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Fine diameter ceramic fibres

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Abstract

Two families of small diameter ceramic fibres exist. The oxide fibres, based on alumina and silica, which were initially produced as refractory insulation have also found use as reinforcements for light metal alloys. The production of SiC based fibres made possible the development of ceramic matrix composites. Improved understanding of the mechanisms which control the high temperature behaviour of these latter fibres has led to their evolution towards a near stoichiometric composition which results in strength retention at higher temperatures and lower creep rates. The SiC fibres will however be ultimately limited by oxidation so that there is an increasing interest in complex two phase oxide fibres composed of α-alumina and mullite as candidates for the reinforcement of ceramic matrices for use at very high temperatures. These fibres show low creep rates, comparable to the SiC based fibres but are revealed to be sensitive to alkaline contamination. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Creep; Fibres; Microstructure; SiC

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1. Introduction

Small diameter ceramic fibres have undergone great changes since their early development due to the need for reinforcements in structural ceramic matrix composite (CMC) materials to be used in air at temperatures above 1000°C. 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] 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.

Initially ceramic fibres were produced in the early 1970s for use as refractory insulation which required the material to withstand high temperatures, typically up to 1600°C, in air but under no applied load. The fibres which were developed at this time were the discontinuous Saffil fibres, with diameters of 3 μm, introduced by ICI in 1972.[2] These fibres were made by the blow extrusion of a sol and consisted of γ-alumina with 3% SiO_2 to inhibit grain growth and control porosity. The Nextel 312 fibre introduced by 3M around 1974 was also made by a sol route and was an amorphous fibre with a mullite composition. Both of these fibres are still in production. Later in the same decade Du Pont produced Fibre FP which was the first continuous α-alumina fibre and was made specifically for the reinforcement of aluminium.[3] However it was the commercial production of the SiC based Nicalon fibres[4] in 1982 by Nippon Carbon which allowed ceramic matrix composites to be developed. The fibres were initially used by SEP to replace carbon fibres in carbon–carbon composites used in rocket nozzles. This improved the oxidative resistance of the material. The carbon matrix was then replaced by SiC to make the first SiC–SiC composites which could be considered for applications at higher temperatures than those at which nickel based super alloys could be used. Efforts have been made since this time to improve the high temperature behaviour of small diameter SiC fibres by making them with compositions increasingly approaching stoichiometry.[5,6] However these fibres are inherently limited by oxidation at very high temperatures. As a result of this limitation a renewal of interest has occurred in oxide systems as a means of making reinforcements capable of operating in air at even higher temperatures than the SiC fibres.

An important characteristic needed in a ceramic fibre reinforcement is flexibility so that preforms can be made by weaving or other related technologies. This is ensured, with materials having even the highest Young's moduli, by a small diameter, as 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. A lower limit in fibre diameter is around 1 μm as at this diameter the fibres become a health hazard, if inhaled, as they block the alveolar structure of the lungs. Also related to the ease of converting the fibres into preforms is the desire for a strain to failure of around 1% and as a Young's modulus of 200 GPa or more is required, this imposes a room temperature strength of more than 2 GPa. Competing materials are usually dense so that a specific gravity of less than 5 would be desirable. The fibres are destined to be used at high temperature and in air so that long term chemical, microstructural and mechanical stability up to and preferably above, 1500°C is required. This means that the structure of the ceramic fibre should not evolve and it should exhibit low creep rates no greater than those of nickel based alloys. Lastly, low reactivity with the matrix is required if the crack stopping process which is the basis of CMC tenacity is to be achieved.

2. Silicon carbide fibres from organic precursors

2.1. SiC from an oxygen cured precursor route

The work of Yajima and his colleagues in Japan was first published in the mid-1970s.[4] The Nicalon and Tyranno fibres produced, respectively, by Nippon Carbon and Ube Industries are the commercial results of this work. These fibres are produced by the conversion of, respectively polycarbosilane (PCS) and polytitanocarbosilane (PTC) precursor fibres which contain cycles of six atoms arranged in a similar manner to the diamond structure of β-SiC. The molecular weight of this polycarbosilane is low, around 1500, which makes drawing of the fibre difficult. The addition of around 2% wt. of titanium, achieved by the grafting of titanium alkoxide between the PCS chains in the Ube precursor, increases molecular weight slightly, which may help with drawing and also may slightly increase thermal resistance by the creation of Ti–C bonds at high temperatures. In these polymers methyl groups ($-CH_3$) in the polymer are included as side groups to the $-(Si-C)_n-$ main chain so that during pyrolysis hydrogen is produced, leaving a residue of free carbon. The production of the first generations of SiC based fibres involved subjecting the precursor fibres to heating in air at around 200°C to produce cross-linking of the structures. This oxidation makes the fibres infusible but has the drawback of introducing oxygen into the structure which remains after pyrolysis. The ceramic fibres are obtained by a controlled increase in temperature in an inert atmosphere up to 1200°C. The properties and composition of these fibres are shown in Table 1.

