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CFCC NEWS

A COMMUNICATION OF THE CONTINUOUS FIBER CERAMIC COMPOSITE PROGRAM

CFCC Process Improvements Now Under Way

Textron Testing

By William Grant,
Textron Systems Corp.

The Textron Systems Corp. CFCC Program Team is developing and demonstrating processing methods for the fabrication of low-cost ceramic composite tubular components for use in commercial and industrial applications.

Textron's approach combines elements of such low-cost forming processes as ceramic slip casting, filament winding, and gas phase nitridation bonding.

The processing approach being pursued by the team combines elements of such low-cost forming processes as ceramic slip casting, filament winding, and gas phase nitridation bonding.

The Textron fabrication process is completely net-shape (after the CFCC green body is wound), requires only one step to effect matrix densification, and is capable of scale-up-to components that are up to three feet in diameter and twelve feet in length.

Industrial applications compatible with these low-cost, robust processes have been sought that will provide adequate testbeds for CFCC technology development and demonstration.

Two such applications are Hauck Manufacturing's immersion heater tubes for molten aluminum furnaces and Williams International's industrial gas turbine engine external combustor.

The team has been fortunate in that both of these applications have provided valuable early opportunities for field test and rapid feedback on component performance under actual operation or simulated operational conditions.

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Fig. 1. CFCC immersion tube.

> *"This process reacts the silicon powder with nitrogen, creating a matrix of silicon nitride to bond the silicon carbide powders and fiber.*

> *"CFCC heater tubes were installed in a test furnace at Doehler-Jarvis, Toledo, Ohio, a production die casting house.*

In the Textron CFCC process, an aqueous-based slurry of silicon carbide powders and silicon metal is applied to a plaster-surfaced, segmented mandrel during filament winding of a +/- 30° array of Textron's 0.0056-in.-diam SCS-6 silicon carbide monofilament.

After winding and air drying, the composite green body is placed in a sealed furnace and heat treated in a nitrogen atmosphere. This process reacts the silicon powder with nitrogen, creating a matrix of silicon nitride to bond the silicon carbide powders and fiber.

During the first half of Phase II, component development activities resulted in the establishment of baseline tooling and composite processing procedures for an immersion burner tube design consisting of a 5.5-in. const-diam, 33-in.-long, closed-end tube with a 0.25-in. wall thickness (Fig. 1).

Integral with this closed tube was a tapered attachment flange for assembly to the burner head. Over 20 of these tubes were fabricated during this period for process development and subscale/bench testing. Following these efforts, CFCC heater tubes were installed in a test furnace at Doehler-Jarvis, Toledo, Ohio, a production die casting house.

In parallel with the immersion heater work, the baseline CFCC process for an 11-in.-long, tapered "bottle-shaped" combustor component was established (Fig. 2).

The external combustor design necessitates a 1-in. diam at the fuel injector end and a 4-in. diam at the exit end. The baseline process yielded a component with a wall thickness of 0.170 in. Due to the small diameter at the fuel injector end of the component, a 0.003-in.-diam silicon carbide monofilament, SCS-9A, was used for this application. Following the fabrication of process development articles, a CFCC combustor component was supplied to Williams International for burner rig testing.

Two 10-h tests have been completed, and combustor temperatures up to 2400°F have been experienced. This first round of testing has been suc-

Fig. 2. CFCC external combustor component.

**Fig. 3.
Close-up of
baseline combustor surface.**

cessful, although there appears to be a need to optimize monofilament reinforcement architecture in the nozzle area of the combustor tube to maximize strength and toughness in this region.

Textron is trying to maximize CFCC materials properties in the highly stressed nozzle region of the combustor so that a new battery of SCS-6/NBSiC new components can be subjected to more extended (>100 h) burner rig test with a high degree of confidence that they will survive successfully.

The first series of field tests on a six-burner set of CFCC immersion tubes was completed at teammate Doehler-Jarvis Die Casting last year. Here again, the outcomes of the field tests were largely successful, with several CFCC burners lasting up to 28 weeks of cyclic exposure in an environment that involved exposure of the CFCC burners tubes to both molten aluminum and high-temperature gas combustion conditions.

This compares very favorably with the one- to four-week lifetimes that are typically observed with monolithic ceramic immersion tubes. However, two CFCC burners failed after approximately four weeks of exposure, although we believe the causes for these premature failures have been identified.

Two primary problem areas seemed to affect burner component durability: (1) low and, even more important, variable fiber content (distribution) within the tube wall cross section and (2) wall thicknesses that are greater than desired and highly variable.

To address these issues, the combustor can component configuration was used to evaluate alternative ceramic slurry formulations, improved fiber/slurry process procedures, and improved filament winding programs. The use of the combustor component for these evaluations allowed shorter processing time and reduced materials input per experiment.

The baseline combustor process, which was used to fabricate the Williams test article, has produced components with a nominal wall thickness of 0.170 in. More important, the fiber crossover configuration results in wall thickness variations from 0.135 to 0.205 in.

Compounding this large thickness variation within the part is a corresponding variation in fiber volume percent, from an estimated 10% at the crossovers, to ~3% in the "picture window" areas framed by the crossover pattern (Fig. 3.)

Alternative winding programs were evaluated that would result in a better distribution of fiber throughout the part. The result of these efforts was a component with a nominal 0.150-in. wall and a thickness variation of only +/- 0.015-in.

In addition to these trials, changes to the ceramic slurry formulations have been made in an attempt to slow the

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Alzeta Corporation Research

Radiant Output

Next Generation, High-Efficiency, Low-Emission Burner Products

By Forrest Long, Alzeta Corporation

As a part of the continuation of Phase II of the CFCC program, Alzeta Corporation, Santa Clara, California, is working as a subcontractor with DuPont Lanxide Composites (DLC) to create next generation, high-efficiency, low-emissions burner products.

Alzeta currently produces radiant burners for use in a wide range of applications from Industrial/Commercial to Residential markets, including warm air furnaces, plastics and paper dryers, residential and commercial water heaters, process heaters, fire- and water-tube boilers, and volatile organic chemical thermal oxidizers.

Increased radiant output is most significant in markets where direct radiative infrared (IR) heating is employed to heat, process, or dry a load. Examples of such applications are drying and curing of paints, epoxies and other coatings, paper, and textiles.

Increased radiant output would result in significantly enhanced process throughput and/or efficiency with reduced energy input requirements and correspondingly reduced emissions, generating the benefits of savings on fuel costs, reduced pollution, and decreased energy use.

