SPRING 1996 • No. 7

A COMMUNICATION OF THE CONTINUOUS FIBER CERAMIC COMPOSITE PROGRAM

Congress, DOE, Industry Attend

CFCC Review

By Sean Yeakle, USACA

The DOE CFCC program review was held in Washington March 19 with representatives from Congress, DOE, and the ceramics industry on hand to hear an overview of the program and to discuss potential applications and opportunities for CFCCs.

J. Michael Bowman of DuPont provided the industry perspective on technology partnerships and the role they should play in a "Third Wave" economy. Bowman said the CFCC program is an excellent example of a successful partnership between government and private industry and noted that the value of technology lies not only in invention but also in production and use. According to Bowman, in a world of constrained resources, such as capital, manpower, and materials, these partnerships increasingly will be the way industry goals will be reached. He said partnerships provide access to ideas and expertise, better products through collaboration, fewer redundant costs, the ability to maintain long-term research and development, and faster return on R&D investment.

In a world of constrained resources, such as capital, manpower, and materials, these partnerships increasingly will be the way industry goals will be reached.

These partnerships, he noted, must be vertical, like CFCC, so that those who have the problems will be involved in developing solutions.

It is vital that the government understand the importance of partnerships,

Continued on page 2

Partnerships provide access to ideas and expertise, better products through collaboration, fewer redundant costs, the ability to maintain long-term R&D, and faster return on R&D investment.

Inside

4 Program Manager

6 GE's R&D

10 B&W Hot Gas Filters

12 3M's Filters

14 CFCC Envelope

17 CFCC Publications

18 Testing Facility

SPONSORED BY THE U.S. DEPARTMENT OF ENERGY, OFFICE OF INDUSTRIAL TECHNOLOGIES

CFCC Review

Continued from page 1

he said. To illustrate this, he said it helps to think of the government as a multitrillion dollar enterprise with high-technology needs.

With that in mind, Bowman explained, it is obvious that the government should sponsor and/or conduct a substantial R&D program to address those needs. For example, if advanced materials are needed to enhance either defense, the civilian infrastructure, or the nation's energy issues, the government must ensure that the enhancement is provided in a timely and cost-effective way.

Solutions

It is not sufficient, he said, to assume the free market will lead to the right technology at the right time. Instead, through proactive involvement of the owners of the problems (in this case the federal government), solutions can be found more efficiently.

Bowman also stressed industry's desire for insertion programs to demonstrate their products. Use of these products is more likely to begin with retrofitting existing systems than with development of new systems.

Industrial Needs

With that in mind, industry needs opportunities to place their products into existing systems, thereby providing a real-time performance database while limiting risks. As the products prove themselves, new systems will be developed.

Congressman Zach Wamp (R-Tenn), whose district is home to the Oak Ridge National Laboratory (ORNL), gave the congressional perspective on the future of science and technology funding, noting that while some have talked about eliminating DOE, there is "no serious threat of that surfacing as part of the fiscal 1996 or 1997 budgets."

Rep. Zach Wamp

Wamp, a member of the House Science Committee, said because individual components of DOE need to remain intact, eliminating the department and moving its programs to another agency would be a "useless exercise."

Restructuring Labs

Wamp is cosponsoring a measure to restructure the national laboratory system by establishing specific mission areas and then requiring the Secretary of Energy to establish and utilize criteria for assigning missions to specific labs. The flow of federal science and technology funding in the future will move toward academia teaming with the national laboratories, he predicted.

Likening science and technology funding to defense spending, Wamp said that during times of peace when there are no apparent military threats, people tend to want to reduce the defense budget. History has shown,

> "It is not sufficient, he said, to assume the free market will lead to the right technology at the right time."

> "The flow of federal science and technology funding in the future will move toward academia teaming with the national laboratories, he predicted."

> "While some have talked about eliminating DOE, there is no serious threat of that surfacing as part of the fiscal 1996 or 1997 budgets."

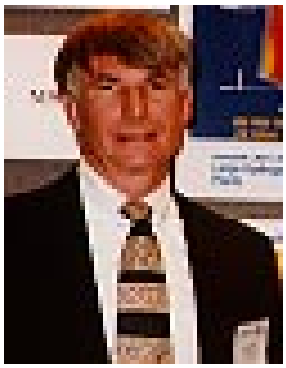
however, that drastic cuts during times of peace create enormous difficulties for bringing spending to needed levels when threats arise. That lesson, Wamp said, should be applied to funding science and technology.

Among several speakers from key industries who discussed potential industrial applications for CFCCs, Jim Wessel of Wessel Associates delivered a presentation on CFCC use in the chemical process industry (CPI).

Jim Wessel, left, of Wessel Associates, discussed "chemical industry applications and opportunities" during the program review. William Werst, right, of USACA, which cosponsored the meeting.

With a million jobs and more than 12,000 plants, CPI is a large and diverse industry representing 3.5% of U.S. energy consumption, Wessel said. CPI equipment includes pipes, pumps, heat exchangers, power generators, power transmission heaters, kilns, and furnaces.

Frequently encountered corrosive chemicals cause various materials



Denise Swink, left, DOE, Deputy Assistant Secretary, Office of Industrial Technologies. J. Michael Bowman, DuPont, right, gave the industry overview talk at the meeting.

problems for which several efforts to find solutions are under way by groups such as the Materials Technology Institute (MTI), Chemical Vision, and DOE.

Wessel said several steps would assist these efforts, including identification of CPI monolithic ceramic experience, identification of high-value applications, leveraging efforts of MTI, Chemical Vision, and DOE, and utilizing national laboratory

Mikio Hiromatsu, Research Institute of Advanced Materials, discussed advanced ceramics for power generation in Japan.

James Weddell, Du Pont Lanxide Composites, at the CFCC display.

”

Drastic cuts during times of peace create enormous difficulties for bringing spending to needed levels when threats arise.

”

With a million jobs and more than 12,000 plants, CPI is a large and diverse industry representing 3.5% of U.S. energy consumption.

A Message from the Program Manager

There has been a great deal of activity in the CFCC Program since my first message in the summer 1995 *CFCC News*. Things have been very busy in Washington because of the unresolved 1996 budget, which I hope will be resolved before the newsletter goes to press.

In January, many of the program participants had the opportunity to report on the substantial progress they have been making in Phase II of the CFCC Program at the meeting in Cocoa Beach.

There was a good turnout at the meeting, and it appeared that the attendance at the CFCC session was high. I have had positive feedback on the meeting from those both in the program and out.

I hope most of you found the Cocoa Beach meeting useful. If not, please let me know how we can make it better because we will be participating in next year's meeting. I have been asked to host another CFCC session and I hope next year we will have an entire day for CFCC-related presentations.

The next programmatic task at hand is to rewrite the CFCC Program Plan. It has become outdated because of the many changes to the program since its publication in 1990. I know some of the applications, schedules, and markets have changed over the past six years. In addition, new opportunities have opened up due to the recent Office of Industrial Technologies "Industries of the Future" strategy. We will also have the opportunity to give a summary of what the program has accomplished. The new plan is scheduled to be completed before the end of the year.

Please feel free to contact me any time. My phone number is (202) 586-3646, and I can be reached through the internet at merrill.smith@hq.doe.gov.

