J MATER SCI 41 (2006) 823–839

A review of the development of three generations of small diameter silicon carbide fibres

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Three generations of small diameter ceramic fibres based on polycrystalline silicon carbide have been developed over a period of thirty years. This has been possible due to studies into the relationships between the microstructures and properties of the fibres. A variety of techniques have been employed by research teams on three continents. The fibres are made by the conversion of polymer precursors to ceramic fibres and all three generations are presently produced commercially. The nature of the precursor and the techniques used for cross-linking have been varied in order to optimise both properties and cost of manufacture. It has been possible to improve the characteristics of the fibres as the processes involved in the cross-linking of the precursor fibres have been better understood and the mechanisms governing both room temperature and high temperature behaviour determined. The result is that, although first generation fibres were limited by a low Young's modulus at room temperature and by creep and instability of the structure at temperatures far lower than those limiting the behaviour of bulk silicon carbide, the third generation fibres shows many of the characteristics of stoichiometric silicon carbide. This remarkable improvement in characteristics has been due to a thorough understanding of the materials science governing the behaviour of these fibres which are reinforcements for ceramic matrix composite materials.

1. Introduction

Silicon carbide fibres, with diameters of around 15 μm, were first produced commercially in 1982 by Nippon Carbon. This industrial production was the direct result of research started in the 1970s and carried out by Professor Yajima and his team at the Tohoku University in Japan. The approach adopted to produce SiC fibres owed much to the experience gained from the development of carbon fibres which involves the spinning of polyacrylonitrile (PAN) precursor fibres, which are stabilised by cross-linking and then pyrolysed under controlled conditions to give carbon fibres. The starting polymer for producing SiC fibres, by necessity, needed to contain silicon and carbon atoms and the polycarbosilane (PCS), which was chosen as the starting material, comprised these elements arranged in a cyclic form consisting of six atoms, which suggested their arrangement in β-SiC. The synthesis of the PCS used dimethyldichlorosilane $(CH_3)_2SiCl_2$ which was converted into polydimethylsilane $[(CH_3)_2Si]_n$, by dechlorination with metal sodium and which in turn was converted into a polycarbosilane polymer by heating in an inert atmosphere at 400°C [1]. The chemical composition of PCS can be simplified as $-[SiCH_3H\text{-}CH_2]_n^-$. The PCS obtained in this way could be melt spun to give weak fibres. Stabilisation was initially by cross-linking of the polymer by heating in air, just as in the carbon fibre production route using PAN precursors. This was followed by heating in vacuum at temperatures, generally around 1200°C and allowed the first generation of small-diameter SiC fibres to be produced. The availability of these SiC fibres brought rapid interest from the aerospace and aero-engine industries as they offered the possibility of producing ceramic fibre reinforced carbon and ceramic matrix composites materials, capable of being used as structural materials to higher temperatures than those attainable with the best nickel based super-alloys. The attraction of silicon carbide is that it is a ceramic, which in bulk form, has a Young's modulus twice that of steel for less than half the density and can be used up to 1600°C. Although oxidised at high temperature, bulk SiC undergoes surface passive oxidation which protects the bulk of the specimen. However it was found that the characteristics of these first generation fibres were not those of bulk SiC. The fibres possessed a Young's modulus less than half that expected. The fibres crept at 1000°C and above and degraded above 1250°C. The understanding of the

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-6566-z

material science involved in the processes governing this behaviour and the use of this knowledge to produce fibres with greatly enhanced properties have been the preoccupation of a number of laboratories across the world for the last quarter of a century. The result has been the development of three generations of fibres, the latest of which has produced fibres with properties approaching the limits of what is physically possible with silicon carbide.

2. First generation fine SiC fibres

The interest in silicon carbide as a reinforcement has prompted the development of several types of fibres including fibres with diameters usually greater than 100 μm made by CVD onto a core filament and also monocrystalline short filaments, known as whiskers, with diameters of the order of 1 μm [2, 3]. The CVD fibre is finding interest as a reinforcement for titanium but its large diameter makes it unsuitable for weaving and other types of fibre handling processes, which are commonly used with finer fibres used in the majority of composite materials. The SiC whiskers also present serious handling difficulties together with worries about health related problems.