The main requirement for a CFCC screen-enhanced IR burner will be durability with respect to both thermal shock and physical impacts. To achieve this, DLC and Alzeta have been working together on a SiC/SiC (CVI matrix) CFCC screen, to be placed as a reverberatory surface above one of Alzeta's burners.

The underlying principle is that the CFCC screen will protect the surface of the burner, while also increasing both the surface temperature and the radiant surface area of the burner system. The result is that a much higher portion of the energy put into

> *"The CFCC screen would protect the surface of the burner, while also increasing both the surface temperature and the radiant surface area of the burner system. The result is that a much higher portion of the energy put into the system as fuel is released as usable radiation.*

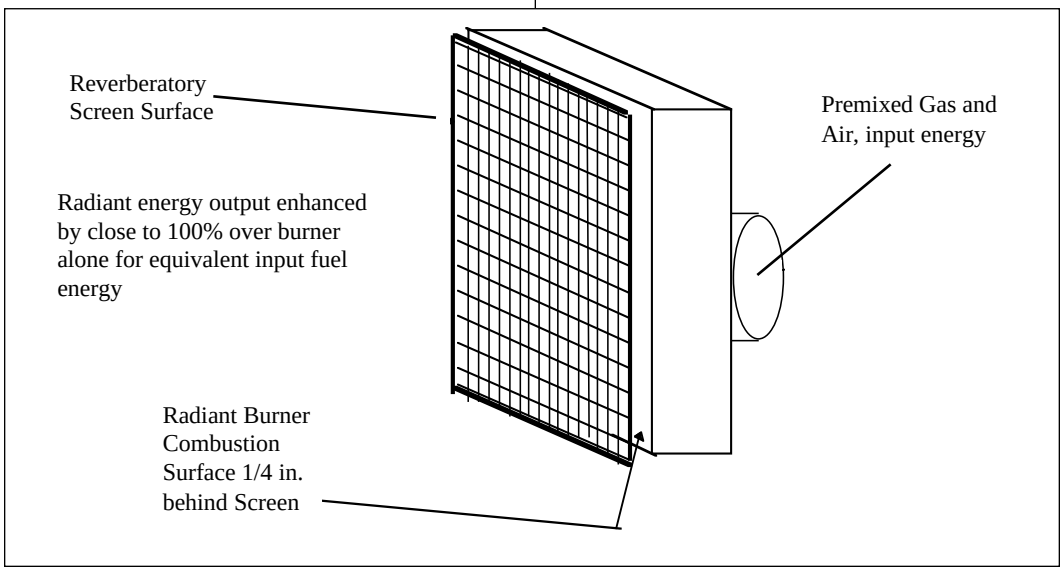

Fig. 1. Schematic diagram of one panel of a multi-panel unit utilizing the CFCC screen product as a reverberatory surface taking advantage of thermal stress resistance and resilience of composite in harsh environments.

the system as fuel is released as usable radiation.

The geometry of the radiant reverberatory screen and burner is shown in Fig. 1. Early tests at Alzeta indicated that this was a very promising method of producing an increase in the radiant portion of the energy released from the burner, as reported in the Summer 1993 issue of *CFCC News*.

Testing Geometries

Following this design concept then, Alzeta has been testing different screen and burner geometries in their combustion lab. The screens have been supplied and analyzed for thermal and oxidation stresses by DLC and tested in a combustion environment for both initial and aged IR radiant performance by Alzeta.

The results of all of these tests have been quite promising. The radiant efficiency of the burner screen system seems to run nearly double that of a baseline Alzeta radiant burner product without the screen. These results are summarized in Fig. 2.

The performance enhancement does not seem to be significantly affected even by use for 1000 h on a cyclic test rig at 6–8 on/off cycles per hour. Reports from DLC indicate that the SiC matrix is not significantly damaged after such tests as well.

The latest design iteration includes an Alzeta Pyromat MF® metal fiber burner with a SiC/SiC open mesh woven screen with a sinusoidal cross-section mounted directly above the surface of the burner.

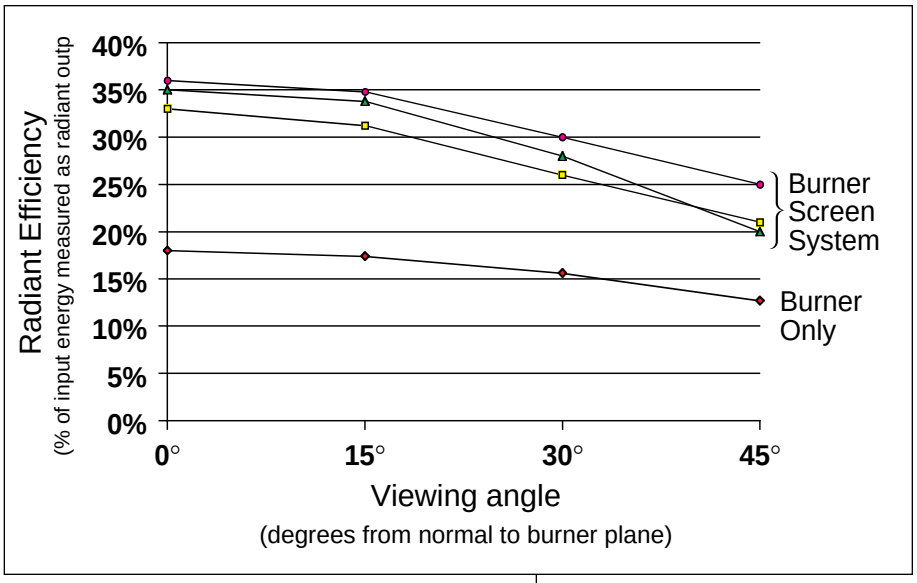

Figure 2. Radiant output and efficiency testing. Burner firing at 100 MBtu/hr-ft.

The pleats in the screen provide enhanced structural resistance to physical impact damage and increased radiant surface area. Both of these effects present improvements over the previous screens and further increase the marketability of the burner/screen system.

A major goal for the project now is the development of a salable product and the introduction of that product into the market for both initial field tests and commercial sales. This burner screen system has already been demonstrated to one prospective customer for use as part of a scientific calorimetry device. The data from that demonstration (Table 1) were positive, and all customer-defined

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Date	S. F. R. MBtu/h-ft2	Separation inches	mV meas.	Meas.Flux kW/m2	Rad. Eff. % at VF=1	VF	VF ratio	scaled flux
8-15-96	150	15.0	4.5	43	29.4	.310	3.04	130.7
8-15-96	152	12.0	6.2	59	26.4	.413	2.27	133.9
8-15-96 [a]	---	12.0	3.2	30	---	.413	2.27	68.1
8-15-96 [b]	131.1	11.81	10.56	100	27	.897	1	100
8-19-96 [c]	137	12.0	5.4	51	25.4	.413	2.27	115.8

Table 1. Burner test results summarized.

