7

Ceramic fibres

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7.1 Introduction

The need for reinforcements for structural ceramic matrix composites (CMC) to be used in air at temperatures above 1000 °C, as well as for the reinforcement for metals (MMCs), has encouraged great changes in small-diameter ceramic fibres since their initial development as refractory insulation. There now exists a range of oxide and non-oxide fibres with diameters in the range of 10 to 20 µm which are candidates as reinforcements.[1] There are also large-diameter ceramic fibres with diameters over 100 µm made by chemical vapour deposition (CVD) and by epitaxial growth from the melt which are also potential reinforcements. Applications envisaged are in gas turbines, both aeronautical and ground-based, heat exchangers, first containment walls for fusion reactors, as well as uses for which no matrix is necessary such as candle filters for high temperature gas filtration.

For all of these applications the structures have to withstand very high temperatures, so excluding the use of organic or glass fibres. The oxidising and corrosive environments in which such structures must operate also prohibit the use of carbon fibres, which would be degraded above 300 °C. Ceramic fibres can withstand such demanding conditions but also are often required to resist static or dynamic mechanical loading at high temperature, which can only be achieved by a close control of their microstructures.

Ideally, ceramic fibres should show sufficient flexibility so that preforms can be made by weaving and subsequently infiltrated by the matrix material. This can be achieved with ceramics, which have high Young's moduli, if the fibres have sufficiently small diameters, because flexibility is related to the reciprocal of the fourth power of the diameter. A diameter of the order of 10 µm is therefore usually required for ceramic reinforcements, together with a strain to failure of around 1%. As the choice of a ceramic material imposes a Young's modulus of 200 GPa or more, this implies a room temperature strength of more than 2 GPa. The fibres are destined to be used at high temperature in air so that long-term chemical, microstructural and mechanical stability and creep resistance above 1200 °C are often required.

Alumina and silicon carbide bulk ceramics are widely used for their high stiffness and good high temperature mechanical properties in air; however, they are generally weak due to the presence of critically sized defects. The low strength of these materials is significantly increased when the ceramics are in the form of fine filaments because the microstructures of the fibres are much finer, being composed of sub-micron grains. This precludes the existence of large defects. The requirements for high-performance reinforcements would therefore be fulfilled if such bulk ceramics were transformed into fibres. However, small diameters required for the fibres impose production processes which result in specific microstructures and properties which are not necessarily those of the bulk ceramics.

Conventional processes for the fabrication of bulk ceramics, which include powder compaction and sintering, cannot be extended to fine fibres. Thermoplastic polymer fibres and glass fibres are obtained by the spinning and drawing from a melt of the desired final composition, a process which is precluded for refractory materials as their melting points can exceed 2000 °C. The production of fine ceramic fibres requires the spinning of an organic or mineral precursor fibre, which is then heat treated and pyrolysed for a very short time. The first ceramic fibres for very high temperature structural applications were commercialised at the beginning of the 1980s and, since then, the fibres have undergone great changes and shown improved properties. This chapter will describe the evolution of both oxide and non-oxide ceramic fibres and show how the small variations in the fabrication processes which have been introduced have induced major modifications in the microstructure and mechanical behaviour of these fibres.

7.2 Silicon carbide-based fibres

7.2.1 Fabrication of silicon carbide-based fibres

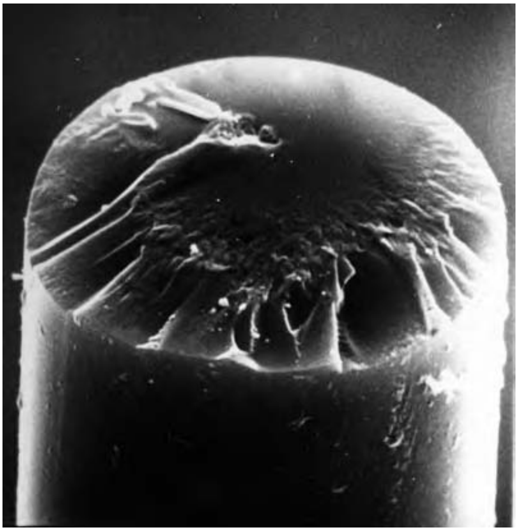
7.2.1.1 General

Fine-diameter SiC fibres are made from precursor fibres that are spun from the melt of an organosilicon polymer, such as a polycarbosilane (PCS) or one of its derivatives. This family of polymers is principally formed of rings of six atoms of Si and C, prefiguring the architecture of the blende structure of SiC. Methyl groups and hydrogen atoms are grafted onto these rings and, in part, remain in the fibres after their conversion to ceramic fibres by pyrolysis above 1200 °C. However, before this process can take place, crosslinking of the precursor fibre is necessary to avoid the softening or melting of the fibre during pyrolysis. The choices of the precursor polymers and of the crosslinking processes have a great influence on the final composition and microstructure of the ceramic fibres.