The fibres obtained by this route have a glassy appearance when observed in SEM, as can be seen from Fig. 1, however a closer examination reveals that they contain a majority of β-SiC, of around 2 nm but also significant amounts of free carbon of less than 1nm and

Table 1
Properties and compositions of silicon based fibres

Fibre type	Manufacturer	Trade mark	Composition (wt.%)	Diameter (μm)	Density (g/cm3)	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 S	SiC + O + C	13	3.0	2.5	0.65	375
	Ube Industries	Tyranno SA	SiC + C + O + Al	10	3.0	2.5	0.75	330
	Dow Corning	Sylramic	SiC + TiB2 + C + O	10	3.1	3.0	0.75	390

excess silicon combined with oxygen and carbon as an intergranular phase.[7,8] Their strengths and Young's moduli show little change up to 1000°C.[9] Above this temperature, in air, both these properties show a slight decrease up to 1400°C. Titanium carbide grains are seen in the Tyranno fibres from 1200°C.[10] Between 1400 and 1500°C the intergranular phases in both Nicalon and Tyranno fibres begin to decompose, carbon and silicon monoxides are evacuated and a rapid grain growth of the silicon carbide grains is observed. The densities of the fibres decrease rapidly and the tensile properties exhibit a dramatic fall. When a load is applied to the fibres, it is found that a creep threshold stress exists above which creep occurs.[11] The fibres are seen to creep above 1000°C and no stress enhanced grain growth is observed after deformation. Creep is due to the presence of the oxygen rich intergranular phase. The fibres made by the above process are the Nicalon NL-200 and Tyranno LOX-M fibres. The Lox-M fibres have been successfully used for the formation of composite material, without the infiltration of a matrix material and with a high fibre volume fraction, under the name of Tyranno Hex.[12] Bundles of fibres, which have been pre-oxidised to give them a thin surface layer of silica, are hot-pressed leading to a dense hexagonal packing of the fibres, the cavities being filled by silica and TiC particles. The strength of Tyranno Hex measured in bending tests has been reported to be stable up 1400°C in air.

Fig. 1. Fracture morphology of a first generation Nicalon fibre, having a diameter of 15 μm and revealing a glassy appearance.

2.2. *Electron cured precursor filaments*

A later generation of Nicalon and Tyranno fibres has been produced by cross-linking the precursors by electron irradiation so avoiding the introduction, at this stage, of oxygen. These fibres are known as Hi-Nicalon,[5] which contains 0.5% wt. oxygen and Tyranno LOX-E[13] which contains approximately 5% wt. oxygen.[10,14] The higher value of oxygen in the LOX-E fibre is due to the introduction of titanium alkoxides for the fabrication of the PTC. The decrease in oxygen content in the Hi-Nicalon compared to the NL-200 fibres has resulted in an increase in the size of the SiC grains and a better organisation of the free carbon. This can be see in Fig. 2. The size of the SiC grains is 5 to10 nm. Carbon aggregates appear by the stacking of four distorted layers over a length of 2 nm on average. A significant part of the

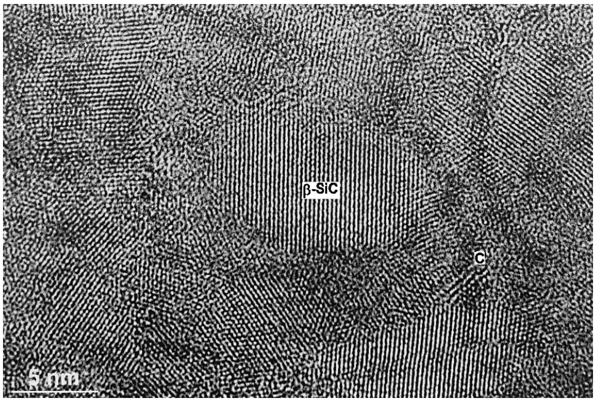

Fig. 2. Lattice fringe image showing regions of lower order between crystallised β-SiC grains of around 10 nm and free carbon in the form of several distorted layers with lengths of around between 2 and 5 nm.

SiC is not perfectly crystallised and surrounds the ovoid β-SiC grains. Further heat treatment of the fibres at 1450°C induces the SiC grain to grow up to a mean size of 30 nm, to develop facets and be in contact with adjacent SiC grains, as is shown in Fig. 3. Turbostratic carbon has been seen to grow preferentially parallel to some of these facets and could in some cases form cages around SiC grains limiting their growth. Significant improvements in the creep resistance are found for the Hi-Nicalon fibre compared to the NL-200 fibre which can further be enhanced by a heat treatment so as to increase its crystalinity. The LOX-E fibre has a microstructure and creep properties which are comparable to those of the LOX-M and Nicalon NL200 fibre. A comparison of the creep behaviour of the LOX-E and Hi-Nicalon fibres is shown in Fig. 4. Despite the electron curing process, the use of a PTC does not allow the reduction of the oxygen in the intergranular phase of the ceramic fibre to the extent seen in the Hi-Nicalon so that, as in the LOX-M, grain growth is impeded below 1400°C and creep is enhanced. A more recent polymer, polyzirconocarbosilane (PZT) has allowed the titanium to be replaced by zirconium and the oxygen content to be reduced. The resulting fibres, known as Tyranno ZE and which contains 2% wt. of oxygen, show increased high temperature creep and chemical stability and resistance to corrosive environments compared to the LOX-E fibre.[15,16]

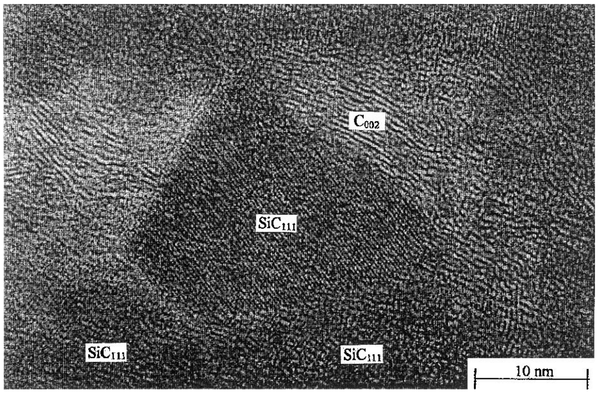

Fig. 3. Growth of faceted β-SiC grains and carbon aggregates parallel to the faces of a SiC grain in the Hi-Nicalon fibre heated at 1400°C for 24 h.

