen and a span of 90 mm. This specimen required more than twice the amount of material as our previous design. The high-temperature flex specimen size had a thickness of 2 mm to maintain the specified L/d ratio.

3.1.3.7.4 Thermal shock testing

Raj N. Singh, Professor, Department of Materials Science & Engineering, University of Cincinnati, Ohio, conducted thermal shock studies on a variety of CFCCs. He tested 2-D SiC/Alumina composites (lot numbers 4461-01-016, 4461-01-018, 4461-01-022, and 4461-01-024). The as-received density and modulus were 2.76 g/cc and 182 GPa.

Thermal shock was measured by dunking samples in water. HACI was interested in participating in this test. However, two concerns existed. First, the relevance of this test to application-specific tests for our customers was questioned. Thermal shocks seldom occur from hot temperatures to room temperature. Instead, they occur from hot temperatures to warm temperatures, such as a 2200°F gas stream lowering to 1000°F rapidly as fuel shuts off in an engine. Seldom do real environments have sufficient water-partial pressure to drive moisture into the composite. Second, HACI was concerned that this test would destroy the BN interface.
Details of the study

Thermal shock tests were performed by heating composites to different temperatures and then inducing thermal shock by a water-quenching technique. In his report, Dr. Singh provided results on the damage to elastic modulus of composites because of the thermal shock as measured by dynamic mechanical resonance (Grindosonic Technique). Figure 13 shows data on the retained Young’s modulus as a function of the quench temperature difference (ΔT).

In this study, composite samples were given a thermal annealing treatment at 500°C in air for 20 minutes. This treatment led to an 11% drop in Young’s modulus of composites. These samples were then thermally shocked from different temperatures. The solid line in Figure 13 shows a change in modulus based on the values after the thermal treatment, and the dotted line represents the expected change in the modulus if composites in their as-fabricated state were used. These results show that a maximum reduction of ~20% in modulus occurred because of the thermal shock damage.

Dr. Singh also evaluated the impact of cumulative thermal shocks. Multiple specimens were exposed to 500°C or 800°C thermal quenches. Each specimen was subjected to a different number of thermal cycles with a maximum of ten cycles. The test specimens were broken and the percentage of retained Young’s modulus was plotted as a function of the number of cycles, as shown in Figure 14. At both 500°C and 800°C thermal quenches, the majority of the property loss (20%) occurred in the first cycle, with an additional 2% loss occurring in the next couple of cycles. No further degradation occurred.
Figure 13. Data on the retained Young’s modulus as a function of the quench temperature difference ($\Delta T$).

Figure 14. Retained Young’s modulus as a function of the number of thermal cycles of 500°C and 800°C.
HACI was concerned that this test would destroy the BN interface. A severe shock, which would create cracks, might allow water to react with the BN. Dr. Singh did not think that it would be a problem because of the short exposure time at high temperatures. The samples were maintained at the selected temperature for 30 minutes and then dropped into water at room temperature. HACI conducted similar tests with SiC/SiC composites (without the seal coating) containing carbon interface coating and did not see any detrimental effect. The hypothesis was that BN should be better than carbon in a similar situation. Exposure to water during thermal shock was very short (i.e., a few minutes), after which samples were immersed in ethanol and dried. Results and conclusions were drawn by microscopic examination of the coupons.

Conclusions

After the test, the SiC/Alumina coupons were microcracked beyond the normal amount from fabrication. Modulus of the samples was reduced probably because of the microcracking. This was similar to tests from HACI and from customers in forced-air cooling tests.

Another interesting observation was evidence of matrix removal. HACI believes the matrix removal occurred during polishing of the coupon for microscopy. When interconnected cracks are present, it is easy for chunks to be dislodged and removed during machining grinding and polishing. Microcracks, when formed, result in separation of material. Their very presence creates a void space (the width of the crack) that directly affects modulus and thermal diffusivity. The decrease in modulus can be attributed to the increasing number of microcracks because of thermal shock. HACI does not believe that there is removal of matrix during thermal shock treatment.

HACI found the thermal shock and microcracking issue to be the primary reason for failure of SiC/Alumina to meet the application needs of these OEM industrial customers. None of the industrial tests saw failure in the rapid time frame of these tests. Over time, however, cracking due to thermal stress and then resultant damage to the interfaces became the dominant failure mode in all cases.
3.1.3.8 Commercialization economics of SiC/Al2O3 materials

During CFCC, HACI generated information on costs of fabricating CFCC parts. For example, process experiments of BN interface coating determined uniformity and allowed prediction of the costs for the scaled-up BN reactors. Run costs were used to make cost determinations for higher volumes of parts and larger-sized components. In addition, process improvements might significantly reduce costs of fabricating CFCCs. The following list provides examples of tasks with high potential to reduce costs.

- Development of low-cost preforming, matrix growth, and metal removal techniques (resulting in reduced labor and materials)
- Development of alternate bedding types
- Higher quality interface coatings (resulting in higher yields)

To refine existing economic models for production costs, HACI used information on the costs of fabricating CFCCs that was generated inside and outside of this program. The impact of process improvements on economics was assessed with cost models. Updated projections of CFCC component prices were compared to the value in use assessments by the OEM team members. To enable predictions of component costs in scale-up quantities, HACI prepared fabrication scale-up plans for preforming, tooling, interface coating, matrix growth, and machining. The plans were based on component test results and designs.

3.2 Materials and Processing of Thin Sheet Alumina

3.2.1 Processing

The evolution of thin sheet DIMOX™ materials is an important step towards low cost material that demonstrates graceful failure and energy absorption of CFCCs rather than the brittle fracture of monolithic ceramics.

Initial experiments used Nicalon™ fibers and SiC interface coatings to create small (12” x 12”) hand sheets. To survive the DIMOX™ process, the Nicalon™-type SiC fiber
needs a protective coating of dense SiC. The following experiments were conducted to demonstrate the feasibility of the concept.

1. Nicalon™-fiber-based woven fabrics were coated with SiC using chemical vapor infiltration.

2. The coated fabrics were randomly broken to provide short length fibers that are typically used in paper-forming processes.

Step 2 (above) yielded some fibers that were individually separated and a majority that were in clump form. The fiber-to-fiber bonding by the SiC coating prevented complete separation of the fibers.

The following experiments were then conducted to demonstrate compatibility of the coated fibers in an in-situ DIMOX™ reaction process.

1. The coated Nicalon™ fibers and clumps of fibers were mixed with powdered aluminum alloy and SiC grits to simulate the constituents of a ceramic fiber paper forming process.

2. The mixture was heated to 950°C (1,740°F) for one hour for the DIMOX™ matrix process.

3. The fibers were examined at the end of the reaction for changes.

Some reaction was observed at the exposed fiber ends, but the reaction was limited. No reaction was observed along the length of the fibers except in the regions where the coating was damaged during post-coating sample preparation steps. These experiments demonstrated the feasibility of the concept that ceramic paper is a viable material system for preforming.

Following these initial experiments, a different ceramic paper technology was found at Lanxide. In June 1993, Lanxide Corporation contributed technology to HACI from Hercules Incorporated. This was technology for fabricating formable ceramic paper with particulate or chopped fiber reinforcement. By using differing mixtures of the in-situ
DIMOX™ process, Lanxide and HACI each demonstrated the growth of an alumina matrix by directed metal oxidation into a ceramic-reinforced paper preform.

Instead of the BN SiC interfaces used on continuous-fiber composites, the thin sheet composites were designed with oxide coatings, with technology from DuPont and from Gateway Technologies. Science support from Institute of Paper Science and Technology was obtained to assist with paper slurries and handling of coated fibers to prevent damage during processing.

The object of this task, added in 1998 into the CFCC program, was to create a sheet-metal-like CFCC material that could be used in industrial applications. The Hercules and Lanxide technologies developed from the idea that formable ceramic papers (to be used as preforms) could be produced by low-speed commercial paper machines. Paper contains various combinations of fibers, coatings, and matrix-type filler materials; the recipe for ceramic composites is similar. Technology from Hercules, Lanxide, and DuPont was combined to create a recipe for a chopped-fiber-reinforced composite that exhibited energy absorption and crack resistance.
3.2.2 Fiber Screening

In general, inorganic ceramic fibers that are available for inclusion into thin sheets can be characterized by price—low-cost insulation fibers or high-priced engineered fibers.

In addition, fibers can be characterized by the effect of fiber modulus. Low modulus fibers did not contribute much to the final composite, but higher modulus fibers tended to reduce firing shrinkage. Based on this difference, fibers are divided generally into the following two groups. Tests were conducted on these fibers.

- Low modulus
  - Cerafiber
  - SF-607
  - Silfa, Siltemp

- High modulus
  - Nextel 312, Nextel 610
  - Millennium SiC
  - Oji SiC

Ceramic-grade Nicalon™ and Tyranno ZM were also tested but only in the initial stage (i.e., the coated reactivity test). Both of these fibers survived, but they were not included in further testing due to their high costs.

Low-modulus fibers

Cerafiber is an insulation-type fiber made by Thermal Ceramics, Atlanta, Georgia. It is made by spraying a melt stream, and it contains significant quantities of shot (i.e., hard particulates of the raw materials that did not convert into fibers). The shot can be removed by washing, which increases the cost. This fiber reacts into the matrix if it is not coated. Primarily because of its low modulus (which causes pilling), Cerafiber coats with great difficulty. Pilling occurs when the fibers wrap around themselves during the coating deposition. It does not then act as a fiber in the thin sheet. Most of the effort in coating this material has addressed this problem.
SF-607, also produced by Thermal Ceramics, is another insulation-type fiber. It is formed in the same way as Cerafiber. However, SF-607 has a different chemical composition than Cerafiber. It was developed for direct contact with molten aluminum metal. This property would be very useful in thin sheet ceramics if aluminum were used as the growth metal; the fiber would not need to be coated.

Silfa and Siltemp are silica fibers made by Ametek, Haveg Division, Wilmington, Delaware. Silfa is a product made by a sol-gel process. It is not being made commercially. There is no demand because it competes with Siltemp. Siltemp is made by leaching out non-silica constituents from glass fibers. It is then thermally treated to consolidate the porous fiber. Silfa is made as fiber tows, and it can be reduced to chopped form easily. Siltemp is made only as cloth and is not readily chopped. Only small quantities were cut using scissors to determine reactivity. Both fibers are subject to pilling.

**High-modulus fibers**

Nextel 312 and Nextel 610 are fibers made by 3M, Minneapolis, Minnesota. Both fibers are made via a sol-gel process and are commercial products. Nextel fibers are not as susceptible to pilling. Although they do make clumps, these clumps are relatively easy to disperse. Our sample of coated Nextel 312 reacted during test firing. It was removed from further consideration and not made into sheets.

Millennium SiC is made by Millennium Materials, Knoxville, Tennessee. It is available only in very short fiber lengths, and it is not yet made on a commercial scale. This fiber is not at all susceptible to clumping.

Oji SiC is made by Oji Paper Company, Tokyo, Japan. It is an experimental material in the process of going to a pilot scale. This fiber remains dispersed during the coating process. All of these fibers were incorporated into handsheets. Three were made into continuous sheets.
3.2.3 Scale-up Fiber Coating at Pressure Chemical

Scale-up of the DuPont coating process was attempted at Pressure Chemical Company, Pittsburgh, Pennsylvania. After a scale-up test, two runs were made—the first on Silfa and the second on Cerafiber. For the scale-up test, Pressure Chemical ran a laboratory-scale coating trial on five pounds of fiber. These coated fibers were then made into sheets and the reactivity, if any, observed. Three coating conditions were made in the test.

The Silfa run was performed in a 50-gallon reactor, and 15 pounds were coated per batch. The desire was to get enough information to do the run in a 1000-gallon reactor. Severe pilling was encountered in the 50-gallon reactor, and there were problems in discharging the material. The coated fibers, even if pilled, form mats that resist flow. Upon discharge, the fibers clogged the valve and did not flow out. The product had to be removed from the top of the reactor. It is possible that discharge from an overflow pipe will work for this material, but Pressure Chemical does not have this type of equipment. Pressure Chemical decided that this material could not be used in their 1000-gallon reactor, since it takes one day just to remove the top cover.

The Cerafiber run was also performed in a 50-gallon reactor, and 15 pounds were coated per batch. Processing conditions were selected based upon the experience from the Silfa batches. The result was that pilling was reduced but not eliminated.

The hydrolysis coating process is relatively simple, involving only one container. However, performing this work at a toll chemical processor was very expensive—well over $100 per pound of fiber. Because of the effort being expended on the fiber coating, it was decided to set up an in-house capability. This facility consisted of a 40-gallon vessel that was designed just for this process, and it included an overflow discharge.

3.2.4 Sheetmaking Trials at Western Michigan University

Western Michigan University operates a prototype paper-making laboratory. The commercial white-paper industry uses very wide sheets fabricated on fast-running machines. These machines are not suitable for ceramic papers, because we wanted to test
small batches of raw materials, and the preform stock paper was not expected to have the strength required for the high speeds. In contrast to white paper, which is only several thousandths of an inch in thickness, our ceramic paper is similar to cardboard stock that is 80 to 120 thousandths of an inch thick. A type of older paper machine, called a Fourdrinier machine, is ideal for experimentation and process development for ceramic papers. Facilities at WMU were inexpensive, and the staff was interested in unique problem solving. For CFCC ceramic paper trials, these conditions led to a good relationship between HACI and Western Michigan University.

Both of the fibers coated at Pressure Chemical (Silfa and Cerafiber) were included in sheets formed on the Fourdrinier machine. In addition, uncoated SF-607 was used in another run. There were no problems encountered in the SF-607 run. However, the extensive pilling of the Silfa fibers presented many problems. Attempts were made to re-disperse the fibers using a high-shear blade (Cowles), which was only partially successful. In the end, the fibers were added to the blend with pills. As a result, the contribution of the fibers in the sheet was reduced.

Dispersion of the coated Cerafiber was more successful. However, there were machine problems that limited the yield of sheets from this batch.

3.2.5 Testing at HACI and ORNL

Mechanical testing was performed at Lanxide Corporation and at Oak Ridge National Laboratory. Samples tested at Lanxide consisted of coupons made from the sheets having dimensions of 0.25"x2.0". Samples supplied to ORNL were larger (0.5" x 6.0") plates from which test parts were machined.

Shrinkage data were obtained from these samples during firing. At Lanxide, room-temperature 4-point flexural tests were made. From these tests, the stress-strain curves were obtained. These samples were also mounted and polished in order to evaluate the microstructure.
At ORNL, 4-point flexural strengths were determined on selected samples at room temperature and at 1200°C. In addition, a few compositions were tensile tested at room temperature.

A machine-made sheet that contained no added inorganic fiber was designated as the baseline material. All other sheets containing fibers were compared with this material in Table 21.
<table>
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<th>Designation</th>
<th>Lanxide Room-Temperature Flexural Test (MPa)</th>
<th>ORNL Room-Temperature Flexural Test (MPa)</th>
<th>ORNL 1200°C Flexural Test (MPa)</th>
<th>ORNL Room-Temperature Tensile Test (MPa)</th>
<th>% Shrinkage</th>
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<td>20</td>
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<td>41</td>
<td>28</td>
<td>NT</td>
<td>1.8</td>
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<tr>
<td>Cerafiber—11%</td>
<td>22</td>
<td>38</td>
<td>30</td>
<td>NT</td>
<td>2.7</td>
</tr>
<tr>
<td>Cerafiber—11% PC coated/WMU</td>
<td>34</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>2.6</td>
</tr>
<tr>
<td>UN SF 607—5.9%</td>
<td>31</td>
<td>40</td>
<td>42</td>
<td>15</td>
<td>2.7</td>
</tr>
<tr>
<td>UN SF 607—8.3% WMU</td>
<td>26</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>3.9</td>
</tr>
<tr>
<td>Silfa—8.3% PC coated/WMU</td>
<td>12</td>
<td>17</td>
<td>17</td>
<td>NT</td>
<td>1.8</td>
</tr>
<tr>
<td>Silfa—10.5% UN Cerafiber—5.3%</td>
<td>32</td>
<td>32</td>
<td>30</td>
<td>14</td>
<td>1.9</td>
</tr>
<tr>
<td>Nextel 610—5.3%</td>
<td>26</td>
<td>33</td>
<td>31</td>
<td>16</td>
<td>0.5</td>
</tr>
<tr>
<td>Millennium SiC—6.6% UN Cerafiber—5.5%</td>
<td>30</td>
<td>33</td>
<td>37</td>
<td>NT</td>
<td>3.1</td>
</tr>
<tr>
<td>Oji SiC—6.3% UN Cerafiber—5.5%</td>
<td>32</td>
<td>35</td>
<td>37</td>
<td>13</td>
<td>1.1</td>
</tr>
<tr>
<td>Oji SiC—11.8% UN Cerafiber—5.2%</td>
<td>28</td>
<td>23</td>
<td>35</td>
<td>NT</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Notes:  
- PC coated = coated at Pressure Chemical  
- UN = Uncoated  
- WMU = Machine made sheets at Western Michigan University.  
- NT = not tested  
- All percentages expressed as weight in initial blend before sheet forming.
Generally, the flexural strengths measured at room temperature at ORNL were higher than those tested at Lanxide. This may be due to the difference in sample preparation; the samples tested at ORNL were fully machined after firing, but the samples tested at Lanxide were "as-fired".