The announcement of the production of SiC based fibres having diameters in the range of 10 to 20 μm, made by the conversion of polycarbosilane precursors, excited considerable interest amongst those people looking for reinforcements capable of operating in an oxidising atmosphere at over 1000°C, above the limits of nickel based alloys [4, 5]. Yajima and his colleagues explored a number of routes to produce polycarbosilane which could be used as a precursor for a ceramic fibre [5, 6]. The difficulty lay in the production of a form of polycarbosilane which could be spun and converted into ceramic filaments. The decomposition of polydimethylsilane (PDS) which was heated in an autoclave at 470°C for 14 h, was eventually chosen as the route for the production of PCS as it gave a precursor which, although difficult to spin, could be spun from the melt and converted into a ceramic fibre. The repeat element in the chemical structure of polycarbosilane is given in Fig. 1. A steric view of this molecule would show that the cycle of carbon and silicon atoms, with some bonds removed, is arranged in the form of a chair configuration, as illustrated in Fig. 2. This reflects the arrangement seen in β-SiC. The numbering of the arrangement of the atoms is so that a comparison can be made to those in Fig. 1. The groups, shown in Fig. 1, numbered 2, 3, 5 and 6 are in the same plane whilst 1 and 4 are out of this plane. "Me" represents the methyl group (CH_3). Unlike most polymers which are spun into fibres, it was found that very high molecular weight was not necessarily best and polymers with molecular weights of around 1500 were eventually used for commercial production. The precursor filaments were then spun from the melt in a nitrogen atmosphere at around 300°C and then cross-linked. The PCS precursor was made infusible, in the first generation of fibres, by crosslinking in air, in the temperature range from 145 to 200°C, which introduced oxygen into the polymer, as shown in Fig. 3. The conversion of the cross-linked precursor fibre into a ceramic fibre was explored again by Yajima *et al.* [7–9] and others [10]. The cross-linked PCS fibres were insoluble in all solvents. Heating the cross-linked precursor up to 550°C induced the evaporation of low molecular weight components in the carbosilanes which led to a considerable weight loss but resulted in an increase in molecular weight. Above this temperature and up to around 800°C, hydrogen and methane were lost from the side groups in the PCS leaving behind free carbon and cross-linking was enhanced. Further heating to 1200°C showed that gas evolution was almost complete at 1000°C. At 1050°C hydrogen was again given off and the XRD patterns became sharper indicating greater regularity in the structure. At and above 1300°C the free carbon created by the destruction of the methyl groups reacted with the Si–O

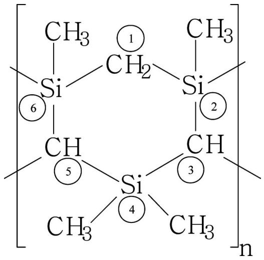

Figure 1 Repeat unit of polycarbosilane (PCS). The numbers allow easy reference to Fig. 2.

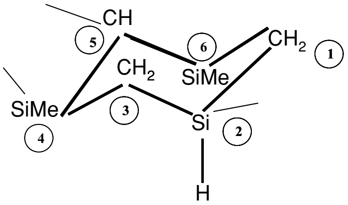

Figure 2 The steric conformation of the repeat unit of polycarbosilane exploited in the production of SiC fibres. The numbers refer to the positions shown in Fig. 1.

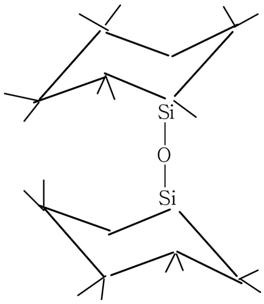

Figure 3 The first generation of fine SiC fibres were made by cross-linking the precursor PCS with oxygen.

TABLE I Compositions of early varieties of first generation SiC fibres produced by Nippon Carbon

	Elemental composition %wt			Chemical composition %wt		
Fibre type	Si	C	O	SiC	SiO_2	C
NLP-101	60	27	13	69	24	7
NLM-102	54	34	12	63	21.5	15.5
NLP-202	54	37	9	66	17	17

TABLE II Compositions, Young's moduli and densities of first generation commercialised SiC fibres

Producer	Nippon Carbon	Ube Industries
Fibre name	Nicalon 200	Tyranno LOX-M
Precursor	PCS	PTC
Cured by	Oxidation	Oxidation
Si (wt%)	56.6	54
C (wt%)	31.7	31.6
O (wt%)	11.7	12.4
Ti (wt%)	0	2.0
C/Si	1.31	1.36
Young's modulus (GPa)	200	185
Density (g/cm^3)	2.55	2.37

group with the evolution of CO gas and forming a Si–C bond. The nascent β-SiC grains, formed at slightly lower temperatures increased in size and the amorphous structure evolved into a semi-crystalline structure consisting of nano sized β-SiC grains surrounded by a much less ordered phase made up of silicon, carbon and oxygen. Heating to 1500°C produced large grain growth, the evolution of carbon monoxide and the disintegration of the fibre.

The first fibres of this first generation, which were made available by Nippon Carbon around 1982, were the Nicalon 100 series but were replaced after about four years by the Nicalon 200 series which became the standard grade for much of the ceramic matrix composite studies subsequently undertaken. These fibres had diameters of around 15 μm but showed variability in diameter along their length because of the difficulties of spinning the precursor fibres, as can be seen from Fig. 4. Table I shows the approximate chemical composition of these fibres.

Yajima and his colleagues had considered several routes to making SiC fibres and one included the addition of titanium to the PCS so as to give polytitanocarbosilane (PTC) [11]. This precursor was obtained by the grafting of titanium alkoxide, $Ti(OR)_4$, in which $R{=}C_nH_{2n+1}$, onto the PCS chains. This linked the polymer chains together, increasing molecular weight and its spinability. In 1987, another Japanese company, Ube Industries announced the production of Tyranno fibres made from PTC precursors and reported that they had better thermal and chemical stability compared with the then-existent Nicalon fibres [12]. The Tyranno fibres could be made with diameters half that of the Nicalon fibres. The precursors of these first Tyranno fibres were also crosslinked in air. Ube Industries used a code to indicate the oxygen content of the fibres so that the fibre which was commercialised was known as Tyranno LOX-M, with the letter M, which is the thirteenth letter in the alphabet, representing an oxygen content of approximately 13% by weight.

