Handbook of Ceramic Composites

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Edited by

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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 aerojet 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, Owen 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 ($Al_2Si_2O_5(OH)_4$). An alternative route is to use mixtures of alumina and silica. The fibers are known collectively at 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.

It has an essentially amorphous structure and is limited to use below 1000°C because of the volatility of boria but it remains the foundation of the 3M Nextel range of oxide fibers. Later in that same decade DuPont produced the first continuous polycrystalline 99.9% alpha-alumina fiber called Fiber FP (4). The fiber was made by spinning in air, a slurry, composed of an aqueous suspension of α-alumina particles and aluminum salts. The as-obtained fiber was then dried and fired in two steps. The incentive for producing this fiber was the possibility of reinforcing aluminum connecting rods in, initially, Toyota engines. The fiber had the high modulus of bulk alumina and this, coupled with its relatively large grain size of around 0.5 μm and a diameter of 20 μm, meant that it could not be easily handled. The fiber had a failure strain of approximately 0.3%. Fiber FP was not developed commercially but is seen as a model fiber against which other polycrystalline oxide fibers can be compared. In an attempt to improve handleability DuPont produced a fiber, called PRD-166, containing 80% by weight of α-alumina and 20% zirconia (5). The presence of the second phase, in the form of grains of 0.1 μm, reduced the grain size of the alumina to 0.3 μm. The presence of tetragonal zirconia in bulk alumina increased room temperature strength by phase transformation toughening and also limited grain boundary mobility, grain sliding and growth at high temperatures. The zirconia phase also reduced the overall Young's modulus of the fiber. However the improvement of the tensile properties was not sufficient to allow commercial development of the PRD-166 fiber. During the 1980s and 1990s a number of companies in Japan and the USA developed oxide fibers which overcame the difficulties encountered by the fibers produced by DuPont. Sumitomo Chemicals produced the continuous Altex fiber in which the 15% of amorphous silica stabilized the alumina grains in the γ-phase which meant that the grain size was 25 nm (6). The Altex fiber had only half the Young's modulus of a pure, dense α-alumina fiber and so could be more easily handled and woven. Mitsui Mining produced the Almax fiber, which in composition and grain size, was very similar to the Fiber FP, however it had only half its diameter (7). The reduction in diameter meant an eight times increase in flexibility and so the fiber could be woven. Later 3M produced the Nextel 610 fiber with the same diameter as that of the Almax fiber but with grain sizes of 0.1 μm which doubled the fiber strength (8).

During this period 3M produced a range of oxide fibers with increasingly high performance properties. The sol-gel process used to produce the Nextel 312 was modified to produce the Nextel 440 fiber. The composition of 3 mol of alumina for 2 mol of silica was maintained but the boria content was reduced to increase its high temperature stability. The Nextel 440 fiber is formed of nano-sized γ-alumina grains in an amorphous silica phase. The fiber has been successfully used to reinforce mullite. The Nextel 720 fiber from 3M is made up of aggregates of mullite grains in which are embedded α-alumina grains (9). Although the grains of each phase are small the aggregates of similarly aligned mullite grains act like single grains of 0.5 μm and this gives the Nextel 720 fiber the lowest creep rate of any oxide fiber at temperatures above 1000°C (10). The fiber is however sensitive to alkaline contamination (11). 3M also produces the Nextel 650 fiber which is reminiscent of the PRD-166 fiber as it contains zirconia as a second phase (12).

The initial interest in small diameter oxide fibers as rivals to small diameter SiC fibers for use in ceramic matrix composites has been largely unfulfilled. Although the oxide fibers do not suffer from oxidation, as do the SiC fibers, they are inherently less mechanically stable above 1000°C. Whereas the co-valent bonds in SiC resist creep the ionic bonds in oxides allow easier movement of the structure. The complexity of the crystal structures of some oxides, such as mullite, does impart good inherent creep properties but ultimately grain boundary sliding and also the metastable state of some of the more complex systems means that oxide fibers are primarily limited to uses below 1200°C if they have to carry loads.

Removing grain boundaries by growing single crystal oxide filaments from the melt either by heating the ceramic in a crucible or by laser has been explored since the 1960s (13). This technique involves a single seeding grain touching the surface of the molten ceramic and slowly being drawn away from it. Such fibers were investigated by Tyco Laboratories (14) and developed commercially by Saphikon in the USA (15). It has been shown that such α-alumina fibers with their C-axis aligned parallel to the fiber axis can resist creep up to 1600°C (16). Saphikon produced fibers composed of single crystal α-alumina and also YAG-alumina, however the large diameters of 100 μm, and above, coupled with their prohibitive cost means that there seems to be no prospect of these fibers leaving the laboratory. A much cheaper process developed in Russia at the turn of this century consists of infiltrating the molten oxide along channels formed by sandwiching molybdenum wires between sheets of molybdenum (17). When the filaments are formed the molybdenum is etched away. The fibers so formed are inevitably of large diameter and are not circular in cross-section but may show the way for this type of fiber being developed in a commercially viable way.

Diameters over 20 μm have been seen to be too great for easy transformation and processing into structures but in the future very fine fibers may also be produced with nanometric sized diameters and these will also require some innovative processing procedures. It has been known since the 1950s that single crystal filaments, of oxides and other materials, with micron size diameters can be grown (18). These filaments, which are known as whiskers, possess very high strengths because of the lack of defects which otherwise weaken larger diameter fibers. Whiskers have diameters in the range of 0.5 to 1.5 μm and lengths which can range from tens of microns to centimeters. The large aspect ratio of length to diameter makes them theoretically interesting as reinforcements for composite materials but difficulties due to their toxicity and simply handling them have meant that they have been little exploited. A technology which is still in the laboratory electrospins sol-gel precursors which can then be pyrolysed to form even finer, nano-oxide fibers. Little is known about the properties which can be expected of such fibers but their development shows that the evolution of oxide fibers is far from over.

