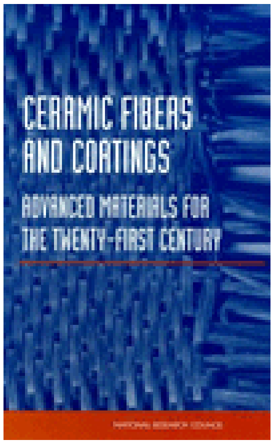

Ceramic Fibers and Coatings: Advanced Materials for the Twenty-First Century

Committee on Advanced Fibers for High-Temperature Ceramic Composites, Commission on Engineering and Technical Systems, National Research Council

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THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

CERAMIC FIBERS AND COATINGS

ADVANCED MATERIALS FOR THE TWENTY-FIRST CENTURY

Committee on Advanced Fibers for High-Temperature Ceramic Composites

National Materials Advisory Board

Commission on Engineering and Technical Systems

National Research Council

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Preface

The U.S. Department of Defense and the National Aeronautics and Space Administration requested that the National Research Council (NRC) conduct a study to recommend future research and development for advanced ceramic fibers and fiber coatings for high-temperature ceramic matrix composites (CMCs). The scope of this study was limited to fibers and their coatings or interfaces, independent of CMC processing and matrix materials, to bring to the forefront the current limitations on the strength and toughness of CMCs, particularly at high temperatures. This report represents the work of the Committee on Advanced Fibers for High-Temperature Ceramic Composites, under the auspices of the National Materials Advisory Board, which was established by the NRC for this purpose.

The properties of the principal classes of high-performance synthetic fibers, as well as several methods of synthesizing and processing them, were discussed in a 1992 NRC report entitled High-Performance Synthetic Fibers for Composites. This report included an excellent assessment of fibers for polymer matrix and metal matrix composites and CMCs, carbon-carbon composites, as well as fibers for nonstructural applications. The 1992 report, however, did not address microstructure/property relationships in ceramic fibers or the relationship between processing and property retention at elevated temperatures. Since the publication of the 1992 report, the need for improved fiber coatings has been more widely identified as critical. In light of the continuing demand for higher temperature performance, this report is focused on the capabilities and requirements of ceramic fibers and ceramic fiber coatings.

The need for improved high-temperature materials is evident in the continuing drive by industry, government, and academia to improve the performance, efficiency, and durability of components used in high-temperature applications. For example, a recent NRC report, Intermetallic Alloy Development: A Program Evaluation, describes the objective of the Oak Ridge National Laboratories intermetallics program as the development of intermetallic alloys for high-temperature structural applications. A 1996 NRC report, Coatings for High-Temperature Structural Materials: Trends and Opportunities, discusses ways to protect the metallic components of turbine engines from their operating environments so they can be used at higher temperatures. Because of the inherent stability of CMCs at high temperatures, they continue to hold great promise for use at high temperatures. Successful implementation of CMCs, however, will require assessing the performance and cost of the constituent fibers and fiber coatings. Therefore, the committee was asked to fulfill the following objectives in this study:

- Characterize the current state of the art in high-temperature fibers and interface materials and identify current domestic and foreign research and development capabilities and production capabilities.
- Assess the capability of current fibers to meet future performance needs.
- Recommend promising directions for research on fibers and coatings to improve performance at high temperatures.
- Identify materials processing technologies that have the potential to produce high-temperature ceramic fibers and coatings cost effectively.
- Identify incentives for and barriers to the development of commercial-scale high-temperature fibers for low volume applications.

Initially, the committee had intended to address Japanese fiber and coating efforts in a separate section. Given the advances that have been made in the United States and Europe, however, the committee determined that a section dedicated solely to Japanese efforts was not warranted. The state of the art in ceramic fiber and coating technology—in the United States, Europe, and Japan—is discussed in Chapter 3.

To address the study objectives, the committee met four times over a period of 15 months interspersed with several teleconferences. Two of the face-to-face meetings were focused on gathering information, and two were devoted to analyzing information and producing the report. Representatives of the National Aeronautics and Space Administration, the U. S. Department of Defense, and the U.S. Department of Energy materials programs, as well as representatives of nongovernmental entities, were invited to discuss the longterm material performance requirements of high-temperature components and the capability of current materials to fulfill them. Current producers of CMCs were requested to define fiber requirements for composite fabrication, as well as composite performance and supply capabilities.

One of the information gathering meetings was held in parallel with the American Ceramic Society's 21st Annual Conference on Composites, Advanced Ceramics, Materials, and Structures, in Cocoa Beach, Florida. At this meeting, the committee attended 15 presentations given by representatives of industry, government, and academe from the United States, Japan, and Germany. Presentations were, for the most part, focused on the current status and future directions of fiber and coatings technologies. In addition, two of the major manufacturers of jet engines presented the general requirements for CMCs to be used in gas turbine engines. The information collected by the committee was used to assess the current state of the art in ceramic fiber and coating technology and to determine the direction researchers and manufacturers should take to further these technologies. At a second information gathering meeting, held at the National Academy of Sciences in Washington, D.C., several representatives of CMC manufacturers discussed their requirements for ceramic fibers and ceramic fiber coating capabilities.

After reviewing these briefings, the committee considered the following questions:

- What requirements for fibers and interfaces are created by CMC processing?
- What are the major CMC markets/applications?
- What are the requirements for fibers and fiber coatings for these markets?
- Do available fibers meet or come close to meeting CMC requirements now?
- How sensitive are current and potential CMC applications to the costs of fibers?

The committee then considered future needs and opportunities for improving the performance and lowering the cost of ceramic fibers and coatings. The discussion included processing improvements that have the potential for improving fibers and coatings, as well as mechanisms for reducing (to some extent) the cost of developing and manufacturing these materials. Finally, the committee developed the conclusions and recommendations presented in this report.

David W. Johnson, chair
Committee on Advanced Fibers for High-Temperature Ceramic Composites

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The committee would like to thank the American Ceramic Society for granting the National Research Council permission to use the following figures in this report: Figure 3-1 , Figure 3-2 , Figure 3-6 , Figure 3-8 , Figure 3-12 , Figure 3-13 , Figure 3-15 , Figure 3-16 , Figure 3-17 , Figure 3-21 , Figure 3-23 , Figure 3-24 , Figure 4-2 , Figure 5-2 , Figure 5-3 , Figure 6-6 , Figure 6-8 , Figure 6-9 , Figure 6-10 , Figure 6-12 , Figure 6-14 , Figure 6-15 , Figure 6-16 , Figure 6-17 and Figure 6-18. These figures were reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, Ohio 43086-6136. The American Ceramic Society maintains copyright to all of the aforementioned figures. All rights reserved.

This report has been reviewed by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the authors and the NRC in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report: Norbert S. Baer, New York University; John J. Brennan, United Technologies Research Center; I. Wei Chen, University of Pennsylvania; Barry S. Draskovich, Allied Signal; Sylvia M. Johnson, SRI International; Harry A. Lipsitt, Wright State University; David B. Marshall, Rockwell International Science Center; and Dennis C. Nagle, Johns Hopkins University.

While the individuals listed above have provided many constructive comments and suggestions, responsibility for the final content of this report rests solely with the authoring committee and the NRC.

The committee wishes to express its sincere appreciation to the staff of the National Materials Advisory Board for its unswerving support. Sandra Hyland, senior program officer, and Charles Hach, research associate, dedicated much time and energy to bringing the report into being. Janice Prisco very effectively handled many issues as the senior project assistant.

The committee chair especially thanks the committee members for their dedication to producing a high-quality report on a tight schedule. Without their freely given time and efforts, this report would not have been possible.

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Acronyms

ACF	activated carbon fiber
BSR	bend stress relaxation
CFCC	continuous fiber-reinforced ceramic composite
CMC	ceramic matrix composite
CTE	coefficient of thermal expansion
CVD	chemical vapor deposition
CVI	chemical vapor infiltration
DTA	differential thermal analysis
DTGA	differential thermal gravimetric analysis
EFCC	externally fired combined cycle
IGCC	integrated gasification combined cycle
IMC	intermetallic matrix composite
MMC	metal matrix composite
NMR	nuclear magnetic resonance
NRC	National Research Council
PAN	polyacrylonitrile
PFBC	pressurized fluid bed combustion
PMC	polymer matrix composite
R&D	research and development
TEM	transmission electron microscopy
TGA	thermal gravimetric analysis
TPV	thermophotovoltaic
UCSB	University of California-Santa Barbara
UF	University of Florida
UHC	unburned hydrocarbons
UTS	ultimate tensile strength

Executive Summary

High-temperature ceramic fibers are the key components of ceramic matrix composites (CMCs). Ceramic fiber properties (strength, temperature and creep resistance, for example)—along with the debonding characteristics of their coatings—determine the properties of CMCs. This report outlines the state of the art in high-temperature ceramic fibers and coatings, assesses fibers and coatings in terms of future needs, and recommends promising avenues of research. CMCs are also discussed in this report to provide a context for discussing high-temperature ceramic fibers and coatings.

Continuous ceramic fibers in CMCs offer the potential for high performance in high-temperature corrosive environments. CMCs can be fabricated into complex shapes for use in thermostructural environments much the way carbon composites are fabricated for use in less aggressive environments. Unlike monolithic ceramic bodies in which the mechanical strength is determined by the largest flaw in a critical position, CMCs are relatively flaw tolerant because the load is borne by a multiplicity of fibers. Thus, CMCs have toughness and damage tolerance comparable to metals with the added advantages of lower density and greater stability at high temperatures.

For the past 15 years, research and development of CMCs has been sustained because of their potential for military and commercial applications. The applications of interest include (1) aircraft engine components, such as combustors, turbines, compressors and exhaust nozzles; (2) ground-based and automotive gas turbine components, such as combustors, first and second stage turbine vanes and blades, and shrouds; (3) aerospace engines for missiles and reusable space vehicles; and (4) industrial applications, such as heat exchangers, hot gas filters, and radiant burners.

Technical shortcomings must still be overcome, however, before CMCs can be widely used in thermostructural applications. These shortcomings provide research opportunities, particularly for the development of fibers and fiber coatings. The following list describes these opportunities:

- Fiber coatings for non-oxide composites have demonstrated adequate performance in short-life applications (e.g., rocket nozzles). These fiber coatings have also been demonstrated to be adequate in composite samples (e.g., test coupons) during long-time exposures to stress at high temperatures in laboratory tests. However, fiber coating technologies for long-life applications (e.g., turbine engine components) have not been demonstrated in component testing.
- Several coatings for oxide ceramic fibers have enabled model composite systems to demonstrate damage tolerant behavior. However, no fiber coatings have been proven to be effective in actual (as opposed to model) oxide composite systems.
- Non-oxide fibers are generally creep resistant but lack chemical stability; they are prone to oxidation. Consequently, stress oxidation limits the durability of nonoxide composites, especially at intermediate temperatures (i.e., 700 to 900°C [1,292 to 1,652°F]) under cyclic loading conditions. There are no known concepts for producing a coating that can prevent oxidation of the fibers for more than 100 hours, after matrix cracks occur (and remain open). Longer life non-oxide composites will require a combination of oxidation resistant fiber coatings and matrix sealing concepts that protect the fiber from oxidation—particularly when the composite is subject to cyclic thermomechanical loads that can cause sealed cracks to reopen. Such concepts have been developed but have not been tested.
- Oxide fibers are generally environmentally stable but are subject to excessive creep at high temperatures. Preliminary work indicates that microstructural modifications have the potential for enhancing creep resistance.

A significant barrier to progress is the paucity of engineering data [1] on CMCs, which reflects a lack of access to data generated by classified projects, as well as a general lack of engineering data. Advances have been further impeded by the high cost of coated fibers, which are attributable to low production volumes and, in some cases, to high precursor costs. Consequently, the stability and breadth of the vendor base for fibers, coatings, and coated fibers is questionable.

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[1] Engineering data are defined as coupon tests, subelement tests, and component tests, as well as design and life prediction results.

APPROACH

To conduct this study, the National Research Council (NRC) convened a committee with expertise in ceramic fiber processing, nanoparticle reinforced ceramics research, ceramic fiber research, high-temperature ceramic fiber-matrix interfacial coatings, and synthesis of nanomaterials. The committee also has expertise in ceramic fiber economics, including cost analysis and the determination of the commercial potential of advanced materials. To accomplish the overall objective of identifying research directions to meet the material property requirements of advanced fibers and coatings for high-temperature ceramic composites, the committee took the following steps:

- characterized the current state of the art in high-temperature fibers and interface materials and identified current domestic and foreign capabilities (both R&D and production capabilities)
- assessed the capabilities of current fibers to meet future performance needs
- recommended promising research directions for developing fibers and coatings for improved performance in high temperature applications
- identified materials processing technologies that have the potential to produce high-temperature ceramic fibers and coatings cost effectively
- identified incentives for and barriers to the development of commercial-scale high-temperature fibers for low-volume applications

By limiting the scope of this study to fibers and their coatings, independent of CMC processing and matrix materials, the committee was able to focus on issues that limit the strength and toughness of CMCs, particularly at high temperatures. The discussion of composite materials in this report is limited to providing a context for discussions, conclusions, and recommendations regarding ceramic fibers and coatings.

TABLE ES-1 Typical Property Ranges for Ceramic Fibers

Property	Non-Oxide Fibers [a]	Oxide Fibers [b]
Tensile Strength (GPa)	1.5–4.0 (220–580 ksi)	1.4–3.0 (260–430 ksi)
Elastic Moduli (GPa)	180–400 (26–58 Msi)	150–380 (22–55 Msi)
Strain to Failure (%)	0.6–1.8	—
Coefficient of Thermal Expansion (ppm/°C)	3–5	3–9
Thermal Conductivity at 1,500°C (2,732°F) (W/mK)	up to 40 (up to 23 Btu/hr foot °F)	—

[a] Representative properties for polycrystalline and amorphous Si-based fibers that contain one or more of the following elements, carbon, nitrogen, or boron

[b] Representative properites for polycrystalline oxide fibers consisting of predominantly Al_2O_3

HIGH-TEMPERATURE CERAMIC FIBERS

Non-Oxide Ceramic Fibers

Non-oxide fibers are typically based on silicon carbide (SiC) and are fabricated by several processes: (1) spinning a melt of organometallic precursors (the most favored route); (2) spinning a solution of organometallic precursors (dry spinning); (3) extrusion spinning of a ceramic powder in a polymeric binder; (4) chemical vapor deposition (CVD) of vapor species onto a monofilament core; and (5) conversion of carbon fiber to SiC using Si-containing vapor species.

Spun non-oxide fibers (i.e., those made by the first three processes above) are produced in tows consisting of hundreds of filaments with diameters of 10 to 20 µm. Typical ranges of properties are given in Table ES-1. All of these fibers are based on SiC except for amorphous Si-B-N-C, a promising new fiber.

The best non-oxide fibers have good creep resistance but are susceptible to degradation by formation of an amorphous silica layer upon oxidation. This layer offers some resistance to further oxidation, but prolonged exposure to oxidizing environments results in oxidative embrittlement of the composite.

Oxide Ceramic Fibers

All currently available commercial oxide fibers are based on aluminum oxides. Examples are alumina (Al_2O_3) yttrium aluminum garnet (YAG) and mullite ($3A1_2O_3$-$2SiO_2$).

Commercial polycrystalline oxide fibers are produced by spinning and hydrolyzing precursors. First a fiber precursor solution is filtered and concentrated to remove excess solvent, forming a viscous spin dope. Then, continuous filaments are extruded by spinning. The filaments are pyrolyzed to remove volatile components and then heat treated above 800°C (1,472°F) to crystallize and sinter the fiber. Polycrystalline oxide fibers are produced in tows of 200 to 1,000 fibers with diameters of 10 to 16 µm (0.39 to 0.63 mils). Typical ranges of properties are listed in Table ES-1.

Oxide fibers are inherently resistant to oxidation but have limited creep resistance because of higher diffusivities compared to SiC. Creep rates decrease with increasing grain size, but this advantage is offset by decreasing strength. However, significant improvements have been achieved in the past decade by reducing the amorphous phase content at the grain boundaries of oxide fibers.

FIBER COATINGS

Damage tolerance in a CMC requires a weak interface between the fibers and the matrix; fiber coatings are engineered to provide this weak interface. Fiber coatings also protect the fiber from environmental attack during composite fabrication and use.

Coatings for Non-Oxide Fibers

Most work on coatings has been concentrated on SiC fibers used in non-oxide CMCs. Tough composite behavior has been reported only when coatings consist predominantly of carbon or boron nitride (BN). Oxidation of the fiber/coating/matrix interface is a major limitation for non-oxide composites. This interface may be exposed to an oxidizing environment when cracks develop in the matrix (which otherwise acts as a barrier to oxygen ingress) under load. Oxidation of the fiber/coating/matrix interface degrades the fiber and its debonding characteristics, reducing both the strength and toughness of the composite.

Carbon coatings can be formed by the in-situ decomposition of Si-C-O fibers or applied by CVD. Carbon coatings are typically 0.1 to 0.3 µm (0.004 to 0.01 mils) thick. During oxidation of the fiber coating, carbon is converted to carbon monoxide (CO) or carbon dioxide (CO_2), leaving a gap. The SiC fiber then oxidizes, forming a silicate glass (SiO_2), which tends to close the gap. However, if the gap is not closed quickly enough, oxidation may proceed along the fiber/matrix interface, bonding the fiber to the matrix and causing embrittlement of the composite. This phenomenon, sometimes called pesting, is most prevalent at intermediate temperatures.

BN is the only other fiber coating that has been demonstrated to enable “tough” composite behavior. BN coatings are typically deposited via CVD and are 0.3 to 0.5 µm (0.01 to 0.02 mils) thick. Because the oxidation product of a BN coating is a borate (B_2O_3) glass, which protects against oxidation at intermediate temperatures, the degradation rate of BN-coated fibers is lower than for carbon-coated fibers. As the temperature is increased, the B_2O_3 reacts with SiO_2 (the oxidation product of either the SiC fiber or the matrix) to form a borosilicate glass. However, in wet atmospheres, the B_2O_3 volatilizes (as boron hydroxides), thus compromising its ability to prevent further oxidation of the fiber, which ultimately leads to embrittlement of the composite.

Coatings for Oxide Fibers

Oxide coatings that are chemically compatible with commercially available oxide fibers have been identified, but adequate debonding and friction have yet to be demonstrated in a composite system. Several coating strategies and materials are being investigated. For example, porous and fugitive coatings have been used, as well as porous matrices (with no coating). These provide toughness as long as sintering between the fibers and particles in the matrix/coatings can be suppressed.

Layered oxides are being studied because of their potential debonding characteristics. A class of sheet silicate minerals known as fluoromicas exhibit easy delamination along crystal planes but are chemically incompatible with current fibers and matrices. Beta alumina (β-Al_2O_3) and magnetoplumbites are compatible with alumina fibers and have sufficiently low fracture energies to provide the weak fiber/matrix interface needed for damage tolerant composites. The magnetoplumbite mineral hibonite, $CaAl_{12}O_{19}$, has been studied extensively, but Ca tends to diffuse into matrices during hot pressing, which degrades composite properties. Other layered oxides that have been studied preliminarily include perovskites, such as $KCaNb_3O_{10}$ and $BaNd_2Ti_3O_{10}$.

“Nonwetting” oxides have shown particular promise. Nonwetting refers to the tendency of the interface between the coating and the fiber to debond readily. The monazite class of compounds (e.g., lanthanide phosphates) and sheelites fall into this category. These compounds have high melting points and are chemically stable (when stoichiometric).

Several coating technologies are used for oxide fibers. CVD can be used, but maintaining stoichiometry is difficult. Solution-based precursors are better for controlling stoichiometry, but maintaining coating uniformity and preventing bridging between fibers in a tow is difficult. The electrostatic attraction between particles in a slurry and the fiber can also be used to deposit fiber coatings. All currently proposed oxide coatings have promising features but have questionable debonding and frictional characteristics, as well as uncertain processing technologies.

RECOMMENDATIONS AND IMPACTS

The committee formulated many specific recommendations on both fibers and coatings that are presented in the body of the report, the most important of which are listed here. The committee also describes the anticipated impact of these recommendations on the field, which is crucial for moving CMC technology forward. These recommendations are followed by a discussion of the rationale for their prioritization. Although the focus of this report is on high-temperature ceramic fibers and coatings, the committee believes that a database of CMC properties is needed to establish research goals and performance criteria to design better fibers and coatings for future CMCs.

Recommendation 1. Building and disseminating an engineering database for actual (as opposed to model) CMCs is essential. The committee recommends the following:

- Existing nonclassified data that are not broadly accessible because they are associated with classified or restricted studies should be made generally available. Wherever possible, agency-owned engineering data should be made accessible, and new programs should avoid restricting data.
- Data that are currently classified should be reassessed to determine if they can be declassified and, if so, they should be made more generally available.
- Low risk government-sponsored insertion programs for CMCs should be expanded to demonstrate the field performance of CMC components.
- Standardized tests for obtaining engineering data on CMCs should be developed and instituted.

Impact. Researchers would be able to determine when ceramic fibers and coatings limit CMC properties and focus materials research on overcoming these limitations. Design engineers would gain confidence in using CMCs when data is available on CMC component performance in operating environments (i.e., field tests). Furthermore, following the recommendations listed above would elucidate composite failure modes, facilitate vetting less viable CMC systems, and establish a foundation for breaking out of the market size-cost impasse that has stymied investments in facilities for the production of fibers and coatings.

Recommendation 2. Coatings for high-temperature ceramic fibers must be improved.

- Non-oxide fiber coatings research should be focused on:
- - concepts that enable high durability with cracked matrices at the “pest” temperature
- - a system approach that includes concepts for improving the oxidation resistance of fiber coatings in dry and moist atmospheres and “sealing” matrix cracks as they form
- - investigating regenerative in-situ coatings

Impact. Durable coatings for non-oxide fibers would provide suitable lifetimes for many applications, such as thermally loaded gas turbine components and heat exchangers.

- Research dedicated to improving the fiber/matrix interface for oxide CMCs should focus on:
- - investigations of weakly bonded, thermally stable oxide coatings for oxide-oxide composites (e.g., nonwetting coatings)
- - approaches that do not use coatings (e.g., porous matrices)

Impact. CMCs that are not susceptible to oxidative degradation could be fabricated for intermediate temperature or intermediate performance applications.

Recommendation 3. Studies should be directed toward improving oxide fiber creep resistance and understanding the underlying scientific mechanisms.

Impact. Oxide fibers with improved creep resistance will allow higher temperature applications (e.g., combustors and heat exchangers) provided that suitable oxide fiber coatings are developed in parallel.

Recommendation 4. The following areas should be investigated for non-oxide fibers:

- emerging amorphous non-oxide fibers, such as Si-B-N-C fibers, to verify the stability, creep resistance, and utility of the in-situ coatings
- microstructural refinement to improve performance in crystalline non-oxide fibers

Impact. The development of higher temperature, higher performance fibers will enable the use of CMCs in long service life, high-temperature applications if the problems of interface durability can be solved in parallel.

Recommendation 5. Efforts to reduce the costs of fiber and coating processing should be focused on the following:

- capital nonintensive approaches
- processes that leverage past investments
- in-situ and liquid precursor coatings

Impact. A broader, more stable vendor base for fibers and coatings would probably be established if costs were reduced. Lower costs for fibers and coatings would also make CMCs more attractive to a larger variety of users.

DISCUSSION OF PRIORITIES

The five recommendations above fall into three categories. Recommendation 1 addresses increasing the knowledge base of, and confidence in, existing CMC technology. The committee anticipates that applications for CMCs will expand if engineering designers have access to the information they need to make materials selection decisions. Thus the committee places a high priority on this recommendation.

Recommendations 2, 3, and 4 (listed in order of decreasing priority) are related to performance, which is also considered to be a high priority. Recommendation 2 is the most important in this category. The oxidation resistance of oxide fibers is attractive, but poor creep resistance is a significant limitation. Thus, Recommendation 3 addresses the need to improve this property. Recommendation 4 (regarding non-oxide fibers) is last in this category because the committee concluded that resources directed toward property improvement in fiber coatings and oxide fibers was more important. The committee is satisfied that the preliminary properties reported for Si-B-N-C amorphous fibers are sufficiently attractive to stimulate the research needed to verify them.

Recommendation 5 is last, not because cost is unimportant but because, at the current stage of the technology, performance rather than cost has limited the use of CMCs. The committee concluded that, at this time, improving properties should be of higher priority than reducing costs.

1

Introduction

Ceramic fibers provide the skeletal structure of ceramic matrix composites (CMCs) and are major contributors to the composite's mechanical and physical properties. The network of ceramic fibers maintains the structural integrity of the composite during matrix cracking, thus increasing the composite's tolerance to damage. Fiber coatings contribute to the chemical stability between the fiber and the matrix and service environments. They also provide a weak interface between the brittle ceramic matrix and the ceramic fiber, enabling “pseudoductility” in the CMC. Fibers and coatings together provide the damage tolerance that gives CMCs their robustness. This report focuses on fibers and coatings and on identifying directions for research and development that would lead to improvements in CMC components for high-temperature applications.

Although the matrix phase of CMCs is not specifically addressed in this report, it is unlikely that ceramic fibers and coatings will be used in the absence of a matrix. Ceramic fibers and coatings are predominantly used as constituent materials for CMCs and enable damage tolerance (in CMCs) that is not inherent to ceramic materials. Therefore, it is relevant to the focus of this report to discuss the potential applications and performance requirements of CMCs (and by analogy fibers and coatings). The discussion of CMCs, however, is limited to providing a context for the discussion of ceramic fibers and coatings.

APPROACH

To conduct this study, the National Research Council (NRC) convened a committee with expertise in ceramic fiber processing, nanoparticle reinforced ceramics research, ceramic fiber research, high-temperature ceramic fiber-matrix interfacial coatings, and synthesis of nanomaterials. The committee also has expertise in ceramic fiber economics, including cost analysis and the determination of the commercial potential of advanced materials. To accomplish the overall objective of identifying research directions to meet the material property requirements of advanced fibers and coatings for high-temperature ceramic composites, the committee took the following steps:

- characterized the current state of the art in high-temperature fibers and interface materials and identified current domestic and foreign capabilities (both R&D and production capabilities)
- assessed the ability of current fibers to meet future performance needs
- recommended promising research directions for developing fibers and coatings for improved performance in high temperature applications
- identified materials processing technologies that have the potential to produce high-temperature ceramic fibers and coatings cost effectively
- identified incentives for and barriers to the development of commercial-scale high-temperature fibers for low-volume applications

By limiting the scope of this study to fibers and their coatings, independent of CMC processing and matrix materials, the committee was able to focus on issues that limit the strength and toughness of CMCs, particularly at high temperatures. The discussion of composite materials in this report is limited to providing a context for discussions, conclusions, and recommendations regarding ceramic fibers and coatings.

POTENTIAL CERAMIC MATRIX COMPOSITE APPLICATIONS

Exceptional high-temperature material and component performance are necessary to realize the benefits of operating systems at elevated temperatures. For example, improvements in gas-turbine efficiency (for power generation, marine applications, or aircraft propulsion) have been driven primarily by significant increases in gas temperatures within the engine. Although the introduction of new materials and processes has led to incremental improvements in high-temperature performance over the five decades that gas-turbine engines have existed, the development of highly engineered cooling schemes has arguably accounted for more than 75 percent of this increase (National Research Council, 1996).

Despite remarkable progress in component cooling and dramatic improvements in engine materials, current superalloys operate at 90 percent of their incipient melting temperatures in some applications. The demand for more efficient engines will require even higher operating temperatures, which will require higher component temperatures. As operating temperatures increase, high-temperature structural applications will require new materials with improved thermomechanical and thermochemical properties. CMCs are recognized as having the potential for providing high strength, toughness, creep resistance, notch insensitivity, and environmental stability at temperatures that will meet the anticipated needs of future high-performance turbine engines and power generators.

In addition to turbine engine components, there are several industrial applications for which a comparatively large market could be realized for a broad range of CMC components. For example, hot gas filters for pressurized fluidized bed combustion (PFBC) and furnace hardware, such as pipe hangers for petroleum refining, represent potential near-term applications for CMCs. These relatively low-risk industrial applications could provide the market volume necessary to lower fiber costs (and prices) significantly, as well as to develop experience and confidence in using CMCs. Longer-range industrial uses for CMCs include heat exchangers for externally fired combined cycle (EFCC) power systems and reforming tubes for the chemical processing industry. Substantial improvements will be required, however, in the thermomechanical and thermochemical properties of ceramic fibers and coatings to enable CMCs to meet the service lifetime requirements.

COMPOSITE MATERIALS

Composite materials derive benefits both from the properties of their constituent phases and from the method of their combination, including the tailoring of interfaces between phases, to achieve properties that none of the constituents exhibits individually. For example, CMCs have well demonstrated damage tolerance, which is attributed to frictional sliding at fiber matrix interfaces (see, for example, Box 1-1). Frictional sliding is enabled by fiber interfacial coatings. Damage tolerance is manifested in ductilities on the order of 1 percent and notch sensitivity comparable to aluminum (Al) alloys. CMCs also have excellent room-temperature fatigue properties, with thresholds (stress below which fatigue does not occur) at about 90 percent of their ultimate tensile strength (UTS). However, fatigue problems are evident at elevated temperatures. The UTS of CMCs (typically 300 MPa [44 ksi]), although not exceptional, is volume invariant because the damage tolerance suppresses the weakest link scaling effects found in monolithic ceramics. That is, because of crack deflection and crack tip blunting mechanisms, CMCs can tolerate cracking that would lead to catastrophic failure in monolithic ceramics. These thermomechanical properties are particularly attractive for large, static, thermally-loaded components.

The CMC market is divided into two classes, oxide and non-oxide materials. Oxide composites consist of oxide fibers (e.g., alumina [Al_2O_3]), interfacial coatings, and matrices. If any one of these three components consists of a non-oxide material (e.g., silicon carbide [SiC]), the composite is classified as a non-oxide composite. These classes have different properties, different levels of development, and different potential applications.

Because most development work has been done on non-oxide materials, particularly SiC fiber-reinforced SiC CMCs (SiC/SiC) with fiber interfacial coatings of either carbon or boron nitride, non-oxide CMCs are more advanced than oxide CMCs. Non-oxide CMCs have attractive high temperature properties, such as creep resistance and microstructural stability. They also have high thermal conductivity and low thermal expansion, leading to good thermal stress resistance. Therefore, non-oxide CMCs are attractive for thermally loaded components, such as combustor liners (see Figure 1-4), vanes, blades, and heat exchangers.

Composite behavior has also been studied in oxide systems (e.g., oxide fiber-reinforced porous oxide matrix composites with no interfacial coatings). Oxide composites have the attractive features of oxidation resistance, alkali corrosion resistance, low dielectric constants, and potentially low cost. Because of these properties, oxide CMCs could be attractive for hot gas filters, exhaust components of aircraft engines, chemical processing equipment, and long-life, lower temperature components.

Both oxide and non-oxide CMCs have demonstrated shortcomings. Embrittlement occurs at intermediate temperatures (~700°C [1,292°F]) in all non-oxide composites, exemplified by SiC/SiC. Embrittlement is most severe with cyclic loading beyond the proportional limit, whereupon matrix cracking occurs because oxygen that ingresses through the matrix cracks reacts locally with the fibers and fiber coatings to form oxide products. These reaction products suppress the internal friction mechanisms that otherwise impart toughness. Although this effect does not occur when the stresses remain below the proportional limit, design studies and end-user experience indicate that stress excursions above the proportional limit must be anticipated. Local embrittlement is, therefore, the dominant life-limiting phenomenon of non-oxide composites. The committee considers the solution to this problem to be imperative for long-life applications of non-oxide CMCs. A systems-level approach that includes considerations of fibers and fiber coatings, as well as ways to diminish oxygen ingress, is discussed in this report.

Oxide CMCs are not subject to oxidative embrittlement but have higher temperature limitations (~1,000°C [1,832°F]) associated with creep and sintering, both governed by the high diffusivities of oxides compared to SiC. Also, fiber coating technologies for oxide materials are less mature than coating technologies for non-oxide materials. In fact, nearly all of the performance data available for oxide CMCs are for systems in which interfacial coatings were not used, and damage tolerance was a result of matrix porosity. Concepts for suppressing the high-temperature degradation mechanisms (e.g.,

BOX 1-1 Damage Tolerant Ceramic Matrix Composites

During the past two decades, significant research has been conducted on structural ceramics because of their promise for use at temperatures higher than currently available nickel-based or cobalt-based super alloys can tolerate. Initial work was focused predominantly on monolithic ceramics, such as SiC and Si_3N_4. Although significant improvements have been made in the strength, strain tolerance, and damage tolerance of monolithic ceramics, they continue to exhibit a catastrophic failure mode. This major performance limitation has prevented their widespread use in thermostructural applications. Ceramic matrix composites (CMCs) are an attractive alternative because they maintain the refractory properties of monolithic ceramics and do not exhibit a catastrophic failure mode.

Figure 1-1 is a schematic representation of the stress-strain behavior of an unreinforced matrix and a CMC. Since unreinforced matrices only show an elastic stress-strain region, they have no mechanism for damage tolerance. CMCs also show stress-strain behavior that is initially linear (elastic). Once the matrix cracking stress has been reached, however, the composite shows stress-strain behavior similar to the plastic deformation demonstrated by metals. This nonlinear behavior is indicative of a non-catastrophic failure mode, thus allowing damage tolerant behavior in CMCs.

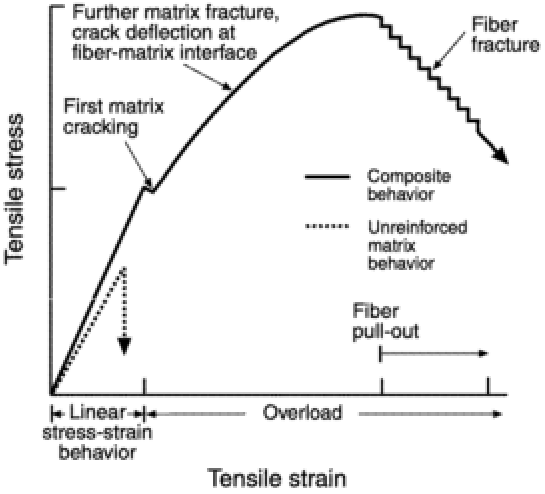


FIGURE 1-1 Ideal stress-strain behavior of continuous fiber-reinforced CMC compared to the stress-behavior of an unreinforced matrix. Source: DiCarlo and Dutta, 1995.

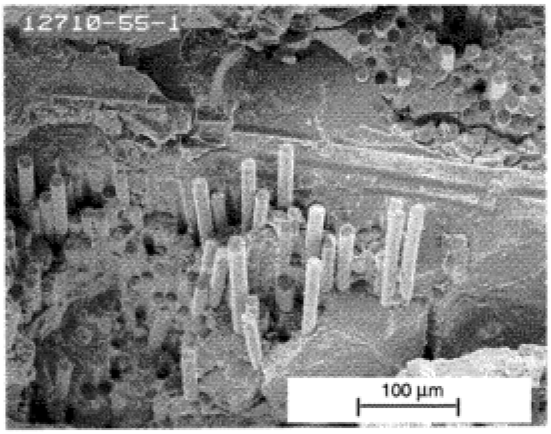


FIGURE 1-3 A scanning electron micrograph of the fracture surface of a Hi-Nicalon™ fiber-reinforced SiC matrix composite made by chemical vapor infiltration (CVI) showing fiber pullout. Source: Dow Corning Company

Figure 1-2 is a schematic representation of the constituents of a CMC, a fiber, a matrix, and one or more fiber-matrix interfacial coatings. In some cases, depending upon the application, an external coating is applied to the composite surface.

The fiber-matrix interface is a key contributor to noncatasrophic behavior in a composite (nonlinear region in Figure 1-1). If the fiber-matrix interface is weakly bonded (which usually requires a fiber coating), cracks that reach the interface are deflected around the fiber rather than through it. Fiber pullout (Figure 1-3) is indicative of this damage tolerant behavior (toughness).

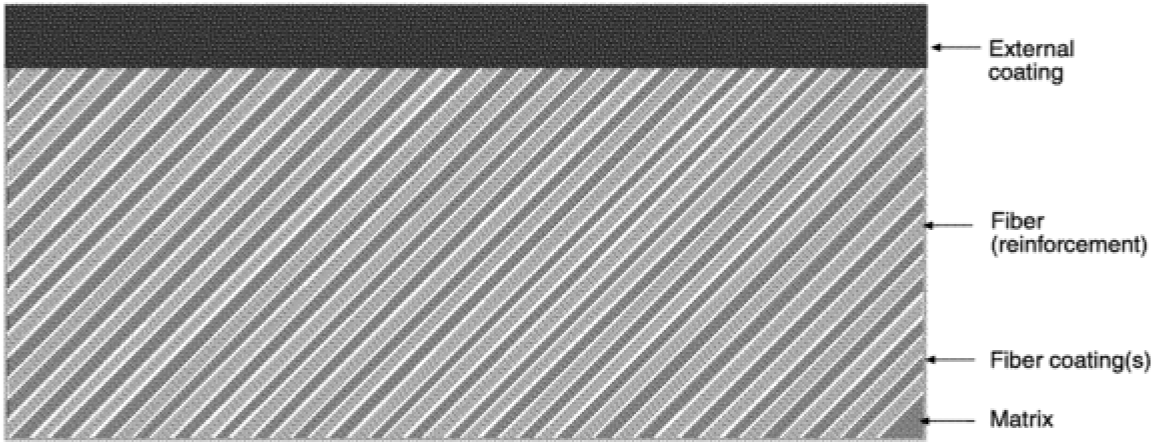


FIGURE 1-2 A schematic representation of the constituents of a CMC. Source: Luthra, 1997a.

creep) in oxide fibers and concepts for fiber coatings that would improve the damage tolerance of oxide CMCs are plentiful but have not been implemented. Opportunities in these areas are presented in this report.

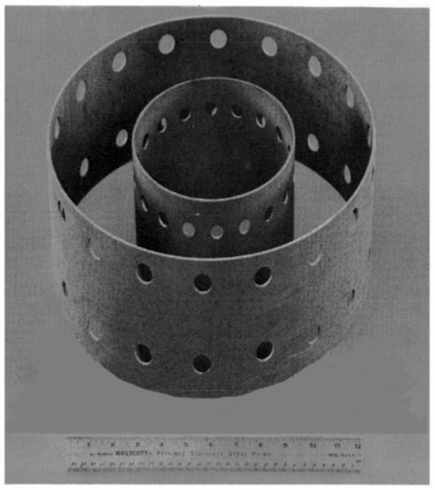
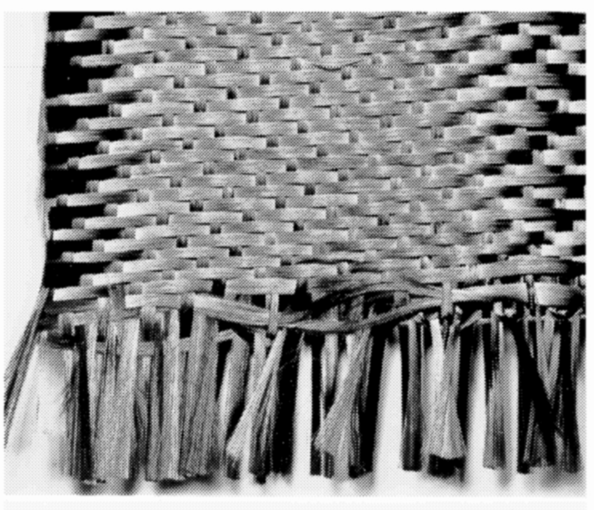


FIGURE 1-4 A set of “Saturn” turbine engine combustor liners (inner and outer) fabricated by DuPont Lanxide Composites, Inc. The combuster liners are composed of Nicalon™ SiC fiber (Nippon Carbon) reinforced enhanced silicon carbide matrix composites fabricated via CVI. These liners were produced for a development program sponsored by the U.S. Department of Energy, Ms. Jill Jonkouski, Program Manager, CFCC Contract DE-FC02-92CE40994. Source: Solar Turbines, Inc.

CERAMIC FIBERS AND COATINGS

Fibers play a critical role in both the processing and performance of CMCs. The thermomechanical and thermochemical properties of fibers dictate the atmosphere, temperature, and weaving capabilities that can be used in composite manufacture (as demonstrated in Figure 1-5). In service, the fibers and their associated interphases are critical to effective composite performance and to maintaining the structural integrity of the composite once cracking of the matrix has been initiated.

Fibers used as reinforcements in CMCs fall into two broad categories: (1) non-oxide fibers, such as SiC, boron nitride (BN), and silicon-boron-nitride-carbide (Si-B-N-C); and (2) oxide fibers, such as aluminum oxide (Al_2O_3, including single-crystal alumina), alumina zirconia mixtures ($Al_2O_3 + ZrO_2$), YAG (yttria-alumina-garnet), and mullite ($3Al_2O_3$-$2SiO_2$). Non-oxide fibers, such as those shown in Figure 1-6, have superior strength and good creep resistance but are susceptible to degradation by oxidation. Oxide fibers, for instance those illustrated in Figure 1-7, are inherently resistant to oxidation but have limited creep resistance at high temperatures due to the higher diffusivities of oxide materials. Creep



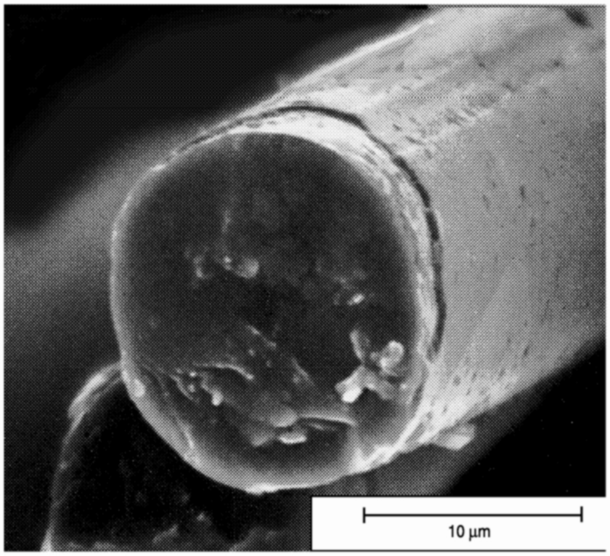


FIGURE 1-5 Eight-harness woven cloth. Each “thread” is a single tow (such as the one shown in Figure 1-7) containing as many as 800 individual filaments (see Figure 1-6). A matrix phase is later introduced to this preform (e.g., by chemical vapor infiltration) to produce a CMC. Source: Dow Corning Corporation.

FIGURE 1-6 Single filament of boron nitride-coated Nippon Carbon Nicalon™ non-oxide ceramic fiber. Non-oxide fibers discussed in this report include polycrystalline SiC fibers and multiphase (amorphous or crystalline) fibers consisting of B,C,N,Ti, or Si. Current manufacturers include Bayer, Dow Corning, Nippon Carbon, Textron, Tonen, and Ube. Source: Dow Corning Corporation.

rates of polycrystalline oxide fibers decrease with increasing grain size, but this advantage is offset by decreasing strength as grain size increases.

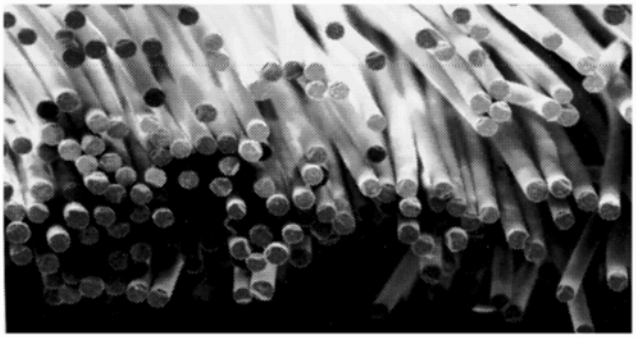


FIGURE 1-7 Tow of 3M Nextel 610 polycrystalline ceramic oxide fibers. Polycrystalline oxide fibers are commercially available in a variety of compositions including alumina, mullite, and others. Current producers include 3M, Mitsui Mining, and Sumitomo, Inc. Source: 3M Company.

Non-oxide fibers are generally derived from polymeric precursors, which often require complicated intermediate processing before they can be pyrolyzed into ceramic fibers. As a class, polymer-derived SiC-based fibers are the strongest ceramic fibers. The early versions of these fibers, typified by Nicalon™, are comprised of very small β-SiC grain sizes and high carbon and/or amorphous phase contents. These fibers have a low elastic modulus that results in strain to failure of greater than 1 percent. Later versions of these fibers have very low oxygen contents and were pyrolyzed at higher temperatures resulting in larger β-SiC grain sizes, very low amorphous phase contents, and higher volume fractions of carbon and SiC. As a result, the room-temperature strength is decreased and the modulus is increased, thus sacrificing strain to failure in favor of dramatically improved high-temperature strength and creep resistance. An interesting development is an amorphous Si-B-N-C fiber (produced using a novel polymer precursor technology) for which high strength, high stiffness, and truly remarkable strength retention and creep resistance have been reported (Baldus, 1997).