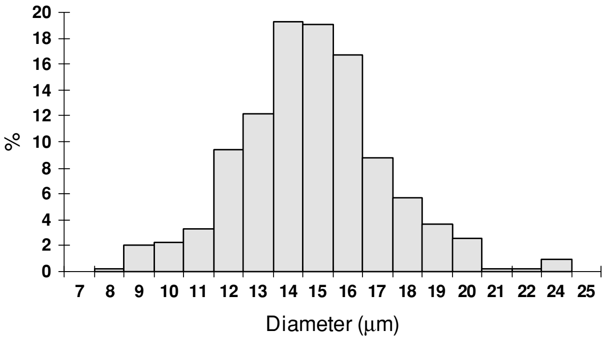

Figure 4 Range of diameters observed with Nicalon NLM 202 fibre taken from the same tow [43].

By the end of the 1980s the two Japanese companies were producing first generation fine diameter SiC fibres and their compositions and densities are shown in Table II. The details of the composition and the nomenclature used to describe the fibres have changed slightly since their initial introduction so that the Nicalon fibres mentioned in Table I are now grouped under the simpler heading of Nicalon 100 or 200 series. Bulk SiC is however the second hardest material known and is crystalline, it possesses a Young's modulus of around 400 GPa and a density of 3.15 g/cm^3 and can be used in air up to 1600°C. At this temperature passive oxidation of the surface to SiO_2 protects it from further degradation. Table II reveals that the properties of the first generation of fine SiC fibres were not those of the bulk material. This has been shown to be due to the non stoichiometric composition of the fibres, which are rich in carbon and contain oxygen, as shown in Tables I and II.

An alternative approach to producing polymer derived SiC fibres, similar to the first generation fibres which have been developed commercially, has been described by university researchers. In contrast to the manufacturing technique described above, it has been shown that such fibres could be produced from precursor filaments made from high-molecular-weight PCS [13]. The infusible PCS was prepared by pressure pyrolysis of polydimethylsilane. Fine fibres were formed by the dry spinning of concentrated PCS-based polymer solutions which were then pyrolised in an inert atmosphere in the temperature range of 1000 to 1200°C. The fibres produced in this manner were reported as possessing very similar properties to those of the commercialised first generation fibres [14].

TABLE III Details of manufacture, elemental composition and approximate cost of all three generations of SiC based fibres

	Trade mark	Manufacturer	Cross linking method	Approximate maximum production temperature	Elemental composition (wt%)	Density (g/cm^3)	Average diameter (μm)	Cost (US $/kg)
First Gen.	Nicalon 200	Nippon Carbon	Oxygen	1200°C	56Si + 32C + 12O	2.55	14	2000
	Tyranno LOX-M	Ube Ind.	Oxygen	1200°C	54Si + 32C +12O + 2Ti	2.48	11	1250
Second Gen.	Hi-Nicalon	Nippon Carbon	Electron irradiation	1300°C	62.5Si + 37C +O.5O	2.74	12	8000
	Tyranno LOX-E	Ube Ind.	Electron irradiation	1300°C	55Si + 37.5 +5.5O + 2Ti	2.39	11	N/A
	Tyranno ZM	Ube Ind.	Oxygen	1300°C	57Si + 34.5C + 7.5O + 1Zr	2.48	11	1500
	Tyranno ZE	Ube Ind.	Electron irradiation	1300°C	58.5Si + 38.5C + 2O + 1Zr	2.55	11	N/A
Third Gen.	Tyranno SA 1	Ube Ind.	Oxygen	>1700°C	68Si + 32C +0.6Al	3.02	11	N/A
	Tyranno SA 3	Ube Ind.	Oxygen	>1700°C	68Si + 32C +0.6Al	3.1	7.5	5000
	Sylramic	COI ceramics	Oxygen	>1700°C	67Si + 29C +0.8O + 2.3B +0.4N +2.1Ti	3.05	10	10000
	Sylramic iBN	COI Ceramics	Oxygen	>1700°C	N/A	3.05	10	>10000
	Hi-Nicalon Type-S	Nippon Carbon	Electron irradiation	>1500°C	69Si + 31C + 0.2O	3.05	12	13000

TABLE IV Details of mechanical and thermal properties of all three generations of SiC based fibres

