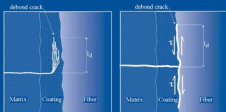


HANDBOOK OF CERAMIC COMPOSITES

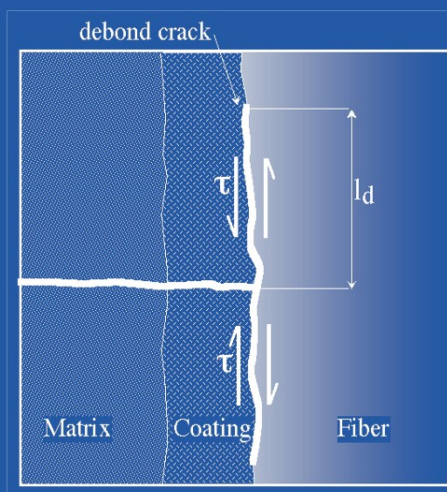
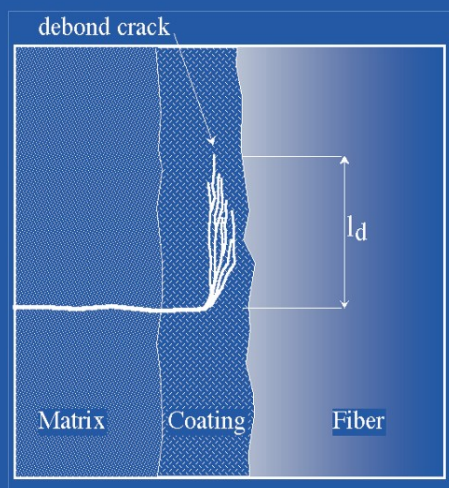
Edited by
Narottam P. Bansal



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*NASA Glenn Research Center
USA*



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Preface

Metallic materials, including superalloys, have reached the upper limit in their use temperatures. Alternative materials, such as ceramics, are needed for significant increase in service temperatures. Advanced ceramics generally possess, low density, high strength, high elastic modulus, high hardness, high temperature capability, and excellent chemical and environmental stability. However, monolithic ceramics are brittle and show catastrophic failure limiting their applications as structural engineering materials. This problem is alleviated in ceramic-ceramic composites where the ceramic matrix is reinforced with ceramic particles, platelets, whiskers, chopped or continuous fibers. Ceramic matrix composites (CMCs) are at the forefront of advanced materials technology because of their light weight, high strength and toughness, high temperature capabilities, and graceful failure under loading. This key behavior is achieved by proper design of the fiber-matrix interface which helps in arresting and deflecting the cracks formed in the brittle matrix under load and preventing the early failure of the fiber reinforcement.

Ceramic composites are considered as enabling technology for advanced aeropropulsion, space propulsion, space power, aerospace vehicles, space structures, ground transportation, as well as nuclear and chemical industries. During the last 25 years, tremendous progress has been made in the development and advancement of CMCs under various research programs funded by the U.S. Government agencies: National Aeronautics and Space Administration (NASA), Department of Defense (DoD), and Department of Energy (DOE). Some examples are NASA's High Temperature Engine Materials Technology Program (HiTEMP), National Aerospace Plane (NASP), High Speed Civil Transport (HSCT), Ultra Efficient Engine Technology (UEET), and Next Generation Launch Technology (NGLT) programs; DoD's Integrated High Performance Turbine Engine Technology (IHPTET), Versatile Affordable Advanced Turbine Engines (VAATE), and Integrated High Performance Rocket Propulsion Technology (IHPRPT) programs; and DOE's Continuous Fiber Ceramic Composites (CFCC) program. CMCs would find applications in advanced aero-jet engines, stationary gas turbines for electrical power generation, heat exchangers, hot gas filters, radiant burners, heat treatment and materials growth furnaces, nuclear fusion reactors, automobiles, biological implants, etc. Other applications of CMCs are as machinery wear parts, cutting and forming tools, valve seals, high precision ball bearing for corrosive environments, and plungers for chemical pumps. Potential applications of various ceramic composites are described in individual chapters of the present handbook.