Flexural strengths tested at 1200°C were usually the same as or higher than the room-temperature values. The reason for increased strength at higher temperature is not known. It could be speculated that there was increased sintering that occurred on these relatively porous materials. However, the time at elevated temperature was very short prior to testing. The only notable exceptions to the increased strength were the Cerafiber samples.

As would be expected, the tensile strengths are lower than the flexural strengths. Fiber additions did not result in higher strengths when compared to the baseline material. The only notable difference due to fiber addition was the lowering of the firing shrinkage. All uncoated fibers react into and become part of the matrix.

In comparison to the baseline material, Cerafiber additions maintained room-temperature flexural strengths. However, the high-temperature strengths did drop significantly, and this was the only fiber to behave in this manner. The reason may be because this is the only glass-type fiber included. Thus, the lower high-temperature strength is a reflection of the softening of the fibers at high temperature.

The SF 607 fibers reacted into the matrix. Although this fiber was developed for molten aluminum contact, intimate mixtures of individual fibers in contact with molten aluminum reduced the fiber completely. The result is a sheet that behaves like the baseline, yet has a lower firing shrinkage. The consumption of these fibers during firing, along with the modest decrease in firing shrinkage, led to the practice of blending low-modulus fibers with high-modulus fibers. The purpose was to decrease the wood pulp content in the sheetmaking step and thus to reduce final porosity. Instead of SF607, Cerafiber was the low-modulus fiber that was actually used in this manner.
The machine-made Silfa sheet suffered from the extensive pilling during coating. The obtained strengths reflected the presence of the undispersed pills. Smaller quantities of Silfa were coated without pilling and mixed with uncoated Cerafiber. This resulted in equivalent strength to the baseline and in a very low firing shrinkage.

The Nextel 610 sheets showed only slightly lower strengths but extremely low firing shrinkage. This is believed to be due to the better dispersion of these higher-modulus fibers in the slurry prior to sheetforming.

The Millennium SiC fiber showed only minimal effect. This may be due to the very short lengths of the fibers. They are similar to thick whiskers with the length visible only under magnification.

The Oji SiC fibers result in sheets that show good strengths and very low firing shrinkage. These fibers are made in a felt- or mat-type of configuration. These are readily crushed into fibers of random lengths. These fibers do not pill or clump during coating and therefore are readily dispersed in the slurry. These fibers are shorter than the Nextel 610 fibers. This probably explains the difference in firing shrinkage.

Both Nextel 610 and the Oji SiC fibers showed the best performance of the fiber-containing sheets. The main disadvantage of Nextel 610 is that it is the most expensive of the fibers under consideration. The main disadvantage of the Oji SiC fiber is that it is not yet in commercial production. It is still in a scale-up mode to pilot scale, and the price has not been established.

### 3.2.6 Sheetmaking Chemical Modification

One of the chemicals used in the sheetmaking step controls the flocculation (e.g. distribution or attachment) of particulates onto fibers. The amount used determines the amount of flocculation. Lightly flocced blends tend to make highly dense sheets but require a longer time to drain water; this can be accommodated in handsheets but sharply reduces throughput on continuous machines. The efficiency can also be reduced on lightly flocced blends because there is a greater chance of unattached particulates flowing
through the screen. Highly flocced blends tend to drain very rapidly but result in a less-dense sheet.

Work with the Institute of Paper Science and Technology in Atlanta, Georgia (IPST), was subcontracted to obtain the assistance of two paper scientists. HACI provided our base chemicals to be used with their experimental setups, which simulate the water drainage in a paper machine. IPST also suggested different additives for wet strength of the paper mix as well as flocculation chemicals. Determination of the amount of chemical used to make sheets was based only upon retention efficiency. To see if variations away from this amount would result in higher mechanical properties of the fired composite, a test was made in which the chemical concentration was varied.

The test was conducted on handsheets, using five different addition levels. Fibers used for this test were coated Oji SiC along with uncoated Cerafiber. Room-temperature 4-point flexural testing was conducted at Lanxide for all addition levels and at ORNL for the end and middle points only. Quantitative image analysis was done on these parts in order to determine porosity values. Table 22 provides the results of the testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lanxide 4-Point Flex Strength Test (MPa)</th>
<th>ORNL 4-Point Flex Strength Test (MPa)</th>
<th>Shrinkage %</th>
<th>% Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1A</td>
<td>18.0</td>
<td>22.1</td>
<td>1.0</td>
<td>36.0</td>
</tr>
<tr>
<td>H1B</td>
<td>20.0</td>
<td>—</td>
<td>1.4</td>
<td>45.0</td>
</tr>
<tr>
<td>H1C</td>
<td>21.0</td>
<td>30.3</td>
<td>1.2</td>
<td>42.3</td>
</tr>
<tr>
<td>H1D</td>
<td>28.0</td>
<td>—</td>
<td>1.2</td>
<td>41.8</td>
</tr>
<tr>
<td>H1E</td>
<td>18.0</td>
<td>26.4</td>
<td>1.0</td>
<td>35.9</td>
</tr>
</tbody>
</table>
The results show that there may be a relation between the strengths obtained and the amount of chemical addition. While the values of the Lanxide and ORNL strengths do not absolutely agree, the trends follow each other at least for the parts tested. The data shows that the highest strength occurs at the level of sample H1D. This happens to be the addition level identified in the previous test for maximum product retention, and it represents the amount currently used in sheet forming.

### 3.2.7 Fiber Coating Alternatives

The DuPont coating process proceeds via heterogeneous nucleation. This means that the chemicals begin to form particulates almost as soon as the coating commences. The ultimate coating thickness is limited as the entire mixture increases in viscosity as more particulates form. Information was found about a similar process that was yielding thick coatings on fabric at Gateway Materials Technology. This presented an alternate coating process. An order was placed at Gateway Materials to compare their process with the DuPont process. The advantage may be thicker coatings on chopped fibers. Cerafiber and chopped Nicalon™ were sent for coating trials. From what was known about the propensity for pilling, process conditions were explored to minimize the effect. From the limited tests to date, it appears that this is also a heterogeneous deposition process, with perhaps different kinetics. Consequently, the same issues faced with the DuPont process remains. However, what has not been determined yet is the ultimate coating thickness achievable with the Gateway process.

Nicalon™ and Cerafiber fibers with alumina coatings were calcined to 900°C to convert the alumina coating to an insoluble refractory alumina. Several small pieces of fabric cut from a square foot of fabric were also coated with alumina. These results were not in a quantity sufficient to produce composites, but were sufficient to identify coating non-uniformity and pilling that was common to the heterogeneous deposition type processes.

In HACI’s agreement with Gateway, no process information was exchanged other than generic work already disclosed or published. Because the results of Gateway coatings seemed similar to DuPont coatings, the DuPont coating process was used for the
remaining work in thin sheet composites. Relations with Gateway remained favorable, leaving future work a possibility.

### 3.2.8 Thin Sheet Laminations and Joining

Early in application development, the issue of joining and attachments was discussed. A survey of the needs for the OEMs for recuperator elements and tube shields revealed that the laminations and the edge sealing were most important.

In the recuperator, the sealed edges form hollow elements for air passages. For the tube shields, straps of thin sheet ceramic were envisioned to go on the backside of the tube, to seal against the tube shield (for attachment). Iterations of processes using the base matrix elements and various heat cycles, with and without added pressure, developed into a first-generation lamination joint. The joints could be made with the preform paper stock and a matrix paste, in a two-step heat-curing cycle. The first stage used pressure in the form of refractory brick for flat shapes, and it incorporated tooling for complex shapes. The second high-heat cycle completed the in-situ DIMOX™ process and finished the process of the thin sheet components and the lamination joint. Laminations of two layers (each of which had already been fully processed through DIMOX™) did not work in this first-generation joining method.

#### 3.2.8.1 Recuperators for gas turbine engines and heat exchangers

The application of recuperators for gas turbine engines and heat exchangers for industrial applications is of high interest. The thin sheet is used to replace metals in the thin-walled elements enabling higher-temperature operations. Two recuperator elements were fabricated. Subsections 3.2.8.1.1 and 3.2.8.1.2 provide descriptions of the designs.

#### 3.2.8.1.1 Parallel-plate, cross-flow test recuperators

These were test data units, about 8” x 8”, with alternating plates flowing air across (e.g. east to west) or down (e.g. north to south), with the total number of layers being 4 to 20 (see Figure 15). These units were flat, and the plates were parallel. Sheets of thin sheet preform stock had edge stock glued to the edges, and the sheets were stacked in an alternating fashion to create the cross flow. Heat exchange occurred because one flow
was hot, and the other was cold. Lamination experiments consisted of keeping plates from curling, and obtaining seals on each edge seal. Materials with low shrinkage were important for this fabrication. In addition, shrinkage needed to be equal in “x” and “y” directions. In the paper machine, this equals the run direction (many feet to one hundred feet length in one process run) by the width of the sheet (24 to 36 inches wide).

![Figure 15. Cross-flow recuperator.](image)

### 3.2.8.1.2 Elements for the counter-flow test recuperator

Each element of this design was about 5" wide by 24" long, hollow at each end, and sealed along both long edges. These elements flowed cold air through the element, and hot air passed over the element for heat exchange. These elements were curved in the width and straight in the length, as shown in Figure 16, so that they could nest together in a cylindrical manifold. Shrinkage in the length was not important to control as long as the shrinkage was uniform. Shrinkage in the width would have been an issue if the elements had warped so that they would not have nested together.
3.2.8.1.3 Fabrication of generic-design cross-flow recuperators

It is during the fabrication of parallel plates and counter-flow elements that the importance of firing shrinkage was seen. The shrinkage is due to the preform minimizing its surface area. It is known from the field of topology that when a flat surface reduces its surface area the result is a saddle shape. Thus, reducing the shrinkage will reduce the saddle effect. Also, maintaining a flat surface results in tensile stresses, and reduced shrinkage will reduce these stresses. Sheets containing no fibers have a linear shrinkage of 4%. Practically all fiber additions reduced this value to 1% or less.

Much effort was expended on developing the techniques needed to fabricate cross-flow recuperators of generic design. The main goal was to form the entire part in the preform stage and to fire it reliably into a monolithic part. This complex part requires very low-shrinkage sheets. Parts measuring up to 8"x 8" x 20 layers were made. Sheets used
to make these parts contained coated Silfa and were machine made. These sheets had the lowest fired strengths, but they were used because of their low firing shrinkage. More successful parts could have been attempted if greater quantities of sheets containing Nextel 610 or Oji SiC fibers had been available; these fibers had the lowest firing shrinkages. Once assembled at room temperature, the flat recuperators were set on refractory plates that had been ground flat. Specific weight was placed on top of the recuperator, for a specific number of plies. After the initial curing-furnace run, the top weight was removed, and the recuperator was fully heated for the DIMOX™ processing.

The cross-flow recuperators made for CFCC have sheet thicknesses that were too thick. Compared to equivalent sheet metal recuperators, the ceramic ones were much thicker (perhaps by 3 times). The means to reduce this is to optimize manufacturing methods—to reduce sheet thickness. However, the edge-sealing methods were proven to work, and flat recuperators were made with good yields.

Process for fabrication of the cross-flow recuperator elements was the same from the materials point, but curved tooling was required for the assembly and firing. The design of the recuperator was such that the elements had ribs inside them to accommodate that the air outside the elements was of a higher pressure. The ribs were formed as strips of the thin sheet with lamination to bond them to the two face sheets. Aluminum tooling was used for the low-temperature process, and monolithic SiC tooling was used for the high-temperature process. Elements were made with baseline particulate-reinforced thin sheet materials and with newer thin sheet with fiber reinforcement. With the higher-shrinkage baseline material, yields through flow testing for individual elements (to ensure no side edge leaks) were only 40%, but yields were nearly 75% with the stronger and lower-shrinkage fiber-reinforced thin sheet.

Table 23 provides data from the testing that was conducted. While the flex data indicates the fiber-reinforced thin sheet is either of the same strength or weaker than the baseline particulate materials, they did not behave this way. In fabrication of the complex curved elements, the fiber-reinforced sheets were less brittle to handle and easier to layup in tooling, and the lower shrinkage produced higher yields in fabrication.
Table 23. Example thin sheet with and without fibers

<table>
<thead>
<tr>
<th>% Fiber (coated at Pressure Chemical)</th>
<th>Flex Strength (room-temperature—Lanxide)</th>
<th>Flex Strength/Weibull Modulus (room-temperature—ORNL)</th>
<th>Flex Strength (1200°C—ORNL)</th>
<th>% Shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Fiber</td>
<td>31±4</td>
<td>40.7 / 4.8</td>
<td>49.3±7.9</td>
<td>4.0</td>
</tr>
<tr>
<td>11.1% Cerafiber</td>
<td>22±2</td>
<td>37.6 / 7.8</td>
<td>29.5±3.9</td>
<td>2.7</td>
</tr>
<tr>
<td>5.9% Cerafiber</td>
<td>19±5</td>
<td>41.3 / 4.4</td>
<td>28.4±6.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

3.2.9 Ceramic Fiber Paper Process Economics

A one-page Excel cost model was developed to easily calculate the fabricated cost of thin sheet materials. With the model, different raw materials and different recipes of the same base materials could be adjusted to show cost variances. Figure 17 illustrates the input data needed and the output data generated for quick comparison of various fabrication scenarios.
Figure 17. Cost model spreadsheet for thin sheet CFCCs.

### 3.2.10 Conclusion and Path Forward

Thin sheet alumina is an interesting and challenging material that has the potential for large-scale commercialization. It is a weak material that needs improvements in fracture toughness and damage tolerance. We found several cases where sheet metal is used in high-temperature processes that could be replaced by thin sheet alumina, including baffles in turbine engines, linings in coal power plants, and edge walls of heat exchangers.

Lamination and joining ideas using preceramic polymers seem technically strong and field workable for component assembly. The need for improvements in toughness and
damage tolerance stems from operations such as drilling holes in the field, for attachment.

The process for large-scale fabrication is not necessarily unique in the ceramics industry, but other materials made in continuous type sheet processes are tape-cast or insulation-type materials. The data sheets indicate these materials are even weaker than thin sheet, and are not made in combination with a process like DIMOX™ that converts the sheet stock into a stable high-temperature material with no remaining binders that burn off.

In the future, consistency and scale-up of the paper-making preform fabrication would need to be improved, and trials for bonding thin sheet ceramics to metals would need to be performed for erosion applications. Additional IOF users would need to be identified to support application development, and fabrication tasks would need to be performed to understand the versatility of this sheet stock.
3.3 Materials and Applications with Foster Wheeler

3.3.1 Application Interest

Foster Wheeler Development Corporation (FWDC) is the research, development, and design division of Foster Wheeler Corporation. At FWDC, HACI worked with material scientists and power plant designers to work on CMC heat exchangers for power plants.

The driving force for FWDC is to increase efficiency of power plants—measured in energy power output versus fuel-burned input—while reducing emissions. In addition, because Foster Wheeler Corporation operates industrial plants and power plants around the world, they are concerned with metal corrosion and other service issues of advanced materials. Replacing super alloys with CMCs offers improved corrosion resistance and higher temperature capabilities.