7.2.1.2 Fibres cured by oxidation

The elaboration of the first fine SiC-based fibres was reported by Yajima and his colleagues in Japan in the mid-1970s[2] and commercialised under the name of *Nicalon* fibres by Nippon Carbon at the beginning of the 1980s. They were produced from a PCS fibre for which crosslinking was achieved by a heat treatment in air at around 200 °C. Lateral Si–H and C–H bonds were oxidised and new Si–O–Si or Si–O–C bonds were created linking pairs of polymer chains. This curing process introduced oxygen into the structure of the precursor fibre which already had hydrogen and methyl side groups in addition to the Si–C of the main chain. This deviation from stoichiometry was reduced during the heat treatment owing to the outgassing of hydrogen, carbon oxides and alkyls between 300 and 900 °C. However, after the pyrolysis at around 1200 °C, significant amounts of oxygen (12% wt) and excess carbon ($C_{at}/Si_{at} = 1.3$) still remained in the ceramic. The fibres that were obtained were described as SiC-based fibres, although their appearance and mechanical properties were not those which could be expected from SiC. The *NL-200 Nicalon* fibres, which are the most representative of this class of ceramic fibres, have a diameter of 14 µm, a glassy appearance, as shown in Fig. 7.1, a Young's modulus of 200 GPa, as shown in Table 7.1, that is half that of bulk SiC, and they show much inferior creep properties as creep is observed from 900 °C. This is explained by the microstructure of the fibre. Only 55% of the fibre is composed of β-SiC, which is in the form of grains of about 2 nm. Oxygen, introduced during curing, forms with carbon and silicon, a metastable Si–C–O phase representing 35 to 40% of the fibre by weight, the rest of the fibre consisting of free carbon particles.[3] The Si–C–O phase impedes grain growth and permits creep. This phase begins to decompose from 1200 °C. Excess carbon and oxygen are lost in the form of oxides of carbon but no densification of the remaining growing SiC grains is possible so that the fibre loses all strength. This degradation of the fibre is more rapid in an inert atmosphere than in air as the outer silica layer that is formed by oxidation slows down the outgassing of the decomposition. However, bubbles of CO which build up at the SiC/SiO_2 interface reduce the fibre strength.

Ube Industries produced a series of fibres from a polytitanocarobosilane (PTC) precursor which was obtained by the grafting of titanium alkoxide between the PCS chains.[4] PTC was reported to be more easily spinnable. *Tyranno LOX-M* fibres, with diameters down to 8.5 µm and containing 13% oxygen by weight, were produced after oxidation, curing and pyrolysis at around 1300 °C. Moreover, it was expected that the germination and growth



7.1 Fracture morphology of a *Nicalon NL-200* oxygen-cured SiC-based fibre. The fibre has a diameter of 14 µm and shows a glassy appearance when observed in SEM (scanning electron microscopy).

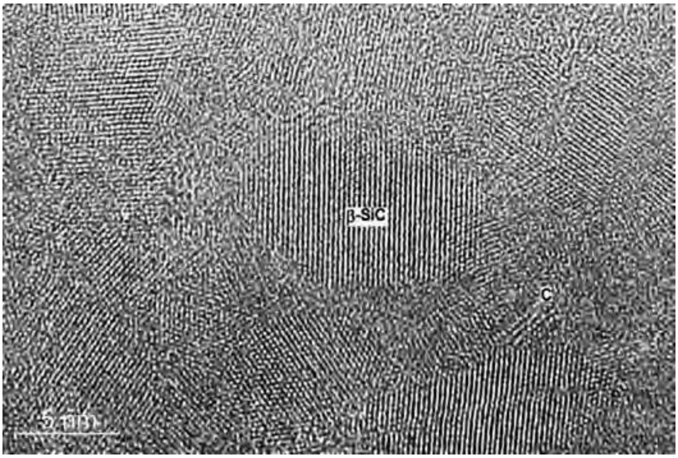
of evenly distributed small grains of TiC could trap excess carbon and inhibit the SiC grain growth responsible for strength loss. Growth of large TiC particles was observed from 1200 °C but no remarkable improvements in the microstructural stability and mechanical properties were noticed and higher oxidation rates were reported.

7.2.1.3 Fibres cured by irradiation

The further improvement of SiC-based fibres required the elimination of oxygen from the structure. This was achieved by Nippon Carbon by irradiating precursor PCS fibres with a 2 MeV electron beam. Si and C atom sited radicals were formed and radical–radical recombination reactions allowed the chains to be crosslinked without introduction of oxygen. These *Hi-Nicalon*[5] fibres were pyrolysed up to about 1400 °C. The oxygen content was decreased to 0.5% wt but the fibre contained more free carbon (C_{at}/Si_{at} = 1.39) as less oxides of carbon could leave the fibre during heat treatment. The fibre encloses ovoid β-SiC grains of 5 to 20 nm, surrounded by poorly organised Si–C and turbostratic free carbon, as seen in Fig. 7.2. The lower oxygen content induced a better chemical stability at high temperature compared to oxygen-cured fibres. The threshold temperature for creep was pushed to 1100 °C and lower creep rates were measured. Creep resistance could further be enhanced by a post heat-treatment for 5 hours in argon

Table 7.1 Properties and compositions of silicon-based fibres. Compositions and densities are those given by the manufacturers