	Trade mark	Manufacturer	Thermal expansion coefficient, ppm/°C (to 1000°C) [15]	Room temperature axial thermal conductivity W/m K [15]	Room temperature strength (GPa)	Room temperature Young's modulus (GPa)
First Gen.	Nicalon 200	Nippon Carbon	3.2	3	3	200
	Tyranno LOX-M	Ube Ind.	3.1	1.5	3.3	185
Second Gen.	Hi-Nicalon	Nippon Carbon	3.5	8	2.8	270
	Tyranno LOX-E	Ube Ind.	NA	NA	2.9	200
	Tyranno ZM	Ube Ind.	NA	2.5	3.4	200
	Tyranno ZE	Ube Ind.	NA	NA	3.5	233
Third Gen.	Tyranno SA1	Ube Ind.	NA	65	2.8	375
	Tyranno SA3	Ube Ind.	NA	65	2.9	375
	Sylramic	COI Ceramics	5.4	46	3.2	400
	Sylramic iBN	COI Ceramics	5.4	>46	3.5	400
	Hi-Nicalon Type-S	Nippon Carbon	NA	18	2.5	400

3. Mechanical behaviour of first generation SiC fibres

At room temperature the fibres show linearly elastic behaviour. The variation in fibre diameter along individual fibres makes the measurement of stress and modulus inherently difficult which explains some discrepancies in the published data for these fibres which in any case have been improved since their introduction. Some typical property data for first generation SiC fibres can be found in Tables III and IV. It should be noted that the Tyranno LOX-M, although still made, is not generally available. Fig. 5 shows the fracture morphology of a first generation Nicalon fibre broken in tension [15]. It can be seen that the fracture suggests a glassy structure of the fibre. A critical stress intensity factor K_{1c} of 2 $MPa.m^{1/2}$ was determined for the Nicalon NLM-202 fibre which is more characteristic of glass than bulk SiC [16].

The behaviour of the first generation fibres remains linearly elastic up to 1250°C but short term strength begins to fall around 1000°C. There is a difference, particularly for the Tyranno LOX-M fibre, when tested in air or in argon, with an earlier onset of strength reduction being observed when the fibres are tested in air indicating a higher sensitivity to carbon oxidation of the surfaces. However the oxidation of the Nicalon 100 series fibres could be beneficial particularly under long term loading conditions as it slowed internal decomposition of the fibres [17]. Growth of silica is observed on the surfaces of both fibres when they are heated in air at 1200°C and above in air. This layer can have an irregular thickness along the fibre and pores are formed at the silica/SiC fibre interface and pores can be formed at 1450°C which induce local decohesion of the silica layer from the fibre. These pores are produced by the outgassing of carbon monoxide from the

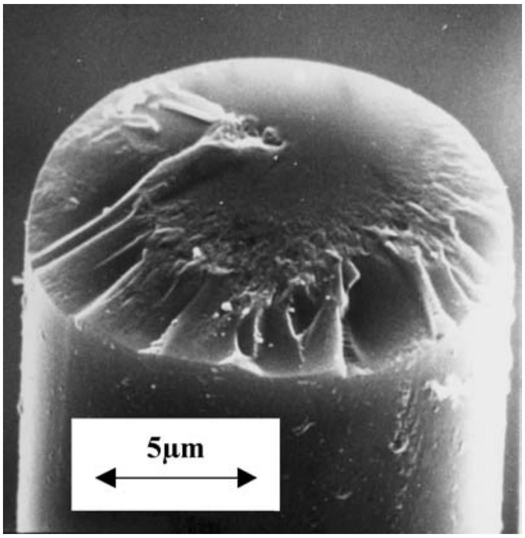

Figure 5 Fracture morphology of a first generation Nicalon fibre [15].

interior of the fibre. Failure surfaces remain brittle at high temperature but new types of defects are seen compared to those found at room temperature. Local chemical inhomogeneities at the fibres' surfaces such as carbon rich zones are preferentially decomposed or oxidized giving rise to porous weak regions.

The fibres were seen to creep from around 1000°C [17], although, when first observed, this was considered a controversial observation as most studies indicated that the fibres shrank on heating above this temperature. These latter conclusions were based on fibres heat treated under no imposed load however the creep observations were made on fibres subjected to loads at temperature. This still leads to some confusion in the literature with some researchers referring to fibre stability as reflecting the characteristics of the fibres, tested at room temperature, after heat treatment. The present authors prefer to consider the characteristics under load at high temperature, which better reflects possible end use conditions. The strength and elastic moduli characteristics of a material are often altered at high temperature with respect to those at room temperature, because of reversible mechanisms at the level of the finest structure of the material and so do not become apparent when the temperature is lowered. Exposure to high temperatures can also, of course, induce irreversible changes in the fibre structure which also need to be understood. The testing conditions for defining stability at temperature will be explained as necessary in this paper.

Further studies on the first generation fibres revealed that, under low loads, the fibres did shrink but, under higher loads they crept. This behaviour was observed from around 1000°C. Studies on the Nicalon 100 series fibres which first revealed this behaviour showed that shrinkage could be attributed to β-SiC grain growth in the fibres which stabilised with grain sizes around 3 nm. The rate of grain growth depended on the temperature but the time to stabilisation corresponded to the period of primary creep observed at higher loads. At temperatures above 1150°C, for the Nicalon 200 fibres and above 1050°C, for the Tyranno LOX-M fibres, and under low loads, it was observed that it was possible to measure an initial shrinkage followed by positive creep showing that two mechanisms were in competition. The variation of steady state creep rate with temperature, T, and applied stress, σ, can often be modelled by:

$$\dot{\varepsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$

where A is a constant depending on the material. The stress exponent, n, and the activation energy for creep, Q, can be deduced from creep experiments and their values can suggest the processes involved. Below 1200°C, the stress component is near to unity for Nicalon 200 fibres revealing Newtonian creep, most probably caused by grain boundary sliding and controlled by the oxygen rich intergranular phase. Above 1200°C, the stress component increases to 2 as the intergranular phase decomposes and grain sliding becomes more difficult.