FWDC studied the feasibility of using CFCCs by performing the following tasks:

1. Component design, in iterations with initial data and then specific data
2. Application-specific materials testing
3. Field exposure testing of basic shapes of CMC materials in realistic environments

In component design, to design part sizes, FWDC used HACI’s fabrication rules and sizes of CMC manufacturing equipment. They designed the number of joints, the assembly methods, and the calculated stresses of new CMC components.

In application-specific testing, to perform tests in small ovens, they used known exact chemistries of different process conditions as static corrosion situations.

In field exposure testing, they sought to place material shapes in accurate positions for dynamic exposures, and they used instrumentation to obtain true exposure data.

Their approach to the use of CMC was serious, sincere, and based on factual material problems in their industrial systems. FWDC used their expertise to seek solutions to
barriers to higher operating efficiency. Key barriers addressed in CFCC included materials properties of use temperature and thermal properties. Added new barriers included component fabrication and cost.

The application of vortex finder panels and tube shields are present day corrosion problems that could be CMC applications if parts were the same cost as metal parts. Other uses such as headers for high-temperature air heaters are fundamental to overcoming barriers for future, new, higher-efficiency industrial plants.

FWDC became the most cost-conscious of all partners over the course of the CFCC program. Many corrosion problems exist in the industrial power plants they work in. These problems are resolved during regularly scheduled (usually annual) shutdowns.

Replacement of one metal part with CMC material can extend the life of that piece, but replacement rarely affects the process efficiency. Except for the incremental savings, (during a shutdown) of replacing the exact part, the value in use is therefore the same. A different metal part becomes the life-limiting component causing the shutdown. Until all the material problems and any related operational problems are solved, to extend the plant run time from one year to two years between shutdowns, the cost savings will be in small increments. In addition, the prevention of quality problems from corrosion and the ability to tolerate hotter temperatures are important benefits for CMCs.

We found the overall resistance to installing CMCs in an industrial plant to potentially be lower with FWDC than with other OEMs. Once FWDC is confident of the component life, the benefit to the plant is one less metals corrosion problem. Accurate application-specific tests were used to build confidence of the CMC’s lifetime. The benefit to HACI is the guaranteed operational test time that the CMC will see, with the comfort of a known inspection or replacement interval for component lifetime planning. For HACI, however, each data point of operational experience took 1 to 2 years, which represented a long waiting time.

The result of these factors signified their project goal of making tests realistic and ensuring that the results and the materials were repeatable. FWDC also sought good
consistency and repeatability in material properties. As a result, they did not embrace the long-life properties of Hi-Nicalon™ fiber (over ceramic-grade Nicalon) because all of the earlier tests might have to be repeated with the new fiber. Another major deterrent was that the premium pushed the price of the CFCC components out of value for their industrial needs.

The materials that FWDC tested in this program included SiC/Alumina with ceramic-grade Nicalon™ and Hi-Nicalon™ fibers, oxide/oxide CMCs including Nextel™ 610/Alumina, and thin sheet alumina CMCs. In addition, the parallel CVI-materials CFCC program encompassed tasks with FWDC. Therefore, many application-specific tests and component designs were completed with several materials in mind, including CVI SiC/SiC.

3.3.2 Application-Specific Materials Testing

Application-specific materials testing included exposures known to corrode current metal components, such as heat exchangers. A material exposure database for corrosion and strength retention in actual and simulated environments was essential for applications such as heat exchangers in coal combustion gas and steam reformers under high-pressure steam.

A discussion of application-specific materials testing is divided into the following sections:

1. C-ring database and baseline data of the fabricated materials
2. Laboratory coupon ash exposure testing
3. High-pressure tube testing
4. Joining
3.3.2.1 C-ring database and baseline data

Twelve straight CFCC tubes approximately 1.5” in diameter by 9” long were fabricated via directed metal oxidation of Nicalon\textsuperscript{TM}/Alumina composite. The as-fabricated tubes were be evaluated to verify that the process conditions produce quality composites in these geometries. These straight tubes were machined into C-rings, for initial database and for exposure tests. FWDC also considered permeability testing, hydrostatic proof testing, mechanical fatigue and pressure fatigue testing, and field-testing on probes.

C-rings were machined by sectioning the tubes into ½”-wide rings and then a ½” section was cut out to create the C shape. C-rings were tested in compression and tension at room temperature to assess composite behavior at the outermost and the innermost diameters of the tubes, respectively. Table 24 provides test result data.
Table 24. Representative C-ring data

<table>
<thead>
<tr>
<th>Tube I.D.</th>
<th>Room-Temperature Tensile</th>
<th>Room-Temperature Compression</th>
<th>1200°C Compression</th>
</tr>
</thead>
<tbody>
<tr>
<td>-001</td>
<td>335 301</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Avg 321 Mpa (46 Ksi)</td>
<td>Avg 272 Mpa (39 Ksi)</td>
<td></td>
</tr>
<tr>
<td>-002</td>
<td>334 331</td>
<td>202</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>343 303</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>272 308</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>268 312</td>
<td>239</td>
<td></td>
</tr>
<tr>
<td></td>
<td>372 301</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Avg 318 Mpa (45 Ksi)</td>
<td>Avg 311 Mpa (44 Ksi)</td>
<td>Avg 210 Mpa (30 Ksi)</td>
</tr>
<tr>
<td>-003</td>
<td>408 316</td>
<td></td>
<td>257</td>
</tr>
<tr>
<td></td>
<td>366 342</td>
<td></td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>350 271</td>
<td></td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>359 352</td>
<td></td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>293 316</td>
<td></td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>Avg 355 Mpa (50 Ksi)</td>
<td>Avg 319 Mpa (46 Ksi)</td>
<td>Avg 216 Mpa (31 Ksi)</td>
</tr>
<tr>
<td>-004</td>
<td>296 246</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>241 218</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Avg 268 Mpa (38 Ksi)</td>
<td>Avg 232 Mpa (33 Ksi)</td>
<td></td>
</tr>
</tbody>
</table>

Additional -004 strengths are reported later in this report, with 4000-hour TVA exposure data.
Data was obtained from 4.4-centimeter (1.75-inch) inner diameter tubes (#1 to #7) and 5.0-centimeter (2-inch) inner diameter tubes (#8 to #10), all with a wall thickness of 0.32 centimeters (0.125 inches). As expected, the mechanical properties (such as compression behavior) showed good retained strength at elevated temperatures.

In order to evaluate any variation in properties along the circumference of the tube, samples were machined such that the cut in the C-ring was at three different orientations—90° intervals. Four samples were tested for each orientation. No significant variation in properties as a function of orientation suggests good uniformity along the circumference within the tube. The C-ring compression strength was also measured as a function of location along the length of the tube, with no significant variations. Figure 18 provides results of the testing.
### C-Ring Compression Strengths

@ 1200°C (2200°F) in Air

<table>
<thead>
<tr>
<th>Orientation</th>
<th>0° Orientation</th>
<th>90° Orientation</th>
<th>180° Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa  ksi</td>
<td>MPa  ksi</td>
<td>MPa  ksi</td>
</tr>
<tr>
<td>288</td>
<td>42</td>
<td>375</td>
<td>54</td>
</tr>
<tr>
<td>348</td>
<td>51</td>
<td>401</td>
<td>58</td>
</tr>
<tr>
<td>390</td>
<td>57</td>
<td>321</td>
<td>47</td>
</tr>
<tr>
<td>324</td>
<td>47</td>
<td>323</td>
<td>47</td>
</tr>
<tr>
<td>Avg.</td>
<td>338  49</td>
<td>355</td>
<td>52</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>43  6</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>320  46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31  5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 18. Testing of C-ring compression strength showed no significant variation of properties along the circumference of the tube.

### 3.3.2.2 Laboratory coupon ash exposure testing

In a coal-fired heat exchanger, construction materials can be subjected to a wide range of temperature and chemistry. During Phase I of CFCC, FWDC identified the air inlet and air outlet as the two extremes in exposure. The air inlet is exposed to the highest temperature, and it is exposed to coal ash and flue gas. The air outlet also is exposed to coal ash and flue gas, but it is exposed to a lower temperature than the air inlet. The lower temperature allows alkalis to condense out of the gas and onto the composite. These alkalis make the environment much more corrosive than plain coal ash does.
Flat-plate-type coupons were placed in an air-atmosphere oven in the laboratory. Coal ash was painted on one side of the coupons for the exposure tests. For laboratory testing, FWDC used both actual coal ash and synthetic mixtures of coal ashes. Laboratory testing was also performed for exposures to the flue gas, without ash contact on the specimens.

The objective of this subtask was to evaluate durability of DMO materials in a coal combustion environment. The initial heat exchanger design was exposed to a coal-burning boiler environment. The temperature ranged between 980°C and 1,175°C (1,800°F to 2,150°F). At high temperatures, the physical state of the coal ash could be that of a dry powder. At low temperatures, the coal ash could become sticky with alkali present. This environment will impact the life of the material through corrosion and erosion of the tubes.

FWDC conducted unstressed-coal-combustion exposure tests on SiC/Alumina and Nextel™ 610/Alumina coupons. Approximately 15 coupons were machined from flat plates and shipped to FWDC. Testing was conducted in the following environments:

- Combustion gas only
- Combustion gas plus coal ash
- Combustion gas plus coal ash plus low alkali
- Combustion gas plus ash plus high alkali
  (representing coal available in the USA)

In Phase I of CFCC, a screening study was performed. The study involved the corrosion of six material systems in five environments for up to 1,500 hours. The air inlet region was simulated by exposing tensile specimens to two types of coal ash plus synthetic flue gas at 2,300°F. The air outlet was simulated by exposing specimens to ash spiked with alkali salts plus flue gas at 1,800 F. Both DIMOX™ alumina and SiC/SiC composites were found to corrode during the 2,300°F exposures. Further, enhanced SiC was severely corroded by exposure to highly alkaline coal ash at 1,800°F. The DIMOX™ alumina material from 1,800°F had bleed-out of the residual aluminum phase, but the composite appeared intact.
In Phase II of CFCC, additional testing was performed with Nicalon™/Alumina, Nextel 610/Alumina, and CVI SiC/SiC. The coal ash exposure tests were conducted at 980°C (1,800°F) and 1,150°C (2,100°F) for 500 and 1,500 hours. Additional coupons were exposed to coal ash and flue gas at 2100°F (200°F lower than in Phase I testing), to flue gas only at 2100°F, and to coal ash spiked with alkali salts at 1800°F. Table 25 outlines the variety of exposure tests that were conducted.

<table>
<thead>
<tr>
<th>Nicalon™/Alumina System</th>
<th>Exposure Test</th>
<th>Nextel™/Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nic #1</td>
<td>As fabricated—no exposure</td>
<td>—</td>
</tr>
<tr>
<td>Nic #2</td>
<td>No ash—500 hrs ;2,100°F</td>
<td>—</td>
</tr>
<tr>
<td>Nic #3</td>
<td>No ash—1,500 hrs ;2,100°F</td>
<td>Nex # 3</td>
</tr>
<tr>
<td>Nic #4</td>
<td>Ash—500 hrs ;2,100°F</td>
<td>Nex #4</td>
</tr>
<tr>
<td>Nic #5</td>
<td>Ash—1,500 hrs; 2,100°F</td>
<td>Nex #5</td>
</tr>
<tr>
<td>Nic #6</td>
<td>Low alkali—1,500 hrs; 1,800°F</td>
<td>Nex #6</td>
</tr>
<tr>
<td>Nic #7</td>
<td>High alkali—1,500 hrs; 1,800°F</td>
<td>Nex #7</td>
</tr>
</tbody>
</table>

To improve on the results from Phase I, the rings of SiC/Alumina were surface-coated. The surface coatings for the DMO tubes originated from methods developed and used in particulate-reinforced SiC/Alumina heat exchanger tube development. Various wash coatings were applied and designed to react with residual aluminum metal within the alumina matrix. Heat-treating resulted in a hard, thick, alumina coating that provided resistance to further aluminum bleed-out. In addition, the coating protected the BN interface coatings from chemical attack and oxidation.

All DIMOX™ samples exposed to coal ash showed surface coating cracks and some spalling. High-alkali coal ash exposure at 982°C (1,800°F) for 1,500 hours appeared to have resulted in some swelling of the specimens. This preliminary evaluation suggests
that this effect is most severe for Nicalon™-fiber-reinforced composites. This type of swelling is not present in the alumina-fiber Nextel™-610-reinforced composites.

Original expectations were that alumina matrix would protect the composite and that it would perform well to coal ash. This expectation resulted from successful tests with particulate-reinforced SiC/alumina. However, the fiber-reinforced coupons did not survive well. Bubbling of the exterior coatings caused swelling of the composite. Swelling created microcracks, which allowed attack of the Nicalon™ SiC fibers. Further analysis revealed that the stoichiometry of SiC particulate is purer, and it is resistant to chemical attack, while the Nicalon™ SiC fibers contain many impurities and are not resistant to chemical attack.

Microscopy showed that the coal ash alkali attack weakens the composite fibers and the interface. Weakening occurred from microcracking of the matrix. In this test, some of the microcracks resulted from CTE differences that caused cracking on fabrication. In addition, cracks were also found between the matrix and the SiC interface. These layers are usually strongly bonded. However, because they were attacked by alkali, cracks occurred in the SiC layer, and a path formed for alkali attack and reaction with the composite.

The composites showed oxidation between the coating and the composite. The mullite coating showed silica below the coating, indicating oxygen ingress and reaction with the interface and fibers in the composite. This indicates that the external mullite coating used with success for SiCp is too hot a process for ceramic-grade Nicalon™; the firing temperatures desired to make the coating most effective will degrade the strength of the fibers.

The tubes were also tested in the field, at the Gallatin Station power plant. The tubes were fabricated with the same alumina-wash coating, but the heat treatment of the coating differed.

In addition, the oxide/oxide work was not successful. The materials presented themselves to the corrosive atmosphere essentially the same as Nicalon™/Alumina using
alumina matrix with residual aluminum and BN/SiC interface. In addition, the materials
had very low high-temperature strength and creep would be an issue if materials had long
lives. Microscopy showed no added damage in the composites from CTE mismatches in
the fiber and interface layers. The SiC layer was applied very thinly. So, CTE of
interface was not an aggravating problem in this case.

3.3.2.3 High-pressure tube testing

The objective of this subtask was to demonstrate that the CFCC materials can function in
the planned applications by testing the materials in environments that simulate actual
conditions. FWDC steam reformer and heat exchanger applications require tubular parts
that can survive temperatures of 1000°C in high-pressure environments without excessive
gas permeability through the tube wall. FWDC and HACI selected The Pennsylvania
State University (Penn State) to establish the permeability and ultimate burst strength at
room and elevated temperature of the CFCC DMO tubes. Professor John Hellmann and
Dr. D.L. Shelleman of Penn State had an existing experimental set-up to perform these
tests. HACI has initiated fabrication of six tubes nominal 5 cm ID (1.75 inches ID) by
45.7 cm (18 inches) long.

A method to fabricate high L/D (length over diameter) tubes was developed during this
task. Prior experience was on cylinders with a diameter greater than the length (and short
tubes—2-inch diameter x 8-inch length). These L/D ratios (L/D<1 to L/D=4) did not
present any difficulty as long as one considered inner tooling design and adopted
methods to remove the inner tooling. The most common tooling method was to make the
inner tooling in four arc segments, held together with rings at the ends. When these tubes
(L/D=9) were fabricated, a number of technical issues arose, which included the
following issues:

- Difficulty in removal of inner tooling
- Thin coatings and poor BN coating uniformity on the inner plies
- Poor BN uniformity from edges to center down the length of the tube
- Unrelated to our fabrication were apparent poor quality fibers that resulted in
  low strength properties
Fabrication of 17 preforms was required for eight parts to be completed through DIMOX™ growth, resulting in four good tubes for Penn State testing. These tubes were machined to the specifications provided by Penn State.

In alignment with the CVI CFCC program, SiC/SiC tubes were also provided to Penn State for high temperature tube testing. Tubes in both CVI and DIMOX™ matrices were fabricated with ceramic-grade Nicalon™ fibers, and should result in similar ultimate tensile strength in durations prior to oxidation damage.

Penn State tested about 8 total tubes from CVI and DIMOX™ CFCCs. The tube rig used high temperature elastomer O-rings to seal argon gas to obtain permeability rates. For temperatures to 2000°F, the O-rings were used with Fiberfrax® insulation and high-temperature RTV, and water-cooled grips were used to hold pressure. Because all parties wanted burst pressures for CFCC tubes, the rig was modified to provide very high flow rates, over 5000 sccm (standard cubic centimeters per minute), to overcome end leakage and provide high peak pressures to burst a tube. Modifications were also made to the Penn State rig to control fragments from the tube, and minimize damage to the rig from the fragments.