Single-crystal oxide fibers are generally stronger and more creep resistant than their polycrystalline counterparts. However, because they are prohibitively expensive they are not discussed at length in this report. Of the polycrystalline oxide fibers, the strongest are those derived from wet chemical precursors to obtain fine grain-sized fibers with avoidance of strength-limiting large grains. Materials with a fine-grained microstructure, however, are less creep resistant than materials of the same composition with a coarse-grained microstructure. Recent work on a two phase alumina-mullite fiber with variable grain morphology shows improved creep resistance with little degradation in strength (compared to fine-grained microstructures).

The purpose of the interfacial coating in a CMC is to provide a weak interface in order to separate cracking in the matrix from the fibers, thus providing damage tolerance in the composite. In addition, interfacial coatings are often used to protect fibers from environmental attack during composite fabrication or while in service. Because most commercial fibers are SiC based, coating research and development has concentrated on these non-oxide fibers. Despite studies of a wide range of interface coatings, tough composites have been reported only when coatings contain carbon or BN as one of the layers (a BN-coated Nicalon fiber is shown in Figure 1-6). Oxidation of the fiber/coating/matrix interface is a major life limitation for these composites. Oxidation of the interface can degrade the fiber or the debonding characteristics of the interface affecting both the strength and toughness of the composite.

The development of ceramic oxide fiber coatings has lagged behind the development of coatings for non-oxide fibers, in part because of the insufficient creep resistance of oxide fibers at elevated temperatures. With the recent development of oxide fibers with improved creep resistance, progress has been made on interface control in oxide systems. Initial approaches to fiber coatings for oxide composite systems (beyond the carbon and boron nitride approaches borrowed from the non-oxide composites) focused on oxide compounds that do not show compound formation with the fibers and the matrices. More recent approaches have focused on oxide interfacial coating materials that mimic the layered crystal structures of carbon and boron nitride, which were used successfully in non-oxide systems. Techniques were developed to provide a mechanically weakened interphase by using porous or fugitive coatings. The newest interface concepts being investigated for oxide systems are focused on creating high energy or nonwetting interfaces between coating compounds and oxide fibers.

ENGINEERING REQUIREMENTS

Opportunities for fiber development can best be discussed in the context of composite performance requirements. Most of the envisaged near- and intermediate-term applications (e.g., static hot-section engine components, such as combustor liners, turbine nozzles, and transition liners) require that components resist thermal loads. These applications, however, have minimal requirements for components to withstand pressure or other mechanical loads. In these cases, the failure strain of a composite is the salient measure of its damage tolerance. In other words, the composite's strain capacity is the metric that characterizes its ability to absorb damage caused by exogenous factors, such as overloads that occur in practice.

Experience suggests that composite failure strains that exceed 0.6 percent provide robust thermostructural charac teristics, whereas failure strains of 0.3 percent result in marginal thermostructural characteristics (Evans, 1997). Moreover, because the composite failure strain is dominated by the failure strain of the fiber bundles (as degraded by weaving, coating, and matrix infiltration), an appropriate goal is the development of fiber bundles with failure strains that exceed ~ 0.6 percent throughout the relevant temperature range for a specific application. These failure strains dictate a preference for low-modulus fibers, although overall stiffness requirements establish a minimum acceptable modulus for the fibers. For typical CMC components, the minimum modulus is approximately 150 GPa (22 Msi).

Most non-aerospace CMC applications require long service lives. For these applications CMC components must avoid creep rupture and must exhibit creep strains lower than ~1 percent after 10,000 hours of service (e.g., at 1,200°C [2,192°F] and 100 MPa [14.5 ksi]); components must also be chemically and microstructurally stable. These stringent demands present major challenges to researchers and engineers, particularly for material development and accelerated testing. The performance objectives limit the material choices to polycrystalline oxides, SiC, or amorphous Si-C-N-B compositions (single-crystal fibers are not affordable).

Balanced research of oxide and non-oxide materials on their specific life-limiting characteristics appears to be necessary because neither class of materials can satisfy design and service life requirements for all of the anticipated applications. For example, SiC-based materials have the high thermal conductivities and low thermal expansion coefficients essential for some components, particularly in high performance turbines for which oxides are inadequate. Conversely, in some corrosive environments (e.g., hot gas filters in coal-fired power systems), oxides provide necessary corrosion resistance.

The interrelationships between performance, manufacturing costs, and life cycle costs for systems containing CMC components have not been well defined. Consequently, the impact of the costs of fibers and coatings on the implementation of CMCs is ambiguous and system dependent. Oxide materials are fundamentally less costly than non-oxide materials, and markets for the former are limited primarily by their poor creep performance and the paucity of engineering data rather than by cost. Decisions regarding the implementation of non-oxide CMCs, however, do appear to be influenced by the costs of fibers and fiber coatings, as well as by performance limitations associated with embrittlement. Thus, the use of CMCs has been caught in the classic chicken-and-egg dilemma. The widespread use of CMCs clearly requires improved fibers at lower prices, but the lack of an established market for these fibers has limited commercial investment in their development and will not support the sales volume needed to reduce costs.

This committee and the high performance ceramics community at large have also been hampered by constraints imposed by end-users and manufacturers on access to engineering data for the most recently developed materials. This problem has been acute for researchers trying to solve problems related to embrittlement in ceramic composite systems who have been unable to assess the viability of various approaches to improving thermomechanical fatigue life. The lack of engineering data has severely limited the committee's ability to make recommendations regarding the use of fiber reinforcements and interfacial coatings for CMCs.

REPORT ORGANIZATION

Chapter 2 presents the current and projected requirements of ceramic fibers and interfacial coatings. Chapter 3 reviews the characteristics of fibers that are commercially available and fibers that are in the advanced stages of development. The characteristics of interest include stiffness, strength, thermal and electrical conductivity, creep and rupture resistance, and oxidation resistance—all as a function of temperature—and strength and stiffness retention as a function of service history. The relationships between processing, cost, and the performance of ceramic fibers is discussed in Chapter 4, and the relationship between material microstructure and properties is discussed in Chapter 5. The current status, needs, and processing approaches for fiber interfacial coatings are presented in Chapter 6. Chapter 7 discusses the relationship between costs and prices, aspects of fiber costs, and the implications of CMC market volume on fiber prices. The overarching research priorities are presented in Chapter 8, along with discussions of their anticipated impact on the field.

2

Current and Future Needs

The demonstrated and potential characteristics of CMCs have excited sufficient interest to sustain research and development for more than 15 years. This long-standing dedication has been based on the hope of creating materials with chemical and environmental stability that approaches the stability of monolithic ceramics, but with sufficient toughness and strength for structural applications. If these goals are achieved, it is anticipated that CMCs could enable improved performance in several commercial and military applications. In this chapter, the current and projected requirements of ceramic fibers and interfacial coatings are discussed in the context of composite fabrication and end-use applications.

Fiber and interface (e.g., fiber coating) requirements are based on the performance requirements of CMCs, which are defined by the performance requirements of intended applications. However, translating application requirements to fiber and interface requirements is difficult for two key reasons:

- CMCs are significantly different from monolithic ceramics, or even from fairly well understood polymer matrix composites (PMCs). The combination of limited ductility of the ceramic matrices and the highly aggressive environments in which they are intended to operate present notable challenges to defining constituent requirements.
- Because of a general lack of field experience, a clear understanding of how CMCs will perform in service has not been developed. Without operational experience, it has been impossible to calibrate knowledge with analytical models of performance.

Nevertheless, three long-term imperatives facing the United States have sustained interest in CMCs. These are:

- **National Defense and Space Exploration.** Aircraft, spacecraft, and missile structures and engines require more efficient (e.g., higher thrust-to-weight ratio), less detectable components.
- **Energy Efficiency.** Expanding global industrialization will continue to put pressure on energy resources, heightening concerns about energy efficiency.
- **Environmental Regulations.** Regulatory mandates to reduce emissions will continue to be an incentive for developing cleaner, more efficient combustion cycles.

CMCs show promise in addressing all of these imperatives because they are inherently refractory, have low density, and have demonstrated damage tolerance in some applications, suggesting that they could be used in light-weight, thermally loaded structures. CMCs also have weaknesses, however, such as oxidation embrittlement in non-oxide ceramics and limited creep strength in oxide ceramics. The useful performance attributes and weaknesses of CMCs are listed in Table 2-1. The advantages of CMCs over competing materials are most apparent when corrosion resistance is required or when benefit can be derived from reducing the cooling requirements of a component. Two examples are presented in Box 2-1.

IMPLEMENTATION OF NEW MATERIALS

The history of implementing new materials systems is littered with the remains of unanticipated failure modes encountered in service. For example, environmental effects and a general lack of understanding of the failures in carbon/epoxy fan blades devastated the early PMC industry in the 1960s. The effects of rain and sand caused significant erosion of the polymer matrices, and the inability of PMCs to survive

TABLE 2-1 CMC Performance Attributes and Weaknesses

Useful Attributes	Weaknesses
Notch insensitivity (high toughness)	Low tensile strength (UTS)
Scale insensitive UTS	Very low interlaminar strength
Some “ductility”	Susceptibility of SiC to “pesting” (oxidation embrittlement)
Low density	Low thermal conductivity (oxides)
Low thermal expansion (SiC)	Limited creep strength (oxides)
High thermal conductivity (SiC)	
Low thermal conductivity (oxides)	
High creep strength (SiC)	
Oxidation resistance (oxides)	
Low dielectric constant and loss tangent (oxides)	

impacts by foreign objects, especially birds, caused a safety/reliability problem that could not be overcome within the design requirements of the blades being considered. Experience with the early Comet aircraft in the United Kingdom (UK) and the F- 111 aircraft in the United States demonstrated that a lack of understanding of fracture toughness and crack growth behavior, and an inability to detect critical flaws could lead to problems, even when systems were designed with comparatively "well understood" metals for which large databases were available. Current knowledge about CMCs and their failure modes is based primarily on extensive laboratory data. These data, however, have not been validated by field experience—which incorporates combinations of effects unique to the operational environment.

BOX 2-1 Sample CMC Applications

Turbine Shrouds

The first stage shroud (see, for example, Figure 2-1) is exposed to some of the highest gas temperatures generated in a gas turbine engine. Current shrouds rely on coated nickel-based superalloys, which are air cooled. The material capabilities of these alloys limit the shroud temperature to approximately 920°C (1,688°F), which requires the use of cooling air, resulting in a substantial penalty in efficiency. CMCs may satisfy the mechanical and environmental requirements, while at the same time substantially reducing the need for cooling air, resulting in improved engine efficiency. For example, by replacing a cooled metal shroud with a CMC shroud in a 160 megawatt industrial gas turbine, a significant annual fuel savings could be realized.

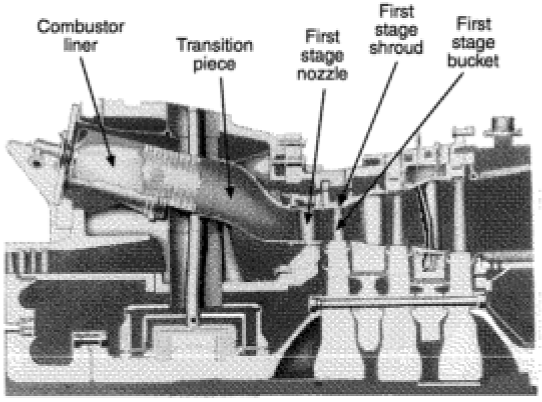


FIGURE 2-1 Cross section of the hot stage components of a large General Electric utility gas turbine. Source: General Electric Corporation.

Combustion Liners

Gas turbine manufacturers throughout the world are currently pursuing technology for reducing emissions of air pollutants in the exhaust. The most common pollutants generated by the combustion of conventional fuels are NO_x, CO, and unburned hydrocarbons (UHC). Lean premixed combustion is a promising method for reducing emissions. Burning the fuel after premixing with excess air is particularly effective at reducing the thermal NO_x, which is formed by oxidation of molecular nitrogen in the air at a high flame temperature. Excess air in the reaction zone of the combustor acts as a heat sink that lowers the flame temperature to the point where oxidation of nitrogen proceeds too slowly to produce any NO_x in the combustor.

To reduce the flame temperature in the reaction zone below the NO_x formation threshold, nearly all of the air available to the combustor must be premixed with fuel upstream of the reaction zone. If the combustion liner is film air cooled, as is necessary with conventional superalloys, the fraction of the combustor air *not available* for premixing with the fuel is 30 to 40 percent. Consequently, it is impossible to operate the combustor lean enough to remain below the NO_x formation threshold.

This problem could be solved using a CMC combustion liner that can withstand the temperature of the hot gas in the reaction zone without film air cooling. Using the available air for lean premixing rather than film air cooling would result in a reduction in NO_x emissions. CO and UHC emissions could also be reduced because the hot surface of a CMC combustion liner could be operated at a temperature high enough to ensure that the fuel oxidation reactions were not quenched at the combustor walls, even if the mixture were lean enough to prevent thermal NO_x formation.

Source: DOE, 1993.

Short development times, which are characteristic of the current manufacturing climate, have exacerbated the problem. Moreover, the complexity of CMC systems and the aggressive nature of the environments they must operate in have made the challenge of implementing them more difficult. Despite great progress in accelerated testing and computational modeling techniques, it is impracticable to simulate all possible scenarios.

For these reasons, it is imperative that intelligent, selective component, rig, and "in service" testing be performed to validate models and laboratory-based data. Although only a few examples of "in service" experience are available, they are instructive because each presents different combinations of materials properties and application experiences.

Glass Matrix Composites

The use of glass and glass-ceramic matrices for CMC fabrication aroused considerable interest and support in the 1970s and 1980s. Efforts to commercialize this technology were unsuccessful, however, because the market base was too small and there were no viable commercial suppliers. Nevertheless, numerous gas turbine engine component demonstrations were successful, and one component for the F-119 engine achieved bill-of-materials status in pilot plant production.

Recently, the Schott Corporation has set up a small plant in Germany that is producing glass matrix composite components for industrial applications. Their first implementation has been machine components for handling hot glass, and the company is beginning to expand its market.

SiC Matrix Composites

SiC matrix composites have been under development since the late 1960s, particularly composites produced by melt infiltration (e.g., General Electric Corporation in the United States) and CVI (e.g., SEP and the University of Bordeaux in France) (Hillig et al., 1975). Laboratory data obtained in the mid-1970s and 1980s demonstrated high temperature stability and encouraged deployment of these materials. The system developed by SEP underwent extensive rig testing, which led to a flight demonstration of a SiC matrix composite engine nozzle at the Paris Air Show and, ultimately, investments in facilities to scale up production in SEP's M53, M88, and EJ-200 engine models. However, large scale deployment never occurred because of unanticipated environmental degradation of the SiC composite components. SEP's experience undermined confidence in these materials, even at this late stage of development.

Oxide/Oxide Composites

Dornier of Germany developed oxide fiber-reinforced mullite matrix composite systems in the 1980s. The system was based on 3M's Nextel 312 fibers and slurry impregnation of a mullite matrix. This composite demonstrated modest levels of strength (120 MPa [17.4 ksi]) and low failure strain (0.2 to 0.3 percent). Several hot gas exhaust nozzles for Dornier's turboprop aircraft were successfully deployed and continue to be used in regular service.

Inhibited Carbon Matrix Composites

An oxidation-inhibited carbon matrix material reinforced with carbon fibers was developed and tested several years ago by the Wright Laboratory Materials Directorate, Hitco, Inc., and General Electric (Aviation Week, 1993). This technology has since been developed further by the replacement of traditional carbon fibers with SiC fibers and the addition of a SiC overcoat. SiC is inherently more resistant to oxidation than carbon and, therefore, retains strength and durability for a longer period of time in service. The oxidation-inhibited carbon matrix offers stiffness—and in the absence of oxidation—remarkable high-temperature mechanical properties. The SiC overcoat protects the composite from oxidation, as well as from other environmental threats. Engine flaps and seals made of this material have improved operating life by 900 percent over metal components (Wright Patterson Materials Directorate, 1995). Thousands of GE-F414 engine hours have been accumulated using this system, and this experience will add valuable information to the knowledge base.

CERAMIC MATRIX COMPOSITE DESIGN AND LIFE PREDICTIONS

Focusing on the CMC applications with the greatest potential for implementation requires placing CMCs within the broad spectrum of thermostructural materials. CMCs differ appreciably from structural metals, monolithic ceramics, and PMCs in their thermomechanical performance. Consequently, the strategies that govern design and life predication for CMCs are unique. The following guiding principles should facilitate the successful implementation of CMCs in targeted applications:

- Applications for CMC components should have loading and thermal profiles that exploit the *attributes of the material;* applications that are sensitive to the weaknesses of the material should be avoided (see Table 2-1).
- Computational design and life prediction codes should be developed explicitly for CMCs. Computational models and predictions should be validated by subelement and component tests that include representative thermomechanical loadings. Rigorous analyses of failure modes should then be performed.
- Designs and fiber architectures that obviate the delamination sensitivity of the critically important joints and attachments should be used (as they are in PMCs).

Because of their damage tolerance, CMCs perform well when they are subjected to thermal loads. However, because of their low UTSs, they are less robust upon inertial loading. Almost all of the applications envisaged for the near-term implementation of CMCs are, therefore, dominated by thermal loading requirements. The greater challenges of using CMCs in inertially loaded components should be deferred until field experience has been gained for thermally loaded components.

Because most CMC applications are dominated by thermal loads, the material temperature depends not only on the component environment (e.g., gas temperature in a turbine engine), but also on material properties and thermal boundary conditions. In a typical environment, material temperatures decrease as their thermal conductivity increases. Therefore, in common thermal environments and boundary conditions, SiC-based materials have lower material temperatures than oxides because of the higher thermal conductivity of SiC.

TABLE 2-2 Industrial Power Generation Applications

Program	Country	Application Type	Components	Typical Goals
Land-based gas turbines	United States	power generation	combustor turbine vanes	1,600°C (2,912°F) for > 25,000 hrs
100kW ceramic gas turbine	Japan	automotive	combustor turbine vanes	1,250°C (2,282°F) for 200 hrs strength 500 MPa (72.5 ksi)
Continuous fiber ceramic composite program	United States	power generation	shrouds combustors thermophotovoltaic power	900°C (1,652°F) for > 25,000 hrs
Continuous fiber ceramic composite program	United States	industrial processing	chemical pumps radiant burners gas filters furnace hardware reforming tubes	350°C (662°F) for 30,000 hrs in an environment containing organic and inorganic chemicals

CERAMIC MATRIX COMPOSITE APPLICATIONS AND REQUIREMENTS

A range of applications have been identified that require the attributes of CMCs listed in Table 2-1. The material requirements are diverse but can be classified into two cross-cutting categories. The first differentiates applications based on use sectors, such as energy and aerospace (see Table 2-2, Table 2-3, and Table 2-4). The second is based on material durability requirements, which are derived from time and temperature profiles (Figure 2-2). The first category is useful because the energy sector could provide a large enough market to reduce fiber costs. Implementation in this sector is, therefore, crucial. The second category facilitates setting goals for fiber properties.

Energy Systems

A high market volume for a broad range of CMC components is more likely in the industrial markets (e.g., power generation) than the aerospace industry. Potential high volume industrial applications could create enough demand for CMCs to lower fiber costs significantly, which would make more cost sensitive applications possible. For example, ground-based turbine engines have less stringent weight restrictions than airborne systems, but they have more stringent cost requirements (e.g., automotive engines) and long-term durability requirements (e.g., land-based power generators). Several potential industrial applications for CMCs are listed in Table 2-2, along with the programs that support their development.

The following near-term, lower risk applications represent product insertions that could provide long-term experience with CMCs:

- hot gas filters for pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycles systems (IGCC)
- furnace hardware, such as pipe hangers for petroleum refining
- reverberatory screens in porous radiant surface burners used for drying, curing, and process heating
- components for melting and handling metals

These near-term applications will probably not require using CMCs at the upper limits of their performance envelope (Figure 2-2). For example, experience is currently being gained with 3M's Type 203 ceramic composite filters (Figure 2-3), which are candle-type filters that consist of a SiC matrix reinforced with Nextel™ fibers. These filters are used to remove particulates from high-temperature (up to 1,200°C [2,192°F]) gas streams. Potential applications include PFBC, IGCC, and incineration. Lower risk applications like these are representative of the product insertions needed to gain long-term experience with CMCs.

Longer-term applications will be at a higher level of risk to end users who have performance requirements for higher temperatures and longer durations. The durability requirements of some industrial (energy) applications are shown in Figure 2-2. These applications include:

- nonrotating components in stationary gas turbines, especially combustion liners and shrouds

- heat exchangers for externally-fired combine cycles (EFCC) power systems, in which the hot air is supplied by a coal-fired heat exchanger and which must operate at approximately 1,400°C (2,552°F) in a coal slag environment for tens of thousands of hours
- thermophotovoltaic (TPV) power systems for household appliances (gas-fired hot water heaters and furnaces that operate in times of electrical outages) and quiet generators for the recreational market (recreational vehicles, yachts), in which a ceramic composite with selective emission characteristics excites matched photovoltaic cells and which must operate at 1,400°C (2,552°F) to achieve the required power densities
- reforming tubes for the chemical processing industry

TABLE 2-3 Aircraft Applications a

Program	Country	Aircraft Type	Components	Typical Goals
Integrated high performance turbine engine technology	United States	military	combustor turbine exhaust nozzle	operate at temperatures > 1,320°C (2,408°F) for > 1,000 hrs
High speed civil transport	United States	commercial supersonic transport	combustor exhaust nozzle	operate at temperatures > 1,600°C (2,192°F) for combustor operate at temperatures > 800°C (1,472°F) for nozzle time at temperature > 10,000 hrs
NASA high temperature	United States	aircraft gas turbines	various	operate at temperatures > 1,320°C (2,408°F) for > 1,000 hrs
Advanced material gas generator	Japan	commercial transport	compressor combustor turbine	turbine inlet temperature of 1,600°C (2,912°F), with 20 percent efficiency improvement, 50 percent weight reduction, and 75 percentNO_x reduction

[a] Note that this table is not a comprehensive representation of program goals.

Aerospace Systems

Aerospace applications can be divided into aircraft, missile, and space systems. Several aircraft programs are focused on tailoring CMCs to improve performance, reduce weight, improve fuel efficiency, and reduce undesirable emissions from gas turbine engines. Some of these programs and their goals are listed in Table 2-3. In general, although the highest exposure temperatures are frequently quoted as “goal” temperatures, performance at lower temperatures and during thermal cycling may be more demanding.

In each case, the CMC components must have the following attributes for a predetermined time:

TABLE 2-4 Space Applications (United States)

Program	Type	Components	Typical Goals
Integrated high performance turbine engine technology	missiles	combustors turbine rotors	operating temperature > 1,400°C (2,552°F)
Integrated high payoff rocket propulsion technology	space vehicles and tactical missiles	turbomachinery thrust chambers nozzles	very high temperature for short periods of time
NASA reusable and expendable launch vehicles	space vehicles	thrust chambers nozzles thermal protection	not available
In-space propulsion	satellites	maneuvering thrusters	operating temperature > 1,700°C (3,092°F) for < 10 hrs

- stability at the goal temperatures indicated and, during thermal cycles, through lower temperatures
- resistance to chemical attack in the gas path flow
- sufficient strength/strain capability to survive normal operating conditions and periodic instances of damage (e.g., overstress)
- reproducible performance

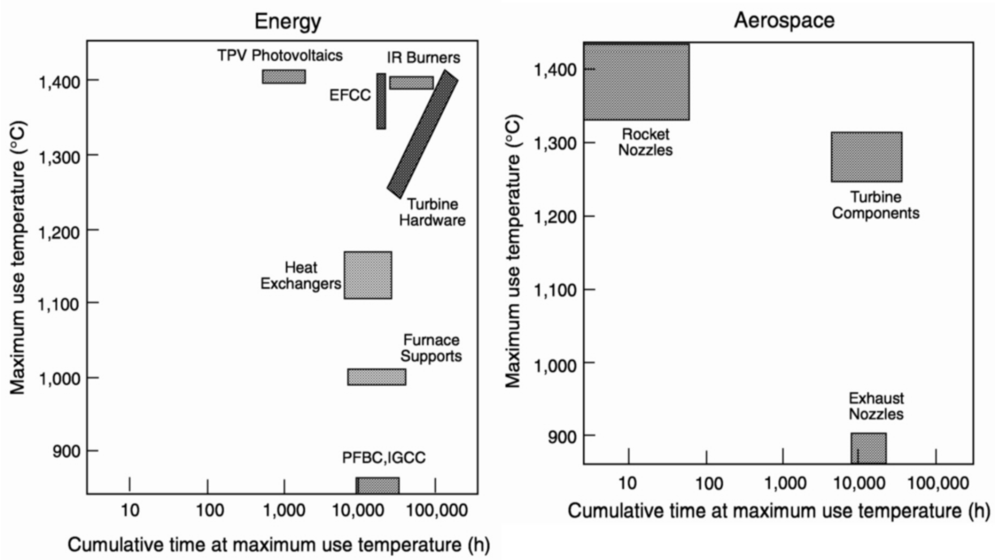


FIGURE 2-2 Thermal performance requirements for various high-temperature applications.

Even though exhaust nozzles in aircraft engines represent a lower temperature, near-term application, the requirements for successful implementation are demanding because unprotected exposure to the atmosphere results in ingress/egress of atmospheric moisture (the same problem that plagued the early deployment of PMCs). The presence of matrix cracks in CMCs makes moisture flow possible. In military aircraft, there is an added requirement for low observability (e.g., low dielectric constant).

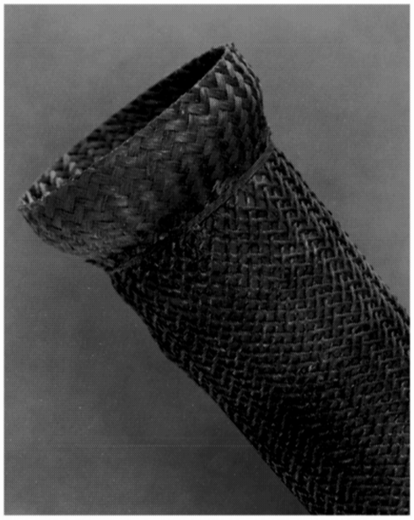


FIGURE 2-3 3M Type 203 Nextel fiber-reinforced SiC matrix ceramic composite candle filter. Source: 3M Company

The implementation of CMCs in spacecraft and uninhabited vehicles is attractive because material life requirements are much less demanding than the requirements for aircraft and industrial applications (Table 2-4). Because the operating environment in space is often non-oxidizing, life limiting oxidative embrittlement of non-oxide ceramics will *not* occur. Consequently, materials based on SiC and C are viable choices and have already been well established from the perspectives of performance and manufacturing characteristics. These limited volume high value applications could add to the production base of CMCs.

MANUFACTURING REQUIREMENTS

Reliability and Reproducibility of Fiber Supplies

One of the key features of emergent materials technologies is the constant changes in processing by materials producers to improve performance and lower costs. Unfortunately the ramifications of these changes are often subtle and cannot always be anticipated. Changes in fiber property requirements and expansion to higher volume production, however, create constant pressure to improve productivity and, hence, to implement processing changes. At some point in the development of ceramic fibers, quality control measures must be put in place to identify and maintain a baseline process configuration (i.e., “frozen” in place). Overly restrictive quality control measures can stifle innovation, whereas uncontrolled process changes can lead to unanticipated performance degradation in end applications.

Handleability and Processability

CMC components have complex shapes, and because of their very low off-axis strength they require multiaxial fiber reinforcement. To attain such complex shapes, the fibers must be able to be readily handled. That is, fibers must be able to be bent through radii of a few millimeters. Furthermore, if coatings are applied to fibers before the final composite fabrication steps (e.g., filament winding, etc.) coating adherence and durability must allow bending, weaving, etc. Ceramic fibers are subjected to temperature extremes and unique environments during processing (Table 2-5). Obviously fibers are needed that do not degrade during exposure to composite processing environments.

IMPLICATIONS FOR FIBER PROPERTIES

Studying the temperature and time-at-temperature requirements for potential CMC applications (Figure 2-2) can provide a perspective on fiber property requirements. It should be noted, however, that material temperature is a function not only of the temperature of the service environment, but also of material thermal conductivity and engineered cooling strategies. Furthermore, fiber durability may not be dictated by property retention at the highest material temperature. For example, non-oxide ceramic fibers demonstrate significant property retention at temperatures as high as 1,600°C (2,912°F). CMCs made from non-oxide fibers, however, have life limiting “pest” problems at intermediate temperatures (e.g., 700 to 900°C [1,292 to 1,652°F]) under cyclic loading conditions in an oxidizing atmosphere.

TABLE 2-5 CMC Processing Environments

Process Type	Process Environment	Maximum Temperature	Time in Process (hours)
Chemical vapor infiltration	multiple inert and corrosive gases	940 to 1,220°C (1,724 to 2,228°F	100
Reaction bonding	molten silicon	1,450 to 1,500°C (2,642 to 2,732°F	1
Polymer infiltration and pyrolysis	various chemical infiltrants with ceramic powders	800 to 1,200°C (1,472 to 2,192°F	multiple steps with 100-hour total
Directed metal oxidation	molten aluminum	950°C (1,742°F)	100

Nevertheless, thermal requirements are useful for setting goals for the microstructural stability and creep resistance of fibers. For example, during component service life, grain growth at the highest use temperature should be less than approximately 20 percent in order to limit the attendant strength reduction to less than 10 percent. Fiber creep strain and creep rupture life must also be at acceptable levels. For example, fiber strains greater than approximately 1 percent are unacceptable because the attendant composite distortions compromise attachments, dimensional tolerance, etc. Defining fiber performance requirements for a temperature-time domain is contingent upon CMC component design—through the expected stress levels—as elaborated below.

General Considerations

The performance of thermally loaded components (in the absence of inertial loading) is dictated by thermally induced strain: $\varepsilon_T = \alpha \Delta T$, where α is the thermal expansion coefficient, and ΔT is the temperature difference between adjacent regions of the component. The relationship between CMC failure strain (ε_f) and thermally induced strain (ε_T) can be used as a metric to rank materials for preliminary designs within regions subject to high thermal flux:

$$\varepsilon_f > \varepsilon_T \quad (1)$$

The relationship between the strain at the proportional limit (ε_p, strain at which matrix cracking occurs) and ε_T ranks materials for general thermal loads:

$$\varepsilon_p > \varepsilon_T \quad (2)$$

Equation 1 can be used as a guide for fiber requirements, because ε_f is approximately equal to the strain-to-failure of dry fiber bundles (provided they are adequately protected against degradation during manufacture by appropriate fiber coatings and matrix infiltration technology). Equation 2 is dictated largely by the matrix.

CMC components are designed so that Equation 2 is satisfied over most of the structure. Similar to other thermostructural systems, however, local exceedences (e.g., $\varepsilon_T > \varepsilon_p$) are likely and are permitted in the design because the precise loads experienced during service are not known. Provided that ε_T does not exceed ε_f, composite durability should be adequate. If local exceedences create a situation that results in a reduction of ε_f (i.e., fiber degradation), however, durability would be compromised. For example, matrix cracking ($\varepsilon_T > \varepsilon_p$) in the presence of oxygen can create pathways for oxygen ingress and concomitant oxidative embrittlement of non-oxide ceramic fibers. Moreover, with thermal loadings, the largest tensile stresses occur in the cooler regions of the structure, where "pest" problems are most debilitating. Therefore, in addition to ε_f and ε_p, system approaches to limit the consequences of matrix cracking must be part of the design.

For composite applications, there are no explicit requirements on the ultimate tensile stress (UTS) of CMCs, although an implicit minimum UTS is dictated by stiffness requirements. Furthermore, there are no requirements for CMC toughness. Instead, the notch performance is more indicative of thermomechanical robustness (i.e., the reduction in net-section UTS upon notching the material). Notch performance is a benchmark for damage tolerance and can be used in the design of holes, slots, and attachments. Damage tolerance is controlled by the frictional characteristics of the interfaces, which is manifested in inelastic deformation. Good notch performance throughout a representative thermomechanical exposure is essential to the implementation of CMCs.

Fiber and Interface Requirements

Given the limited amount of field experience and the limited analysis of that experience, it is premature to be explicit about property requirements. Thermal loadings tend to be benign because inelastic strains redistribute the stresses caused by thermal expansion. Design calculations that do not take these stress redistributions into account can lead to overly pessimistic conclusions. Creep and rupture requirements cannot be directly related to fiber creep rupture diagrams (Chapter 3) because the stresses on fibers in thermostructural applications are unknown. Unlike thermal loads, pressure and inertial loads continue to act and cause strain accumulation throughout the operating cycle of a CMC component. Therefore, matching material properties to application requirements requires distinguishing between thermal and mechanical loadings. This distinction is rarely made in finite element computations.

Classifying applications by the maximum use temperature (T_{max}) and the time (t_m) at that temperature is not always relevant because life limiting mechanisms may operate at lower temperatures, thus negating high-temperature performance in medium-duration (e.g., aircraft engines) and long-duration (e.g., land-based power turbines) applications. Some applications (e.g., rocket nozzles), however, require very short-duration performance at extreme temperatures. Because the service environment affects the relevance of T_{max} and t_m, focusing exclusively on T_{max} or t_m is imprudent.

For robust thermomechanical performance, the toughness and ductility manifest in the notch behavior cannot be compromised. Presently, no guidelines have been established for setting requirements for these properties. Experience indicates that tensile "ductility" (i.e., fiber failure strain) that exceeds approximately 0.6 percent gives good toughness and desirable notch behavior. But there are also examples of strain-at-failure of 0.3 percent being adequate when the materials exhibit appreciable shear ductility (carbon/carbon composites, for example). In short, fiber failure strain requirements have not been rigorously defined (Evans, 1997).

Although determining whether available fibers are adequate or inadequate for current CMC applications is impracticable without input from component and subelement testing, the following statements can be made:

- Fibers must be microstructurally stable at T_{max} for t_m.
- Dry bundle failure strains greater than 0.3 percent seem to be a prerequisite for robust behavior, but $\varepsilon_f > 0.6$ percent virtually assures robust behavior.
- Enhancing the creep and rupture properties of fibers is undoubtedly beneficial, but explicit goals cannot be set until component testing is done.

The committee made two assumptions to formulate the interrelationships between application requirements and fiber properties. First, the combination of tensile strength, creep resistance, and rupture resistance exhibited by available SiC fibers is approaching theoretical limits. Second, enhancing the creep strength of oxide fibers by several hundred degrees centigrade may be possible although this has not been demonstrated.

Fiber/matrix interface requirements are also difficult to define. It appears, however, that CMCs are limited, for the most part, by insufficiently engineered interfaces. That is, CMC performance is limited by the inability to maintain a weakly bound fiber/matrix interface at elevated temperatures. Solving this problem is a prerequisite for realizing the benefits of improved fiber properties.

3

State of the Art in Ceramic Fiber Performance

Continuous-length ceramic fibers used to reinforce CMCs must have optimal mechanical, physical, and chemical properties (described in Chapter 2). This chapter reviews the characteristics of fibers that are commercially available and fibers that are at an advanced stage of development. The performance characteristics of interest include stiffness (i.e., Young's modulus), strength, thermal and electrical conductivity, creep and rupture resistance, oxidation resistance, all as a function of temperature, and strength and stiffness retention as a function of service history. The critical issue of chemical compatibility with prospective interface coatings and the ceramic matrix is addressed in Chapter 4 and Chapter 6.

CANDIDATE FIBERS

The physical characteristics, fabrication methods, and key microstructural features of all ceramic fibers, both oxides and non-oxides, are tabulated in Table 3-1. The characteristics of fibers that are commercially available are summarized in Table 3-2, including maximum use temperature, current uses, and current prices. Ceramic oxide fibers (often referred to as oxide fibers) are composed of oxide compounds, such as alumina (Al_2O_3), mullite ($3Al_2O_3$-$2SiO_2$), and zirconia (ZrO_2). Unless specifically identified as a single-crystal fiber, oxide fibers are assumed to be polycrystalline. The nonoxide fibers discussed in this report are polycrystalline SiC fibers or multiphase (amorphous or crystalline) combinations of boron (B), carbon (C), nitrogen (N), titanium (Ti), or silicon (Si).

Two monofilament fibers have been included in Table 3-1, Saphikon (single-crystal alumina) and SCS-6 (a multilayered C/SiC fiber produced by chemical vapor deposition on a carbon fiber substrate), both of which have been used extensively in research on CMCs. They also represent the two extremes of creep resistance (Saphikon) and creep rupture strength (SCS-6). Some of the fibers listed in Table 3-1 are no longer available, having been discontinued as commercial or developmental fibers by the manufacturers. They are included in the table because significant property databases have been generated for them indicating fruitful directions for future research to improve fiber properties. Table 3-1 does not include every member of each fiber product family (e.g., some fiber versions in the Nextel and Tyranno product lines) either because they are not of general interest for CMCs or high temperature use or because they represent incremental changes in properties and may not be commercialized.

In general, oxide fibers are poor thermal and electrical conductors and have higher coefficients of thermal expansion (CTEs) than non-oxide fibers. In addition, oxide fibers are usually more dense than non-oxide fibers. Non-oxide fibers generally have higher electrical and thermal conductivities, and SiC-based fibers are more conductive than Si(N)-based fibers.

Comparison of Fiber Categories

As a class, polymer-derived SiC-based fibers are the strongest ceramic fibers known. Those with very small β-SiC grain sizes and high carbon and/or amorphous phase contents (e.g., Nicalon, Tyranno, University of Florida [UF], SiC) also have a low elastic modulus, which results in high strain-to-failure (i.e., greater than 1 percent). As the β-SiC grain size increases or the amorphous phase content decreases, the carbon content increases in some fibers (Hi-Nicalon, Tyranno Lox E) resulting in a decrease in strength and an increase in the modulus, thus sacrificing strain-to-failure. These microstructural changes are induced by (1) using a curing step during fiber processing that incorporates very little oxygen into the structure and (2) by conducting pyrolysis at higher temperatures.

In the Tyranno family of non-oxide fibers, Ti was originally incorporated into the fiber during processing to create a very fine β-SiC grain size. In the Tyranno ZM fiber and its derivatives, zirconium (Zr) is included to improve its high-temperature properties and resistance to NaCl corrosion.

Recent research worldwide has focused on producing a stoichiometric SiC fiber to enhance high-temperature properties (e.g., creep resistance, strength retention, and oxidation resistance). Hi-Nicalon S fiber consists of nearly stoichiometric β-SiC with a very slight carbon excess and very low oxygen (~ 0.2 percent) content. The β-SiC grain size is about twice the grain size in Hi-Nicalon fiber. Thus, the strength of Hi-Nicalon S fiber is somewhat lower than Hi-Nicalon fiber, and the modulus approaches the modulus expected for fully crystalline SiC. The high-temperature property improvements of these fibers are discussed in more detail below.

The Carborundum sintered α-SiC fiber, which has been discontinued, was formed by extruding a melt spinning compound, which had been formed by mixing a sinterable submicron SiC powder and sintering aids (e.g., B and excess C) with a suitable polymer. The extruded fibers were then drawn down to the desired diameter and sintered at temperatures in excess of 2,000°C (3,632°F). The fibers produced were nearly fully dense, with an average α-SiC grain size of ~1.7 µm (0.07 mils). Their strength was limited by the largest grains and, occasionally, by pores. This fiber had the best creep resistance of all the polycrystalline ceramic fibers fabricated to date.

The developmental Dow-Corning Sylramic SiC fiber is a B-doped, fully crystalline fiber with a β-SiC grain size on the order of 0.1 to 0.5 µm (0.004 to 0.02 mils). The Sylramic fiber is a polymer-derived SiC fiber in which B is incorporated prior to sintering, resulting in a fully crystalline material. Because this fiber is sintered at higher temperatures than most other fibers, the creep resistance is comparable to the Carborundum fiber while strength is retained or slightly increased. The Sylramic fiber is much stronger than other stoichiometric SiC fibers. The high-temperature properties of this fiber are superior to finer grain size, carbon-containing, polymer-derived SiC-based fibers.

The University of Florida, in collaboration with 3M, has developed a potentially lower cost, dry spun polymer-derived analogue of Hi-Nicalon fiber. It appears that this process can produce the same microstructural evolution that produced the high-performance Nicalon/Hi-Nicalon family of SiC fibers. Processing costs may be lower because this fiber does not require a separate thermal cross-linking (cure) step. This advantage may, however, be somewhat offset by the controlled evaporation and recovery of solvent, which is inherent in the dry spinning process.

Textron's SCS-6 SiC fiber was included in Table 3-1 primarily because it has excellent room-temperature strength and creep-rupture resistance. It is currently made in monofilament form, but multifilament tow fabrication is being researched. The excellent mechanical properties of this fiber apparently arise from its uniform, fine grained (~ 0.04 to 0.1 µm [0.002 to 0.004 mils]) microstructure and its single-phase stoichiometric β-SiC composition.

An amorphous Si-B-N-C fiber produced by novel polymer precursor technology is currently being developed by Bayer HG in Germany. This fiber has high room-temperature strength and stiffness and is reported to have remarkable strength retention and creep resistance at elevated temperatures. In addition, the $SiBN_3C$ version of this fiber develops a hexagonal BN layer under the conventional SiO_2 oxidation product upon oxidation at 1,500°C (2,732°F), thus holding out the promise of producing a crack deflecting interface in situ.

Among the oxide ceramic fibers, single-crystal alumina fibers are much stronger than polycrystalline oxide fibers. Recent work on single-crystal fiber growth by Ali and co-workers (Sayir, 1993) reinforces this conclusion, particularly when pore-free fibers are drawn. The strengths of the polycrystalline oxide fibers are generally limited by processing defects or by the largest grains in the fibers. The strongest single-phase polycrystalline oxides at room temperature are the ones with the finest grain size and are generally fabricated from a sol-gel precursor. For example, the Nextel 610 fiber, which is a single-phase polycrystalline α-Al_2O_3 fiber with a grain size on the order of a 0.10 µm (0.004 mils) has a room-temperature strength of 3.0 GPa (430 ksi). Because of this fine grain size, however, this fiber has poor creep resistance.

Several of the commercially available oxide fibers are multiphase materials. For example, Nextel 312 fibers contain an amorphous phase along with mullite, and Altex fibers contain an amorphous phase and γ-Al_2O_3. Several oxide fibers incorporate a second crystalline phase. For example, PRD-166 fibers consists of α-Al_2O_3 and ZrO_2, and Nextel 720 fibers are composed of α-Al_2O_3 and mullite. Although these fibers are not the strongest polycrystalline oxides available, the incorporation of secondary phases yields significant benefits in high-temperature creep and rupture resistance. The strength of multiphase oxide fibers could be increased with grain refinement.

TEMPERATURE AND TIME DEPENDENCE OF PROPERTIES OF NON-OXIDE FIBERS

Strength and Stiffness as a Function of Test Temperature

The strength and Young's modulus of "early" Nicalon and Tyranno fibers are shown in Figure 3-1 and Figure 3-2a, respectively. Note that the room-temperature strengths shown in Figure 3-1 are lower than in Table 3-1 because the fiber gauge lengths used in the strength test reported in Figure 3-1 were much larger than the standard one inch length used for the

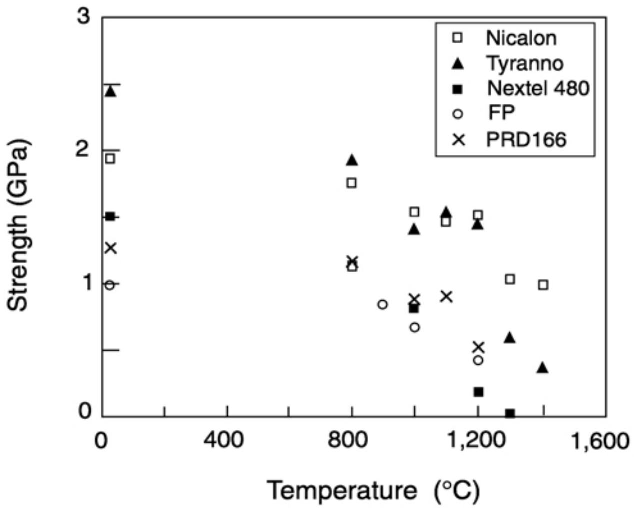


FIGURE 3-1 Strength vs. temperature of SiC-based fibers and oxide fibers. Source: Pysher et al., 1989.