[a]Test point for determining minimum stable burner operation heat flux.

[b]Theoretical target point with calculated surface firing rate required to generate 100kW/m2 at 27% radiant efficiency on a 1.6 m x 1.6 m burner array with 300 mm (11.81 in.) separation between burners and sample.

[c]Secondary data point taken later with screens moved closer and higher excess air.

How CFCCs Have Changed

Charting Progress

By Bill Werst, USACA

"Today, affected primarily by consolidation and corporate redirection, USACA stands at 18 member companies."

"In an oft quoted 1984 Department of Commerce report on the global future of Advanced Ceramics, the market by the year 2000 was estimated to be $5.9 billion. . . ."

Ever since the inception of DOE's CFCC program, there has been a cooperative and synergistic relationship between DOE and the United States Advanced Ceramics Association (USACA), the industry trade association that represents the people and companies working on CFCC developments.

USACA History

In October 1985 fourteen charter member companies came together in Washington, D.C., to form USACA. In the ensuing 11 years USACA membership has fluctuated from that initial 14 to a high of 31 companies in 1987. Today, affected primarily by consolidation and corporate redirection, USACA stands at 17 member companies.

In the early days of USACA, members pursued market opportunities in sectors as diverse as automotive, aerospace, defense, electronics, machine parts, and perishable tooling. Members have always included raw material producers, structural and electronic parts producers, and structural parts users.

Much of USACA's early activity focused on gathering information from the member companies on the progress of their research and development activities. That information on the definition, economic advantages, uses, and applications of advanced ceramic materials was disseminated to policy makers and the general public. In some rare cases commercial products were being sold.

Although initially founded to promote the interests of U.S.–owned companies against competition from Japan and Europe, USACA's bylaws were eventually modified to make membership available to all companies with production capability in North America. This was done when many of the original member companies were being acquired by European and Japanese firms.

Advanced Ceramics—1984

In an oft quoted 1984 Department of Commerce report on the global future of Advanced Ceramics, the market by the year 2000 was estimated to be $5.9 billion with $3.5 billion being in electronic ceramics and the rest in various structural ceramic applications. That same report reached the following conclusions:

- Japan dominates electronics.
- Japan dominates supply of advanced ceramic powders.
- R&D effort is larger and more organized in Japan.
- Japanese products have better initial cost/performance.
- Japan invests for the long haul.
- Japan is superior at developing & implementing commercial manufacturing processes.
- The United States will fall further behind.

Advanced Ceramics—1996

By 1996 several things had changed that brought that 1984 forecast into question:

- The competitive position of U.S.–based ceramics producers was enhanced by the reduction in the exchange rate for the yen—from 150 to 110 yen to the dollar.

- Japan's success with automotive turbochargers has not transferred to the United States even in Japanese brands.
- The environmental market for catalytic converters and diesel exhaust filters is a U.S.-driven success story.
- Corporations have different R&D payoff patience:

  U.S., European Corporations—2 to 5 years.

  Japanese Corporations—10 to 15 years.
- A chicken and egg situation exists with non-oxide raw materials. The costs are too high because there is not a large enough demand, and the demand is low because it depends on lower-cost parts that are, at least partially, dependent on low-cost raw materials.
- Machining and grinding costs are a significant portion of the cost of high-performance parts.
- The electronic ceramic market growth has slowed as producers find other ways to manage their thermal problems.

Severe Challenges

In 1996 USACA has successfully faced severe challenges brought on by the budget-cutting climate in Washington. Despite these challenges, USACA has been instrumental in securing congressional support for several specific programs.

It has accomplished this by serving as the primary forum for industry/federal government interaction in advanced, monolithic and ceramic matrix ceramics.

Throughout its history, USACA has spent much of its time educating policy makers in the Executive and Legislative Branches of government on the advantages and applications of advanced ceramics and advocating positions of interest to the industry on legislative and regulatory proposals. In particular USACA urged Congress to sustain funding for the Clinton Administration's PNGV Program, the Department of Energy's Office of Transportation Technology's Propulsion Materials programs for both automotive and heavy duty vehicles, and the Office of Industrial Technology's Ceramic Turbine Retrofit and the ATS programs.

Industries of the Future

Additionally, USACA is heavily supporting the crosscutting role of advanced ceramics in allowing the Industries of the Future to reach their energy efficiency and pollution reduction goals. Also, USACA activated a grass roots effort to prevent the Congressional budget hawks from eliminating the DOE Offices of Energy Efficiency and Fossil Energy.

For example, a report published by the Department of Defense (DoD) claimed that the U.S. was not vulnerable to shortages of key advanced materials. However, it is clear to the U.S. advanced materials industrial base that these new materials are being used in DoD systems and system upgrades at a slow pace.

In spite of the DoD report, USACA was instrumental in getting language inserted in the FY97 DoD Authorization Bill signed into law by the President that instructs the Secretary of Defense to institute a materials insertion program in the military services. The plans for this directed program are to be submitted to Congress by April 1, 1997.

1997 and Beyond

In 1997 USACA is planning to conduct a study for DOE to determine where government-supported R&D on advanced ceramics has contributed and may in the future contribute to energy efficiency and pollution prevention in the Industries of the Future market segments. The study will define a roadmap for industry/government cooperation to continue integration of advanced ceramics into the

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A Message from the Program Manager

A number of important events have taken place since our last newsletter was published: several meetings, many accomplishments, lots of budget battles, and much progress in the program.

We are currently in the middle of the fiscal year 1998 budget process. So far, things are going smoothly and we are hoping to receive the budget that we requested. Regarding accomplishments, we have begun some longer term testing of components and several components will be produced in larger quantities (at least 50) in the coming year.

We just concluded our annual working group meeting in San Diego. From all accounts it was very successful, with two days of speakers and a tour of Solar Turbines' facilities. In addition, we have several important meetings coming up.

The participants of the CFCC Program will be taking part in the 21st Annual Conference on Composites, Materials, and Structures in Cocoa Beach January 26–31. On Monday afternoon the 27th, there will be an Overview of Government Ceramic Programs; on Wednesday the 29th, there will be a full day of presentations on the DOE CFCC Program; on Thursday morning the 30th, there will be presentations on the DOE Program on Joining of Ceramics and CMCs; and on January 28 a session is scheduled on Ceramic Pressure Equipment.