The conclusion of the testing was that the DIMOX™ tubes had high permeability, and allowed argon gas leakage after about 200 psi of internal pressure. Subsequent pressurizations made the permeability worse. This was found to be a combination of gas flow through the internal pores from the DIMOX™ processing, and also later from matrix microcracking damage on repeat pressurizations.

CVI tubes in contrast had very low permeability up to about 600 psi of internal pressure. Even after high pressure testing to 1900 psi, the CVI tubes had some leakage but still at very low flow rates. This was viewed as evidence of graceful failure of the composite tubes. Three CVI tubes were burst, all at very high pressures of 2300 psi to 2600 psi.

These tests were closely monitored by FWDC, and the CVI results were of high comfort to FWDC's engineers. Most of the application work studied for CFCC materials at 2” diameter sizes were 150 psi or so. Header connections for heat exchangers were larger,
up to 6” and 8” diameter, but also at 150 psi. The permeability rates and burst pressures provide a high factor of safety to their designs, and were data that were unknown prior to CFCC.

This testing proved to be a real problem for the DIMOX™ materials to FWDC applications. HACI tried several post treatments to convert residual aluminum in the matrix to ceramic, to block microchannels, but none of the treatments were sufficient for small inert gas molecules. The process needs for CFCC tubes are in situations where cross-contamination may or may not be dangerous, but is certainly contrary to high efficiency of operation.

Fabrication work on DIMOX™ headers and some work on materials continued to be of interest to FWDC, but the primary focus for near term applications work switched to the CVI matrix materials.

3.3.2.4 Joining

Joining of CFCC materials to other materials will be necessary in many of the potential applications. To realize the potential benefit of CFCCs, the joints will have to survive at high temperatures and pressures in corrosive environments. Joints must therefore have adequate strength, temperature resistance, corrosion resistance, and impermeability.

Applications where joining will be necessary include several joints in FWDC’s design for a high temperature heat exchanger. In initial designs, tubes and headers for a ceramic heat exchanger were thought to be CFCC materials. As cost projections were made, the cost of a CFCC header seemed reasonable but the CFCC tubes were very expensive. FWDC made the design change to use monolithic tubes, such as SiC-particulate/Alumina or SiC. The design used put all the joints from the side header to process tubes inside the hot zone to minimize joint stresses, and only one or two header connections were designed to pass from the hot zone for outside connections. Therefore, the design required many high-temperature ceramic-to-ceramic joints.

Chemical bonding (as opposed to mechanical attachment) was explored to maintain corrosion resistance of the CMC materials. Mechanical attachments were designed by
FWDC for the CMC to metal joints outside the hottest process area, using expansion bellows and metallic bolts that have temperature limitations much lower than the 1100°C to 1200°C process temperature required.

Lanxide Corporation owned technology for unique low-cost preceramic polymers that sintered to make silicon carbide, silicon nitride, and aluminum nitride matrices. These easy to process chemicals became the building block for ceramic-to-ceramic joints. In addition, in the CFCC program, HACI also explored commercial ceramic bonding pastes. Brazes of high melting alloys had been tried prior to CFCC, and they produce good strong joints, but have high temperature limits in the range of 800°C to 900°C, and the FWDC design required 1100°C to 1200°C.

Prior to CFCC, HACI had determined that Ceraset™ SN preceramic polymer provides good bonding between two SiC-particulate-reinforced alumina composites produced by the DIMOX™ directed metal oxidation process. Coverage of the joint surface has exceeded 75 percent even in initial scouting experiments. After curing the polymer, the joint appears to be a combination of SiC, alumina, and possibly AlN. Initial tests of the joining techniques on particulate-reinforced alumina composites have shown that a good quality joint can be fabricated which will survive under mild thermal shock condition, such as heating and cooling in air between room temperature and 1400°C. The strength of the bond is maintained through 500 hours of exposure at 1400°C. There is a high probability of success with SiC/Alumina because the composite is chemically identical to the particulate/alumina composite.

Lap joint configuration samples were prepared using two machined stepped coupons. The specimens were about 1.9 cm long, 1.27 cm wide with 1.27 cm step section as the mating surface (0.75" long, 0.5" wide, and 0.5" long step). Once the joining studies on lap joint coupons were complete, two 1.5" to 2" diameter tubes were joined for strength testing. Bonds were fabricated using preceramic polymer, and they were tested at room temperature and at elevated temperature. In addition, the joints were also pressure tested to check the permeability of the bond. Broken tubes were analyzed to understand the nature of the failure. Preform construction was 2-D fabric reinforcement by hand layup.
Test coupons were made from both ceramic-grade Nicalon™, which FWDC favors for lower costs, and Hi-Nicalon™, which HACI favors for high-temperature strength retention after joint curing cycles. In addition, with the parallel CVI CFCC program, joining of CVI SiC/SiC composites was performed with similar methods.

Two other joining methods were evaluated via initial experiments, but, in favor of the preceramic polymer methods, they were not continued. The two other methods are preforming joining, and alumina cements.

In preform joining, two sections are preformed and interface coated. They are then mechanically joined for the DIMOX™ process. Iterations were tried with tongue-and-groove flat coupons joined after BN coating and joined after SiC coating. In both cases, the final composite had only 30% of the flex strength of a standard plate. Work on this method was not continued after the size and complexity of the FWDC components was understood.

New alumina-based cements offered by Cotronics and Aremco were evaluated. Both used sodium silicate as the bonding medium. These cements gave a good level of bonding after cure. However, the microstructural analysis of the polished samples showed poor cement coverage of the bonding surfaces.

With the lap joint coupon, Aremco cemented sample showed the calculated shear strength of 1.5 MPa (10.5 Ksi). The low shear strength is believed to be caused by poor cement coverage in the joint area, only 50% of the surface, and excessive thickness of the cement layer. The next set of tests included variables such as additives to the cement solution to improve flow and to reduce the thickness of the cement layer. Further coupons were joined with the cement solution viscosity was adjusted to improve the coverage of the composite surfaces. The two surfaces were placed in contact and held by clamps. A two-step curing cycle was employed, with the first step at 100°C (212°F) for one hour and heated at 1,100°C (2,012°F) for six hours. The joint was cut for microstructural evaluation. The polished surfaces of the joint showed more uniform coverage by the cement in the bond area. Optically, there was more cement present prior to polishing; which suggested a good chemical bonding, as there was a fair amount of
pullout during polishing. The part was also fractured at the joint area by a hammer. It took several blows to develop the break. Once again, this suggested that the bond was strong. Work on these cements was stopped after the corrosion resistance of the sodium silicate was believed to react with coal ash constituents and thought that the preceramic polymer would be more stable to different kinds of environments. In addition, initial cost modeling revealed that the cost of the raw materials for the preceramic polymer joints was much lower than the cost of the cements (both of which had similar processing requirements).

Processing experiments with Ceraset™ SN polymers were performed on flex bars with shear tests to determine joint strength. (See Table 26.) The polymer is used as an adhesive, which initially thermosets at about 200°C in air. The joined pieces are then placed in an argon or ammonia atmosphere and heated to 1200°C for conversion to a ceramic joint. Experiments were conducted to determine the optimum resin, filler, and atmosphere combinations to keep ceramic conversion high but processing temperature as low as possible to avoid damaging the Nicalon™ fibers.

<table>
<thead>
<tr>
<th>Joint Combination</th>
<th>Shear Strength</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Nicalon™/Alumina CFCC</td>
<td>19.9 Mpa average</td>
<td></td>
</tr>
<tr>
<td>Gold alloy brazes</td>
<td>As high as 26 Mpa</td>
<td>Same strength as base material, but limited to 700°C to 800°C maximum temperature.</td>
</tr>
<tr>
<td>Preform joining</td>
<td>As high as 8.5 Mpa</td>
<td>Joint not as strong as base composite.</td>
</tr>
<tr>
<td>Ceraset™ SN with boron alloy fillers</td>
<td>As high as 11.2 Mpa</td>
<td>Joint not as strong as base composite.</td>
</tr>
<tr>
<td>Ceraset™ SN with aluminum alloy fillers</td>
<td>As high as 21.8 Mpa</td>
<td>Same strength as base material, maximum temperature same as base composite.</td>
</tr>
</tbody>
</table>
3.3.3 Design of Representative Components

In the Phase I application assessment, two component geometries were thought to represent the shapes necessary to begin development and evaluation of CFCCs for the ceramic air heater for FWDC, straight tubes, and tubes with U-bends. The tubes consisted of 10-foot-long sections joined with U-bends, with all tubes passing from the air heater process module to the ambient-temperature outside header connections. This design caused each tube to incur a high stress in the transition area from hot process to ambient temperature.

The design of the air heater heat exchanger was very detailed. FWDC performed stress and vibration analysis of the heat exchanger tubing. Their conclusion was that with proper positioning of supports, the stress and vibration problems could be eliminated. They looked at continuous operation of the unit to heat air from 1400°F to 1800°F, by using tubing with 2100°F to 1800°F hot gas inside them. The heat exchanger was designed so that, through the wall, temperature gradients might only be 50°F or so. The following conclusions were reached:

1. Stresses of dead weight of the tubes themselves are about 1000 psi, which is very low.
2. Adding thermal stresses to this caused peak stresses to reach 7600 psi, which was judged to be within the design stresses allowable for SiC/Alumina.
3. Worst-case contact stresses at support positions can reach 12,100 psi, which is judge to be too high.
4. Multiple supports reduce the loads of the contact stresses. While this increases the mechanical complexity of the unit, they are feasible.

As the CFCC program progressed, a new revised design was developed by Foster Wheeler. FWDC developed a second design for a large-scale heat exchanger for a power plant having 300 million Btu/hour heat transfer rate using CFCC tubes and manifolds. The purpose was to have an alternate design, in case the L-and U-bends and supports for
long straight tube sections proved more difficult and more expensive. Cost modeling by FWDC found the cost of CFCC tubes to be very high versus cost of monolithic ceramic tubes. The new design placed the tubes solely in the hot process section, so that monolithic tubes would be used with stresses low enough for long life. The ceramic tubes in the new design were 3.8 m (12.5 ft.) long and were joined to CFCC headers. The headers were connected to refractory-lined metal manifolds by bellows to allow for thermal expansion. The CFCC headers contained a few tubes as inlets and outlets that passed through the wall of the module, which allowed the high stress of hot-to-cold transitions. The headers were defined as 4-inch- to 10-inch-diameter tubes with a means for joining tubes to them—such as holes or stub ends.

Because the SiC/Alumina did not perform well in corrosion testing, the design efforts were interrupted and slowed down. Detail designs of the header and stress levels were not released to HACI because they were not completed. A representative component header was fabricated to help illustrate and learn about design issues of tube attachment and header fabrication.

### 3.3.4 Fabrication of Representative CMC Header

HACI fabricated a representative header component in order to help assess the manufacturing feasibility. The header fabricated was 10cm ID x .85m long (4" diameter by 30" long) with a closed end. The full-size headers were nominal, 25.4-cm-ID x 1.5-m-long (10"-ID x 5-ft.-long) closed-end tubes.

An alternate “D” cross-section was proposed by HACI engineers to facilitate joining of tubes to the headers. FWDC calculations showed that the diameter of the header would have to be increased from 25 cm to 36 cm (10 inches to 14 inches). And the stress analyses predicted high bending stresses from the internal pressure. To accommodate these stresses, thickness would have to have been increased to approximately 5 cm (2 inches), which was impractical. A circular cross section was retained in the design concept.
One of the tools used by HACI was a computer-aided analysis of fabric shapes on the surface of the desired part. In this case, the 4” diameter tubes required a closed end. HACI’s preform design program was used to design ply shapes for the heat exchanger headers. A ply of fabric could be conformed to a shape, to an angle amount of skewing or rack where the tows of the fabric rest against each other. This angle of skewing can not be allowed over large surface areas, because the fabric then forms a solid barrier to gas and liquid flows for interface coating and matrix densification. A CAD file of the part shape was created in PATRAN. The CAD analysis was used to help define ply shapes for an optimum closed end tube.

Another design concept was a header module based on a cylinder, about 18 inches long by 10 inches in diameter. One end had a dome-shaped end protruding out, but the other end had the dome-shaped end turned in. The idea was based on the design for stacking of short header modules to reduce fabrication risk of long headers. In the cylinder, two tube stubs would be fabricated-in, such as 2-inch-diameter stubs extending 4 inches from the cylinder wall. Two versions were conceived: first, a stub emanating at right angles from the axis of the tube and second version, for a 2-row heat exchanger, where the stubs are parallel but join on a tangent angle. This header style was not fabricated.

The heat exchanger header tube (4” diameter by 30” long) was fabricated with simulated threads on the outer diameter at the open end. Fabric layup technique was used to form the rounded end of the header tube. Graphite tooling was fabricated to allow gas flow through the inside of the tube, which worked well. Multiple-piece tooling allowed the preform to be removed after BN without delaminations. DIMOX™ growth was performed in a special layup that suspended the tube upright, with alloy on the outside of the tube. Air was supplied to the inside of the tube for consistent matrix growth at the closed end.
The header fabrication trials demonstrated the following:

1. The large ID of the header eliminated some of the interface non-uniformity issues found with long L/D tubes.

2. The logistics of very large graphite tools and preforms require fixtures for handling, versus the many small hand-held parts that HACI normally handles.

3. Use of octagon furnaces stacked vertically provided a reasonable manufacturing arrangement for DIMOX™ growth without specialty furnaces.

3.3.5 Field Exposure Testing

In parallel with the laboratory exposure tests, Foster Wheeler tested tube samples in the combustor of the coal-fired Gallatin Station power plant. This allowed a correlation between field and laboratory testing because the coal types in all tests were known and recorded by FWDC.

A favorite test site for FWDC is the TVA’s (Tennessee Valley Authority) Gallatin Station power plant in Gallatin Station, TN. The testing was performed with the permission of the TVA facilities management, at their request but without their involvement. FWDC was allowed to perform the exposure tests they wanted, using through-wall probes into the process. However, this did not provide an opportunity for HACI to discuss the test results or to learn about materials issues with this power plant operator. FWDC was unwilling to push this arrangement. They realized that the ability to perform materials testing might be different if the testing became recognized as a TVA program or if TVA operators had to seek permission to conduct materials testing.

In-service tests were performed by placing representative CFCC component probes in operating coal-fired plants for long periods. Foster Wheeler has developed an air-cooled retractable corrosion probe assembly for field exposures of metallic components. These probes have been installed in three different utility stations and have been used to study exposures up to two years in duration. These probes are remotely monitored for temperature, position, and status by FWDC, and they are independent of the boiler
operation. The probe and material sample can be removed and examined at any time while the power plant is in operation. This type of field test provides very credible data to FWDC. The use of probes to hold tubular test coupons is FWDC’s design, and they have significant experience in this testing for new metal alloys.

In the application of this test to CFCCs, the probe location was changed to expose the tubes to hotter temperatures. The risk of this test was that the combustion zone of older power plants does not have uniform temperatures, and the locations available for a probe may not have had uniform air flow velocities. These non-uniformities simulated real-life exposure.

Another difficult factor to determine was ash build-up on the samples. In the case of the actual heat exchangers in the power plant, the unit was equipped with soot blowers, which are devices that blow a directed jet of air onto the metal heat exchanger tubes, to blow off ash accumulation. The ash is not desired as a surface layer on the heat exchanger tube because the ash layer promotes corrosion of the metals, and reduces the total heat transferred from the combustion hot air, to the working fluid in the heat exchanger. Wall probes used in this test were located where soot blowers would blow onto the CFCCs, but we found their effectiveness to be directional. Upon analysis of the tube samples, one wall surface facing the soot blower would be relatively clean, but the backside of the tube had thick ash cake layers.

The test was arranged so that each probe held four short CFCC tubes, each 5 cm x 7.62 cm long (2 inches ID x 3 inches long). Temperatures were nominally 2000°F to 2200°F, and the flue gases contained fly ash particulate. One set of samples was removed and destructively evaluated after 4000 hours. The other was removed and destructively evaluated after 8000 hours. Visual observations were made at 2000, 4000, 6000, and 8000 hours.