2.3. Near stoichiometric fibres

Efforts to reduce the oxygen content by processing in inert atmospheres and cross linking by radiation have produced fibres with very low oxygen contents. These fibres are not, however, stoichiometric as they contain significant amount of excess free carbon affecting oxidative stability and creep resistance. Near stoichiometric SiC fibres from polymer precursors are produced by the two Japanese fibre producers and in the USA by Dow Corning by the use of higher pyrolysis temperatures. This leads to larger grain sizes and the development of a sintered material.

Nippon Carbon has obtained a near-stoichiometric fibre, the Hi-Nicalon S, from a PCS cured by electron irradiation and pyrolysed by a modified Hi-Nicalon process in a closely controlled atmosphere above 1500°C.[5] As a result it is claimed by the manufacturer that excess carbon is reduced from C/Si = 1.39 for the Hi-Nicalon to 1.05 for the Hi-Nicalon S. The fibre has a diameter of 12 μm and SiC grain sizes of between 50 and 100 nm. The microstructure of the type S fibre is shown in Fig. 5. Considerable free carbon, which could help pin the structure at high temperature, can be seen between the SiC grains.

Ube Industries has developed a near stoichiometric fibre made from a polyaluminocarbosilane.[17] The precursor fibre is cured by oxidation, pyrolysed in two stages, first to 1300°C, to form an oxygen rich SiC fibre, then up to 1800°C to allow first the outgassing of CO, between 1500 and 1700°C, and sintering. The addition of aluminium as a sintering aid allows the degradation of the oxicarbide phase at high temperature to be controlled and catastrophic grain

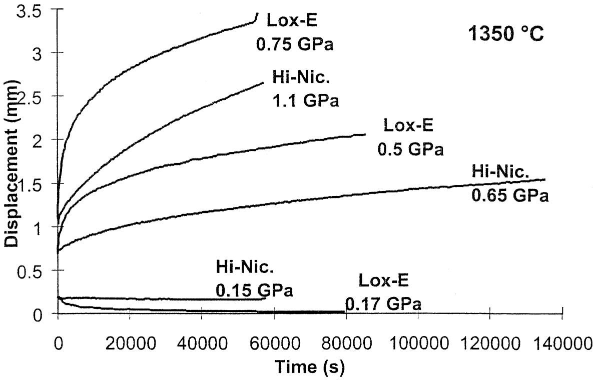

Fig. 4. A comparison of creep curves obtained at 1350°C with the Tyranno LOX-E and Hi-Nicalon fibres.

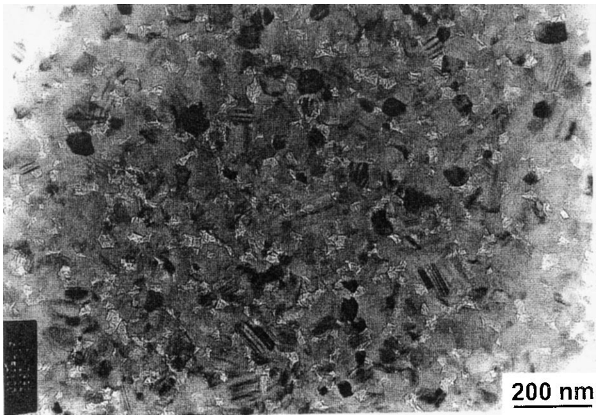

Fig. 5. The microstructure of the Hi-Nicalon type S, near stoichiometric SiC fibre, revealing SiC grains of 50–100 nm and free turbostratic carbon at triple points.

growth and associated porosity, which occurred with the previous oxygen rich fibres, avoided. The precursor fibre can then be sintered at high temperature so that the excess carbon and oxygen are lost as volatile species to yield a polycrystalline, near-stoichiometric, SiC fibre. This Tyranno SA fibre has a diameter of 10 μm and SiC grain sizes of about 200 nm. The microstructure of the fibre is shown in Fig. 6 which also reveals considerable excess carbon. Less than 1% wt. of Al has been added as a sintering aid and the manufacturer claims that it gives better corrosion resistance compared to other metals. A fracture surface of the Tyranno SA fibre is shown in Fig. 7 and can be seen to be noticeably more granular than the earlier generations of fibres.

Dow Corning has produced stoichiometric SiC fibres using PTC precursors containing a small amount of titanium, similar to the precursors described above for the earlier generation Ube fibres. These fibres are cured by oxidation and doped with boron which acts as a sintering aid. The precursor fibre is pyrolysed at around 1600°C to form a near stoichiometric fibre called SYLRAMIC fibre.[18] Such a fibre has a diameter of 10 μm and SiC grain sizes ranging from 0.1 to 0.2 μm with smaller grains of TiB_2 and B_4C. Fig. 8 shows the microstructure of the Sylramic fibre which has also be seen to contain excess carbon.