The two mechanisms which were in competition were therefore grain growth and perfection and grain boundary sliding. The results are that the creep curves of first generation fibres show primary creep which lasts several hours followed by secondary creep with no tertiary creep stage up to 1250°C. Shrinkage could be reduced in these fibres by heat treatment at 1200°C in Argon for 5 h which induces densification and an increase in Young's modulus of around 15 GPa. The creep activation energy was found to be around 250 kJ/mol.

As the applied stress was increased, at a given temperature, the period during which shrinkage was observed decreased until a stress was reached at which only positive creep was measured although, as intimated above, the processes inducing shrinkage still occurred and controlled the period of primary creep. Table V shows the stresses as a function of temperature below which shrinkage has been observed for the two fibres.

Creep curves of the first generation fibres revealed the existence of stress level thresholds, defined as a creep rate

TABLE V Maximum stress at which shrinkage has been detected in first generation SiC based fibres

Temperature (°C)	Nicalon 200	Tyranno LOX-M
1050	-	1.00 GPa
1150	-	0.65 GPa
1250	0.34 GPa	0.40 Gpa
1350	0.18 GPa	0.08 GPa
1450	0.06 GPa	0.19

lower than 10^{-10} s^{-1}, which reduced as the temperature increased.

Similar mechanical data have been reported for the laboratory produced fibres produced from high-molecular-weight PCS, both in tension and in creep [18].

The creep data given in this paper, which come from the authors' laboratory, have been obtained using machines dedicated to the high temperature testing of small diameter filaments. These machines have been described elsewhere [19] and are capable of conducting tensile, relaxation, creep and, if necessary, fatigue tests on very small diameter filaments over a wide range of temperatures. Other research teams have conducted creep tests using dead weights supported by the fibres. An alternative and rapid way of ranking the creep or relaxation behaviour of ceramic fibres is to put them into the form of a loop around a former and to heat treat them. If the fibre remains perfectly elastic during the test its form returns to its original, straight form on cooling and removal from the former. However if any anelastic behaviour occurs the fibre retains a curvature. The degree of the induced curvature is taken as a mean of ranking the probable creep behaviour of the fibre compared to that of other fibres [20].

3.1. Compositions and microstructures of first generation fibres

Fig. 5 shows a typical failure surface of a first generation SiC fibre. There is no sign of any granular texture so that the fibre appears to be glassy and possibly amorphous, as was originally concluded. However, wide angle X-ray diffraction (XRD) studies and later examination by transmission electron microscopy (TEM) showed that the first generation fibres were nano-crystalline with sizes of β-SiC grains generally being in the range 1.7 to 2 nm although some variation occurred in early fibres due, presumably, to optimisation by the manufacturers in the duration of pyrolysis [17].

The compositions by weight percentages and densities of the fibres are given in Table II, together with the carbon-to-silicon atomic weight ratios. It is clear that the first generation fibres were far from being stoichiometric silicon carbide and that they contained an excess of oxygen and carbon. This observation was the beginning of an understanding of the reasons why the fibres had such different characteristics from those of bulk SiC. Although the manufacture of these fibres from PCS and PTC was analogous to that of carbon fibres made from PAN, an important difference quickly became evident, which was that the oxygen, used to crosslink and render infusible the precursors before pyrolysis, introduced into the PAN fibres, is entirely removed at high temperatures but that used to stabilise the PCS and PTC fibres remains. The excess carbon in the SiC fibres came from the methyl groups present in the PCS and PTC polymers. The presence of oxygen in the precursor fibres induced the out-gassing of carbon oxides between 400 and 600°C at the beginning of the pyrolysis so reducing the final carbon content of the ceramic fibre. Most important was the understanding that the presence of the oxygen produced an amorphous phase in which the small SiC grains and the free carbon aggregates were embedded.