A tubular probe with thermocouples was installed to monitor temperatures of the coal combustion gases at a new location for FWDC. The probe also allowed them to obtain a pre-test sample of physical nature of the coal ash. The temperature at this boiler location
was expected to be in the range of 1,200°C (2,200°F). However, the temperature rose as high as 1,315°C (2,400°F), and thermocouples failed.

This unexpected temperature was due to the installation of a new, low-NOx coal firing system. The probe was relocated to expose the tube sections in the cooler (i.e., 800°C [1,500°F]), part of the boiler. The temperature information was transmitted to FWDC computers in Livingston, NJ, via a data acquisition system. Graphs of actual temperatures showed the temperature range in a given month to be from 675°C to 955°C (1250°F to 1750°F).

Some test rings were surface coated to enhance long-term durability. The surface coatings for the DMO tubes came from methods developed and used in particulate-reinforced SiC/Alumina heat exchanger tube development. Various wash coatings were applied and designed to react with residual aluminum metal within the alumina matrix. Heat-treating resulted in a hard, thick, alumina coating that provided resistance to further aluminum bleed-out, and it protected the BN interface coatings from chemical attack and oxidation. Table 27 describes the three different types of heat treatment used for the protective coating.

<table>
<thead>
<tr>
<th>March 1996 Gallatin Station Exposure Samples</th>
<th>Nicalon™-fiber-reinforced Alumina CFCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube Tracking Number</td>
<td>Surface coating</td>
</tr>
<tr>
<td>4462-01-001-1T</td>
<td>1100°C for 6 hours</td>
</tr>
<tr>
<td>4462-01-001-1M</td>
<td>1100°C for 6 hours</td>
</tr>
<tr>
<td>4462-01-001-1B</td>
<td>1100°C for 6 hours, ramp to 1325°C for 1 hour</td>
</tr>
<tr>
<td>4462-01-003-3T</td>
<td>1100°C for 6 hours, ramp to 1325°C for 1 hour</td>
</tr>
<tr>
<td>4462-01-003-3B</td>
<td>1200°C for 31 hours</td>
</tr>
<tr>
<td>4462-01-004-4T</td>
<td>1200°C for 31 hours</td>
</tr>
</tbody>
</table>
Figure 19 depicts the results of the C-ring strengths of specimens exposed in the TVA boiler for 4000 hours (coal ash, temperature from RT to 1850 F). One set of as-fabricated tube data is shown for comparison to the 4000 hour exposed tubes. The unexposed tube (4462-01-004) also had an alumina external coating applied to it.

The effects of TVA exposure are interesting. Two sets of specimens had significantly lower strength than the control, and one set (001-1T) had much less reduction in strength. Macroscopically (10X), all of the fracture surfaces of exposed surfaces look rather brittle.

Figure 19. C-ring strength of Nicalon™/Alumina exposed for 4000 hours in the TVA boiler. Data for an unexposed control is shown at the top.

The exposed samples were observed for any changes, weight loss was noted, and some residual mechanical properties were established. This data was one of the several bases in establishing material suitability for the application.

The strength loss after only 4000 hours was disappointing to FWDC, combined with the fracture results showing brittle failure. With the parallel CFCC CVI program, tubes of SiC/SiC composites, also with ceramic-grade Nicalon™ fibers showed much less
strength degradation. This field data confirmed the laboratory exposure data; the alumina matrix is not protective for the long durations required in FWDC's applications.

### 3.3.6 ASME Code Acceptance

In their Phase I commercialization plan, Foster Wheeler expressed the desire to obtain ASME code acceptance for CFCC materials. The ASME code is used here as an abbreviation for the *American Society of Mechanical Engineers Boiler and Pressure Vessel Code*—specifically, section VIII for un-fired vessels such as heat exchangers. If CFCC materials are to be used in pressure-vessel applications, the American Society of Mechanical Engineers (ASME) codes and standards for design and construction of pressure components must be established for CFCC materials. No codes for CFCCs exist today. The ASME Boiler and Pressure Vessel Code Section VIII committee will have to approve CFCC components use in heat exchanger and steam reformer applications prior to full commercial introduction across the US.

For Foster Wheeler, this part of their plan was a routine part of new materials acceptance into the heat exchanger and power plant industry. As a critical-path item for CFCC materials acceptance, the code efforts could be obviated, at least temporarily, by enclosing the heat exchanger or reformer tubes in a code-accepted internally insulated metallic vessel. Foster Wheeler engineers also believed the code activities were important to widespread industry acceptance of CFCC materials because of the standard tests and database that could come from the activities. They believed many small users would not have the patience for long design and experimentation but would try CMCs once the procedures and data were in the ASME code. Lastly, Foster Wheeler engineers hoped that the code meetings and activities would provide positive publicity for the use of ceramic composites, to attract others' interest.

Foster Wheeler engineer Dr. T.V. Narayanan took the lead to initiate the development of ASME code acceptance of CFCC materials in the appropriate ASME committees. Foster Wheeler, HACI, and others attended these ASME committee meetings, determined ASME requirements, and gathered data from various sources to satisfy committee requirements.
This activity was led by Foster Wheeler jointly under the CFCC DIMOX™ and CVI Material CFCC programs. The HACI CVI Program had the lead responsibility and lead funding for this subtask. Only the incremental work on ASME code acceptance for DMO CFCC material was included in this DMO Program subtask.

The process used to develop a case for ASME code to include ceramic composite materials was to first solicit standing members for the ASME committee. That committee drew upon any interested individual to write a specific section of the code, for which they had knowledge and interest. As a draft, the committee used two other works, one of which was a preliminary draft of the ceramic code. This draft was based on ASME Boiler and Pressure Vessel Code Section X. The second source was code cases from individual states within the US, presented by manufacturers of monolithic graphite for heat exchangers. From these draft documents, sections specific to CMCs were added. Meetings were held at CFCC working group sessions, ASME annual working meetings, Cocoa Beach Ceramic Conferences, and specially convened ASME meetings.

Typical issues reviewed were the database and the overall scope of the codes for CMCs. At one meeting, several people from a company that manufactures and commercially sells graphite-based heat exchangers also attended. Their success in satisfying code needs for some of the individual states within the US would be an excellent guidance in setting CFCC-based components acceptance by the users. One example from the graphite users is ASME proposed code case, RP 77-780. All of them showed keen interest in developing design and material codes for ceramic composites. Mr. Jerry Sandifier of Babcock & Wilcox emphasized the need to identify the issues confronting designers and their vision of where the use of these materials will be in the short-, medium- and long-term exposures. The design group highlighted the need for the understanding of material failure modes so acceptance criteria can be established pursuant to standards development. Specifically, this includes distinguishing CFCCs from monolithic ceramic material systems in terms of significant higher toughness with fiber-reinforced ceramic composite systems.
Testing and design requirements for pressure vessel materials include the following:

1. Definitions of design stress and allowable stress, supported by testing.

2. Designs will use a factor of safety of 5, so that ultimate stress from testing is 5 times the maximum allowable stress value in the component design.

3. To accommodate for material variations and factor of safety, the code rules for graphite are planned to eliminate higher stress vessels even if they use high strength graphite—by stating that maximum design allowable is limited to a value, in their case, 1000 psi, even for 13,000-psi-strength graphite.

4. Design and testing are related; for most components, a hydrostatic test of 1.5 times operational values is required. For CMCs, a concern is that the test maximum stress should be below the proportional limit, to avoid damaging the vessel in testing. The required material ultimate strength would guide the design.

5. It also seems that more testing in the area of strain history beyond yield will be necessary. This should also be an area where CFCCs will shine in providing excellent factors of safety. The strains at 33 MPa are so small that they should provide many times more strain capability than allowable.

6. The sonic modulus methods can be effectively used for NDE in the field and for complex shapes. While not well quantified, it is known that SiCf/Alumina has a modulus relaxation after high stresses and cyclic stresses. One turbine engine company has used sonic modulus, and sonic natural frequencies of the parts, to detect a shift in modulus caused by damage, from overstress. Thus, some inspection methods can be identified, but more data will need to be gathered from the material to quantify a generic modulus affects.

The efforts on the ASME Code are continuing with the CFCC CVI materials program. Hard copies of the ASME code for CFCCs are available from HACI or FWDC; electronic copies are not available.
3.3.7 Thin Sheet Applications Work with Foster Wheeler

Test parts for industrial alkali environments were considered with Foster Wheeler Development Corporation. Tube shields are an interesting application development because they represent an immediate sheet metal replacement opportunity for CFCCs. In the application, shields are used to protect heat exchanger tubes and process piping from erosion and further corrosion in particulate laden gas streams. Large manifolds of piping sit in the hot combustion gas streams, but only the first row or two of tubes that are hit with particulates from the combustion process need shields.

Current shields cover tubing from 1 1/2-inch diameter to 4-inch diameter, and they are fabricated in lengths up to 8 feet long. They are currently materials such as Inconel, and they cover 180 degrees to 210 degrees of the tube diameter. They can be bent slightly to fit over the tube, and area welded in place with back straps. The current tube shields have only the same corrosion resistance as the primary tubes, and, because of welding, they require a shutdown and sometimes scaffolding to install.

Currently, shields are only installed after the primary tubes show erosion and corrosion damage ahead of planned replacement times. The strategy for use of thin sheet ceramics is to provide a tube shield that has greater corrosion resistance than the base metal tube, and it therefore lasts longer in service. Ceramic tube shields offer the potential to be designed and built into the manifold of piping at the original installation, if their life can be predicted to be as long as the process piping.

Laboratory testing of particulate-reinforced thin sheet materials was performed while materials processing of fiber-reinforced thin sheet progressed in parallel. Testing demonstrated encouraging erosion performance to the application temperature of 1800°F. Testing also included laminated plates up to 9 layers, to obtain erosion results on thick samples. Laminations did not seem to affect erosion results versus the base material. Table 28 provides details of this testing.
Table 28. Details of laboratory testing of particulate-reinforced thin sheet materials

<table>
<thead>
<tr>
<th>Date</th>
<th>Materials Sent</th>
<th>Lab performing Testing</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct 1996</td>
<td>Bars for testing</td>
<td>ORNL</td>
<td>• Flex strength data at 32 to 44 Mpa.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Room temperature to 1100°C shows little strength reduction.</td>
</tr>
<tr>
<td>Nov 1997</td>
<td>20 bars for Municipal Solid Waste ash corrosion testing</td>
<td>FWDC</td>
<td>Joined laminates show joint material has same corrosion resistance as base material.</td>
</tr>
<tr>
<td>Nov 1997</td>
<td>20 bars for flue gas corrosion testing</td>
<td>FWDC</td>
<td>Heat treatments to 100 hours at 1200°C show little degradation.</td>
</tr>
<tr>
<td>Nov 1997</td>
<td>80 bars for high temperature exposure and SEM study</td>
<td>ORNL</td>
<td>Erosion performance is good at 1800°F.</td>
</tr>
<tr>
<td>Oct 1997</td>
<td>2-ply to 5-ply laminates for disc erosion testing</td>
<td>FWDC</td>
<td></td>
</tr>
</tbody>
</table>
Table 29 describes how all the thin-sheet-material characteristics compared to CFCCs and monolithic ceramics.

Table 29. Comparison of material properties for CFCCs and thin sheets

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Fiber-Reinforced CFCCs</th>
<th>Monolithic Ceramics</th>
<th>Fiber-reinforced Thin Sheet Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>Very High</td>
<td>High</td>
<td>Low processing cost</td>
</tr>
<tr>
<td>Shape Making</td>
<td>Thin shell type structures</td>
<td>Moldable shapes</td>
<td>Shell, Sheet, Corrugated structures including some formability such as “Origami” shapes</td>
</tr>
<tr>
<td>Temperature Ranges</td>
<td>To fiber stability temperature, 1100°C to 1300°C</td>
<td>Very High, to 1600°C.</td>
<td>1200°C stability for 100 hours verified.</td>
</tr>
<tr>
<td>Strength and Characteristics</td>
<td>10 to 30 Ksi, graceful failure</td>
<td>20 to 60 Ksi, brittle</td>
<td>3-to 8-Ksi, tears, but some brittle.</td>
</tr>
<tr>
<td>Fabrication and Manufacturing</td>
<td>Parts made one at a time with individual tooling.</td>
<td>Semi-continuous process with lots of shrinkage.</td>
<td>Low cost, high volume sheet structures, less than 1% shrinkage.</td>
</tr>
</tbody>
</table>

3.3.8 Conclusion and Path Forward

CFCC began with the DIMOX™ materials holding a high interest because it was believed that the oxide matrix would hold up superior to carbide matrix materials. FWDC and HAC1 each had experience with monolithic alumina- or particulate-reinforced alumina materials that demonstrated good corrosion resistance. For highly stressed and pressurized components, the use of fiber reinforcement was necessary.

Overall, they found SiC/Alumina not to be the best CMC for their use because SiC/SiC composites seem to naturally resist the alkaline environments of their industrial applications. In the SiC CVI CFCC program, the program with FWDC will continue. After the CFCC program, we expect commercial programs with FWDC to continue, as
long as HACI has the means to cost-subsidize the fabrication cost of parts in exchange for the test time in the field.

The results of the testing show that the DIMOX™ materials do not hold up consistently to coal ash atmospheres. Specifically, the matrix microcracks provided ingress for alkaline elements to attack the BN interface, which causes strength loss and brittle behavior over time. In addition, the material advancements sought by other CFCC partners, such as use of Hi-Nicalon™ fibers, was a negative factor to FWDC due the increased cost of the composite. External coatings provided some benefit to seal microcracks, but, at the end, SiC/SiC composites sealed with CVI SiC provided better strength over long periods than DIMOX™ composites provided. There are no short-term uses of composites in FWDC’s application areas, and materials must have 8,000 hours of utility for commercial consideration.

For any CFCC materials, plans must include considerations for testing of header modules. Hydrostatic testing with low-pressure water was considered the safest test, to be followed by high pressure testing at Foster Wheeler. High pressure testing would need to be conducted inside special rooms that can contain fragments in the event of a failure. Such explosion barricades exist at the DuPont Experimental Station, Wilmington, Delaware, and at different Foster Wheeler sites.
3.4 Materials and Applications for GEPG

3.4.1 Application Interest

In CFCC Phase I, GE performed an extensive study on the use of ceramic composites in industrial turbo machinery, which may provide substantial payoff for components such as first-stage turbine rotor buckets (aka “rotor blades”) and shrouds (aka “tip shrouds”). These components would be GE’s first choice for application of CFCCs. Due to very high stresses in the turbine rotor buckets, the shroud presents a more realistic first CFCC candidate component.

The first stage shroud is a stationary component that defines the airflow stream from the exit of the combustor, the outside diameter of the first stage rotor, and transition into the second stage of the engine. The shroud sees very high temperatures and thermal stresses, and in metal it requires cooling air on the backside and at all edges.

Reduction or elimination of cooling air, using CFCCs, provides fuel savings for the engine (either fuel savings at constant power output or more power output for constant fuel usage). Emissions reduction represents another benefit. This reduction results from the reduction in film cooling and from the gradients caused by film cooling that are known to create CO formation and unburned hydrocarbons.

GEPG formulated a plan for design review of a CFCC shroud, database extensions, and shroud testing in a small combustion rig. Because the end-use application is for very large power generation turbine engines, no test engine exists. Database and application-specific testing were shared by GEPG and HACI.

The shroud test rig was built using an existing combustion rig in Schenectady, New York. The rig was used in multiple tests to simulate different engine conditions. The most severe tests were turbine trips, in which fuel is shut off from a full-load operating situation. This creates a very rapid thermal down-shock. Other tests for thermal cycling and short duration hot operation were planned.
GE’s plan to start testing with the most severe test seem partly unfair to the developmental needs of the CFCC companies who desired many rounds of incremental testing (i.e., progressing from the least severe test to the most severe test). This incremental test approach also allows for incremental materials, processing, and fabrication improvements. However, GE’s management did not share the desire for incremental testing; they preferred to quickly understand how close to commercialization the CFCC materials might be.

CFCC shrouds were also provided for rig testing from HACI’s CVI Materials CFCC Program and GE CR&D’s MI Materials CFCC Program. While the SiC/Alumina shrouds were not selected as the best material for this application, the very positive results of the shroud testing on CFCC has lead to continued efforts on the other CFCC Programs and on private GE funding.