3.0. PROCESSING

1.1. Glass Fibers

The basic material for making glass is sand, or silica, which has a melting point around 1750°C, too high to be extruded through a spinneret. However combining silica with other elements can reduce the melting point of the glass which is produced. Fibers of glass are produced by extruding molten glass, at a temperature around 1300°C, through holes in a spinneret, made of a platinum-rhodium alloy, with diameters of one or two millimetres and then drawing the filaments to produce fibers having diameters usually between 5 and

TABLE 1. Compositions (% wt) of various glasses used in fiber production. Soda lime glass is known as A-glass. The type E is the most widely used glass fiber, types S and R are glasses with enhanced mechanical properties, type C resists corrosion in an acid environment, type Z in an alkaline environment and type D is used for its dielectric properties.

Glass type	A	E	S	R	C	Z	D
SiO_2	72	54	65	60	65	70	74
Al_2O_3	1	15	25	25	4	1	
CaO	10	18		9	14		0.2
MgO	3	4	10	6	3		0.2
B_2O_3		8			5.5		23
Li_2O						1	
F_2		0.3					
Fe_2O_3		0.3					
TiO_2						2	0.1
Na_2O	14				8	11	1.2
K_2O		0.4			0.5		1.3
ZrO_2						15	

15 μm. The spinnerets usually contain several hundred holes so that a strand of glass fibers is produced.

Several types of glass exist but all are based on silica (SiO_2) which is combined with other elements to create specialty glasses. The compositions of the most common types of glass fibers are shown in Table 1. A-glass is alkali or soda lime glass and is most usually used for bottles and not in fiber form. The most widely used glass for fiber reinforced composites is called E-glass, glass fibers with superior mechanical properties are known as S- and R-glasses which contain a higher amount of alumina. However the higher the content of refractory solids such as alumina and silica the more difficult it is to obtain a homogenous melt and this is reflected in the cost of the final product. C-glass is resistant to acid environments and Z-glass to alkaline environments. Type D-glass is produced so as to have a low dielectric constant. The temperature of the molten glass is chosen so that a viscosity of around 500 P (slightly less viscous than molasses) is achieved. The best production temperature is that which gives the desired viscosity and is at least 100°C higher than the liquidus temperature, which is the temperature above which devitrification cannot occur and is around 1100°C for type E glass. This ensures that any slight variation in the temperature of the spinneret bushings does not lead to them being blocked. A lower temperature risks causing breaks in the fiber however a lower viscosity could induce instabilities into the glass stream. The cost of glass fiber production is sensitive to the purity of the raw materials, for which only very small amounts of iron are desired, for example, and to the use of expensive batch materials, such as materials containing boron oxide and sodium oxide (19). Typical values of forming parameters for glass fiber spinning are given in Table 2.

Drawing takes place at high speed and as the glass leaves the spinneret it is cooled by a water spray so that by the time it is wound onto a spool its temperature has dropped to around 200°C in between 0.1 and 0.3 seconds. An open atomic network results from the rapid cooling and the structure of the glass fibers is vitreous with no definite compounds

TABLE 2. Typical drawing conditions for forming glass fibers.

Typical drawing speeds (Upper limit)	450 to 4500 m min^{-1} $<$ 5000 m min^{-1}
Typical nozzle bore diameters in the spinneret	1 to 2 mm
Nozzle lengths	2 to 6 mm
Typical draw-down diameter ratios	96 to 321
Extension ratios	9230 to 103,224

being formed and no crystallization taking place. Despite this rapid rate of cooling there appear to be no appreciable residual stresses within the fiber and the structure is isotropic. The glass fibers which are produced have slightly lower densities than the equivalent bulk glass. The difference is approximately 0.04 g/cc. The higher the draw speed used the lower the density of the glass fiber which is produced. Heating glass fibers above around 250°C will produce an increase in density.

The strength of glass fibers depends on the size of flaws, most usually at the surface, and as the fibers would be easily damaged by abrasion, either with other fibers or by coming into contact with machinery in the manufacturing process, they are coated with a size. The purpose of this coating is both to protect the fiber and to hold the strand together. The size may be temporary, usually a starch-oil emulsion, to aid handling of the fiber, which is then removed and replaced with a finish to help fiber matrix adhesion in the composite. Alternatively the size may be of a type which has several additional functions which are to act as a coupling agent, lubricant and to eliminate electrostatic charges.

Continuous glass fibers may be woven, as are textile fibers, made into a non-woven mat in which the fibers are arranged in a random fashion, used in filament winding or chopped into short fibers. In this latter case the fibers are chopped into lengths of up to 5 cm and lightly bonded together to form a mat, or chopped into shorter lengths of a few millimeters for inclusion in molding resins.

1.2. Discontinuous Oxide Fibers

1.2.1. Melt-Spun Aluminosilicate Fibers

The Chemical Abstract Service has defined these materials under the CAS number 142844-00-6 as: Refractories, fibers, aluminosilicates. Amorphous man-made fibers produced from melting, blowing or spinning of calcinated kaolin clay or a combination of alumina (Al_2O_3) and silica (SiO_2). Oxides such as zirconia, ferric oxide, magnesium oxide, calcium oxide and alkalines may also be added.

These aluminosilicate fibers are produced by a melt-spun process in which the starting material is melted, at around 2000°C, by passing an electric current through it. The molten ceramic is poured into a stream of compressed air which carries the ceramic with it, producing drawing. The molten ceramic should be viscous but have a low surface tension in order to be drawn into fiber form, even so a considerable fraction of the ceramic is not drawn and is known as ‘shot’. Turbulence breaks the filaments which are formed into discontinuous lengths with irregular cross sections but a mean diameter would be of the range of 2.5 to 3.5 μm. The need for a low surface tension restricts the alumina/silica ratio to an upper limit of 60/40 and pure alumina is not drawn into filament form if produced by this technique (20).

Alternatively the molten ceramic can be fed to a rapidly rotating disk, or series of disks, from which short fibers are thrown by centrifugal force. This latter process is similar to that used in Germany during WWI to produce short glass fibers to replace asbestos. It produces longer fibers with a slightly larger diameter (3–5 μm) than the first process, which however is more common. Both techniques produce fibers of great variability in diameter which however are generally within the range of (1–8 μm) and lengths (up to several centimeters) and a considerable fraction of non-fibrous shot. The specific surface area of these fibers is in the range of 0.4–0.8 m^2/g.