The first fibre of this generation to be studied by XRD and TEM was the Nicalon NLM-102 fibre with a 16 wt.% content [17]. This study was followed by others on the same type of fibre and gave greater information on the bonding of the oxygen atoms with neighbouring silicon and carbon atoms [21, 22]. These studies revealed that the fibre consisted of very small β-SiC grains with an average size, as calculated from the XRD patterns using the Sherrer method, of 1.7 nm in size and these were embedded in an oxygen rich amorphous silicate phase. The β-SiC grains were the only crystalline phase detected by XRD and electron diffraction. The early grade was later replaced by what was called the ceramic grade Nicalon NLM-202 fibre, the composition of which differed slightly from the earlier grade as it had a lower oxygen content of 12%. Studies on this fibre, which became the standard and most widely studied first generation fibre, by TEM, allowed the structure of the free carbon to be determined and the mean composition of the amorphous phase to be proposed [23]. Originally the oxygen was presumed to be included in an amorphous silica phase. Further studies showed that only a fraction of the oxygen was in the form of SiO_2 and the rest was present in the fibre in the form of a ternary phase SiO_xC_y [21]. The fibre was therefore seen to be composed of a continuum of SiO_xC_y tetrahedra with $x + y = 4$. The Nicalon 200 grade fibre with a 11 wt.% oxygen content was determined as being composed of SiC_4 tetrahedra formed into small crystallites of 1.4 nm with a diamond-like structure separated by two SiO_xC_y tetrahedra ($x \neq 0$), whereas the 100 grade fibres with 16 wt.% of oxygen had a lower crystallinity. The Nicalon 200 grade fibre was composed of 55 wt.% β-SiC grains, 40% of an intergranular phase with a mean composition of $SiO_{1.15}C_{0.85}$ and 5% of randomly oriented free carbon aggregates, 1 nm in size. C_{002} lattice fringe images showed small stacks of two fringes around 0.7 nm in size suggesting that the basic structural unit (BSU) was a face-to-face association of aromatic rings, called dicoronenes, in which the hydrogen-to-carbon atomic ratio is 0.5. With such a model for the microstructure of the fibre, a porosity level of more than 2% was calculated [23]. Other authors proposed that the intergranular phase should be written as $SiO_xC_{1-x/2}$ which suggests that the composition could vary continuously from SiC to SiO_2 as the oxygen concentration varied [24]. This gave a composition by weight of 56% SiC, 10% C and 34% $SiO_{1.12}C_{0.44}$.

The existence of porosity in the first generation ceramic fibres was proposed so as to account for the outgassing of the hundreds of volumes of gas per volume of fibre, which occurs during the transformation from an organic to a mineral structure, which occurs during the manufacture of the fibre [25]. It was reasoned that nanometric channels must exist in the fibres during the transformation stage as diffusion through a solid phase would be too slow. These nanochannels collapse on further heating above the temperature at which the gas is evolved. A porosity of 6.2% was shown to exist experimentally by X-ray scattering measurements on Nicalon NLM-202 fibres pyrolized at 1400°C [26, 27].

The result of the studies on the first generation fibres was the conclusion that it was the non-stoichiometric composition of the fibres which were limiting their physical characteristics. The presence of the amorphous intergranular phase was clearly due to the oxygen which remained in the fibres after pyrolysis making a Si–O–C phase. The low fraction of a granular SiC phase accounted for the Young's modulus of the fibres being only half that of bulk SiC. The amorphous phase also explained why the fibres began to lose strength and creep at temperatures around 1000 or 1100°C whereas bulk SiC would be expected to resist to higher temperatures [28]. Heating to above 1500°C induced rapid grain growth and outgassing of SiO and CO which came from the oxygen in the amorphous Si–O–C phase and also the free carbon in the fibre, as described by the following relationship.

$$\mathrm{SiC}_x\mathrm{O}_y \rightarrow \mathrm{SiC}\,(\mathrm{s}) + \mathrm{SiO(g)} + \mathrm{CO(g)}$$

It had been noticed in early studies that the rate of strength loss of first generation fibres was lower in oxidizing atmospheres than in an inert argon atmosphere [17, 29, 30]. It was concluded that heating the fibres in air produced a silica coating which hindered outgassing of the products of the decomposition of the Si–O–C phase; this was further studied by heating fibres made from both the PCS and PTC precursors over a wide range of oxygen partial pressures and in carbon dioxide [31, 32]. These authors also showed that the formation of a barrier coating of SiC laid down by chemical vapour deposition on the fibre surface suppressed gas evolution and slowed the degradation process. They also showed that, what had been presumed in earlier studies was actually the case and that a solid layer of SiO_2 formed on the surface of the Nicalon fibres and a SiO_2 layer with a small amount of TiO_2 was formed on the surfaces of the Tyranno fibres [33].

It should however be noted that increasing the pressure of an argon environment also hindered the onset of decomposition. When the first generation fibres were heated in Argon at a pressure of 138 MPa the onset of fibre weight loss increased from 1200 to 1500°C [34].

If improved fibres were to be made, which could go some way to meeting the promise of a pure SiC, it was clear that a more stoichiometric composition had to be achieved. As mentioned above, it had been seen that the presence of oxygen in the fibre resulted in a poorly organised phase in which the SiC grains were embedded. It was clear that the oxygen content had to be considerably reduced if improvements were to be made. As the primary reason that the oxygen was in the fibres was that it was introduced to render the precursor fibres infusible, it was clear that other means of cross-linking the polymer precursors had to be investigated.