From the Phase I CFCC component analysis, GE expressed an interest in combustors for uncooled low-emissions operation. These parts are secondary to shrouds in economic payoff in GE’s large power generation engines. However, shapes of combustors, economical fabrication methods, and cost modeling were discussed. Fabrication work on combustors was not pursued on this program, but because of positive benefits from the CFCC Program, work also continued on other government programs and on private GE funding.

3.4.2 Database

The early discussions with GE illustrated a serious plan to develop a database and understanding of CFCC materials. HACI was more anxious for component fabrication and rig testing, but GE insisted on the database and testing route. Now, many years after the original Statement of Work was prepared, GE continues to drive commercialization of a ceramic composite shroud, based on the solid knowledge gained from the CFCC programs.

In Phase I, GE and HACI worked together to create an extensive chart of SiC/Alumina material properties (see Table 30). That chart was updated in Phase II with additional
data. To aid designers in understanding the tradeoffs in material properties, a right column was added that suggested means by which HACI could improve material properties. Some of these were explored in general material tasks, and the only real modification in materials for GE shrouds was the use of Hi-Nicalon™ fibers over ceramic-grade Nicalon™, even after some data points were obtained in ceramic-grade reinforced materials.

Additional data was desired by GE designers, in the properties of creep. To help establish stress ranges for creep tests, a few new stress rupture tests were performed by HACI.

Stress rupture tests were performed by HACI. One 2-D Nicalon™/Alumina composite specimen at 1200°C in air under a constant tensile stress of 70 MPa completed over 5500 hours of exposure without failure. An additional tensile stress rupture test was conducted to evaluate composite intermediate temperature behavior. A tensile stress of 83 MPa was applied to a Nicalon™/Alumina composite at 600°C in air. The test was stopped after the specimen completed 1500 hours at temperature without failure.

Creep testing was performed by University of Dayton Research Institute (UDRI). They tested DIMOX™ and CVI matrix materials. Tests were designed to be similar in specimen geometry and test method to ORNL high-temperature creep tests, so that data could be readily compared. The following test data was requested:

- 35-140 MPa (5-20 Ksi)
- Temperatures—1000°C and 1100°C (1832°F and 2010°F)
- Desired test points—50, 100, 1,000, 5,000 and 8,000 hours
**Table 30. SiC/Alumina material properties for GE's shroud design**

<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature</th>
<th>Model</th>
<th>Recommended</th>
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<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>1000°F</td>
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<td></td>
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<td></td>
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<td>54</td>
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<td>2</td>
<td>54</td>
</tr>
<tr>
<td>K33 (BTU/in/hr/°F)</td>
<td>61</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>CP (Btu/lb-m)</td>
<td>0.17</td>
<td>3</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Creep (2% @ 2200°F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Creep</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCF (ksi, A=1,10^7 cycles)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fatigue</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermal shock</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTES**
- Data for 2D plain-woven Nicalon/A2O3 preform. Vf=0.36, Vv=0.00
- DuPont Lamixide SC/A2O3

*Source of datum
- No data available
1 Micromechanical estimates
2 Engineering estimates
3 Test data
Creep simulates the movement of components during long-term service under mechanical loads and is a prime mode of super-alloy failure in gas turbine engines. Creep failure normally occurs because component deformation disrupts seals or opens up clearances. Creep was simulated by isothermal tensile testing at several elevated temperatures using a fixed stress level. Several samples of each material was exposed and tested.

Figure 20 and Figure 21 depict the creep data conducted on our CG Nicalon™ materials. To generate the plots shown, some manipulation of the data received from UDRI was necessary. An explanation of this manipulation is necessary. UDRI’s current creep testing systems measures the creep strain exhibited by a specimen subsequent to its loading to the test stress level. In other words, their system measures incremental creep strain. To convert this measurement to total creep strain, the strain exhibited by the specimen during the initial loading to the test stress level must be determined. While the actual value is not attainable, there was a group of high-temperature (1100°C) fast fracture tests done on each batch of material prior to shipping the specimens to UDRI (6 specimens of S/E-S and 4 specimens of DIMOX™). From these tests, an average stress-strain curve was computed for each material system. Using these average curves, a good estimate of the strain exhibited by a specimen of each material during the initial loading was determined and added to the incremental values measured by UDRI. The actual values added to each specimen are shown in Table 31.

This data represents the first time that HACI had created fan-fold-type creep data for ceramic materials. These types of charts are widely used with metals, and they have high value and create a sense of predictability and confidence with mechanical designers.
Table 31. Creep data obtained for Nicalon™/Alumina materials from testing at University of Dayton Research Institute (UDRI)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>982</td>
<td></td>
<td>DIMOX™</td>
<td>5.0</td>
<td>0.07779</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td></td>
<td>34.0</td>
<td>0.06745</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>DIMOX™</td>
<td></td>
<td></td>
<td>0.06298</td>
<td>119 Survived 2185.0 hrs</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td>Stopped</td>
<td></td>
<td>0.05814</td>
<td>118 Survived 1028.0 hrs</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td>0.04814</td>
<td>137 Survived 1490.0 hrs</td>
</tr>
</tbody>
</table>

903

|            |                   | DIMOX™          | 2.3                   | 0.06745                   |                        |                                 |
|            | 90                |                 |                       |                           |                        |                                 |
|            | 85                |                 | 16.5                  | 0.06298                   |                        |                                 |
|            | 80                | DIMOX™          | 320.0                 | 0.05814                   |                        |                                 |
|            | 75                |                 | Stopped               |                            | 0.05298                | 131 Survived 1250.2 hrs        |
|            | 70                |                 |                       |                            | 0.04814                | 119 Survived 1010.0 hrs        |
Creep Testing Results for CG Nicalon/Alumina at 982°C (1800°F) in Air.

The reverse strain was the result of specimen rotation during fracture.

Figure 20. Creep testing results for ceramic-grade Nicalon™/Alumina.
Figure 21. Creep curves generated for Ceramic-Grade Nicalon\textsuperscript{TM}/Alumina CFCC at 982°C and 1093°C.
3.4.3 Application-Specific Tests at GEPS

Long-term service life in a power generation gas turbine requires predictable material systems performance in high-temperature oxidizing environments. GE and HACI performed tests to establish thermal shock, thermal cycling, creep, and other long lifetime capability of the material. The test conditions were established to provide data that would let them predict the performance of turbine engine components. This was successfully performed by focusing on one shroud application for one set of engine conditions, and then using a battery of tests to look at the various thermal shocks and cycling behavior that occur as the engine starts up, runs for long duration, and shuts down. The following tests were recommended to help evaluate CFCC materials for this specific gas turbine application:

- Thermal fatigue—using a JETS (Jet Engine Thermal Shock) tester
- Thermal gradient—using several severe thermal gradients without cycling
- Low-cycle fatigue—at room temperature and high temperature
- High-cycle fatigue—at room temperature and high temperature
- Steam oxidation testing—15% steam at 150 psi at 1200°C

Table 32 outlines the GEPS test plan.

HACI fabricated over 85 machined test specimens of Nicalon™/Alumina as needed for the tests. Most tests used CFCC tensile specimens cut from flat plates, exposed as the test performs, and followed up with testing for retained tensile strength.
<table>
<thead>
<tr>
<th>Test Type</th>
<th>Test Site or Vendor</th>
<th>Number of Specimens</th>
<th>Temperatures</th>
<th>Test Conditions</th>
<th>Specimen Geometry</th>
<th>Residual Tensile Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Fatigue</td>
<td>Materials Characterization Laboratory—Scotia, NY</td>
<td>16</td>
<td>2100°F Hot Gas</td>
<td>500, 1000, 1500, &amp; 2000 cycles</td>
<td>2.0” dia.</td>
<td>Yes**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 sec. Cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Gradient</td>
<td>Materials Characterization Laboratory—Scotia, NY</td>
<td>10</td>
<td>2100°F Hot Gas</td>
<td>0, 100, 500, 1000, &amp; 1500 cycles</td>
<td>2.0” dia.</td>
<td>Yes**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>800°F Cold Gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Cycle Fatigue</td>
<td>Composites Testing &amp; Analysis—Ann Arbor, MI</td>
<td>24</td>
<td>1832 &amp; 2012°F</td>
<td>20 cycles/min @</td>
<td>UMTensile</td>
<td>Yes*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A ratio =.25 &amp; 1(r=.6 &amp; .05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60-300, 1000, 10,000, 100,000, &amp; 1,000,000 cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Cycle Fatigue</td>
<td>Composites Testing &amp; Analysis—Ann Arbor, MI</td>
<td>24</td>
<td>1832 &amp; 2012°F</td>
<td>180 cycles/min. @</td>
<td>UMTensile</td>
<td>Yes*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>A ratio =.25 &amp; 1(r=.6 &amp; .05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60-300, 1000, 10,000, 100,000, &amp; 1,000,000 cycles</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4.3.1 Thermal fatigue testing
Thermal fatigue testing simulates the effect of multiple exposures of a thermal gradient across or along a component. Thermal fatigue testing was conducted via a JETS (Jet Engine Thermal Shock) tester. The sample is exposed to a flame, such as oxy-acetylene, from a nozzle for a specified number of seconds. The exposure produces a specific surface temperature on one face while the other face is either cooled by an air stream or left exposed to ambient air. It is possible to obtain about 1000 exposure cycles in five days. A comparable number of cycles to the exposure expected for the metal we expect to replace in the shroud will be performed and the residual tensile strength of the CFCC measured. Fifteen samples of each material were exposed and tested.

3.4.3.2 Thermal gradient testing
Thermal gradient testing simulates the influence of severe thermal gradients on properties. This is a key test for CFCCs since thermal stress levels exceed mechanical stresses in many high-temperature applications where CFCCs are currently considered as candidate materials. This test will be performed by exposing samples to several gradients without cycling. Ten samples of each material will be exposed and tested. Neither the thermal fatigue nor thermal gradient testing caused a SiC/Alumina coupon to crack. The results of the tests allowed exact calibration of material emissivity, which the engine designers need; but overall were rather un-dramatic. The reason for the material to survive this testing, but crack in the engine test rig is probably due to the small sample size in this test, and constrained attachments in the test rig. Results of the testing are discussed in detail in a Materials Characterization Laboratory report. 8

3.4.3.3 Fatigue testing
Low-cycle fatigue testing simulates service from start-up to operating temperature and then back to room temperature at shut down. To understand the fatigue behavior over a range of temperatures, fatigue testing was performed at constant temperature using room temperature for a baseline and then several elevated temperatures to simulate the gas turbine environment. The gripping system was critical and was carefully designed to
allow the sample to be cycled from tension to compression without buckling. Twenty samples were tested. The testing showed that SiC/Alumina has very little temperature dependency for fatigue strength, in that lowering the temperature produces the same run-out stress as higher temperatures. The Hi-Nicalon™ fiber provides 200°F improved durability.

High-cycle fatigue testing simulates the vibratory influences at long service times while at elevated temperature. The simulation is performed by stressing the sample, and then cycling the stress about this average stress level. Isothermal fatigue testing was performed at room temperature and at several elevated temperatures. Twenty samples were tested. The SiC/Alumina composites perform well in fatigue at 30 Hertz, with 10 million cycles without failure. The ceramic-grade Nicalon™ reinforced composites run-out at 10 Ksi at 2000°F, while the change to Hi-Nicalon™ fiber provides the same performance but at 2200°F. For higher stress operation, at 15 Ksi, the temperatures need to be lower by 200°F for each fiber.

Details of the fatigue test plan are provided in Table 33. Results of the fatigue testing are discussed in detail in a final report by Composite Testing & Analysis (Ann Arbor, Michigan).
Table 33. SiC/Alumina fatigue test plan at Composite Testing & Analysis

<table>
<thead>
<tr>
<th>High Cycle Fatigue Testing</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard Ceramic Grade Nicalon</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Material System</strong></td>
<td><strong># of Specimens</strong></td>
</tr>
<tr>
<td>SiC/C2A2O3</td>
<td>5</td>
</tr>
<tr>
<td>SiC/C2A2O3</td>
<td>5</td>
</tr>
<tr>
<td>E-SiC/SiC</td>
<td>5</td>
</tr>
<tr>
<td>E-SiC/SiC</td>
<td>5</td>
</tr>
</tbody>
</table>

| **Hi-Nicalon** |  |
| **Material System** | **# of Specimens** | **Test Temperature** | **Test Conditions** | **Planned # of Cycles** |
| 200°F(982°C) | 5 | 180 CPM | r = 6 | 30-300,1k,10k,100k,1,000k |
| 220°F(1204°C) | 5 | 180 CPM | r = 6 | 30-300,1k,10k,100k,1,000k |
| 200°F(1093°C) | 5 | 180 CPM | r = 6 | 30-300,1k,10k,100k,1,000k |
| 220°F(1204°C) | 5 | 180 CPM | r = 6 | 30-300,1k,10k,100k,1,000k |

Notes: May adjust 180 CPM to 500 CPM to maximize the highest frequency. John Holmes can record strain rate at 1100°C with Edge Loaded Specimens and existing extensometers.

<table>
<thead>
<tr>
<th>Low Cycle Fatigue Testing</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hi-Nicalon</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Material System</strong></td>
<td><strong># of Specimens</strong></td>
</tr>
<tr>
<td>SiC/C2A2O3</td>
<td>5</td>
</tr>
<tr>
<td>SiC/C2A2O3</td>
<td>5</td>
</tr>
<tr>
<td>E-SiC/SiC</td>
<td>5</td>
</tr>
<tr>
<td>E-SiC/SiC</td>
<td>5</td>
</tr>
</tbody>
</table>

Notes: There will be no Low Cycle Fatigue Testing performed on Standard Ceramic Grade Specimens.

3.4.3.4 Steam oxidation testing

Steam oxidation testing (see Figure 22) was added late in CFCC for combustion atmosphere testing. GE built a tube furnace test rig to test tensile bars, to similar exposure conditions that ORNL’s furnace tests flex bar coupons. The test addressed the long-term service life of CFCCs in a power generation gas turbine in high-temperature oxidizing environments. This category of data represented the most significant set of new data points that was required. Unfortunately, SiC/Alumina did not do well in this test. The steam is able to penetrate the matrix via microcracks, and oxidize the BN interface. The resulting reaction creates a tight bond of fiber through interface to matrix, resulting in a brittle material.
Figure 22. Results of steam-oxidation testing at GE.

Conclusions on the testing and the affect on GE's design are discussed in detail in a report by GE's Materials and Processes Group.  

---

10
3.4.4 Design, Fabrication and Testing of Shrouds

The original CFCC shroud design was a duplication of the metal shroud. It is a slightly curved box with four sides, like a soap dish. This shape allows sealing edges up and away from the immediate hot gas flow, and provided stiffness for the metal alloys when hot. The original CFCC design was also considered for fabrication with GE’s in-house tape laydown process, not 2-D fabric reinforcement. Because of the very high thermal conductivities of cast super alloys, this design works, and the raised edges served to provide stiffness and mating edges from shroud to shroud.

HACI evaluated the design and sought changes from the four walls of the existing GEPS-cast, super alloy metal turbine shroud. With cuts and seams at every corner in a CFCC material, the four raised edges immediately cause a fabrication concern—for the bending and formation of fabric layers. It would also have high stress levels as the corners and walls would be different temperatures than the base shroud. In meeting with GE design engineers, a shroud was agreed upon, which had only two walls on opposite sides. Further design studies looked at means of attachment, and the large radius bend for the sides was created. Shroud design and representative shroud components were also fabricated. (See Figure 23.)

Other design details, important later to an engine designer, were not dealt with at this early test stage. Some of those issues are surface finish, geometric tolerances beyond basic dimensions, and air seals part to part and shroud to engine. Also, an extensive design optimization was not made, but later would include minor changes in the design, such as changes in wall thickness, fillet radii, hole geometries, attachment points, and tolerances.
The shrouds were preformed by hand layup and compressed to dimension and proper fiber volume fraction in a multi-piece aluminum tool. Two graphite tools were fabricated to process the shrouds through BN. New with this program was a definition of common manufacturing batch. For traceability, all cycles and all parts were recorded individually, but parts were considered to be in a manufacturing batch by SiC cycle. Parts from several preforming times and several BN cycles were the processed together in a SiC cycle. From that point on, this group of parts was considered the same lot of parts. In further fabrication steps, the intention was that the parts stay together. For example, parts from several DIMOX™ growth layups were used, but these parts were run in the same furnace batch.
Table 34 briefly lists fabrication data for shrouds. They were processed in 2 different SiC cycles, each with 4 preforms. In this case, the first batch of shrouds received a SiC coating of 90% to 110% weight gain, which is higher than specification. An adjustment was made, and the second batch of shrouds received 60% to 70% weight gain, which was preferred.