Shot is undesirable as it does not contribute to the strength and insulation properties of the product. It is of irregular shape and size and is considerably larger than the fibers which are formed, ranging from tens of microns to several hundred microns. Shot content can be reduced to less than 25% by sifting using a standard 212 μm mesh.

The range of compositions of melt-spun aluminosilicate fibers is 45–60 wt% Al_2O_3 with $Al_2O_3SiO_2$ as the other major component together with minor amounts of Fe_2O_3, TiO_2, CaO and other oxides (21). The limit to the composition is the resistance of the material to devitrification of the glass with, for example, the nucleation and growth of mullite ($3Al_2O_3 \cdot 2SiO_2$) which reduces strength dramatically. Strength at temperature increases with alumina content so that some compositions have 52 wt% Al_2O_3, for use as an insulation up to 1250°C. The highest levels of alumina allow insulation blankets to be produced for use up to 1400°C. Small additions of Cr_2O_3 improve temperature resistance.

These melt blown aluminosilicate fibers are produced in several forms by companies such as Morgan Thermal Ceramics and the Unifrax Corporation : they can be a loose collection of fibers which is known as 'bulk fiber' and are used as fillers; 'blankets which can be needle punched felts; the fibers can be made as a laminated felt or paper; stronger 'boards' or 'modules' are formed by a wet vacuum process to produce a felt in which the fibers are held together by an organic binder and these products are typically used in electrical furnaces; 'blocks' are made by stacking squares of blanket material, typically twelve layers 300 × 300 × 25mm are stacked to form blocks of 300 × 300 × 100 mm with the fibers aligned normal to the larger surfaces to give higher strength in the thickness direction. The fibers can also be mixed with binders to form product which can be cast or molded or used as a reinforced refractory cement.

1.2.2. The Saffil Fiber

The Saffil fiber which contains 4% of silica is produced by the blow extrusion of partially hydrolyzed solutions of some aluminum salts with a small amount of silica, in which the liquid is extruded through apertures into a high velocity gas stream. The fiber contains mainly small δ-alumina grains of around 50 nm but also some α-alumina grains of 100 nm. The widest use of the Saffil type fiber in composites is in the form of a mat which can be shaped to the form desired and then infiltrated with molten metal, usually aluminium alloy. It is the most successful fiber reinforcement for metal matrix composite.

For refractory insulation applications heat treatments of the fiber above 1000°C induce the delta alumina to progressively change into alpha alumina. After 100 hours at 1200°C, or one hour at 1400°C, acicular alpha alumina grains can be seen on the surface of the fiber and mullite is detected. After 2 hours at 1400°C the transformation is complete and the equilibrium mullite concentration of 13% is established. Shrinkage of the fiber and hence dimension of bricks are controlled up to at least 1500°C (21). Saffil was originally produced as a refractory insulation but, in addition, has become the most widely used reinforcement for light alloys.

1.3. Fine Continuous Oxide Fibers

1.3.1. Manufacture

Continuous fine oxide fibers are based on alumina in one of its forms, often combined with silica or other phases such as zirconia or mullite (22). Precursors of alumina (Al_2O_3) can be obtained from viscous aqueous solutions of aluminum salts Al X_n $(OH)_{3-n}$, where X can be an inorganic ligand (Cl^-, NO^{3-}...) or an organic ligand ($HCOOH^-$...). The precursor gel fibers which are spun are then dried and heat treated. Heating these precursors causes the precipitation of aluminum hydroxides, such as boehmite (AlO(OH) and the outgassing of large volumes of residual compounds. The associated volume change and porosity at this step has to be carefully controlled if useful fibers are to be produced. It is also possible to spin aqueous sols based on aluminum hydroxide directly. Heating the precursor fibers induces the sequential development of transition phases of alumina which if heated to a high enough temperature all convert to the most stable form which is alpha alumina. Above 400°C and up to around 1000°C transitional phases of alumina are produced with grain sizes in the range of 10 to 100 nm. Above 1100°C α-alumina is formed. However this transformation is followed by a rapid growth of porous α-alumina grains, of micron sizes and above, giving rise to weak fibers. It is essential that this rapid grain growth is controlled or retarded if fibers with useful properties are to be obtained. Applications of alumina fibers above 1100°C requires that the nucleation and growth of the α-alumina grains be controlled and porosity limited. This is achieved by either adding silica precursors or seeds for α-alumina formation to the fiber precursors. This has led to the development of two families of alumina based fibers, one consisting of primarily of α-alumina grains and the other of transitional alumina phases together with another phase.

If alumina is combined with silica (SiO_2) the transformation to alpha alumina can be retarded and controlled. The microstructures of such fibers depend on the highest temperature the fibers have seen during the ceramisation. Very small grains of η, γ or δ alumina in an amorphous silica continuum are obtained with temperatures below 1000–1100°C. The combination of alumina and silica phases changes the inherent rigidity of the fibers as the Young's modulus of alumina is around 400 GPa and that of silica approximately 70 GPa, as can be seen in Figure 1.

Strength is not effected by the silica content, as can be seen by Figure 2. The differences in the strengths of the α-alumina fibers are principally due to differences in grain size. The Nextel 610 fiber is composed of α-alumina of around 0.1 μm whereas the other two fibers shown have grains or 0.5 μm. The lower strength of the Almax fiber compared to the Fiber FP is due to porosity although the former's smaller diameter makes it easier to handle (22). Silica softens at around 1000°C so that alumina fibers which contain amorphous silica are not suitable for applications at higher temperatures. However the fibers are inherently resistant to oxidation and are stable in molten metals. They have been used successfully in reinforcing light metal alloys. It should be noted however that alumina is not easily wetted by many molten metals so that attention has to be taken to improve fiber-matrix interface.