TABLE 3-1 Commercially Available and Developmental Ceramic Fibers for CMCs

OXIDES

Trade Name	Manufacturer	Composition (wt%)	Density (g/cm^3)	Grain Size (µm)-Microstructure	Diameter (µm)	Fibers-Tow	Process	Elastic Modulus (GPa)	Strength (GPa)	CTE [c] (ppm/°C)	Thermal Conductivity	Electrical Conductivity	Comments
Fiber FP [a]	DuPont	> 99% α-Al_2O_3	3.92	0.5	20	200	slurry spinning	380	1.38	~ 9	—	—	—
PRD-166 [a]	DuPont	~80% α-Al_2O_3 ~20% ZrO_2	4.2	0.5 (α-Al_2O_3) 0.1–0.3 (ZrO_2)	20	200	slurry spinning	380	2.3	~ 9	—	—	—
Nextel 312	3M	62% Al_2O_3 24% SiO_2 14% B_2O_3	2.7	< 0.5 mullite in glass	10–12	740–780	sol-gel	150	1.7	3	—	—	dielectric constant 5.2 at 9.375 GHZ
Nextel 720	3M	85% Al_2O_3 15% SiO_2	3.4	< 0.5 α-Al_2O_3 + mullite	10–12	—	sol-gel	260	2.1	6	—	—	dielectric constant 5.8 at 9.375 GHZ
Nextel 550	3M	73% Al_2O_3 27% SiO_2	3.03	< 0.5 mm γ/δ Al_2O_3+ glass	10–12	—	sol-gel	193	2.0	5.3	—	—	dielectric constant 5.8 at 9.375 GHZ
Nextel 610	3M	0.2–0.3% SiO_2 0.4–0.7% Fe_2O_3 > 99% α-Al_2O_3	3.88	0.1	14	390	sol-gel	373	2.93	7.9	—	—	dielectric constant 9.0 at 9.375 GHZ
Almax	Mitsui Mining	> 99% α-Al_2O_3	3.6	0.4	10	1,000	slurry spinning	210	1.8	8.8	—	—	—
Altex	Sumitomo	85% γ-Al_2O_3 15% SiO_2	3.2	0.02 γ-Al_2O_3 in glass	16	1,000	sol-gel	193	2.0	7.9	—	—	—
Saphikon	Saphikon	100% Al_2O_3	3.96	single-crystal α-Al_2O_3	125	mono filament	edge defined film-fed growth	470	3.5	9	—	—	developmental fibers

NONOXIDES

Trade Name	Manufacturer	Composition (wt%)	Density (g/cm^3)	Grain Size (μm)-Microstructure	Diameter (μm)	Fiber Tows	Process	Elastic Modulus (GPa)	Strength (GPa)	CTE^c (ppm/°C)	Thermal Conductivity	Electrical Conductivity	Comments
Nicalon NL200	Nippon-Carbon	57% Si 31% C 12% O	2.55	5nm β-SiC in Si-O-C amorphous phase	14	500	polymer pyrolysis	220	3.0	—	—	(10^3–10^4 ohm-cm)	1.4% elongation to failure
Hi Nicalon	Nippon-Carbon	62% Si 32% C 0.5% O	2.74	~ 10nm β-SiC, C	14	500	polymer pyrolysis	270	2.8	—	—	(1.4 ohm-cm)	1.0% elongation
Hi Nicalon-S	Nippon-Carbon	68.9% Si 30.9% C 0.2% O	3.10	~ 20 nm β-SiC, C	12	500	polymer pyrolysis	420	2.6	—	—	(0.1 ohm-cm)	0.6% elongation, developmental fiber
Tyranno Lox M	Ube	55.4% Si 32.4% C 10.2 % O 2% Ti	2.48	~ 2 nm	11	800	polymer pyrolysis	187	3.3	3.1	—	(30 ohm-cm)	1.8% elongation
Tyranno ZM	Ube	55.3% Si 33.9% C 9.8% O 1.0% Zr	2.48	~2 nm	11	800	polymer pyrolysis	192	3.3	—	—	(10 ohm-cm)	1.7% elongation, developmental fiber
Sylramic	Dow-Corning	66.6% Si 28.5% C 2.3% B 2.1% Ti 0.8% O 0.4% N	3.0	0.1–0.5 β-SiC 0.05 TiB_2	10	800	polymer pyrolysis and sinter	380	3.2	5.4 (20–1,320°C)	40 W/mK	—	developmental fiber
SiBN(C)	Bayer	$SiBN_3C$ with 1–3% O	1.8–1.9	amorphous	8–14	300	melt spin polymer pyrolysis	358	3.0	3.5	0.4 W/mK at 1,500°C	insulating	developmental fiber
Tonen	Tonen	58% Si, 37% N 4% O, trace C	2.5	—	10	—	polymer pyrolysis	250	2.5	—	—	—	—
SCS-6	Textron	SiC on C	3.0	0.04–0.1 β-SiC on C core	140	mono-filament	CVD on C	390	4.0	4.6	—	—	—
UF SiC^b	University of Florida/3M	SiC, 1.17% O	2.7	< 0.05 μm β-SiC amorphous carbon	10–12	120	dry spin polymer pyrolysis	210–240	2.8	—	—	—	developmental fiber

[a] Discontinued by the manufacturer.

[b] There is also a high modulus version of this fiber (E = 420 GPa) with a larger β-SiC grain size (0.5 μm) and a higher density (~ 3.15 g/cm^3).

[c] CTE = Coefficient of thermal expansion.

Data obtained from Baldus (1997), Hasegawa (1997), Lipowitz (1997b), Pysher and Tressler (1991), Sacks et al. (1997), Takeda (1996, 1997), Wilson (1997).

TABLE 3-2 Selected Commercially Available Ceramic Fibers

Trade Name	Prime Composition [a]	1,000 Hour Maximum Use Temperature (°C) (rupture strength = 100 MPa) [a]	1,000 Hour Maximum Use Temperature (°C) (rupture strength = 500 MPa) [a]	Projected Applications	Price
Nicalon NL200	Si-C-O	<1,300	<1,100	reinforcement in CMCs, projected application in turbine engine components and heat exchangers	\$1,250/kg for 1 kg to several hundred kg
Hi-Nicalon	Si-C	<1,400	1,200	reinforcement in CMCs, projected application in turbine engine components and heat exchangers	\$6,900/kg for 1 kg to several hundred kg
Tyranno Lox M	Si-C-O-Ti	n/a	n/a	n/a	n/a
Sylramic	SiC, TiB_2	>1,400	1,200	reinforcement in CMCs, projected application in turbine engine combustor liners	\$10,000/kg for <5 kg \$8,500/kg for 5–50 kg \$6,700/kg for > 50 kg
Tonen	Si-N-C	n/a	n/a	n/a	n/a
SCS-6	SiC	> 1,400	< 1,300	n/a	\$8,800/kg for 0.5–4.5kg \$5,500/kg for > 90kg
Altex	Al_2O_3-SiO_2	n/a	n/a	n/a	\$326/kg
Nextel 312	Al_2O_3-SiO_2-$B2O_3$	n/a	n/a	flexible thermal insulation for furnace linings, seals and curtains, high-temperature sleeving, aircraft firewalls, ceramic composites, and hot gas filters	\$227/kg for <227kg \$206/kg for 227–682 kg \$187/kg for >682kg
Nextel 610	Al_2O_3	950	850	reinforcement of CMCs, hot gas filters	\$1,100/kg for <455 kg \$594/kg for >455 kg
Nextel 720	Al_2O_3-SiO_2	1,050	950	reinforcement of CMCs, hot gas filters	\$1,012/kg for <455 kg \$550/kg for > 455 kg
Almax	Al_2O_3	n/a	n/a		
Saphikon	Al_2O_3 (single crystal)	> 1,400	1,250		~ \$66,000/kg

[a] Source: DiCarlo and Dutta, 1995

data presented in Table 3-1. [1] In the late 1980s, the Nicalon fiber was clearly superior to the Tyranno fiber.

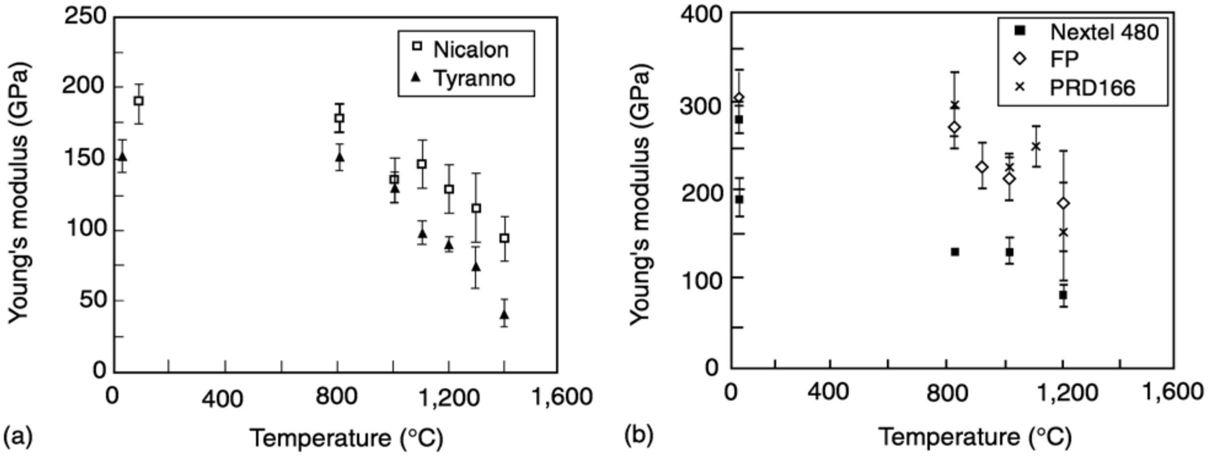
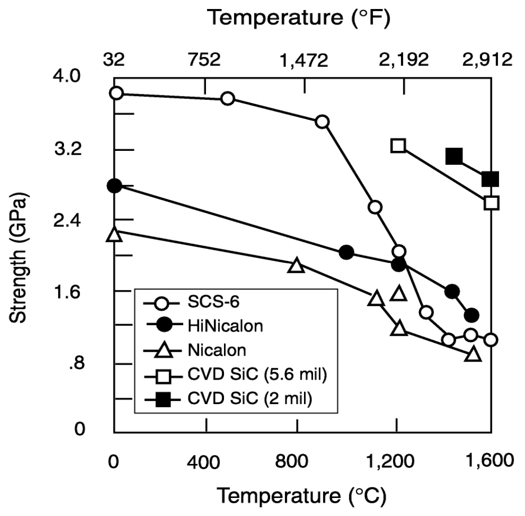


FIGURE 3-2 (a) Young's moduli vs. temperature for SiC-based fibers. Each point represents the average of at least 10 tests. Error bars represent 95 percent confidence limits. (b) Young's moduli vs. temperature for oxide fibers. Each point represents the average of at least 10 tests. Error bars represent 95 percent confidence limits. Source: Pysher et al., 1989.

Tensile strength as a function of temperature for some later SiC fibers is shown in Figure 3-3 (Misra, 1994). However, surprisingly few reports of fast fracture strength as a function of temperature for these and other recently developed nonoxide fibers are available. The trends in fast fracture strength of both oxide and non-oxide ceramic fibers as a function of temperature are given in Figure 3-4 (DiCarlo and Dutta, 1995). The SiC fibers produced by chemical vapor deposition (CVD) are clearly superior in fast fracture strength to most of the polymer-derived polycrystalline fibers. Low oxygen content, polymer-derived fibers (e.g., Hi-Nicalon) show higher strengths at high temperatures than the higher oxygen content polymer-derived fibers (e.g., Nicalon). The low oxygen content Tyranno and UF SiC fibers are expected to follow this trend. Although the Dow Corning Sylramic fiber is expected to exhibit good strength retention in the 1,000 to 1,300°C (1,832 to 2,372°F) range, no data are available in this temperature range. The Carborundum-sintered SiC fiber showed fast fracture strengths of ~800 MPa (120 ksi) at 1,400°C (2,552°F) in air and ~750 MPa (110 ksi) at 1,200°C (2,192°F) in air, thus retaining more than 90 percent of its roomtemperature strength (Tressler et al., 1995). This suggests that



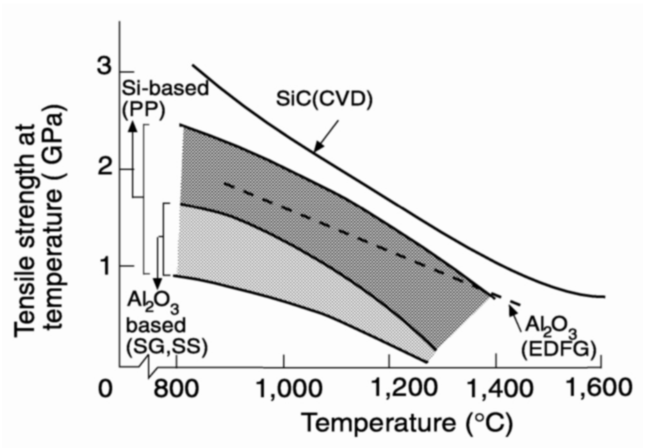


FIGURE 3-3 Tensile strength vs. temperature of various SiC fibers. Source: Misra, 1994.

FIGURE 3-4 Fast fracture strength at temperature for commercial fibers based on silicon compounds and alumina. PP = polymer pyrolysis, SG = sol gel, SS = slurry spinning, EDFG = edge defined film growth, CVD = chemical vapor deposition. Source: DiCarlo and Dutta, 1995.

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[1] Ceramic materials often fail well below their inherent theoretical strengths as a result of critical flaws. For a given fiber thickness, a larger gauge length represents a larger volume of material and, therefore, an increased probability of a critical flaw, which results in a lower average measured strength.

fully crystalline, near stoichiometric SiC fibers will show very little strength degradation between room temperature and 1,200 to 1,400°C (2,192 to 2,552°F).

Room-Temperature Strength and Modulus as a Function of Aging

The literature is rich with experimental data on the room-temperature strength of non-oxide fibers after exposure to high temperatures in air, inert atmospheres, and reducing atmospheres.

- Aging studies (usually at high temperatures in an inert environment for short times) are often conducted to assess the effects of fiber pyrolysis temperatures on room-temperature strength.
- The effects on fiber properties of exposure to composite fabrication conditions can be simulated by a relatively short exposure of fibers to high temperatures in an inert or reducing environment.
- The effects of decomposition of polymer-derived fibers in long-term service in inert or reducing conditions can be simulated by long-term exposure to such environments at temperatures above the pyrolysis condition.
- The effects of oxidation on the SiC, C, or Si-N-C phases have been simulated by short- to long- term exposure in air or oxygen.

Figure 3-5 is a general view of the effect of high-temperature exposure for one to ten hours in argon on the room-temperature strength of ceramic fibers. Polymer-derived fibers that contain some Si-O-C phase lose strength due to the decomposition of this phase to form gaseous SiO(g) and CO(g) at temperatures greater than or equal to the original pyrolysis temperature. This decomposition is accompanied by β-SiC grain growth and the generation of pores within the fiber. This kind of degradation has been suppressed by heat treatments in CO (Bodet et al., 1996). The very low oxygen content polymer-derived fibers (e.g., ZE and Hi-Nicalon Type S) retain their strength much better than oxygen containing Si-based fibers after high-temperature exposure in argon (Figure 3-6 and Figure 3-7) because of the improved microstructural stability in

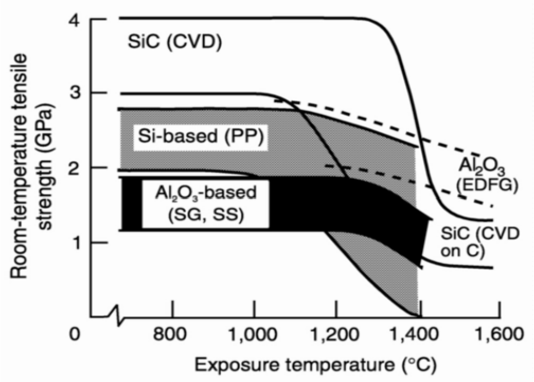


FIGURE 3-5 Room-temperature strength retention after short thermal exposure (one to ten hrs) of commercial silicon-based and alumina-based fibers. PP = polymer pyrolysis, SG = sol gel, SS = slurry spinning, EDFG = edge defined film growth, CVD = chemical vapor deposition. DiCarlo and Dutta, 1995.

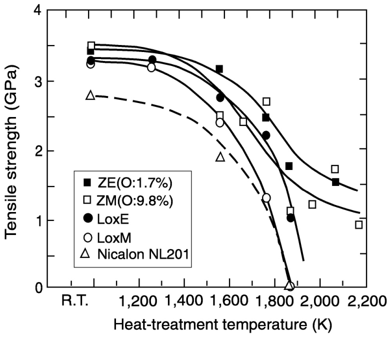


FIGURE 3-6 Tensile strength of SiC fibers after heat treatment in argon for one hour. Source: Kumagawa et al., 1997.

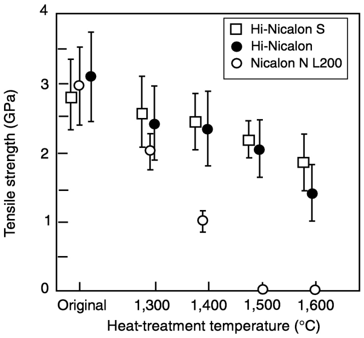


FIGURE 3-7 Room-temperature tensile strength of SiC fibers after 10hour thermal exposure in argon. Source: Takeda, 1997.

fibers that do not have a significant amount of Si-O-C phase. That is, reducing the oxygen content of SiC fibers increases their resistance to microstructural degradation associated with high-temperature exposure.

High temperature thermal exposure in argon shows very little affect on the room-temperature strength of the Dow Corning Sylramic fiber or the Carborundum fiber. Figure 3-8 shows the effect of thermal aging on the room-temperature strength of Sylramic fiber in comparison to other polymer-derived fibers.

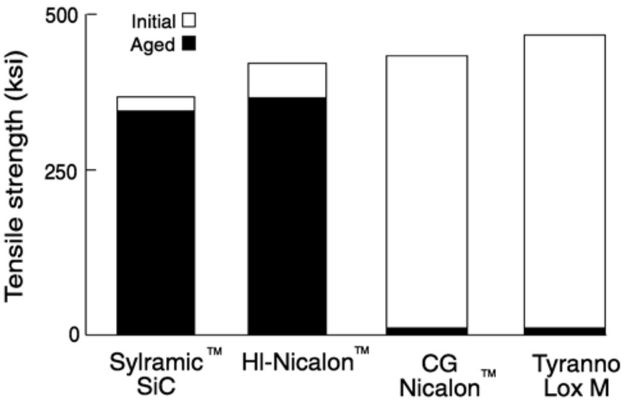
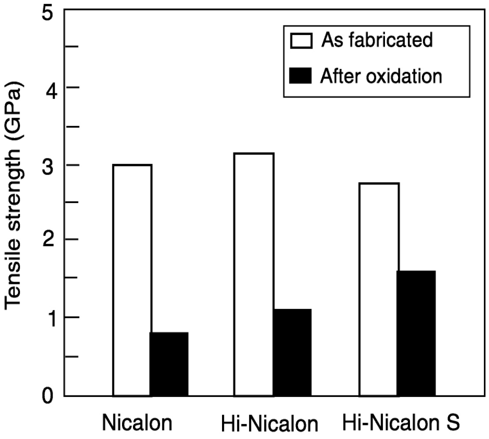


FIGURE 3-8 Tensile strength of SiC fibers after aging for 10 hours at 1,550°C (2,822°F) in argon. Source: Lipowitz et al., 1997.

Exposure of polymer-derived non-oxide fibers to air or oxygen can result in rather dramatic decreases in room-temperature strength (Figure 3-9 and Figure 3-10). In all cases, a passivating film of SiO_2 is formed. In fibers containing large amounts of oxygen (e.g., 10 weight-percent O_2), however, the SiO_2 films contain bubbles and pores, presumably caused by CO generation. The decrease in room-temperature strength after oxidation has been related to the thickness of the SiO_2 film, suggesting that cracks in the oxide act as surface flaws that initiate fracture of the fiber. This theory is supported by findings that indicate removal of the oxide film restores the fiber strength to its original level (Parthasarathy et al., 1997). Recent results for Sylramic fibers also support this finding (Lipowitz, 1997b).



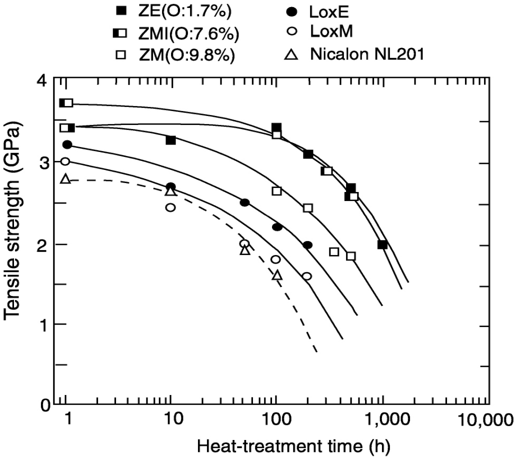


FIGURE 3-9 Tensile strength of SiC fibers after exposure for 10 hours in dry air at 1,400°C (2,552°F). Source: Takeda, 1997.

FIGURE 3-10 Tensile strength of SiC fibers after heat treatment at 1,000°C (1,832°F) in air. Source: Kumagawa, 1997.

The reasons for the lower strengths of CVD SiC fibers after heat treatment have been debated for more than 25 years. For CVD fibers deposited on a carbon fiber core, the most likely explanation for the dramatic drop in strength is the melting and volatilization of free silicon in the fiber. However, larger grains of α-SiC have been found on some fracture surfaces after heat treatments at 1,500°C (2,732°F) and higher, suggesting that transformation of β-SiC to α-SiC with accompanying exaggerated grain growth—is the cause of reduced strength.

The relatively new, amorphous Si-B-N-C fiber produced by Bayer has been reported to show promise for use at high temperatures. For example, it has been reported that the Bayer fiber has excellent thermal stability, remaining amorphous after extensive heat treatments of up to 1,800°C (3,272°F) in an inert environment. This fiber is also unusually resistant to oxidation (for a non-oxide fiber), producing only a 1µm thick oxide film after 48 hours of exposure to air at 1,500°C (2,732° F) (Figure 3-11). Another interesting aspect of this fiber is the hexagonal BN (h-BN) interlayer that forms in situ under the SiO_2 film. This interlayer appears to act as a crack deflector much the way a CVD BN film does (Baldus, 1997). However, the remarkable strength retention and creep resistance of the Bayer fiber (as well as of the Tonen and University of Florida fibers) have not been verified and are not well understood. In view of its impressive thermal stability, however, this new material should be extensively researched.

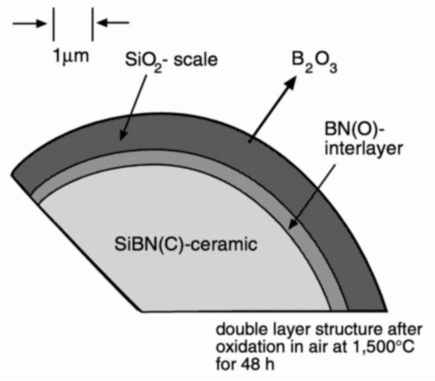


FIGURE 3-11 Structure of the diffusion barrier coating forming on oxidation at the surface of $SiBN_3C$. Source: Baldus, 1997.

Very little data in the literature relate room-temperature modulus values to aging history. Given that stiffness is a critical property for CMC engine applications (Chapter 2), research in this area is certainly warranted.

Thermal Conductivity (Diffusivity) and Electrical Conductivity (Resistivity) as a Function of Temperature and Aging History

Very little data in the literature deal with the influence of test temperature and aging history on the thermal conductivity and electrical conductivity of CMCs. The data on electrical resistivity in Table 3-1 suggest that the reduction in oxygen content in polymer-derived fibers reduces the resistivity so that the near stoichiometric fiber has a rather low resistivity. Narisawa and coworkers (Narisawa et al., 1995) have systematically studied the effects of heat-treatment temperature and measurement temperature (i.e., temperature at which electrical conductivity was measured) on the electrical conductivity of Nicalon fibers (Figure 3-12). They found that the dissociation of the Si-O-C phase during heat treatment leads to much higher electrical conductivity, which appears to be controlled by two different semiconducting paths, one of which is eliminated as the Si-O-C phase disappears. They also found that in the Si-C fibers (low or no oxygen) the highest resistivity corresponds to the stoichiometric SiC. Excess carbon or silicon creates lower resistivity paths in the microstructure (Figure 3-13).

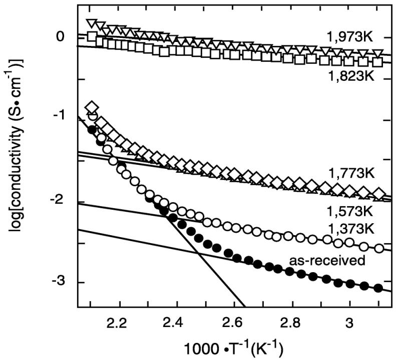


FIGURE 3-12 Temperature dependence of electrical conductivity in heat-treated Si-C-O fibers. Source: Narisawa et al., 1995.

Creep Behavior of Non-Oxide Fibers and Effects of Heat Treatment, Oxidation, and Aging

Reviews by Tressler and DiCarlo (1993, 1995) cover the main features of creep behavior in non-oxide fibers, particularly SiCbased materials (Parthasarathy et al., 1997; DiCarlo, 1994). All crystalline and microcrystalline SiC-based fibers exhibit primary creep to very long creep times (> 1000 hrs).[2] Recent developments that have resulted in low oxygen content polymer-derived fibers and near stoichiometric or stoichiometric SiC fibers have dramatically improved the creep resistance of nonoxide fibers. These results are illustrated in a composite figure (Figure 3-14) using bend stress relaxation (BSR)[3] data obtained by Nippon Carbon and National Aeronautics and Space Administration (NASA) Lewis Research Laboratory (Parthasarathy et al., 1997). These test results are presented as a function of temperature for many of the commercially available and developmental fibers (the higher the m value the more creep resistant the material). The Carborundum fiber has the highest creep resistance (except for the annealed Hi-Nicalon S); the Hi-Nicalon S and the Dow Corning fiber follow. The highest ranked production fiber is Hi-Nicalon.

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[2] primary creep occurs after the initial elastic extension (or strain) of the material under load and continues until the creep rate reaches a steady state. Creep rate decreases asymptotically to the steady state rate in the primary creep region.

[3] The bend stress relaxation (BSR) technique involves forcing a fiber into a loop of radius (R_0). After thermal exposure, a creep induced radius of curvature (R_0) is observed in the fiber at room temperature. The salient parameter of the BSR test is the BSR ratio, $m = 1 - R_0/R_a$. The higher the value of *m*, the more creep resistant the material. For a complete description of the BSR technique, see DiCarlo and Dutta, 1995.

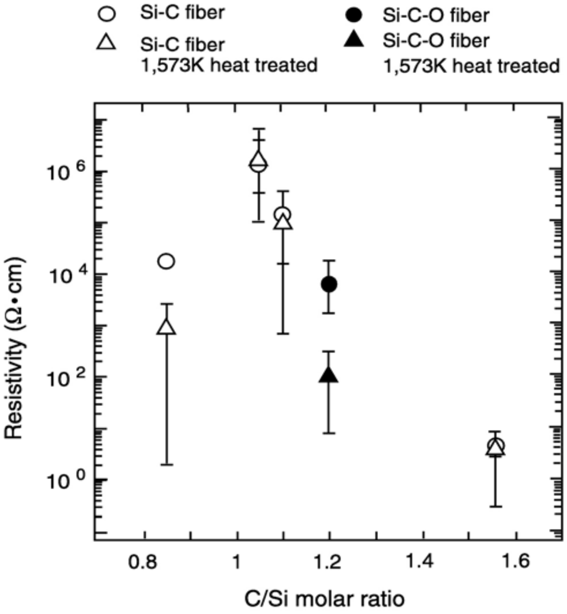

FIGURE 3-13 Relationship between electrical resistivity and C/Si molar ratio in Si-C fiber. Source: Narisawa et al., 1995.

Based on these results and extensive tensile creep tests on as-received and annealed fibers of several types (DiCarlo and Dutta, 1995; Yun et al., 1995a; Yun et al., 1995b; Yun et al., 1994), certain generalizations can be made about SiC-based fibers produced by a given technique (e.g., polymer-derived vs. sintered vs. CVD). SiC grain size and volume fraction control the creep resistance. The composition and spatial locations and sizes of secondary phases also affect creep behavior. For example, in the Nicalon family, the Hi-Nicalon fiber is much more creep resistant than the Nicalon fiber because the Si-O-C secondary phase is essentially replaced with turbostratic (nongraphitic) carbon. If the SiC grain size is increased by annealing, the creep resistance increases. In fact, annealing for one hour at 1,600°C (2,912°F) in argon causes the Hi-Nicalon fiber to approach the creep resistance of the Carborundum fiber (Rugg et al., 1995). Similarly, the creep performance of experimental non-stoichiometric University of Florida fibers after annealing for one hour at 1,700°C (3,092°F) also approaches the performance of the Carborundum fiber. Increasing the volume fraction of β-SiC to near stoichiometry, with a concomitant doubling of grain size, drastically increases the creep resistance of the Hi-Nicalon S fiber.

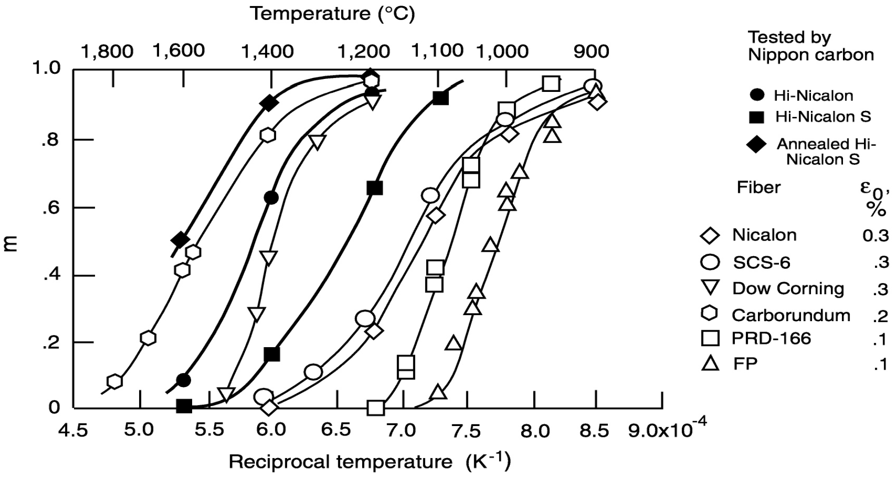

FIGURE 3-14 One-hour bend stress relaxation ratio of polymer-derived SiC fibers and other polycrystalline SiC and Al_2O_3 fibers. Source: Reprinted from Composites Science and Technology, Volume number 51(2), J.A. DiCarlo, Creep limitations of current polycrystalline ceramic fibers, Pp. 213–222. Copyright© 1994, with permission from Elsevier Science.

The Dow Corning and Carborundum fibers are comparable in terms of microstructure in the final product, except that the grain size of the Carborundum material is three to ten times the size of the Dow Corning fiber. The resultant creep resistance scales as one would expect for diffusional creep. The change in creep rate of the CVD-SiC has been quantitatively accounted for by the effects of grain coarsening on the diffusional creep rate (Lewinsohn et al., 1994).

However, a quantitative explanation for the observed creep rates across the various classes of SiC fibers remains elusive. For example, the creep rate of the annealed Hi-Nicalon fiber is very similar to the creep rate of the Carborundum fiber although the grain sizes are 10 to 100 times larger in the Carborundum fiber. The CVD β-SiC fibers have grain sizes on the order of 4 to 10 times larger than the Hi-Nicalon fiber, but creep rates are 10 to 100 times those of Hi-Nicalon. Lowering the boron content of the Sylramic fiber appears to improve creep resistance, but the effect has not been quantified.

Thus, fundamental questions remain about what controls the creep rates of SiC-based materials. What is the role of carbon, of solid solution dopants? Do the stacking faults in β-SiC grains play a role? Is the α-SiC microstructure intrinsically more creep resistant? All of these questions remain to be answered.

Rupture Behavior of Non-Oxide Fibers in Oxidizing and Non-Oxidizing Environments and the Effects of Heat Treatment and Oxidation

The literature on creep rupture and stress rupture (time-to-failure at a given stress) is meager. Researchers at the NASA Lewis Laboratory have done comparative stress rupture studies of various SiC-based fibers in air and argon (Yun et al., 1995a). Figure 3-15 presents the data for the Dow Corning, Carborundum, Hi-Nicalon, and annealed Hi-Nicalon (1,600°C [2,912°F], one hour, argon) fibers. The fibers generally performed better in air, except for the annealed Hi-Nicalon, in which the oxidation of internal porosity is thought to accelerate creep failure. Rugg et al. (1995) have shown that failure of the Carborundum fiber at these stress levels in the 0 to 100 hour time frame is caused by slow crack growth and not creep-induced damage. Although the Carborundum fiber has about 50 percent of the room-temperature strength of the other fibers, it has about the same 100 hour rupture strength at 1,400°C (2,552°F). The behavior of the other fibers appears to be controlled by creep-generated flaws at higher temperatures and lower stresses, with a regime of slow crack growth at lower temperatures and higher stresses.

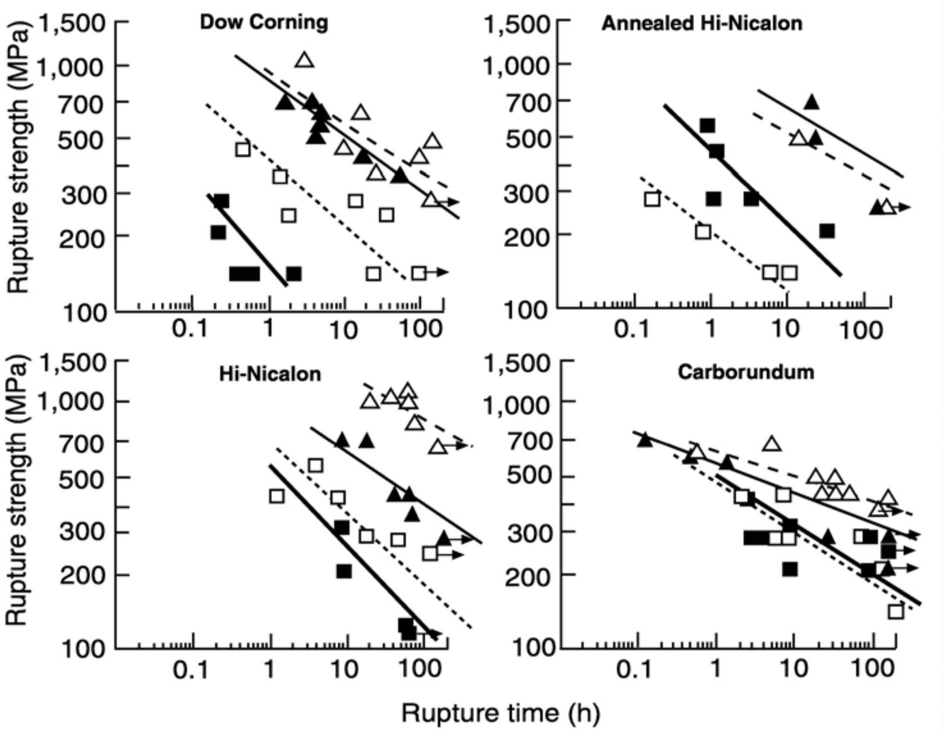

FIGURE 3-15 Rupture strength of SiC fibers in air (open symbols) and argon (closed symbols) at 1,200°C (2,192° F) (Δ) and 1,400°C (2,552°F)(▫) Source: Yun et al., 1995a.

Yun and DiCarlo (1996) have characterized the high-temperature rupture strength of ceramic fiber using the Larson-Miller formulation of thermally-activated rupture. For the rupture of SiC and Al_2O_3 based fibers, the average rupture strength (S) can be described as a function of a parameter q:

$$S = S(q) \quad (1)$$

$$\text{where } q = T(\log t + D) \quad (2)$$

The parameter q is a function of fiber rupture time (t) and temperature T). Here $D = \log(\theta_0) = 22$ for the SiC and Al_2O_3 fibers in the high-temperature range where creep cavitation controls failure ($q > 32{,}000$ for Nicalon SiC fibers; $q > 20{,}000$ for the polycrystalline oxide fibers), where θ_0 is the activation time parameter (Yun et al., 1993).

Yun and DiCarlo merged the slow crack growth dominated regime and the creep-generated flaw controlled regime into a rupture plot for Hi-Nicalon using the q parameter, as described above (Figure 3-16) (Yun and DiCarlo, 1996). Thus stress rupture at various stresses and temperatures can be represented in one plot. Using the same approach, comparable data for Nicalon, CVD SCS-6, and a small diameter CVD SiC fiber by Textron (Ultra-SCS) can be presented with the curve for the Hi-Nicalon data (Figure 3-17). Over a significant range of temperatures and stresses (starting at 1,000°C [1,832°F] for ~1,000 hours) the performance of Hi-Nicalon is superior to SCS-6. However, the performance of Ultra-SCS is superior over the whole temperature range.

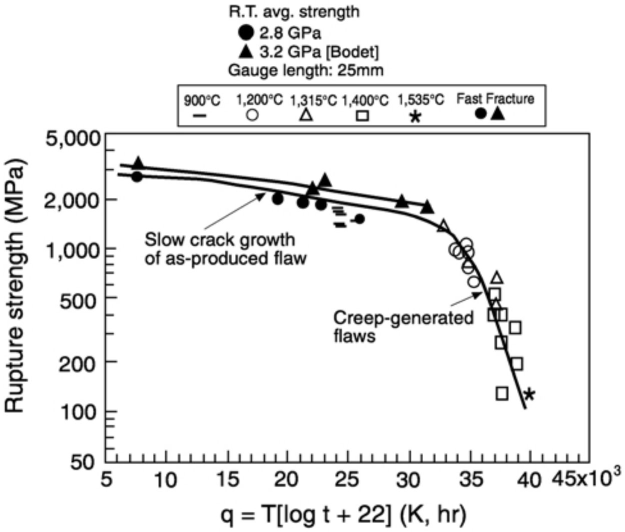

FIGURE 3-16 Thermal activation plot for Hi-Nicalon fast fracture and rupture strength in air. Source: Yun and DiCarlo, 1996.

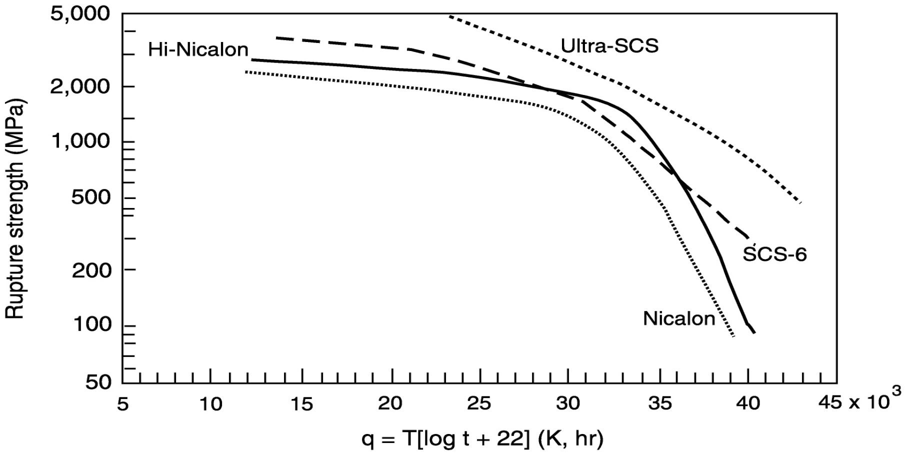

FIGURE 3-17 Thermal activation plots for average strength of as-produced SiC fibers. Source: Yun and DiCarlo, 1996.

It should be noted that these comparisons are based on very small data sets that represent relatively short times. Future studies should focus on longer-term durability, particularly with coated fibers and in oxidizing environments. Rupture strength studies are needed for all non-oxide fibers.

The effects of oxidizing and non-oxidizing environments are included in the preceding discussion. In general, if the oxidation seals the fiber from gas-phase degradation (SiO and CO volatilization, for example), the oxidizing environment results in longer life than for comparably stressed fibers in an argon environment. If internal oxidation occurs, or, if dopant oxidation and/or rearrangement can occur, oxidation can be deleterious to the rupture life. The role of boron additives has not been thoroughly studied, but there is some evidence that boron degrades creep resistance and rupture strength. In general, the onset of measurable creep is accompanied by a degradation in rupture strength suggesting that improvements in creep resistance would lead to improvements in rupture resistance (as predicted by the Monkman-Grant relationship) (Tressler and DiCarlo, 1993).

The effects of aging have been included in the above data for Hi-Nicalon. However, no systematic study has been done of the effects of heat treatment or aging on the rupture strength of other fibers. Furthermore, no data are available on the rupture strength of the Bayer Si-B-N-C fiber or the Tonen Si-N fibers at elevated temperatures.

Microstructural Stability

The dependence of room-temperature properties and, to a lesser extent, high-temperature properties on the pyrolysis temperature for polymer-derived non-oxide fibers is well documented and well understood in terms of amorphousphase decomposition and SiC and carbon grain growth. Many of these studies have been cited above. However, a fundamental understanding of the role of the carbon phase in the grain growth process and the creep process is still not complete. Similarly, the effects of and basic mechanisms involving dopants, such as boron, have not been systematically studied.

The CVD SiC fiber has been shown to undergo accelerated β-SiC to α-SiC transformation under stress with exaggerated α-SiC grain growth (Giannuzzi et al., 1997). It has been suggested that the stacking faults in β-SiC act as nucleation sites for this transformation, but no clear proof has been presented in the form of transmission electron microscopy. This raises the question of whether all β-SiC-based fibers are subject to this potentially deleterious microstructural change.

Finally, the crystallization behavior of the remarkably stable Si-B-N-C fiber must be studied under anticipated service conditions in order to determine the limits of the material and to establish its comparative advantages or disadvantages over other non-oxide fibers.

TEMPERATURE AND TIME DEPENDENCE OF PROPERTIES OF OXIDE FIBERS

Strength and Stiffness as a Function of Test Temperature

Figure 3-1 illustrates the trends in tensile strength, as a function of temperature, for the small diameter ceramic fibers that were available in the late 1980s (Pysher et al., 1989). The tensile elastic modulus was also measured as a function of temperature (Figure 3-2a and Figure 3-2b). Data on fiber strength have been updated and generalized by DiCarlo and Dutta (1995) and are included in Figure 3-4. The stiffness properties of ceramic fibers are very similar to those of bulk ceramics with comparable microstructures (e.g., the elastic modulus of bulk glass-bonded mullite is similar to 3M Nextel 480 fiber).

Oxide-based polycrystalline fibers lose short-term strength (i.e., load is continually increased until failure) in the 1,200 to 1,300°C (2,192°F to 2,372°F) range. These are fine grained oxide fibers that contain glass at the grain boundaries. Their strength, therefore, drops precipitously at elevated temperatures due to crystallization of the amorphous phase. The strength of the more recently developed Nextel 720 (multiphase alumina-mullite) fiber is well above the range indicated in Figure 3-4. A direct comparison of the fine grained alumina Nextel 610 and the multiphase Nextel 720 in terms of strength as a function of temperature is shown in Figure 3-18.

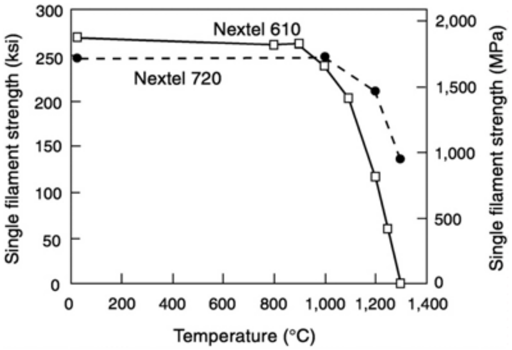

FIGURE 3-18 Tensile strength as a function of test temperature for Nextel 610 and Nextel 720 single fibers (heated gauge length = 25 mm [1 in], overall gauge length = 220 mm [8.8 in]). Source: Wilson, 1997.

Room-Temperature Strength and Modulus as a Function of Aging History

The effect of short-term exposure (one to ten hrs) at various temperatures on the room-temperature strength of ceramic fibers is shown in f 3-5. [4] Oxide fibers were exposed in air; the non-oxides were exposed in argon. The oxide fibers lose strength after exposure to temperatures above 1,200°C (2,192°F), which is directly related to microstructural changes in the ceramic fibers when they are subjected to more severe thermal conditions than conditions imposed during processing. In the case of Nextel 312 (mullite in glass) fibers, for example, crystallization of the amorphous phase (that occurs at high temperature) is known to degrade strength. Furthermore, grain growth in fine grain Al_2O_3 fibers (e.g., Nextel 610 and Fiber FP) during exposure to high temperatures results in a loss of room-temperature strength.

Thermal Conductivity (Diffusivity) and Electrical Conductivity (Resistivity) as a Function of Test Temperature and Aging History

Little can be found in the literature concerning the effect of thermal aging history on the thermal conductivity (diffusivity)

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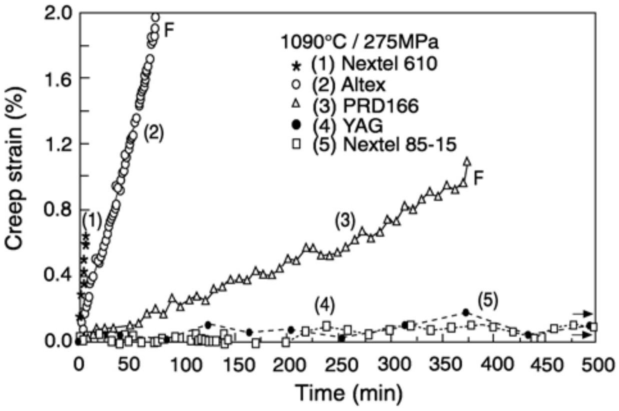
[4] Note that this measurement is useful for predicting the ability of a fiber to retain its strength after composite fabrication. In many cases, the most aggressive environment a fiber is exposed to is during composite fabrication.

and electrical conductivity (resistivity) of ceramic fibers. In general, the monolithic ceramic oxides are poor thermal and electrical conductors, and, therefore, they are often used as thermal or electrical insulators (beryllium oxide is an exception in terms of thermal conduction). There is no reason to expect that the properties of the fibrous forms of these oxides will be substantially different from their bulk ceramic analogues. Thus, discussion of bulk ceramics also applies to these materials (Kingery et al., 1976).