Merrill Smith

> *"The next programmatic task at hand is to rewrite the CFCC Program Plan. It has become outdated because of the many changes to the program since its publication in 1990.*

Merrill Smith

Year's Accomplishments

CFCC Program Manager Merrill Smith outlined for participants at the CFCC review meeting in Washington, D.C., some of the year's accomplishments. Included were the following:

- **AlliedSignal's** engine rig tests showed that the CFCC valve guides exhibited 1/6–1/4 of the wear of the baseline cast-iron guides and 1/2 of the wear of stems running against guides.
- **Amercom** successfully formed an Industrial filter and pump Fibrosic ™ candle filter around a CFCC Strongback™.
- **Babcock & Wilcox's** manufacturing technology for the CFCC hot gas filters was transferred from the company's R&D division to the operating division.
- **Dow Corning** fabricated and delivered CFCC tube hangers to Chevron and a subscale combustor liner to Solar Turbines for simulation testing.
- **DuPont Lanxide**, using the DIMOX™ process, manufactured a representative combustor liner for solar turbines. The liner passed nondestructive evaluation and will be rig tested for 100 hours.

• AlliedSignal
• Amercom
• Babcock & Wilcox
• Dow Corning
• DuPont Lanxide
• General Electric
• Textron Specialty Materials

• **DuPont Lanxide's** chemical vapor infiltration silicon carbide/silicon carbide reverberatory screens passed 1000 hours of static burner rig exposure and 300 thermal cycles at Alzeta Corporation.

• **General Electric** fabricated representative shroud parts of silicon carbide/silicon matrix composites and demonstrated tough ceramic joints in monofilament-reinforced composites.

• **Textron Specialty Materials** installed and began field testing SCS-6/NB SiC CFCC immersion burner tubes in a commercial aluminum holding furnace.▲

CFCC News Notes

■ USACA Spring Meeting

The U.S. Advanced Ceramics Association (USACA) held its annual Spring meeting March 20–21, 1996, in Alexandria, Virginia, with several speakers from industry discussing potential applications for CFCCs. Among those speakers were

- Joseph Luckett, E.I. DuPont, discussing the chemical process industry;
- Robert Hillery, GE's aircraft engine group, discussing coatings for high-temperature structures;
- Donald Blomquist, National Institute of Standards and Technology (NIST), on NIST's advanced ceramic high-speed grinding program;
- Daryl Treger, Strategic Analysis, Inc., on applications for high-temperature superconductors; and
- Jerome Persh, Institute for Defense Analysis, discussing Defense Department trends for advanced materials.

■ "Older, Cheaper, Greener"

Discussions were held at two recent meetings on the armed services' shift in focus from developing new systems to retrofitting existing systems.

In March at a meeting of the American Society for Metals' Government and Public Affairs Committees, Vincent Russo, who heads the Air Force's Materials Laboratory at Wright Patterson Air Force Base, said the services are shifting their focus from new materials for new systems to new materials to solve problems with existing systems. The aim, he said, is to make existing systems more environmentally friendly at a lower cost. The motto, he noted, is changing from "Higher, Faster, Farther" to "Older, Cheaper, Greener."

At another meeting, this one called by the U.S. Advanced Ceramics Association (USACA) with Department of Defense officials, Jerry Persh of the Institute for Defense Analysis indicated the DoD Advanced Research Projects Agency is moving from structural materials to functional materials to solve problems with existing equipment. He urged industry to show how advanced materials are essential to this effort and to communicate that information to Congress.

"*Vincent Russo, who heads the Air Force's Materials Laboratory at Wright Patterson Air Force Base, said the services are shifting their focus from new materials for new systems to new materials to solve problems with existing systems.*

GE Research & Development

Toughened Silcomp

New Strategies Improve Performance, Reliability

By Greg Corman and Krishan Luthra, GE

"Utilization of CFCC shrouds and combustor liners is expected to give an annual fuel cost savings per machine of over $800 thousand with substantial reductions in NO_x emissions."

GE Industrial and Power Systems is the world's premiere producer of large-scale (>20 MW) industrial gas turbine engines. To maintain this position, GE constantly evaluates new strategies for improving engine performance and reliability. Utilization of CFCC components has the potential for significantly increasing the efficiency and lowering pollutant emissions of gas turbines, thus representing real value to turbine users.

Benefits

Obtaining the maximum benefits from CFCCs would require a complete redesign of an engine around the unique capabilities and limitations of these materials; however, such an undertaking is clearly outside the scope of the CFCC program. Rather, the use of CFCCs for specific retrofit components in an existing engine (MS7001FA class) was considered to be the fastest route to commercialization.

In Phase 1, two components—the first stage inner shroud and the combustor liner—were selected for CFCC utilization based on a subjective evaluation of the potential benefits versus the difficulties and risks of implementation. The assessment of CFCCs for these components was discussed previously (*CFCC News*, No. 3, Fall 1993).

The major conclusions of the assessment were (1) utilization of CFCC shrouds and combustor liners is expected to give an annual fuel cost savings per machine of over $800 thousand with substantial reductions in NO_x emissions; (2) Toughened Silcomp can meet the short-term material property requirements for these two applications; and (3) extensive material testing and development of life prediction methodology will be needed to ensure the necessary reliability of CFCC components before their utilization.

Silcomp

Silcomp is the name given to GE's version of reaction-formed silicon carbide made by melt infiltration of silicon into a porous preform containing carbon and/or SiC. During infiltration the silicon metal reacts with the carbon in the preform, yielding two interpenetrating, continuous networks of SiC and residual silicon.

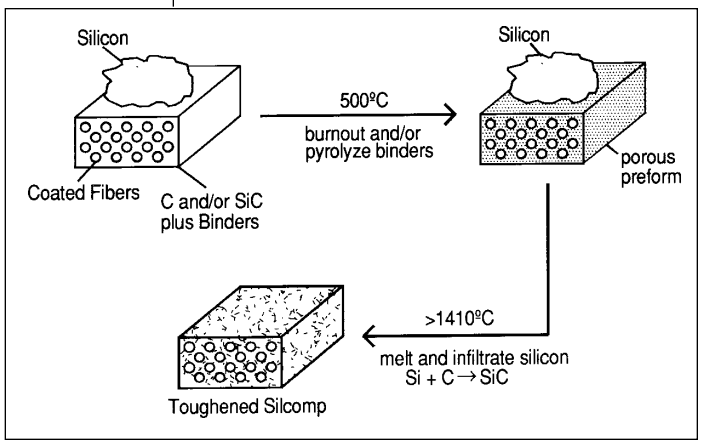


Fig. 1. Schematic of the melt infiltration process for making Toughened Silcomp.

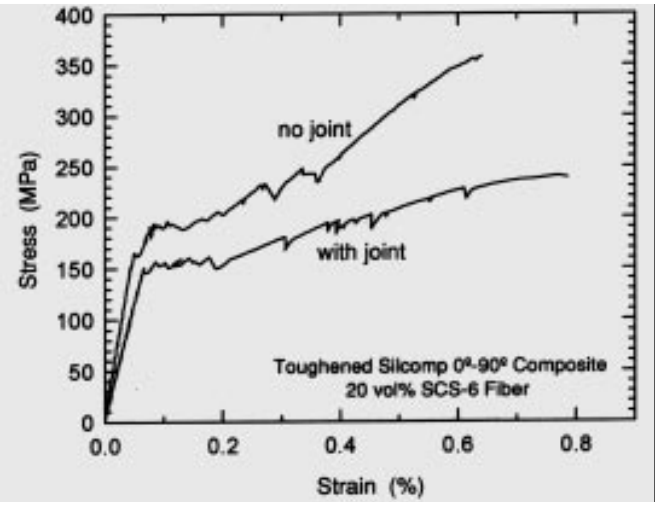


Fig. 2. Room temperature tensile fracture behavior for 0–90° Toughened Silcomp composites reinforced with 20 vol % SCS-6 or 25 vol % Hi-Nicalon SiC fibers. Curves are offset for clarity.