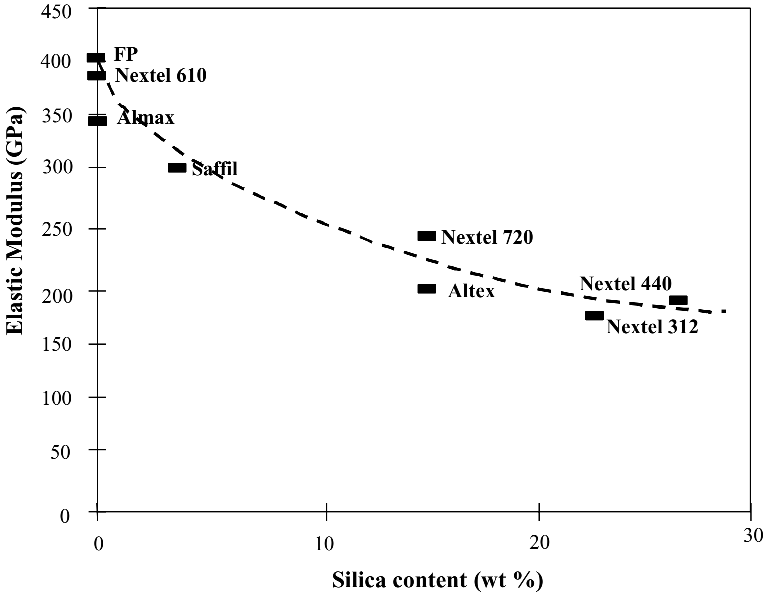

FIGURE 1. The variation of Young's modulus as a function of silica content for a number of alumina based fibers.

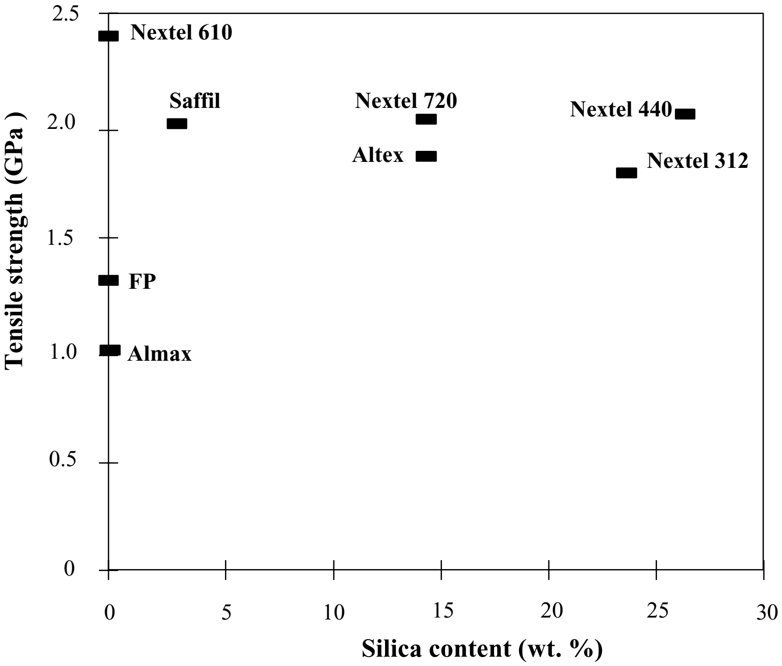

FIGURE 2. There is no direct link between the silica content and the strength of alumina fibers.

Many metal matrix composites are made by squeeze casting in which the molten metal is infiltrated under pressure into a fiber perform. The applied pressure is sufficient to achieve good interfacial bonding with fibers composed of γ- or δ-alumina because of the small sizes of the grains leading to large active contact surfaces.

When heated to around 1200°C alumina combined with silica is partially converted to mullite which can have a range of compositions from $2Al_2O_3{\cdot}SiO_2$ to $3Al_2O_3{\cdot}2SiO_2$. The interatomic bonds governing creep in alumina which are ionic and covalent lead to creep at temperatures above 1000°C. The development of fibers combining both alumina and another phase, such as mullite or zirconia, which can hinder creep processes has encouraged interest in the possibility of oxide fibers being used to reinforce ceramics.

1.3.2. Continous Alumino-Silicate Fibers

1.3.2.1. The Altex Fiber The Altex fiber is a fiber produced by Sumitomo Chemicals. The fiber is circular in cross section and has a smooth surface. The fiber is obtained by the chemical conversion of a polymeric precursor fiber, made from a polyaluminoxane dissolved in an organic solvent to give a viscous product with an alkyl silicate added to provide silica (18). The precursor is then heated in air to 760°C, a treatment which carbonises the organic groups to give a ceramic fiber composed of 85% alumina and 15% amorphous silica. The fiber is then heated to 970°C and its microstructure consists of small γ-alumina grains of a few tens nanometres intimately dispersed in an amorphous silica phase. Subsequent heat treatment produces mullite above 1100°C. At 1400°C the conversion to mullite is completed and the fiber is composed of 55% mullite and 45% alpha alumina by weight.

1.3.2.2. The Nextel Fibers The 3M corporation produces a range of ceramic fibers under the general name of Nextel. The Nextel 312 and 440 series of fibers are produced by a sol-gel process. They are composed of 3 moles of alumina for 2 moles of silica with various amounts of boria to restrict crystal growth. Solvent loss and shrinkage during the drying of the filament produces oval cross sections with the major diameter up to twice the minor diameter. They are available with average calculated equivalent diameters of 8–9 μm and 10–12 μm A more crystalline version of the Nextel 440 fiber was produced under the name of Nextel 480 but appears to no longer to be available.

The Nextel 312 fiber, which first appeared in 1974, is composed of 62% wt Al_2O_3, 24% SiO_2 and 14% B_2O_3 and appears mainly amorphous from transmission electron microscopy observations although small crystals of aluminium borate have been reported. It has the lowest production cost of the three fibers and is widely used but has a mediocre thermal stability as boria compounds volatilise from 1000°C inducing some severe shrinkage above 1200°C. To improve the high temperature stability in the Nextel 440 and 480 fiber, the amount of boria has been reduced. These latter fibers have the same compositions: 70% Al_2O_3, 28% SiO_2 and 2% B_2O_3 in weight but their microstructures are different. Nextel 440 is formed in the main of small γ-alumina in amorphous silica whereas Nextel 480 was composed of mullite. These differences may be due to different heat treatments of similar initial fibers, the Nextel 440 fiber being heated below the temperature of mulitisation.