A comparison of the Young's moduli of the three near stoichiometric SiC fibres gives different results suggesting that they are not fully dense SiC materials. The Hi-Nicalon-S fibre has an elastic modulus 375 GPa and a density of 3.0 g/cm^3. The Tyranno SA fibre has a Young's modulus of 330 GPa and a density of 3.0 g/cm^3. The elastic modulus of the Sylramic fibres is 390 GPa and its density is 3.1 g/cm^3. A comparison of the strengths as a function of temperature of the three near stoichiometric SiC fibres is shown in Fig. 9. The three fibres show much improved creep properties with creep rates are 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 creep

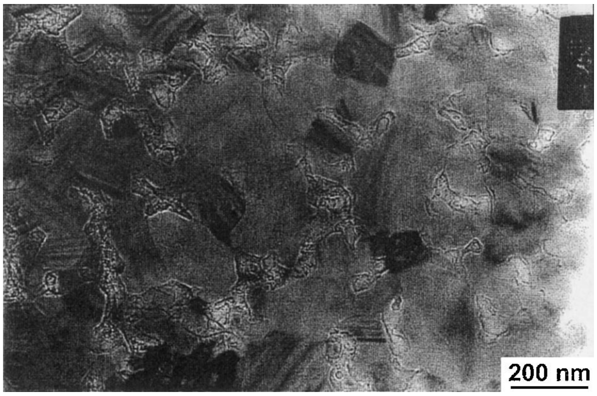

Fig. 6. The microstructure of the Tyranno SA, near stoichiometric SiC fibre, revealing SiC grains of 200 nm and free turbostratic carbon at triple points.

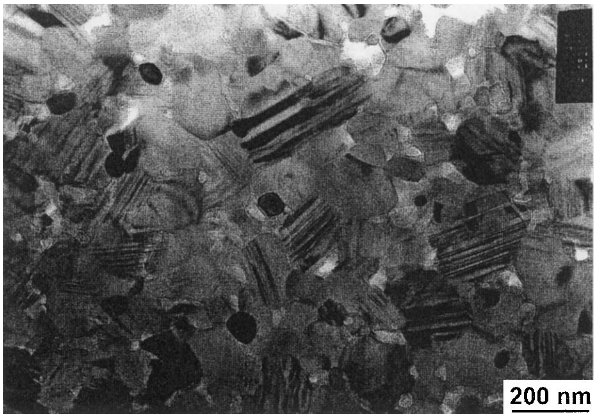

Fig. 8. The microstructure of the Sylramic, near stoichiometric SiC fibre, revealing SiC grains of around 200 nm, TiB_2 grains of 50 nm and free turbostratic carbon at triple points.

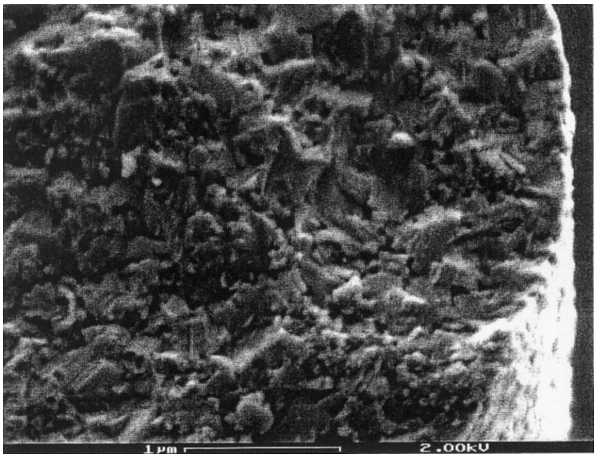

Fig. 7. Fracture morphology of a Tyranno SA fibre revealing its granular structure.

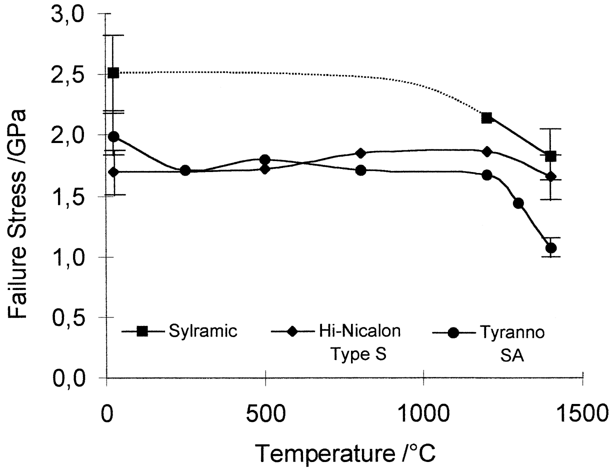

Fig. 9. Comparison of mean failure stress for near stoichiometric silicon carbide fibres.

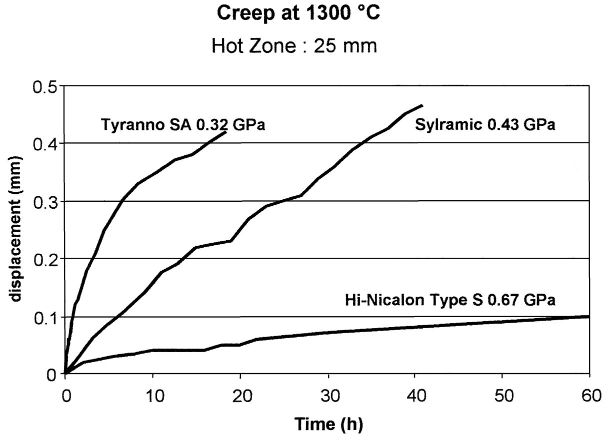

Fig. 10. Typical creep curves obtained at 1300°C for near stoichiometric silicon carbide fibres.

behaviours of the three fibres are shown in Fig. 10. It can be seen that 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 within the fibres at high temperatures. The characteristics of the three near stoichiometric SiC fibres are shown in Table 1.

The emerging generation of stoichiometric SiC fibres represents a solution to the instability of earlier fibres however the accompanying increase in Young's modulus and a slight loss in strength due to larger grain sizes leads to fibres which become more difficult to handle and convert into structures. This difficulty may be overcome by transforming partially converted Si–C–O fibres, into the woven or other form of fibre arrangement followed by pyrolysis and sintering to convert them into a stoichiometric dense form. The fibre structure could then be infiltrated to form the matrix, giving an optimised ceramic matrix composite. However even stoichiometric silicon carbide fibres will suffer from oxidation from 1200°C resulting in the formation of a silica surface layer. CMCs rely for their tenacity on their ability to accumulate cracks which are however paths for oxidation of the fibres. Silica layers created on the fibres in the vicinity of cracks would fuse the fibres to the matrix seriously reducing fibre pull-out and the absorption of failure energy of the composite. For this reason this family of fibres are likely to be limited to a maximum temperature of 1400°C.