The melt infiltration process is relatively fast (infiltration rates are on the order of several cm/min; total part infiltration requires only 10–20 min) and results in fully dense, net size and shape (dimensional changes <0.3%) parts.

The dimensional stability, short processing times, and fully dense end product make the melt infiltration process ideal for the production of CFCCs. Thus Toughened Silcomp, which is a Silcomp matrix reinforced with continuous silicon carbide fibers (primarily Textron's SCS type fibers or Hi-Nicalon™), was developed at GE Corporate Research and Development.

Protection

The melt infiltration process utilized, similar to that used for monolithic Silcomp, is shown schematically in Fig. 1. The proper fiber coating, which serves to protect the fibers during melt infiltration and provides the proper fiber-matrix debond characteristics, is key to the performance of the composite.

Initial development of Toughened Silcomp was done primarily with Textron SCS-6 monofilament SiC fibers and CVD fiber coatings applied in a batch mode.

By teaming with the fiber supplier, Textron Specialty Materials, we were able to jointly develop continuous fiber coatings that made possible the use of a drum-winding process for the fabrication of composite preforms.

Unidirectional pre-preg tapes are first fabricated using the drum winding process. These tapes are then stacked to give the desired fiber architecture, laminated either by die pressing or autoclaving, and then melt infiltrated.

We have subsequently demonstrated tough composite behavior with continuously coated SCS-6, SCS-9, and SCS-0 type fiber.

Recent Work

More recently work has been done on incorporating Hi-Nicalon™ SiC fibers into Toughened Silcomp.

The fabrication process is nearly identical to that mentioned above for monofilaments. Typical tensile stress-

Property	SCS-6 Fiber	Hi-Nicalon™ Fiber
Fiber volume fraction (%)	20	25
Matrix cracking stress (MPa)	148	146
Initial modulus (GPa)	227	272
Matrix cracking strain (%)	0.065	0.053
Ultimate strength (MPa)	354	300
Strain at maximum stress (%)	0.74	0.8
Interlaminar shear strength (MPa)	55	33
Thermal conductivity at 1200°C (W/m•K)	19	15.5

Table 1. Mechanical and Thermal Properties of Toughened Silcomp (0–90° crossply composites)

”

By teaming with the fiber supplier, Textron Specialty Materials, we were able to jointly develop continuous fiber coatings that made possible the use of a drum-winding process for the fabrication of composite preforms.

”

More recently work has been done on incorporating Hi-Nicalon™ SiC fibers into Toughened Silcomp.

strain curves for both SCS-6 and Hi-Nicalon™ reinforced composites are shown in Fig. 2. Representative properties of SCS-6 reinforced composites and some preliminary Hi-Nicalon™ composites are listed in Table 1.

Stronger

Although somewhat weaker than the SCS-6 reinforced composites, the Hi-Nicalon™ reinforced Toughened Silcomp with only 25 vol % fiber is stronger than most competing CFCC materials which utilize up to 40 vol % fiber.

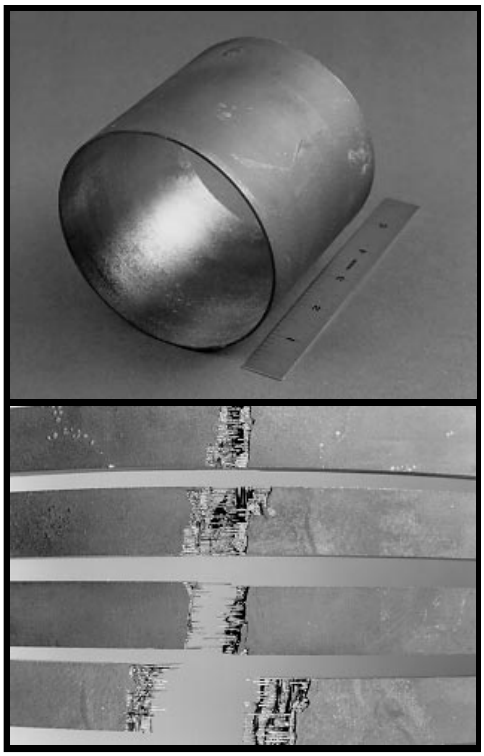


Fig. 3. Top: Toughened Silcomp cylinder made by drum winding. Bottom: Failed sections of tested rings cut from such a cylinder.

With the use of the drum-winding fabrication process we have obtained CFCCs with excellent mechanical and thermal properties, as shown in Table 1. Of particular interest are the high values of matrix cracking stress and thermal conductivity. As with most CFCCs, the high temperature use stress limit of Toughened Silcomp for long-term applications is directly related to the matrix cracking stress.

Also, the turbine components of interest in this program, namely the first stage shroud and combustor liner, are primarily thermally loaded, (i.e., the largest source of operating stresses are the thermal gradients within the components). With a high thermal conductivity the thermal gradients are lessened, thereby decreasing the stresses on the components.

> *"As with most CFCCs, the high temperature stress limit of Toughened Silcomp for long-term applications is directly related to the matrix cracking stress.*

> *"With a high thermal conductivity the thermal gradients are lessened, thereby decreasing the stresses on the components.*

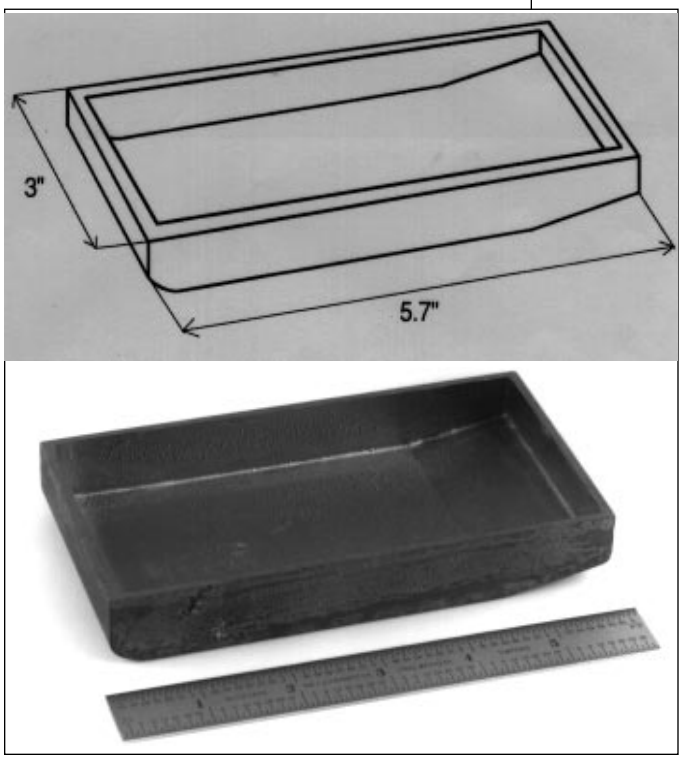


Fig. 4. Top—Schematic of the CFCC shroud segment design. Bottom—Toughened Silcomp representative shroud segment reinforced with Textron SCS-6 fiber. Similar shroud segments have been fabricated with Hi-Nicalon™-reinforced Toughened Silcomp.

The high thermal conductivity and high matrix cracking stresses make Toughened Silcomp the most suitable CFCC for these and other thermally loaded applications, such as heat exchanger tubes.