The Nextel 720 contains the same alumina to silica ratio as in the Altex fiber, that is around 85% wt Al_2O_3 and 15% wt SiO_2. The fiber has a circular cross section and a diameter of 12 μm. The sol-gel route and higher processing temperatures have induced the growth of alumina rich mullite and alpha alumina. Unlike other alumina-silica fibers the Nextel

720 fiber is composed of a mosaic of mullite grains of around 0.5 μm consisting of several slightly mutually misoriented grains in which elongated α-alumina grains are found. This structure results in the Nextel 720 being the oxide fiber with the lowest creep rate. Post heat treatment leads to an enrichment of α-alumina in the fiber as mullite rejects alumina to evolve towards a 3:2 equilibrium composition. Grain growth occurs from 1300°C (10).

1.3.3. Alpha Alumina Fibers

Alpha alumina is the most stable and crystalline form of alumina to which all other phases are converted upon heating above around 1000°C. As we have seen above, fibers based on alumina can contain silica as its presence allows the rapid growth of alpha-alumina grains to be controlled. However the presence of silica reduces the Young's moduli of the fibers and reduces their creep strength. High creep resistance implies the production of almost pure alpha alumina fibers however to obtain a fine and dense microstructure is difficult. The control of grain growth and porosity in the production of alpha-alumina fibers is obtained by using a slurry consisting of alpha alumina particles, of strictly controlled granulometry, in an aqueous solution of aluminium salts. The rheology of the slurry is controlled through its water content. The precursor filament which is then produced by dry spinning is pyrolysed to give an alpha-alumina fiber.

1.3.3.1. Fiber FP The FP-fiber, manufactured by Du Pont in 1979, was the first wholly α-alumina fiber to be produced (4). Its production involved the spinning in air of a slurry composed of an aqueous suspension of Al_2O_3 particles and aluminium salts. The as obtained fiber was then dried and fired in two steps, the first to control shrinkage and followed, at a higher temperature, by flame firing to obtain a dense microstructure of α-alumina. A final step, involving a brief exposure to a high temperature flame to produce a fine surface layer of silica, had the effect of improving fiber strength and aiding wettability with metal matrices. It was a continuous fiber with a diameter of 18 μm This fiber was composed of 99.9% alpha alumina and had a density of 3.92 g/cm^3 and a polycrystalline microstructure with a grain size of 0.5 μm, a high Young's modulus of 410 GPa, a tensile strength of 1.55 GPa at 25 mm but a strain to failure of only 0.4%.This brittleness made it unsuitable for weaving and although showing initial success as a reinforcement for light alloys, production did not progress beyond the pilot plant stage and commercial production ceased. Never-the-less Fiber FP represents an example of an almost pure alumina in filament form and as such allows the fundamental mechanisms in this class of fiber to be investigated (23). This fiber was seen to be chemically stable at high temperature in air, however its isotropic fine grained microstructure led to easy grain sliding and creep, excluding any application as a reinforcement for ceramic structures.

Other manufacturers have modified the production technique to reduce the diameter of the alpha-alumina fibers that they have produced. This reduction of diameter has an immediate advantage of increasing the flexibility and hence the weaveability of the fibers. Mitsui Mining and 3M Corporation have introduced polycrystalline fibers, the Almax and the Nextel 610 fibers with diameters of 10 μm, that is half the diameter of Fiber FP.

1.3.3.2. Almax Fiber An alpha-alumina fiber which is still commercially available was produced first in the early 1990s by Mitsui Mining (7). It is composed of almost pure alpha alumina and has a diameter of 10 μm. The fiber has a lower density of 3.60 g/cm^3 compared to Fiber FP. Like Fiber FP the Almax fiber consists of one population of grains of around 0.5 μm however the fiber exhibits a large amount of intragranular porosity, and associated with numerous intragranular dislocations without any periodic arrangement. This indicates rapid grain growth of alpha alumina grains during the fiber fabrication process without elimination of porosity and internal stresses. As a consequence, grain growth at 1300°C is activated without an applied load and reaches 40% after 24 hours, unlike that with the other pure alpha alumina fibers, for which grain growth is related to the accommodation of the slip by diffusion.

1.3.3.3. Nextel 610 A continuous alpha-alumina fiber, with a diameter of 10 μm, was introduced by 3M in the early 1990s with the trade-name of Nextel 610 fiber (24). It is composed of around 99% alpha alumina although a more detailed chemical analysis gives 1.15% total impurities including 0.67% Fe_2O_3 used as a nucleating agent and 0.35% SiO_2 as grain growth inhibitor. It is believed that the silica which is introduced does not form a second phase at grain boundaries although the suggestion of a very thin second phase separating most of the grains has been observed by transmission electron microscopy. The fiber is polycrystalline with a grain size of 0.1 μm, five time smaller than in Fiber FP.

1.3.4. Alumina Zirconia Fibers

1.3.4.1. PRD-166 Fiber Du Pont synthesised the PRD-166 fiber in which 20% wt of partially stabilised tetragonal zirconia was added to increase the elongation to failure of the fiber (5). The intention was to produce a fiber which, compared to Fiber FP, was easier to weave. The dispersion of zirconia intergranular particles of 0.15 μm limited grain growth of the alumina grains which had a mean diameter of 0.3 μm instead of 0.5 μm for Fiber FP for a similar initial alumina powder granulometry. These particles underwent a martinsitic reaction in the vicinity of the crack tips, which in a similar bulk ceramic results in the partial closure of cracks and in an increase of the fiber strength. It is not clear if this process was significant in the fiber form or if the reduction in grain size was more important but the PRD-166 fiber was stronger than the Fiber FP with a failure strength of 1.8 GPa at a gauge length of 25 mm. The resulting stiffness of the reinforced alumina was lower than that of Fiber FP, $E = 344$ GPa, due to the lower Young's modulus of zirconia ($\approx$200 GPa) compared to that of alumina ($\approx$400 GPa). However the increase in strain to failure was not sufficient to allow weaving with the PRD-166 fiber and production of the PRD-166 fiber did not progress beyond the pilot stage, however the study of this fiber permits a greater understanding of the mechanisms of toughening and the enhancement of creep behaviour of alumina fibers.