The Office of Industrial Technologies' big event will be February 24–27, 1997. This is the date of OIT's 2nd Annual Exposition and Symposium. There will be a session on the CFCC and Advanced Industrial Materials Programs from 2:00–3:30 p.m. and a session on Cogeneration from 4:00–5:30 on February 25. In addition to the sessions, the exposition will include an exhibition hall with 90 booths, including participants from AlliedSignal, Alzeta, Babcock and Wilcox, Dow Corning, Du Pont Lanxide, Oak Ridge National Laboratory, and Solar Turbines. General Electric is one of the cosponsors of the meeting. We hope that many of you will be able to attend this symposium.

Please feel free to contact me any time. I can be reached by telephone at (202) 586-3646, and through the Internet at merrill.smith@hq.doe.gov.

With my regards,

Merrill Smith

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Model Applied to CFCC Designs

Macro Mechanics

By John Kibler,
Materials Sciences Corporation

Supporting Technologies

The supporting technologies task of the CFCC program has been supporting the development of a mini mechanics based material model for predicting the properties and performance of CFCC components.

This model has been reported at annual reports and was featured in *CFCC News* No. 5, pp 12–15. The model has been applied to the development of several CFCC material components under the CFCC program, with excellent success.

Materials Sciences Corporation (MSC) has been applying the analytical model to assist both Amercom and Textron in their material/component development efforts.

Primary Benefit

The model's primary benefit to the materials and component developers is that it can provide early guidance to the development efforts.

There is a continuing need for simultaneous material and component design with materials that have not been fully characterized.

In general, limited constituent property data are available, but usually no composite properties are available for the designer of the component.

Materials Sciences Corporation (MSC) has been applying the analytical model to assist both Amercom and Textron in their material/component development efforts.

Although the model was still being developed, it was anticipated that some benefit could be derived from applying its capabilities to the Amercom and Textron material/component development efforts.

Model Background

The analytical model is composed of a number of modules which permit storing a database of constituent fiber, matrix, particle, and layer properties for analysis within the code. The user supplies definition of the fiber type and volume fraction, void volume fraction, and particulate type and volume fraction, as well as the orientation of each layer within the composite material.

The code then computes the thermo-structural properties of the composite as specified and permits the user to apply loading conditions and to predict when failure will occur. In addition, the code will predict the first fiber and first ply strengths of the composite material. All analyses may be conducted at a specified temperature, and temperature may be applied as a loading condition to the material, along with a general set of applied loads.

Prediction Ability

Another feature of the model, and one which is very useful to the materials developer, is its ability to predict the nonlinear stress-strain behavior of the composite based upon the fiber and matrix statistical strength characteristics. The matrix is assumed to microcrack when stress levels within the

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matrix exceed the lower Weibull strength levels. These micro-cracks result in localized debonding at the crack/fiber/matrix interface, with the potential for partial or complete fiber debonding.

The influence of the micro-cracking is a localized softening of the composite, which is accounted for in the model by integrating the localized properties through the volume of the test specimen.

The micro-cracking feature of the model required that the user supply such parameters as

- fiber and matrix Weibull strength characteristics,
- fiber/matrix interface strength,
- fiber/matrix interface friction coefficient after debonding,
- strength between 0- and 90-degree plies,
- loading orientation relative to fiber axial direction, and
- loading increments to be applied.

The capability of the model is demonstrated in Fig. 1, where predicted and measured unidirectional behaviors are compared. This type of data comparison has also been achieved with cross-ply laminated ceramic matrix composites.

The early application of the model to component/material design identified that there were essentially

- no composite properties available,
- few definitions of component requirements as a ceramic composite,
- limited constituent property data available, and
- lots of enthusiasm for applying the model and assisting the material manufacturers.

The approach in each case was the same:

- Assemble known constituent properties.
- Identify the principal structural requirements.
- Determine the sensitivity of the component to material construction parameters that could be controlled by the material manufacturer.
- Identify the desirable constructions.
- Recommend material configurations to be fabricated.

Amercom Hot Fan

The original fan assembly being used in hot gas furnaces is fabricated from a complex, heavy metal casting. It is a single piece, and weighs nearly 150 lb. The fabrication of a single piece unit in a CFCC material would be extremely complex because of the fiber management that would be required.

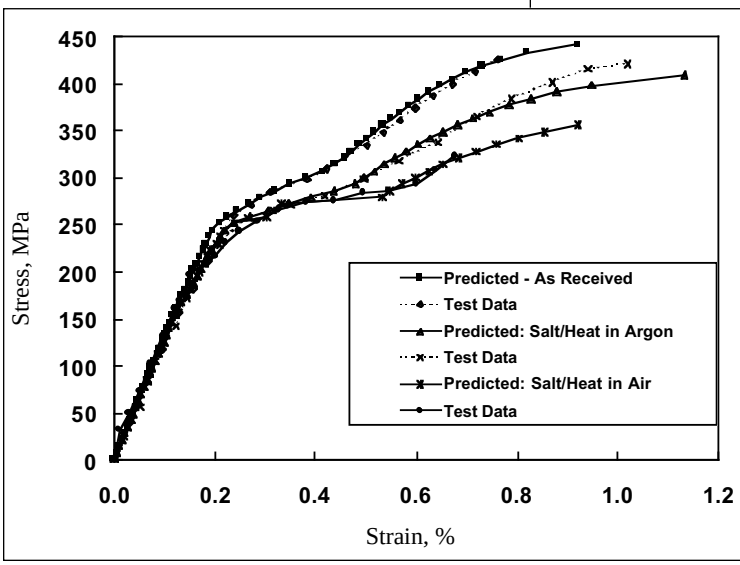

Fig. 1. Predicted and measured unidirectional stress-strain behavior of Nicalon/CAS subjected to several environmental conditions.

Consequently, MSC approached the problem by totally redefining the fan configuration. To avoid extreme costs in fiber handling and placement, the approach was to utilize a basic ceramic fabric and to create three full blades which would be attached at the shaft hub.

The basic blade is shown in Fig. 2. The construction requires that the blade be fabricated with two twists. Variations in length of the twist or of the blade area produced different stresses in the material. Lower stresses result from a long twist length, but better fan performance is achieved with a long blade area, hence short twist length.

The final configuration was a compromise between blade area and twist length. Stress analysis showed that the material fiber stresses were on the order of 15% of the fiber ultimate, thus stresses were low.

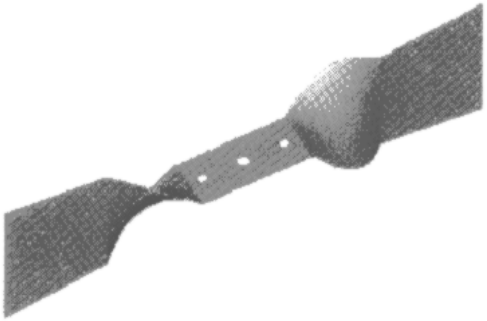

Fig. 2. Single ceramic composite fan blade.