Parts

The fabrication of cylindrical shapes is very simple using the drum winding process. Figure 3 shows an illustration of a 4-in.-diameter Toughened Silcomp cylinder fabricated by drum winding in the as-infiltrated condition.

The fracture properties of such cylinders have been measured using a split disk tensile test and have been found to be comparable to those of flat tensile specimens. Failed sections of some of the tested rings, displaying significant crack deflection and branching and extensive fiber pullout, are also shown in Fig. 3.

Although the Application Assessment considered both shrouds and combustor liners, only the shroud application is being pursued currently. The conceptual design for the CFCC shroud segment is shown in Fig. 4.

Fabrication of such a shape using SCS-type monofilament fibers requires joining of the side, end, and bottom faces. Fortunately, joined structures can easily be formed in Toughened Silcomp in the preform stage. Figure 4 also shows a picture of a representative shroud segment fabricated with 20 vol % SCS-6 fiber by using such joining technology. The use of joints in component fabrication is feasible only because tough composite joints can be made with Toughened Silcomp, as demonstrated by the stress-strain curves in Fig. 5.

To the best of our knowledge, this is the first demonstration of tough CFCC joints. Demonstration shrouds have also been fabricated using Hi-Nicalon™ fiber without the need for composite joints.

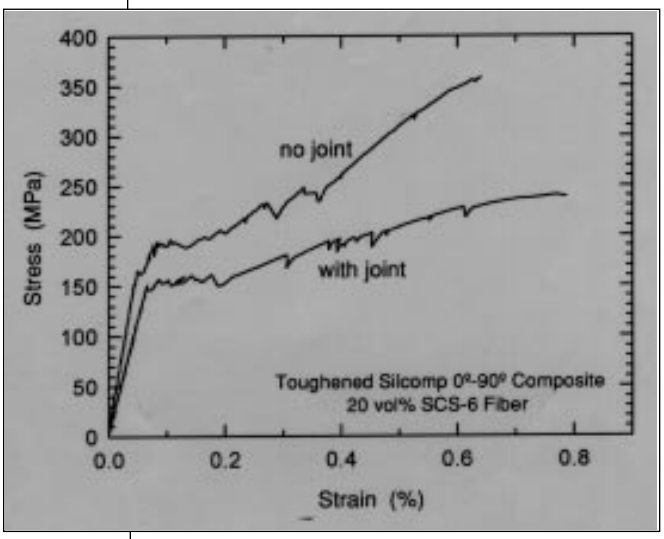


Fig. 5. Tensile stress-strain behavior of Toughened Silcomp both with and without a joint. Though strength is decreased somewhat, the joint area remains tough.

Current Focus

Activities/developments currently being pursued include the following:

1. Demonstration of a composite system with the necessary oxidation/environmental resistance to survive the required 48,000-hour life of the shroud component.
2. Transition of composite fabrication technology to appropriate material vendors (Textron Specialty Materials and Carborundum Company).
3. Generation of a materials property data base using materials supplied by the vendors and tested at GE and ORNL.
4. Fabrication and rig testing of representative shroud components.▲

”

To the best of our knowledge, this is the first demonstration of tough CFCC joints.

”

Although the Application Assessment considered both shrouds and combustor liners, only the shroud application is being pursued currently.

Durable Filters

Hot-gas filter elements for advanced power generation

By Rich Wagner,
Babcock & Wilcox

"The level of mechanical durability exhibited by the currently available filters in field tests indicates that more rugged filters are required to meet the demands of large power generation systems.

"The B&W ERI division's expertise in filament winding has been utilized in the fabrication of program samples. The division will be the ultimate manufacturing facility for commercial filter element production.

The objective of this DOE/Morgantown Energy Technology Center (METC) program is to develop more durable hot gas filter elements for advanced power generation systems.

Background

Pressurized fluidized bed combustion (PFBC) and integrated coal gasification combined cycle (IGCC) systems are among the advanced coal-based energy cycles being considered for low-cost, clean power generation.

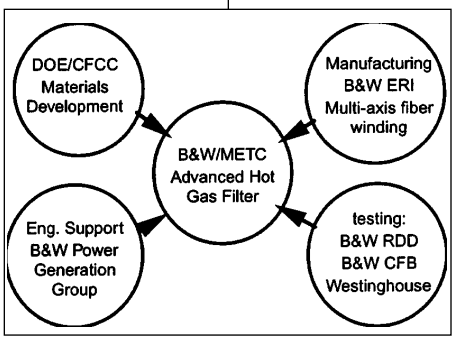


Fig. 1. Organization of DOE/METC Advanced Hot Gas Filter Program.

Hot-gas filters are required to remove particulates from the high-temperature turbine inlet stream in order to protect turbine components from excessive erosive wear and to meet clean air requirements.

The level of mechanical durability exhibited by the currently available filters in field tests indicates that more rugged filters are required to meet the demands of large power generation systems. Furthermore, long-term corrosion resistance of currently available filters has yet to be demonstrated in PFBC systems. The essential requirements of a composite material designed to meet the program objective for a toughened hot-gas filter include

- stable continuous fiber,
- rigid porous matrix,
- engineered fiber-matrix interface, and
- cost-effectiveness.

The key to achieving the goal of this program is to apply the composite technology developed under the DOE CFCC program to the special requirements of a toughened hot-gas filter.

Figure 1 illustrates the roles of the various contributors to this program. In addition to the DOE/CFCC materials development support, two Babcock &Wilcox operating divisions play key roles in the development and commercialization of an advanced hot-gas filter.

The B&W ERI division's expertise in filament winding has been utilized in the fabrication of program samples. The division will be the ultimate manufacturing facility for commercial filter element production.

The experience of B&W's Power Generation Group (PGG) in the design of advanced power systems including hot-gas filter systems provides valuable guidance to this program. PGG would utilize the composite filter elements produced by B&W ERI in the B&W Advanced Ceramic Tube Filter system.

A porous oxide-oxide composite system was selected based on the predicted chemical stability in advanced combustion environments.

In Phase I, porous composite fabrication technology developed under the CFCC program was transferred to the B&W ERI facility.

A modified filament winding process was used to fabricate porous composite preforms containing both continuous reinforcement fibers and chopped fibers. Initial testing performed on open end tubes demonstrated that an improved fiber coating process was required.

An immiscible liquid coating process developed under the CFCC program was implemented for the fabrication of subscale closed-end flanged tubes.

Four compositions of subscale filter elements were tested for 250 hours in the 1500 to 1625°F region of a 55 MW(e) circulating fluidized-bed combustor (CFB). One third of the samples in the CFB received a 90-psi ambient air back pulse at 15-min intervals to simulate the thermal fatigue produced by filter cleaning.

Compressive C-ring tests performed at 1600°F were used to assess the effects of the exposure and thermal fatigue testing on the mechanical properties of candidate compositions.

The results of these tests were used to select the composition for the fabrication of full-scale filter elements for testing in a PFBC simulator in Phase II of the METC program.

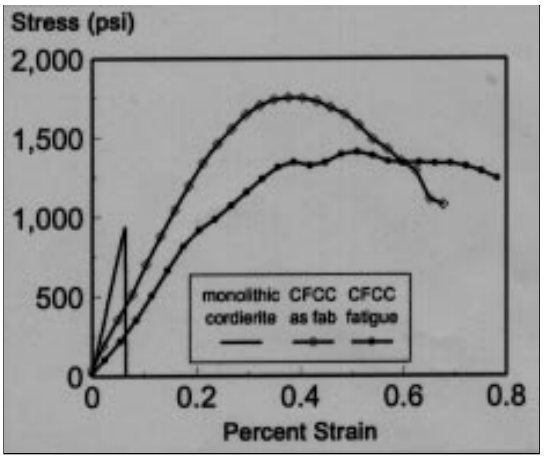


Fig. 2. The 1600°F C-ring results for CFCC hot gas filter element before and after the 250-hour CFB exposure/thermal fatigue test compared to monolithic cordierite filter.