Fibre type	Manufacturer	Trademark	Composition (wt %)	Diameter (μm)	Density (g/cm^3)	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
Si-C based	Nippon Carbide	*Nicalon NLM 202*	56.6% Si 31.7% C 11.7% O	14	2.55	2.0	1.05	190
	Nippon Carbide	*Hi-Nicalon*	62.4% Si 37.1% C 0.5% O	14	2.74	2.6	1.0	263
	Ube Industries	*Tyranno Lox-M*	54.0% Si 31.6% C 12.4% O 2.0% Ti	8.5	2.37	2.5	1.4	180
	Ube Industries	*Tyranno Lox-E*	54.8% Si 37.5% C 5.8% O 1.9% Ti	11	2.39	2.9	1.45	199
Near stoichiometric SiC	Nippon Carbon	*Hi-Nicalon Type-S*	68.9% Si 30.9% C 0.2% O	13	3.0	2.5	0.65	375
	Ube Industries	*Tyranno* *SA1* *SA3*	SiC Al < 1% +small amounts of C + O	 10 7.5	 3.0 3.1	 2.6 2.9	 0.75 0.8	 330 340
	Dow Corning	*Sylramic*	SiC ~ 96% TiB_2 ~ 3.0% C ~ 1.0% O ~ 0.3%	10	3.1	3.0	0.75	390



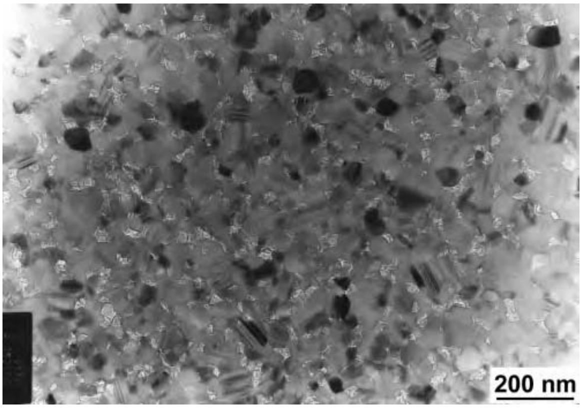
7.2 High-resolution transmission electron microscopy (TEM) image of a *Hi-Nicalon* fibre, showing β-SiC grains of about 10 nm, surrounded by a poorly organised Si–C phase, and turbostratic carbon.

at 1450 °C, a temperature just above the pyrolysis temperature, so as to increase the crystallinity. Turbostratic carbon has been seen to grow preferentially parallel to some of the SiC grain facets and could in some cases form cages around them, so limiting their growth.

The radiation curing process was also used by Ube Industries to crosslink PTC fibres. After a pyrolysis at around 1300 °C, the *LOX-E* fibre that was obtained contained 5% wt of oxygen. This higher value of oxygen in the *LOX-E* fibre compared to that of the *Hi-Nicalon* was due to the introduction of titanium alkoxides for the fabrication of the PTC. As a result, this fibre possessed a microstructure and high-temperature behaviour that were comparable to those of the previous oxygen-rich fibres.[6] A subsequent series of *Tyranno* fibres was obtained from a PCS polymer onto which zirconium acetylacetonate was grafted.[7] The use of these compounds introduced less oxygen and allowed the oxygen content to be decreased to 2% wt. The microstructure and creep behaviour of the *Tyranno ZE* fibres obtained by radiation curing were close to those of the *Hi-Nicalon*.

7.2.1.4 Sintered fibres

Three new sintered fibres, referred to by their manufacturers as being stoichiometric, have been developed by Ube Industries, Dow Corning and Nippon Carbon and called respectively, *Tyranno SA*,[8] *Sylramic*[9] and *Hi-Nicalon Type-S*.[10] Ube Industries and Dow Corning start with precursor fibres cured by oxidation, as for the first generation of fibres, but introduce



7.3 Microstructure of a *Hi-Nicalon Type-S* fibre revealed by TEM. The fibre is composed of SiC grains of 50 to 100 nm and pockets of free carbon.

sintering aids in the precursor, by reaction of aluminium acetylacetonate with PCS for Ube Industries or by doping the PTC with boron for Dow Corning. By these processes, ceramic fibres containing an oxygen-rich intergranular phase, similar to the first generation of fibres, are produced. These fibres are then pyrolysed up to 1600 °C for the *Sylramic* and 1800 °C for the *Tyranno SA*, so that the excess carbon and oxygen can be lost as volatile species. Unlike in the previous generations of fibres, densification of the fibres can take place because of the sintering aids. Grain sizes are of 200 nm, with TiB_2 particles in the *Sylramic* fibres whereas no crystallised aluminium compounds are formed in the *Tyranno SA* fibres. The process adopted by Nippon Carbon is reported as being a 'modified *Hi-Nicalon* process'. The PCS precursor fibres are cured by irradiation and pyrolysed in a hydrogen-rich atmosphere up to 1500 °C to reduce the free carbon content. The grain sizes are 50 to 100 nm, as seen in Fig. 7.3. Sintering aids cannot be detected in these fibres. The three types of fibres contain a significant amount of free carbon, located at pockets between clusters of SiC grains, which explains why their Young's moduli are still lower than that of bulk sintered SiC. The three fibres show much improved creep properties, with creep rates of the order of $10^{-8}\,s^{-1}$ at 1400 °C when compared to the earlier generations of fibres which have rates of $10^{-7}\,s^{-1}$ at the same temperature. The *Nicalon Type S* fibre shows lower creep rates than the other two fibres and this fibre is also seen to maintain its room temperature strength up to 1400 °C. The use of the electron-curing process for the PCS precursor is clearly of benefit, although it imposes a cost penalty. The sintering aids used in the other two fibres are seen to increase creep rates by increasing diffusion rates.