Creep Behavior of Oxide Fibers

The creep behavior of ceramic fibers has been reviewed extensively by Tressler and DiCarlo (1993, 1995). For example, DiCarlo and coworkers have investigated the time dependent mechanical properties of ceramic fibers (Yun et al., 1995a, 1995b, 1994). Tensile tests on single fibers have been used to study creep, and the BSR technique has been used as a screening test to compare the creep behavior of various fibers (Sabol and Tressler, 1990).

Figure 3-19 shows creep curves at 1,090°C (1,994°F) with a tensile stress of 275 MPa (40 ksi) for several oxide fibers (Yun et al., 1995c). The curve labeled Nextel 85-15 represents an earlier form of Nextel 720. The curve labeled YAG represents the creep behavior of a polycrystalline yttrium aluminum garnet fiber made by General Atomics, which is in the research phase (none of these fibers are commercially available). Data shown in Figure 3-20 compares the creep behavior of several 3M Nextel fibers to other alumina fibers at various temperatures. The diffusional creep of the fine grain oxides is simply too high at temperatures above ~900°C (1,652°F) to be useful. Second phase particles, however, were shown to reduce the creep rate of polycrystalline alumina significantly (e.g., Fiber FP compared to PRD-166) (Pysher and Tressler, 1992a). Preliminary studies of ceramic oxide fibers indicate that grain elongation holds promise for improving the creep resistance of these fibers.



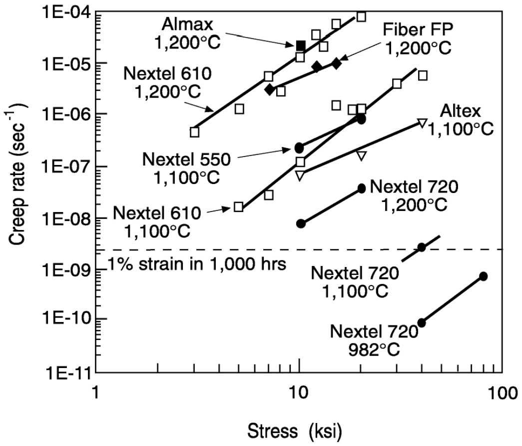


FIGURE 3-19 Typical creep curves for polycrystalline alumina-based oxide fibers at 1,090°C (1,994°F) in air. Source: Wilson, 1997.

FIGURE 3-20 Creep rate of Nextel 720 compared to other commercial oxide fibers. Source: Wilson, 1997.

The Nextel 720 fiber has both a secondary phase and elongated grains incorporated into its microstructure. The (~55 volume percent) mullite is present primarily as needles surrounding the Al_2O_3 grains (~45 volume percent). Thus, the creep resistance of the Nextel 720 is better than for other oxide fibers. However, the use temperature under a 100 MPa (15 ksi) load (1 percent strain in 1,000 hrs) is lower than 1,200°C (2,192°F).

In Figure 3-21, BSR data (one hour) for several oxide fibers are compared, including the single-crystal alumina monofilament (Morscher et al., 1995)

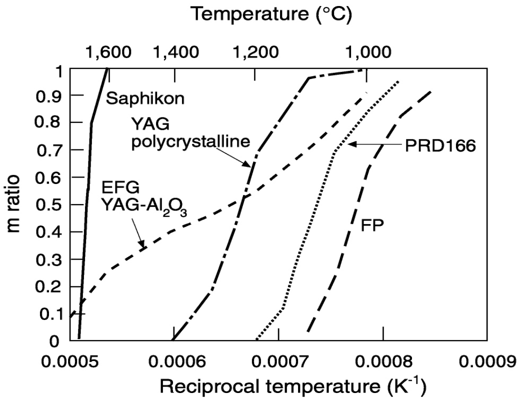


FIGURE 3-21 One-hour bend stress relaxation ratio for directionally solidified eutectic YAG/alumina fibers grown by edge-defined film growth (EFG), for polycrystalline alumina-based fibers, and for c-axis sapphire fibers. Source: Morscher et al., 1995.

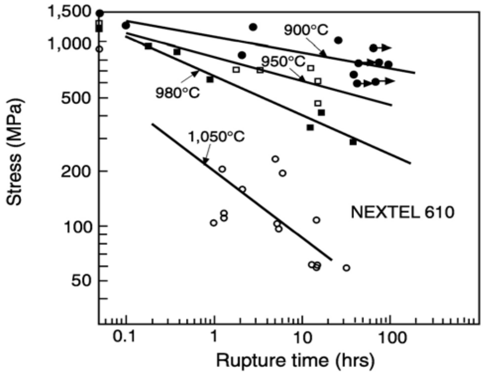


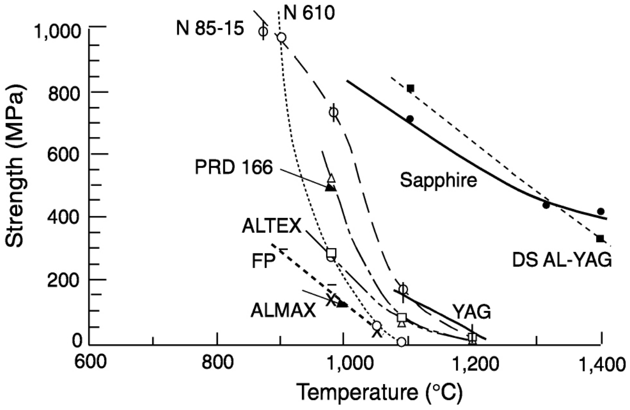
FIGURE 3-22 Stress rupture for Nextel 610 fibers. Source: Tressler and DiCarlo, 1993.

Preliminary studies of oxide fiber creep rupture behavior have been summarized in review papers by Tressler and DiCarlo, and others (Kingery et al., 1976; Tressler and DiCarlo, 1993, 1995; Yun et al., 1994, 1995a, 1995b; DiCarlo and Dutta, 1995). At temperatures of 900 to 1,000°C (1,652°F to 1,832°F), the strength of polycrystalline oxide fibers degrades with long-time exposure to relatively high stress (> 500 MPa [75 ksi]), as shown for Nextel 610 fibers in Figure 3-22. This behavior suggests that the failure mechanism is slow crack growth of pre-existing (e.g., processing-induced) flaws. From 1,150 to 1,300°C (2,102 to 2,372°F), however, polycrystalline oxide fibers, such as Fiber FP and PRD-166, exhibit rupture times that are inversely proportional to their creep rates (Monkman-Grant relationship), which is indicative of creep damage-induced failure (Pysher and Tressler, 1992b). This may also explain the low-stress rupture of Nextel 610 at 1,050°C (1,922° F) (Figure 3-22) (Tressler and DiCarlo, 1993).

The 100-hour rupture strength of several polycrystalline and single-crystal oxide fibers are compared in Figure 3-23 (Yun et al., 1995c). It is apparent that not even the recently developed creep resistant polycrystalline oxide fibers have rupture strength after 100 hours of exposure to more than 1,200°C (2,192°F). Only Nextel 720 [5] fibers have significant load bearing capability after 100 hours of exposure above 1,000°C (1,832°F).

A plot of rupture strength vs. the *q* parameter (described above) for Nextel 720, Nextel 610, and Saphikon fibers is given in Figure 3-24. This figure shows failure by creep-induced flaws that arise in the high-temperature, low stress region and the slow crack of existing (processing-induced) flaws in the lower temperature, higher stress region. The multiphase Nextel 720 oxide fiber is clearly superior to the fine grain Al_2O_3 Nextel 610 at higher temperatures and longer exposure times, whereas the single-crystal Saphikon fiber is superior to both polycrystalline Nextel 610 and 720 fibers at high temperatures.

No extensive study of the effects of heat treatment or aging on the creep rupture behavior of oxide fibers has been undertaken. However, heat treatments that coarsen the microstructure, thereby improving creep resistance, should increase the rupture strength of polycrystalline oxides, as indicated by the Monkman-Grant relationship.



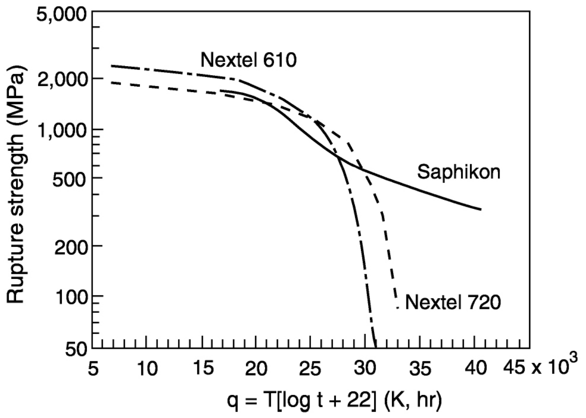


FIGURE 3-23 The 100-hour rupture strength of polycrystalline and monofilament alumina-based fibers. Source: Tressler and DiCarlo, 1995.

FIGURE 3-24 Thermal activation plots for average strength of asproduced Al_2O_3-based fibers at a gauge length of ~25 mm (1 in). Source: Yun and DiCarlo 1996.

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[5] Note that the Nextel 720 fiber was referred to as a N85-15 fiber during development and is often referred to that way in the literature.

Microstructural Stability

Single-phase, fine grain oxide fibers experience grain growth at exposure temperatures above the final sintering/pyrolysis temperatures used during their fabrication. Fiber FP and PRD-166 can be dramatically weakened by heat treatments. This weakening is expected in all of the polycrystalline oxides being considered for CMC reinforcements. Although grain boundary crystalline phases and certain dopants that segregate the grain boundaries can suppress grain growth (Harmer, 1997), detailed studies of grain growth (on Nextel 720, for example) have not been published. Therefore, specific data relating heat treatment and grain growth to strength and creep rupture are not available.

PERFORMANCE CHARACTERISTICS COMPARED TO PERFORMANCE GOALS

Detailed comparisons of fiber properties and performance goals requires a knowledge of the thermostructural requirements for a CMC component (e.g., a combustor liner for an aircraft engine). At this early stage of component design and materials development, this information is either not known or it is proprietary. DiCarlo has attempted to use generic performance goals for the CMC material to identify minimum property goals for ceramic fibers. These property goals are sometimes expressed in terms of tensile overload stresses (which gives a goal for the fast fracture stress) or in terms of sustained service stresses.

In studies by Tressler and DiCarlo (1993, 1995), the target rupture strength and 1 percent creep strength defined for the best superalloy (PWA 1480 Ni-based superalloy) were compared to the corresponding data for fibers. Of the commercially available fibers, only Hi-Nicalon had a clear advantage over the superalloy when corrected to 20 volume percent fibers along the load axis. Developmental fibers, such as Hi-Nicalon S, Sylramic, and other non-oxide fibers, also promise to meet these minimum goals.

More recently, DiCarlo (1997) has compared ceramic composites to the best superalloy using the strength-to-density ratio versus the Larson-Miller parameter, *q*. In this analysis (Figure 3-25), the Nextel 720 fiber-reinforced composite is inferior to the metal in short-term fracture but comparable to the superalloy in long-term rupture. On this basis, the Hi-Nicalon fiber is superior to the superalloy except at short times and high stress levels, when fiber failure is dominated by slow crack growth.

Non-oxide fibers cause composites to be susceptible to oxidative degradation, particularly when the matrix is cracked. Thus, the limiting stress at the present time is the matrix cracking stress (on the order of 100 MPa [14.5 ksi]).

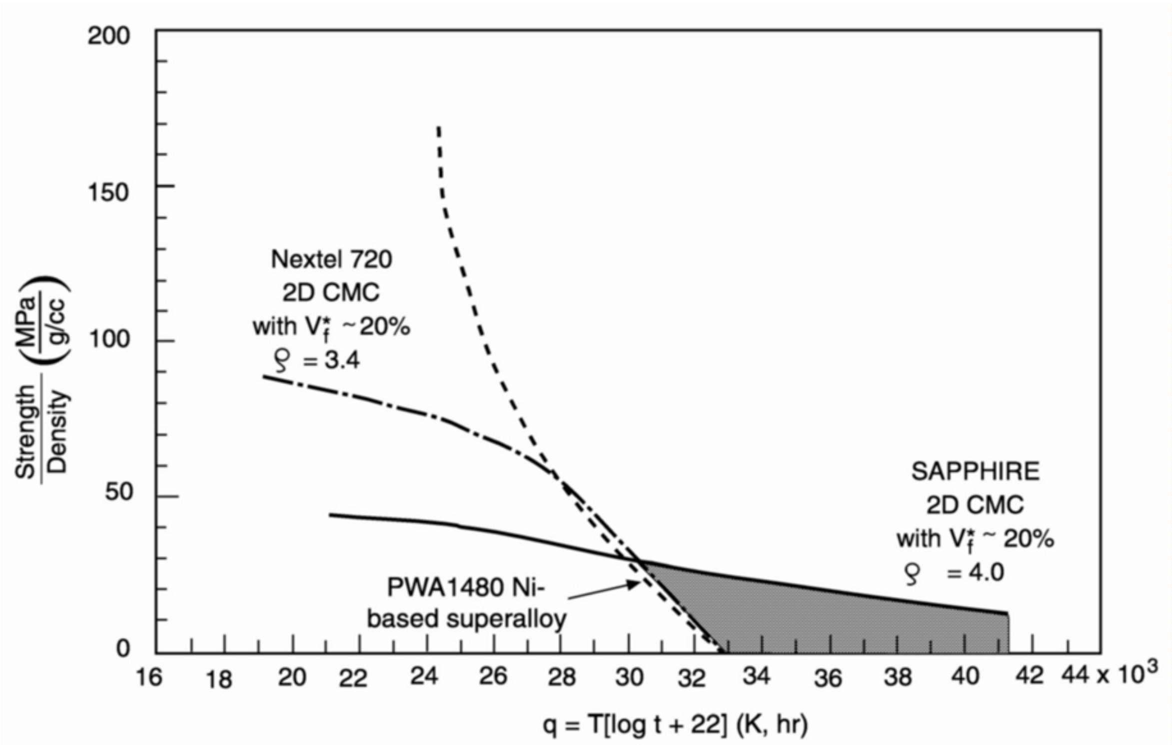


FIGURE 3-25 Comparison of optimum strength map of Al_2O_3 fiber-reinforced CMC with strength behavior of an advanced superalloy. Source: DiCarlo, 1997.

This means that until more oxidation tolerant matrix-interface-fiber systems are developed, service conditions will be rather limited for non-oxide fiber-reinforced CMCs. CMCs do have a large weight advantage over superalloys, however, as well as low observability to radar.

RECOMMENDATIONS AND FUTURE DIRECTIONS

Assessing the state of the art in ceramic fibers requires a thoughtful definition of performance requirements and comparisons of these requirements to current capabilities. Defining the state of the art also requires the rigorous characterization of available materials, particularly the properties that are relevant to CMC applications. Microstructural stability, stiffness (elastic modulus), and creep behavior, as a function of temperature and time at temperature in actual service environments, are the most critical fiber properties. Therefore, research should focus on determining these properties, including understanding microstructural and compositional relationships to these properties.

The Bayer Si-B-N-C fiber is reported to have impressive thermal stability (i.e., it remains amorphous at high temperatures) as well as excellent creep resistance (Baldus, 1997). To understand the performance capabilities of this material in terms of time, temperature, and stress conditions, however, the crystallization behavior of the Si-B-N-C fiber must be studied under anticipated service conditions. Continued study is also needed to establish its advantages or disadvantages in relation to other non-oxide fibers. Therefore, the committee recommends that detailed, high-temperature studies of the Bayer Si-B-N-C fiber, especially long-term durability studies, be done to verify preliminary results.

Fundamental questions about factors that control the creep rates of ceramic materials have not been answered. The effects of carbon and solid solution dopants on the creep rate of SiC materials need to be better understood. The role of intragranular stacking faults on β-SiC creep rates should also be determined. Furthermore, a determination must be made as to whether the microstructure of α-SiC is intrinsically more creep resistant than the microstructure of β-SiC. For oxide ceramics, the role of microstructure in controlling creep rate and creep rupture strength must be determined, particularly for multiphase microstructures.

The effects of thermal aging on creep rupture strength have been studied for the Hi-Nicalon, Dow Corning, and Carborundum fibers, but no systematic studies of the effects of heat treatment or aging on the creep rupture strength of more recently developed fibers, such as Hi-Nicalon S, and Sylramic, have been conducted. Furthermore, no creep rupture strength data are available for the Bayer Si-B-N-C fiber, the University of Florida SiC fiber, or Tonen Si-N fibers. Therefore the committee recommends that creep rupture studies be conducted on the Bayer, Sylramic, Hi-Nicalon S, UF-SiC, and Tonen Si-N fibers. These studies should include the effects of thermal aging and the effects of microstructure on creep behavior.

Creep and creep rupture in oxide ceramic fibers have been studied extensively by Tressler and DiCarlo (1993, 1995). However, no detailed studies of the effects of heat treatment or aging on the creep rupture behavior of oxide fibers have been done. These studies will be important in light of the fact that single-phase oxides experience grain growth that dramatically reduces the fiber strength at temperatures that exceed their fabrication (i.e., sintering) temperatures. It is, therefore, critical that the role of dopants and multiphase microstructures on in-service grain growth, and ultimately on creep rupture, as a function of temperature, be determined for oxide fibers. Studies should focus on creep rupture and the effects of heat treatment on polycrystalline oxide fibers.

Finally, there are essentially no data in the literature relating room-temperature modulus values to aging history. Because stiffness is a critical property for CMC engine applications, research should be done in this area.

4

Ceramic Fiber Processing

Most CMCs are reinforced with continuous, multifilament tow ceramic fibers. Fiber tows typically consist of 500 to 1,000 filaments, with a diameter of 10 to 15 µm (0.40 to 0.59 mils) each. These fiber tows are flexible, easy to handle, and can be woven into fabrics and used to fabricate complexshaped composites. Monofilament fibers have also been used to reinforce ceramic composites, but they have several disadvantages. For example, monofilaments (especially singlecrystal fibers) are expensive, and their large diameter (> 75µm [3.0 mils]) limits their minimum bend radius, which can make fabricating complex-shaped composites difficult. This chapter, therefore, focuses on small diameter, multifilament ceramic fibers.

A wide variety of precursors and processing techniques are available for the production of both oxide and non-oxide ceramic fibers. With these techniques, microstructural development and a variety of fiber properties, such as modulus, density, dielectric constant, and tensile strength, can be controlled. In addition, the curing and pyrolysis processes can be used to control the composition of non-oxide fibers prepared by preceramic polymer routes. The key characteristic of reinforcement fibers is their ultrafine, or even nanoscale, microstructure. For example, a grain size below 0.5 µm (0.02 mils) is optimal for high strength although it has the disadvantage of increasing the rate of high-temperature creep. In the last decade, however, improvements in fiber processing have made fibers with significantly improved high-temperature creep properties possible (see Chapter 3). Fiber costs can be reduced by using improved, more efficient processing methods (see Chapter 7). The relationships between the processing, cost, and performance of ceramic fibers are discussed in this chapter.

NON-OXIDE FIBER PROCESSING

The majority of non-oxide ceramic fibers that have been studied are Si-based (tending toward SiC in composition). Their microstructures can be crystalline, amorphous, or a mixture of crystalline and amorphous material. Although other compositions have been studied, including Si_3N_4, B, BN, HfC, and others, efforts to develop a high-temperature fiber have focused predominantly on Si-based ceramics. Therefore, the following discussion of non-oxide fiber processing will be limited to techniques applicable to these materials, including CVD (chemical vapor deposition), chemical conversion, extrusion/sintering, and preceramic polymer processing.

The oldest commercial process for producing non-oxide fibers is CVD of a ceramic material (typically SiC) onto a heated core monofilament (e.g., carbon fiber or tungsten wire). This process is still used by Textron Company. These fibers are used primarily to reinforce metal matrix composites (MMCs) and intermetallic matrix composites (IMCs). SiC fibers prepared by CVD, however, are typically large-diameter (generally ≥ 75 µm [0.30 mils]) monofilaments that are stiff and unsuitable for weaving or other preforming techniques. In addition, commercially available CVD SiC mono-filaments are prohibitively expensive for use in CMCs. Recent attempts to deposit SiC (via CVD) on fine-diameter, multifilament carbon fibers are described in the literature (Lackey et al., 1995; Kowbel, 1997), but high strength, multifilament fiber tows have yet to be demonstrated. A key requirement for this potentially lower-cost approach is the development of a technique for spreading the core fiber tow to achieve uniform CVD of the individual filaments without causing interfilament bonding (which would compromise the mechanical properties of the fiber tow).

Chemical conversion of carbon fiber (C_f) to SiC fiber (SiC_f) is another approach to producing non-oxide ceramic fibers. Conversion typically involves reacting a carbon fiber with either silicon or silicon monoxide vapor via the following reactions:

$$C_f + Si(g) \rightarrow SiC_f \quad (1)$$

$$2C_f + SiO(g) \rightarrow SiC_f + CO(g) \quad (2)$$

Attempts to produce a viable SiC fiber by Reaction 1 have not been successful because the approximately 87 percent increase in volume that occurs upon conversion disrupts the microstructure and, therefore, compromises the mechanical properties of the fiber. Reaction 2 proceeds, theoretically, with approximately 6 percent shrinkage. However, recent attempts by MER Corporation (Kowbel, 1997) to convert entire filaments via Reaction 2 have been unsuccessful. Furthermore, earlier attempts to fully convert oriented carbon fiber were also unsuccessful. The interior of these carbon fibers generally remains unconverted graphite; attempts by the New Oji Paper Company (Okada et al., 1995) using a porous, activated carbon fiber (ACF), have been successful in converting carbon filaments to SiC. The complete conversion to SiC_f is possible because the ACF fiber has extensive surface-connected nanoporosity, which permits the diffusion of SiO vapor throughout the fiber. The ACF fiber, however, is intended for use in the purification of gases and liquids and not intended for use as a structural fiber. Because of processinduced surface flaws and extensive porosity, which remain in the converted fiber, the ACF fiber has low strength and low modulus.

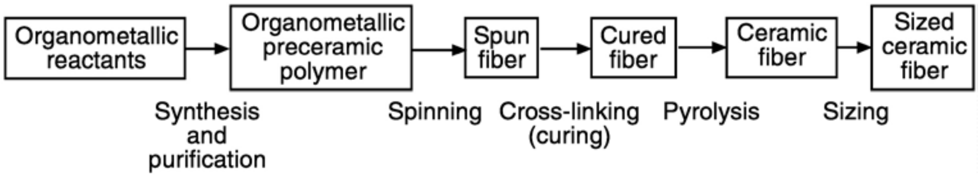


FIGURE 4-1 Typical processing scheme for producing ceramic fibers from organometallic polymer precursors. Source: Dow Corning Corporation.

A third approach to producing non-oxide fibers involves extrusion (spinning) of a ceramic powder, generally SiC, in a polymeric binder, followed by sintering. It is difficult, however, to produce fibers of less than 30 µm (1.2 mils) in diameter using this technique because the largest grain size of the powder (in the extruded fiber) must be no more than a small fraction of the fiber diameter to retain the strength and integrity of the fiber during the slurry spinning process. The tensile strength of the sintered fiber has been limited to approximately 1.4 GPa (200 ksi) because the largest grains have been critical strength-limiting flaws. Using very fine powders in extruded fiber production leads to the formation of agglomerates that also act as critical, strength-limiting flaws. The weak large-diameter fibers produced by ceramic powder extrusion have not yet been successfully woven. Two unsuccessful approaches tried by the DuPont and Carborundum companies, respectively, involved using polycarbosilane as a preceramic polymer binder (Silverman et al., 1991) or a fugitive organic binder (Frechette et al., 1994). Both efforts have been discontinued.

Preceramic Polymer Processing

Commercial and developmental fine-diameter fibers (that can be woven) have been produced by melt-spinning or solution (“dry”) spinning of organometallic polymer precursors, followed by a cross-linking (curing) step to prevent melting [1] during a subsequent pyrolysis step. This technique is known as preceramic polymer processing.

The preceramic polymer process is similar to the process used to produce carbon fiber from pitch or polyacrylonitrile (PAN) fiber. A general process scheme is shown in Figure 4-1. Several reviews of the many variations of this process are available in the open literature (Lipowitz, 1991, 1997a; Lipowitz et al., 1993; Laine et al., 1995). Although preceramic polymer processing is simple in principle, producing fibers with high tensile strength and high thermal stability requires high purity polymers, high quality spinning, and minimal impurities and mechanical damage introduced during spinning, curing, pyrolysis, and sizing (Haider and Clark, 1986; Salinger et al., 1988; Freeman et al., 1993). Multifilament spinning, generally of 200 or more filaments simultaneously, is necessary to increase throughput and reduce costs. Spinning involves two simultaneous processes: (1) extrusion of a melt or viscous solution through an orifice and (2) drawing the extruded fiber by winding at a higher velocity than the extrusion velocity.

Table 4-1 summarizes the processes used to prepare commercially available polymer-derived ceramic fibers, as well as fibers being actively developed. Although the fiber compositions vary widely, they are all prepared by a process route similar to the one shown in Figure 4-1. Advantages inherent to the polymer approach include (Lipowitz, 1997a):

- control of fiber purity
- control of ceramic morphology (amorphous or crystalline) and crystallite size
- ability to produce fine diameter (30 µm [1.2 mils]), multifilament, continuous fibers suitable for weaving and knitting
- ability to produce new metastable compositions unobtainable by other means

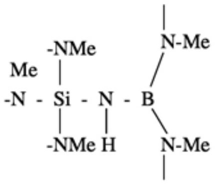
The following properties are desirable for conversion of polymers to ceramic fibers:

- a polymer that can be pyrolyzed to the desired ceramic composition (although final composition may be modified by the cure chemistry or by using reactive gases, such as NH_3 or H_2 and N_2 during pyrolysis)
- a high purity polymer with minimal particulate content (particulates interfere with spinning and introduce critical flaws)
- a highly branched polymer (which increases the ceramic char yield necessary to produce a ceramic fiber, the end product)

---

[1] Note that melting is not required for dry-spun polymers.

TABLE 4-1 Processes for Commercial and Developmental Polymer-Derived Ceramic Fibers

Company	Fiber	Polymer [g]	Spin Method	Cure Method	Pyrolysis [h]	Ceramic [i] Composition
NCK [a]	CG NICALON	$(Me_2SiCH_2)_x (MeHSiCH_2)_y$ x/y=1-2M Me=CH_3 polycarbosilane	melt	air oxidation	N_2, ~1,400° C	Si-C-O
	HI-NICALON	same	melt	electron beam	N_2, ~1,400° C	SiC + C
	HI-NICALON S	same	melt	electron beam	$N_2 + H_2$, ~1,400°C	SiC
Ube [b]	TYRANNO	same + several % Ti	melt	air oxidation	N_2, ~1,400° C	Si-C-O-Ti
		same + several % Ti	melt	electron beam	N_2, ~1,400° C	Si-C-Ti
	TYRANNO-Z	same + several % Zr	melt	air oxidation	N_2, ~1,400° C	Si-C-O-Zr
		same + several % Zr	melt	electron beam	N_2, ~1,400° C	Si-C-Zr
MER/UM [c]	—	$(MeSiH)_x$ polymethylsilane	solution dry	thermal + chemical	N_2 or Ar 1,400–1,600°C	SiC
3M/UF [d]	—	higher molecular weight polycarbosilane + additives	solution dry	thermal + chemical	N_2 or Ar ~1,400°C	SiC + C or SiC
DCC [e]	SYLRAMIC		melt	air oxidation	Ar ≥ 1,600° C	SiC + TiB_2
Bayer [f]	—		melt	chemical	N_2/1,500° C or NH_3/1,200° C	Si-N-B-C-O or Si-N-B-O

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[a] Nippon Carbon Company, Tokyo, Japan
[b] UBE Industries, Ltd., Tokyo, Japan
[c] MER Corporation, Tucson, Arizona, and University of Michigan
[d] 3M Corporation, Minneapolis, Minnesota, and University of Florida
[e] Dow Corning Corporation, Midland, Michigan
[f] Bayer Company, Leverkusen, Germany
[g] Idealized, simplified polymer molecules; all am highly branched, three-dimensional structures
[h] Pyrolysis conditions are inferred in many cases
[i] Si is listed first, followed by other elements in order of decreasing atomic abundance

- a polymer displaying rheological and thermal stability in the melt (or solution) that can be readily spun into high quality fibers
- a polymer capable of easy cross-linking to an infusible fiber after spinning
- an air-stable and moisture-stable polymer
- a low cost polymer

A highly-branched, low to moderate molecular weight, globular-shaped polymer molecule inherently produces a fragile, low strength preceramic polymer fiber because it is incapable of molecular orientation. This polymer can be contrasted with the commercial polymer fibers (nylons, polyesters, polyethylene, polypropylene, etc.), which are all high molecular weight, linear molecules capable of molecular orientation along the fiber axis, as well as of partial crystallization during drawing, which leads to high strength. The fragile nature of preceramic polymer fibers limits spinning and drawing speeds, imposing an economic penalty on throughput of the high capital-cost spinning fine. Limitations, such as moderate rates of cross-linking and pyrolysis, further restrict throughput rate and increase costs. Similar limitations in carbon fiber processing, however, have been overcome as the technology has matured.

Some polymer systems do not require a separate crosslinking step because the polymer undergoes thermal crosslinking in the early pyrolysis stage (Sacks et al., 1995; Zhang et al., 1994; Kowbel, 1997), which could reduce processing costs. However, these polymers are dry (solution) spun, which requires controlled evaporation and the recovery of the organic solvent, which would detract from the cost reduction achieved by eliminating the separate cross-linking step.

Microstructural Development

During the curing step, polymer fiber is converted to a highly cross-linked, infusible gel (with infinite molecular weight). Cross-linking can be accomplished by chemical, thermal, or radiation methods. Cure chemistry may modify the composition of the polymer and, thus, the ceramic product during the introduction of chemical cross-links (e.g., adding oxygen during oxidative air cure).

During the pyrolysis step (Figure 4-2), loss of volatile polymer components followed by thermal degradation and further cross-linking of the polymer occurs, ultimately producing an inorganic, ceramic composition. This process involves the simultaneous loss of a large volume of gas and a two-fold or greater shrinkage in volume, largely because of the increase in density from the polymer stage (p ~ 1g/cm^3 [0.04 lb/in^3]) to the ceramic stage (p ≥ 2g/cm^3 [0.07 lb/in^3]). The loss of a large volume of pyrolysis gases and the simultaneous densification of the solid phase leads to nanometer-size channels for gas evolution in region B. In region C, viscous flow of the predominantly glassy ceramic product leads to collapse of the nanochannels, which closes the nanopores (Lipowitz et al., 1990; Suzuya et al., 1996). Subsequent heating above the pyrolysis temperature, even without further gas evolution or crystallization, causes fiber shrinkage as pore volume decreases (Lipowitz, 1991).

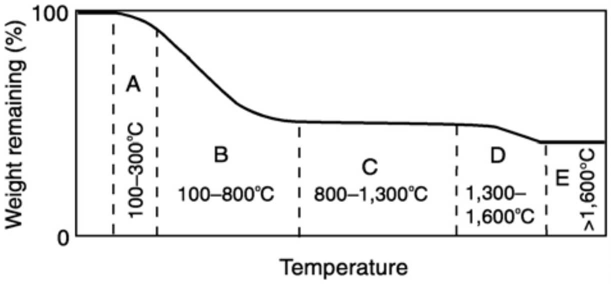

FIGURE 4-2 Schematic illustration of the pyrolysis process. Region A (~100 to 300°C [212 to 572°F]): loss of volatile oligomers. Region B (~300 to 800°C [572 to 1,472°F]): loss of pyrolysis products. Region C (~800 to 1,200°C [1,472 to 2,192°F]): continued loss of some hydrogen and methane. Region D (~1,300 to 1,600°C [2,372 to 2,912°F]): thermal degradation-loss of carbon monoxide, some silicon monoxide, and nitrogen (if present); loss of strength. Region E (~1,600°C [2,912°F]): little or no further weight loss. Source: Lipowitz, 1991.

Generally, pyrolysis takes place in an inert atmosphere, such as argon or nitrogen, with a maximum temperature of 1,100 to 1,400°C (2,012 to 2,552°F). In some instances, however, reactive atmospheres are used to modify the composition of the ceramic fiber. For example, an ammonia atmosphere will remove carbon from the polymer and replace it with nitrogen, (Okamura et al., 1987) thus permitting preparation of Si-N or Si-N-O compositions from organosilicon polymers containing carbon or carbon + oxygen, respectively. A hydrogen atmosphere removes carbon from polycarbosilane without substituting another element into the ceramic product. Hydrogen atmospheres have been used to prepare a near-stoichiometric SiC fiber from polycarbosilane, which otherwise produces a carbon-rich ceramic fiber (Ichikawa et al., 1995).

The initial ceramic produced during pyrolysis (region C) tends to be primarily, if not completely, a metastable, amorphous structure. Crystallization tends to occur more readily, and at a lower temperature, as the fiber approaches the composition of a stoichiometric crystalline material (e.g., SiC, Si_3N_4, Si_2N_2O, BN, . . .). Thus, a nonstoichiometric Si-N-B-C-O composition (Baldus, 1997; Baldus and Jansen, 1997)—which is significantly different in composition from any simple crystalline material—does not crystallize until the temperature exceeds ~1,800°C (3,272°F) in a nitrogen atmosphere. In contrast, ceramic grade Nicalon™ (an Si-C-O composition) begins to form nanocrystallites of β-SiC at approximately 1,200 to 1,300°C (2,192 to 2,372°F) in argon.

Si-C-O (made by Nippon Carbon Company) and Si-C-O-Ti (or Zr) compositions (made by UBE Industries) undergo carbothermal reduction above approximately 1,300°C (1,372°F) to form large grains of crystalline SiC, eventually resulting in a significant loss of strength:

$$4C + 2SiO_2 \rightarrow SiC + 3CO + SiO \quad (3)$$

Both UBE Industries and Nippon Carbon Company have improved the thermal stability of recently introduced products by minimizing the oxygen content in the fiber. This was accomplished by using an electron beam rather than an oxidative air cure process (Hasegawa, 1997; Takeda, 1996). In addition, UBE Industries has recently developed a series of fibers containing several weight percent Zr instead of Ti, which UBE claims reduces salt corrosion and oxidative strength loss.

Dow Corning Corporation has introduced a polycrystalline SiC fiber (Sylramic™) that incorporates up to several weight percent boron in a Si-C-O or Si-C-O-(Ti) fiber prior to a high temperature (≥ 1,500°C [2,732°F]) carbothermal reduction process (i.e., reaction 3), producing a stoichiometric β-SiC (or β-SiC + TiB_2) fiber (Lipowitz, 1997a). It is well known that boron suppresses exaggerated grain growth and aids in sintering of SiC. The incorporation of boron, which can be added to the polymer or added during the cure or pyrolysis steps, permits formation of a high strength, high modulus polycrystalline SiC fiber after sintering (or densification) at high temperature. Increasing the sintering temperature leads to increasing grain size, density, elastic modulus, strength, and creep resistance over a wide temperature range.

OXIDE FIBER PROCESSING

Commercial polycrystalline oxide fibers used to reinforce ceramic composites are produced by spinning and pyrolyzing chemically-derived precursors. These chemical processes are commonly referred to as sol-gel or metal-organic processing. Chemical processing produces fibers with high temperature properties not attainable by traditional processing methods, such as melt-spinning (e.g., spinning molten glasses). Although alternative melt-spinning approaches are being investigated, a high SiO_2 content is characteristic of melt-spun fibers, which reduces the high-temperature properties of the fibers.

One novel process, which allows fiber drawing from refractory oxide melts, is called containerless processing. Amorphous mullite and YAG (yttria-alumina-garnet) fibers with strengths as high as 5 GPa (725 ksi) have been produced from levitated, undercooled melt droplets. However, because these fibers crystallize at elevated temperatures, resulting in significant strength degradation, they will not be considered further in this report. The preparation of single-crystal fibers by drawing from a melt are also excluded because the slow production rates inherent in this process will preclude commercialization of these fibers for the foreseeable future. [2]

Extreme care must be taken at all stages of fiber processing to prevent the formation of strength-limiting defects and flaws, such as particulate inclusions, pores, bubbles, blisters, cracks, and surface damage. For example, current Nextel 610 fibers have a significantly higher tensile strength (3.0 GPa [435 ksi]) than other commercially available oxide fibers, and 50 percent higher than the originally introduced Nextel 610 fiber. This improvement is the result of an intensive program to eliminate flaws by improving process cleanliness during precursor preparation and by improving fiber processing techniques (Wilson, 1997).

In the last decade, many new oxide fibers with improved high-temperature performance have been commercialized. The keys to these improvements has been (1) the design of fiber microstructures to reduce the volume of amorphous phases and (2) the development of multiphase polycrystalline fibers. Eliminating amorphous phases prevents rapid, viscous deformation under load at high temperatures. Multiphase polycrystalline microstructures appear to inhibit creep, particularly at elevated temperatures. Examples of developmental fibers with improved high-temperature properties include polycrystalline Al_2O_3, YAG, and mullite fibers.

Chemical Processing

Chemical processing was first used to produce ceramic oxide fibers in the 1960s (Walner et.al., 1965; Lockhart and Walner, 1966). Initially, most work focused on fibers with high alumina content, although several other compositions, including those based on ZrO_2 and TiO_2, were also produced. A number of chemically-derived alumina-silica fibers, notably Saffil (noncontinuous 95 percent Al_2O_3- 5 percent SiO_2 fibers) and Nextel 312 (mullite in a borosilicate glass), were commercialized in the late 1970s. However, these fibers had poor load-bearing capability above 800°C (1,472°F) and, therefore, were not optimal for reinforcing high-temperature ceramic composites. They were (and continue to be), however, used for thermal insulation, where load-bearing capability is not a major concern. The first commercial oxide fibers designed specifically to reinforce composites was DuPont's Fiber FP, a polycrystalline Al_2O_3 fiber with significantly better high-temperature capability than Al_2O_3-SiO_2 fibers. However, Fiber FP, and the improved PRD-166 Al_2O_{3-} ZrO_2 fiber, had poor tensile strength and handleablity, which

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[2] The drawing rate of single-crystal fibers from a melt is fundamentally limited by the rate of heat transfer from the growing tip of the fiber. For Al_2O_3, the maximum rate is ~25 mm/min. (1 in./min.) for a 5 rail fiber. At this rate, it would take ~5,000 hours to make a single pound of fiber. Drawing multiple filaments (e.g., 25) from a single melt has been demonstrated but is still too slow, even for high value applications.

eventually prevented full commercialization. Neither fiber has been produced since 1985.

Figure 4-3 is a flow diagram showing the chemical processing of ceramic oxide fibers. Because all commercially available oxide fibers are based on alumina, these fibers are the focus of this discussion. As indicated in Figure 4-3, an alumina precursor is mixed with inorganic additives (e.g., a silica precursor) and organic additives to modify the precursor chemistry and allow the preparation of a viscous liquid suitable for fiber spinning. The fiber precursor is typically synthesized as a dilute solution so it can be filtered to remove particulate contamination. After filtration, the precursor solution is concentrated in a vacuum to remove excess solvent and form a viscous spin dope (the material from which fibers are drawn). Most oxide fibers are extruded into continuous filaments using dry-spinning; the spin dope contains a solvent, usually water, which is evaporated during spinning to produce a rigid fiber. The "green" (i.e., unfired) filaments are then pyrolyzed at temperatures of 300 to 500°C (572 to 932°F) to remove volatile components of the precursor, producing ceramic fibers. Heat treatment above 800°C (1,472°F) results in crystallization of the fiber into alumina or other ceramic compounds, depending on the composition of the precursors. Sintering (densification) may occur before or after crystallization.

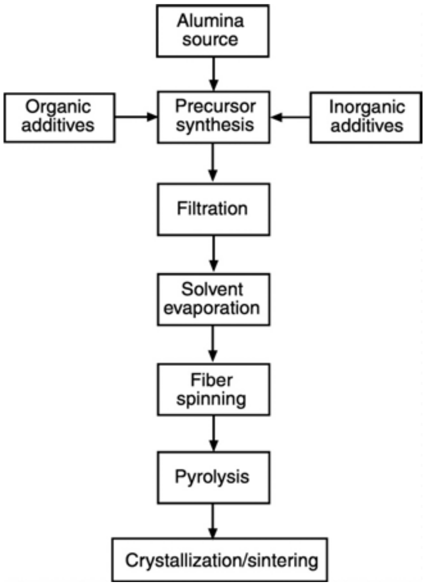


FIGURE 4-3 Flow chart of chemical processing of ceramic oxide fibers. Source: 3M Company

Chemistry of Oxide Fiber Precursors

One distinct advantage of oxide fibers in terms of processing is that several alumina precursors suitable for forming fibers are available. The aqueous chemistry of aluminum allows for the formation of viscous basic aluminum salt solutions that can be made into fibers by dry-spinning. Polymeric aluminoxane precursors have also been used to produce alumina-based fibers. Recently, aluminoxanes that can be melt-spun into fibers have been produced. Details of both types of chemical precursors are given below.

The spinning solution, or spin dope, must be stable with respect to the crystallization and precipitation of insoluble salts and organic-containing complexes, and with respect to rapid increases in viscosity (gelation) resulting from the progression or cross-linking of precursor species. Spin dopes prepared exclusively from colloidal sols (e.g., boehmite, AlOOH) are not suitable for forming continuous fibers because they are shear thinning. Colloidal SiO_2, however, is commonly used as a component in oxide fiber spin dopes (Table 4-2). Other SiO_2 precursors, such as partially hydrolyzed alkoxides and polysiloxanes, have also been used as a method of introducing SiO_2 into fiber compositions. Other inorganic modifiers to oxide fiber compositions can be readily added using soluble salts (e.g., nitrates).

Basic Aluminum Salts

The aqueous chemistry of aluminum has been extensively studied (Bertsch, 1989; Singhal and Keefer, 1994). Fully hydrolyzing aluminum salts, such as $AlCl_3$, produce insoluble aluminum hydroxides upon reaction with certain additives (e.g., 3 moles of base, such as NaOH). However, soluble aluminum complexes can be formed by partial hydrolysis with less than the stoichiometric 3 moles of anion per Al. These are commonly called basic aluminum salts with the nominal formula $AlX_n(OH)_{3-n}$, where X is either an inorganic ligand (e.g., Cl^-, NO_3-, etc.) or an organic ligand (e.g., $HCOOH^-$). Basic aluminum salts can be formed using a number of methods, including dissolution of Al metals in salt solutions, dissolution of Al hydroxides in acid, hydrolysis of alkoxides in the presence of complexing ligands, ion exchange, and neutralization of acidic salt solutions.

The aluminum species present in solution are typically octahedrally coordinated, hydroxy bridged species. A number of polynuclear aluminum species, including monomers, dimers, oligomers of intermediate molecular weight, and an Al_{13} complex (a cage of 12 octahedrally coordinated aluminums surrounding a single tetrahedrally coordinated aluminum), have been identified in aqueous solutions by Al_{27} nuclear magnetic resonance (NMR). Recently, Al_{27} NMR data suggesting 5-coordinated Al species have been produced (Wood et al., 1990). These polynuclear complexes are stabilized against further cross-linking and hydrolysis by complexing ligands. An aluminum dimer complexed with two carboxylate ligands, acetic acid, and lactic acid is shown below (Everitt, 1988):

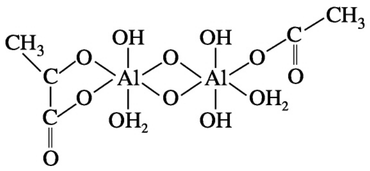


TABLE 4-2 Composition and Precursors of Commercially Available Oxide Fibers [a]

Composition (%)						
Fiber	Manufacturer	Al_2O_3	SiO2	B_2O_3	Al_2O_3 precursor	SiO_2 precursor
Nextel 312	3M	62	24	14	aluminum carboxylates	colloidal silica
Nextel 440	3M	80	28	2	aluminum carboxylates	colloidal silica
Nextel 550	3M	73	27	—	aluminum carboxylates	colloidal silica
Nextel 610	3M	100	—	—	aluminum carboxylates	—
Nextel 720	3M	85	15	—	aluminum carboxylates	proprietary
Altex	Sumitomo	85	15	—	tri-isopropyl aluminoxane	polysilicate ester
Alcen	Nitivy	70,60,80	30,40,20	—	$AlCl_x(OH)_y$	colloidal silica
Rubilon	Nichias	68	27	5	aluminum carboxylates	colloidal silica
Almax	Mitsui	100	—	—	$AlCl_x(OH)_y + Al_2O_3$ particles	—
Fiber FP	DuPont [b]	100	—	—	$AlCl_x(OH)_y + Al_2O_3$ particles	—
PRD-166	DuPont [b]	80 [c]	—	—	$AlCl_x(OH)_y + Al_2O_3$ particles	—

[a] Fiber composition taken from vendor specifications, precursor composition from the patent literature
[b] No longer commercially available
[c] 20 percent ZrO_2

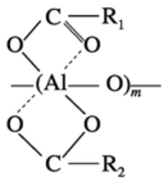
Ligands can be monodentate, such as acetic acid ($COCH_3$, upper right above), or bidentate, such as lactic acid (C_2OCH_3, left). In many cases, mixtures of ligands are used. The relative amounts of each type of Al complex in solution vary with the type and amount of anion ligand present, concentration, heat treatment time and temperature, and preparation route. In general, lower anion levels result in higher levels of polymerized or clustered aluminum species. Viscosity in basic aluminum salts is not derived from the presence of linear polymers but is believed to result from hydrogen bonding between adjacent Al complexes.