The combination of both continuous and chopped fibers results in a very lightweight composite material with a bulk density in the range 0.8 to 0.9 g/cc compared to 1.4 to 1.9 g/cc for monolithic filter materials.

The combined effect of the lower filter density and the thinner tube walls results in significant potential weight savings in the filter system (about 10 lb per filter element or 60,000 lb in a 350 MW(e) plant).

Examples of the 1600°F failure behavior of the optimized B&W filter element before and after the CFB thermal fatigue test are shown in Fig. 2.

Figure 2 also includes the room temperature fracture behavior of a monolithic cordierite filter material. The observed brittle fracture is typical of monolithic ceramic materials.

In comparison to the monolithic material, the B&W composite filter exhibited relatively non-brittle failure behavior both before and after the 250-hour thermal fatigue/exposure test in the CFB. A photograph of the B&W subscale filter following the CFB exposure/thermal fatigue test is shown in Fig. 3.

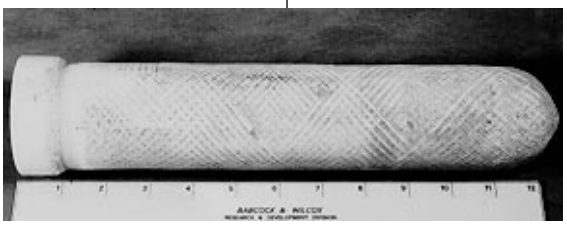


Fig. 3. B&W composite filter element following 250-hour CFB exposure/thermal fatigue test.

In the next work phase, full-scale filter tubes will be fabricated and tested in a PFBC simulator. Successful completion of this program is expected to lead to full-scale testing in a PFBC or IGCC demonstration plant.▲

”

The combined effect of the lower filter density and the thinner tube walls results in significant potential weight savings in the filter system.

”

Successful completion of this program is expected to lead to full-scale testing in a PFBC or IGCC demonstration plant.

3M's Composite Candle Filters

Ceramic Filters

By Dave Stinton and Rod Judkins, ORNL, and Bob Smith and Ed Fischer, 3M

> *"The extensive strain tolerance demonstrated by these composites led researchers to investigate the concept of fiber-reinforced hot-gas filters in 1986 when monolithic candle filters were observed to fail in a brittle fashion as a result of thermal or mechanical shock.*

Researchers at Oak Ridge National Laboratory (ORNL) have been funded since 1983 by the U.S. DOE Office of Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program to develop dense composite materials for use as heat exchangers in advanced coal-fueled gas turbine technologies.

The extensive strain tolerance demonstrated by these composites led researchers to investigate the concept of fiber-reinforced hot-gas filters in 1986, when monolithic candle filters were observed to fail in a brittle fashion as a result of thermal or mechanical shock.

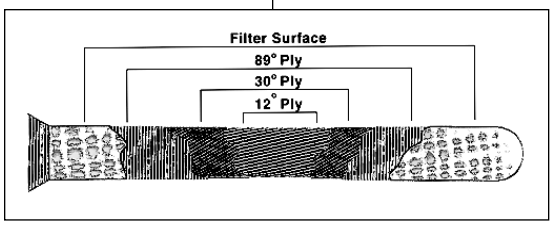


Fig. 1. First-generation 3M Company ceramic composite filter.

Initially, fibrous preforms about 1.5 cm thick (comparable to monolithic filters) were partially infiltrated to produce porous-filter materials.

Improved Shock Resistance

Thinner structures were developed in an effort funded by the DOE Morgantown Energy Technology Center (METC) Surface Gasification Materials Program to reduce the weight, back pressure, and thermal gradients experienced by the filters, and thus significantly improve the thermal shock resistance.

Several concepts of ceramic composite filters, including fibrous mats reinforced with ceramic fabric, were evaluated at ORNL, Acurex Corporation, and the Coal Research Establishment (United Kingdom). The results were so promising that several companies requested that ORNL fabricate full-size candle filters for testing and evaluation.

3M Contract

Because the fabrication of full-size filters at ORNL was impractical, the 3M Company was awarded a contract in FY 1989 by the AR&TD Materials Program through competitive bidding to produce full-size candle filters.

In the first quarter of 1993, the 3M Company completed the development of its first-generation ceramic composite candle filter. The first-generation filter (Fig. 1) was a filament-wound structure with three plies of Nextel 312, an alumina-boria-silica fiber, with a barrier layer of chopped random fibers on the exterior of the candle.

3M replaced the fibrous mat with a chopped fiber surface, which had a controlled pore size that would be easier to clean and prevent blinding. The binder for the filter is a silicon carbide matrix deposited by chemical vapor deposition (CVD).

A disciplined approach has been taken for the testing and demonstration of the 3M Ceramic Composite Filter. As part of the AR&TD Materials Program funded effort, two test campaigns were conducted at

Westinghouse Science and Technology Center.

First Test

The first test that involved two first-generation 3M filters was very promising but indicated a need for modification of the structure.

The most significant changes were the replacement of the filament-wound structure with a much less expensive tightly braided structure and the addition of an open-braided outer layer to prevent sloughing off of the filter surface.

Six of these filters were included in the second Westinghouse test, and all performed successfully. Tests were also successfully completed at the University of North Dakota Energy and Environmental Research Center.

The next phase was a demonstration of three filters at the Tidd PFBC Demonstration Project (see Fig. 2). Two of the three filters were broken as a result of an ash buildup and bridging phenomenon in which hardened ash spans the space between the filters and support structures. During cooling, this contracts, resulting in lateral forces that bend and eventually break the filters.

The filters were again improved by strengthening the flange area. Also, a better way to hold the filters in the tubesheet without damage was developed.

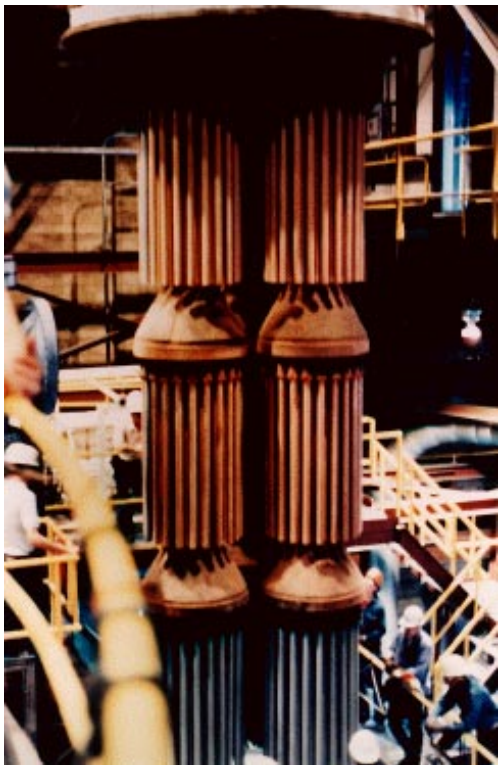


Fig. 2. Westinghouse advanced particle filter system at the Tidd Pressurized Fluidized-Bed Combustion Demonstration Project in Brilliant, Ohio

In a second demonstration at Tidd in which ash buildup and bridging did not occur, ten 3M Ceramic Composite filters survived the entire, 1000-hour campaign (see Fig. 3). Demonstration

Continued on page 19

Fig. 3. Ed Fischer examines 3M Ceramic Composite Filters after exposure in the Tidd plant (ash brushed from filter at right).