As the composition of the fibres approaches stoichiometry, lower creep and oxidation rates are obtained. Nevertheless, this family of fibres are likely to be limited by oxidation to a maximum temperature of 1400 °C.

7.2.1.5 SiC fibres made by chemical vapour deposition

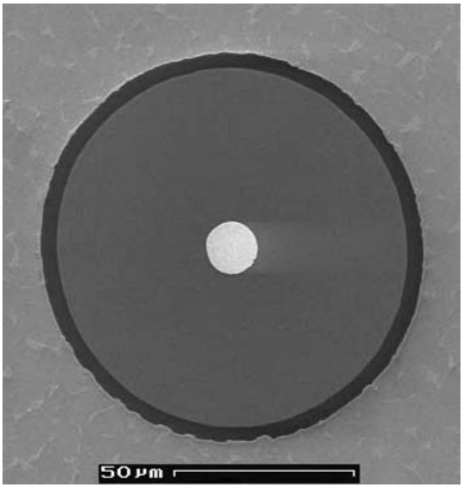
Silicon carbide fibres made by CVD are produced on both tungsten and carbon cores.[11] In commercial production, the gas mixture is introduced at multiple injection points of the vertical reactor, which is about two metres in length. The temperature along the reactor passes through a maximum between 1400 and 1500 °C at an early stage of deposition. Passage through the reactor is of the order of one or two minutes and results in a fibre with a diameter greater than 100 μm. Various carbon-containing silanes have been used as reactants. In a typical process, with CH_3SiCl_3 as the reactant, SiC is deposited on the core as follows:

$$CH_3SiCl_3 \rightarrow SiC + 3HCl$$

SiC fibres produced on a tungsten core of 12 μm diameter show a thin reactive layer between the SiC and tungsten which forms reaction products of α-W_2C and W_5Si_3. Heating above 900 °C leads to growth of this reactive layer and degradation of the properties of the fibre.

The carbon fibre cores of 33 μm diameter, which are used for the CVD production of SiC fibres, are themselves coated with a 1–2 μm thick layer of pyrolytic carbon which covers surface defects on the core and produces a more uniform diameter. The fibres on a carbon core show a gradation of composition, which is richer in carbon near the interface and becomes stoichiometric SiC towards the fibre surface. The fibres on a tungsten core have a mantle of stoichiometric SiC. The specific gravity of a 100 μm diameter SiC-W fibre is 3.35 whilst that of a 140 μm diameter SiC-C fibre is around 3.2.

Early SiC fibres were found to have a wide scatter in tensile strengths and this was alleviated by coating them with a thin layer of carbon. This had the disadvantage, however, of reducing interfacial bonding, particularly with light alloys. To overcome this, the SiC fibres made on a carbon core and destined to reinforce light alloys, are produced with a surface coating, the composition of which is made to vary from being carbon rich to silicon carbide at the outer surface. The fibres which are to be used to reinforce titanium have a protective layer which varies from being rich in carbon to being rich in silicon to a composition which is again rich in carbon at the surface. The outer sacrificial layer protects the fibre during contact with the molten and highly reactive titanium during composite manufacture. This type of fibre is produced by Textron under the designation *SCS-6*, as the



7.4 Cross-section of a SiC fibre made by CVD onto a tungsten core.

coating increases the fibre diameter by 6 μm. The fibre shows no degradation after 5 hours at 900 °C when embedded in Ti (6Al4V) matrix. A cross-section of a typical 100 μm diameter SiC fibre on a tungsten core, made by DERA, is shown in Fig. 7.4. This fibre has surface coating that is 3–4 μm thick and that varies from being carbon rich to becoming a thin layer of less than 1 μm of TiB_2 at the surface.

The room-temperature strengths of the fibres are around 4 GPa. Low failure stresses are due to surface flaws whereas higher strengths are controlled by defects at the core mantle interface. Strength decreases in air when the fibres are heated to above 800 °C for long periods most probably due to oxidation of the carbon-rich outer layers. At temperatures above 900 °C, interfacial reactions between tungsten cores and mantles cause degradation of properties. At higher temperatures still, grain growth in the SiC mantle may be the cause of further falls in strength.

7.3 Other non-oxide fibres

Various non-oxide fibres have been developed at a laboratory or pilot scale from other silicon containing precursors such as polysilazane. The fibres obtained have amorphous structures based on Si–C–N–O, Si–N or Si–B–N–C, but recrystallise from 1200 °C or show poor oxidation resistance. Boron nitride fibres with oriented turbostratic structures are also being developed for specific applications, but they are intrinsically not adapted to resist oxidation.