3. Oxide fibres

Oxide fibres are clearly of interest for high temperature use in air and alumina combined with silica fibres began to be produced in the early 1970s for high temperature insulation. Silica was added to maintain the transitional forms of alumina and inhibit α-alumina grain growth. Such fibres show poor creep resistance however. Later in that decade pure and stiffer α-alumina fibres were produced for the reinforcement of aluminium to obtain light weight composites with a high Young's modulus. The brittleness of such fibres posed difficulties of handling. This has been ameliorated by reductions in fibre diameter and by the additions of second phases. The latest fibres in this family of reinforcements consist of α-alumina together with mullite which show remarkable high temperature properties and good creep resistance if contamination from alkaline elements can be avoided.

3.1. Alumina silica fibres

The difficulties in producing pure alumina fibres, which are the control of porosity and grain growth of the alpha phase, as well as the brittleness of these fibres can be overcome by the inclusion of silica in the structure. The microstructures of these fibres depend on the highest temperature the fibres 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. Above this range of temperatures a rapid growth of α-alumina porous grains is observed in pure alumina fibres.[19] The introduction of silica allows this transformation to be limited, as it reacts with alumina to form mullite ($3Al_2O_3{:}2SiO_2$). The presence of mullite at grain boundaries controls the growth of the α-alumina which has not been consumed by the reaction.[20]

The Young's moduli of these fibres are lower compared to that of pure alumina fibres, and such fibres 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 fibres are also used to reinforce aluminium alloys in the temperature range of 300–350°C. Continuous fibres of this type can be woven due to their lower Young's moduli.

3.1.1. The Saffil fibre

The Saffil fibre[20,21] is a discontinuous fibre with a diameter of 3 μm and was introduced by ICI in 1972. It consists of δ-alumina and 4% of silica and is produced by the blow extrusion of partially hydrolysed solutions of some aluminium salts with a small amount of silica. The fibre 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 fibre 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 fibre reinforcement for metal matrix composites.

Heat treatments of the fibre above 1000°C induce the δ–alumina to progressively change into α-alumina. After 100 h at 1200°C or 1 h at 1400°C acicular α-alumina grains can be seen on the surface of the fibre and mullite is detected. After 2 h at 1400°C the transformation is complete and the equilibrium mullite concentration of 13% is established. Shrinkage of the fibre and hence the dimensional stability of bricks is controlled up to at least 1500°C.

3.1.2. The Altex fibre

The Altex fibre is produced by Sumitomo Chemicals.[22] It is produced in two forms with diameters of 9 and 17 μm. The fibre is obtained by the chemical conversion of a polymeric precursor fibre, produced from a sol and then heated in air to 760°C, a treatment which carbonises the organic groups to give a ceramic fibre composed of 85% alumina and 15% amorphous silica. The fibre is then heated to 970°C and its microstructure, as shown in Fig. 11, consists of small γ-alumina grains of a few tens of nanometres intimately dispersed in an amorphous silica phase. The fibre has a room temperature tensile strength of 1.8 GPa and an elastic modulus of 210 GPa as shown in Table 2. Subsequent heat treatment produces mullite above 1100°C. At 1400°C the conversion to mullite is completed and the fibre is composed of 55% mullite and 45% α-alumina by weight. The presence of silica in the Altex fibres does not reduce their strength at lower temperatures compared with pure alumina fibres, however a lower activation energy is required for the creep of the fibre.[23] At 1200°C the continuum of silica allows Newtonian creep and the creep rates are higher than those observed with fibres composed solely of α-alumina and which are described below. The Altex fibre is produced as a reinforcement for aluminium alloys.

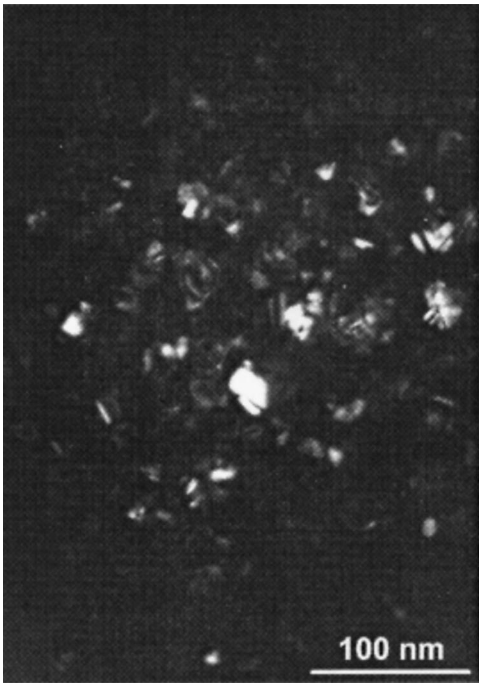

Fig. 11. TEM dark field image of the Altex fibre showing γ-alumina grains.

3.1.3. The Nextel 312-440 fibres

The 3M corporation produces a range of ceramic fibres under the general name of Nextel. The Nextel 312 and 440 fibres are produced by a sol–gel process.[24,25] They are composed of 3 mols of alumina for 2 mols of silica with various amounts of boria to restrict crystal growth. Solvent loss during the rapid 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 and 10–12 μm. Their mechanical properties are reported in Table 2.