1.3.4.2. The Nextel 650 Fiber The Nextel 650 fiber is produced by 3M, in order to combine the properties of a fiber which was above all resistant to alkaline contamination, as this was important for a reinforcement for high temperature composites, and second have improved creep resistance compared to the Nextel 610 pure α-alumina fiber (25). The Nextel 650 fiber has been produced, like others in the Nextel series, by sol-gel processing with the use of iron compounds as nucleating agents and SiO_2 to restrict grain growth compared to the PRD-166 fiber. The addition of α-Fe_2O_3, which has a similar structure to that of α-alumina, to the sol is to lower the temperature at which transitional phases of alumina are converted to α-alumina and this helps in the production of a low porous structure.

The Nextel 650 fiber is continuous and circular in cross-section with a diameter of 11.2 μm and is composed of α-alumina and 10%wt of cubic zirconia stabilized by 1%wt of

Y_2O_3. The zirconia has been added to increase the elongation to failure and to limit alumina grain growth. The microstructure obtained is very fine with alumina grains of 0.1 μm and a bimodal zirconia grain size distribution: 5 to 10 nm in size for intra-granular grains and 20–30 nm for inter-granular grains. No other phase can be detected in the as-received fiber and inter-granular porosity was quasi-inexistent.

1.3.5. Continuous Monocrystalline Filaments

The techniques for producing single ceramic crystals as filaments has been known since the 1960s and they offer the possibility of producing filaments containing no grain boundaries with associated high strength (13, 14). Continuous α-alumina monocrystalline filaments have been commercially produced by the Saphikon company in the USA. (15). This type of filament is grown from molten alumina by a modified Czochralsky-Stepanov edge-defined film-fed growth method in which an oriented seed crystal is slowly drawn from the molten ceramic. The ceramic is either heated by radio frequency induction furnace in a molybdenum crucible or by a technique known as laser-heated float zone in which the surface only of a ceramic feed rod is melted by a laser beam. The crystal orientation which is induced in the filament is that of the seed crystal, which is attached to a molybdenum rod, although regular patterns of bubbles can be seen in filaments produced by the induction furnace heating process and which are due to convection in the molten ceramic. The production rate is extremely slow and the high cost of producing the filaments together with their large diameters, usually in excess of 100 μm, means that they are not being considered for industrial use. The stoichiometric composition of these fibers with the absence of grain boundaries ensures that they should be able to better withstand high temperatures above 1600°C. Careful orientation of the seed crystal enables the C-axis of the α-alumina fiber can be aligned parallel to the fiber axis so that creep resistance can be optimized.

The same manufacturing processes have been employed to produce an eutectic fiber consisting of interpenetrating phases of -alumina and $Y_3Al_5O_{12}$ (YAG) (25). The structure depends on the conditions of manufacture, in particular the drawing speed but can be lamellar and oriented parallel to the fiber axis. This fiber does not show the same fall in strength seen with the single phase alumina fiber. However such fibers are seen to relax from 1100°C but their strengths do not have as strong a dependence on temperature as with the polycrystalline oxide fibers.

The growth process is extremely slow, typically 100 mm/hr but can easily be adapted to a wide range of ceramic systems for growing single crystal and directionally solidified eutectic filaments (27, 28). Although the crystal structure is continuous and Saphikon produced lengths of up to 3000 m of fiber, usually the lengths of filaments produced in laboratories are short, being typically tens of centimeters.

An alternative approach to making single crystal fibers and one which is potentially much cheaper than the technique described above is to infiltrate the molten ceramic in the channels formed by sandwiching molybdenum wires between molybdenum sheets (17). These dies are prepared and the wires and sheets diffusion bonded together. The processing zone is heated using a 8 kHz induction heated graphite susceptor and molybdenum crucible. Seeds, which are used to control crystal growth and orientation are placed on the top surface of the molybdenum die. The crucible is filled with the raw material which is melted. As the raw material becomes molten the molybdenum die is lowered into it and the molten ceramic is drawn up the channels by capillary forces. The die is then withdrawn and the ceramic solidifies from the top down. The seed crystal determines the crystal orientation of the filaments formed. The technique has been used to produce eutectic ceramic filaments for which it is not necessary to use a seed (26). Systems which have been made by this technique include Al_2O_3, Al_2O_3-$Al_5Y_3O_{12}$, Al_2O_3-$ZrO_2(Y_2O_3)$ and Al_2O_3-$AlGdO_3$. Mullite filaments have also been produced by this process. Many fibers can be produced simultaneously by this technique. Drawing rates are around 10mm/min.

The length of the zone which can be heated limits the length of filament which can be produced but lengths of up to 250 mm have been announced. Processing is carried out under inert gas or vacuum. Several batches of fiber can be processed simultaneously to produce up to 150 g of filaments at a time.

The molybdenum die material is finally removed by etching. Two routes are possible to remove the molybdenum using the following chemical reactions:

$$Mo + 3H_2O_2 = H_2MoO_4 + 2H_2O \tag{1}$$

Reaction (1), in which hydrogen peroxide is used is more ecologically friendly however the reaction takes up to three times longer than the second. The cost of hydrogen peroxide is

$$3Mo + 6HNO_3 \xrightarrow{HCl} \xrightarrow{H_2SO_4} 3H_2MoO_4 + 6NO \tag{2}$$

higher than for the acids in the second reaction. Both reactions produce a rise in temperature which however is easier to control in the second reaction. Reaction (2) requires approximately thirty hours to remove the molybdenum so as to release the fibers.

1.3.6. Whiskers

Whiskers are fine high purity monocrystals in the form of filaments. The potential of whiskers as reinforcements has been discussed for many years as their small diameters, usually between 0.5 and 1.5 microns means that they contain very few defects and must posses extremely high strengths, perhaps up to the theoretical strength for matter, which is approximately one tenth of its Young's modulus. In addition their aspect ratios of length to diameter can be considerable as they can be produced with lengths between 20 μm and it is claimed, several centimeters. A high aspect ratio is just what is required to achieve reinforcement in composites.

Amongst the oxides which have been produced as whiskers are Al_2O_3, MgO, MgO-Al_2O_3, Fe_2O_3, BeO, MoO_3, NiO, Cr_2O_3 and ZnO. Typically the whiskers are produced by heating the metal in a suitable atmosphere such as wet hydrogen, a moist inert gas or air. The most commonly produced whiskers are of alumina and silicon carbide.