Natural frequencies were computed and indicated that the fan operating speed fell between the first and second natural frequency of the blades. The fan natural frequencies are a strong function of the blade stiffness. Because MSC was predicting all composite properties using assumed constituent properties, it is important that the actual blades be tested for structural properties to confirm the analysis input. Additionally, blade natural frequency should be measured to ensure that the operating frequency is away from a natural frequency.

The final blade configuration is to be attached to a hub and shaft as shown in Fig. 3. The resulting fan weight is about 10 lb. This is to be compared with the metal design which is about 150 lb. This significant weight savings offers the potential for the fan installation to require one person, rather than the current two persons, and thus installation costs will be reduced.

The assembly shown in Fig. 3 is currently in fabrication at Amercom. Single blades are being produced, and will be assembled into the final fan assembly after fabrication.

Although stresses were not a governing factor in this design, the analyses showed that the trade-off between twist length and blade length could be utilized to select a geometric configuration for the application.

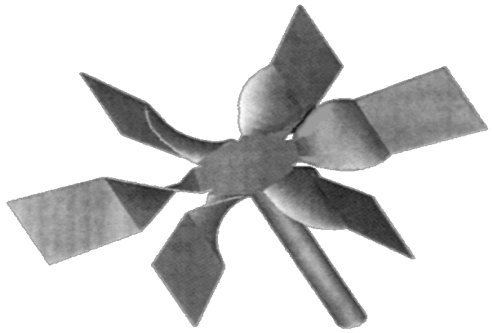

Fig. 3. Computer rendering of assembled ceramic fan.

Textron Immersion Heater Tube

The immersion heater tube for aluminum re-heater furnaces must withstand repeated cycles of applied temperatures. The inside of the tubes are subjected to flame temperatures, and structurally, the tubes must be capable of withstanding handling during assembly and opening of furnaces.

The material design and support evaluated a number of material construction parameters, including fiber/matrix interface properties, fiber volume fraction, fiber orientation, and residual stresses after processing. The primary output from the analytical

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Lower stresses result from a long twist length, but better fan performance is achieved with a long blade area, hence short twist length.

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> *"It is expected that increasing the fiber volume fraction will provide both a stronger and more "ductile appearing" material behavior, which will be capable of withstanding the severe gradients being developed within these furnaces.*

study was that the intended fiber volume fractions were so low, and the matrix modulus so high, that the fiber orientations have an extremely small influence upon the composite stiffness and strength properties.

It was likewise shown that the fiber/matrix interface strength which Textron was achieving was well over a threshold level required to initiate a relatively smooth stress-strain response for the unidirectional material.

Important Result

Another important result was a definition of a minimum fiber content required to eliminate a brittle stress-strain response. Figure 4 shows that one can expect a brittle jump at first matrix cracking stress levels for materials with fiber volume fractions less than eight percent. This establishes an eight percent minimum target for the material development efforts.

Based upon the analytical studies, the fiber winding angles were established to achieve good mandrel coverage and good coverage over the closed dome end. Hoop fiber wraps are to be included both to provide increases in hoop strength and to provide additional consolidation of the angle-ply layers so that the fiber volume would be increased. The target eight percent volume fraction fiber content has been adopted as a material goal.

MSC also investigated the potential start-up stress levels in the immersion tube during operation. Severe start-up gradient conditions were postulated, and analyzed assuming that the tube could be started while immersed in aluminum at room temperature.

These conditions, coupled with the maximum flame temperatures occurring at the aluminum/air interface, resulted in very severe strains being predicted in the tube wall.

Studies are continuing on this subject, with efforts being directed at defining actual severe start-up conditions as well as potential changes in burner location to alleviate some of the severe conditions.

Fracture Surfaces

Initial tubes have been field tested, with both successes and tube cracking being evidenced. However, the initial tubes tested all had fiber volume fractions that were on the order of two percent, and the fracture surfaces indicated little or no presence of fibers on the surface (see Fig. 5 on next page).

It is expected that increasing the fiber volume fraction will provide both a stronger and more "ductile appearing" material behavior that will be capable of withstanding the severe gradients being developed within these furnaces.

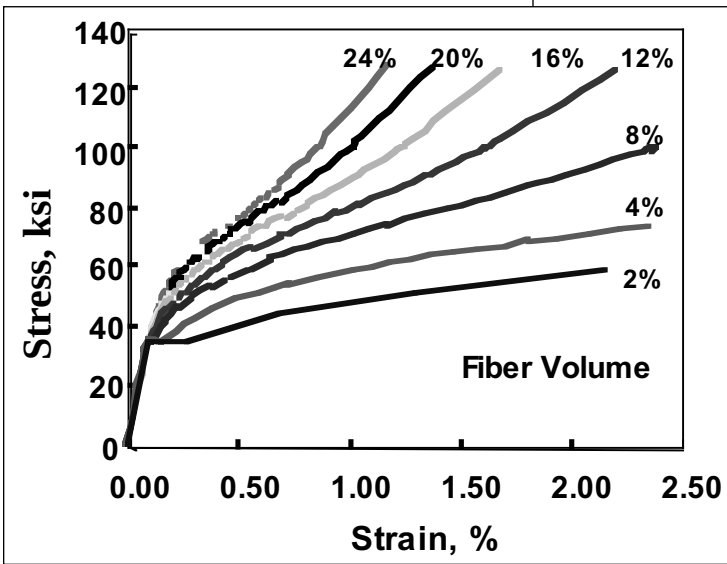

Fig. 4. Influence of fiber content upon stress-strain response on Textron's material.

Fig. 5. Section of completed immersion tube.

Summary

The analytical modeling tool that has evolved under the supporting technologies task is sufficiently well developed to permit good engineeringdecisions to be made relative to material and structural configurations definitions for CFCC components.

The model has provided good direction for the development of several components, and in continuing applications, it provides confidence that material behavior can indeed be predicted with relative accuracy, given basic constituent properties and material construction parameters.

As further confidence in the model is developed, other applications will be identified for which the modeling efforts can reduce the time and effort required to develop an appropriate material and component geometry for CFCC components.

Ultimately, the goal is for the analytical modeling capability to be available for both component designers and material fabricators, such that the number of experimental cycles needed to bring a component to market will be drastically reduced.▲

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CFCC Publications

■ CFCCs Featured in *Chemical Engineering* Magazine

James Wessel, president of Wessel and Associates in Oak Ridge, Tennessee, authored a comprehensive look at the state of CFCC research and development programs for the October 1996 issue of *Chemical Engineering*.