"Current demonstrations include nine 3M Filters in Foster Wheeler Energia's circulating fluidized- bed combustion plant in Karhula, Finland."

"These demonstrations are proving the viability of the 3M Ceramic Composite Filters and are moving this important technology toward a fully commercialized status."

Supporting Technologies

How Properties Change

Setting the Envelope for CFCC Development

By Paul F. Becher,
H. T. Lin, Karren L. More,
Metals and Ceramics,
ORNL

CFCC systems have sparked considerable interest because they can offer protection against unexpected failures as they exhibit large strains to failure and are resistant to in-service damage.

However, many applications for CFCC systems also demand extended service life at elevated temperatures while subjected to mechanical loads.

The exceptional performance of CFCCs is based upon maintaining the desired fiber strength and interfacial properties that lead to gradual fiber pullout that prevents catastrophic failure. So there is concern as to how interfacial and fiber properties may change during exposure to various environments and temperatures and what this might do to the ability of the composite to survive.

Answering questions about exposure to environments and temperatures

Insights

An underlying issue is to gain insights about modifying the CFCCs to further improve their service life. Under Task 2.0, the life of CFCCs subjected to applied loads (stresses) at various temperatures is being examined by H. T. Lin and P. F. Becher to provide the temperature-stress-environment conditions or working envelope for various CFCCs.

Collaborations with other subtasks that are examining the oxidation response (P. F. Tortorelli), the mechanical behavior (E. Lara-Curzio and S. Raghuraman), and the microstructural characteristics (K. L. More) for these composites allow us to both characterize the service life of CFCCs and to understand the various constituents of the composite that could be altered to extend its life.

Evaluation

The working envelope for a CFCC in the desired environment is evaluated by determining the lifetime of test specimens subjected to selected applied bending stresses at different temperatures.

To see this, let us examine the behavior of a composite consisting of a Forced Chemical Vapor Infiltrated (FCVI) SiC matrix containing ~ 43% Nicalon fibers in the form of plain weave cloth where the cloth layers are stacked with a 30° rotation between layers, and a low open porosity level (≤ 10%).

Before being infiltrated with SiC, a 0.3-µm carbon layer was applied by chemical vapor deposition (CVD) to the fibers to promote the desired fiber pullout. Some of the test bars were also sealed with a 40-µm CVD SiC external layer to cover and protect the

fibers exposed during the machining of the test bars.

Figure 1 reveals that the lifetime of this composite in air at each selected temperature decreases as the applied stress is increased. On the other hand, there is no limit in life when the applied stress is decreased below a certain level (~ 100 MPa here). In addition, the lifetime curve is shifted to shorter times-to-failure with increase in temperature.

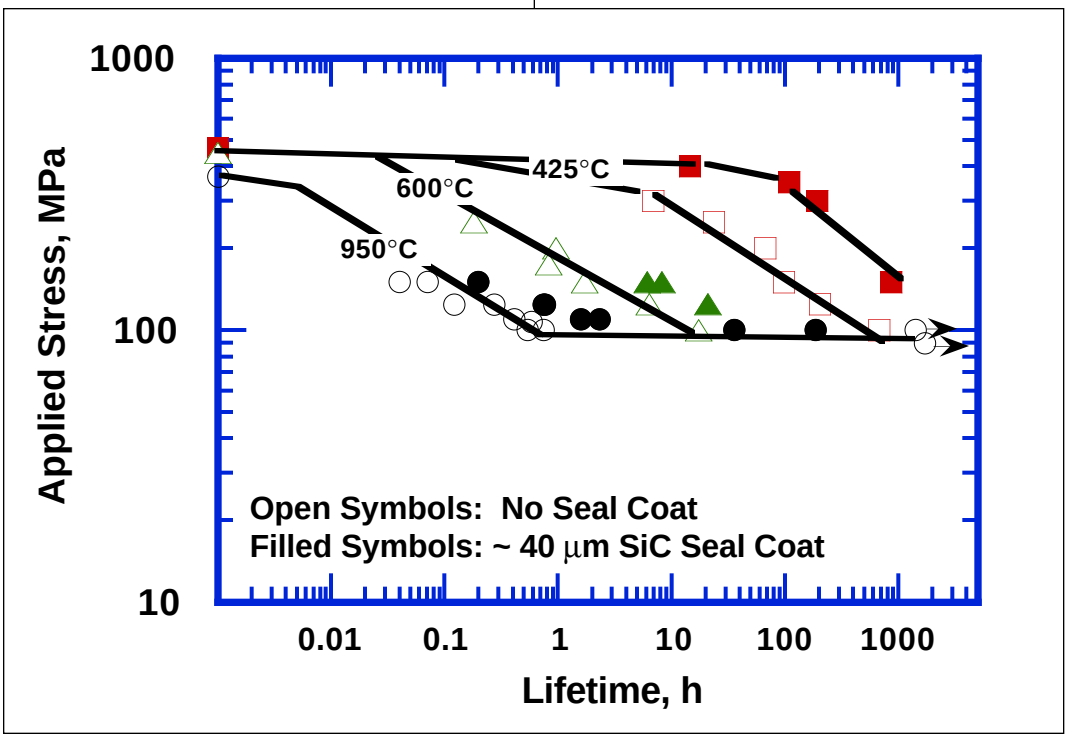


Fig. 1. In an oxidizing atmosphere, the life of a SiC matrix composite reinforced with carbon-coated Nicalon fiber cloth is a function of both the applied flexure stress and the test temperature.

Safe stress levels

Note also that the CVD SiC seal coat had no effect on lifetime except in tests conducted at 425°C. With these results, we can establish the maximum safe stress levels for the temperature range of interest that will ensure the life of the component under oxidizing conditions.

In the past, researchers had shown that similar composites could have limited life above 900°C due to the strong matrix–fiber interface formed by the oxidation of the fiber, its carbon coating, and the SiC matrix.[1] The transmission electron microscopy studies reveal that a thick silica layer is formed by the more rapid oxidation at 950°C of the fiber as compared to the SiC matrix, Fig. 2a. The white curved boundary indicates the position of the interface between the two brittle silica layers that have replaced the carbon interfacial layer.

This is the reason for the limited life seen for the current composite tested at 950°C at stresses > 100 MPa. This occurs when the applied stress is raised above 100 MPa as cracks form in the SiC matrix and the SiC seal coat which allow oxygen to penetrate into the interior of the composite.

Lower Temperatures

However, it was not clear what happens to the composite at lower temperatures where the fiber and matrix were not expected to oxidize. We do know that carbon materials, such as those comprising the fiber coating, oxidize at temperatures as low as

”

The working envelope for a CFCC in the desired environment is evaluated by lifetime of test specimen subjected to selected applied bending stresses at different temperatures.

”

With these results, we can establish the maximum safe stress levels for the temperature range of interest that will ensure the life of the component under oxidizing conditions.

300°C. Thus, one needs to determine what changes in the interfacial carbon coating and/or other constituents of the composite occur below 950°C and their role is in composite life.

Tortorelli's studies show that this composite does oxidize even at 600°C, and one step involves the loss of the carbon interface.[2] Researchers elsewhere have shown that Nicalon fibers can also oxidize at measurable rates at temperatures as low as 600°C, resulting in the formation of surface defects.[3]

> "Tortorelli's studies show that this composite does oxidize even at 600°C, and one step involves the loss of the carbon interface

Channel Formed

Transmission electron microscopy observations (Fig. 2-lower) of the composite tested at 425°C show that a channel is formed at the interface due to the loss of a portion of the carbon coating, which allows the fiber surface region to be oxidized.