The Nextel 312 fibre, 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 TEM observation although small crystals of aluminium borate have been reported. It has the lowest production cost of the three fibres and is widely used but has a mediocre thermal stability as boria compounds volatilise from 1000°C

Table 2
Properties and compositions of alumina based fibres

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 de Nemours	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	610	99% Al_2O_3;0.2–0.3;SiO_2 0.4–0.7;Fe_2O_3	10–12	3.75	2.6	0.7	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	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	440	70 Al_2O_3;28 SiO_2;2 B_2O_3	10–12	3.05	2.1	1.11	190
	3M	720	85 Al_2O_3;15 SiO_2	12	3.4	2.1	0.81	260

inducing some severe shrinkage above 1200°C. To improve the high temperature stability in the Nextel 440 fibre, the amount of boria has been reduced. This latter fibre is composed of 70% Al_2O_3, 28% SiO_2 and 2% B_2O_3 by weight and is formed in the main of small γ-alumina in amorphous silica. The fibre is of interest for the reinforcement of aluminium.

3.2. Alpha-alumina fibres

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, fibres based on alumina can contain silica as its presence allows the rapid growth of large and porous α-alumina grains to be controlled. However the presence of silica reduces the Young's modulus of the fibre and reduces their creep strength. High creep resistance implies the production of almost pure α-alumina fibres however to obtain a fine and dense microstructure is difficult. The control of grain growth and porosity in the production of α-alumina fibres is obtained by using a slurry consisting of α-alumina particles, of strictly controlled granulometry, in an aqueous solution of aluminium salts. These alumina particles act as seeds to lower the formation temperature and rate of growth of the α-alumina grains. 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 α-alumina fibre.

3.2.1. Fully dense α-alumina fibres

The FP-fibre, manufactured by Du Pont in 1979, was the first wholly α-alumina fibre to be produced.[3] It is no longer produced but is a useful reference for a pure α-alumina fibre. It was continuous with a diameter of 18 μm. This fibre was composed of 99.9% α-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 410 GPa, a tensile strength of 1.55 GPa at 25 mm but a strain to failure of only 0.4%.[26] This brittleness together with its diameter 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. Up to 1000°C the Fibre FP showed linear macroscopic elastic behaviour in tension. Its granular fracture morphology can be seen in Fig. 12. Above 1000°C, the fibre was seen to deform plasticity in tension and the mechanical characteristics decreased rapidly. At 1300°C, strains in tension increased and could sometimes reach 15%. Creep was observed from 1000°C. Very little primary creep was reported, but steady state creep was seen followed by tertiary creep. This small and continuous increase of the strain just before failure indicated an accumulation of damage in the fibre that preceded failure. Grain growth of 40% was revealed for a fibre which failed with a strain of 30%, with an applied stress equal to 17% of the failure stress. There was no overall preferential direction for the grain growth but the development of cavities at some triple points was noticed due to the pile up of intergranular dislocations at triple points caused by insufficient accommodation of the deformation. The external surfaces of the FP fibres broken in creep at 1300°C after large deformations showed numerous transverse microcracks, which were not observed for smaller strains. No modification of the granulometry was observed after heat treatment without load at 1300°C for 24 h but large deformations resulting from tensile and creep tests conducted at 1300°C were observed to induce grain growth. The strain rates from 1000 to 1300°C were seen to be a function of the square of the applied stress and the activation energy was found to be in the range of 550 to 590 kJ mol^{-1}. The creep mechanism of Fibre FP has been described as being based on grain boundary sliding achieved by an intergranular movement of dislocations and accommodated by several interfacial controlled diffusion mechanisms, involving boundary migration and grain growth. The failure of the fibre, at high temperature, occurred after a short period of damage, by the growth of transverse intergranular microcracks from the cavities, the coalescence of which led to a non-flat failure surface.

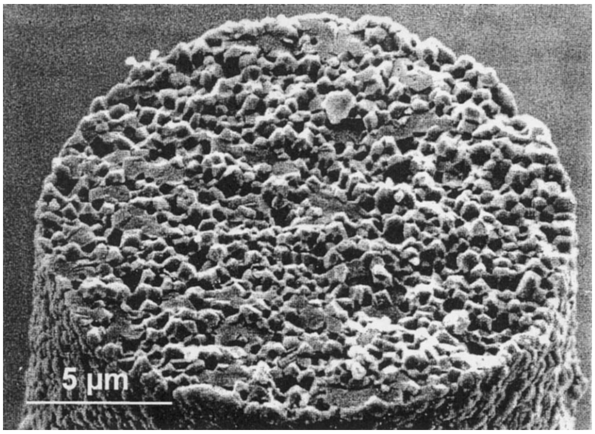

Fig. 12. Fracture morphology of fiber FP revealing its granular structure.

This fibre 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 fibres that they have produced. This reduction of diameter has an immediate advantage of increasing the flexibility and hence the weaveability of the fibres.

A continuous α-alumina fibre, with a diameter of 10 μm, was introduced by 3M in the early 1990s with the tradename of Nextel 610 fibre.[27] It is composed of around 99% α-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. As can be seen from Fig. 13, the fibre is polycrystalline with a grain size of 0.1 μm, 5 times smaller than in Fibre FP. As shown in Table 2. this smaller grain size together with the smaller diameter leads to a fibre strength which is twice the tensile strength measured for Fibre FP.