In practice, 0.5 to 2.0 moles of anion ligand are used per mole of Al for fiber spinning precursors. A variety of ligands have been used to produce spinnable alumina precursors, including chloride, nitrate, and carboxylates. Small amounts of ligand can allow gelation via the cross-linking of polynuclear clusters; larger amounts, however, cause problems during fiber heat treatment because of the excessive amounts of fugitives that must be removed during pyrolysis. Large ligands, such as lactic acid or acetyl acetonate, can be used to produce spinnable precursors, but ceramic yield on firing is lower than when smaller ligands, such as Cl, are used.

Aluminum chlorohydrates ($AlCl_x(OH)_y$) are used to prepare a number of commercial fibers, including Fiber FP and PRD-166, Almax, and Alcen (Table 4-2). Rubilon and the Nextel series of fibers are produced using aluminum carboxylates.

Polymeric Aluminoxane

Alumina fibers based on polymeric aluminoxanes were initially developed in the late 1970s (Horikiri et al., 1978). Aluminoxanes consist of an Al-O backbone polymer coordinated by chelating ligands, such as carboxylates and acetoacetonates, as shown below (R_1 and R_2 are organic ligands, and m is the degree of polymerization):



Ligands that have been used as components in spinnable aluminoxanes include ethyl acetylacetonate (Yogo et al., 1993), propionic acid (Glaubitt et al., 1994), 3-ethoxypropionic acid (Kimuta et al., 1989), acetic acid (Yogo and Iwahara, 1992) and isobutyric acid (Glaubitt, et al., 1994).

Aluminoxanes are synthesized by adding the ligand to aluminum alkyls or alkoxides to partially chelate the aluminum, followed by the addition of 0.5 to 1 mole of water per mole or Al to polymerize the aluminoxane. Additional ligands are usually added to modify precursor rheology to improve spinning and pyrolysis behavior. Depending on the ligands used, the precursors can be either melt-spun (Kadokura et al., 1990) or dry-spun. Melt-spun fibers are cured (to make them infusible) by completing hydrolysis on exposure to humid atmospheres. The ceramic yield of aluminoxane polymers can be as high as 50 weight percent. Sumitomo Altex fibers are produced using this technique.

Dry Spinning

Figure 4-4 is a schematic drawing of the dry-spinning process. The spin dope is pumped by a metering pump through a spinneret. Spinning is performed by extruding the fiber into a spinning tower under carefully controlled humidity, temperature, and air flow conditions. Spin dope viscosity is typically 100 to 1,000 Pa-s for fiber spinning. It is desirable for the spin dope to exhibit Newtonian (i.e., nonshear thinning) behavior so its viscosity remains consistent as it is extruded through the orifice of the spinneret. Fiber diameter is controlled by varying the volumetric pumping rate relative to the speed of the draw wheels. The diameter is reduced substantially during spinning; the draw ratio (speed of the draw wheels relative to the extrusion rate) is typically between 4 and 25. In order to stabilize spinning, the forces acting on the fiber must be in balance:

$$F_{\text{draw}} + F_{\text{grav}} = F_{\text{visc}} + F_{\text{inertia}} + F_{\text{surf}} \quad (4)$$

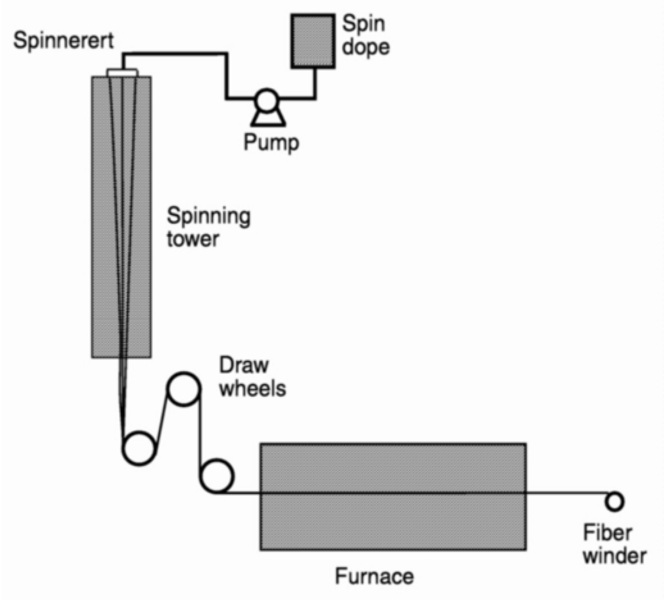


FIGURE 4-4 Schematic illustration of the dry-spinning process. Source: 3M Company

The downward forces from the draw wheel and gravitation must, therefore, equal the restraining forces generated by the viscosity and surface tension of the spin dope plus the inertial drag of the fiber as it is accelerated. Low viscosity leads to insufficient rheological force to resist gravitation; fiber diameter is reduced to the point where fracture occurs by necking. High viscosity can lead to capillary fracture, which occurs when the draw force exceeds the stretching capability of the fiber. Maintaining a balance of forces is very difficult because all of these factors are continuously changing. As the fiber progresses down the spin tower, the fibers are drawn down to smaller diameters, fiber velocities are increased, and the viscosity of the spin dope increases as the solvent evaporates, resulting in the fiber becoming rigid.

Pyrolysis

After spinning, the green fibers are conveyed into a furnace for heat treatment. Pyrolysis (the conversion of the chemical precursor into a ceramic) typically involves the loss of 50 to 80 percent of the initial weight of the green fiber. In addition, volumetric shrinkage can be 80 percent or higher. Volatile components (including CO, CO_2, H_2O, produced by oxidation, and low molecular weight organics, depending on precursor chemistry) must diffuse out of the fiber during pyrolysis. Thus, pyrolysis must be performed with care to decompose the green fiber to the oxide form gently so as not to introduce defects or flaws. Removing fugitive components becomes increasingly difficult as fiber diameter increases. Typically, a fiber diameter of 20 μm (0.80 mils) is the upper limit for chemically-derived fibers. Defects that can occur during pyrolysis include the partial melting of fusible fiber components, the evolution of gases causing pinholes, the formation of bubbles or voids or even bloating, the entrapment of carbon, phase separation, and cracking. Adding colloidal or particulate materials to fiber precursors increases ceramic yield, thereby reducing shrinkage and facilitating pyrolysis. Colloidal additives may, however, have a detrimental effect on fiber properties.

The results of simultaneous thermal gravimetric analysis (TGA), differential TGA (DTGA), and differential thermal analysis (DTA) of a chemically-derived alumina fiber produced from aluminum carboxylates are given in Figure 4-5. The TGA curve shows a weight loss of 10 to 15 percent at 100°C (212°F). This corresponds to an endotherm on the DTA plot and is indicative of water loss. A series of weight loss peaks appear on the DTGA curve in the temperature range of 300 to 450°C (572 to 842°F). Two DTA exotherms at 420°C (788°F) and 455°C (851°F) are also present. These peaks correspond to the exothermic decomposition of the organic components in the green fiber. A weight loss of ~50 percent occurs during this process. By the time a temperature of 650°C (1,202°F) is reached, weight loss ceases. At this point, the fiber is alumina but is x-ray amorphous. At 860°C (1,580°F), an exotherm occurs as the fiber crystallizes to cubic alumina spinel (η- Al_2O_3). An exotherm at 1,030°C (1,886°F) indicates the temperature at which the transformation to α-Al_2O_3 occurs.

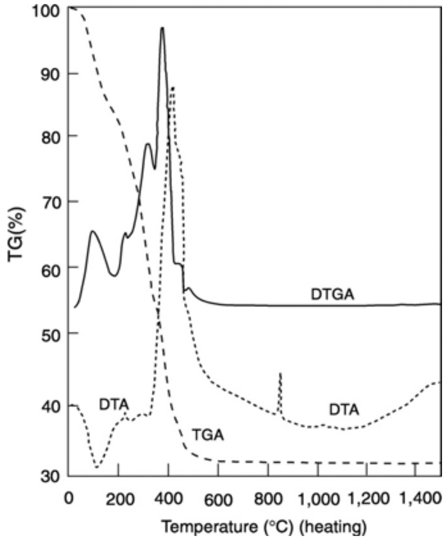


FIGURE 4-5 Differential thermal analysis (DTA), differential thermogravimetric analysis (DTGA), and thermogravimetric analysis (TGA) of chemically-derived alumina fiber. Source: 3M Company

Heat Treatment and Fiber Microstructure

The goal of heat treatment is to develop a ceramic microstructure with both good strength and good high-temperature properties (i.e., low creep rate, high creep rupture strength, and resistance to thermal degradation via grain growth). Fiber microstructure is determined by both the chemistry and composition of the fiber precursor. High fiber strength at room temperature requires a small grain size (≤ 0.5 µm [0.02 mils]). The Griffith equation, $\sigma_f = K_{Ic}/\sqrt{\pi c}$, indicates that for Al_2O_3, (fracture toughness, $K_{Ic} = 4$), a fracture strength (σ_f) of 3 GPa (435 ksi) can only be achieved if the flaw size (c) is ≤ 0.6 µm (0.02 mils). Thus, not only must defect concentration be kept low by careful fiber processing, but grain size must not exceed this limit. Unfortunately, creep rates increase with small grain size. Thus, optimizing overall performance requires making a trade-off between strength and creep resistance.

Microstructure development in alumina-based fibers is strongly influenced by transformation sequences that occur as alumina precursors crystallize. The stable phase of alumina at all temperatures is α-Al_2O_3. However, a series of cubic alumina spinels, commonly called transition aluminas, form during heat treatment of alumina precursors. The nature of the transformation (i.e., temperature, porosity, grain size) depends on the precursor. However, for amorphous precursors, like basic aluminum salts and aluminoxanes, η-Al_2O_3 (cubic) or γ-Al_2O_3 (tetragonal) crystallize in the range 800 to 900°C (1,472 to 1,652°F) (Figure 4-5). In many systems, δ-Al_2O_3 and Θ-Al_2O_3 are formed with additional heating in the range 1,000 to 1,150°C (1,832 to 2,102°F). These polymorphs are similar to γ-Al_2O_3 but have a higher degree of ordering on the cation lattice. The transformation to α-Al_2O_3 occurs between 1,000°C (1,832°F) and 1,200°C (2,102°F). These transformation sequences are determined by the chemistry of the fiber precursor (Wood et al., 1990). In transition aluminas, the Al^{3+} cations are present on both tetrahedral and octahedral sites.

The chemistry of the alumina precursor used for fiber spinning varies with synthesis technique. This chemistry is maintained throughout the pyrolysis process and affects the nature of the crystals formed at higher temperatures. For instance, the presence of the Al_{13} complex leads to highly ordered spinel structures, whereas the presence of 5-coordinated Al species in solution produces poorly ordered crystals (Wood et al., 1990).

Adding inorganic components to alumina-based precursors also has a strong affect on crystallization behavior and the fiber microstructure. For instance, small grain size can be achieved by stabilizing transition alumina by adding SiO_2

(Stacey, 1988). Most commercial oxide fibers have a major phase of transition alumina stabilized by silica (Table 4-2). The grain size of alumina spinels is very small, typically 100 nm (0.004 mils) or less. Adding SiO_2 increases the temperature of the α-Al_2O_3 transformation by as much as several hundred degrees (to 1,400°C [2,552°F]) if the Al and Si precursors are intimately mixed. SiO_2-stabilized alumina spinels are very resistant to grain growth at temperatures up to 1,200°C (2,192°F) for extended periods. The crystallization of spinels can be eliminated, leading to the direct formation of mullite at 980°C (1,796°F) through the synthesis of atomically-mixed Al_2O_3-SiO_2 precursors (e.g., Al alkoxides + tetraeth-oxysilane) (Schneider et al., 1992). Similar effects have been observed with other aluminates, such as YAG (King et al., 1993) and $MgAl_2O_4$. If colloidal silica or aluminas are used (i.e., “diphasic” precursors), the crystallization of mullite occurs at 1,280°C (2,536°F). Dopants can also affect crystallization. For instance, B_2O_3 reduces the transformation temperature of mullite (Richards et al., 1991).

Microstructural stability and creep performance can be improved by crystallizing the fiber to eliminate amorphous phases and form creep-resistant phases, such as mullite or YAG. However, control over the nucleation process during the crystallization of high-temperature phases is essential to attaining the fine grain sizes (≤ 0.5 µm) required for high strength. In alumina-silica fibers, large grain sizes often result from the crystallization of new phases, such as mullite and α-Al_2O_3. A low volumetric nucleation density, which leads to large grain sizes, is typical of both alumina and mullite.

In addition to large grains, crystallization often leads to high levels of porosity, which inhibits sintering. Figure 4-6 shows a crystalline α-Al_2O_3 fiber heated to 1,400°C (2,552°F). The grain size is more than 2 µm (0.08 mils), which leads to very poor strength. Enhancing the nucleation rate to improve microstructures can be done using seeding or nucleating agents. Figure 4-7 shows Nextel 610 fiber, which has a nucleation agent added, producing a uniform, high density microstructure with a grain size of ~100 nm (0.004 mils). Fiber FP/PRD-166 and Almax fibers, which are made by adding crystalline α- or γ-Al_2O_3 particles, respectively, are other examples of seed or nucleation sites reducing grain size.

Grain growth is another factor to be considered in the design of fiber microstructures for high-temperature applications. The degradation of fiber strength at high temperatures occurs via grain growth, which generates critical flaws in the microstructure. The presence of second phases on grain boundaries can reduce grain boundary migration rates and limit degradation associated with grain growth. For instance, PRD-166, which contains 20 percent ZrO_2, retains good strength to higher temperatures than Fiber FP, a similar fiber with only a single phase of α-Al_2O_3. Grain growth of alumina is also inhibited in Nextel 720, which consists of a two-phase mixture of α-Al_2O_3 and mullite.

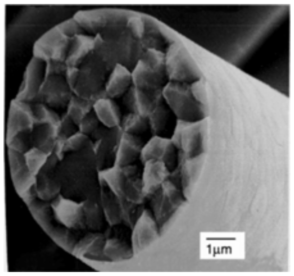


FIGURE 4-6 α-Al_2O_3 fiber with large grain size resulting from low nucleation density. Source: 3M Company.

Recently, several laboratories have produced polycrystalline YAG fibers. Successful processes included using colloidal sols (King and Halloran, 1995), carboxylates (King and Halloran, 1995; Budd and Wilson, 1993; Pak and Kimel, 1994), alkoxides (King et al., 1993), and mixed yttrium-aluminoxane polymers (Chen and Mazkiyasni, 1995). BSR creep experiments on polycrystalline YAG fibers have demonstrated creep resistance at 100 to 200°C (212 to 392°F) higher than the useful operating temperatures for commercially available oxide

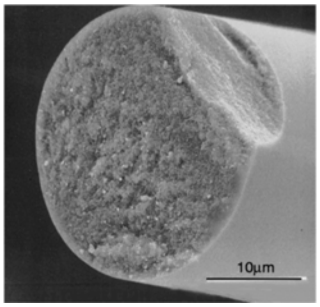


FIGURE 4-7 Nextel 610 fiber showing small grain size resulting from the addition of nucleation agents. Source: 3M Company.

fibers (Morscher et al., 1994). In this last instance, second phase particles of ZrO_2 were reported to reduce grain growth and improve creep resistance in YAG fibers (Morscher et al., 1994).

Unfortunately, the strength of these experimental YAG fibers is generally below 1.0 GPa (145 ksi). In many cases, these low fiber strengths resulted from process-related flaws, such as large pores and cracks created by imperfect pyrolysis of the precursor. However, crystal growth during crystallization of the YAG phase produced fibers with relatively large grain sizes (> 0.5 µm [0.02 mils]), which limited potential fiber strength. The production of high strength YAG fibers will require development of novel precursor chemistries that can be spun and pyrolyzed to form flaw-free fibers on a commercial scale, as well as a better understanding of factors that affect crystallization and grain growth.

RECOMMENDATIONS AND FUTURE DIRECTIONS

Although the oxidation resistance of *oxide* fibers is attractive, their poor creep resistance is a limiting factor. A number of the recommendations below suggest promising processing improvements that could improve this situation. Recommendations regarding property improvements of *non-oxide* fibers are less of a priority because, for many applications, adequate properties have already been attained. Therefore, the committee concluded that directing resources toward improving the properties of oxide fibers was more important. Note, however, that fiber processing costs for both oxide and non-oxide fibers can be reduced.

Non-Oxide Fibers

The extraordinary structural and oxidative stability claimed for the amorphous Bayer Si-N-B-C(O) fiber and the formation of an in situ BN layer on oxidation suggest directions for further investigation. Non-oxide, multi-element glasses may be a fertile area for the discovery of compositional variants that have unexpectedly useful thermomechanical and thermochemical properties. Amorphous fibers composed of combinations of elements that form strong covalent bonds (e.g., Si, C, N, B, O, and possibly Al, Ge, P, and S) may produce stable, amorphous compositions that are resistant to crystallization because of their high activation energies for bond rearrangement and a lower probability (entropy factor) of rearrangement to simple crystalline structures.

Methods for reducing the costs of processing steps in preceramic polymer processing routes for non-oxide fibers should be pursued. For example, spinnable, low-cost polymer precursors that cross-link (cure) rapidly on line or thermally cross-link in the early stage of pyrolysis have the potential to increase throughput and lower costs. These fibers should preferably be melt-spun rather than dry-spun to eliminate the need for the extra steps of solvent evaporation and recovery. Low-cost polymers with molecular structures suitable for rapid spinning and rapid on-line curing are also promising. Faster on-line pyrolysis, using polymer structures that maximize ceramic yield and minimize pyrolysis gas formation, is also a desirable goal. Non-polymer precursor processing routes should also be investigated.

New ceramic compositions and microstructures with thermomechanical and thermochemical properties beyond the capability of SiC will be required for the next generation of high-temperature materials. Developing and commercializing new non-oxide fibers that cost less and/or have improved properties are likely to be lengthy and expensive processes. Because non-oxide ceramic fibers have not been profitable so far, industry alone is unlikely to support further development.

Oxide Fibers

Although the creep resistance of oxide fibers is inferior to Si-based non-oxide fibers, recently developed oxide fibers, such as Nextel 720 and YAG fibers, have demonstrated adequate creep resistance for use in structural composites in the 1,000 to 1,200°C (1,832 to 2,192°F) range. A fertile area for research is the development of chemical precursors that can be used to produce fine-grained, fully crystalline fibers of creep-resistant complex oxides, such as YAG and mullite. A thorough understanding of the crystallization of creepresistant phases with the proper microstructures will be required to improve creep properties without decreasing strength. In many cases, intermediate phases form prior to the crystallization of the desired phase. The demonstration of reduced rates of thermal degradation in multiphase oxide fibers complicates matters but also suggests directions for future research. The use of dopants that reduce diffusion rates to minimize grain growth kinetics should be investigated as a way of improving creep resistance. Other opportunities for improving the creep-resistant properties of oxide fibers are discussed in Chapter 5.

Si-based non-oxide fibers are covalently bonded, which leads to very high fiber strength compared to oxide fibers. However, the high strength of Nextel™ 610 fibers, attained via a targeted flaw reduction program, suggests that new types of creep-resistant oxide fibers may benefit from similar programs, which will probably be necessary for the development of high strength, creep-resistant oxide fibers, which may have relatively large grain sizes compared to most commercially available oxide fibers. The committee recommends that efforts be made to determine the effect of grain size, microstructure, and flaw population on the strength and creep resistance of oxide fibers.

The utility of oxide fibers in composites can also be enhanced by using heat treatments to produce in-situ interface coatings. For instance, Nextel 312 (which contains 14 percent

B_2O_3) develops a BN-coating up to 10 nm (4 x 10^{-4} mils) thick when it is heated in NH_3 (Khasgiwale et.al., 1995). This process has led to the development of low cost Blackglass™ ceramic composites. Other fiber surface modifications have also been demonstrated, for example, the formation of fibers with metal-modified surfaces by exposing spinel fibers to reducing environments (Sowman, 1988). The committee recommends that research on ceramic oxide fiber processing include fiber surface modifications and the development of in-situ coatings.

5

Materials and Microstructures

The performance objectives described in the previous chapters limit the material choices of ceramic fibers for CMCs to polycrystalline oxides (e.g., Al_2O_3, mullite), non-oxides (e.g., SiC, Si_3N_4), and amorphous Si-C-N-B-O compositions. Single-crystal monofilaments have certain performance advantages, but their cost is prohibitive. Therefore, they are not discussed in this chapter.

Once fabrication flaws have been eliminated, the strain-to-failure of ceramic fibers is dominated by grain size (*d*), scaling as $\sim d^{-1/2}$. Typically, the grain size must be 0.1µm to 0.5µm (0.004 to 0.02 mils) to achieve the strain-to-failure goal of 0.6 percent for ceramic fibers (Evans, 1997). The creep rate (ε') of fine-grained polycrystalline ceramics typically *increases* as the grain size *decreases* because of the dominate diffusive deformation mechanisms in these materials. In single-phase ceramics, the creep rate is controlled by the following relationship:

$$\varepsilon' \sim D_b/d^n \quad (1)$$

D_b is the diffusivity, and n is an exponent between 1 and 3, depending on the dominant creep mechanism (e.g., $n = 3$ for grain boundary diffusion). However, these mechanisms are not sufficiently understood for creep rates to be explicitly predicted from the grain size and diffusivity of the material. The recent experimental findings described below highlight this deficiency and also indicate the opportunity for developing polycrystalline materials that combine high tensile strength with excellent creep resistance.

OPPORTUNITIES FOR FIBER DEVELOPMENT

To facilitate the discussion of potential improvements in fiber properties through microstructural enhancement, some recent creep studies (and the associated mechanistic understanding) are summarized below. Ceramic fibers consisting of mullite and alumina mixtures (e.g., Nextel 720 fibers) have demonstrated creep strengths considerably greater than those observed in single-phase alumina or mullite fibers (Chapter 3). In general, two-phase mixtures exhibit less grain growth than single-phase materials and tend to be more microstructurally stable (French et al., 1990). However, the mechanism by which multiphase ceramic oxide fibers resist creep rupture is not understood. The microstructure of the Nextel 720 fiber consists of needle shaped mullite grains and elongated α-Al_2O_3 grains, suggesting that grain morphology plays a key role in creep retardation. For example, calculations have implied that grain elongation along the fiber axis can enhance creep strength, when diffusion mechanisms dominate creep rate (Figure 5-1) (Sabol, 1994).

Adding SiC nanoparticles to bulk samples of alumina has been shown to enhance the creep strength of alumina (see Figure 5-2), particularly when the SiC particles are preferentially located at the alumina grain boundaries (Ohji et al., 1995). It has been postulated that the SiC particles inhibit grain boundary sliding, setting up a “back stress” that resists creep. It has also been inferred, from sintering studies, that SiC particles decrease the overall grain boundary diffusion rate and that creep inhibition is due to slow diffusion along the alumina/silicon carbide interface (Stearns et al., 1992). However, the fundamental mechanisms whereby SiC particles inhibit creep are not known.

The addition of yttrium and other oversized isovalent cations to alumina has also been shown to enhance creep strength (Figure 5-3) (French et al., 1994). The oversized ions segregate to the alumina grain boundaries (Figure 5-4). One

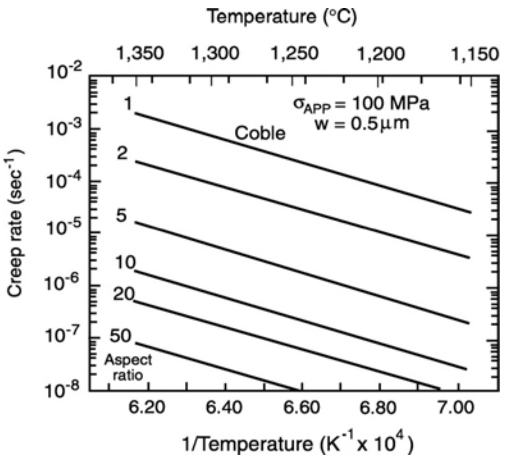


FIGURE 5-1 Predicted creep rates for alumina fibers as a function of aspect ratio using a two-dimensional model. Source: Sabol, 1994.

hypothesis is that the retardation in creep results from inhibition of the grain boundary diffusion kinetics by a simple “steric hindrance” effect. There is also some evidence in the literature that the presence of dopant ions can significantly increase the proportion of special (i.e., coincident site lattice) grain boundaries in alumina (Lartigue-Korinek et al., 1994). Perhaps the diffusivities along these boundaries are diminished, resulting in grain boundary sliding rates that are also diminished. A comprehensive understanding of the mechanism by which oversized isovalent cations inhibit creep, however, remains elusive.

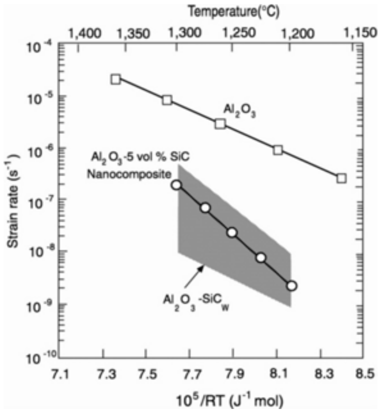


FIGURE 5-2 Tensile creep rate of Al_2O_3-SiC nanocomposite containing 5 volume percent of 0.15 µm (0.006 mils) SiC particles and undoped Al_2O_3 of the same grain size. The hatched band represents flexural strain rate data for SiC whisker-reinforced alumina Source: Thompson et al., 1997b.

Although the findings described above regarding creep in fine-grained polycrystals have been limited to oxides, it is anticipated that analogous effects are possible for non-oxide ceramics. For example, certain additives and second-phase particles (e.g., Ti, C, and B_4C) enhance the creep strength of polycrystalline SiC, while others (e.g., B and Al) degrade it (recall Chapter 3). The mechanisms, however, are not understood.

The development of an amorphous fiber in the Si-N-C-B system has revealed two unexpected possibilities. First, this fiber appears to be stable in the amorphous state up to ~1,600°C (2,912°F), even in air, and retains its tensile strength up to 1,600°C (2,912°F). Second, oxidation of the Si-N-C-B fiber forms silica at rates comparable to the rate that silica is formed upon oxidation of crystalline SiC, and also creates a thin (~50 nm [0.002 mils]) buried interphase of hexagonal BN. It has been hypothesized that this in-situ BN would act as a crack deflection layer in a CMC. If so, the regenerative nature of the deflection interphase could avert composite degradation by stress oxidation.

These findings imply that there is a realistic potential for discovering materials with superior creep strength, through a mechanism-based research approach. Complex oxides and carbides, as well as multiphase materials, could be tailored to create attractive combinations of properties.

POLYCRYSTALLINE OXIDES

Fine-grained (grain size < 1µm [0.04 mils]) oxide poly-crystals creep in accordance with diffusive deformation mechanisms, accompanied by sliding of the grain boundaries. (Note that the stress/temperature domain in which dislocation is the dominant creep mechanism has yet to be rigorously identified). Therefore, if all other parameters remained fixed, the creep rate would simply scale with the grain boundary diffusivity (D_b) and vary inversely with the grain size (d) to the first, second, or third power (n) depending on whether the process is controlled by interface control (or sliding), lattice diffusion, or grain boundary diffusion (see Equation 1).

One implication that has been adequately validated by experiment is that complex oxides with low D_b, particularly mullite, have creep strengths superior to single-phase oxides, such as alumina, yttria, and magnesia. However, the findings that solid solutions and nanoparticles profoundly affect creep rates in bulk polycrystalline oxides was not obvious from

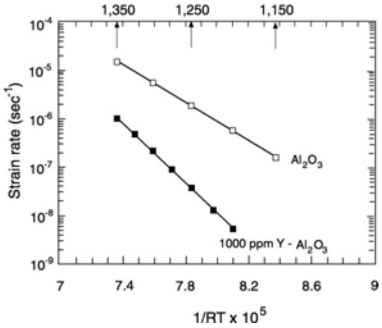


FIGURE 5-3 The steady-state tensile creep rate for undoped alumina and alumina doped with 1,000 ppm Y_2O_3. Note that yttria doping dramatically reduces the creep rate. Source: French et al., 1994.

prior knowledge of the creep mechanism. The current theory is that (1) some solid solutions diminish the diffusivity, and (2) some intergranular nanoparticles inhibit the sliding and rotation of the grain boundaries. The specific mechanisms that dictate the diffusivity and sliding are not clear, but the findings are compelling and suggest trajectories for future research and development.

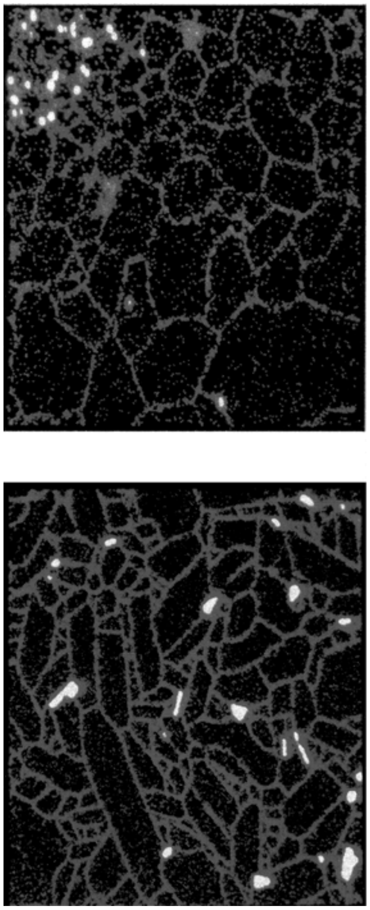


FIGURE 5-4 High resolution secondary ion mass spectroscopy compositional maps showing dopant segregation in yttrium and lanthanum doped alumina. Source: Chabala et al., 1997.

The best creep results on nanoparticle-reinforced alumina have been achieved with intergranular SiC (at about 5 volume percent). The effect of SiC nanoparticles was unexpected because simple theory indicates that diffusion would occur rapidly around SiC particles located along sliding grain boundaries because of their small size. However, there is no evidence that this occurs. The mechanism(s) responsible for this counterintuitive effect need to be understood so this behavior can be realized in other systems. Despite the promising results indicating excellent creep resistance in Al_2O_3 reinforced by SiC nanoparticles, SiC nanoparticle-reinforced Al_2O_3 does not appear to be appropriate for use as a fiber for reinforcement of CMCs subject to oxidizing conditions. That is, the oxidation characteristics of this material are problematic. Oxidation measurements indicate that a silica outer layer forms on Al_2O_3 reinforced with SiC nanoparticles at a rate comparable to the rate it would form on SiC. However, a much thicker SiO_2 layer forms below the surface of SiC nanoparticle-reinforced Al_2O_3, wherein the SiC particles have a modified chemistry and morphology. Such a thick SiO_2 layer would result in the degradation of a fiber made of this material. The benefit of creep strengthening with nanoparticles could be realized without oxidative degradation, *if* oxide ceramics were reinforced with oxide ceramic nanoparticles. The committee recommends that this possibility be investigated.

Certain solutes can also have a profound, beneficial effect on creep resistance. For example, it has recently been discovered that the addition of small quantities (less than 1,000 ppm) of rare earth dopants, such as yttrium, lanthanum, or neo-dymium, to fine grained Al_2O_3 (1µm to 2µm [0.04 to 0.08 mils] grain size) can reduce the creep rate by several orders of magnitude. The effect seems to be strongly correlated with the fact that these ions are highly oversized for the alumina lattice and thus segregate very strongly to the grain boundaries. Other isovalent dopant ions, such as chromium and iron, which are closer in size to aluminum and do not segregate strongly to the grain boundaries, do not affect creep strength.

The mechanism for creep reduction is not understood although the relationship between dopant concentration and creep resistance has been confirmed to be a true solid-solution effect. One school of thought is that creep is controlled by grain boundary diffusion and that large segregated ions simply hinder diffusion in the core sites at the boundary. This theory is supported by kinetic measurements of self-diffusion in undoped and yttria-doped alumina and by studies of the oxidation of aluminum alloys (Le Gall et al., 1995). There is also some evidence to suggest that yttria may promote the formation of special (i.e., high coincidence site lattice) grain boundaries in alumina (Lartigue-Korinek et al., 1994). This theory argues that grain boundary diffusion would be retarded along these boundaries because of their greater structural order, which would lead to slower creep kinetics. The committee recommends that research be continued on the effect of isovalent doping on the creep properties of oxide ceramics.

Much of the work on doping has been performed on bulk materials with grains several times larger than those present in most fibers. An important aspect of future research should be to determine the extent to which these findings translate to fibers with ultrafine grains.

In general, when material deformation is dominated by diffusion, fibers may be strengthened by texturing and elongating grains along the fiber axis. Methods for developing these microstructures should be investigated in the future.

POLYCRYSTALLINE SILICON CARBIDE

The creep mechanisms in fine-grained polycrystalline SiC should be the same as the mechanisms that operate in fine-grained oxides. The major difference is the inherently low grain boundary diffusivity of SiC compared to most oxides. Consequently, the baseline creep properties of SiC, before either solid-solution or particle strengthening, are superior to those of oxide ceramics. The only information available regarding solid-solution or particle strengthening of SiC ceramics, however, concerns an apparent solid-solution weakening effect caused by boron-doping, and an apparent particle strengthening caused by excess carbon and, possibly, titanium diboride. It seems that the potential of these mechanisms for creep strengthening has not been explored at all. The committee recommends this area as a focus of future research.

As opportunities for enhanced creep strength are explored, it is essential that the chemistries be retained within a domain that ensures that oxidation rates are comparable to, or better than, the rates for nominally pure SiC. Otherwise oxidative degradation of the composite will reemerge as *the* performance limiting mechanism. The rupture strength of polycrystalline SiC fibers at elevated temperatures has not been evaluated comprehensively and should be further investigated. A few systematic studies on the effect of heat treatment (aging) on rupture strength have been conducted, but this area is worthy of future research.

AMORPHOUS FIBERS

The development of amorphous fibers composed of Si, C, B, and N with exceptional creep resistance and thermal stability (against crystallization) has been reported by several domestic and foreign researchers independently (Baldus, 1997). These reports suggest that the creep resistance of amorphous Si, C, B, and N (Si-C-B-N) fibers are comparable to stoichiometric, crystalline SiC. The committee recommends that research be undertaken to verify these results and to develop a basic understanding of the Si-C-B-N material. The object of this research is to find ways to produce these fibers using less expensive precursors. A successful outcome would be the development of an affordable fiber with the same performance characteristics as crystalline SiC. However, confirming the utility of this fiber for CMCs would require that the following issues be rigorously investigated:

- susceptibility to crystallization at long exposure to high temperatures, including the influence of oxidation, temperature, and stress (the expectation is that the onset of crystallization would cause rapid degradation)
- stability of the surface oxide and of the in-situ BN layer at intermediate temperatures (for many non-oxides, intermediate temperatures are the most critical for property retention)
- creep viscosity

RECOMMENDATIONS AND FUTURE DIRECTIONS

The properties of ceramic fibers are dominated by fabrication flaws and fiber microstructure. These two factors are not mutually exclusive and have been discussed in this report in several different contexts. Recommendations pertinent to fiber processing to reduce fabrication flaws and develop tailored microstructures were discussed in Chapter 4. Here the committee recommends directions for research that are likely to determine the microstructures required for attaining the properties that would facilitate the use of ceramic fibers in advanced high-temperature CMCs.

Oxide fibers (which are inherently resistant to oxidation) with improved creep resistance will, with the concurrent development of suitable fiber-matrix interfaces, enable CMCs to be used in higher-temperature applications in oxidative environments (e.g., gas turbine engine exhaust nozzles and heat exchangers for externally-fired combined-cycle power systems). Therefore, the committee recommends that the following research be supported:

- determining the mechanism by which certain solutes lower the creep rate of bulk polycrystalline oxides (e.g., yttria in alumina) and applying them to oxide fibers and determine if analogous effects exist in non-oxide systems
- establishing the mechanism(s) by which SiC nanoparticle dispersions inhibit creep in oxide ceramics and developing oxide nanoparticle systems analogous to the alumina (SiC) nanocomposite system
- exploring and exploiting multiphase microstructures for enhancing high-temperature microstructural

stability (e.g., resistance to grain growth) and improving creep resistance in both oxide and non-oxide systems

Non-oxide fibers, which are inherently more creep resistant than oxide fibers, could provide the higher-temperature performance needed for near-term CMC applications (e.g., furnace hardware, such as pipe hangers). But a systems approach to preventing oxidative degradation (pesting) of nonoxide CMCs will have to be developed. With further improvements in the creep resistance of non-oxide fibers, they could be used in longer-term applications (e.g., gas turbine engine combustor liners). Therefore, the committee recommends that research in the following areas be supported:

- verification and study of the mechanisms of creep enhancement, stability against crystallization, and oxidation resistance in amorphous Si-C-B-N fibers and the exploration of other families of amorphous non-oxide fiber systems
- the development of new materials conducive to the formation of in-situ coatings either during fiber processing or in service (e.g., the BN layer formed by oxidation in amorphous Si-C-B-N fibers)
- clarification of the effect of solid-solution and second-phase additives (especially C and TiB_2) on the creep behavior and grain growth of polycrystalline SiC fibers
- study of the effects of texture on the creep strength of fibers and the development of processing methods to induce the optimum orientation
- systematic studies of the effects of high-temperature heat treatment (aging) on the rupture strength of polycrystalline SiC fibers

6

Interfacial Coatings

CMCs typically consist of a ceramic fiber, a matrix, and one or more fiber/matrix interfacial coatings (fiber coatings). The purpose of the fiber coating is to provide a weak fiber-matrix interface that prevents matrix cracking from penetrating the fibers—thus providing damage tolerance (toughness) to the composite. Fiber coatings also protect fibers from environmental degradation during composite fabrication and use. The fiber coating must be chemically and mechanically stable in high-temperature corrosive environments in order to maintain the fiber-coating-matrix debond characteristics necessary for damage tolerance. Unfortunately, the development of interfacial coatings has not kept pace with the development of ceramic fibers, which has limited the use of CMCs. Current fiber coatings either do not have adequate oxidation resistance or are not stable with fibers and matrices at elevated temperatures. Generally, these limitations have resulted in the degradation of the strength and toughness of CMCs during use.

In this chapter, the current status, major issues, and needs for fiber coatings are discussed. This discussion includes the status of the vendor base needed to commercialize fiber coatings. Although ceramic fibers were discussed in Chapter 4 and matrix materials are beyond the scope of this report, the effectiveness of the fiber/matrix interface is system dependent. Therefore, system approaches, such as the use of matrix additives to inhibit oxidation, will also be discussed in this chapter.

COATINGS FOR NON-OXIDE COMPOSITES

This section centers on fiber coatings for non-oxide composites in which either the fiber or the matrix is a non-oxide ceramic. Although oxide fiber-reinforced composites have been studied, most of the research available in the literature has focused on SiC fiber-reinforced composites. For example, mullite ($3Al_2O_3$-$2SiO_2$) fiber-reinforced SiC matrix composites have been fabricated by CVI (chemical vapor infiltration). However, SiC fiber-reinforced SiC matrix (SiC/SiC) composites are superior for the following reasons: (1) mullite fiber-reinforced composites do not improve resistance to oxidation, one of the major factors limiting the use of non-oxide composites; and (2) SiC fibers have mechanical properties superior to those of mullite fibers. This section will be concerned primarily with SiC fiber-reinforced ceramic composites, which offer the best oxidation resistance of any non-oxide fiber at high temperatures (particularly above ~1,100°C [2012°F]).

Both oxide and non-oxide matrices have been used with SiC reinforcements. Examples include alumina matrix composites fabricated by oxidation of an aluminum melt (DIMOX process) (Newkirk et al., 1986), glass-ceramic matrix composites fabricated by hot pressing (Prewo and Brennan, 1980), SiC matrix composites made by CVI (Stinton et al., 1986), SiC or SiC/Si_3N_4 matrix composites made by polymer pyrolysis, and SiC-Si matrix composites produced by silicon melt infiltration (Luthra et al., 1993).

CMCs must be thermally stable. That is, they must retain a significant fraction of their room-temperature properties, such as strength and toughness, after long-term (desired service life) exposures at operating temperatures. They must also maintain these properties under oxidizing conditions. A composite that is thermally stable, however, may not remain stable when high temperatures are combined with high stresses under oxidizing conditions, a situation that is likely to be encountered in a composites operating environment. A wide variety of fiber coatings have been studied, but tough, thermally stable, non-oxide ceramic composites have only been demonstrated when C or BN fiber coatings were used.

Oxidation of the fiber-coating-matrix interface is one of the major problems that have prevented the widespread use of non-oxide ceramic composites (Luthra, 1997b). This interface can be exposed to oxidizing environments when the ends of coated fibers are exposed to the surrounding atmosphere or when matrix cracks are present, allowing atmospheric oxygen to reach the fiber coatings.

Matrix cracks develop when the composite is exposed to stresses above the matrix cracking strength (proportional limit), which can occur inadvertently even if CMC components are designed to operate below the proportional limit. Once matrix cracks have formed, they remain open even after the operating stress is reduced below the matrix cracking strength. Matrix cracks allow oxygen ingress and, therefore, oxidation of the fiber coating, and, potentially the degradation of the fiber itself. Oxidation of the coating also degrades the debond characteristics of the interface thereby degrading both the strength and toughness of the composite.

Carbon Coatings

Composite Behavior

Carbon was one of the first fiber coatings that produced tough behavior in ceramic fiber-reinforced CMCs. Carbon coatings can form in-situ by the decomposition of Nicalon fibers, as has been observed in glass-ceramic matrix composites prepared by hot pressing, or they may be applied via CVD (chemical vapor deposition) techniques. Composite toughness appears to increase as the thickness of the coating increases. The load transfer between the fibers and the matrix, however, is reduced as the thickness of the coating is increased. Therefore, the coating thickness is typically on the order of 0.1 to 0.3 µm (0.004 to 0.01 mils). Tough composite behavior is demonstrated in carbon-coated Nicalon fiberreinforced SiC matrix composites prepared by CVI (chemical vapor infiltration), as shown in Figure 6-1 (Headinger et al., 1994).

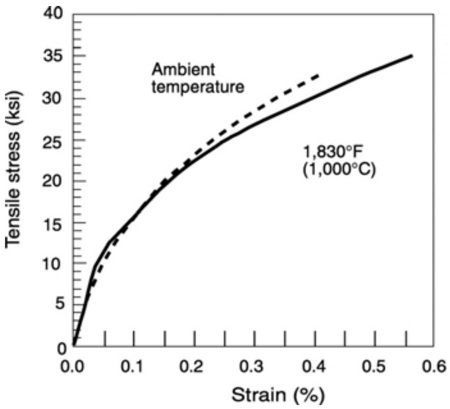


FIGURE 6-1 Tensile test results of Nicalon fiber-reinforced SiC matrix composites prepared by CVI. Source: Headinger et al., 1994.

Oxidation Behavior

The oxidation of carbon fiber coatings has been extensively analyzed in the literature. Fillipuzi and Naslain (Fillipuzi et al., 1994; Fillipuzi and Naslain, 1994) were the first to conduct a careful, systematic study of carbon coating oxidation in Nicalon fiber-reinforced composites. Figure 6-2 is a schematic representation of the oxidation phenomenon in carbon-coated SiC fiber-reinforced SiC matrix (SiC/SiC) composites. Carbon oxidation results in the formation of CO and CO_2, leaving behind a gap between the fiber and the matrix, which exposes the fiber side and the adjacent matrix to oxidation, producing SiO_2, which tends to close the gap. Oxidation of carbon and the corresponding depth of recession of the carbon coating along the fiber continue by gas phase diffusion of oxygen until the SiO_2 formed by the oxidation of the fiber and the matrix seals the gap. Based on the parabolic rate constants of the oxidation of the Nicalon fibers and the SiC matrix, Luthra (Luthra, 1994) calculated the time needed to seal the gap, which varies inversely with the oxidation rate constants of the fiber and the matrix and varies directly with the thickness of the fiber coating.