Alumina whiskers are produced by high temperature chemical vapor deposition at the tip of a substrate particle (21). The temperature has to be high enough for the vapor pressure of the whisker or whisker forming material to become significant, in which case the atoms become attached to the tip of the whisker and contribute to its growth. Alumina whiskers can be produced by passing a stream of moist hydrogen over aluminum powder heated to around 1400°C. A mass of acicular α-alumina crystals are deposited in the cooler part of the furnace. This commonly used reaction is as follows:

$$2Al(g) + 3H_2O(g) \longrightarrow Al_2O_3(s) + 3H_2(g)$$

Alternatively the following reaction can be used :

$$2AlC_3(g) + 3CO_2(g) + 3H_2(g) \Rightarrow Al_2O_3(s) + 6HCl(g) + 3CO(g)$$

Considerable difficulties have to be overcome if whiskers are to be used as reinforcements however. They are extremely small so that plastic bag containing whiskers seems to contain dust. This means that alignment of the whiskers in a matrix is very difficult. There are potential uses for whiskers combined with more conventional fibers so as to provide some reinforcement of the matrix in the transverse direction. Their fineness is also another handicap in their exploitation as one micron is just the size to block up the alveolar structure of the lungs. For this reason, above all, whiskers remain an intriguing possibility as reinforcements but one which is little exploited.

1.3.7. Nano-oxide fibers

An emerging technology is the production of fibers of very small diameter, of the order of 50nm. These fibers are produced by the spinning of a precursor organic fiber from a pipette to a collecting plate. A high voltage (tens of kilovolts) is passed between the pipette and the plate and the polymer is drawn from the pipette to the plate. The fibers are generally collected on the plate to form a random array although work is proceeding to align the fibers. The fibers are too fine to be tested by conventional techniques but can be tested as bundles. The fibers can also be subjected to the same cycles of pyrolysis that have been used to produce larger diameter ceramic fibers. At present this technology is still at the laboratory stage so that few data are available however the nanometric diameter could be expected to confer on the filaments perhaps exceptional properties which are not obtained with larger diameter fibers. This is primarily because dislocation movement should be restricted so that high strengths and low creep rates could be expected. At the laboratory scale oxide fibers such as Al_2O_3, ZrO_2 and TiO_2 as well as carbon fibers have been made but they are far from having being fully evaluated.

4.0. PROPERTIES

1.1. Glass Fibers

The mechanical properties of a range of glass fibers are shown in Table 3. As strength and failure strains are not intrinsic properties of a material it is possible to find a range of values in the literature (29). Physical properties of glass fibers are shown in Table 4.

Glass fibers are known to fail when subjected to steady unvarying loads. This is not creep failure but is sometimes known as static fatigue. In this process microscopic defects grow under the influence of the applied stress. When the defect attains the critical flaw size for the applied stress the fiber breaks. The growth of flaws in glass was first treated by Griffith who discussed the energy necessary to propagate a crack in an elastic medium (30). The energy necessary to separate the two fracture surfaces can be modified by the environment in which the glass is held. Water, for example can reduce the threshold stresses for crack propagation. Table 5 gives details about the chemical resistance of the glass fibers in different environments.

TABLE 3. Mechanical properties of a number of different types of glass fibers.

Glass type	A	E	S	R	C	D
Strength (20°C) GPa	3.3	3.5	4.65	4.65	2.8	2.45
Elastic Modulus (20°C) GPa	69	73.5	86.5	86.5	70	52.5
Failure Strain (20°C) %	4.8	4.5	5.3	5.3	4.0	4.5
Specific Gravity	2.44	2.54	2.48	2.48	2.49	2.16
Poisson's ratio	–	0.2	–	–	–	–
Coefficient of Thermal Expansion ($\times 10^7 \cdot C^{-1}$)	73	54	16	33	63	25

TABLE 4. Physical properties of a number of different types of glass fibers.

Properties	A	E	S	R	C	D
Refractive Index	1.538	1.558	1.521	1.546	1.533	1.465
Dielectric constant 1 MHz	6.2	6.6	5.3	6.4	6.9	3.8
Specific heat cal $g^{-1}{}^{\circ}C^{-1}$	0.796	0.810	0.737	–	0.787	0.733
Softening temperature °C	705	846	1056	952	750	771
Annealing temperature °C	–	657	816	–	588	521
Volume resistivity (ohms-cm)	1.0E + 10	4.20E + 14	9.03E + 12	2.03E + 14	–	–

TABLE 5. Chemical resistance of glass fibers immersed in different environments.

Durability (% weight loss)	A-Glass	E-Glass	E-Glass	R-Glass	C-Glass	D-Glass
H_20 : 24 hr	1.8	0.7	0.5	0.4	1.1	0.7
168 hr	4.7	0.9	0.7	0.6	2.9	5.7
10% HCl : 24 hr	1.4	42	3.8	9.5	4.1	21.6
168 hr		43	5.1	10.2	7.5	21.8
10% H_2SO_4 : 24 hr	0.4	39	4.1	9.9	2.2	18.6
168 hr	2.3	42	5.7	10.9	4.9	19.5
10% Na_2CO_2 : 24 hr		2.1	2.0	3.0	24	13.6
168 hr		2.1	2.1		31	36.3

TABLE 6. Examples of typical melt spun short fibers and their characteristics.

Property	Kaowool	Kaowool 1400	Kaowool 1500	Cera-chrome
Maximum service temperature	1260°C	1400°C	1500°C	1427°C
Melting point	1760°C	1815°C	–	>1760°C
Average fiber diameter	2.8 μm	2.5 μm	2.6 μm	3.5
Specific gravity	2.6	2.8	2.65	2.65
Chemical analysis (%)				
Al_2O_3	47.3	56.3	41.2	42.5
SiO_2	52.3	43.3	56.6	55.0
Cr_2O_3			2.1	2.5

1.2. Aluminosilicate Fibers

The Young's moduli of these fibers are lower compared to that of pure alumina fibres, and such fibers are produced at a lower cost. This, added to easier handling due to their lower stiffness, makes them attractive for thermal insulation applications, in the absence of significant load, in the form of consolidated felts or bricks up to at least 1500°C. Such fibers are also used to reinforce aluminum alloys in the temperature range of 300–350°C. Continuous fibers of this type can be woven due to their lower Young's moduli. However microstructural changes occur if the fibers are heated to sufficiently high temperatures. All transitional phases are changed in to α-alumina around 1100°C. If any amorphous silica is present in the fiber it will begin to soften at these temperatures and facilitate grain boundary sliding and creep of the fiber. In addition mullite may begin to be formed around 1000°C and cristobalite around 1200°C. The ionic bonds which occur in oxides allow faster creep rates than are found in ceramics which possess only co-valent bonds such as silicon carbide.