Creep occurs from 900°C and strain rates are 2 to 6 times larger than those of Fibre FP, due to the finer granulometry and possibly to the chemistry of its grain boundaries. A stress exponent of approximately 3 is found between 1000 and 1200°C with an apparent activation energy of 660 kJ/mol. Failure frequently occurs via the coalescence of cavities into large cracks over the whole gauge length and the failure surfaces are rougher compared to those obtained at room temperature, in the same manner as was seen with Fibre FP. Local cavitations and necking around heterogeneities sometimes induce failure.

3.2.2. *Porous α-alumina fibres*

An α-alumina fibre which is still commercially available was produced first in the early 1990s by Mitsui Mining.[28] It is composed of almost pure α-alumina and has a diameter of 10 μm. The fibre has a lower density of 3.60 g/cm^3 compared to Fibre FP. Like Fibre FP, the Almax fibre consists of one population of grains of around 0.5 μm; however, the fibre exhibits a large amount of intragranular porosity, and associated with numerous intragranular dislocations without any periodic arrangement.[26] This indicates rapid grain growth of α-alumina grains during the fibre 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 h, unlike that with the other pure alpha alumina fibres, for which grain growth is related to the accommodation of the slip by diffusion.

Fig. 13. TEM image of Nextel 610 fibre revealing α-alumina grains of around 0.1 μm.

The fibre exhibits linear elastic behaviour at room temperature in tension and brittle failure. The mechanical properties of the Almax fibre are shown in Table 2. Its Young's modulus is lower than that of the Fibre FP, because of the greater amount of porosity. The reduction of the measured failure stress of the Almax compared to those of the FP and the more pronounced intragranular failure mode for this fibre compared to the FP fibre show a weakening of the grains by the intragranular porosity. The fibres exhibit linear macroscopic elastic behaviour up to 1000°C. Above 1000°C the mechanical characteristics decrease rapidly, with a more severe drop than for Fibre FP. Tensile failure of the Almax fibre at 1250°C has revealed isotropic grain growth up to 55%. No extended regions of damage could be observed, as seen on the Fibre FP surface.

Creep occurs from 1000°C for the Almax fibres and the fibres show a lower resistance to creep than Fibre FP. Diffusion and grain boundary sliding are facilitated by the growth of intergranular porosity and much higher strain rates are obtained. This intergranular porosity which appears in the fibre during creep may have been created by the interception of intragranular pores by the boundaries of the growing grains. This intergranular pore growth, rapidly induces failure.

3.3. *Alpha-alumina fibres containing a second phase*

3.3.1. *Zirconia-reinforced alumina fibres*

Du Pont further developed the Fibre FP to produce a fibre called PRD-166 which consisted of 80% wt. α-alumina with 20% wt. of partially stabilised zirconia.[29] The introduction of tetragonal zirconia resulted in a toughening of the fibre and a decrease of its Young's modulus allowing some increase in strain to failure. The fibre began to creep at 1100°C, 100°C above the temperature creep threshold for Fibre FP and showed lower strain rates, however this advantage, compared to Fibre FP, was lost at 1300°C.[26] PRD-166 was not produced commercially as its large diameter prohibited weaving despite the small increase in flexibility.

3M has announced the development of a zirconia reinforced alumina fibre, Nextel 650, with a smaller diameter than that of the PRD-166 fibre which may allow it to be woven.[30]

3.3.2. *The Nextel 720 alumina mullite fibre*

The Nextel 720, produced by 3M, contains the same alumina to silica ratio as in the Altex fibre, that is around 85% wt. Al_2O_3 and 15% wt. SiO_2.[31] The fibre 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, composed of 2 mols of alumina to one of silica (2:1 mullite) and alpha alumina. Unlike other alumina–silica fibres the Nextel 720 fibre is composed of mosaic grains of about 0.5 μ with wavy contours, consisting of several slightly mutually misoriented mullite grains in which are embedded α-alumina grains some of which are elongated, as shown in Fig. 14.[32] At room temperature its Young's modulus and tensile strength at 25 mm are 260 and 2.1 GPa, respectively, as shown in Table 2. Post heat treatment leads to an enrichment of α-alumina in the fibre as mullite rejects alumina to evolve towards a 3:2 equilibrium composition. Grain growth occurs from 1300°C and at 1400°C the wavy interfaces are replaced by straight boundaries, as shown in Fig. 15. The fibre has been shown to be sensitive to contamination by alkalines which are thought to create a silicate phase at the fibre surface. Such phases can have melting points lower than 1000°C, and if formed, allow rapid diffusion of elements and grain growth so that strength has been shown to depend on the test conditions. In the presence of such contaminants strength falls at temperatures above 1000°C due to crack initiation at large α-alumina platelets which develop at the surface, as Fig. 16 reveals. If contamination is avoided and creep experiments are carried out Dorn plots indicate that 2 orders of magnitude exist between the strain rates of the Nextel 720 fibres, at 1200°C and any other oxide fibre so far produced commercially. Results from creep tests conducted at 1400°C are shown in Fig. 17 and give a creep rate of the order of 10^{-6} s^{-1}. This improved creep resistance is attributed to the particular microstructure of the fibre which is composed of aggregates of mullite, which is known as possessing very good creep properties, rather than the two-phase nature of the structure.