Still others have reported that the strength of Nicalon fibers exposed to oxidizing conditions for short periods can be measurably degraded at 600°C,[4] probably due to the surface defect noted in ref. 2.

Applying Stress

At temperatures below 900°C in air, the steps leading to failure are initiated when the applied stress is sufficient (here ≥ 100 MPa) to generate cracks in the SiC matrix (and the seal coat).

This allows oxygen to reach the coated fibers. Next, the carbon fiber coating begins to be oxidized forming volatile CO (or CO_2) which can escape along the associated interfacial channels. However, this process is limited by the ability of the carbon monoxide formed to escape (i.e., if the partial pressure of CO (or CO_2) gets too high, the oxidation of carbon is suppressed). The use of thinner carbon fiber coatings can slow the oxidation process down by restricting the channel size through which the CO (or CO_2) escapes. Indeed, our studies show that composite life is improved when the thickness of the carbon layer applied to the fibers is reduced.

> "The use of thinner carbon fiber coatings can slow the oxidation process down by restricting the channel size through which the CO (or CO_2) escapes.

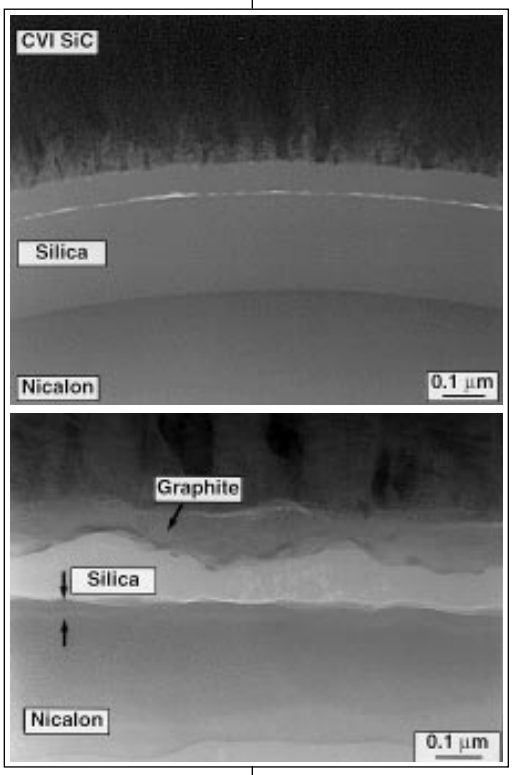


Fig. 2. Transmission electron microscopy studies of the CFCC samples tested reveal changes in the structure of the matrix-fiber interface region.
The upper picture shows that the graphite interfacial film is completely replaced by a thick brittle silica layer during testing at 950°C in air.
The lower picture shows that a micro-channel is formed in the graphite layer during tests at 425°C in air allowing the fiber surface to oxidize to form a silica skin.

Oxidation

However, the loss of the carbon layer would not result in failure at these lower temperatures, but its loss does allow the fiber to begin to oxidize. As oxidation of the fiber progresses, the strength of exposed fibers is reduced with time until some fibers start to fail.

If these processes continue, the composite will eventually fracture. Note that each of these steps is time- and temperature dependent, and the extent to which the fiber strength

must be reduced to cause it to fail is dependent upon the applied stress. This reflects the observed dependence of the composite's life on both temperature and applied stress.

Protecting

One can view the carbon coating as a means of protecting the fiber against oxidation at these lower temperatures. With the gradual loss of the carbon coating, the clock starts to count down to failure.

Then we must examine methods by which the composite life can be improved. Current studies are evaluating advanced fiber coatings, and the initial results show that some of these can provide substantial improvements in the life of such composites.

These collaborative studies establish not only the working envelopes for current CFCCs but also provide insight on ways to modify them to extend their performance.▲

References

1. R.D. James, R.A. Lowden, and K.L. More, *Ceramic Transactions* **19**,925–35 (1991).

2. P. F. Tortorelli, J. R. Keiser, L. Riester, and E. Lara-Curzio, pp. 51–54 in *CFCC Program Task 2 Bimonthly Progress Report for April–May 1994*, U. S. Department of Energy.

3. T. Shimoo, H. Chen, and K. Okamura, "Mechanism of Oxidation of Si-O-C Fibers," *J. Ceram. Soc.*, Japanese edition., **100**,918–24 (1992).

4. G. Emig and R. Wirth, "Tensile Strength of Silicon Carbide Fibre Bundles at Elevated Temperatures," *J. Mater. Sci.* **30**,5813–18 (1995).

"Current studies are evaluating advanced fiber coatings, and the initial results show that some of these can provide substantial improvements in the life of such composites."

CFCC Publications

■ Textron's Research & Development Contract Noted

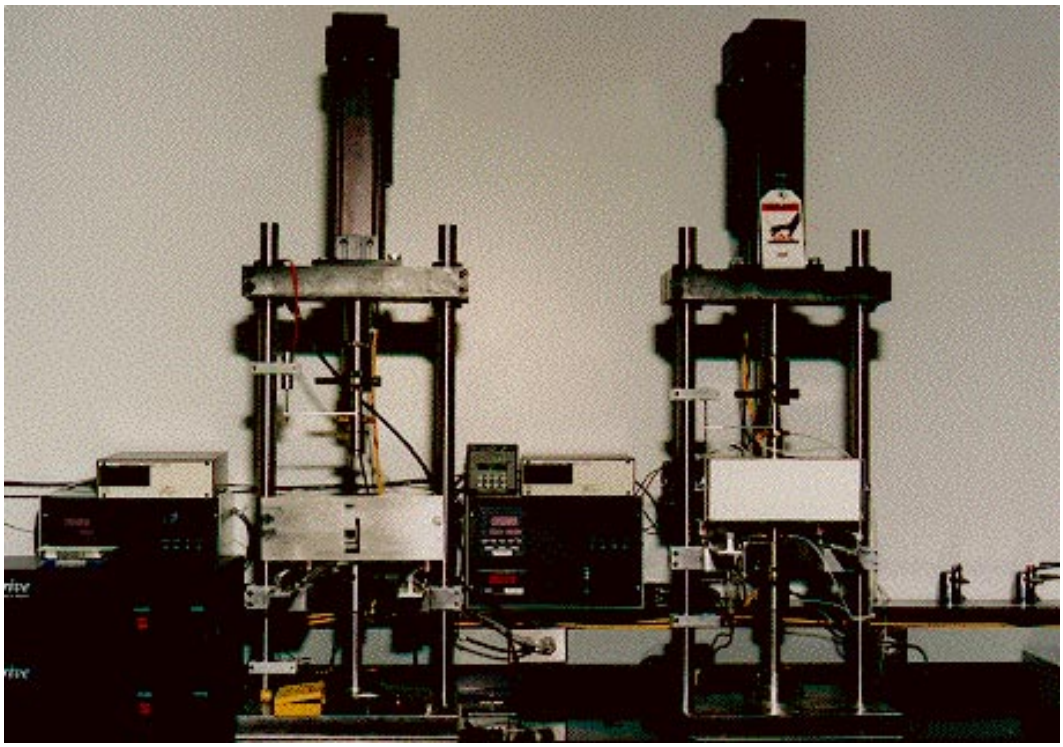
Textron Specialty Materials' winning a $4.2 million contract from DOE was noted recently in the newsletter Ceramic Industry. The contract is to continue to improve the efficiency and capability of CFCC processing methods for fabrication of components for industrial applications. The article noted that Textron has successfully demonstrated a process to make ceramic composite furnace tubes and gas turbine combustors.