7.4 Alumina-based fibres

If high-performance fibres are to be exposed to oxidising atmospheres and temperatures above 1400 °C, they will have to be made from oxides with high melting points. α-alumina is widely used for it refractory properties. Its complex structure provides large Burgers vectors so that high stresses are necessary to generate plasticity in monocrystals. Monocrystalline α-alumina fibres showing no creep up to 1600 °C can be obtained if the fibre axis strictly corresponds to the [0001] axis. However no viable processes exist at present to produce fine and flexible continuous monocrystalline fibres. Therefore, only polycrystalline fibres can be considered for the reinforcement of ceramics. Various processing routes exist for making such fibres and these lead to a large range of microstructures and behaviours at high temperature. The properties of such fibres are shown in Table 7.2.

7.4.1 Fabrication of alumina fibres

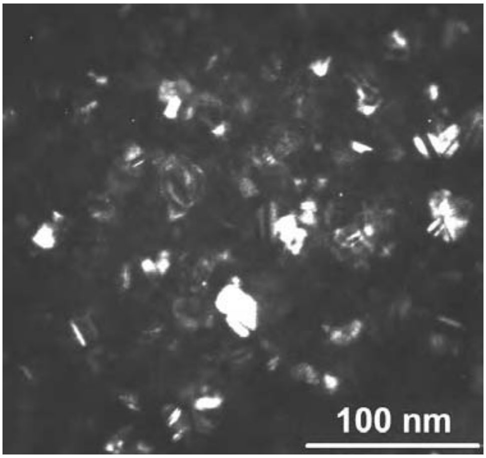
Precursors of alumina are viscous aqueous solutions of basic aluminium salts, $Al\ X_n\ (OH)_{3-n}$, where X can be an inorganic ligand (Cl^-, NO^{3-} . . .) or an organic ligand ($HCOOH^-$ . . .).[12] Spinning of the precursor produces a gel fibre which is then dried and heat treated. Decomposition of the precursor induces the precipitation of aluminium hydroxides, such as boehmite AlO(OH), and the outgassing of a large volume of residual compounds. The associated volume change and porosity at this step has to be carefully controlled. It is also possible to spin aqueous sols based on aluminium hydroxides directly. Above 400 °C and up to around 1000 °C the fibre is composed of grains, in the range of 10 to 100 nm, of transitional forms of alumina associated with finely divided porosity. Above 1100 °C, stable α-alumina nucleates and a rapid growth of micron-sized grains occurs together with the coalescence of pores. The fibres become extremely brittle owing to large grain boundaries emerging at the fibres' surfaces and cannot be used in this form. The use of alumina fibres above 1100 °C therefore requires the control of the nucleation and growth of α-alumina and porosity. This has been achieved by adding either silica precursors or seeds for α-alumina formation to the fibre precursors and has led to two classes of alumina-based fibres, one consisting primarily of α-alumina grains and the other of transitional alumina phases together with another phase.

7.4.2 Alumina–silica fibres

Alumina–silica fibres were the first ceramic fibres produced in the early 1970s, for thermal insulation applications. A small amount of silica (≈3% wt in the *Saffil* short fibres from ICI) allows the sintering of the transitional

Table 7.2 Properties and compositions of alumina-based fibres. Compositions and densities are those given by the manufacturers

Fibre type	Manufacturer	Trade mark	Composition (wt %)	Diameter (μm)	Density (g/cm^3)	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
α-Al_2O_3 fibres	Du Pont	*FP*	99.9% Al_2O_3	20	3.92	1.2	0.29	414
	Mitsui Mining	*Almax*	99.9% Al_2O_3	10	3.6	1.02	0.3	344
	3M	*Nextel 610*	99% Al_2O_3 0.2%–0.3 SiO_2 0.4–0.7 Fe_2O_3	10–12	3.75	1.9	0.5	370
Alumina-silica fibres	ICI	*Saffil*	95% Al_2O_3 5% SiO_2	1–5	3.2	2	0.67	300
	Sumitomo	*Altex*	85% Al_2O_3 15% SiO_2	15	3.2	1.8	0.8	210
	3M	*Nextel 312*	62% Al_2O_3 24% SiO_2 14% B_2O_3	10–12 or 8–9	2.7	1.7	1.12	152
	3M	*Nextel 440*	70% Al_2O_3 28% SiO_2 2% B_2O_3	10–12	3.05	2.1	1.11	190
	3M	*Nextel 720*	85% Al_2O_3 15% SiO_2	12	3.4	2.1	0.81	260
Alumina-zirconia fibres	3M	*Nextel 650*	89% Al_2O_3 10% ZrO_2 1% Y_2O_3	11	4.1	2.5	0.7	360