The article, featured as the publication's cover story, notes that CFCCs have solved the brittleness problem associated with traditional ceramics and explains that their resistance to heat, erosion, and chemical activity make them excellent candidates for use in the chemical process industries.

Also discussed in the article is the variety of applications for CFCCs, including pump components, gas turbines, radiant burners, gas filters, heat exchangers, furnace fans, and waste incinerators. ▲

Environmental Effects: Comprehensive Characterizations

High-Temp Effects Studied at ORNL

Influence of Environments on Properties and Lifetime of CFCCs

By P.F. Tortorelli, E. Lara-Curzio, K.L. More, H.T. Lin, J.R. Keiser, M.K. Ferber, and P.F. Becher, Oak Ridge National Laboratory

Industrial applications of CFCCs span a broad range of high-temperature environments. Conditions of relevance include temperatures of 300–1400°C, high pressures, thermal cycling, and a wide variety of possible environmental reactants such as air, H_2O, H_2S, HCl, alkali species, ash/char deposits, or molten metals.

This wide variety of conditions complicates any attempt to generally assess high-temperature environmental effects of a ceramic composite being considered for a broad spectrum of industrial applications. However, it is typical to first evaluate environmental susceptibility in the presence of oxygen as many composites are exposed to this species either during processing or service.

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Furthermore, because composites present numerous sites and pathways (multiple phases, interfaces, and extended defects) for reaction with environmental species, exposures in high-temperature air or oxygen often are used to determine the most likely ways other reactive species can also interact with the various solid constituents (through cracks, along particular interfaces, etc.).

Subsequently, depending on the results from these studies and any particular targeted applications for the composite, more complex exposure schemes are utilized. This essentially is the approach being used at ORNL for comprehensive characterization of high-temperature environmental effects.

The process starts with establishment of general trends for a particular composite system based on rather generic conditions as appropriate for a given composite, (dry air, oxygen, added H_2O) and, if needed for a particular use, then moves toward in-house laboratory facilities or external test beds capable of simulating application-specific environments.

The first part of such efforts focuses on examination of the underlying processes of environmental degradation through thermochemical stability considerations, experiments, microstructural and mechanical characterization, and modeling.

Exposures in controlled atmospheres are used to (1) establish operating envelopes, (2) provide data relevant to predicting materials behavior, (3) evaluate new or modified oxidation-resistant interfaces, and (4) examine the effectiveness of protective external coatings (seal coats).

Over the past few years, environmental effects work at ORNL has principally involved thermogravimetric analysis (TGA); microstructural characterization by scanning and

transmission electron microscopy (SEM/TEM); and mechanical testing using flexure, tensile, and C-(O-)ring approaches.

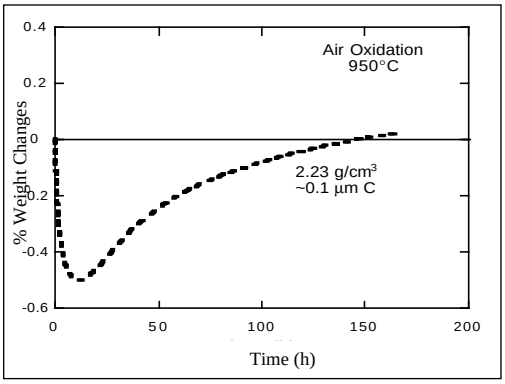

Fig. 1. Thermogravimetric analysis is used to evaluate overall oxidation kinetics. These results are for a Nicalon-reinforced SiC with a carbon fiber coating approximately 0.1 μm in thickness and no external seal coating The extent of weight loss is a function of exposure temperature, density, and thickness of the carbon interphase.

Recently, specific efforts have been made to better integrate reaction kinetics (that is, TGA measurements), related microstructural changes, and associated effects on mechanical properties by using a characterization sequence in which the same specimen is first exposed to an oxidizing environment in a microbalance to generate the TGA data (see Fig. 1), then tested in flexure at room-temperature to assess the effects of oxidation on mechanical properties, and, finally, examined by SEM and TEM.

In this way, the important relationships between reaction kinetics, microstructure, and properties can be established and, hopefully, used to spotlight any material factors critical to environmental susceptibility.

Figure 1 shows that the subject CFCC (Nicalon-reinforced SiC with carbon interphases but no external coating) suffered a weight loss consistent with removal of carbon by oxidation and subsequent weight gains associated with formation of silica on external and internal surfaces (some of which were created by the carbon loss).

The relative contributions of these competing oxidation reactions were shown to depend on exposure temperature and the starting specimen density. For the conditions corresponding to the gravimetric behavior shown in Fig. 1, postexposure flexure testing revealed a substantial, rapid decrease in strength and, at long exposure times, complete brittle behavior when this type of kinetic behavior was observed by TGA.

Scanning and transmission electron microscopy of composite specimens oxidized for various times clearly established the microstructural basis for the interpretation of reaction kinetics and the corresponding effects on mechanical properties.

Evidence of open channels created by carbon oxidation are found, and subsequent filling of these with silica are observed.

As shown in Fig. 2, measurements of reaction product thickness by TEM allows precise determination of the

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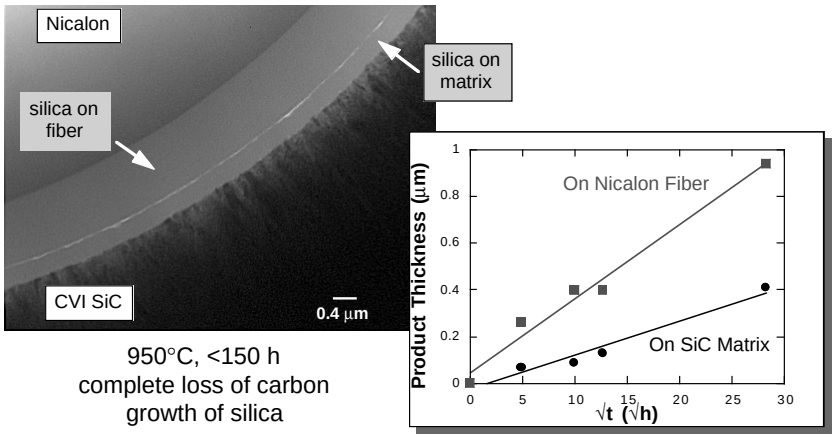
Fig. 2. Transmission electron microscopy is used to link environmental effects to microstructural changes and reaction kinetics.