Figure 6-3 shows the corresponding depths of oxidation of a carbon coating as a function of temperature. Even for a fiber coating only 0.1 µm (0.004 mils) thick, the depth of oxidation of the fiber coating is very high, on the order of millimeters. Thus, the oxidation of fiber coatings is a serious concern when fiber ends are exposed. The depth of oxidation varies inversely with temperature in the range of 900 to 1,200°C (1,652 to 2,192°F). At high temperatures, the gap created by carbon oxidation is sealed fairly quickly, thus limiting the depth of oxidation. Consequently, the ends-on oxidation

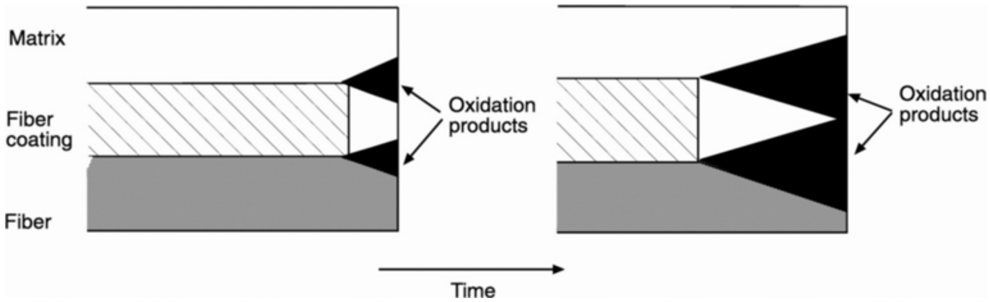


FIGURE 6-2 Schematic representations of the progression of oxidation along the fiber/coating/matrix interface of uniaxial SiC/C/SiC composites with fiber ends exposed. Only one section of the annular region along the fiber/coating/matrix interface is shown. Source: Luthra, 1994.

problem is most damaging at intermediate temperatures of around 700 to 800°C (1,292 to 1,472°F) when it causes embrittlement of the composite. Embrittlement at intermediate temperatures is frequently called pesting.

Non-oxide composite components will be designed to operate below the proportional limit, but occasional accidental exposures above the proportional limit must be anticipated. When they occur, oxygen can diffuse through the matrix cracks and oxidize carbon fiber coatings. In these cases, the oxidation front will migrate laterally along the length of the fiber, and the depth of oxidation will be similar to the depth observed for the ends-on oxidation described above. Furthermore, sealing by the oxidation of SiC to produce SiO_2 does not work effectively at intermediate temperatures of ~ 700 to 800°C (1,292 to 1,472°F). Therefore, an alternative mechanism must be found to seal matrix cracks faster and minimize oxidative degradation.

In the case of carbon fiber-reinforced carbon (C/C) composites, boron has been added to the matrix to help seal the matrix cracks in the intermediate temperature regime. B_2O_3 glass, formed by the oxidation of boron, acts as the crack sealant. DuPont Lanxide (Gray, 1992) has applied this boron sealing concept to enhanced CVI SiC/SiC composites. It was not clear, however, whether boron additives work fast enough to prevent the degradation of carbon fiber coatings when matrix cracks develop. Further work will be necessary to determine if performance can be improved in non-oxide systems after matrix cracking occurs.

Boron Nitride Coatings

Composite Behavior

Aside from carbon, boron nitride (BN) is the only fiber coating that has enabled graceful failure in non-oxide ceramic composites. It should be noted, however, that not all BN coatings are the same. When deposited at low temperatures, BN can be amorphous or turbostratic. When deposited at high temperatures (e.g., over ~ 1,500°C [2,732°F]), BN typically has an ordered hexagonal crystal structure (the desired structure for providing toughness to CMCs). BN deposited by CVD invariably contains carbon or oxygen impurities. Finally, silicon-doped BN is an intentional variation being evaluated for improved oxidation resistance.

Like the toughness of carbon-coated fiber-reinforced CMCs, the toughness of BN-coated fiber-reinforced CMCs appears to increase with the thickness of the coating. The optimum thickness of the BN coatings might be in the range of 0.3 to 0.5 µm (0.01 to 0.02 mils), thicker than for the carbon coatings. Figure 6-4 shows the tensile test results of Hi-Nicalon SiC fiber-reinforced SiC-Si matrix composites made by melt infiltration. Figure 6-5 shows the tensile test results for Nicalon SiC fiber-reinforced glass-ceramic matrix composites made by hot pressing. Both have BN fiber coatings. Tough composite behavior is indicated by the nonlinear stress-strain curve (suggesting inelastic deformation) and a strain-to-failure of > 0.6 percent.

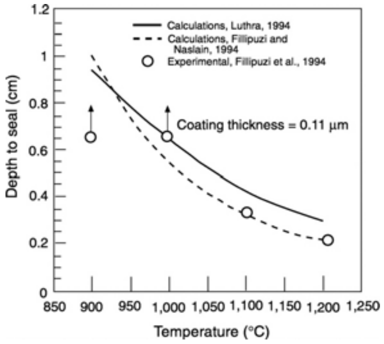


FIGURE 6-3 Depth of oxidation of fiber coatings for uniaxial SiC/C/SiC composites with fiber ends exposed. All of the data is for Nicalonreinforced composites made by CVI. Source: Luthra, 1994.

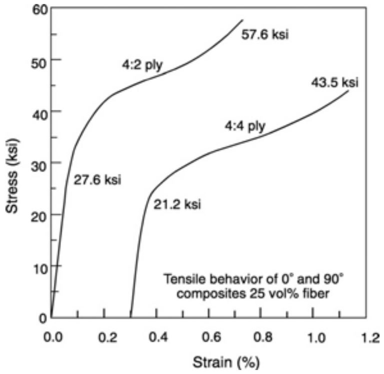


FIGURE 6-4 Tensile test results of Hi-Nicalon fiber-reinforced SiC-Si matrix composites prepared by melt infiltration. Results are for 4:2 and 4:4 fiber layup indicative of the number of plies in 0° and 90° directions, respectively. Source: Corman et al., 1996.

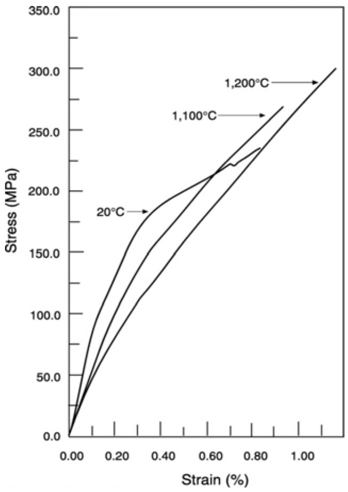


FIGURE 6-5 Tensile test results for hot pressed Nicalon SiC fiberreinforced glass-ceramic matrix composites with a BN fiber coating. Source: Sun et al., 1996.

Oxidation Behavior

The oxidation rate of BN, in dry air or oxygen, is expected to be much lower than that of carbon because the BN oxidation product is a liquid boron oxide rather than a gaseous oxide. The lower rate is reflected in ends-on oxidation studies of composites. The depth of oxidation of the BN coatings in SiC-Si matrix composites has been observed to be very low, on the order of 10 µm (0.4 mils) or less for times up to 100 hours at 700 to 1,200°C (1,292 to 2,192°F) (Brun and Luthra, 1997). It is believed that BN oxidation produces a boron oxide liquid that interacts with silica, the oxidation product of the fiber and the matrix, to form a borosilicate glass. The composition of the glass changes with time due to surface volatilization of the boron oxide. The depth of oxidation is much shallower than the oxidation for carbon coatings. Therefore, BN coatings should perform much better than carbon in dry oxidizing environments.

In wet environments, the oxidation behavior of BN coatings appears to be similar to carbon in oxidizing environments. The oxidation product (B_2O_3) volatilizes as boron hydroxides before a borosilicate glass forms that can seal the gap created by BN oxidation and volatilization. Figure 6-6 shows the depth of oxidation of the BN coating in SiC-Si matrix composites reinforced with Hi Nicalon fibers with a nominal coating thickness of 0.5 µm (0.02 mils). At 1,200°C (2,192°F) oxidation proceeds for only about one hour before sealing prevents further oxidation; at 900°C (1,652°F) oxidation stops after approximately four hours. At 700°C (1,292°F), however, sealing does not occur and oxidation continues for up to 100 hours. Thus, it appears that embrittlement of these composites will occur more readily at intermediate temperatures of about 700 to 800°C (1,292 to 1,472°F) than at high temperatures of ~1,200°C (2,192°F).

In the presence of matrix cracks, oxidants (oxygen and water vapor) can rapidly diffuse through the cracks and oxidize fiber coatings. The coatings are normally 1 µm thick or less. Therefore, coatings are expected to oxidize very rapidly (in minutes at operating temperatures of more than ~900°C (1,652°F) (Jacobson et al., 1997), and the damage will then extend to the fiber. In dry environments, the damage should be confined because the lateral growth of the oxidation product will be slow, as suggested by ends-on oxidation studies. In wet environments, however, the damage will be more extensive because the BN coating can oxidize rapidly.

Therefore, approaches must be developed to seal the matrix cracks caused by overstressing. Two possible mechanisms by which the matrices could seal cracks are: (1) matrix heating or deformation (e.g., via creep); and (2) matrix additives that (upon oxidation) provide oxidation products that help seal cracks. In principle, the matrix sealing approach can work as long as the sealing occurs before significant damage is done to the composite. Results of stress rupture tests (Sun et al., 1996) on Nicalon fiber-reinforced glass-ceramic

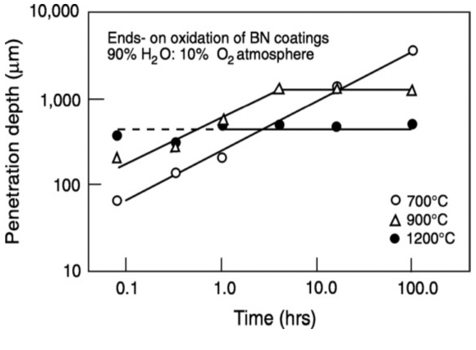


FIGURE 6-6 Depth of coating oxidation in Hi-Nicalon fiber-reinforced SiC-Si matrix composites prepared by melt infiltration. The BN coating had a nominal thickness of 0.5 mm (0.02 mils). Source: Brun and Luthra, 1997.

composites, with a layered BN/SiC fiber coating, indicate that sealing does indeed occur. A sample was exposed at a temperature of 1,100°C (2,012°F) in air at a stress of 138 MPa (20 ksi) (well above the fast fracture proportional limit stress of 88 MPa [13 ksi]). The sample lasted for more than 1.7 years, and the residual strength was comparable to the strength of the unoxidized sample.

Figure 6-7 shows a cross-section of a sample exposed at 1,200°C (2,192°F). The oxidation is confined to a surface depth of about 100 μm (4 mils). Although the microstructure of the sample at 1,100°C (2,012°F) was not shown, the degradation mode was presumably similar. There were no boron additives in the matrix, but the fiber coating was a layered BN/SiC coating. Sealing occurred by either creep deformation of the matrix or by oxidation products of the fiber coatings. There is little or no information in the literature as to whether boron additives will work effectively with BN fiber coatings, particularly in wet environments where BN can volatilize as boron hydroxides.

Crystalline BN and silicon-doped BN have been suggested to improve the oxidation resistance of amorphous BN in water vapor environments (Morscher et al., 1997). Silicon-doped BN should be particularly attractive because it is expected to maintain the debond characteristics of the BN and to improve oxidation resistance significantly over BN, in both dry and wet environments. Although the effect of silicon on oxidation resistance has not been quantitatively evaluated, it is reasonable to expect that the addition of silicon to BN would significantly decrease the oxidation rate of the coating. The oxygen diffusivity through B_2O_3, the oxidation product of BN, is about 3 orders of magnitude higher than through silica, the oxidation product of SiC and Si_3N_4. The volatility of silicon as silicon hydroxide is also very much lower than of boron hydroxide. Silicon doping in BN is also expected to reduce the volatilization of the coating in water vapor environments. Thus, silicon-doped BN is potentially an attractive coating that should be explored further.

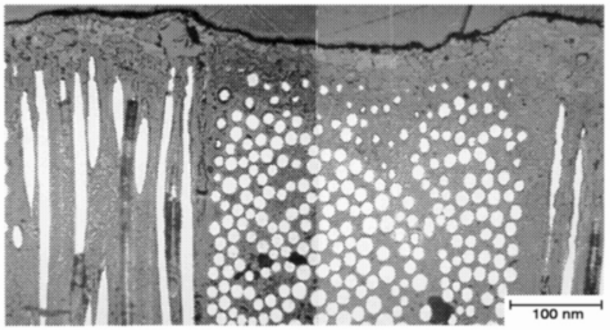


FIGURE 6-7 Polished section of a hot pressed SiC fiber-reinforced glassceramic matrix composite with a BN fiber coating exposed to a tensile stress rupture experiment at 1,200°C (2,192°F), 69 MPa (10 ksi), 11,725 hours in air. Fiber ends and lengths are visible. Source: Sun et al., 1996.

Alternative Fiber Coatings

Coating Compositions

Several alternative fiber coatings have been evaluated in non-oxide fiber-reinforced composites, either to improve the oxidation resistance of composites or to improve the stability of carbon and BN coatings. Alternatives include layered coatings (Luthra et al., 1994; Brennan, 1997), such as BN/C/BN, BN/C/Si_3N_4, SiC/C/SiC, and BN/SiC. Multiple iterations of these layered coatings have also been evaluated. Because each carbon or BN layer in multilayer coatings is not as thick as a single carbon or BN coating, multilayer coatings may be more resistant to oxidative degradation. Multiple layers may also provide multiple debond layers.

Other coatings that have been proposed include carbides, such as Ti_3SiC_2 (Christian et al., 1991); nitrides, such as AlN; and a variety of oxides. However, no information is available in the literature describing whether or not any of these alternative fiber coating systems provide damage-tolerant, tough ceramic composites in the absence of a carbon or BN layer. Fiber coatings or coating systems that provide improved oxidation resistance (compared to carbon or BN coatings), as well as acceptably tough composites, will have to be developed.

Oxidation Behavior

It is difficult to assess the oxidation resistance of all of the coatings that have been proposed in the literature. However, it is worthwhile to discuss the potential capabilities of the best oxidation-resistant coatings. In order to maintain a practical level of load transfer between the matrix and fiber, fiber coatings can be a maximum of ~ 1 μm (0.04 mils) thick for fiber bundles and several microns for monofilaments that are more than 100 μm (4 mils) in diameter. For the present discussion it was assumed that the coating was about 1 μm (0.04 mils) thick.

Because oxide ceramics cannot oxidize, it is commonly believed that oxide coatings represent the best choice in terms of oxidation resistance. Although this is true for the prevention of oxidation of fiber coatings, it is not true for the protection of the underlying non-oxide fibers from oxidation or for the maintenance of weak fiber-matrix interfaces. Using diffusion analysis, Luthra (1997b) demonstrated that non-oxide fibers can start oxidizing at the interface between the fiber and the oxide coating within a matter of seconds, even with an oxidation barrier like SiO_2. Once oxidation is initiated at the fiber-coating interface, the fiber bonds to the coating, which may also bond to the matrix, which renders the composite intolerant to damage. The coating composition also changes, which is particularly important if the coating is weak and debonding occurs within the coating (e.g., mica substances), rather than at the fiber-coating interface. Because fiber-coating reactions can occur at typical composite fabrication temperatures, it is difficult even to fabricate non-oxide fiber-reinforced composites with oxide fiber coatings without degrading the fiber and composite properties.

For non-oxide coatings, silica-forming materials provide the best protection against oxidation at temperatures above ~ 1,100°C (2,012°F) because silica has the lowest oxygen permeability of any oxide. However, Luthra (1997b) has demonstrated that the oxidation protection provided by a 1 µm (0.04 mils) coating of silica-forming material, such as SiC or Si_3N_4, is limited, theoretically, to a maximum of ~100 hours at 1,200°C (2,192°F). Therefore, no non-oxide coating can protect SiC fibers for more than 100 hours in the presence of oxygen. Oxidation resistance should be considered in terms of the overall composite system to determine how oxidation degrades composite properties and how the system, including the fiber, coating, and matrix, can be modified to alleviate this problem.

Systems Approach to Inhibiting Oxidative Embrittlement

In the presence of open matrix cracks, no fiber coating can (or will likely ever) protect the fiber from oxidation for more than 100 hours at 1,200°C (2,192°F) in an oxygen containing environment. This does not, however, eliminate the need for fiber coatings with improved oxidation resistance because theoretical limitations have not yet been reached. Therefore, a two pronged approach should be pursued:

- The oxidation resistance of non-oxide fiber coatings must be improved, from the current calculated value of a few minutes (at 1,200°C [2,192°F]) for 1 µm (0.04 mils) BN coatings to the maximum possible calculated value of ~ 100 hours for 1 µm (0.04 mils) silica-forming coatings.
- Techniques should be sought for rapidly sealing matrix cracks once they form. The crack sealing time should be less than the time it takes to oxidize the fiber coating.

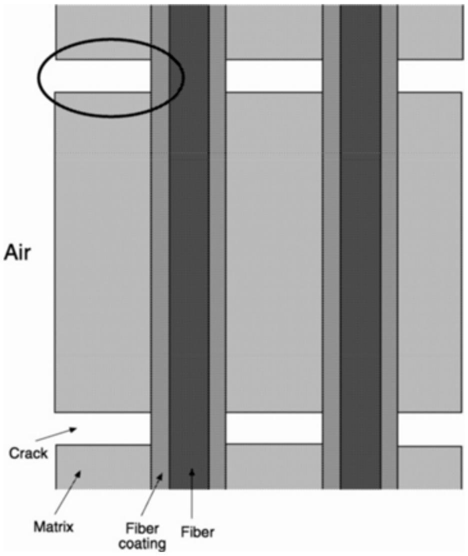


FIGURE 6-8 A schematic representation of matrix cracking on exposure to stresses above the matrix cracking strength in continuous fiber-reinforced ceramic composites. Source: Luthra, 1997b.

A schematic representation of a cracked CMC is shown in Figure 6-8. The crack width is similar to the thickness of the coating, on the order of 1 µm (0.04 mils) or less. The effect of oxidation on one of the crack/coating/matrix regions schematically shown in Figure 6-8 is presented in Figure 6-9. Various processes that occur in the cracked region are shown in Figure 6-9a. Oxidants, such as oxygen and water vapor, diffuse through the open crack to the interior of the composite, oxidizing the sides of the cracks and the fiber coating (indicated by three arrows). Upon oxidation, the volume of the oxidation products is higher than the volume of the oxidizing constituents. For example, the oxidation of SiC to form silica results in a volume expansion of ~100 percent. Therefore, the oxidation products can fill the cracked region and prevent the oxidation of the underlying composite. Figure 6-9b shows schematically the progression of the oxidation region. In this case, the crack is still open, although its width has been reduced, and the coating is not fully oxidized. Figure 6-9d shows a coating that has been breached before the crack was sealed. Oxygen diffusing through the crack can continue to oxidize the fiber by diffusing through the oxidation product of the coating, indicated by a semi-spherical region. The best situation is shown in Figure 6-9c, where the crack has been sealed before the coating was oxidized, thus preventing significant damage to the fiber-coating-matrix interface. This approach might be feasible with multilayer coatings that provide multiple debonding layers.

If cracks develop near the fiber/coating interface, some oxidation of the interface will inevitably occur before the cracks are sealed. If there are multiple debond layers, the debond characteristics of the interface can be maintained even after sealing. However, this has not been demonstrated for any composite system. Questions regarding the survivability of the sealed regions under the cyclic loading conditions that will be encountered in an operating environment have not been addressed. Therefore, in addition to developing matrix crack sealing concepts and fiber coatings with improved lifetimes, the performance of these materials should be evaluated under conditions representative of operating environments.

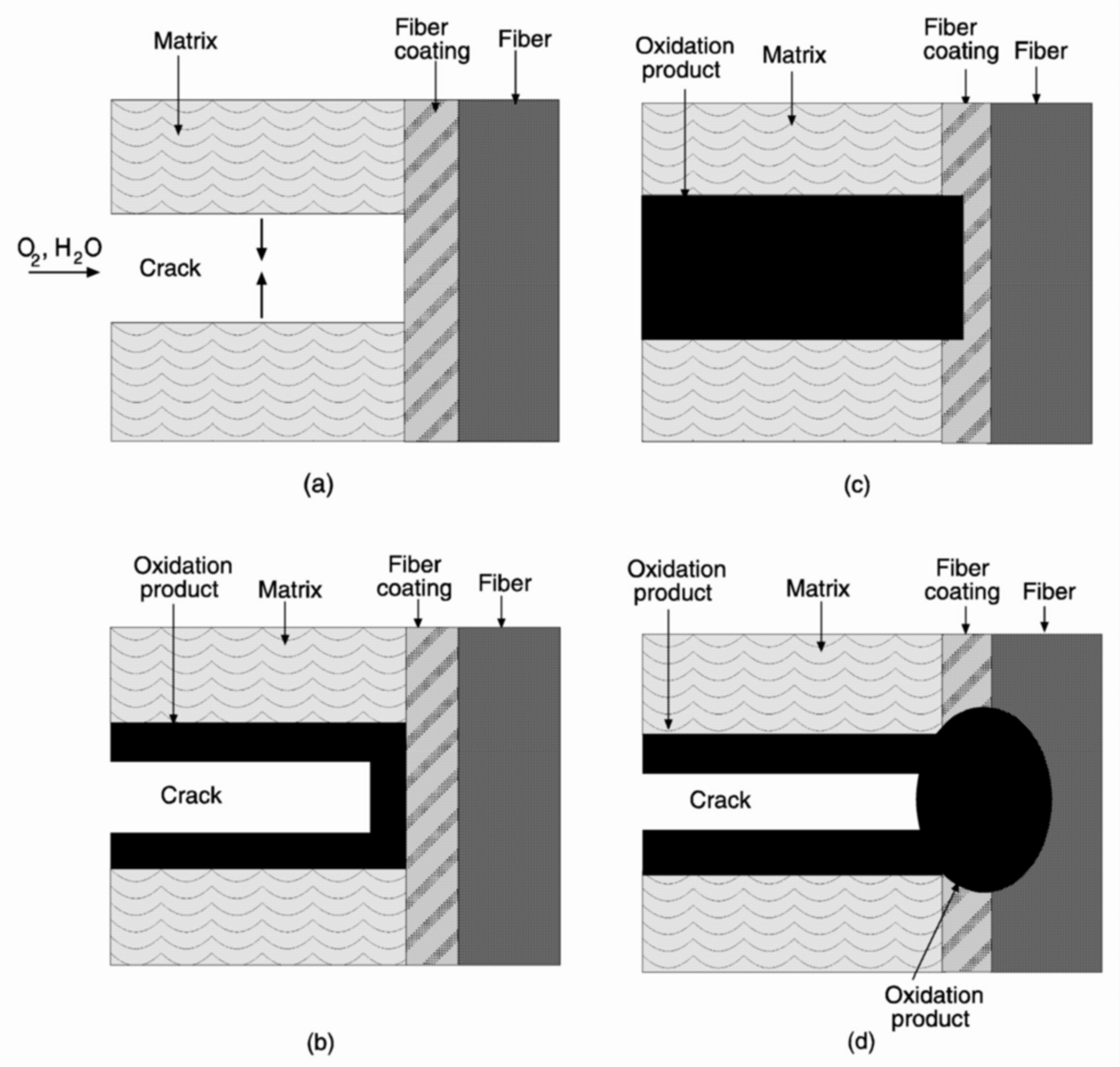


FIGURE 6-9 Schematic representations of the progression of oxidation in a crack/matrix/fiber coating region shown in the elliptical region in Figure 6-8. Source: Luthra, 1997b.

Coating Processes and Vendors

Chemical Vapor Deposition

CVD is the most common method of depositing fiber coatings for composite systems because it is a conformal process that can deposit fairly uniform coatings on a wide variety of structures. CVD is perhaps the only method that has been used successfully to provide tough composites with acceptable mechanical properties. A wide variety of coatings have been deposited by CVD, including carbon, BN, silicon-doped BN, Si_3N_4, and SiC.

Carbon is usually deposited by cracking hydrocarbons, such as CH_4 and C_2H_2 at temperatures of 1,000 to 1,800°C (1,832 to 3,272°F). BN is usually deposited using a boron trichloride precursor with ammonia and a nitrogen carrier gas at temperatures of 800° to 1,600°C (1,472 to 2,912°F). Other precursors, such as borozine and BF_3, have also been used. The crystallinity and deposition rate of BN increases with temperature. However, the coatings also become less uniform as temperature is increased. The non-uniformity is expected to be less prevalent when fiber tows are coated and most prevalent when three-dimensional composite lay-ups are coated. The chemistry of the BN coatings depends upon the precursors, as well as a range of other variables. For example, BN coatings produced in silica reactors are subject to oxygen contamination, but coatings produced in carbon furnaces contain carbon contaminants. Patibandla and Luthra (1992) observed up to 12 atomic percent oxygen in their BN coatings; Sun, Nutt, and Brennan (1994) intentionally used coatings with 40 atomic percent boron, 40 atomic percent nitrogen, and 20 atomic percent carbon. Unfortunately, the effects of BN chemistry and crystallinity on the mechanical properties of composites, both as fabricated and after environmental exposure, are not well characterized or understood.

Silicon nitride is usually deposited using one of the following silicon precursors: silane, dichlorosilane, trichlorosilane, or silicon tetrachloride. Silicon tetrachloride, the most common silicon precursor, is used with an ammonia and nitrogen mixture to obtain silicon nitride at temperatures of 800 to 1,400°C (1,472 to 2,552°F). Silicon carbide is usually produced by cracking methyl trichlorosilane at 800 to 1,400°C (1,472 to 2,552°F).

Vendors

This section discusses the domestic coating vendor base. The capabilities of foreign vendors are not available in the open literature and are, therefore, not covered.

The applicability of specific deposition technology to coating a particular ceramic fiber depends on the fiber architecture. For example, CVI is most suitable for depositing multilayer coatings on woven cloth or fibers with a three-dimensional architectures. In the United States, CVI process vendors include—but are not limited to—DuPont Lanxide, BF Goodrich, and Amercom. To produce uniform CVI coatings, deposition has to be carried out at relatively low temperatures of (e.g., 800 to 1,000°C [1,472 to 1,832°F]). However, significant variations in coating uniformity have been observed from one filament to another within fiber bundles, as well as from the inside ply to the outer ply of a three-dimensional layup. The effect of non-uniformity in the fiber coating on composite behavior has not been well characterized. Non-uniformity is expected to increase if crystal-line BN coatings are used because they require deposition temperatures of 1,400°C (2,552°F) or even higher. Chemical non-uniformity is expected to be another important factor in the deposition doped BN coatings, such as silicon-doped BN.

Vendors are available for coating single plies of woven cloth and individual tows. For example, Synterials currently uses a batch reactor to deposit coatings, and Advanced Ceramics uses a semicontinuous process in which the uncoated woven cloth is carried though the CVD furnace and spooled at the other end. Advanced Ceramics has a 3-spool reactor and a 12-spool reactor for coating fiber tows, which is the most attractive approach if uniform fiber coatings are needed. Unfortunately, to date it has not been possible to weave coated fibers without degrading the fiber coating. Therefore, coated fibers have been successfully used only in processes that do not require a woven cloth or three-dimensional lay-up, such as prepregging.

Alternative Approaches

Although oxide fiber coatings have been successfully deposited using a wide variety of non-CVI processes, such as sol-gel or particulate slurry, only CVD has been successfully used for non-oxide coatings, including carbon and BN. It should be possible, however, to deposit non-oxide coatings by other means. For example, Kim, Cofer, and Economy (1995) obtained a BN matrix using a borazine oligomer.

The costs of fibers and coatings constitute a very large fraction of the high costs of CMCs. The costs of coatings currently are on the order of a few thousand dollars per pound of fiber. Although cost analyses have not been reported as a function of processing conditions, it is expected that uniform coatings will be more expensive to produce than non-uniform coatings. For example, although lowering the coating deposition temperature typically improves uniformity, it also decreases the deposition rate, which is expected to increase costs. Furthermore, it has been demonstrated that moving from multiple layers of cloth (i.e., three-dimensional lay-ups) to a single layer of cloth (i.e., two-dimensional lay-ups) to fiber tows (i.e., one-dimensional lay-ups) improves coating uniformity. Coating several fiber tows prior to weaving them into cloth, however, is expected to be more costly than coating the cloth itself. The development of additional low cost approaches will be necessary to reduce the costs of coatings and, ultimately, of composites.

One approach that appears to be particularly attractive is insitu coatings formed during fiber processing or by subsequent heat treatment. An example of an in-situ coating discussed in Chapter 3 was developed by Bayer of Germany, which has reportedly formed an in-situ BN layer in a Si-B-N-C fiber. It should be possible to form a BN and/or silicon-doped BN coating on SiC fibers doped with boron by appropriate heat treatment in an nitrogen-containing gas environment. These coatings should be more uniform in thickness and much cheaper to produce than coatings produced by CVD. However, it is not clear what the debond characteristics of in-situ formed coatings will be in a finished composite. The behavior of in-situ coated fibers in a composite system should be studied.

OXIDE FIBER COATINGS

The development of ceramic oxide composites has lagged behind the development of non-oxide composites because of the poor creep resistance of oxide fibers (compared to SiC fibers) and because of the lack of adequate oxide fiber coatings that promote fiber-matrix debonding. Recent advances in creep-resistant oxide fibers (e.g., Nextel 720) and progress on interface control has improved the potential for using oxide composites in industrial and defense applications. However, an effective coating for oxide fibers that provides a weak fiber/matrix interface (and therefore tough composite behavior) remains to be demonstrated.

Oxide fiber coatings are most commonly applied to oxide fibers. Using oxide fiber coatings on silicon-based non-oxide fibers has generally been avoided because these fibers have a tendency to react with the oxide fiber coatings, thus creating strongly bonded interfaces. There are notable exceptions, however (e.g., SiC fibers coated with a $SiO_2/ZrO_2/SiO_2$ multilayered coating).

Carbon-based and BN-based coatings for oxide composite systems have not been investigated as fervently as they have for non-oxide systems. One reason for this is that a primary advantage of using an oxide system is its inherent oxidation resistance, which could be hindered by the presence of an interface that was prone to oxidation. This is especially true for BN, the oxidation product of which (boria) can react with the fiber and the matrix. Using carbon coatings as fugitive interfaces in oxide systems as a means to debond the fiber from the matrix is an example of taking advantage of a coating prone to oxidation. This is discussed in more detail later.

The initial approach to developing fiber coatings for oxide composite systems, beyond the carbon and BN approaches borrowed from non-oxide composites, focused on oxide compounds that do not form compounds with the fibers or the matrices. The focus later shifted to oxide interfacial coatings that mimic the layered crystal structures of carbon and BN, which provide weak interfaces in non-oxide composite systems. Techniques were also developed to provide mechanically weakened interfaces between the fiber and matrix by using porous, or fugitive, coatings. The latest concepts being investigated for oxide systems are focused on creating high energy interfaces between coating compounds and oxide fibers (described further in the following sections).

Porous Coatings and Porous Matrix Approaches

Porous Coatings

In order to decrease the debond strength of fiber/matrix interfaces, porosity has been incorporated into the fiber coating to provide a weak path along which matrix cracks can be deflected away from the fiber (Davis et al., 1993). Various techniques have been tried for incorporating porosity in a fiber coating, including sol-gel and co-deposited CVD. Porosity within the coating often has to be generated after processing of the composite matrix to prevent the pores from being filled during composite fabrication. To achieve this porosity, the as-deposited coatings often contain carbon, which is removed to create pores after matrix processing has been completed. For example, porous alumina coatings have been obtained by sol-gel processing using boehmite sols in a polyelectrolyte ammonium polymethacrylate (Darvan C) solution (Boakye et al., 1997). After the fibers were coated with this solution, they were fired in an argon atmosphere to yield an oxide-carbon coating (Figure 6-10). No data has been generated for composites that use these fiber coatings, however, nor has a deposition technique that yields high quality coatings over long lengths of fiber been demonstrated.

A major concern about porous coatings is maintaining the stability of the pore morphology after prolonged high-temperature exposure, as there may be a tendency for these coatings to densify. Thus far, porous coatings on fine-diameter fibers have not been subjected to long-term thermal exposures to evaluate their microstructural stability. If coarsening of the porosity proves to be a problem, it may be necessary to use oxides with sluggish diffusion kinetics to prevent sintering of the coating. Possible compounds for porous coatings include mullite, rare earth aluminum garnets, and mixed phases, such as mullite-alumina or alumina-garnet.

CVD has been investigated as a method for creating a porous zirconia coating by co-depositing carbon and zirconium carbide in a ratio that yields a 40 percent porous zirconia coating upon oxidation (Goettler, 1997a). Oxidation of the coating at 1,100°C (2,012°F), however, caused sintering of the zirconia to a dense coating. Some fiber pullout from an alumina matrix was observed when these coatings were used. However, this was probably caused by shrinkage of the fiber

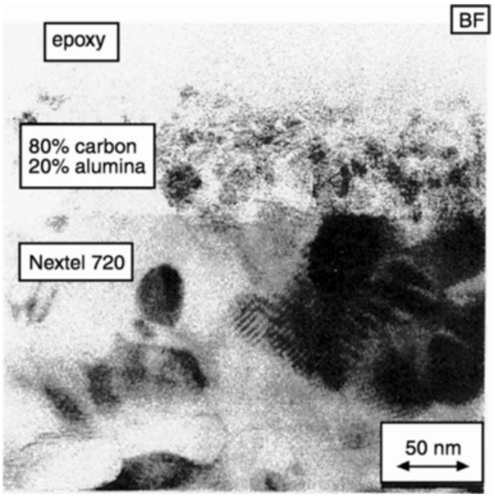


FIGURE 6-10 Porous alumina fiber coating deposited from a mixture of boehmite and Darvan C. Source: Boakye et al., 1997.

coating (away from the alumina matrix) upon oxidation and sintering of the coating following composite processing.

No Coating/Porous Matrix Approach

The cost of ceramic composites could be lowered and the overall processing simplified if the fiber coating step could be eliminated. This approach is being investigated by General Electric and researchers at the University of California at Santa Barbara (UCSB) for oxide systems composed of Nextel 610 or Nextel 720 fibers in an alumina-mullite matrix. The General Electric material uses a matrix containing alumina particles and a silicon containing organic polymer (Harrison et al., 1994)). The silicon polymer provides green strength to the preform and generates silica upon decomposition, which then reacts with and bonds the alumina matrix particles. The UCSB material uses a bimodal distribution of coarse mullite particles and finer alumina particles to create the majority of the matrix through a pressure filtration technique (Levi et al., 1997). Bonding of the matrix particles is achieved by additional infiltrations with an aluminum hydroxychloride solution. The key to success is retaining sufficient porosity within the matrix to allow for crack branching within matrix regions and crack deflection around the continuous fibers. Total composite porosities typically fall within the 20 to 25 percent range depending on the total fiber loading. This approach is similar to the porous coating approach described above except that the porous interfacial region extends throughout the entire matrix.

The range of potential components that could be fabricated from porous matrix ceramic composites may be limited because of the poor mechanical properties of the porous matrix. Porous matrices generally yield composites with low compressive and interlaminar properties, making it difficult to design structures capable of carrying out-of-plane loads. Furthermore, it is difficult to attach porous matrix composites to neighboring structures. Three-dimensional fiber architectures rather than two-dimensional laminate structures will probably be required for the components made from a porous matrix ceramic composite.

A potential problem with this type of composite system is the possibility of reaction or sintering between matrix particles and the fibers at points of contact. Exposure tests of UCSB Nextel 610 composite at 1,200°C (2,192°F) for 100 hours shows reasonable mechanical property retention (Figure 6-11). Similar tests have yet to be performed on Nextel 720 composites. Therefore, the data on long-term exposure is insufficient to address the issue of matrix-fiber bonding (Levi et al., 1997). Because degradation is likely to be kinetically driven, residual fiber strength will be dictated by time at temperature.

Many industrial applications (e.g., industrial gas turbines or heat exchangers) require that composites operate nearly continuously for many years at high temperatures. Over time, the fiber properties, and hence the composite properties, may deteriorate as matrix particles react or sinter with fibers. Another concern is the potential densification of the matrix after long-term exposure at operating temperatures, causing a change in the pore-size distribution of the matrix and probably changes in the mechanical properties of the composite. Coarsening of the fine porosity within the silica bond phase of the General Electric Gen IV system reportedly limits the maximum operating temperature for the material (Hay, 1991). This characteristic of the Gen IV system was the motivation for the development of the more stable porous

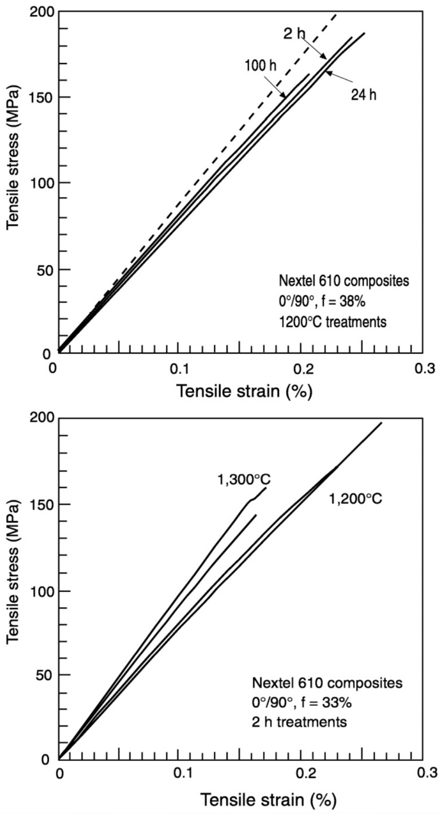


FIGURE 6-11 Effect of thermal exposure on the ambient stress-strain behavior for all-oxide composites in the 0°/90° orientation. (a) shows the effect of different times at 1,200°C (2,192°F). (b) shows the effect of two-hour treatments at two different temperatures. Source: Levi et al., 1997.

matrix of the UCSB composite system, which has an alumina bond phase.

The stability of the interface and matrix morphology may not be as critical for defense applications, where the service time of the ceramic component, especially at peak temperatures, is relatively short. Uncoated fibers in a porous matrix, however, may subject the fibers to corrosive species in the operating environment that could degrade fiber strength. These composite systems must be tested in their service environments to determine if the absence of a fiber coating accelerates the degradation of fiber strength.

Fugitive and Segregant Weakened Interfaces

Fugitive Interfaces

The concept of fugitive interface coatings is based on processing a composite with a carbon coated fiber (molybdenum coatings have also been proposed) (Sambasivan et al., 1993). After composite densification, this coating can be oxidized away to create a void along the fiber-matrix interface (Mah et al., 1991; Keller et al., 1993). In essence, the fibermatrix interface is debonded from the start rather than relying on the stress intensity of a propagating crack front to initiate fiber-matrix debonding.

A major technical issue with this approach is how to ensure load transfer to the fibers if the interface is totally debonded. Test data, based on the rule of mixtures, shows that, even with the carbon coating removed, some load transfer appears to occur between the matrix and fiber (Keller et al., 1993). The degree of load transfer may depend on the thickness of the fugitive layer (which is present during composite processing) relative to the roughness of the fiber surface and the variation in diameter along the fiber's length.

If the fugitive zone (between the fiber and matrix) is not too thick in comparison to these fiber characteristics, some contact may be made between the matrix and the fiber, allowing for load transfer. Fiber-matrix contact, however, raises the possibility that fiber strength could be degraded by reaction or sintering between the fiber and the matrix. Good strength and modulus retention have been demonstrated for a Nextel 720 fiber-reinforced, calcium aluminosilicate glassceramic matrix composite (with carbon coating removed) following a 500 hour, 1,000°C (1,832°F) unstressed heat treatment (Figure 6-12) (Keller et al., 1997).

A second issue with this concept is that bare fiber surfaces are exposed to the operating environment, which could lead to the degradation of fiber strength. Composites that utilize the fugitive interface coating concept must be tested under realistic operating conditions. This is a fairly cost effective coating approach because of the ease with which carbon coatings can be deposited by both sol-gel and CVD techniques.

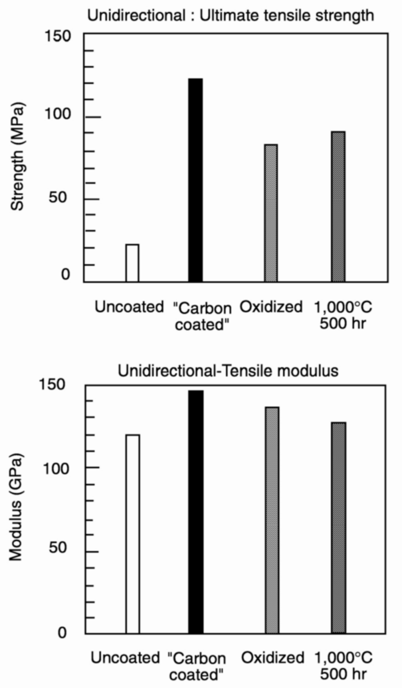


FIGURE 6-12 Nextel 720 fiber-reinforced calcium aluminosilicate glass-ceramic matrix composites show significant modulus retention following carbon interface burnout indicating matrix-to-fiber load transfer. Source: Keller et al., 1997.

Segregant Weakened Interfaces

Segregant weakened interfaces is an intriguing debonding concept based on the development of a nonporous, weak fiber/matrix interfacial boundary. It has been proposed that the fiber-matrix interface in dense oxide ceramic composites may be weakened by using segregants (Sambasivan et al., 1993). The basis for this approach was the observation that adding calcia to alumina reduces the fracture toughness of alumina (Jupp et al., 1980). Model composites were investigated in which a single crystal of YAG (yttria-alumina-garnet) was hot pressed in a matrix of either strontium oxide (SrO) or calcia (CaO) doped alumina (Sambasivan et al., 1993). Strontium and calcium were found to exist preferen tially at the YAG-alumina interface. Using Vickers indentations, the segregant enhanced interfaces were shown to be weaker than an undoped YAG-alumina interface. These results raise the possibility that this low cost approach could be used to produce high-temperature ceramic composites. So far, only preliminary research has been performed on this coating concept, and only on model composite systems. Quantitative tests will have to be done to determine if interfacial weakening is sufficient to promote crack deflection in CMCs. Furthermore, preliminary results were for a single crystal-polycrystalline matrix interface. Selective segregation may be much more difficult for a polycrystalline-polycrystalline fiber-matrix interface.

Dense Oxide Fiber Coatings

Nonreactive Oxides

A prerequisite for an effective fiber coating is chemical stability with the fiber and matrix phases of a composite. If reactions occur, the fiber-coating-matrix interface would become strongly bonded, and the composite would exhibit brittle fracture behavior. Based on currently available phase diagrams, oxide compounds have been identified that do not show compound formation with commercially available oxide fibers. Particular attention has been paid to fibers that show the highest temperature capability (alumina fibers, such as Fiber FP, PRD-166, and Nextel 610). Oxide compounds identified as stable with alumina included tin oxide, zirconia, titania (at temperatures below ~1,150°C [2,102°F]), zirconia titanate ($ZrTiO_4$, also at temperatures below ~1,150°C [2,102°F]), and possibly zirconia tin titanate ($Zr(Sn,Ti)O_4$).

Tests on tin oxide fiber coatings in model composite systems indicated some crack deflection at the coating-fiber interface (Siadati et al., 1991; Venkatesh and Chawla, 1992). However, tensile tests of tin oxide coated alumina fiber-reinforced alumina matrix composites demonstrated a decrease in the extent of fiber pullout as the density of the matrix phase was increased. This led to increasingly brittle fracture behavior in these composites (Goettler, 1993). Tin oxide also has thermal stability problems at elevated temperatures (Norkitis and Hellmann, 1991). For example, in the presence of air at temperatures above 1300°C (2,372°F), tin oxide (solid) decomposes into SnO (gas) and O_2 (gas). This decomposition occurs at even lower temperatures when the partial pressure of oxygen in the test environment is reduced.

Zirconia coatings require intercoating porosity to allow for crack deflection at the alumina-zirconia interface in zirconia coated alumina fiber-reinforced alumina matrix composites (Davis et al., 1991). Testing of titanate coatings is incomplete, but in general these nonreactive isotropic oxides appear to provide a reaction barrier between the fibers and the matrix. Because they are dense coatings, however, their interfacial debond strengths are too high to allow for crack deflection around alumina fibers. Therefore, they do not enable graceful failure in ceramic composites.

Layered Oxides

Many layered oxides have been identified as potential fiber coatings for oxide ceramics as analogs to the layered carbon and BN fiber coatings used for non-oxide composites. One of the first layered oxides to be investigated was a class of sheet silicates known as fluoromicas. A potassium-tetrasilic mica ($KMg_{2.5}(Si_4O_{10})F_2$) and a potassium fluorphlogopite ($KMg_3(A1Si_3O_{10})F_2$) have been examined (Beall et al., 1990; Chyung and Dawes, 1993). These synthetic micas exhibit easy delamination along the crystal planes containing the fluorine and interlayer alkali cations. The presence of these weak crystal planes along the fiber-matrix interface encourages crack deflection. Because of the complex chemistry of these multicomponent compounds, however, they are chemically incompatible with the currently available fibers and matrices, which causes the composite to become unstable and ineffective after prolonged exposure to elevated temperatures (Cooper and Hall, 1993).