7.5 Dark field image of an *Altex* fibre revealing γ-alumina grains that are embedded in amorphous silica.

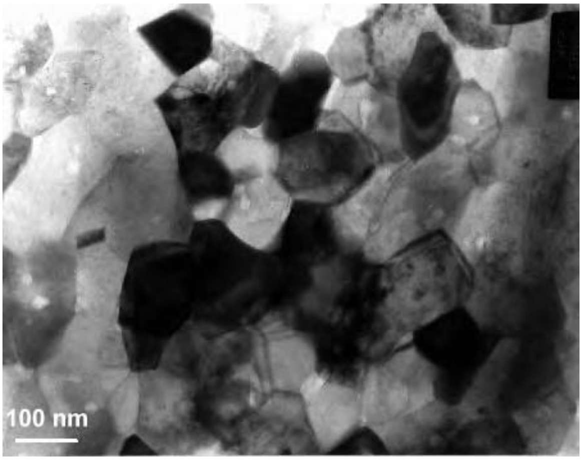
forms of alumina and delays the nucleation and growth of α-alumina to 1300 °C.[13] Larger amounts (15% wt in the *Altex* fibre from Sumitomo) produce γ-alumina grains of around 25 nm in amorphous silica,[14] as shown in Fig. 7.5. Mullite, with a composition between $2Al_2O_3.SiO_2$ and $3Al_2O_3.2SiO_2$, crystallises above 1100 °C, before the formation α-alumina, the growth of which is then restricted. The α-alumina formation can be totally suppressed if enough silica is added to consume the metastable alumina by mullite formation. 3M began to produce the *Nextel* series of fibres having the composition of mullite. Boria additions lowered the temperature of mullite formation, helped sintering and increased the fibre strength. Various degrees of crystallinity can be obtained according to the amount of boria and the pyrolysis temperature. *Nextel 312*, with 14% B_2O_3, is a quasi-amorphous fibre,[15] the high temperature properties of which are limited by the volatilisation of boron compounds from 1100 °C. *Nextel 440* contains 2% B_2O_3 and is composed of γ-alumina in amorphous silica. The same fibre composition, heated above the mullitisation temperature, yields fully dense crystallised mullite with 50 to 100 nm grain sizes.[16] However, the good high-temperature creep resistance which could be expected from the complex mullite structure is not obtained owing to the presence of an amorphous borosilicate intergranular phase.

The effect of silica on the room-temperature properties of alumina fibres is to reduce their overall stiffness ($E(SiO_2) \approx 70$ GPa, $E(Al_2O_3) \approx 400$ GPa) and to increase their room temperature strength by avoiding the formation of large grains.[1] This results in flexible fibres that can be used in the form of bricks or woven cloths for thermal insulation. Strength loss at high temperature occurs from 1000 °C. The main drawback of silica is that it facilitates creep, which begins from 900 °C so that these fibres cannot be used for structural applications above this temperature.

7.4.3 Single phase α-alumina fibres

To obtain creep-resistant alumina fibres, they have to be deprived of intergranular silicate phases. This imposes processes other than the addition of silica to control α-alumina growth. A pure α-alumina fibre was first produced by Du Pont in 1979.[17] *Fiber FP* was obtained by the addition, to an alumina precursor, of more than 40% wt of α-alumina powder having a grain size of less than 0.5 μm. The use of a lower fraction of precursor reduces the porosity owing to its decomposition and to the dehydration of hydrous aluminas. α-alumina particles act as seeds for the growth of α-alumina and so remove the problems associated with the delay of nucleation and rapid grain growth. In the case of *Fiber FP*, the grain size of the powder included in the precursor precluded the spinning of fine filaments. The *Fiber FP* had a diameter of 20 μm, and this, added to the intrinsic high stiffness of α-alumina ($E_{FP} = 410$ GPa) and low strength (1.5 GPa at 25 mm) owing to its large grain size (0.5 μm), made the fibre unsuitable for weaving. Flexible α-alumina fibres require diameters of around 10 μm. This was first achieved by Mitsui Mining by reducing the size of the α-alumina powder.[18] However, this affected the control of porosity and the resulting *Almax* fibre encloses a significant amount of pores inside alumina grains, which are of 0.5 μm in size.[1] Later, 3M produced the *Nextel 610* fibre,[19] which is a fully dense α-alumina fibre of 10 μm in diameter, as seen in Fig. 7.6, with a grain size of 0.1 μm and possesses the highest strength of the three α-alumina fibres described, as shown in Table 7.2.

The high-temperature behaviours of these three fibres are controlled by their microstructures, which are made of fine isotropic grains.[20] Plasticity occurs from 1000 °C and superplastic behaviour can be obtained at 1300 °C with the *FP* fibre. No intragranular plasticity can develop in these fibres as the small distances between two grain boundaries, perpendicular to the load axis, prevent the formation of dislocation sources and pin dislocation movement. However, the large number of boundary surfaces allows the relaxation of the imposed stress by grain boundary sliding. This mechanism involves movement of intergranular dislocations and is accommodated by interfacial controlled diffusion mechanisms. Amongst the three fibres, the lowest deformation rates are obtained with the *FP* fibre ($\sim 10^{-3}\,s^{-1}$ at 1300 °C). Diffusion and deformation are facilitated by porosity in the *Almax* and by grain size in the *Nextel 610*, which is five times smaller than in the other two fibres. Damage occurs by the growth of cavities at triple points and the coalescence of intergranular microcracks induces failure. The times



7.6 Microstructure of a *Nextel 610* fibre composed of α-alumina grains of around 100 nm.

to failure in creep are considerably reduced in the *Almax* fibre by the build-up of large intergranular pores.