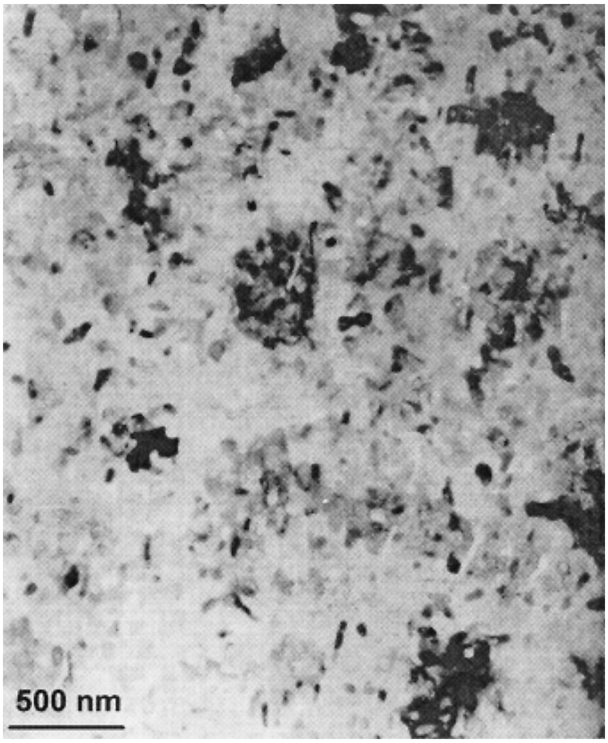

Fig. 14. Microstructure of Nextel 720 fibre exhibiting mullite aggregates enclosing elongated α-alumina grains.

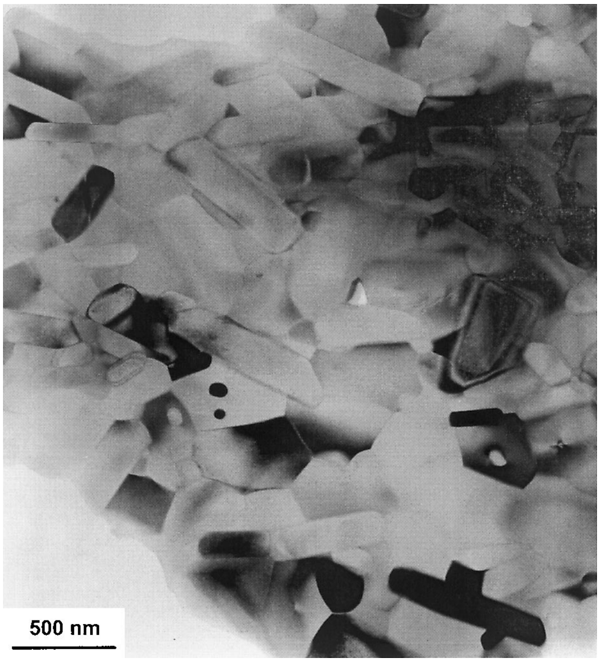

Fig. 15. Microstructure of Nextel 720 fibre after heat treatment at 1400°C for 4 days.

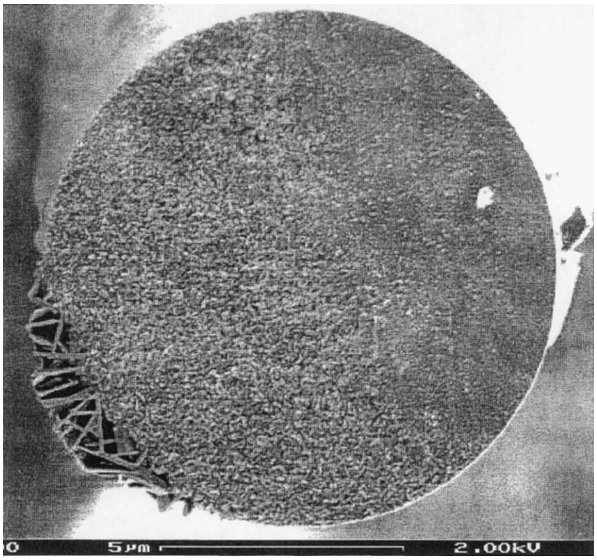

Fig. 16. Fracture morphology of Nextel 720 fibre failed in tension at 1200°C. Failure is initiated by the growth of large α-alumina grains.

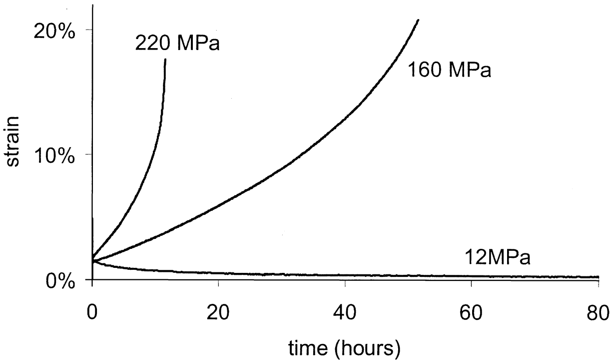

Fig. 17. Creep curves for Nextel 720 fibre at 1400°C under different stresses.

4. Conclusions

Two families of small diameter ceramic fibre have been developed based on SiC and alumina, often combined with silica. The SiC based fibres have allowed CMCs to be developed and in order to meet the requirements of the applications foreseen for these composite materials, the microstructures of the fibres have evolved towards stoichiometry. The elimination of a less well organised intergranular phase has been seen to improve both high temperature stability and creep behaviour. Such near stoichiometric fibres seem to be candidates for applications up to 1400°C but surface oxidation ultimately limits them from use at higher temperatures.

Oxide fibres have been used as refractory insulation and reinforcement for light metal alloys. Alumina in one of its transition phases combined with silica can be made into flexible fibres which can be woven and used for the reinforcement of metals however softening of the silica and grain transformation limits these fibres to applications lower than 1000°C. Alpha alumina fibres have greater stiffness, which also results in greater brittleness and show creep from 1000°C. These fibres are also used for reinforcing light alloys but are not suitable for CMCs. The Nextel 720 fibre which consists of both mullite aggregates and α-alumina show similar creep rates as the SiC fibres and is potentially a reinforcement for CMCs but its sensitivity to alkaline contamination has to be better understood.

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