This handbook is markedly different than the other books available on Ceramic Matrix Composites. Here, a ceramic composite system or a class of composites has been covered in a separate chapter, presenting a detailed description of processing, properties, and

applications. Each chapter is written by internationally renowned researchers in the field. The handbook is organized into five sections. The first section “**Ceramic Fibers**” gives details of commercially available oxide fibers and non-oxide (silicon carbide) fibers which are used as reinforcements for ceramic matrices in two separate chapters. The next section “**Non-oxide/Non-oxide Composites**” consists of seven chapters describing various composite systems where both the matrix and the reinforcement are non-oxide ceramics. Special attention has been given to silicon carbide fiber-reinforced silicon carbide matrix (SiC_f/SiC) composite system because of its great commercial importance. This CMC system has been covered in three separate chapters as it has been investigated extensively during the last thirty years and is the most advanced composite material system which is commercially available. The section “**Non-oxide/Oxide Composites**” comprises of six chapters presenting the details of various composites which consist of oxide matrix and non-oxide reinforcement or vice versa. The composites where both the matrix and the reinforcements are oxides are covered in three chapters in the section “**Oxide/Oxide Composites**”. The final section “**Glass and Glass-Ceramic Composites**” contains three chapters describing composites where the matrix is either glass or glass-ceramic.

This handbook is intended for use by scientists, engineers, technologists, and researchers interested in the field of ceramic matrix composites and also for designers to design parts and components for advanced engines and various other industrial applications. Students and educators will also find the information presented in this book useful. The reader would be able to learn state-of-the-art about ceramic matrix composites from this handbook. Like any other compilation where individual chapters are contributed by different authors, the present handbook may have some duplication of material and non-uniformity of symbols and nomenclature in different chapters.

I am grateful to all the authors for their valuable and timely contributions as well as for their cooperation during the publication process. Thanks are due to Mr. Gregory T. Franklin, Senior Editor, Kluwer Academic Publishers, for his help and guidance during the production of this handbook. I would also like to express my gratitude to Professor Robert H. Doremus for helpful suggestions and valuable advice.

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Part I

Ceramic Fibers

1

Oxide Fibers

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ABSTRACT

Oxide fibers find uses both as insulation and as reinforcements. Glass fibers, based on silica, possess a variety of compositions in accordance with the characteristics desired. They represent the biggest market for oxide fibers. Unlike other oxide fibers, glass fibers are continuously spun from the melt and are not used at temperatures above 250°C. Short oxide fibers can be melt blown whilst other aluminasilicate and alumina based continuous fibers are made by sol-gel processes. Initial uses for these fibers were as refractory insulation, up to 1600°C, but they are now also produced as reinforcements for metal matrix composites. Continuous oxide fibers are candidates as reinforcements for use up to and above 1000°C.

1.0. INTRODUCTION

Synthetic fibers, both organic and inorganic, were developed in the twentieth century and represent an enormous market. Their development has had a marked effect on the textile industry, initially in long established industrial nations and increasingly in developing countries. The processing and handling techniques of synthetic fibers are often related to traditional textile processes but a considerable fraction of even organic fibers are used for industrial end products. This fraction is considerably greater for inorganic fibers. More than 99% of the reinforcements of resin matrix composites are glass fibers and most of these are of one type of glass. The diameters of glass fibers are of the order of 10 μm or about one eighth the diameter of a human hair. The fineness of the filaments makes them very flexible despite the inherent brittleness and stiffness of the material. It is the development

of glass fibers which has laid the foundations for the present composite materials market. The fibers are produced as tows of continuous filaments which are then converted into many different products. The fibers can be woven by the same techniques as other continuous synthetic fibers. The fibers can also be wound around a mandrel and, impregnated with a resin, made into filament wound tubes, for example. Alternatively they can be formed into a non woven mat which can then be draped around a form and impregnated with a resin or put into a mould and impregnated. The resin then can be cured to form a structural composite material. Glass fibers can be chopped into short lengths and mixed with an uncured resin which can then be placed into a mould and formed into a structure or mixed with a resin to be injected into a mould so as to form a structure. Glass fibers are also chopped and projected with the resin against a mould to make cheap large scale structures. Glass fiber reinforced resin composites are ubiquitous materials which find uses in applications such as pipelines, parts of car bodies, boats, pressure vessels and a thousand and one other applications. It is particularly useful as it resists many corrosive environments and so is used for chemical storage tanks and for other applications for which chemical inertness is required. Glass is however limited in its use as it has a low Young's modulus, about the same as that of aluminum and it has limited high temperature capabilities. It is also sensitive to extreme variations in pH.