These three fibres are stiff and chemically stable. They can therefore be used to reinforce matrices, such as light alloys, working in intermediate temperature ranges, or for applications at higher temperatures for which no load bearing capacity is required, as in thermal insulation. They were not developed to work in the conditions for which their poor creep behaviours have been demonstrated. However, the creep mechanisms that have been revealed have allowed the microstructure that would improve the high temperature behaviour of α-alumina based fibres to be better defined. These fibres must have fine grains, as large grains are detrimental to the fibre strength, but grain sliding has to be inhibited. Inclusions of second phases and fine but elongated oriented grains have been considered as possible solutions to achieve these goals.

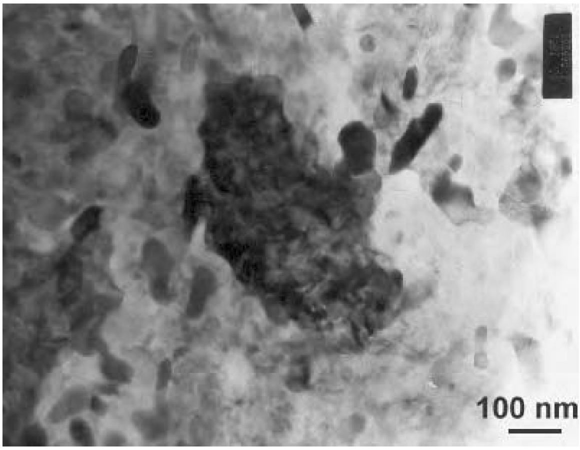
7.4.4 α-alumina/zirconia fibres

The dispersion of small particles of tetragonal zirconia between α-alumina grains was first employed by Du Pont, with the aim of producing a modified *FP* fibre with improved flexibility. This fibre, called *PRD-166*,[21] was obtained by the addition of zirconium acetate and yttrium chloride to the blend of the alumina precursor and α-alumina powder. The fibre had a diameter of 20 μm and contained 20% wt of tetragonal zirconia in the form of grains of 0.1 μm, which restricted the growth of α-alumina grains to 0.3 μm, on average.[20] The Young's modulus was lowered to 370 GPa because of the lower stiffness of zirconia ($E(ZrO_2)$ ~200 GPa). Tetragonal to monoclinic transformation of zirconia around the crack tip at room temperature toughened the fibre and a higher strength was obtained. However, this was not sufficient to ensure flexibility and production did not progress beyond the pilot stage. A flexible α-alumina-zirconia fibre, *Nextel 650* has been announced by 3M, with the aim of increasing the creep resistance with respect to that of the α-alumina *Nextel 610* fibre.

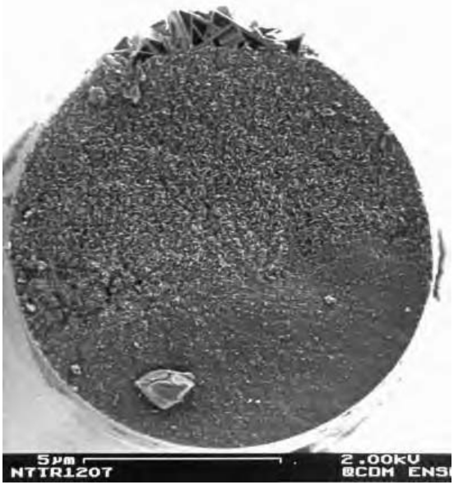
The effect of the addition of zirconia on the high-temperature mechanical behaviour is to delay the onset of plasticity to 1100 °C and to decrease the strain rates in creep. The mechanisms proposed have been the pinning of the grain boundaries by the intergranular zirconia particles and the modification of the Al^{3+} diffusion rates at the alumina/alumina grain boundaries by the presence of Zr^{4+} ions. However, these mechanisms are less efficient as the temperature exceeds 1100 °C and at 1300 °C the creep rates of *FP* and *PRD 166* fibres are similar.[20]

7.4.5 α-alumina/mullite fibres

The complex crystalline structure of mullite provides creep resistance materials if a sintered microstructure can be obtained without the help of an excess of silica. 3M produced a dense mullite/α-alumina fibre, called *Nextel 720*,[22] by using an aqueous sol composed of intimately mixed silica and alumina precursors, with iron compounds used as the seeds for α-alumina. The fibre is composed of a continuum of mullite mosaic grains of about 0.5 μm with wavy contours, with no silicate intergranular phase. Each mosaic grain consists of several mullite grains that are slightly mutually misoriented, and encloses spherical and elongated particles of α-alumina of respectively 50 nm in diameter and 100 nm in length, as can be seen in Fig. 7.7. The elongated particles show some preferential alignment with respect to the fibre axis and their long facets correspond to the basal plane of α-alumina. After heat treatment, from 1300 °C, the microstructure evolves towards faceted mullite ($3Al_2O_3 : 2SiO_2$) grains deprived of intragranular alumina particles, together with larger α-alumina particles which become intergranular. Some of the elongated α-alumina grains show exaggerated growth. This evolution of the microstructure is accelerated by the combination of temperature and load. When tested in creep, these fibres show much reduced creep rates as compared to pure α-alumina fibres and creep rates of the order of $10^{-6}\,s^{-1}$ have been measured at 1400 °C.[23] This remarkable behaviour is attributed to the high creep resistance of mullite and to the presence of the elongated and oriented α-alumina grains. The fibres are, however, very sensitive to alkaline-containing environments. Mullite decomposes in the presence of a low concentration of alkalines to form aluminosilicate phases of melting points lower than 1200 °C. The fast growth



7.7 Microstructure of a *Nextel 720* fibre revealing diffracting mullite aggregates and α-alumina grains that are enclosed in other non-diffracting mullite grains. Some of these alumina grains are elongated and oriented preferentially parallel to the fibre axis.