950°C, <150 h
complete loss of carbon
growth of silica

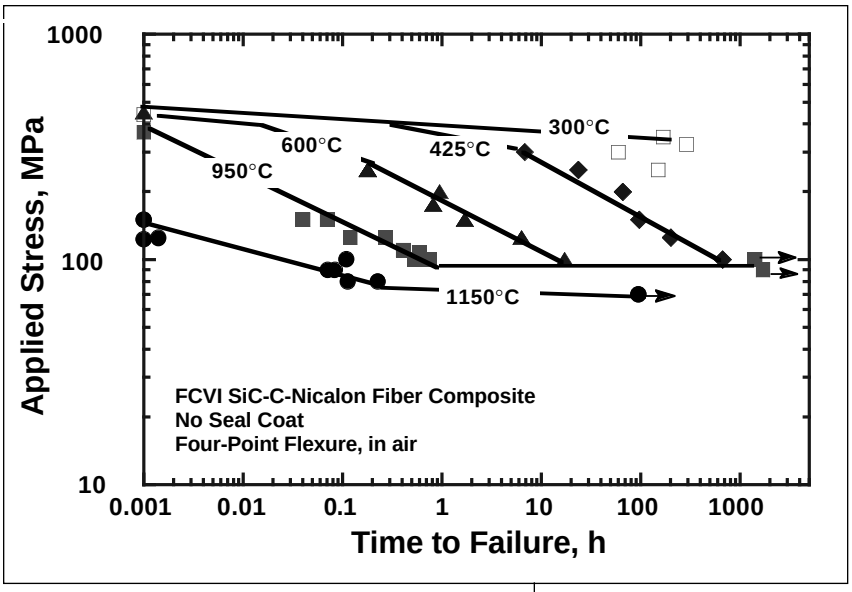


Fig. 3. Stress rupture is used to determine regimes of environmental susceptibility.

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> *"A number of potential applications for CFCCs involve cylindrical components (for example, heat exchangers and hot-gas filters), and it is often important to evaluate as-fabricated material in this product form.*

rates of silica growth on both the fiber and matrix phases and allows the deconvolution of the TGA curves (such as the one shown in Fig. 1), which represent the superposition of a number of different oxidation processes.

These findings provide a consistent explanation of not only the flexure results, but also data on fiber pushout as a function of exposure time. A similar integrated approach is now being applied to CFCCs with other fiber coatings (such as BN and multilayers) and matrices.

Stress-Rupture Testing

In addition to the effort to examine the relationships among reaction kinetics, microstructure, and properties for selected CFCCs, stress-rupture testing is used to examine the simultaneous effects of corrosion and stress.

These tests allow evaluation of the general environmental resistance of a particular type of ceramic composite by mapping the stress-time-temperature regimes of susceptibility. An example of such flexural results is shown in Fig. 3; such observations have been particularly valuable in examining the effects of composite density and exposure temperature on environmental stability, in judging the effectiveness of external coatings in improving oxidation resistance under an applied load, and in identifying particularly susceptible composite variants.

Much of the stress-rupture work to date has involved four-point bending, but similar tests under tensile loading have now begun. Composites with SiC and oxide matrices and a variety of fiber coatings have been or are being examined, and efforts to evaluate the effects of controlled additions of water vapor on stress-rupture are being initiated.

Long-Term Testing

In addition, several of the flexure machines are now devoted to long-term testing of CFCCs with promising environmental resistance, as such lifetime tests have important implications in qualifying composite components for industrial applications.

A number of potential applications for CFCCs involve cylindrical components (for example, heat exchangers and hot-gas filters), and it is often important to evaluate as-fabricated material in this product form. To do so, C- or O-rings can be cut from tubular products, exposed to a corrosive environment, and then mechanically tested via standard methods for these specimen shapes.

Such an approach has been pursued at ORNL for several CFCCs exposed to air or a synthesis gas (H_2-CO) in support of the development of high-

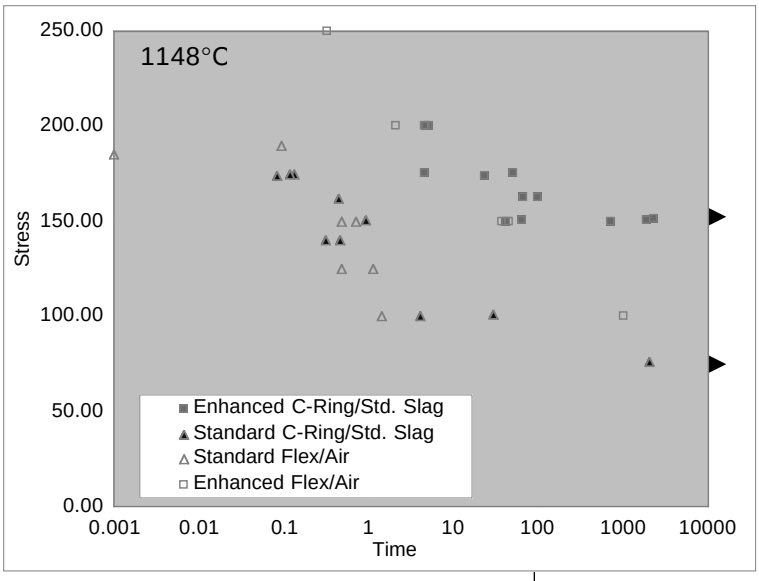

Fig. 4. C-ring stress-rupture tests for Nicalon/SiC composites with carbon interfaces yielded equivalent results to flexure data and showed little effect of ash layer. Results for composites with standard and enhanced (DuPont Lanxide Composites proprietary process) SiC matrices are shown.

temperature heat exchangers. Stress-rupture tests with C-rings are also being conducted, and results-to-date indicate good agreement between data obtained with these specimens and those gotten from flexure experiments (see Fig. 4).

With potential applications in fossil-fuel-fired systems in mind, C-rings of Nicalon-reinforced SiC are coated with char and placed under load in air at elevated temperatures. As shown in Fig. 4, the presence of this dry ash had a negligible effect on stress-rupture behavior up to 1148°C. Similar experiments at higher temperatures are now under way.

Oxidation/Corrosion

Another aspect of the environmental effects work involves the evaluation of existing models of how oxidation/corrosion affects the mechanical behavior of CFCCs and the development of new or improved approaches to explaining and predicting the influences of reactive species on properties.

While models based on oxidation of various composite constituents can qualitatively explain loss of fracture resistance in a number of cases, more quantitative treatments are being pursued so as to develop more rigorous links between reaction processes and resulting mechanical behavior. A good example of this is a recently developed model that accurately describes apparent time-dependent behavior of a CFCC under constant load in terms of oxidation-induced progressive fiber failure.

