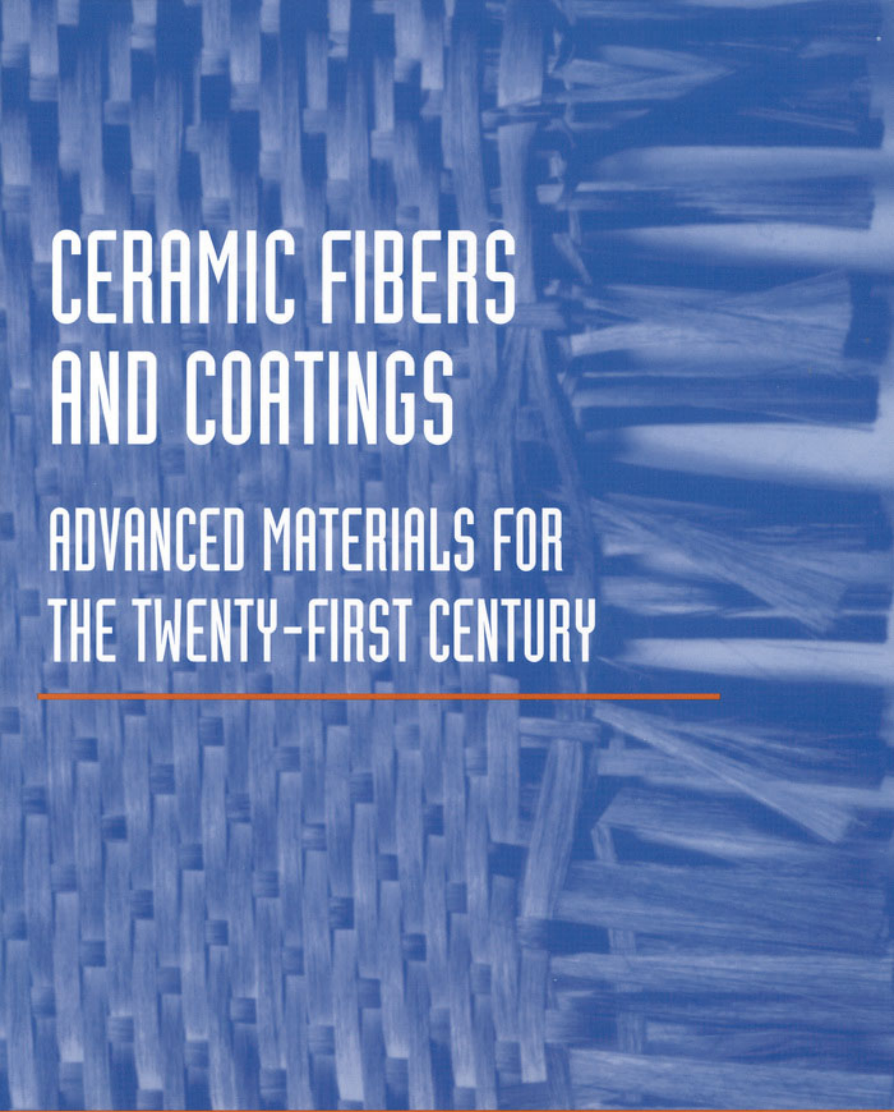

CERAMIC FIBERS AND COATINGS

ADVANCED MATERIALS FOR THE TWENTY-FIRST CENTURY

NATIONAL RESEARCH COUNCIL

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

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

Publication NMAB-494

National Academy Press
Washington, D.C. 1998

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

The National Academy of Sciences is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. Upon the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Bruce M. Alberts is president of the National Academy of Sciences.

The National Academy of Engineering was established in 1964, under the charter of the National Academy of Sciences, as a parallel organization of outstanding engineers. It is autonomous in its administration and in the selection of its members, sharing with the National Academy of Sciences the responsibility for advising the federal government. The National Academy of Engineering also sponsors engineering programs aimed at meeting national needs, encourages education and research, and recognizes the superior achievements of engineers. Dr. William A. Wulf is president of the National Academy of Engineering.

The Institute of Medicine was established in 1970 by the National Academy of Sciences to secure the services of eminent members of appropriate professions in the examination of policy matters pertaining to the health of the public. The Institute acts under the responsibility given to the National Academy of Sciences by its congressional charter to be an adviser to the federal government and, upon its own initiative, to identify issues of medical care, research, and education. Dr. Kenneth I. Shine is president of the Institute of Medicine.

The National Research Council was organized by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and advising the federal government. Functioning in accordance with general policies determined by the Academy, the Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in providing services to the government, the public, and the scientific and engineering communities. The Council is administered jointly by both Academies and the Institute of Medicine. Dr. Bruce M. Alberts and Dr. William A. Wulf are chairman and vice chairman, respectively, of the National Research Council.

This study by the National Materials Advisory Board was conducted under Contract No. MDA972-92-C-0028 with the Defense Advanced Research Projects Agency. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors(s) and do not necessarily reflect the views of the organizations or agencies that provided support for the project.

Available in limited supply from:
National Materials Advisory Board
2101 Constitution Avenue, N.W.
HA-262
Washington, DC 20418
202-334-3505
nmab@nas.edu

Additional copies are available for sale from: National Academy Press Box 285 2101 Constitution Ave., N.W. Washington, DC 20055
800-624-6242 202-334-3313 (in the Washington Metropolitan Area) http://www.nap.edu
Library of Congress Catalog Card Number: 98-84558
International Standard Book Number: 0-309-05996-8

Cover: Eight-harness woven cloth. Each “thread” is a single tow containing as many as 800 individual filaments. Source: Dow Corning Corporation.

Copyright© 1998 by the National Academy of Sciences. All rights reserved.