Glass fibers are predominantly formed with silica but also contain alumina. Fibers which are rich in alumina have been produced since the late 1940s. This type of fiber was initially produced in a low cost discontinuous form and used for refractory insulation, typically in furnace linings, and has found a very large market. Alumina is about five times stiffer than silica so that, in the form of fine filaments, it is attractive as a potential reinforcement for light alloys and even vitreous ceramics. The development of ceramic matrix composites, in the 1980s, originally based on silicon carbide based fibers, opened up other horizons to oxide fibers. Unlike SiC based fibers they were insensitive to oxidation and held out the promise of enhanced properties far above the best metal alloys and even silicon carbide ceramics. Such fibers are used as reinforcements for light alloys such as aluminum but also with matrices such as mullite.

2.0. DEVELOPMENT OF OXIDE FIBERS

The primary component of glass filaments is SiO_2 , followed by CaO , Al_2O_3 and other oxides. A number of types of glass fiber exist with different compositions according to the desired characteristics. Glass filaments have probably been formed since or before Roman times and more recently the production of fine filaments was demonstrated in Great Britain in the nineteenth century and used as a substitute for asbestos in Germany during the first World War. In the latter application molten glass was poured onto a spinning disc to produce discontinuous fibers. In 1931 two American firms, Owens Illinois Glass Co. and Corning Glass Works developed a method of spinning glass filaments from the melt through spinnerets. The two firms combined in 1938 to form Owens Corning Fiberglas Corporation. Since that time extensive use of glass fibers has been made and there are major producers in several countries. Initially the glass fibers were destined for filters and textile uses however the development of heat setting resins opened up the possibility of fiber reinforced composites and in the years following the Second World War the fiber took

a dominant role in this type of material. Today, by far the greatest volume of composite materials is reinforced with glass fibers.

The development of more refractory fibers dates from 1942 and in 1949 a patent was awarded to Babcock and Wilcox in the USA for the melt blown production of aluminosilicate filaments (1). Refractory insulation is most usually produced in the form of a felt consisting of discontinuous fibers and other non fibrous forms, depending on the manufacturing process used. The usual starting material for production is kaolin, also known as china clay. It is a natural form of hydrated aluminum silicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). An alternative route is to use mixtures of alumina and silica. The fibers are known collectively as aluminosilicate Refractory Ceramic Fibers or simply RCFs. The progressive replacement, in the earlier fibers, of silica by alumina improved their refractory characteristics but made manufacture more difficult. The fibers made from kaolin contain around 47% by weight of alumina. Shot, or non fibrillar particles, levels are high and can be of the order of 50% of product mass. These products continue to find important markets and are continuing to develop. A concern for these classes of fibers is the possibility of risks to health. This concern comes from the proven carcinogenic effects of asbestos fibers and which cause all fiber producers to take the possibility of health hazards seriously. An important consideration is the diameter of the fibers being made which if they are similar to the alveolar cellular structure of the lungs can mean that they can become blocked in the lungs. Even if no long term morbidity occurs the efficiency of the lungs would be reduced. The critical size seems to be one micron however even if no effects are proven the industry is developing low biopersistent fibers, to be used as thermal insulation. These are vitreous fibers containing calcium oxide, CaO, magnesia, MgO, and silica, SiO_2 , in variable proportions. Other oxides may be added to optimize temperature resistance or other properties. The fibers are more soluble than the traditional RCFs and would reside for less time in the lungs if inhaled.

The aluminosilicate RCF fibers are most widely used in the form of a non-woven blanket or board for furnace linings in the metallurgical, ceramic and chemical industries. An alternative refractory brick would be up to ten times heavier. The use of aluminosilicate felts allows fast heating and cooling cycles of furnaces, because of the reduced mass which has to be heated or cooled and this allows considerable cost savings to be made compared to other types of insulation.

Producing oxide fibers by sol-gel processes is more expensive than the melt blown process but greater control of the final product is possible and the fibers can be made with a much higher alumina content. Another advantage is that the precursor is spun at low temperatures before being pyrolysed. A British patent was awarded to Babcock and Wilcox in 1968 for the production of oxide fibers by this process and since then a considerable number of other companies, mostly in the USA, UK and Japan have made fibers using the sol-gel route (2). ICI developed a short fiber with a diameter of 3 μm called Saffil in 1974 (3). This fiber is 97% alumina and 3% silica and was originally developed for high temperature insulation up to 1600°C. The increased interest during the late 1970s for metal matrix composites saw Saffil used to reinforce aluminum and it remains the most widely used fibrous reinforcement for light alloys. The successful use of Saffil fiber reinforced aluminum by Toyota to replace nickel based alloy inserts to maintain oil rings in diesel engines has encouraged other firms to produce similar products.

The first alumina based continuous fiber was produced in 1974 by 3M and is sold under the name Nextel 312. It contains only 62% alumina together with boria and silica.