Less chemically complex layered oxides, which have the β-alumina ($Me^{1+}Al_{11}O_{17}$) and magnetoplumbite ($Me^{2+}Al_{12}O_{19}$) structures, have also been investigated. These materials are phase compatible with alumina making them promising candidates for alumina fiber-reinforced composites (Morgan and Marshall, 1992; 1993). Although these layered oxides are not as readily cleaved at the basal planes as fluormicas, their fracture energies appear to be sufficiently low to promote crack deflection along the fiber-matrix interface (Phillips and Griffin, 1981; Beevers and Ross, 1937). The structures of both β-alumina and magnetoplumbite consist of layered spinel blocks ($(Al_{11}O_{16})^+$) with alkali, alkaline-earth, and rare-earth cations in *c*-axis planes between the spinel layers (Beevers and Ross, 1937; Utsonomiya et al., 1988). The similar structures of these two classes of compounds are shown in Figure 6-13.

Investigations into β-alumina fiber coatings have been discontinued because of problems with alkali loss during heat treatment, especially with sodium and potassium β-aluminas. However, it has been reported that the use of larger alkali cations, such as rubidium, which has a reduced mobility within the β-alumina structure because of its larger ionic radius, may minimize vaporization (Sambasivan et al., 1996). The magnetoplumbite structures containing alkaline-earth or rare-earth cations do not exhibit this vaporization problem and are, therefore, more promising candidates for fiber coatings. Compatibility studies between Nextel 720 fiber and $RbAl_{11}O_{17}$ show a degradation of fiber strength for coated fibers after a one hour heat treatment at 1,100°C (2,012°F) (Goettler, 1996). $RbAl_{11}O_{17}$ appears to be stable with Nextel 610 after similar heat treatment; however, the lower temperature capability of Nextel 610 precludes its use in many high-temperature structural applications.

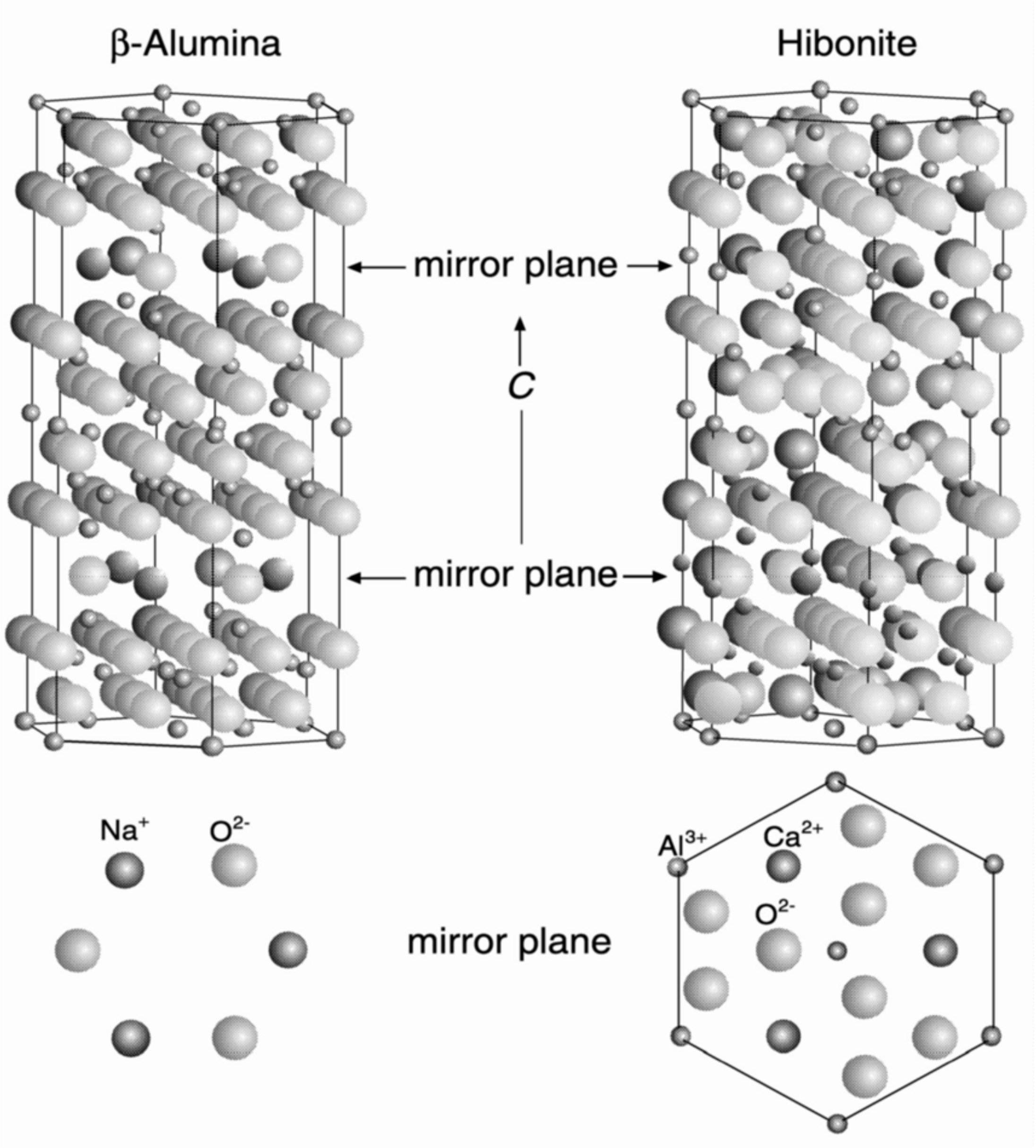


FIGURE 6-13 Hexagonal β-alumina ($NaAl_{11}O_{17}$) and magnetoplumbite (hibonite[$CaAl_{12}O_{19}$,]) structures. Below each structure is the interspinel mirror plane viewed along the *c*-axis. Source: Cinibulk and Hay, 1996.

The most detailed investigations of a layered oxide have focused on the magnetoplumbite known as hibonite, $CaAl_{12}O_{19}$ (Cinibulk and Hay, 1996). No composites have yet been fabricated from fibers with hibonite coatings. Studies of model composite systems consisting of hibonite coated, single-crystal fibers (both Al_2O_3 and YAG fibers) in hot pressed matrices of alumina and YAG have shown encouraging crack deflection results. Figure 6-14 is a transmission electron micrograph of a cross-section of a hibonite-coated sapphire fiber that shows the desired crack deflection along the basal plane (Cinibulk and Hay, 1996). There are, however, several technical obstacles to incorporating this coating into actual composite systems. First, high-temperature processing of the coating, typically higher than 1,300°C (2,372°F), is required to generate the magnetoplumbite structure with the layered planes parallel to the fiber axis (Cinibulk, 1997b). This temperature is higher than the temperature at which commercially available polycrystalline oxide fibers show strength degradation. Solution-based precursors in which calcium-aluminum inorganic polymers are created or in which nucleating agents are added to induce lower temperature formation of the magnetoplumbite structures may have to be developed.

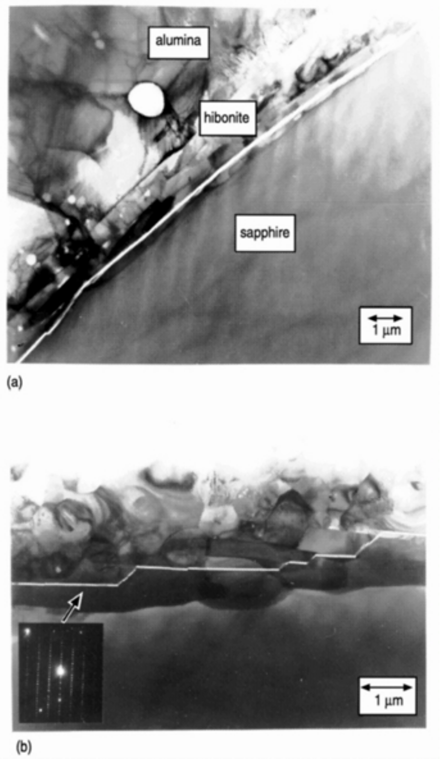


Figure 6-14 Transmission electron micrographs of cracks propagating transgranularly along the basal planes of the textured hibonite interphase. Source: Cinibulk and Hay, 1996.

Another problem with hibonite is the tendency for calcium to diffuse from the coating into the matrix during hot pressing (Cinibulk, 1994). The use of alternate basal plane cations, which would have less of a tendency to diffuse into the matrix and fibers, may solve this problem.

Hibonite has been chosen for initial investigation because it can be converted to the magnetoplumbite structure at a lower temperature than other layered oxides with basal plane cations other than calcium. Novel solution precursor chemistry that would enable lower temperature conversion to the magnetoplumbite structure could expand the compositional ranges to include cations less susceptible to migration within the matrix and fiber. Magnetoplumbites that contain alkaline-earth and rare-earth elements are likely to be chemically incompatible with fibers that contain mullite, such as Nextel 720 (as was observed with the β-aluminas). In order to utilize magnetoplumbite fiber coatings, a higher-temperature fiber that does not contain Si, such as YAG or creep-resistant doped alumina, will probably be required to ensure interfacial stability and allow for the high processing temperatures currently required to generate the magnetoplumbite structure.

The latest class of layered oxides to be proposed as fiber coatings are layered perovskites, including potassium calcium niobate ($KCa_2Nb_3O_{10}$) and barium neodymium titanate ($BaNd_2Ti_3O_{10}$) (Petuskey et al., 1996). Potassium calcium niobate has a melting temperature of only 1,460°C (2,660°F), whereas barium neodymium titanate has a melting temperature of greater than 1,800°C (3,272°F). Only preliminary investigations have been made thus far to assess these compounds as coatings in oxide composites. The main concern with these complex chemical compounds is their stability with candidate fibers and matrices. Both compounds appear to be stable with alumina, at least up to moderate temperatures of 1,250°C (2,282°F) (Petuskey et al., 1997), but their stability with fibers of more complex chemistry, such as Nextel 720 fiber (which contains mullite) and YAG fibers, is suspect. The potassium in potassium calcium niobate shows some volatility and thin films of the niobate heated to 800°C (1,472°F) exhibit a significant loss of potassium. However, there are indications that a sodium calcium niobate may exhibit less volatility.

One favorable aspect of these layered compounds is their ability to form a layered structure from sol-gel precursors at temperatures as low as 600°C (1,112°F). This ability is critical, especially with complex chemistries, because a lower formation temperature can help avoid reactions between the fibers and intermediate coating phases. Additional work will be required to determine if these classes of compounds are stable with potential and commercially available fiber reinforcements.

Weakly Bonded, Nonlayered Oxides

The segregant approach described earlier has the potential for creating a weak fiber-matrix interface without fiber coatings. An alternate approach is to use a fiber coating that exhibits a high energy, therefore weak, interface with the fiber or the matrix, or both. The high energy interface created between the coating and the fiber will have a tendency to debond readily in the presence of the stress intensity created by a propagating crack. Compounds that exhibit weak bonding to alumina include the rare-earth phosphates of the general formula $Me^{3+}PO_4$ (Morgan and Marshall, 1996), including the monazite family of minerals, which is composed of the larger rare-earth elements of the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, and Tb) that are sometimes substituted with divalent and tetravalent cations, such as calcium or strontium. Also included are the xenotime family of minerals comprised of scandium, yttrium, and the smaller rare-earth elements of the lanthanide series (Dy, Ho, Er, Tm, Yb and Lu). In general, the rare-earth phosphates have a high melting point. For example, monazite ($LaPO_4$) melts at 2,072 ± 20°C (3,761± 68°F).

Model composite systems of monazite-coated fibers in hot pressed billets of alumina have shown very promising interfacial debonding induced by propagating cracks generated by Vickers indentations (Figure 6-15) (Morgan and Marshall, 1995). Micromechanical analysis, based on theoretical models incorporating interfacial energies and elastic mismatches (He and Hutchinson, 1989), predict debonding at the monazitealumina fiber interface (Morgan and Marshall, 1995). The ease of debonding observed in the model composite systems has yet to be fully demonstrated in an actual dense composite system.

A significant obstacle to implementing these coatings has been depositing fiber coatings with a stoichiometric lanthanum-to-phosphorous ratio. It appears that nonstoichiometric monazite can significantly degrade the strength of the fibers and may affect the ability of the interface to debond (He and Hutchinson, 1989). Monazite appears to be stable with Nextel 720 fibers when the stoichiometry is met (Goettler, 1997b), which correlates with geological information showing that monazite is stable with aluminosilicates (Morgan and Marshall, 1995).

Additional compounds of the general ABO_4 formula have been proposed as weakly bonded, nonlayered oxide fiber coatings for alumina-based fibers. These include the broad family of tungstates ($Me^{2+}WO_4$), molybdates ($Me^{2+}MoO_4$), tantalates ($Re^{3+}TaO_4$), and niobates ($Re^{3+}NbO_4$) (Goettler et al., 1997a). Alkaline earth tungstates have melting temperatures ranging from 1,358°C (2,476°F) for $MgWO_4$ to 1,580°C (2,876°F) for $CaWO_4$ (scheelite). Molybdates have lower melting temperatures than the corresponding tungstates. Data is incomplete on the melting points of many tantalates and niobates although they generally have higher melting temperatures than tungstates and molybdates. Tantalates have melting temperatures near 1,900°C (3,452°F), whereas niobates melt at approximately 1,600°C (2,912°F).

Detailed investigations have been performed for scheelite and $ErTaO_4$ fiber coatings on Nextel 610 fibers in duplex matrices of alumina-scheelite and alumina-$ErTaO_4$, respectively. Scheelite appears to be chemically compatible, as well as show easy debonding, with Nextel 610 fibers (Figure 6-16) (Goettler et al., 1997a). Unidirectional composites have shown strengths of more than 340 MPa (50 ksi) and extremely fibrous pullout at composite porosity levels of approximately 20 percent at room temperature (Goettler et al., 1997a). The scheelite-alumina debonding mechanism must still be verified, however, at the high temperatures representative of projected operating environments. Preliminary investigations suggest that, like sheelite, $ErTaO_4$ is stable with alumina although substantial debonding of this coating from Nextel 610 fiber was not observed (Goettler et al., 1997a). Because tantalates have a crystal structure similar to monazite, the debonding characteristics are also expected to be similar. Additional investigations must be done, however, to demonstrate this. The grain size of the $ErTaO_4$ fiber coatings were about an order of magnitude smaller than the grain size of $CaWO_4$ coatings, indicating that the grain size of the ABO_4 coatings may have a strong affect on the interfacial energy and, hence, the ability of the interface to debond readily.

Initial mechanical testing and transmission electron microscope studies of scheelite-coated Nextel 720 fiber-reinforced oxide composites suggest compatibility between scheelite and Nextel 720 fibers (Goettler et al., 1997b). Furthermore, scheelite is found in nature with quartz deposits, providing some geological evidence that scheelite should be stable with silica-containing fibers, such as Nextel 720. However, detailed testing will be required to verify the applicability of scheelite as a fiber coating for Nextel 720. The fact that only some ABO_4 compounds (all of which fall into closely related crystal groups) show weak bonding to alumina and aluminasilicate-based fibers underscores the need for basic studies of oxide-oxide interfaces on the atomic scale. Determining the reason for the weak bonding of these interfaces may lead to other candidate interfaces that could extend the range of oxide composite systems that can survive the environments to which these composites may be subjected.

Coating Processes and Vendors

Immiscible Liquid Coating Technique

The most promising oxide fiber coatings appear to be multicomponent oxides. Liquid-based techniques are generally the most viable for producing these complex oxide coatings. Using CVD, it is often very difficult to maintain stoichiometry in the coatings, although some success has been achieved with $LaAl_{11}O_{18}$ (Brown, 1995) and monazite (Chayka, 1997). Using CVD precursors are often expensive, and using a precursor in a continuous coating process is often inefficient. Solution-based precursors allow accurate stoichiometric control, and, with inorganic polymer chemistry, it is possible to create precursor solutions that convert to the desired phases at low temperatures upon decomposition. For instance, monazite has been reported to form at as low a temperature as 100°C (212°F) from an aqueous solution (Morgan, 1996; Goettler and Sambasivan, 1996).

The major drawback of solution-based coating techniques is the difficulty in obtaining continuous, uniform, bridge-free coatings. CVD coatings are typically superior, morphologically, to coatings obtained by sol-gel techniques. A new technique that minimizes the bridging problem exhibited by solution-derived coatings involves using immiscible liquids to displace excess coating solution that is normally retained between fibers within a tow bundle after passing through a coating precursor (Figure 6-17a and Figure 6-17b) (Hay, 1991). The basic idea behind this technique is to take advantage of surface energy relationships to keep the individual fibers, which are covered by the coating precursor, separated from one another by a layer of hydrocarbon, such as pentadecane, until the coating precursor gels. Figure 6-18 shows $CaWO_4$ fiber coatings obtained by making multiple passes through an immiscible layer formed by the coating precursor and pentadecane (Goettler et al., 1997b). This technique can yield fairly uniform, thick coatings. Because the nature of the precursor determines the quality of the coatings, the most desirable precursors will form thin films upon drying and exhibit minimal gas evolution upon decomposition. Excessive gas evolution tends to dislodge coatings from the fibers and leads to fiber bridging.

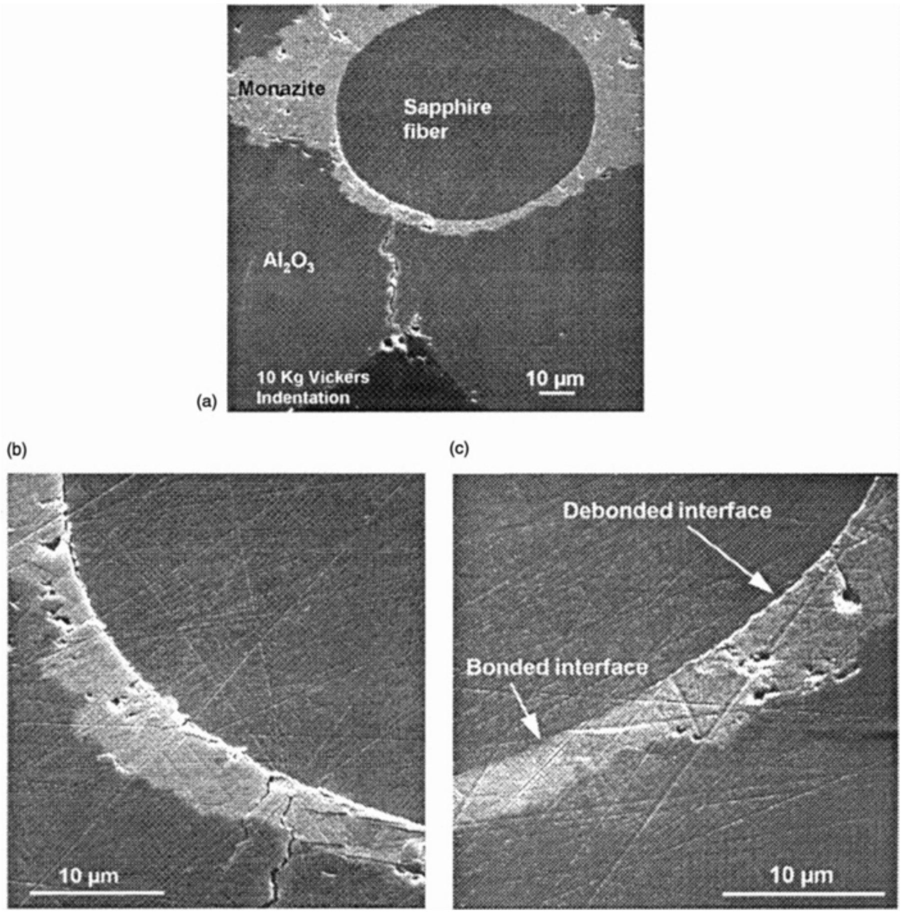


FIGURE 6-15 Scanning electron micrograph showing crack deflection at alumina-monazite interfaces. Cracks initiated by Vickers indentation. Source: Morgan and Marshall, 1995.

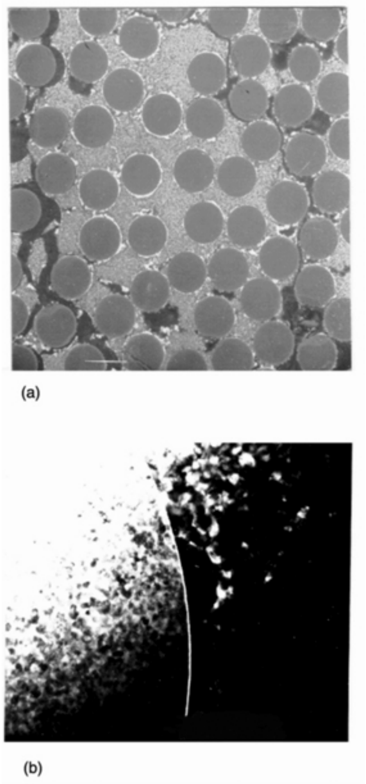


FIGURE 6-16 Scanning electron micrograph and transmission electron micrograph showing debonding along scheelite-Nextel 610 interfaces. Source: Goettler et al., 1997a.

Only a few organizations are known to be using the sol-gel immiscible liquid coating technique to produce moderate quantities of fiber; these include the U.S. Air Force Wright Laboratory and McDermott Technology Incorporated (formerly Babcock and Wilcox), Lynchburg Research Center. An advantage of this technique is the relatively low capital cost required to establish a coating capability. The critical element of this technique is the chemistry of the liquid coating precursor.

Heterocoagulation Technique

The heterocoagulation technique takes advantage of electrostatic attraction, which can be generated between fibers and slurry or colloidal particles in liquid media of high dielectric constant, such as water (Malghan et al., 1990; Cinibulk, 1997a). Surfactants are often required to shift the isoelectric point of either the fiber or the coating particle in order to create electrostatic attraction at a given pH. Figure 6-19 shows $LaPO_4$ fiber coatings obtained by dipping Nextel 720 fibers in Betz 1260 flocculant, washing them, and dipping them in a milled monazite slurry (repeated six times) (Goettler, 1997a).

The attractions of this technique are twofold. First, it utilizes an electrostatic driving force to help ensure the uniform coating of fibers. Second, the coatings are deposited as the desired phase, eliminating the chance of reaction between the fibers and intermediate phases often encountered during sol-gel decompositions. A less attractive characteristic of the technique is that it often requires multiple passes to achieve sufficient coating thickness. A continuous coating process utilizing this technique is complicated by the need to perform multiple passes, combined with the need to wash away excess sol after the electrostatic attraction, often (depending on the fiber/coating system) reabsorbing a surfactant, and then washing away the excess surfactant before reexposing the fiber to the sol. Complete washing of the surfactants is often necessary to prevent contamination of the sol, which could change the zeta potential of the sol and therefore the electrostatic relationship between the sol bath and the fibers.

Research into maximizing the electrostatic potential between common oxide fibers and candidate coating particles using surfactant technology in order to obtain sufficiently thick coatings in a single pass of a fiber tow through a colloidal sol would be useful. The technique would still be limited by having to use fine particle slurries or colloidal sols of the desired coating composition. Formation of these slurries or sols could be difficult for some of the complex oxides being considered as fiber coatings.

Currently, no organizations are known to be using the heterocoagulation technique to coat large quantities of fiber tow. Organizations that have evaluated the technique for composite processing include the U. S. Air Force Wright Laboratory and McDermott Technology, Incorporated, Lynchburg Research Center. Neither group is active in this area currently. This technique is attractive, however, because it would require relatively low capital costs to establish a significant coating capability.

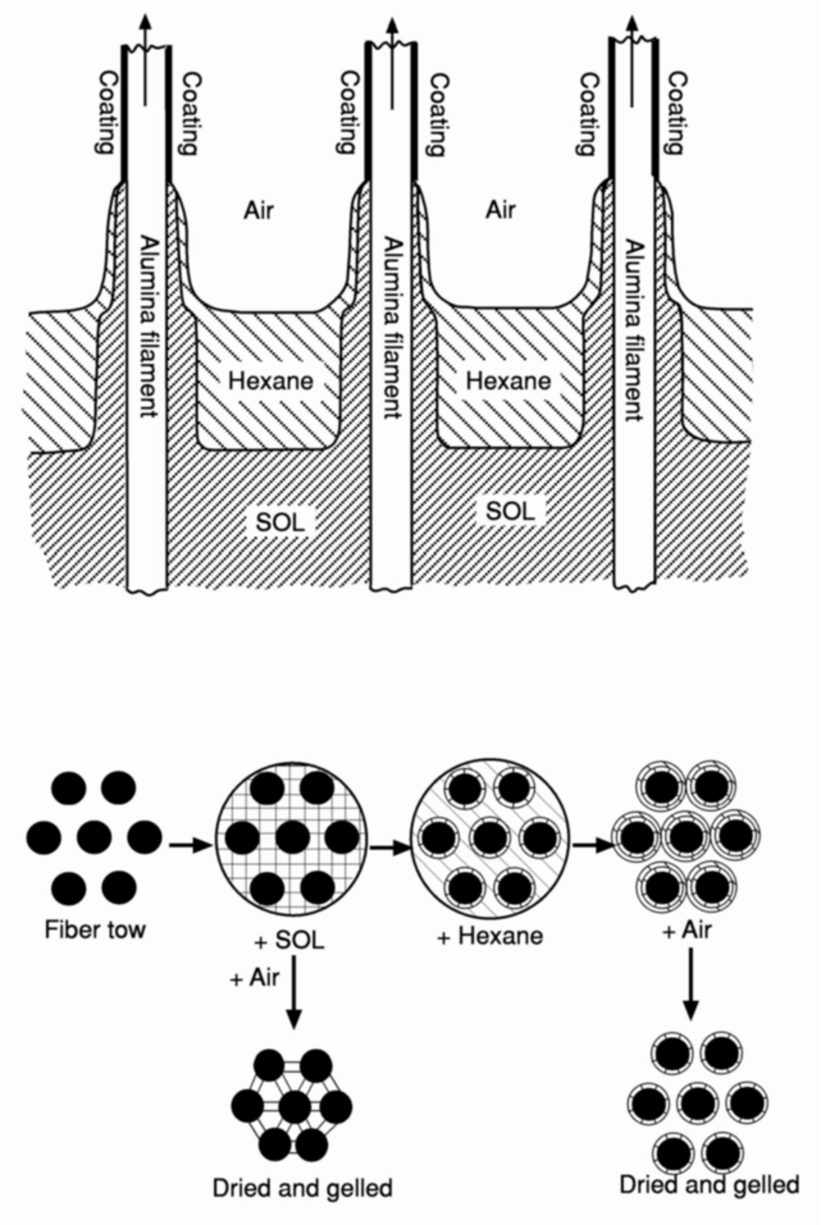


FIGURE 6-17 Schematic illustration of immiscible liquid coating technique. (a) Sequence of events during coating of a fiber tow, lengthwise view. (b) Idealized sequence of events during sol-gel coating of a fiber tow in a two-phase liquid (in cross-section). Source: Hay, 1991

RECOMMENDATIONS AND FUTURE DIRECTIONS

Non-Oxide Fiber Coatings

CMCs reinforced with SiC fibers have used a wide variety of fiber-matrix interface coatings, but acceptable toughness (debond characteristics) has only been demonstrated with coatings that contain either a carbon or a BN layer. Oxidation of both carbon and BN has been a major factor limiting the widespread use of non-oxide CMCs. Carbon coatings can readily oxidize in all oxidizing environments, and BN coatings are particularly vulnerable in environments that contain water vapor. However, not all BN coatings are alike, and the effects of BN chemistry and crystallinity on composite properties have yet to be systematically evaluated.

Composites are generally designed to operate below the proportional limit or matrix cracking strength. However, matrix cracking will inevitably occur by accidental exposures to stresses above the matrix cracking strength. Therefore, a non-oxide, silica-forming fiber coating—capable of preventing oxidation of the fiber-matrix interface—with adequate debond characteristics is highly desirable. Unfortunately no fiber coating can prevent the oxidation of this interface for more than 100 hours at the desired operating temperatures (~ 1,200°C [2,192°F]). Long-term applications such as industrial gas turbines and commercial aircraft engines, however, have life requirements on the order of several thousand hours. Because occasional matrix cracking probably cannot be prevented, oxidation of fiber coatings is a serious concern—limiting the widespread use of non-oxide composites. Therefore the committee recommends the following approach to inhibiting oxidative embrittlement of non-oxide CMCs:

- The oxidation resistance of non-oxide fiber coatings should be improved from the current calculated value of a few minutes (at 1,200°C [2,192°F]) for 1 μm (0.04 mils) BN coatings to the theoretical limit of ~ 100 hours for 1 μm silica-forming coatings.
- Techniques should be developed for sealing matrix cracks rapidly.

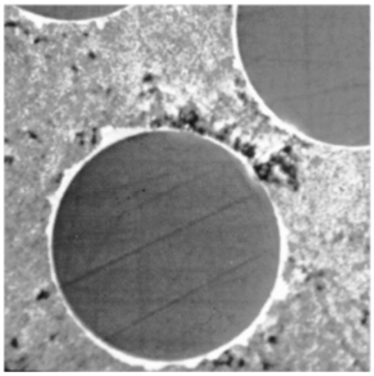


FIGURE 6-18 Example of oxide fiber coatings deposited via the immiscible liquid coating technique ($ErTaO_4$-coated Nextel 610 fibers in an alumina-$ErTaO_4$ matrix). Source: McDermott Technology, Inc.

Clearly, the crack sealing time should be less than the time it takes to oxidize the fiber coatings, which are typically on the order of 1 μm (0.04 mils) thick. Coatings that could potentially improve oxidation lives are silicon-doped BN, AlN, multilayer coatings of BN, and silicon-doped BN with SiC and Si_3N_4. Boron-additives might be useful for sealing matrix cracks in matrices that contain SiC. A critical question that remains to be addressed is whether the sealed cracks will hold under the cyclic stresses encountered during operation, even if the stress is below the incipient cracking strength of the unoxidized matrix. Therefore, the committee recommends that materials be evaluated under conditions representative of their operating environments.

CVD is the most common method of producing fiber coatings for non-oxide composites. This method is limited in some respects because coating non-uniformity increases with the complexity of the substrate architecture (i.e., from tows to weaves to three-dimensional layups). Because the costs of fiber coatings constitute, perhaps, the largest fraction of the cost of composites today, approaches that lower costs and produce more uniform coatings are needed. Coatings formed from liquid precursors represent one possible approach. Another is in-situ coatings, which have been demonstrated with the Bayer fiber. Therefore, the committee recommends that fiber coatings derived from liquid precursors and in-situ coating approaches be investigated further.

Oxide Fiber Coatings

The development of coatings for ceramic oxide fibers has lagged behind the development of coatings for non-oxide fibers partly because of the insufficient creep resistance of

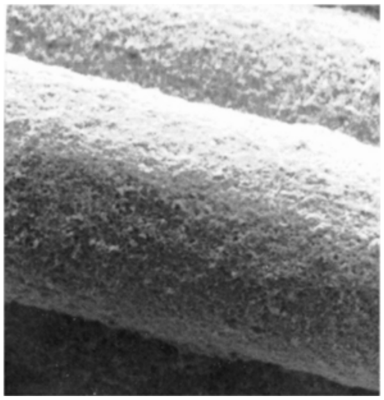


FIGURE 6-19 $LaPO_4$ coatings on Nextel 720 fibers deposited by heterocoagulation techniques. Source: McDermott Technology, Inc.

oxide fibers at elevated temperatures. Recent improvements in creep-resistant oxide fibers, however, have improved interface control in oxide systems. The majority of oxide composite studies, however, have been conducted with porous matrix composites (with no coatings). All oxide coating concepts discussed in the literature have been demonstrated only with model, rather than actual, composite systems. Therefore, although several coating approaches promise of providing damage tolerant oxide composites, they will require further study to prove or disprove their viability. These coating concepts are discussed below.

Porous Coatings and Porous Matrix Approaches

Research will be needed to identify porous coating compositions that are microstructurally stable enough to prevent densification of the coating during composite use. Multiphase coatings may be required to suppress the tendency for porous coatings to become dense, which would make chemical compatibility between the fiber, coating, and matrix more difficult to maintain.

More research is needed to support long-term exposure under anticipated operating conditions for systems without an interfacial coating that rely on porous matrices for graceful failure. For example, mechanical testing and interface characterization, especially transmission electron microscopy, of these porous matrix composites will be required to assess the stability of fiber-porous matrix interfaces and the degree of possible fiber degradation. For applications that require longer operating times at elevated temperatures, alternatives to the UCSB alumina-mullite matrix that are more chemically stable with the fiber reinforcement and more resistant to densification may have to be developed.

Fugitive and Segregant Weakened Interfaces

Both fugitive and segregant-weakened interface concepts represent potentially lower cost options because fugitive carbon interfaces can easily be deposited by CVD or solgel techniques, and the use of segregants eliminates the need for fiber coatings. Therefore, these concepts merit further investigation.

Fugitive interfaces will require substantial long-term testing to confirm that fiber strength does not degrade by contact with the matrix. Most long-term testing of fugitive interfaces has involved only unstressed oxidation heat treatments. Heat treatments under load, when the matrix and fibers are more likely to be in contact, and subsequent mechanical testing have not been done. Fugitive interfaces could also benefit from research into alternative matrices that are stable with commercially available fibers for extended exposures to high temperatures.

Segregant-weakened interfaces are an attractive concept based on the possibility of eliminating the coating phase from the composite fabrication process. This concept has only been demonstrated, however, on model composite systems. A major technical issue is whether the matrix or fiber, or both, would have to be doped to control the fiber-matrix interfacial energy. If polycrystalline fibers require doping, then the effects of dopants on creep performance must be considered. Therefore, additional basic research of this interface concept, utilizing available polycrystalline fibers and candidate oxide matrices, is recommended.

Dense Oxide Fiber Coatings

Many layered oxide coatings show promise as crack deflecting interfaces for oxide-oxide composites. Although the β-aluminas have been shown to be unstable with Nextel 720 fibers, they are still candidate fiber coatings (especially the less volatile $RbAl_{11}O_{17}$) for ceramic composites if other creep-resistant oxide fibers become available. Research into an improved creep-resistant Nextel 610 fiber that incorporates additions of rare-earth oxides or garnet-based fibers, may make the β-aluminas more viable as fiber coatings.

The same recommendations hold true for magnetoplumbitebased coatings. Additional research is needed into sol-gel or solution-based inorganic polymers that could convert to the β-alumina and magnetoplumbite structures at lower temperatures. The development of ceramic oxide fibers with improved high-temperature creep resistance that are stable with these layered oxides would reduce the need for a low-temperature coating process. It would be preferable, however, to create the desired coating phase at as low a temperature as possible to prevent intermediate phases from reacting with the fibers.

Additional investigation of the layered perovskites ($KCa_2Nb_3O_{10}$ and $BaNd_2Ti_3O_{10}$) should be limited because of the low probability that these compounds will be stable with available creep-resistant fibers. Layered perovskites may be stable with a creep-enhanced polycrystalline alumina fiber although it has been reported that these coatings are stable with alumina only at moderate temperatures (~1,250°C [2,282°F]). The simpler chemistry of layered β-aluminas and magnetoplumbites are more likely to be used as coatings for available oxide fibers.

Basic research of weakly bonded, nonlayered oxides will be required to understand the mechanism that controls debonding of some ABO_4 compounds from alumina and aluminamullite fibers. Preliminary data on the strength retention of monazite-coated fibers underscore the need for testing the potentially detrimental effect of cation diffusion (solid solubility) on the strength of the polycrystalline fibers. Perhaps certain “A” cations for the ABO_4 coating will have to be selected that have limited fiber grain boundary solubility. Substantial, long-term exposure and mechanical testing programs will be required to prove the viability of ABO_4 compounds as fiber coatings.

Coating Processes and Vendors

Only two institutions are known to be using the sol-gel immiscible liquid coating technique (Wright Laboratories and McDermott Technology, Incorporated, Lynchburg Research Center). The immiscible liquid coating process is rather slow. For example, McDermott Technology, Incorporated, deposits carbon coatings onto Nextel 610 fiber at a rate of approximately 152 cm (60 in.) of fiber tow per minute. If coating speeds could be increased, integrating the coating step into the fiber manufacturing process would become much more feasible, thus potentially lowering costs. Therefore, programs focused on investigating and improving the quality of these coatings as a function of coating speed are recommended.

No organizations are known to be using the heterocoagulation technique for coating large quantities of fiber tow, despite its potential for depositing uniform coatings without (often problematic) intermediate phases. This is most likely because the heterocoagulation technique often requires multiple passes to build up sufficient coating thickness. Heterocoagulation, however, is attractive because it requires a relatively low capital investment. Therefore, the committee recommends that research be done on surfactants that could yield higher charges on the coating particles and/or fibers. It may be possible to absorb soluble inorganic polymer precursors onto the fiber surfaces by heterocoagulation, which would eliminate the need to form a fine powder of the desired coating composition. The inorganic polymer-derived coatings would probably be very thin, however, and would therefore work best for coating concepts that rely on debonding at the interface rather than within the interphase.

7

Cost Issues

The performance, manufacturing, and life cycle costs for systems containing CMC components, including ceramic fibers and coatings, are interconnected. The *prices* of ceramic fibers, fiber coatings, and composites, however, do not always reflect manufacturing *costs*. These issues have not been widely explored and are even less widely understood. Consequently, the influence of fiber and coating costs on the manufacture and implementation of CMCs remains ambiguous and system dependent. This chapter discusses the relationship between costs and prices, aspects of fiber costs, and the implications of CMC market volume on fiber prices.

PRICE VS. COST

The words price and cost are often used interchangeably. There are, however, important distinctions between price and cost in the commercialization of a new technology.

Price can be defined as what the market will bear for a product or service. Price levels for competitive goods and services under normal circumstances are set by the marketplace. For new materials, price levels are determined by assessing the price/performance ratio of existing materials. In general, the price and performance of CMCs will be compared to superalloys and other turbine engine materials, as well as to monolithic ceramics for the components of small industrial turbine generators.

Costs are determined by actual expenditures for producing a good. Costs are governed by physical realities, for example, the cost of buying machines and the cost of labor to operate them. Costs can fluctuate widely depending on how much is being produced per unit of time or how efficiently the manufacturer uses resources. In general, there are two types of cost: costs associated with production (i.e., manufacturing costs) and costs associated with operating a continuing business (i.e., administrative and marketing costs). The most important factor for commercializing a new technology is potential manufacturing costs. If the product can be manufactured efficiently, it is assumed that a suitable “business structure” can be put in place for delivering the product to the market.

As products flow along the supply chain, the prices for one entity become the costs for the next. Thus, for the commercialization of new technology, the word cost has different meanings for producers and users. For users, the price and cost of a product or service are the same. For producers, however, cost is the expense incurred to produce a product or supply a service. To earn a profit and a return on investment, the producer's *aggregate costs* over time must be lower than the *aggregate revenue. Time* becomes the key element in the equation. In the short run, costs are often higher than prices; but there must be an expectation that, in the long run, prices will exceed costs.

For producers, profit is the difference between cost and price. Making a profit is the goal of every commercial enterprise, and the definition of successful “commercialization” of a new technology should be when a new technology is either earning a profit or is on a trajectory to do so. Even if a new technology is available for consumption, it will eventually be removed from the market if it does not show promise to earn a sufficient profit.

TYPES OF COST

Some costs are incurred all at once, but their effects are felt over a period of time. Other costs increase or decrease depending on the level of business. Because of the difference in how costs occur, categories have been developed (see, for example, Figure 7-1) to aid in the analysis of financial alternatives:

- Variable costs are costs that vary, *in the aggregate*, with production volume. Raw materials are the best example of a variable cost. As production increases, the aggregate cost of raw materials increases.

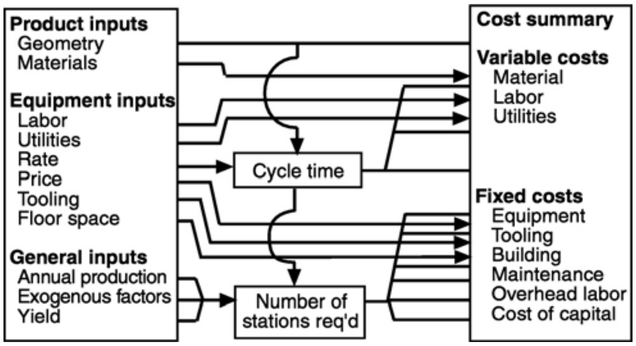


FIGURE 7-1 Elements in manufacturing costs. Source: IBIS Associates,Inc.

- Fixed costs are costs that, *in the aggregate*, are constant (fixed) regardless of the level of production. The best example is machinery, which is put in place with a one-time expense. No matter how much of the capacity of the machine is used, the aggregate expense does not change.

However, these distinctions can almost be reversed when considering the cost of a single unit. Variable costs are constant for each unit of production regardless of volume. For example, if the output of a brick plant doubles, the amount of clay consumed *per brick* is the same. The only time this principle doesn't hold is if something else changes, if the amount of scrap is somehow reduced, for example, along with the increase in volume. Fixed costs, however, account for less cost *per unit of production* as volume is increased to capacity. For commercializing a new technology in the manufacturing environment, the two types of cost have important implications.

Variable Costs

The aggregate manufacturing costs that change with production volume fall into three basic categories: materials, direct labor, and utilities. Materials include the input materials that end up in the final product, as well as scrap losses and other consumable items affected by production volume. For example, mold release coatings, although they are not part of the final product, are still required to make the part and are accounted for as a materials cost. Direct labor is the cost of the manpower to operate the machinery in the factory; as production increases, more labor is required. It is assumed that if a machine is not running, the machine operator can “do something else” and that cost (associated with running that machine) is not incurred; in practice this is obviously not always the case. Also, workers can “learn” some processes to improve the production rate, for example, composite lay-up. In this case, the labor cost decreases on a per unit basis, although it still increases in the aggregate. Utilities are the flat-rate consumables needed to operate a factory, such as electric power and water provided by a utility. Once again, the aggregate costs increase with production volume, but the per unit costs are constant.

For analytical purposes, it is best to treat the per-unit variable costs as constant throughout the range of production volumes. Factors that will change the per-unit variable costs are theoretically independent of production volumes, although in practice they become easier to affect as volumes increase. For example, reductions in scrap losses lower the cost of material per unit, as well as in the aggregate. It is easier to identify the root causes of scrap losses when capacity utilization is high, but in theory there is no correlation between scrap losses per unit and production volume. Although the “learning curve” effect reduces direct labor content per unit, manufacturing philosophies dramatically affect the extent of this phenomenon.

Fixed Costs

Manufacturing costs that do not change, in the aggregate, with production volume include: the cost of equipment; the cost of tooling; the cost of the building; the time value of the money invested in equipment, tooling, and the building; and the labor and maintenance expenses needed to operate the plant and equipment.

The first four items are relatively easy to understand. Let's say General Motors decides to build a new electric vehicle. It builds a new plant with special machinery and orders tooling that can only be used to make that specific car. It builds a new building for the assembly of this unique vehicle and invests money borrowed from a bank or shareholders, on which it will owe interest or dividends, to put everything in place.

If the new technology (i.e., the electric vehicle) is accepted by the public, the factory will increase production, and the cost of the investment in the fixed plant will be spread over a great many cars. If the electric vehicle is a flop in the market, the investment costs will be spread over many fewer cars, and per unit costs will be higher. The number of cars produced doesn't affect the aggregate spending on facilities; but it does affect the amount of spending per car.

It's easy to see that fixed facilities require up-front cash expenditures and that only future events will determine if the investments were sound. Thus, fixed costs are the most significant for commercialization; companies must take risks that fixed costs, *investments*, will be paid back at a later date.

Some costs are generally regarded as fixed costs but are in somewhat of a “gray area.” Examples are factory “overhead,” labor, and maintenance costs. A scheduler is necessary regardless of the plant's utilization, whereas an extra press operator is not. Thus the scheduler is dubbed a fixed cost, and the press operator a variable cost. This designation is made even though the press operator may be given something else to do, and the cost still incurred, if production is not up to capacity. Similarly, maintenance costs can be based on time or on production (akin to changing your car's oil every 3,000 miles or every three months, whichever comes first). Accountants generally put maintenance in the “fixed” category, although it often functions more like a variable cost.

The Bridging Factor—Cycle Time

Time is the governing issue in profitability; how much can be produced and sold in a given time for a given investment. Let's say engineers figure out a way to halve the time it takes to produce a unit on a given machine. The output of that machine per unit time doubles; the fixed cost per unit is halved. The full capacity of the machine, however, must be used to achieve the cost savings. For example, if throughput is doubled, but sales remain constant, the only effect would be to idle the machine half the time. Only if the number of workers to operate the machine and the amount of power consumed by the machine remain constant, do the elements of variable cost get halved (as a result of halving production time per unit). Labor and power costs are reduced regardless of production volume (after all, these are variable costs).

Cycle time is, therefore, one of the key cost predictors of a new technology. As an example, car companies have looked towards polymer-based composite structures to reduce the weight of vehicles. Steel panels, however, can be formed in just a few seconds. Although much larger, vastly more expensive stamping machines are required for steel panel production, high sales volumes easily allow the cost of these stamping presses to be minimized on a per unit basis. Thus steel has remained the low-cost way to build automobiles.