As a particular CFCC material is further developed with respect to oxidation-resistance and appropriate applications are identified, the environmental effects work progresses toward use of more specific exposure tests for experimental examination of possible changes in properties.

As mentioned above, such exposures involve the presence of H_2O, H_2, H_2S, SO_2, or other gaseous species and the possibility of ash/salt deposits. With a few exceptions, most of these application-specific environmental tests consist of exposures followed by characterization.

These exposures can take place in experimental simulation (laboratory) systems, industrial test beds, or in actual industrial systems for which the CFCC is being targeted. Examples of these types of studies involving ORNL include those examining environmental effects of composites being considered for particle filtration, steam reforming, ethylene cracking, turbine combustor cans, and waste incineration.

Future issues of this newsletter will include articles about several of these efforts.▲

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Dow Corning Corporation

High-Temp Filters

Benefits for Process Stream Efficiency & Effluent Cleanup

By Theodore Besmann, Oak Ridge National Laboratory

"The proposed project . . . is designed to assess the applicability of high temperature filter materials to solve these problems.

"Replacement with filter media that can withstand both corrosive and high-temperature environments, yet are robust to mechanical and thermomechanical stress, can significantly improve energy efficiency and product throughput.

Dow Corning Corporation is a market leader in the production of dimethylsiloxane, which is utilized as an intermediate in a wide variety of silicone products.

In Carrollton, Kentucky, the company operates the largest plant of its type for the production of dimethyl-siloxane, housing several generations of production streams.

The facility could benefit substantially both in process stream efficiency and effluent cleanup from improved high temperature filtration technology.

The results . . . should have applicability across a wide range of chemical industry problems in high-temperature filtration.

The proposed project, which is under a cooperative research and development agreement (CRADA) between Dow Corning and Oak Ridge National Laboratory, is designed to assess the applicability of high-temperature filter materials to solve these problems.

CRADA Program

The results of the proposed CRADA program should have applicability across a wide range of chemical industry problems in high-temperature filtration.

Within gaseous process streams there is often a need to remove particulates before further processing can be accomplished. Yet conventional filtration materials and techniques either are inefficient or insufficiently rugged to survive in the process environment.

Their replacement with filter media that can withstand both corrosive and high-temperature environments, yet are robust to mechanical and thermo-mechanical stress, can significantly improve energy efficiency and product throughput.

The proposed filtration concepts can result in filter cleaning in place via back-pulsing, with almost indefinite life.

Effluent Cleanup

Effluent cleanup for chemical process streams can also be energy inefficient, often requiring electrostatic systems for particle removal coupled with liquid scrubbers for vapor removal.

The ability to filter particles from a hot-gas waste stream offers two advantages. The first is the elimination of electrostatic systems that require cooling of the waste stream, are energy consumers, and are capital and maintenance intensive.

The second is that a particle-free hot-gas waste stream is available for heat recovery. Thus many chemical plants that produce particle-laden hot-gas waste streams could substantially improve their energy efficiency and productivity through the use of stable, high-temperature filtration systems.▲

Textron Testing

—Continued from page 3

air drying time and thereby further improve the wall thickness and reduce the tendency to form shrinkage micro cracks. The demonstration of these improvements resulted in a component having a nominal 0.12-in. wall. These process improvements have been implemented on the combustor component, and an improved test article is being prepared for a 100-h burner rig test. Transition of these same improvements to the immersion tube component are under way, and should result in significant durability improvements.▲

USACA & CFCCs

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identified industries. At the same time USACA will continue to support, via its Surface Transportation Working Group, the continued use of advanced ceramics in hybrid propulsion systems and in various programs supported by the Heavy Vehicles Initiatives.

Environmental Impact

USACA believes that the environmental impact of advanced ceramics in pollution prevention and energy efficiency is severely underpublicized. With the cooperation of our member companies who are active in this market segment, a study for publication and public awareness enhancement will be conducted in 1997.

USACA's Spring Conference will take place in Gaithersburg, Maryland, where topics will include the latest information on advanced ceramics processing, grinding, and metrology, along with a tour of the National Institute of Standards and Technology ceramics related facilities for the members who are currently unfamiliar with them.

As the leading advocate for advanced ceramics in the United States, USACA will continue to support the DOE and its various programs that utilize advanced ceramics and ceramic matrix composites throughout 1997 and beyond.▲

Alzeta Burners

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objectives were met or surpassed. Unfortunately, that customer has not yet been able to guarantee the purchase of such a system.

Further contacts are being pursued, however, in the scientific test equipment and in the previously mentioned drying/curing industries. The biggest competition in these markets, is from cheaper, low-capital-cost gas systems and high-efficiency, so-called "zero-emissions" electric systems. The increased efficiency of the screen allows much more effective competition between Alzeta's enhanced IR product and the electric systems, especially when the energy cost savings are included.

The major hurdle now seems to be the cost involved in making and selling the product. The CFCC enhanced radiant burner product is on its way to commercialization and utility to the industrial, commercial, and residential markets of the near future.▲

"Transition of these same improvements to the immersion tube component are underway, and should result in significant durability improvements

"USACA believes that the environmental impact of advanced ceramics in pollution prevention and energy efficiency is severely underpublicized.

CFCC NEWS

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

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***CFCC News* URL**

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

A COMMUNICATION OF THE CONTINUOUS FIBER CERAMIC COMPOSITE PROGRAM

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

Calendar

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

USACA Annual Spring Meeting and Conference.
March 19–20, 1997, Gaithersburg Hilton, Gaithersburg, Maryland.
The conference, "Advanced Ceramics Programs at the National Institute of Standards & Technology (NIST)," will include programs on ceramic machining, ceramic coatings, national and international standards, ceramic data via the World Wide Web, and the ceramic processing characterization consortium. For registration information, contact: Rebecca Hainsey, USACA meetings director, (703) 812-8740.

Euromat 97: 5th Conference on Advanced Materials Science & Materials Technology.
April 21–23, 1997, Maastricht, The Netherlands.
For registration information, contact: Euromat 97 secretariat, P.O. Box 390, NL 3330 Aj Zwijndrecht, The Netherlands.
Telephone 37-78-619-26-55, Fax 31-78-619-57-35.
Internet: bvm@metropolis.nl.

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. For registration, contact: ACerS Meetings Department, 735 Ceramic Place, P.O. Box 6136, Westerville, OH 43081-8720.
Telephone (614) 890-4700, Fax (614) 899-6109.