7.8 Fracture morphology of a *Nextel 720* fibre at 1200 °C in the presence of alkaline contaminants.

of large alumina grains, under load, occurs by liquid transportation leading to large platelets as can be seen in Fig. 7.8 and which are detrimental to fibre strength. This observation could seriously limit the use, in real environments at high temperature, of fibres based on the Al_2O_3–SiO_2 system.

7.5 Other polycrystalline oxide fibres

Attempts to produce creep-resistant oxide reinforcements have led to the experimental development of polycrystalline fibres from complex crystallographical systems such as mullite, chrysoberyl or garnet-like structures. Among them, yttrium aluminium garnet (YAG) ($Y_3Al_5O_{12}$) fibres seem the most promising.

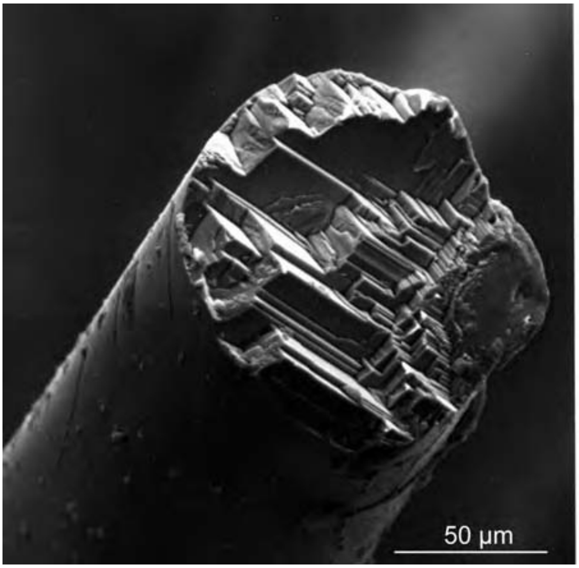
7.6 Single-crystal oxide fibres

Continuous monocrystalline filaments have been developed by the Saphikon company in the USA.[24] These filaments are grown from molten alumina, either heated in a crucible or from the end of an alumina rod heated by a laser, and, as a consequence, are produced at a slow rate and high cost and with large diameters usually in excess of 100 µm. The stoichiometric composition of these fibres with the absence of grain boundaries means that they should be able to better withstand high temperatures above 1600 °C. Careful orientation of the seed crystal enables the crystalline orientation to be controlled so that creep resistance can be optimised. Published data on the strength of *Saphikon* fibres as a function of temperature reveal that strength variation is not a simple function of temperature. The observed fall in strength around 300 °C, which is then followed by an increase in strength around 500 °C, could be due to stress corrosion followed by crack blunting.[24] These fibres are not without defects and characteristic bubbles can be seen in the fibres, most probably due to convection during fibre growth at the meniscus point between the solid and the melt. The crystalline fracture morphology of these fibres is shown in Fig. 7.9.

The same manufacturing processes have been employed to produce an eutectic fibre consisting of interpenetrating phases of α-alumina and YAG. The structure is lamellar and oriented parallel to the fibre axis. This fibre does not show the same fall in strength seen with the single-phase alumina fibre. However, such fibres are seen to relax from 1100 °C but do not have as strong a dependence on temperature as the polycrystalline oxide fibres.[25]

7.7 Conclusions

The requirement to have reinforcing fibres capable of operating at very high temperatures and under corrosive environments has been addressed by the development of two families of small-diameter reinforcements and large-diameter fibres made by CVD or grown from the melt. The former SiC- and alumina-based fibres have been improved by a greater knowledge and control of the relationships between process and microstructure that governs the ultimate mechanical properties. The reduction of amorphous



7.9 Room-temperature fracture morphology of a monocrystalline α-Al_2O_3 fibre produced by *Saphikon*.

phases, in both classes of fibres, has largely overcome the poor creep behaviour and structural instability at high temperatures of earlier generations of these fibres. The latest SiC fibres have sintered microstructures showing excellent creep resistance and strength retention up to 1400 °C. These fibres are, however, limited by oxidation. The large diameter SiC fibres made by CVD are of primary interest for reinforcing titianium. Polycrystalline alumina fibres do not suffer from this limitation but can exhibit superplastic behaviour at 1300 °C. The addition of second phases, such as zirconia or mullite, can inhibit grain boundary sliding.

The large diameter oxide fibres resist much better the effects of very high temperatures but their high costs and the inability to weave such fibres means that they have attracted little industrial interest. The development of polycrystalline oxide fibres for very high temperatures is still in its infancy and considerable advances may be expected from the production of fibres based on oxides with complex crystallographic structures.

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