4. Second generation small diameter SiC fibres

The route adopted to reduce the oxygen content in the second generation of small diameter SiC fibres was to eliminate the oxygen induced cross-linking step used to render the PCS precursor fibre infusible. This was possible by using different types of irradiation which could interact with the precursor polymers to produce free radicals and gaseous products by the scission of the chemical bonds of Si–CH_3, Si–H and C–H. This allowed Si–Si and Si–C bonds to be formed. A number of different types of radiation were investigated by both fibre producers working in collaboration with the Japanese Atomic Energy Research Institute. Gamma irradiation was investigated but finally electron radiation in a helium atmosphere was used to make the second generation fibres. The cross-linking step was followed by heat treatment at 327°C for a short time to eliminate the remaining free radicals which were trapped in the irradiated precursor fibre [35]. An example of how the hydrogen atom, bonded to the silicon atom, as shown in Fig. 2, is removed by electron bombardment, so as to allow direct bonding between the two silicon atoms in neighbouring molecules, is shown in Fig. 6 [36].

Below 550°C cross-linking between main chains dominates and is induced by the dehydrogenation condensation of the Si–H groups. From 550°C to 800°C, the side chains on the cross-linked polymer begin to decompose and CH_4 and H_2 are given off producing an inorganic fibre. Above 800°C and up to 1000°C, hydrogen is given off, most probably associated with the decomposition of

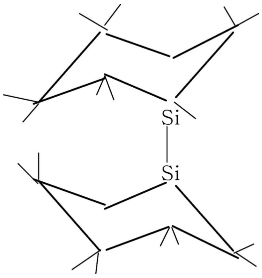

Figure 6 Direct cross-linking of the PCS precursor polymer by irradiation curing.

C–H bonds remaining in the PCS. Above 1000°C, β-SiC grains, free carbon aggregates and a poorly organised intergranular phase comprising of silicon and carbon atoms are formed [37, 38]. The presence of the free carbon aggregates is considered to hinder grain growth so allowing the SiC grains to remain small during fibre production which takes place at around 1300°C as indicated in Table III.

The radiation cross-linking process, although costly, was successful in reducing the oxygen content of fibres produced from PCS precursors to 0.5 wt.% and gave rise to the Hi-Nicalon fibre produced by Nippon Carbon [39, 40].

When the radiation process was applied to the PTC precursor fibres, it was found that, although the oxygen content fell, it was only reduced to around 5 wt.%. The explanation was that the Ti addition to the PCS, so as to make the PTC polymer, was achieved by adding a titanium alkoxide, $Ti(OR)_4$, which added oxygen by another route than that of oxygen cross-linking. This alkoxide grouping formed links between the PCS molecules through Ti–O bonds which were stable up to 700°C. Above this temperature Ti–C began to be formed. Intermediate species such as TiC_xO_y were produced with the formation of SiC_xO_y. The result was that, although cross-linking occurred by the process described above for the PCS fibres, there remained a significant presence of oxygen in the Tyranno LOX-E fibre which Ube Industries produced by this method. Fig. 7 shows the atomic carbon to silicon ratios and oxygen contents for the first and second generation fibres.

Ube Industries took the decision not to commercially produce the Tyranno LOX-E fibre as the irradiation process was expensive and the improvement in properties not sufficiently adequate. The company produced other fibres with the intention of reducing the oxygen content by changing the metal added to the PCS polymer and the titanium was replaced by zirconium. This substitution reduced the oxygen concentration as the compound used to graft the zirconium onto the PCS polymer contained less oxygen than was the case with titanium alkoxide [41]. Two types of fibre were produced. The Tyranno ZM fibre was cured by oxidation and was commercially produced and an experimental Tyranno ZE fibres cured by electron irradiation, which was not commercialised. The former fibre was produced with an oxygen concentration of 10 wt.% and also 7.8 wt.%. The stability of the intergranular phase which contained zirconium was said to be improved, compared to the titanium containing intergranular phase, as weight loss began at 1600°C for the Tyranno ZM fibre which was 200°C higher than for the Tyranno LOX-M. The Tyranno ZM fibre found a market, for some time, in filters for engines running on sulphur rich diesel.

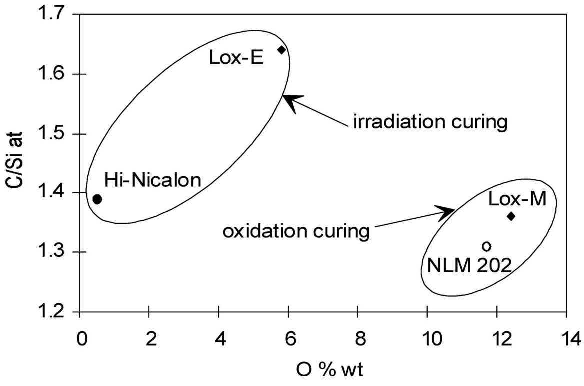

Figure 7 The carbon/silicon atomic ratios and oxygen contents in the first and second generation SiC fibres [42].