The shrouds were fabricated over size, to provide cut off stock on the edges for tensile bars. Also, some of the shrouds with high SiC deposition were cut up immediately for as-fabricated properties.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Part Number</th>
<th>Material System</th>
<th>Comments</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4470-01-001</td>
<td></td>
<td>90% SiC gain</td>
<td>Shipped to GE</td>
</tr>
<tr>
<td></td>
<td>4470-01-002</td>
<td></td>
<td>100% SiC gain</td>
<td>Retained at HACI for properties.</td>
</tr>
<tr>
<td></td>
<td>4470-01-003</td>
<td>HiNicalon™/BN/SiC/Alumina</td>
<td>105% SiC gain</td>
<td>Retained at HACI for show.</td>
</tr>
<tr>
<td></td>
<td>4470-01-004</td>
<td></td>
<td>110% SiC gain</td>
<td>Retained at HACI for show.</td>
</tr>
<tr>
<td></td>
<td>4470-01-005</td>
<td></td>
<td>65% SiC gain</td>
<td>Shipped to GE</td>
</tr>
<tr>
<td></td>
<td>4470-01-006</td>
<td></td>
<td>62% SiC gain</td>
<td>Shipped to GE</td>
</tr>
<tr>
<td></td>
<td>4470-01-007</td>
<td></td>
<td>70% SiC gain</td>
<td>Shipped to GE</td>
</tr>
<tr>
<td></td>
<td>4470-01-008</td>
<td></td>
<td>68% SiC gain</td>
<td>Shipped to GE</td>
</tr>
</tbody>
</table>

Table 34. Batch data for Hi-Nicalon™ SiC/Alumina CFCC shrouds
These representative shrouds were tested in GE's test rig. Shrouds were tested under simulated engine operating conditions, including the temperature gradients expected across the thickness of the components during their service. Testing included the following components:

1. Cyclic fatigue test to evaluate the high-cycle fatigue stress in the shroud.
2. Actual attachment methods, for a static load test to estimate whether the CFCC shroud has the structural integrity to withstand the pressure load induced by the cooling air.
3. Rig test operation for approximately 200 hours to evaluate shroud performance in simulated gas turbine conditions. The test objectives included low-cycle type engine cycling, cooling flow variation, and simulated turbine trips.

After testing, shrouds were cut up into tensile bars to obtain retained properties, and as-fabricated comparison. (See Figure 24.) The SiC/Alumina shrouds survived, but they cracked and lost modulus in thermal cycling.

### 3.4.5 Test Results and Conclusions

The result of this effort was that shrouds were successfully designed, fabricated, and tested in the GE shroud test rig. Material properties and testing from coupons were found to be appropriate for the component design. Component design was changed from the metal component in a way that the engine designer agreed.

In the most severe testing of thermal shock, the SiC/Alumina material cracked, and was down-selected from the shroud component. Other CFCC materials also cracked, and were found not as durable as newer melt-infiltration-matrix CFCC materials. The melt infiltration matrix materials are favored for this application due to their high thermal conductivity creating lower stresses in severe operation.

Due to this successful CFCC work, the shroud is viewed today as a realistic component. The program is continuing with the basic design established here and with the aim of commercialization of a ceramic composite shroud.
Figure 24. SiC/Alumina shrouds retained strength versus as-fabricated properties.
3.5 Materials and Applications for Solar Turbines, Inc.

3.5.1 Application Interest

In Phase I of CFCC, Solar reviewed benefits and preliminary design for CFCC materials to replace metals in industrial gas turbine engines. In that analysis, first stage nozzles were found to require material properties in excess of the Nicalon™/Alumina material, but uncooled combustor liners seemed to be a good match. In this subtask, subscale combustor liner components were designed at Solar Turbines. Combustor liners 8" in diameter x 8" long were fabricated and shipped to Solar Turbines for testing in a combustion rig. Solar tested the combustors on a rig in iterations up to 100 hours.

One of the differentiation points of the CFCC tasks with Solar, from other CFCC applications is the emphasis on NDE and relationship with Argonne National Laboratory. Prior to and in between rig testing, NDE was performed to look at the density, and flaws, in the materials. NDE was provided by Argonne National Laboratory, Dr. Bill Ellingson. Combustor liners were photographed and dimensioned prior to testing. At the end of the test, the combustor was photographed and then destructively tested.

In the early stages of CFCC, Solar reported on CFCCs being tested for industrial heat exchangers in the DOE sponsored HiPHES Program. One of the goals of HiPHES was long duration testing of CFCC materials, which in turn builds confidence for long-term use in a turbine engine. The goal is 2 years of exposure at 1800°F at 100 psi. Two SiC/SiC and one SiC/Alumina DLC HiPHES tubes reached 6,000 hours of pressurized exposure. They were removed from the furnace; the dimensions were inspected, and then the tubes were re-pressurized. The DIMOX™ tube failed a few months later at 6984 hours of exposure. The appearance of the fragments from the HiPHES DIMOX™ tube that failed after is consistent with interface embrittlement that is seen in DLC's long-term stress rupture testing coupons. This data alerted Solar of the failure mechanism of the SiC/Alumina CFCC, and the combustor testing proceeded.

Other CFCC materials were tested by Solar Turbines in the same timeframe of the SiC/Alumina materials testing. On other CFCC Programs, SiC/SiC materials from the
DLC CVI CFCC Program were tested. In addition, SiC/SiCNO materials from Dow Corning Corporation were tested.

Regarding combustors, Solar plans to continue the work from CFCC into the ceramic stationary gas turbine (CSGT) program. CSGT is designed to support long-term 1000-hour endurance testing on a CFCC combustor in an engine field test. The CFCC 100-hour testing helped determine which CFCC materials should go into engine testing.

### 3.5.2 Application-Specific Materials Testing

Solar Turbines reviewed the database for 2-D Nicalon™ fabric reinforced DIMOX™ alumina matrix composites. For the combustor liner application, Solar Turbines recommended the following additional testing:

- Fatigue testing at a frequency of 480 Hz
- Residual strength measurement following thermal cycling between 650°F and 2150°F with 1 minute holds at temperature and 1 minute ramp times between temperatures

The existing fatigue data on Nicalon™/Alumina composites did not include cycling at such a high frequency of 480 Hz. Similarly, while thermal cycling data for Nicalon™/Alumina composites exists, the ramp rates were not as fast as those required by Solar Turbines. HACI did not find facilities for fatigue testing at frequencies as high as 480 Hz and furnaces for rapid (forced cooling) thermal cycling.

### 3.5.3 Representative Components

The representative component for the combustor in a small industrial gas-fired turbine engine is an open-ended cylindrical liner (see Figure 25). The liners are approximately 20 cm OD, 30.5 cm high, and 0.3175 cm thick (8" OD; 12" length; 0.125" thick). Combustors were preformed with Nicalon™ fabrics, with 8 separate plies of fabric. This allowed the joints of each ply to be staggered from each other.
Design and fabrication discussions also included features that may be required for future engine combustors. Features such as flanges, dovetails, ribs, holes or slots may be required for mechanical attachment and anti-rotation reasons in the gas turbine. The only feature required in this liner is a .060-inch-diameter hole for a through-wall thermocouple, as shown in Figure 25.

Several liners suffered fabrication flaws including plies not demolding cleanly from tooling and low-density region, due to incomplete metal growth. However, three liners were successfully fabricated for testing at Solar Turbines. The best liner that passed the x-ray NDE test at HACI was shipped to William A. Ellingson of Argonne National Laboratory for thermal diffusivity (see Figure 26) and x-ray NDE analysis to establish the quality of the liner prior to testing. The liner was also CAT scanned at Argonne. Ellingson reported verbally that this was the most uniform liner he had tested so far.
After exposure, the liner was NDE-analyzed again and destructively tested to establish the material integrity.

Figure 26. Thermal Diffusivity Map of combustor 4460-01-006 as-fabricated prior to any rig testing. Uniform density distribution through a Nicalon™/Alumina combustor liner is exhibited.

3.5.4 Component Testing

The representative components fabricated for Solar Turbines were tested in short-term rig tests. (See Table 35.) Temperature profile and lean limit emissions tests were performed. The lean-limit emissions test established the correct air to fuel ratios and fuel flow rates for stable combustion and defined combustion parameters for longer combustion rig tests.
Table 35. Rig testing of combustor 4460-01-006 (ceramic-grade Nicalon™/Alumina)

<table>
<thead>
<tr>
<th>Date</th>
<th>Test Activities</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 1995</td>
<td>Initial scan of thermal diffusivity by Argonne</td>
<td>Very uniform diffusivity</td>
</tr>
<tr>
<td>January 1996</td>
<td>2 hours rig time</td>
<td>No visual damage or indications</td>
</tr>
<tr>
<td>February 1996</td>
<td>Second scan of thermal diffusivity by Argonne</td>
<td>No NDE indications of damage or change</td>
</tr>
<tr>
<td>June 1996</td>
<td>10 additional hours rig</td>
<td>Cycles unknown</td>
</tr>
<tr>
<td>October 1996</td>
<td>Third scan of thermal diffusivity by Argonne</td>
<td>No NDE indications of damage or change</td>
</tr>
<tr>
<td>December 1996</td>
<td>90 additional rig hours, total 102 hours</td>
<td>Several flameouts were performed to create thermal downshocks</td>
</tr>
<tr>
<td>April 1997</td>
<td>Thermal diffusivity and air-coupled ultrasound NDE of liner.</td>
<td>New camera used for diffusivity; new 400 kHz focused transducer for ultrasound</td>
</tr>
</tbody>
</table>

Solar Turbines modified an existing atmospheric pressure combustion rig to accommodate ceramic matrix composite combustor subelements. Test parameters were selected to represent different conditions to which a full-scale combustor may be exposed. Examples included isothermal operation, step changes in temperature (simulating start up or shut down) and cyclic temperature changes (simulating operation under swing load conditions). Temperature of the liner was controlled by backside cooling and fuel amount. Temperatures were kept consistent for all tests of that liner, and they were kept appropriate for the fiber and matrix of the material system.
The rig testing of the liner for the first 2 hours determined temperatures for the testing. The hot side of the liner was kept below 1,204°C (2,200°F) while keeping the maximum temperature on the outer wall at 1,066°C (1,950°F).

The liner with 2 hours test exposure was processed through the thermal diffusivity NDE testing at Argonne National Laboratory. The thermal diffusivity plots of before and after rig tests showed no significant changes (see Figure 27). HACI x-rayed the liners to establish microstructural changes through thickness. Subsequent to NDE tests, the liner was tested for 10 and 100 hours at Solar.

After rig testing of the liner for 102 hours was completed, Solar reported no visually detectable changes on the inner and outer surfaces of the liner. Along the inner diameter of the outer liner, however, some scale (which developed from combustion), appeared to have flaked off, but the scale did not seem to penetrate the composite. Figure 28 provides photos of the liner after testing.
Figure 27. Comparisons of three thermal diffusivity scans showing no significant changes in composite density from first two rig tests, to 12 hours.
Figure 28. Combustor 4460-01-006 after 102 hours of rig testing. Red color is apparently from the fuel and combustion. Enlargement shows scale from ID and intact fabric pattern on composite wall.
3.5.5 Conclusion and Path Forward

During this CFCC Program, Solar initiated their CSGT program for combustor testing using the larger Centaur engine. Due to two factors, the embrittlement of DIMOX™ HiPHES tubes and current CVI interface manufacturing size capability, they chose to start CSGT with CVI SiC/SiC materials. Later, they were interested in the melt infiltration matrix materials and improved coatings for high-pressure steam combustion environments.

Solar Turbines was also very interested and supportive of life assessment methodology and predictive models. They believed predictive models could be important to reduce qualification-testing times for ceramic components and would encourage use of ceramics for designers and engineers to become more familiar with CFCC materials. Results of representative components testing in this task were planned to contribute a great deal of useful data on the effects of high-temperature oxidizing environments on CFCC materials. However, the test times obtained on CMCs in the CSGT program quickly surpassed the 100 hours of CFCC test time, and life prediction was not done on this CFCC program.

In conclusion, Solar did not obtain a failure with the SiC/Alumina materials in short-term combustor testing. However, because of database testing and the HiPHES data, they believed that other materials would provide longer-term service in their applications. Because the goal of their application is 30,000 hours in an engine, the embrittlement after 6000 hours became a decision factor.

In this DIMOX™ CFCC program, the evolution of the materials technology used in very long life combustors tested in CSGT was partially discovered. The combustor materials, which started as carbon interface ceramic-grade Nicalon™, moved to BN interface Hi-Nicalon™ fiber materials. This was possible due to BN scale-up started in this program, as well as the use of multipiece tooling and preform construction and compaction methods used in these tasks.
3.6 Materials and Applications with Teledyne

3.6.1 Application Interest

Recuperators for high efficiency turbine engines represent one of the industrial applications of thin sheet material. Thin sheet material is being considered to replace metals in the thin-walled heat exchanger elements. Replacement would enable operations at higher temperatures. Under a cost-shared program with DOE-OTT (US Department of Energy and Office of Transportation Technologies), and the PNGV program (Partnership for New Generation Vehicles), Teledyne Engine Company initiated design and development for a novel recuperator for an automotive turbine engine. The recuperator was a very compact cylindrical structure with high surface area for heat exchange. The cylinder had approximately a 9-inch inner diameter and an 18-inch outer diameter. The annulus contained about 80 elements in an axial arrangement. The hollow elements held the cool intake air through the inside of the element, and they held the high-pressure hot-exhaust airflows outside and between the elements. The elements were about 20 inches long and about 4 inches wide.

This recuperator was designed to contain ceramic elements, so that very high temperature turbine engine technology from aircraft and missile engines could be used for high-efficiency gas turbine and electric hybrid cars. This program was stopped after thin sheet elements had been designed and prototyped but prior to any testing of thin sheet ceramic elements.

Despite the fact that the PNGV program was stopped, knowledge was gained from the design and prototyping. One of the immediately noticeable shortcomings of the initial thin sheet material used for elements was its low strength and the resulting cracking of elements. Experimentation determined that some of the cracking occurred because of the material’s high CTE and its fabrication as laminated structures. One of the positive elements from the initial prototyping was the successful process that used aluminum curing tools and silicon carbide high-temperature tools.
Teledyne reviewed their design and did not make any changes between the PNGV and CFCC Programs.

Materials work on the CFCC program for fiber-reinforced thin sheet materials yielded stronger and more stable materials than the particulate-reinforced materials first used for PNGV recuperator elements. Specifically, demonstrations of lower-shrinkage materials and laminate-type joints were relevant to solving fabrication problems for the recuperator. Small 8”x 8”parallel-plate recuperators were made in practice fabrication and helped solve warpage and lamination problems. When the CFCC materials work was demonstrated, it was clear that the materials techniques were sufficiently improved to revisit the Teledyne recuperator and fabricate a full size unit for testing.

This project continued to allow a hot-air heat transfer test to obtain actual data to validate modeling performed for the recuperator. Actual data enabled Teledyne to continue designs for recuperator applications—for hybrid vehicles or distributed power systems. HACI will use the experience for thin sheet element recuperators in the Industries of the Future, including the glass and aluminum industries.

Teledyne’s design partner, Rensselaer Polytechnic Institute (RPI), performed the hot-air heat exchange testing.

3.6.2 Representative Components

Parallel-plate cross-flow recuperators were made (see Figure 29). The units were similar to monolithic ceramic recuperators field-tested in a DOE program, and they were similar to military air-to-air heat exchangers fabricated by HACI. Fabrication challenges were overcome by laminating a multi-layered and multi-dimensional control in high-temperature firing for strength. Parallel-plate recuperators (consisting of up to 20 layers) were made.
The rectangular units were easy to fixture into a heat exchange assembly. The recuperators were designed for low-stress laminar flow, versus higher flow rates with turbulent flow. Testing showed that the units exhibited heat transfer that matched predictive modeling to 1000°C.\(^\text{11}\)

### 3.6.3 Component Fabrication

Complex curvature designs with high surface area for counter-flow recuperators were made. Elements from the PNGV program were visually checked, but, because most were cracked, none of them was used. New elements were fabricated. Existing element design was used, as were existing tools for shaping and fabrication of the recuperator elements and the assembly fixture. Aluminum tools (see Figure 30) were used for initial curing of the assembled element. After final firing, the tools were used as fixtures for
minor grinding for edge attachments. Elements were held with ceramic end rings inside a stainless steel can to complete the recuperator assembly.