1.2.1. Melt Spun Aluminosilicate Fibers

The irregular shapes and fine diameters of these fibers make them difficult to characterize and most available data concerns the properties of finished products. However, Table 6 gives some data on typical fibers made by the melt spun process (20).

The standard grade products account for most of the ceramic fibers produced and are made into a variety of products. Their composition of 47–51% alumina and 49–53 silica allows fibers to be produced with small diameters. Within this composition range there is little variation in thermal resistance however when natural kaolin is the starting material there is a possibility of contamination by alkaline oxides (Na_2O and K_2O) which has a detrimental effect on the thermal insulation of the fibers produced. Thes alkaline contaminants can combine with the silica in the fiber to form a low melting point phase and this can cause failure of the fibers. The presence of vanadia (V_2O_3) can further exacerbate the fiber damage by producing a low melting point phase and reacting with the alkaline contaminants. Increased thermal resistance is achieved by increasing the alumina content although the increased difficulty in producing this grade means that a higher

TABLE 7. Property and microstructural changes during the processing of Al_2O_3 fibers containing approximately 4% SiO_2.

Major phases	η	η/γ	γ	γ/δ	δ	δ/θ	θ-mullite	α-mullite
Grain size	6 nm				50 nm		100 nm	>200
Crystallinity (%)	50	62	68	77	79	86	97	100
α-alumina (%)					7	16	20–50	100
Pore volume (mm^3/g)	200		187	121	73	46	0	0
Shrinkage at 1400°C after 1h (%)	18	17	14	8	6.5	3.5	0.5	0
Tensile strength for 3.5 μm diameter fiber (GPa)	1.8				1.5			0.5

shot content should be expected as well as a higher specific gravity. Both of the former materials can suffer from significant shrinkage upon heating above 1200°C due to temperature induced phase changes. The addition of chromia (Cr_2O_3) retards these phase changes and reduces shrinkage. The low biopersistent fibers which contain calcia (CaO), magnesia (MgO) and silica (SiO_2) show lower thermal resistance and are probably limited to around 1000°C.

All of these fibers are subject to changes to their microstructures at high temperature and these ultimately limit their use. Alumina and silica will combine to form mullite from around 970°C and crystoballite, which is a crystalline form of silica, is formed at around 1260°C. These changes can occur progressively over a period of time when the fibers are subjected to temperatures in these ranges. The standard RCF starts to precipitate crystobalite at 1100°C after around 3000 hours, but at 1200°C this is reduced to 300 hours and 50 hours at 1300°C. The 1400°C grade takes two to three times longer at the same temperatures. The effects of these phase changes are to cause the mullite grains to grow from, initially, around 30 nm at 1100°C and 100 nm at 1300°C. The development of these mullite grains is to reduce the flexibility of the fibers and eventually to lead to the fusing together of the fibers and the product becomes brittle. Shrinkage of the fiber structure also occurs when crystallization is initiated and the higher the alumina content the greater the shrinkage. The standard grade heated for 100 hours at 1100°C will shrink 2% and 2.8% at 1200°C whereas the 1400 grade will shrink 2.1% and 3.6% under the same respective conditions.

1.2.2. Alumina based fibers produced from precursors

The alumina based fibers discussed in section 3.2 possess a range of compositions. They can be short, as with the Saffil fibers or continuous, as with the others described. Their properties at room temperature depend on the α-alumina content and at high temperature, the presence of any second phase (31). The Saffil fiber contains a few percent of silica with the remainder of the composition being alumina in one of its transition phases or as a mixture of transition phases and α-alumina. Table 7 shows the changes in processing of fibers of this type (32).The properties of alumina based fibers areshown in Table 8. Figure 3 shows the tensile curves of a pure α-alumina fiber, the Fiber FP, which had a grain size of 0.5 μm (23).

TABLE 8. Properties and compositions of alumina based fibers

Fiber Type	Manufacturer	Trade Mark	Composition (wt%)	Diameter (µm)	Density (g/cm^3)	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)	CTE $10^{-6}/°C$
α-Al_2O_3 based fibers	Du Pont	FP	99.9% Al_2O_3	20	3.92	1.2	0.29	414	5.9 (25–900°C) 9.6 (900–1500°C)
	Mitsui Mining	Almax	99.9% Al_2O_3	10	3.6	1.02	0.3	344	7
	3M	Nextel 610	99% Al_2O_3 0.2%–0.3SiO_2 0.4–0.7 Fe_2O_3	10–12	3.75	1.9	0.5	370	8 (100–1100°C)
	Du Pont	PRD 166	80% Al_2O_3 20% ZrO_2	20	4.2	1.46	0.4	366	9.0
	3M	Nextel 650	90.4 Al_2O_3 7.9% ZnO_2 1.1% Y_2O_2 0.6% Fe_2O_3	11	4.1	2.3	0.6	370	8.0
Alumina silica based fibers	Saffil	Saffil	95% Al_2O_3 5% SiO_2	1–5	3.2	2	0.67	300	6
	Sumitomo Chemicals	Altex	85% Al_2O_3 15% SiO_2	15	3.2	1.8	0.8	210	6
	3M	Nextel 312	62% Al_2O_3 24% SiO_2 14% B_2O_3	10–12 and 8–9	2.7	1.7	1.12	152	3 (25–500°C)
	3M	Nextel 440	70% Al_2O_3 28% SiO_2 2% B_2O_3	10–12	3.05	2.1	1.11	190	5.3
	3M	Nextel 720	85% Al_2O_3 15% SiO_2	12	3.4	2.1	0.81	260	6 (100–1100°C)