■ Materials Research Society Publishes Proceedings

The Materials Research Society has published a new collection of symposium proceedings, *Ceramic Matrix Composites—Advanced High-temperature Structural Materials*. It was edited by Richard Lowden, Mattison Ferber, John Hellman, Krishan Chawla, and Stephen DiPietro. Papers in this 478-page volume were originally presented at the symposium "Ceramic Matrix Composites: Advanced High-Temperature Structural Materials" held at the 1994 MRS fall meeting in Boston.

The symposium's objective was to bring together researchers concerned with the various aspects of ceramic composites to stimulate interaction between the disciplines involved in successful utilization of these advanced structural materials. The symposium was organized such that papers concerning constituents—fibers and matrices—were presented first, followed by composite processing, modeling of mechanical behavior, and thermomechanical testing.

Two days were devoted to fiber-matrix interfaces in CFCCs. Talks were organized into four sessions: mechanical modeling, test methods, interface behavior, and modification and control. For information about purchasing the proceedings, which is MRS volume 365, please telephone (412) 367-3003 or Fax (412) 367-4373.



The Environmental Effects Testing Facility at Oak Ridge National Laboratory consists of six in-house-developed small universal testing machines. Each test frame has an electromechanical actuator with 2300 lb of capacity and 8 nm resolution, small igniter furnaces capable of 1400°C, a load train with self-aligning capabilities, and a chamber for conducting tests in a controlled environment up to 1200°C.

Environmental Effects Testing Facility

CFCCs Tested for Stresses

The selection of CFCCs for energy-related industrial applications, where component service lives are measured in thousands of hours, will be determined in great part by their durability and reliability under thermal and mechanical loading in harsh environments.

To investigate the simultaneous effect of stress, temperature, and environment on the long-term thermomechanical behavior of CFCCs, the DOE CFCC Program sponsored the development and construction of the Environmental Effects Testing Facility at Oak Ridge National Laboratory.

This facility consists of six in-house-developed small universal testing machines. Each test frame consists of an electromechanical actuator a capacity of 10,000 N and displacement resolution of 8 nm, igniter furnaces capable of 1400°C, a load train with self-aligning capabilities, and a chamber for conducting the tests in a controlled environment.

Although specimens with different geometries and gripping arrangements can be accommodated, typically 4-in.-long shoulder-loaded specimens are used. The test machines are interfaced to a personal computer for data acquisition and control.

The Environmental Effects Testing Facility was inaugurated in March 1996 with a series of long-term duration tests scheduled by the team formed by Dow Corning Corporation, Solar Turbines and Oak Ridge National Laboratory.

To obtain more information contact:
Edgar Lara-Curzio
Metals and Ceramics Division
Oak Ridge National Laboratory
(423) 574-1749
laracurzioe@ornl.gov
or
Peter F. Tortorelli
Metals and Ceramics Division
Oak Ridge National Laboratory
(423) 574-5119
tortorellipf@ornl.gov

“

Although specimens with different geometries and gripping arrangements can be accommodated, typically 4-in.-long shoulder-loaded specimens are used.

CFCC NEWS

This newsletter is intended to facilitate communication among industrial, government, and university researchers working on the CFCC Program.

Managing Editor
Gloria M. Caton
E-mail: mgc@ornl.gov

Newsletter Designer and Technical Writer/Editor
Tim Elledge
E-mail: x3x@ornl.gov

Suggestions and contributions are invited and should be sent to:

Gloria M. Caton
Oak Ridge National Lab.
1060 Commerce Park
MS 6480
Oak Ridge, TN 37830

Phone: (423) 574-7759
Fax: (423) 574-9888
E-mail: mgc@ornl.gov

This newsletter is prepared at the request of the DOE Office of Industrial Technologies by the Health and Safety Research Division at Oak Ridge National Laboratory, which is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy, under Contract DE-AC05-96OR22464.

A COMMUNICATION OF THE CONTINUOUS FIBER CERAMIC COMPOSITE PROGRAM

3M Ceramic Filters

Continued from page 13

of the current generation of filters continues under PFBC and gasification conditions in the United States, Europe and Asia.

Finland Test

Current demonstrations include nine 3M Filters in Foster Wheeler Energia's circulating fluidized-bed combustion plant in Karhula, Finland.

A demonstration of over 3000 hours duration has been completed in a gasification plant; no detectable degradation of properties occurred in this demonstration.

Commitments have been made for additional demonstrations in another PFBC and in at least two incinerator applications.

Discussions are in progress with respect to including 3M Ceramic Composite Filters in the Wilsonville Advanced PFBC facility. These demonstrations are proving the viability of the 3M Ceramic Composite Filters and are moving this important technology toward a fully commercialized status.

> ”
> *A demonstration of over 3000 hours duration has been completed in a gasification plant; no detectable degradation of properties occurred in this demonstration.*

New Agreement

In a related development, 3M has announced an agreement with BF Goodrich to produce ceramic composite products for 3M.

BF Goodrich will manufacture 3M Hybrid U-tubes used for industrial furnaces and the 3M Ceramic Composite Filters.

BF Goodrich has the largest CVD furnace in the United States, and this teaming of capabilities will dramatically increase the production capability of and improve the economics for the 3M Ceramic Composite Filters.▲

World Wide Web

CFCC Program on line

The CFCC Program is happy to announce that its home page is now available on the World-Wide Web (WWW) at:

http://www.ms.ornl.gov/cfcc/home1.htm

The CFCC home page is still under development. Information and links will continue to be added.

If you have suggestions for links relevant to the CFCC Program page, send them to mgc@ornl.gov.

We are also happy to announce that the *CFCC News* is available on the WWW through the CFCC Program home page. It can also be accessed directly at:

http://www.hsrd.ornl.gov/cfcc/newshome.html

Calendar

1996 Materials Research Society Fall Meeting.
December 2–6, 1996, Boston, Massachusetts.
Meeting chairs are Werner Lutze, University of New Mexico, (505) 277-7964, Fax (505) 277-5433, brbl@unmb.unm.edu; Karen Maex, IMEC, (32) 1628-1358, Fax (32) 1628-1214, maex@imec.be; Karl Sieradzki, Arizona State University, karl@icarus.eas.asu.edu.
URL: http://www.mrs.org/meetings/future_meetings.html

21st Annual American Ceramic Society Cocoa Beach Conference and Exposition.
January 12–16, 1997, Cocoa Beach, Florida.
Sponsored by the Engineering Ceramics Division of the American Ceramic Society.

2nd Industrial Energy Efficiency Symposium & Exposition.
February 25–27, 1997, Hyatt Regency Crystal City, Alexandria, Virginia.
Sponsored by the DOE Office of Industrial Technologies. The symposium will spotlight the way the "Industries of the Future" process, industry-government partnerships, and crosscutting technologies are helping U.S. industry address energy, environmental, and technology challenges. For registration, contact: Energetics, Inc., 7164 Gateway Dr., Columbia, MD 21046, Attn: Conference Services, Fax (301) 621-3329, E-mail: OIT.EXPO97@hq.doe.gov
URL: http://www.oit.doe.gov/News/expo97.html

99th Annual Meeting & Exposition of the American Ceramic Society.
May 4–7, 1997, Cincinnati, Ohio.
Sponsored by the Engineering Ceramics Division of the American Ceramic Society.