![Figure 30. Aluminum tool and cured recuperator element.](image)

To assemble the recuperator, a fixture was built (see Figure 31) so that each element could be set in place on the inner cylinder of the can, at the proper angle. End rings were made of particulate-reinforced SiC/Alumina. A layer of Fiberfrax® insulation was used between the elements and the outer can. The stainless steel can was not manufactured to simulate the automotive recuperator, and it was assembled with flanges and bolts.
3.6.4 Component Testing

RPI performed heat exchange analysis and then testing to obtain heat-exchange data to correlate with FEA predictions and modeling. Heat-transfer measurements were obtained from both types of recuperator assemblies that were made from thin sheet ceramics. The RPI high-temperature gas loop was configured to obtain flow and heat-transfer characteristics for the recuperators. The cross-flow parallel-plate recuperators were tested to obtain measured values of friction factors and thermal effectiveness versus calculated values. The large recuperator was tested only for heat exchange values versus total pressure drop.

A microprocessor with feedback control regulated the hot- and cold-side airflow and heater control, to maintain temperatures within ±2°C. Airflow was provided by 5- and 3-horsepower blowers. Heat was produced by 60 kW and 280 kW burners, such that inlet temperature to the test section was 30°C on the cold side and either 400°C or
1000°C on the hot side. Flow rate was obtained from measurements of pressure drop across orifice plates within a measurement uncertainty of 2%. K-type (cromel-alumel) thermocouples measured inlet and outlet temperatures on both hot and cold sides. On the outlet, eight thermocouples were arranged in a matrix, to obtain the bulk temperature, which is the average gas temperature used in calculations of thermal effectiveness. Surface pressure taps located in the inlet and outlet provided pressure drop to within an uncertainty of 0.001-inch water column. These measurements were corrected for inlet and outlet effects so that the overall friction factor of only the heat exchanger was determined. Figure 32, Figure 33, and Figure 34 show the results obtained on one stack assembly.

The parallel-plate units compared very favorably to experimental correlations in rectangular channels with fully developed laminar flow and constant surface temperature.
Figure 32. Friction factor measurements obtained on one recuperator stack assembly—high-pressure side.
Figure 33. Friction factor measurements obtained on one recuperator stack assembly—low-pressure side.
Figure 34. Thermal effectiveness measured obtained on one recuperator stack assembly.
The counter-flow unit could not be compared to design calculations because the number of units in the design was different from the number of units in the fabricated unit. In initial flow testing, it was found that the recuperator suffered from numerous broken elements. Breakage apparently occurred between the assembly, the transportation, the rigging of the unit at RPI, and the testing. HACI technicians partially disassembled the counter-flow unit at RPI, and they sealed closed about 20% of the elements with Ceraset™ adhesives. Once the cross-flows between the hot and cold circuits were brought to a reasonable level, the unit was tested, and heat transfer data was obtained. While the heat exchange was a fraction of the theoretical value, high temperatures (of nearly 1000°C) were obtained in testing, which were too hot for normal sheet metal alloys used in recuperators.

In later analysis, the sheet-metal can (see Figure 35) was determined to be fabricated too weak to provide support for the ceramic elements. In the future, the can would need to be designed to provide lifting attachments for the assembly (for transportation and rigging), such that the ceramic elements are not put into bending loads for which they are not designed.
Figure 35. End view of recuperator assembly in Houston can.
3.6.5 Improved Heat Transfer

During the testing of laminar flow recuperators, RPI suggested a task for increased heat exchange for laminar flow recuperators. Most industrial heat exchangers operate in turbulent flow modes, which create higher system pressure than available in a turbine-engine-based system. Techniques to modify the surface roughness of the recuperator elements can be used to improve heat exchange in laminar flows. The formation of a corrugated surface would render them more advantageous than sheet metal. In very thin sheet metals, corrugations formed by ribbed rollers during sheet production are expensive, and they can limit the fabrication of the sheet metal. In the thin sheet ceramic, corrugations might also be made with rollers but in the soft-preform paper stage of fabrication. RPI performed research that identified corrugation height and width (i.e., corrugation wave period) for different laminar flows and heat exchange results. An example of these results is shown in Figure 36.

This work was not tested either in methods to emboss the thin sheet with corrugations or in fabrication work to test the heat transfer effectiveness. The testing performed by RPI in this research was completed with corrugated sheet metal pieces. Figure 37 shows the equipment used in this testing.

Recuperators transfer waste heat from combustion products to reactants so that energy efficiency of Brayton-cycle microturbines is increased. Minimal pressure loss and maximum heat transfer represent the goals in recuperator design. Fabrication features such as sheet embossing were explored for increased heat transfer in low velocity laminar flow rates.\(^1\)
Figure 36. Streamlines above sinusoidal surface calculated with RANS CFD method—from wall to centerline.

Figure 37. Windtunnel configuration.
The rate of convective heat transfer in laminar flow through a channel, such as each element of a recuperator, can be enhanced by the introduction of advection mechanisms. Stream-wise vorticity to increase mixing represents an example of such a mechanism. Surface treatments that include vortex generators, delta wings and winglet pairs, and airfoils at incidence improve heat exchanger performance through the generation of stream-wise vortices. Other research showed the effect of different-shaped vortex generators on heat transfer. From this research, it was concluded that the secondary flow direction and strength were the dominant factors in the heat transfer enhancement.

The objective of this research effort was to investigate techniques by which heat transfer could be enhanced in high-aspect ratio channels without excessive increase in pressure loss. Equations and laboratory testing identified corrugations that increase heat transfer at various Reynolds numbers of flow. RPI may be contacted for specific details.

3.6.6 Conclusion and Path Forward

Heat-exchanger testing provided validation that simple heat exchangers designed with metals could be designed with thin sheet ceramic materials. The laminar flow performance region limits the data’s use to low-flow and low-back pressure systems, but it can include very hot temperatures. From previous field trials of parallel-plate ceramic heat exchangers, we learned of their primary issues of unexpected corrosion and ineffective filtering, both of which caused corrosion and blocking of the channels. None of the research in CFCC addressed solutions to those issues.

The fabrication and test tasks were important in validating the material system of fiber-reinforced thin sheet and in providing sample components made with laminated joints and curved components. Additional tasks are still necessary for thin sheet component work, including new hurdles identified in this work of attachment and fixturing of thin sheet elements to prevent fracturing.

In the future, consistency and scale-up of the paper-making preform fabrication needs to be improved. An IOF user needs to be identified to support heat exchanger development, corrosion testing, and expansion of the database.
4 Conclusions

The following five conclusions were drawn from the DMO CFCC program:

1. SiC/Alumina CFCC was found not durable enough for long term use

2. Thin Sheet low cost ceramic sheet metal type material was optimized in a novel approach using papermaking machines

3. Fabrication steps were found important and beneficial for other compositions of CMC—
   - CVI-densified and silicon melt infiltrated (MI) composites
   - C/SiC and MgO/AlN for brakes
   - C/C enhancements

4. Commercial applications for CMC materials were advanced. Many engineers were educated about CMCs for the future.

5. Long-lasting relationships were formed between commercial companies and National Labs

SiC/Alumina composites were tested in industrial environments of high temperatures, of steam, of alkaline elements contained in processes for natural gas and coal combustion, and of heat exchange. In these tests the SiC/Alumina material performed well at no or very low stresses, in short periods of time, and in single cycle applications. In tests involving higher stresses or multiple cycles combined with longer exposure times, the SiC/Alumina material failed due to microcracking of the matrix alumina which allowed the exposure elements to damage the interface layers and reinforcing fibers, which lead to structural failure of the material. Different enhancements to modify the matrix, the interface layers, and the reinforcing fibers all produced single improvements, but no combination was found that produced a SiC/Alumina CMC material that satisfied a long-duration industrial application.
Ceramic composite matrix systems such as Enhanced CVI SiC/SiC and MI SiC/SiC have shown superiority over the DIMOX™ SiC/Alumina for long-life industrial applications such as industrial turbine engine components and municipal solid-waste vortex finder panels. A satisfactory composite material solution still does not exist for other industrial applications such as heat exchangers.

Thin sheet alumina material was explored as a low cost route for high-temperature, sheet-metal-type materials. Its novel manufacturing route uses technology from the paper making industry, which contributes to its low cost. This material was brought to the proof-of-concept stage and, it will hopefully be matured via commercial applications. In addition, processes used and optimized for this material have found application in other chopped-fiber-reinforced materials, such as C/SiC and C/C.

Fabrication steps that were optimized for SiC/Alumina have now found value as improved process steps for other CMCs such as enhanced SiC/SiC and MI SiC/SiC. These process steps are practiced today with the technical knowledge gained from this program. Specific examples include some tooling and preforming practices and dual layer interface coating of BN/SiC. (See Table 36.)
Table 36. Fabrication steps valuable in applications beyond SiC/Alumina

<table>
<thead>
<tr>
<th>Technology or Fabrication Step</th>
<th>New Application Other Than SiC/Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite tooling practices</td>
<td>Melt Infiltration SiC/Si/SiC CMCs</td>
</tr>
<tr>
<td>Detooling after BN interface</td>
<td>MI and CVI composites that use BN</td>
</tr>
<tr>
<td>Modifications of BN for interfaces</td>
<td>MI and CVI composites that use BN</td>
</tr>
<tr>
<td>Dual layer BN/SiC interface</td>
<td>MI and CVI composites</td>
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<tr>
<td>BN process improvements</td>
<td>All low temperature BN CVI</td>
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<td>DIMOX™ matrix process</td>
<td>Thin Sheet Alumina</td>
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<td></td>
<td>MgO/AlN composites for brakes</td>
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<tr>
<td>Release agents and bedding materials experience</td>
<td>MI composites</td>
</tr>
<tr>
<td>Slurry interfaces from Thin Sheet composites</td>
<td>C/SiC materials using chopped fiber reinforcement for brakes and glass handling</td>
</tr>
<tr>
<td>Oxidation resistance experience</td>
<td>C/C and C/SiC materials for brakes and glass handling</td>
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The significance of the relationship between HACI and Honeywell Aircraft Landing Systems (ALS) is the opportunity for the ceramics technology to make an immediate impact on a commercial product, brakes for aircraft, trucks, and cars. Current applications of ceramics for commercial brakes include MgO/AlN brake pads for use with C/SiC rotors for automotive and truck brakes. Process combinations using thin aqueous slurry coatings have yielded lower cost C/SiC materials for applications such as glass handling parts.

Commercial projects and/or military projects with significant testing milestones have benefited from CFCC. Companies such as Foster Wheeler, Solar Turbines, GE Power
Systems, and Teledyne Engines engaged in detail testing of CMCs. The results of these tests will be in their materials database for future use. These companies performed significant, detailed, application-specific tests with data and results backed with microscopy, so that they will be meaningful in the future when other advanced materials are considered. Foster Wheeler accomplished several design iterations of CMC heat exchangers. Solar Turbines accomplished multiple sets of combustor testing, which verified correlations between size scales and enabled thousands of hours of engine testing on their CSGT program. GE Power systems performed physical and rig tests prior to turbine tip shroud rig tests and established correlations between the data and testing. To enable automobile-size recuperator performance predictions, Teledyne Engines performed several design iterations of recuperators, with three scales of heat transfer testing.

In the process of performing the work on CFCC, multiple presentations were given each year to many audiences. The affect of presenting work on CMCs to audiences of ceramic engineers via ACS, mechanical engineers via ASME, chemical and materials engineers via NACE, as well as company-specific and university-specific talks, many people were exposed to CMCs. The presentations provided exposure of CMCs to thousands of people in technical communities who work on advanced materials.

A significant, meaningful partnership was established between HACI and The Oak Ridge National Laboratory. HACI also worked with other national laboratories including Sandia Livermore and AMES Laboratory. The relationship between scientists at ORNL and HACI resulted in annual private meetings where honest and frank dialogues about HACI's materials were conducted. During these annual reviews, strengths were highlighted and weaknesses were clarified, and potential experiments for the upcoming year were discussed. The work with Sandia created peer relationships for CVI process-modeling discussions. Both relationships became forums for HACI scientists to discuss questions without commercial fears of proprietary information.
5 Recommendations

The CFCC program was a very successful method for many CMC producers, researchers, and users to come together over a significant period, to advance the material's state of the art. HACI recommends that programs such as this continue to be funded by the DOE for energy-saving technologies.

In addition, HACI recommends that the DOE consider cost-sharing methods to enable advanced-material producers and users to obtain partial funding for CMC components for tests and evaluation, to overcome purely financial hurdles for application-specific testing. This is envisioned as a source of funding that would be rapid in response and simple to apply for, to continue to encourage commercial testing of CMCs without the huge cost of full R&D programs.

A hurdle to commercialization and the cost reduction of CMCs is the cost of the reinforcing fiber. HACI recommends that the DOE or the National Labs continue research into other uses for SiC fiber to increase volume usage, that they attempt to merge commercial and military fiber selection, and that they continue to monitor fiber manufacturers for methods to assist with low-cost fiber manufacturing.
6 Acknowledgments

DOE Program Managers—Washington, DC
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DOE Project Officer—Chicago Field Office
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6.1 HACI Contributors to DMO CFCC Efforts

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Atul Shah  Phase II—January 1995 to December 1996
Phil Craig  Phase II—January 1997 to end

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### 6.2 Other Contributors to DMO CFCC Efforts (listed alphabetically)

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
</tr>
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<tbody>
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<td>Manny Subvasian</td>
<td>Ames National Laboratory at Iowa State University</td>
</tr>
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7 Appendices
Appendix 1 is the first page of patent number US 6,228,453 B1, Composite Materials Comprising Two Jonal Functions and Methods for Making the Same.
Appendix 1 First page of patent number US 6,228,453 B1

(12) United States Patent
(10) Patent No.: US 6,228,453 B1
(45) Date of Patent: May 8, 2001

(54) COMPOSITE MATERIALS COMPRISING TWO JONAI. FUNCTIONS AND METHODS FOR MAKING THE SAME.

(75) Inventors: All Syed Fareed; John Edward Garnier; Gerhard Hans Schirsky; Christopher Robin Kennedy, all of Newark, DE (US); Bird Sonuparlak, Longmont, CO (US)

(73) Assignee: Lanzide Technology Company, I.P.; AlliedSignal Composites Inc., both of Newark, DE (US)

(57) Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 08/958,685
(22) Filed: Oct. 27, 1997

Related U.S. Application Data

(63) Continuation-in-part of application No. 08/472,613, filed on Jan. 7, 1995, new Pac. No. 5,842,594.


Field of Search: 428/43, 428/403, 428/549, 428/552, 610, 704, 698, 699, 701, 702

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ABSTRACT

The present invention generally relates to mechanisms for preventing undesirable oxidation (i.e., oxidation protection mechanisms) in composite bodies. The oxidation protection mechanisms include getterer materials which are added to the composite body which gather or scavenge undesirable oxidants which may enter the composite body. The getterer materials may be placed into at least a portion of the composite body such that any undesirable oxidant approaching, for example, a fiber reinforcement, would be scavenged by (e.g., reacted with) the getterer. The getterer materials may form at least one compound which acts as a passivation layer, and/or is able to move by bulk transport (e.g., by viscous flow as a glassy material) to a crack, and sealing the crack, thereby further enhancing the oxidation protection of the composite body. One or more ceramic filler materials which serve as reinforcements may have a plurality of super-imposed coatings thereon, at least one of which coatings may function as or contain an oxidation protection mechanism. Specifically, a coating comprising boron nitride which has been engineered or modified to contain some silicon exhibits improved corrosion resistance, specifically to oxygen and moisture. The coated materials may be useful as reinforcing materials in high performance composites to provide improved mechanical properties such as fracture toughness. The present invention also relates to improved composites which incorporate these materials, and to their methods of manufacture.

27 Claims, 17 Drawing Sheets
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