GENERAL FIBER MANUFACTURING COSTS

The manufacture of fibers presents three unusual cost issues: fibers have a very high length per unit mass; the machinery used for fiber production is highly specialized; and materials to be formed into fibers require special treatments or additives.

The cost of most materials is scaled by cost per unit of mass. Fibers have a tremendous amount of length per unit mass, and processing that length incurs additional costs relative to mass (see, for example, Figure 7-2). The additional cost can be seen as a cycle time penalty. For example, it takes less time to produce a kilogram of bulk polymer than a kilogram of the same polymer spun into a fiber. The cost premium for engineering materials that have been "stretched" to fiber diameters is significant, especially in the linear density range of interest for composite materials.

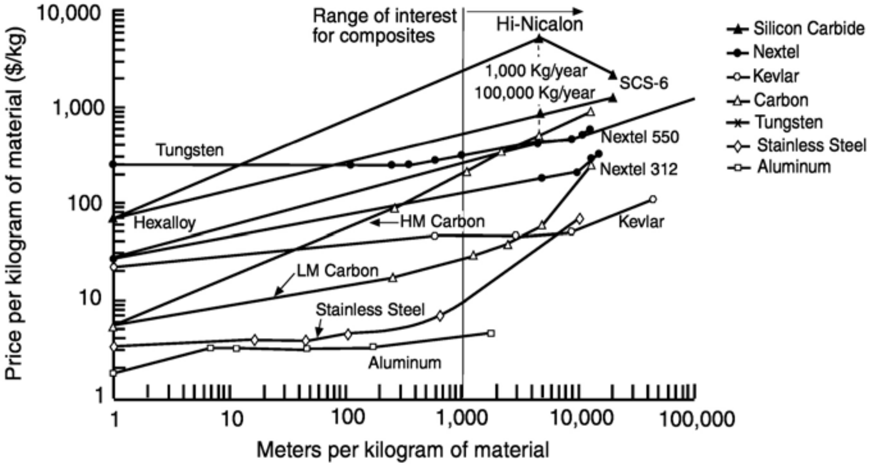


FIGURE 7-2 Fiber price premiums. Source: IBIS Associates, Inc.

The machinery used for fiber production is highly specialized; there is little in the way of off-the-shelf fiber spinning, drawing, or heat treating machinery. The low volume, customized nature of this machinery extracts a considerable investment premium. For example, plastic injection molding machines are available on a turn-key basis in a range of sizes from a large number of suppliers. Plastic fiber spinning machines, however, are only available on a custom basis from a limited number of suppliers.

Finally, there is an added premium to materials prices that are formed into fibers. This is because fiber drawing materials (e.g., spin dope) must be exceptionally pure and require special treatments or additives. For example, the cost of carbon pitch is measured in dollars per ton. The purification required to spin carbon pitch into carbon fiber, however, raises the raw materials costs to dollars per pound, an increase of three orders of magnitude.

Taken together, these three factors make fiber production for composites a dubious business proposition. The time it takes to learn how to use the fiber and qualify the material for specific applications has resulted in slow market development, during which time the manufacturer must hold a tremendous amount of underutilized invested capital. The fiber manufacturer is thus in a precarious situation. If the fiber manufacturer produces fiber at full capacity to reduce manufacturing costs per unit, he will produce more fiber than can be sold and will lose money through excessive variable costs. If the fiber manufacturer produces only the amount of fiber that can be sold, he will incur high underutilized fixed costs, resulting again in his losing money.

Take, for example, the two major commercialized advanced composite fibers, Kevlar and carbon fiber. When Kevlar was first developed, DuPont believed it would be used as a replacement for fiberglass in ropes, tire cords, and many other applications. Therefore, DuPont spent heavily on research and development and production capacity, but a large market did not materialize rapidly enough for DuPont to make a return on its investment. If DuPont had simply put all of the money it invested in Kevlar "in the bank," it would be earning more in interest, from doing nothing, than it earns in profits from Kevlar production.

A similar situation occurred in the carbon fiber industry. Carbon fiber was expected to be the material of choice for aircraft structures, but the drop-off in the production of military aircraft and the hurdles of qualifying for civil aircraft production resulted in inadequate market development and large losses for the early developers. Over time, however, the understanding of carbon fiber has matured and manufacturers have improved processing, thus reducing production costs. As a result, carbon fiber is now a large, growing, profitable business. It currently has important uses in commercial aerospace, automotive, and electronic markets and may even become a significant material in civil engineering. But its "commercialization" took 25 years, well beyond the purview of any single commercial enterprise.

Ceramic fiber producers are in the same situation that DuPont was in with Kevlar and that several manufacturers were in with carbon fibers. The fixed costs of producing ceramic fibers are high. The only way to reduce the fixed cost per pound of fiber is to produce more fiber than can be sold because the market is not significant, regardless of price. Offering a long-run price to the market would certainly help the market grow, but market development still takes time, and manufacturers would incur losses until the market becomes substantial.

MANUFACTURING CERAMIC FIBERS

There are three basic steps in the manufacture of high performance, continuous ceramic fibers, all of which have important cost considerations: (1) preparation of bulk, preceramic material to be spun; (2) spinning the bulk material into a green fiber; and (3) heat treating the spun green fiber to convert it into ceramic fiber.

The preparation of preceramic material involves processing a high purity, easily spinnable material, usually a preceramic polymer or sol. In either case, specialized equipment is required to produce the material because there is no other market for these exact materials (although there are some close relatives). The high level of purity, the delicate balance of material properties, and the dedicated, customized equipment make preparation an expensive process.

Spinning involves pumping the material through very fine, precise holes in a plate (called a spinneret) into a controlled environment where the material is solidified. This environment can be gaseous (dry spinning) or liquid (wet spinning). As the material is forced through the spinneret, it takes fibrous form. The diameter of the fiber is usually reduced by taking up the bundle of fiber on a spool at a faster rate than it is being produced at the spinneret.

At this point the fiber is called green fiber and is usually extremely delicate and difficult to handle, resulting in reduced yield. Controlling the spinning environment is challenging. If the fibers are too dry, they will break apart. If they are too wet, they will stick together and form a useless cord when they are squeezed into a bundle on the spool. The lower yield that results from these processing complexities results in increased costs.

Heat treating involves ramping the temperature of the green fiber to the temperature of its conversion to ceramic material, holding it at that temperature until the fibers are fully converted, and ramping the fiber temperature back down. The environment must be carefully controlled throughout this process. The time and temperature required to convert the fiber, the controlled environment, and the custom furnaces all make this an expensive process.

The combination of high fixed costs for all three steps and the long cycle times of the last two steps result in extraordinarily high costs per unit mass for low volumes (often thousands of dollars per pound). The most effective way to lower the costs of ceramic fibers is to increase the volume of production. Other efforts to reduce fiber cost will have far less impact than increases in production volume.

OXIDES VS. NON-OXIDES

Oxides appear to have a distinct manufacturing cost advantage over non-oxides. Oxides generally require shorter heat treatments at lower temperatures in less difficult environments (e.g., the presence of oxygen is not a complicating factor). This translates into significant savings in fixed costs. Lower temperature furnaces, for example, are less expensive than higher temperature furnaces. Furthermore, eliminating oxygen from the cure environment for non-oxides is expensive and adds costs that are not incurred for oxide fibers. Shorter heat treatment times for oxides result in faster cycle times. There is also a strong possibility that the cost of raw materials for producing oxide fibers can be reduced to well below the cost of raw materials for non-oxide fibers.

FINDINGS

Relationship between Price and Volume

Fiber prices could be reduced by a market-driven increase in production volume, which would lower the fixed cost per unit. Although current fiber manufacturers and independent consultants have conducted studies to predict fiber prices and cost levels, exact predictions are elusive because of the difficulty in precisely forecasting future yields and process improvements. Furthermore, prices will depend on the pricing policies of individual manufacturers as much as on actual costs.

Assuming that the performance of ceramic fibers is suitable for thermostructural applications, implementing these materials still poses great business risks. CMC manufacturers have said that fibers that meet their performance requirements must be priced at approximately $1,100/kg ($500/lb) for large volumes to be in demand. Ceramic fiber developers/ manufacturers, however, have indicated that ~ 23,000 kg (50,000 lbs) of fiber must be sold annually to attain a price of $1,100/kg ($500/lb) (see Figure 7-3). The math is simple; 23,000 kg (50,000 lbs) of fiber at $1,100/kg ($500/lb) results in a total of ~ $25 million in revenue for the fibers alone. Even if an assumption is made that the cost of the fibers constitutes 25 to 50 percent of the cost of the final composite, $50 million to $100 million in composite sales will be necessary to support $25 million in fiber sales.

The problem is that no single current application of continuous fiber composite material within one company totals $100 million. This includes applications that utilize carbon fibers, Kevlar, or even fiberglass. In fact, a large application for a composites manufacturer is $10 million. The largest single applications of continuous fiber composites (by dollar value), within one company are carbon fiber golf clubs, pultruded fiberglass ladder rails, and certain aerospace applications (e.g., Boeing's 777 empennage structure). Even by the standard of the jet engine component industry, $100 million represents a tremendous volume of sales. Current suppliers of metal jet engine components, such as Wyman Gordon and Howmet, measure sales in hundreds of millions of dollars, but these sales are spread over several individual components for a large number of engines.

Therefore, it is extremely unlikely that the commercialization of CMCs and their constituent fibers can be supported by one application. Several applications will have to be developed to reach $50 million to $100 million in CMC sales. Materials suppliers typically solve this problem by offering new materials to the market at a long-run price below cost (on the assumption that several applications will be developed) and incur losses until a market develops.

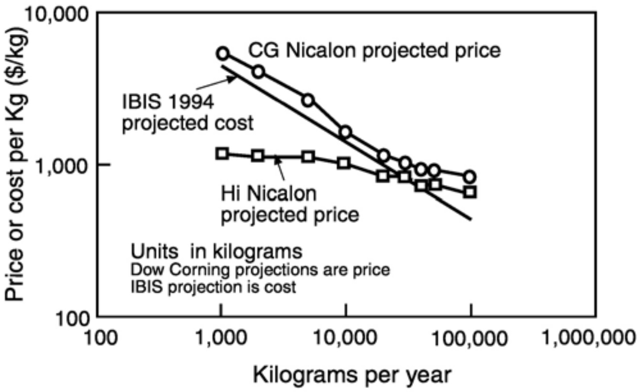


FIGURE 7-3 Projected costs of fibers as a function of annual production. Source: IBIS Associates Inc.

If a ceramic fiber manufacturer were to take this approach, he would face a daunting task. For example, if Dow Corning were to offer Hi-Nicalon fiber at a *price* of $500/kg ($227/lb) and could develop a CMC market of $20 million the first year (a tremendous accomplishment by the standards of the composite materials industry), this would equate to fiber sales of roughly 10,000 kg (22,000 lbs) in the first year. Dow Corning, however, projects that the *cost* of manufacturing Hi-Nicalon fiber, at 10,000 kilograms (22,000 lbs) of annual production, would be in the range of $1,250/kg ($568/lb) (a dramatic drop from its current cost of more than $3,000/kg [$1,363/lb]), as can be seen in Figure 7-3. Thus the payoff for developing the market is a loss of $750/kg ($340/lb) of fiber and a total loss of $7.5 million to Dow Corning in the first year alone.

Given the typical rate of market development for composite materials, fiber manufacturers may face many years of these large losses. Clearly, one of two situations must develop for the commercialization of successful ceramic fibers: (1) high-value applications must be developed that support fiber prices of much more than $500/kg ($227/lb); or (2) very large volume applications (by composites standards) must be developed that allow fiber manufacturers to produce fibers efficiently and offer them at a low price (e.g., $500 per kilogram [$227/lb]). Given the historical rate of market development for composites and the niche applications targeted for CMCs, the first situation is more likely to develop.

Is Fiber Price Really the Key Issue?

Figure 7-2 shows that the Nextel ceramic oxide fibers are currently available within the price range of commercially available carbon fibers. That is, they cost more than low modulus carbon fibers but less than high modulus carbon fibers. There are even specialty grades of carbon fiber that sell for much more than the carbon fiber prices shown in Figure 7-2. Thus, by current standards, the Nextel family of ceramic fibers cannot truly be labeled expensive.

The SiC fibers shown in Figure 7-2 (the upper line shows the projected price level at 1,000 kilograms [2,200 lbs] per year; the lower line shows 100,000 kilograms [220,000 lbs] per year) do indeed appear to be “expensive,” well above the price line for carbon fibers. It may not be appropriate, however, to compare the cost of SiC fibers, which are produced at a rate of 100,000 kilograms (220,000 lbs) per year to the cost of carbon fibers, which are typically produced in millions of kilograms per year per manufacturer. Note that when carbon fibers were first used in aerospace, the price was several hundred dollars per kilogram in late 1960s dollars, which corresponds to much more than $1,000/kg ($455/lb) in

1997 dollars. If aerospace grade carbon fibers were made in a factory today with only tens of thousands of kilograms of capacity, the cost would rise to hundreds of dollars per kilogram.

Finally, the metal parts in aerospace applications (e.g., turbine engines) that CMCs would replace are already expensive. Given the projected prices for SiC fibers of $1,250/kg ($568/lb) (at sales of 10,000 kilograms [22,000 lbs] per year) and the weight savings and improvements in performance offered by CMCs, one must ask if cost is really the limiting factor? The answer is probably not. It seems more likely that the limiting factor is lack of confidence by potential CMC end users that the application will be successful and reluctance to incur the initial costs of implementation.

Improving Performance vs. Lowering Prices

Given the difficulties of fiber manufacturing (high fixed capital cost and slow cycle times) and the low sales volume, the only way to lower prices (at low sales volumes) is to produce the fiber with much less capital equipment. Even if cycle time is dramatically improved, the only way to capitalize would be to set up a factory that could produce small volumes of fiber quickly with a small amount of equipment. After 30 years of research and development on ceramic fibers, however, there is no indication that such a development is forthcoming.

Over the past 30 years, however, the performance of ceramic fibers has continued to improve. Today's low modulus carbon fiber has a modulus that was attainable only by the highest grades of early carbon fiber. The latest version of 3M Nextel oxide ceramic fibers show thermal stability far above the Nextel grades that were first commercialized. The Hi-Nicalon SiC fibers manufactured by Nippon Carbon Company are superior to the original Nicalon fibers. It is possible, therefore, that ceramic fibers will eventually reach a level of performance that will justify their price to design engineers of thermostructural components.

System Costs

The fiber is only one of three constituents of a CMC system, which also includes an interface and a matrix. Matrix processing is clearly beyond the scope of this report, but fiber-matrix interfaces (or interphases) are not. The manufacturing cost of potential interphase materials and the processes used to apply them to fibers and preforms is not well defined or understood. Interphase coatings are not mature at this point, and the cost impact of the interphase application process should be an important consideration in future efforts to commercialize CMCs. Therefore, the committee concludes that efforts should be made to determine the impact of the cost of fiber interphases on the cost of the total CMC system.

Implementation Costs

Despite the high cost of producing fibers and composites, some applications appear to offer favorable cost/benefit ratios for incorporating CMCs. The reason these applications have not been commercialized is most likely the cost and risk of implementation. Implementation costs include all qualification costs, such as generating an engineering database, design and development costs, and the cost of gaining regulatory approval. The probability of unforeseen problems that would require additional time and money to address add a considerable risk to those attempting to qualify CMC applications. The combination of known qualification costs and a risky payback have made the incorporation of CMCs, even when applications appear to be favorable, an unacceptable business proposition.

CONCLUSIONS

High manufacturing costs are barriers to the commercialization of ceramic fibers for advanced composites. Barring a tremendous technical breakthrough, manufacturers will likely view entering the market as a highly risky investment that is more likely to lose money than make it. The up-front costs and competition versus the potential future payback presents a stark contrast. That is, a material supplier would have to invest significant capital up-front for development and capital equipment and would face certain competition from currently available, relatively inexpensive, well understood materials. In addition, the product may not work, the market may take a long time to develop, and favorable pricing and volumes may never materialize. Early producers of advanced fibers for composite materials, such as Kevlar and carbon, lost money despite the high capabilities and promise of those materials. These experiences are ominous reminders of the precarious nature of the advanced fibers business.

Despite the tremendous financial risks and, in some cases, financial losses incurred by fiber manufacturers, society has benefited significantly from the development of advanced fibers. For example, Kevlar fibers have saved lives, in bullet-proof vests for policemen, in helmets for soldiers, in rescue hoists on helicopters, but almost none of that value has been translated into profits for DuPont. Carbon fibers are making light, efficient satellites possible that will allow worldwide portable telecommunications. Despite the tremendous market value of this innovation, however, Union Carbide, the original pioneer of carbon fibers in the United States, has long since gone out of the carbon fiber business after writing off the financial losses incurred during development. The lack of short-term, or even longer-term, return on investment from fiber development makes it difficult for a commercial enterprise to justify developing advanced fibers independently.

Developers of ceramic fibers for CMCs are in a similar situation. The use of CMCs in turbine engines can both improve efficiency and lower polluting emissions. Although real value can be put on these advantages, in the form of lower electricity costs and cleaner air, it is not likely that enough of this value would be realized in the form of profits to motivate a company to single-handedly invest in making ceramic fibers a viable commercial business. Without cooperation between the commercial and governmental entities that stand to benefit from the development of advanced ceramic fibers and composites, the technology will almost certainly remain in the laboratory, and the potential benefits will not be realized.

RECOMMENDATIONS AND FUTURE DIRECTIONS

Although advanced fibers and composites offer tremendous potential value to the marketplace, historically fiber manufacturers have not realized enough profits to justify their investments. This has resulted in difficulty in maintaining a reliable fiber supply. In the absence of outside support, fiber manufacturers will continue to lose money until a viable market for CMCs develops. Because they cannot control how the market develops, however, they are in a more tenuous business position than other CMC stakeholders.

The successful commercialization of ceramic fibers will require a price level at which initial commercial sales are feasible. In other words, ceramic fibers, and ultimately CMCs, must be judged by end users to be economically and functionally viable to justify the cost of qualifying and implementing them. The price of CMCs (and therefore fibers) must be at a level that will supply the market initially (perhaps at a loss to the CMC and fiber producers) with hopes that the market will grow to the point where a profitable return on investments can be made. This condition has not occurred at the price/performance levels of currently available ceramic fibers. The committee has identified three mechanisms for improving the market potential of ceramic fibers and CMCs: (1) improving fiber performance; (2) reducing the risk of commercializing ceramic fibers; and (3) expanding the potential market.

Improving Fiber Performance

The committee has identified two models for the business development of advanced materials that might be applicable to improving the performance of ceramic fibers. The first model is creating a new material with exceptional performance properties and marketing this material to high value applications that can afford to pay the high initial price. As the market grows, prices can be lowered as a function of reduced fixed costs per unit and the development of lower value, higher volume markets. The second model is improving the performance level of an existing commercial base of technology. In this model, fixed cost investments have already been made, which allows for lower fixed costs at initial volumes.

The first model is based on the carbon fiber experience. Once the high-performance aerospace business had been established, other markets, such as racing cars, sporting goods, and industrial products, were developed. All of these applications have grown in volume as prices have come down. The second model is based on the Kevlar fiber experience, in which DuPont was skilled in polymer fiber technology prior to the development of Kevlar.

Both models have established track records in the aerospace industry, which is a well known proving ground for truly new materials. Carbon fiber, glass fiber, titanium, and even aluminum owe their initial commercialization to the aerospace industry. All of them were supported, however, by military demand that could pay high initial prices. The losses faced by the materials supplier, however, are inevitable, and only if they appear to be short-lived and not excessive will the manufacturer take the risk of supplying the market. These two models suggest several recommendations for future investment.

Given the current state of the art, neither model is producing ceramic fiber suitable for applications that would justify paying the short-run price and the high cost of implementation. The goal is to improve performance, either in a unique environment or in an environment that can leverage existing assets. Therefore, the committee recommends research that focuses on improving the properties of polycrystalline ceramic fibers, recognizing that leveraging existing assets will help reduce fixed costs.

Reducing the Risk of Commercializing Ceramic Fibers

The costs and risks of incorporating CMCs into existing applications can be addressed by obtaining data from tests of CMC components to alleviate concerns about encountering “unknowns” during materials qualification. The focus should be on bench testing and insertion programs because data from coupon tests of composites are already widely available. Thus far, the results of bench testing and field testing, such as the tests of the Dornier material in Germany (see Chapter 2), have been promising. Therefore, the committee recommends that low risk government sponsored insertion programs for CMCs be expanded to demonstrate the field performance of CMC components.

Another way to advance the commercialization of ceramic fibers is for the initial high costs of fiber production to be subsidized, thus reducing the risk incurred by fiber developers and manufacturers. In effect, this is what occurred as a result of the early military procurement of carbon fibers. The current low build rate of new military aerospace products and a procurement environment that favors lower purchase costs over higher performance do not bode well for this approach. The outright subsidization of production, without a military demand, has generally not been a policy of the United States although other countries, notably Japan, have employed this policy.

Expanding the Potential Market

CMCs are targeted largely toward applications in turbine engines. In terms of material consumption, this is a relatively small market. Because of the large production volumes needed to support fiber manufacture, every potential outlet for the use of ceramic fibers should be investigated. Multiple applications must be developed because individual applications can constitute only a small part of the production necessary to support the development and manufacture of advanced ceramic fibers.

8

Recommendations and Future Directions

The principle focus of this study is on two of the three constituent phases of CMCs, ceramic fibers and the fiber-matrix interface (e.g., fiber coatings). The committee has formulated many specific recommendations regarding ceramic fibers and coatings for overcoming the challenges to implementing these promising materials. These recommendations were presented throughout the body of the report. The key overarching research priorities are presented here along with discussions of their anticipated impact on the field. The committee believes that these priorities are crucial to moving CMC technology forward and, ultimately, to the widespread application of CMCs. Although the focus of this report is on high-temperature ceramic fibers and coatings, the committee believes that a database of CMC properties is necessary for the establishment of research goals and performance criteria to facilitate the development of better fibers and coatings for future CMCs.

ENGINEERING DATA

Assessing the state of the art of CMCs, including ceramic fibers and coatings, requires a thoughtful definition of performance requirements and a subsequent comparison of these requirements to current capabilities (Chapter 2 and Chapter 3). A general lack of substantiation through field experience has, however, prevented the committee from establishing a clear understanding of how CMCs will perform and how they will age in service. Without operational experience, it has been impossible to calibrate knowledge with analytical performance models. Performance requirements must be made available to those responsible for meeting them, and the evaluation of composite performance must include tests of CMC components in their operating environments. Similar in-service component testing has been done for other structural composite systems, such as Kevlar-49-reinforced epoxy fairings and graphite-reinforced epoxy ailerons. Service experience would enable the establishment of CMC design guidelines that could be included in reference works like the MIL 17 Composite Materials Handbook, Ceramic Matrix Composites (MIL-HDBK-17), which is currently under development.

Recommendation 1. An engineering database for actual (as opposed to model) CMCs should be produced and disseminated. Producing the database will require the following steps:

- existing nonclassified data that is not broadly accessible because of its association with classified or restricted studies be made generally available (in particular, the committee recommends that, wherever possible, agency owned engineering data be made accessible and that new programs avoid restricting data)
- data that is currently classified be reassessed to determine if it can be declassified and, if so, that it be made more generally available
- low risk, government sponsored insertion programs for CMCs be expanded to demonstrate the field performance of CMC components
- standardized tests for obtaining engineering data on CMCs be instituted or developed.

The committee anticipates that following this recommendation would facilitate the design of better fibers and coatings while simultaneously increasing confidence in the use of CMCs. Researchers would be able to determine when ceramic fibers and coatings limit CMC properties and thus focus materials research to overcome these limitations. Design engineers would gain confidence in using CMCs when data is available on CMC component performance in operating environments (i.e., field tests). If CMCs are demonstrated to satisfy a need or outperform existing materials, they should begin to gain experience in the market. This would establish a foundation for breaking the market size-cost dilemma that has hindered investment in research and development in production facilities for high-temperature ceramic fibers and coatings.

In addition to facilitating the acceptance of CMCs by designers, field tests will also determine CMC component degradation mechanisms and life-failure modes in operational environments. On the basis of these tests, promising composite systems can be refined, and less viable CMCs can be vetted.

FIBER COATINGS

Adequate fiber coatings are requisite for providing damage tolerance (toughness) to CMCs. Fiber coatings also protect fibers from environmental attack during composite fabrication and use. Fiber coatings must demonstrate chemical and mechanical stability in high-temperature corrosive environments in order to maintain the necessary fiber-coating-matrix debonding characteristics for damage tolerance in the composite. Unfortunately, the development of interfacial coatings has lagged behind the development of ceramic fibers. Therefore, the widespread use of CMCs has been limited, to a large extent, by inadequate fiber coatings.

Current fiber coatings either have inadequate oxidation resistance or are not stable with fibers and matrices at elevated temperatures. Generally, these limitations result in degradation of the strength and toughness of the composites during use. The issues for coatings for non-oxide fibers differ from issues for oxide fibers and are discussed separately below.

Coatings for Non-Oxide Fibers

Although tough, thermally stable, non-oxide ceramic composites have only been demonstrated with carbon or BN fiber coatings, oxidation of the fiber-coating-matrix interface (i.e., pesting) is one of the major life-limiting issues preventing the widespread use of non-oxide ceramic composites. Pesting is particularly prevalent at intermediate temperatures (e.g., 700 to 900°C [1,292 to 1,652°F]) and occurs when the interface is exposed to an oxidizing environment via matrix cracks that allow atmospheric gases to come into contact with fiber coatings.

Recommendation 2a. Concepts should be pursued that enable high durability CMCs with cracked matrices at the temperatures where pesting is prevalent. Future development should be directed toward a system approach that includes improving the oxidation resistance of fiber coatings—in dry and moist atmospheres—and “sealing” matrix cracks as they form. Regenerative in-situ coatings should also be investigated.

The development of oxidation-resistant coatings that maintain the necessary debond characteristic for non-oxide fibers would enable the development of CMCs suitable for applications that demand longer component lifetimes, such as heat exchangers and thermally loaded gas turbine engine components. Furthermore, efficient matrix crack sealing mechanisms (particularly at the “pest” temperature) would also enable the use of CMCs. Finally, regenerative in-situ coatings could provide damage tolerance after initial oxidation of the fiber-matrix interface, provided that the coating has sufficient debond characteristics with SiO_2, the oxidation product of Si-based non-oxide ceramics (e.g., SiC).

Coatings for Oxide Fibers

The development of ceramic oxide composites has lagged behind the development of non-oxide composites because of the poor creep resistance of oxide fibers (compared to SiC fibers) and because of the lack of adequate oxide fiber coatings that promote fiber-matrix debonding. Recent advances in creep-resistant oxide fibers and progress on interface control has improved the potential for oxide ceramic composites in industrial and defense applications. However, an effective coating for oxide fibers that provides a weak fiber-matrix interface (and therefore tough composite behavior) remains to be demonstrated. As was discussed in Chapter 6, all oxide coating concepts discussed in the literature have been demonstrated with model systems rather than actual composite systems.

Recommendation 2b. Coating approaches that promise to provide damage tolerant oxide composites should be evaluated to prove or disprove their viability. Based on the preliminary results discussed in Chapter 6, the committee has concluded that research should be focused on the following areas: weakly bonded, thermally stable oxide coatings (e.g., rare-earth phosphates of the general formula $Me^{3+}PO_4$); and the development of oxide composites that do not require fiber coatings (e.g., porous matrices).

The impact of developing a viable interface for oxide CMCs would be twofold. First, it would enable near-term implementation of CMCs that are not susceptible to oxidative degradation for intermediate-temperature or intermediate-performance applications. Second, the performance of oxide CMCs would no longer be limited by the fiber-matrix interface. Therefore, future advancements in oxide fiber capabilities could be readily utilized in CMCs.

DEVELOPMENT OF OXIDE FIBERS

Ceramic oxide fibers are attractive because they are inherently resistant to oxidation and, therefore, are not susceptible to oxidative embrittlement. They have higher temperature limitations (e.g., T>1,000°C [1,832°F]), however, associated with creep and microstructural instability. This is problematic because oxide fibers must resist creep and maintain microstructural stability in order to be successfully used in high-temperature applications. For example, during CMC component service life, grain growth at the highest use temperature should be less than ~ 20 percent in order to limit strength reduction to less than 10 percent. Furthermore, fiber strains greater than ~ 1 percent are unacceptable because attendant composite distortions compromise attachments and dimensional tolerance. Work to address these performance requirements is ongoing.

Ceramic fibers consisting of mullite and alumina mixtures have demonstrated creep strengths considerably greater than the creep strengths observed in single-phase alumina or mullite fibers (Chapter 3). The mechanism by which multiphase ceramic oxide fibers resist creep rupture is not understood, however, although it is known that two-phase mixtures (in general) exhibit less grain growth than single-phase materials and, therefore, tend to be more microstructurally stable. The addition of yttrium and other oversized isovalent cations to alumina has also been shown to enhance creep strength. The addition of SiC nanoparticles to bulk samples of alumina has been shown to enhance the creep strength of alumina, particularly when the SiC particles are preferentially located at the alumina grain boundaries.

Recommendation 3. The results discussed in Chapter 3 and Chapter 5 suggest that continued study and increased understanding of dual-phase microstructures, solutes (e.g., yttria in alumina) and nanoparticle reinforcement will lead to improvements in the high-temperature creep resistance, rupture strength, and stability of oxide fibers. Therefore, the committee recommends that research be directed towards: establishing the mechanism(s) by which SiC nanoparticle dispersions inhibit creep in bulk oxide ceramics (including developing oxide nanoparticle systems, analogous to the alumina-SiC nanocomposite system, that can be applied in an oxide fiber); determining the mechanism by which certain solutes lower the creep rate of bulk polycrystalline oxides (e.g., yttria in alumina) and applying them to oxide fibers; and using multiphase microstructures to promote increased high-temperature microstructural stability (e.g., resistance to grain growth) and increased creep resistance in oxide fibers.

The committee believes that oxide fibers with improved creep resistance will enable the use of oxide CMCs in higher temperature applications (e.g., gas turbine combustors and heat exchangers) provided that suitable oxide fiber coatings are developed in parallel. Improved oxide fibers would allow higher operating temperatures and, therefore, greater efficiencies than are attainable with current thermostructural materials.

DEVELOPMENT OF NON-OXIDE FIBERS

Most work on CMCs has been done on non-oxide materials, particularly SiC-fiber-reinforced SiC CMCs (SiC/SiC) with carbon or BN fiber interfacial coatings. These composites have attractive high-temperature properties, such as good creep resistance and microstructural stability. They also have high thermal conductivity and low thermal expansion, leading to good thermal stress resistance. Because of their high thermal conductivity, non-oxide CMCs are attractive for thermally loaded components, such as combustor liners, vanes, blades, and heat exchangers. The most pressing limitation of these materials is oxidative embrittlement at the fiber-matrix interface (addressed in Recommendation 2). Although non-oxide CMCs are not limited by the fibers themselves, some recent improvements in non-oxide fiber performance nonetheless warrant further attention.

One promising development is an amorphous Si-B-N-C fiber produced using a novel polymer precursor technology, for which high strength, high stiffness, and high-temperature strength retention and creep resistance have been reported. In terms of polycrystalline non-oxide fibers, preliminary results suggest that incorporating up to several weight percent boron in a Si-C-O or Si-C-O-(Ti) fiber produces a stoichiometric polycrystalline, high strength, high modulus β-SiC (or β-SiC + TiB_2) fiber.

Recommendation 4. The key areas of investigation recommended for non-oxide fibers are recently developed amorphous non-oxide fibers, such as Si-B-N-C fibers, to verify their stability and creep resistance and the utility of the reported in-situ coatings, and microstructural refinements to improve performance in crystalline non-oxide fibers.

The development of higher temperature, higher performance fibers will enable the use of CMCs in long service-life, high-temperature applications (e.g., thermally loaded gas turbine engine components and heat exchangers for externally fired combined cycle power systems) if the problems of interface durability are solved in parallel.

MANUFACTURING COSTS

The manufacture of fibers has three unusual cost issues: (1) fibers have a very high length per unit mass; (2) the machinery used for fiber production is highly specialized; (3) materials to be formed into fibers require special treatments or additives. The cost of most materials is scaled by cost per unit of mass. Fibers have a tremendous amount of length per unit mass, and processing that length incurs additional cost relative to mass. The cost premium for engineering materials that have been “stretched” to fiber diameters is significant, especially in the linear density range of interest for composite materials.

Fiber prices could be reduced, however, if there was a market-driven increase in production volume, thus lowering the fixed cost per unit. Current fiber manufacturers and independent consultants have conducted studies to predict fiber prices and cost levels. Exact cost predictions have been elusive, however, because of the difficulty of precisely forecasting future yields and process improvements. Furthermore, prices will depend upon the pricing policies of individual manufacturers as much as on actual costs.

The fact that an increase in the market for fibers would reduce the cost of ceramic fibers raises the question of why the ceramic fiber market hasn't grown already. Ceramic fibers are currently available within the price range of commercially available carbon fibers and, by current standards, cannot be labeled expensive. Furthermore, the development costs of specialty materials for jet engines have historically been readily justified for rather modest increases in temperature capability. But cost alone has not kept ceramic fibers or CMCs from entering the market. Significant efforts must still be directed towards increasing the performance capabilities of these materials. The following guidelines can help reduce development and manufacturing costs.

Using capital non-intensive equipment for fiber production will lower fixed costs, thus lowering cost per unit. Processes that leverage past investments can further reduce fixed costs. The development and use of less expensive fiber precursors also offer a potential reduction in variable costs. Finally, because applying coatings to fibers via CVD adds considerably to the final cost of CMCs, liquid precursor coatings or coatings developed on the fiber in-situ (without a separate processing step) can also lower costs.

Recommendation 5. Efforts to reduce the costs of fiber and coating processing should be directed toward using capital non-intensive equipment; developing less expensive fiber precursors; using processes that leverage past investments; and developing in-situ and liquid precursor coatings.

A broader, more stable vendor base for fibers and coatings could probably be established if costs could be reduced. Lower costs for fibers and coatings would make CMCs more attractive to a larger variety of end-users.

PRIORITIES

The five recommendations above fall into three categories. Recommendation 1 addresses increasing confidence in existing CMC technology. By providing engineering designers with the information they need to make materials selection decisions, it is anticipated that applications for CMCs will increase. Thus the committee places a high priority on this recommendation.

Recommendations 2, 3, and 4 fall into the second category, performance. As a group, these recommendations, which are also considered to be of high priority, are listed in the order of decreasing priority. The committee found that fiber coatings and other interface technologies for both non-oxide and oxide systems are the major technical limitation to CMC development. That is, improved fiber coatings are needed to enable CMCs to meet the higher temperature performance requirements for many applications. Recommendation 2 has the highest priority in this category because even though the oxidation resistance of oxide fibers is attractive the creep resistance of these fibers must be improved. Recommendation 3 addresses this priority. Recommendation 4 (regarding non-oxide fibers) has a lower priority because for many applications adequate properties have already been attained in non-oxide fibers. Therefore, the committee concluded that resources directed toward improving the properties of fiber coatings, and oxide fibers was more important. However, the committee is satisfied that the preliminary properties reported for Si-B-N-C amorphous fibers are sufficiently attractive to stimulate the work needed to verify them.

Although cost is an important issue, Recommendation 5 is considered lower in priority. The committee concluded that at the current stage of technology performance rather than costs have limited many CMC applications, making improved properties a higher priority than lower costs.

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DAVID W. JOHNSON (chair) is head of metallurgy and ceramics research at Bell Laboratories, Lucent Technologies, and adjunct professor of materials science at Stevens Institute of Technology. His research activities include fabrication and processing of spinel ferrites and sol-gel processing of glass and ceramics. He is a fellow of the American Ceramic Society, has chaired an American Society of Testing and Materials subcommittee, and is a member of several other professional societies. Dr. Johnson has won the Taylor Lecture Award from Pennsylvania State University, the Fulrath Award from the American Ceramic Society, and the Ross Coffin Purdy Award for the best paper in ceramic literature. Dr. Johnson was elected to the National Academy of Engineering in 1993 for his discovery of new compositions and processing techniques and their transfer to manufacturing.

ANTHONY G. EVANS is the Gordon McKay Professor of Materials Engineering at Harvard University. His research interests include the mechanical properties of brittle materials particularly the fracture of ceramics under conditions of impact; thermal and mechanical stress; and failure prediction based on nondestructive evaluation. He is a recipient of the American Ceramic Society's Ross Coffin Purdy Award and has authored and co-authored several publications. Dr. Evans is a member of the National Materials Advisory Board and has served on several National Research Council committees. Dr. Evans was elected to the National Academy of Engineering in 1997 for his contributions to the development and understanding of structural materials.

RICHARD W. GOETTLER has been active in the development of ceramic matrix composites through his employment for the last five years as a research engineer at McDermott Technology Incorporated (formerly Babcock & Wilcox), and the previous three years at McDonnell Douglas Aircraft Company. He is making advances in many of the key enabling technologies, including cost processing routes and the tailoring of fiber-matrix interfaces, which are necessary for the successful implementation of ceramic matrix composites in the defense and commercial industries. Mr. Goettler's work on engineering nonreactive, weak fiber-matrix interfaces makes him cognizant of the chemical requirements of fibers, in combination with the interface and matrix materials. In addition, he has worked with turbine suppliers to assess fiber performance requirements for an oxide continuous-fiber ceramic composite combustor.

MARTIN HARMER is the Alcoa Foundation Professor of Materials Science and Engineering and the director of the Materials Research Center at Lehigh University. He has played a major role in initiating and developing the ceramic research program at Lehigh University and has published more than 100 articles in the general area of ceramic processing and microstructure-property relations in ceramics. Dr. Harmer's current research interests include the design of novel multiphase microstructures for improved mechanical performance of ceramics. In addition to several other honors, he is a former National Science Foundation Presidential Young Investigator, a fellow of the American Ceramic Society, twice the recipient of the Rowland B. Snow Award from the American Ceramic Society, and a recent recipient of the National Science Foundation's Creativity Award. Dr. Harmer is a past chair of the Gordon Conference on Solid State Studies in Ceramics, was a representative at the United States-Japan Joint Seminar on Ceramic Processing in 1990, and is involved in several other professional activities.

JONATHAN LIPOWITZ, Dow Corning Corporation, has more than 30 years of industrial research experience. Among other topics, his research interests include the micro- and nanostructure of ceramic fibers derived from organosilicon precursors and polycrystalline silicon carbide fibers derived from organosilicon polymers. Dr. Lipowitz has nearly 20 U.S. patents and more than 50 publications to his credit. He is a member of several professional and honorary societies, including the American Ceramic Society, the Materials Research Society, Sigma Xi, and the New York Academy of Science.

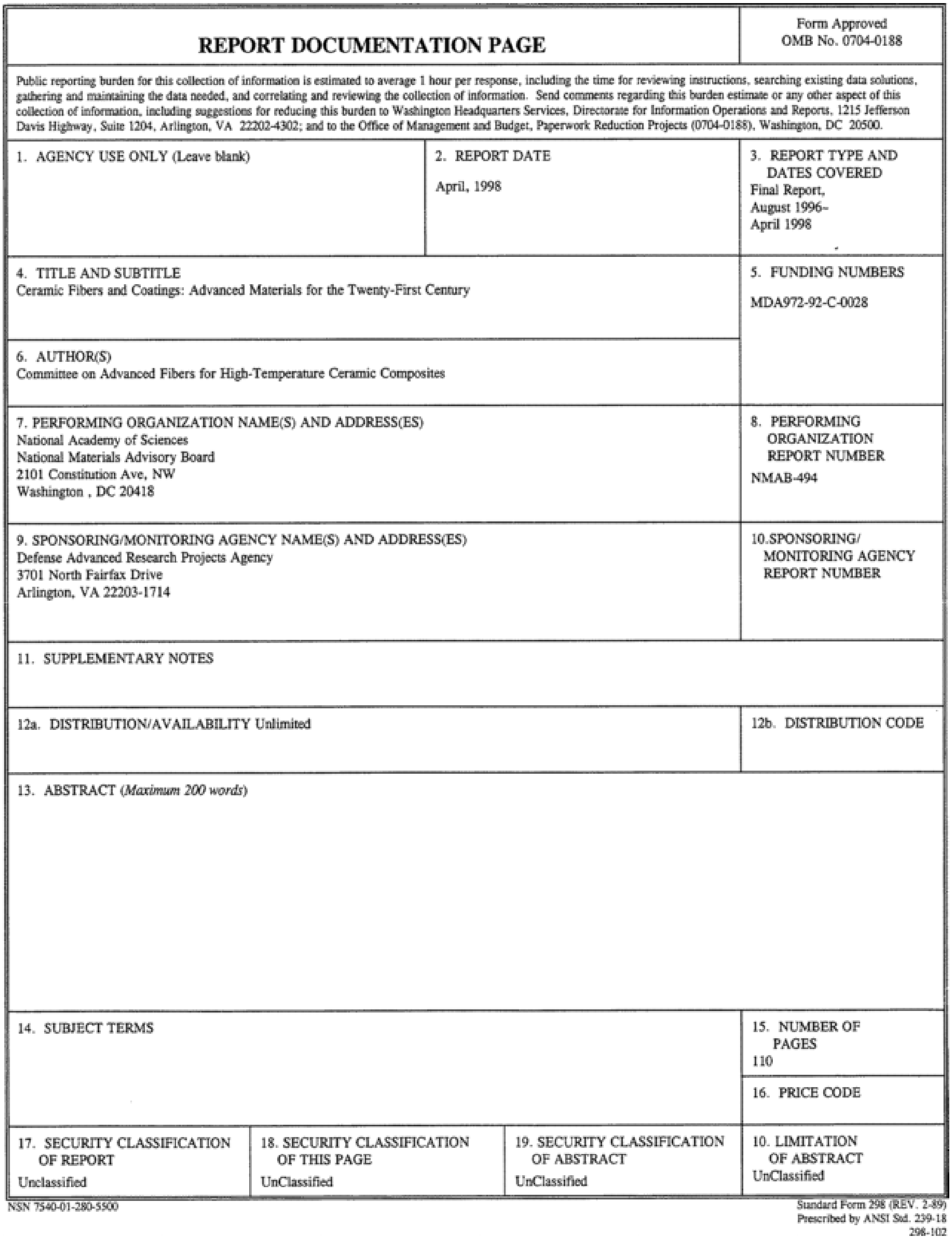
KRISHAN L. LUTHRA, General Electric Corporation, has 20 years of corporate research and development experience in high-temperature materials. His research interests include thermodynamics and kinetics of high-temperature reactions and corrosion at elevated temperatures, particularly in the context of fiber-matrix interfaces in high-temperature composites. Dr. Luthra is a member of the Electrochemical Society, the Metallurgical Society, and the American Institute of Mining, Metallurgy, and Petroleum Engineers. He is a past research fellow at the Department of Metallurgy and Materials Science, University of Pennsylvania.

PAUL PALMER has more than 10 years of experience in business and product development, marketing, planning, and related analysis with aerospace and related industries. His current emphasis is on commercializing new materials technologies at Thermo Fibergen. As a project manager at IBIS Associates, Inc., Mr. Palmer led consulting engagements with aerospace companies and government-industry consortia for advanced technology commercialization. Projects have included studies in the manufacturing costs of advanced ceramic fibers and their composites for the Integrated High Performance Turbine Engine Technology Consortium. He also has experience performing airframe structural analyses for General Dynamics Corporation (now the Tactical Aircraft Division of Lockheed-Martin).

KARL PREWO is manager of materials sciences at United Technologies Research Center. In this position, he directs a research group in the area of ceramics, metals and metal matrix, and ceramic matrix composites. He has more than 20 years of industrial research experience and has written many articles in the area of fiber-reinforced metals and ceramics. He is a recipient of United Technologies' highest award for engineering achievement, the George Mead Medal, the Medal of Excellence in Composite Materials from the University of Delaware Center of Composite Materials, and is a fellow of the American Society for Materials. Dr. Prewo has served on two previous National Research Council committees.

RICHARD E. TRESSLER is the head of the Department of Materials Science and Engineering at Pennsylvania State University. His research interests include the fabrication and mechanical behavior of structural ceramic fibers and composite materials, fracture and strengthening mechanisms for structural ceramic materials, and integrated circuit processing and properties. Dr. Tressler is the recipient of the Science Achievement Medal from the U.S. Air Force and the Pace-Schwartz Walter Award from the American Ceramic Society. He is a fellow of the American Ceramic Society and a member of the Metal-lurgical Society of the American Institute of Mining, Metal-lurgical, and Petroleum Engineers, the Electrochemical Society, Sigma Xi, and Keramos. Dr. Tressler has also served on five previous National Research Council committees.

DAVID WILSON is a research specialist with 3M and has more than 10 years of research and development experience in the synthesis of new ceramic fibers using sol-gel techniques and is the inventor of the Nextel™ 610 and Nextel™ 720 ceramic fibers. His experience includes the development of novel fiber precursor formulations, continuous fiber processing, and characterization of ceramic fibers at room and elevated temperatures. Current research activities include preceramic polymer-derived SiC fibers and MOCVD coating and composite fabrication for the Mullite Matrix Composite Consortium Program. Mr. Wilson holds four patents and is the author of several publications.



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