Printed in the United States of America.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

COMMITTEE ON ADVANCED FIBERS FOR HIGH-TEMPERATURE CERAMIC COMPOSITES

DAVID W. JOHNSON (chair), Lucent Technologies, Murray Hill, New Jersey
ANTHONY G. EVANS, Harvard University, Cambridge, Massachusetts
RICHARD W. GOETTLER, McDermott Technology-Lynchburg Research Center, Lynchburg, Virginia
MARTIN P. HARMER, Lehigh University, Bethlehem, Pennsylvania
JONATHAN LIPOWITZ, Dow Corning Corporation, Midland, Michigan
KRISHAN L. LUTHRA, General Electric Corporate Research and Development, Schenectady, New York
PAUL D. PALMER, Thermo Fibergen, Bedford, Massachusetts
KARL M. PREWO, United Technologies Research Center, East Hartford, Connecticut
RICHARD E. TRESSLER, Pennsylvania State University, University Park
DAVID WILSON, 3M Corporation, St. Paul, Minnesota

National Materials Advisory Board Staff

SANDRA HYLAND, senior program manager
CHARLES T. HACH, research associate
JANICE M. PRISCO, project assistant
ROBERT E. SCHAFRIK, director (until November 1997)
RICHARD CHAIT, director (after February 1998)

Government Liaison Representatives

ERNEST CHIN, Army Research Laboratory, Aberdeen Proving Ground, Maryland
JAMES A. DICARLO, NASA Lewis Research Center, Cleveland, Ohio
STEVEN FISHMAN, Office of Naval Research, Arlington, Virginia
RONALD KERANS, Wright-Patterson Air Force Base, Ohio
S. CARLOS SANDAY, Naval Research Laboratory, Washington, D.C.
MERRILL SMITH, U.S. Department of Energy, Washington, D.C.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

NATIONAL MATERIALS ADVISORY BOARD

ROBERT A. LAUDISE (chair), Lucent Technologies, Murray Hill, New Jersey
G.J. ABBASCHIAN, University of Florida, Gainesville
MICHAEL I. BASKES, Sandia/Livermore National Laboratory, Livermore, California
JESSE (JACK) BEAUCHAMP, California Institute of Technology, Pasadena
FRANCIS DiSALVO, Cornell University, Ithaca, New York
EARL DOWELL, Duke University, Durham, North Carolina
EDWARD C. DOWLING, Cyprus Amax Minerals Company, Englewood, Colorado
THOMAS EAGAR, Massachusetts Institute of Technology, Cambridge
ANTHONY G. EVANS, Harvard University, Cambridge, Massachusetts
JOHN A. GREEN, The Aluminum Association, Washington, D.C.
SIEGFRIED S. HECKER, Los Alamos National Laboratory, Los Alamos, New Mexico
JOHN H. HOPPS, JR., Morehouse College, Atlanta, Georgia
LISA KLEIN, Rutgers, The State University of New Jersey, Piscataway, New Jersey
MICHAEL JAFFE, Hoechst Celanese Corporation, Summit, New Jersey
SYLVIA M. JOHNSON, SRI International, Menlo Park, California
HARRY LIPSITT, Wright State University, Yellow Springs, Ohio
ALAN G. MILLER, Boeing Commercial Airplane Group. Seattle, Washington
RICHARD S. MULLER, University of California, Berkeley
ROBERT C. PFAHL, Motorola, Schaumburg, Illinois
ELSA REICHMANIS, Lucent Technologies, Murray Hill, New Jersey
KENNETH L. REIFSNIDER, Virginia Polytechnic Institute and State University, Blacksburg
JAMES WAGNER, Case Western Reserve University, Cleveland, Ohio
BILL G.W. YEE, Pratt and Whitney, West Palm Beach, Florida

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

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

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

Acknowledgments

The Committee on Advanced Fibers for High-Temperature Ceramic Composites gratefully acknowledges the information provided by the following individuals: Hans-Peter Baldus, Bayer AG; Ted Besmann, Oak Ridge National Laboratory; John Brennan, United Technologies Research Center; Mike Burke, Westinghouse; Phillip Craig, DuPont Lanxide, Inc.; Said El-Rahaiby, Department of Defense-Ceramics Information Analysis Center; Dick Enghalt, Synterials; Doug Freitag, Dupont Lanxide; Hans Friedericy, AlliedSignal; Randy Hay, Wright Patterson Laboratory; Bill Hong, Institute for Defense Analysis; K. William Householder, Dow Corning; Hiroshi Ichikowa, Nippon Carbon Company; Kioyshi Kumagawa, UBE Industries; Withold Kowbel, Materials and Electrochemical Research Group; Gary Linsey, Pratt and Whitney; Richard Lowden, Oak Ridge National Laboratory; Michael Millard, General Electric; Peter Morgan, Rockwell International; Koichi Niihara, Osaka University; Paul Nordine, Containerless Research Corporation; John Porter, Rockwell International; Michael Sacks, University of Florida; Andrew Szweda, Dow Corning; Michio Takeda, Nippon Carbon Company; Tom Tompkins, 3M Company; Richard Wagner, McDermott Technologies, Inc.; and Richard Weber, Containerless Research Corporation.

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.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

Contents

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

Tables, Figures, and Boxes

TABLES

FIGURES

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

BOXES

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

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

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

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.

---

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

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.

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.

About this PDF file: This new digital representation of the original work has been recomposed from XML files created from the original paper book, not from the original typesetting files. Page breaks are true to the original; line lengths, word breaks, heading styles, and other typesetting-specific formatting, however, cannot be retained, and some typographic errors may have been accidentally inserted. Please use the print version of this publication as the authoritative version for attribution.