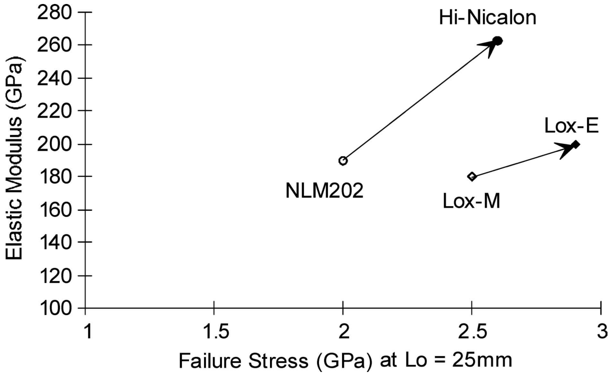

Figure 8 The second generation fibres showed increased Young's moduli compared to the first generation fibres [42].

5. Mechanical behaviour of second generation SiC fibres

The reduction of the oxygen content in the fibres, made by irradiating PCS, produced Hi-Nicalon fibres which were approximately 35% stiffer than the first generation fibres, as can be seen from Fig. 8. However the increase was not nearly as significant for the Tyranno LOX-E fibre which, unlike the Hi-Nicalon, was not developed as a commercial second generation fibre. There was no change in appearance of the fracture surfaces between the first and second generation fibres which remained devoid of any obvious signs of an ordered microstructure, as seen in the scanning electron microscope.

Strength retention at high temperatures of the Hi-Nicalon fibre was improved, when compared to the first generation fibres [42]. These second generation fibres remained linearly elastic up to 1350°C which was 100°C higher than the first generation fibres and room strength was retained up to around 1200°C in both argon and air, although the Tyranno LOX-E fibres, heated in air, showed a fall in strength at temperatures lower than 1000°C. This was not observed in argon, suggesting a sensitivity to carbon oxidation at the surface of the fibres. Such sensitivity could be seen in the Hi-Nicalon fibres but at higher temperatures, as is revealed by Fig. 9 which shows such a fibre broken in tension at 1400°C, which is 100°C higher than the temperature used for fibre manufacture. Growth of a silica layer was observed on the surfaces of the fibres when heated in air at 1200°C and pores at the silica and SiC fibre interface were observed at 1450°C induced by the decomposition products of the fibre.

The Hi-Nicalon fibre was found not to creep below 1000°C and to possess the highest creep threshold and the lowest strain rate of the first and second generation fibres. The Tyranno LOX-E fibre was found to creep from 950°C. The strain rates of the fibres, under an applied stress of 1 GPa at 1050°C, were 10^{-10} s^{-1} for the Hi-Nicalon fibre, 6×10^{-8} s^{-1} for the Tyranno LOX-E fibre, 2×10^{-8} s^{-1} for the Nicalon 200 fibre and 2×10^{-10} s^{-1} for the Tyranno LOX-M fibre, although it should be noted that the latter fibre showed much higher creep rates at slightly higher stresses. The creep rates of all the first and second generation fibres were very similar at 1400°C, at around 5×10^{-7} s^{-1} under a stress of 0.3 GPa, as can be seen from Fig. 10. The activation energy for the creep of Hi-Nicalon fibres was around 360 kJ/mol and could be explained by grain boundary sliding accommodated by interface-controlled diffusion mechanisms. The carbon layers, between the grains, could facilitate this sliding. Ultimate failure in creep of the fibres was found not to be due to a lack of accommodation, as is the case for bulk ceramics, but related to surface defects, such as cavities or porous zones growing from local chemical heterogeneities, as shown in Fig. 9.

The Tyranno ZM and Tyranno ZE fibres showed improved strength retention at high temperatures, compared to their titanium containing homologues. Similar strength retention at 1400°C was seen by the Tyranno ZE fibre when compared to the Hi-Nicalon fibre [43].

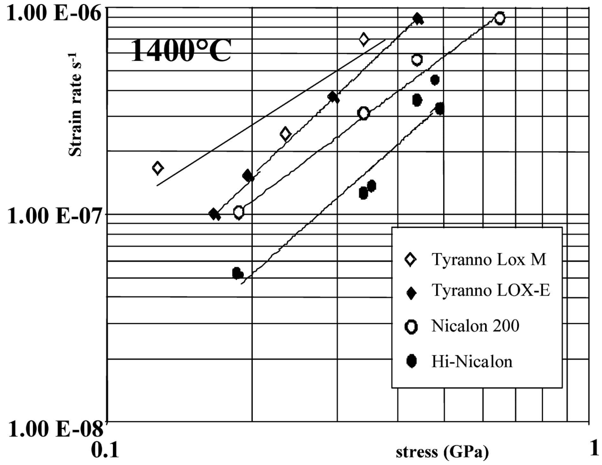

Figure 10 Creep rates at 1400°C for the first and second generation fibres [42].

The mechanical properties of the second generation SiC based fibres are given in Table IV.

5.1. Compositions and microstructures of second generation fibres

The removal of oxygen from the cross-linking process used to make the Hi-Nicalon fibres, made from electron irradiated PCS precursors, resulted in an increase in size of the β-SiC grains which were seen, in the as received fibre, to be in the range of 5 to 10 nm, as shown in the TEM micrograph shown in Fig. 11 [44, 45]. This accounts for the slightly higher thermal conductivity of these fibres compared to the first generation fibres, as can be seen in

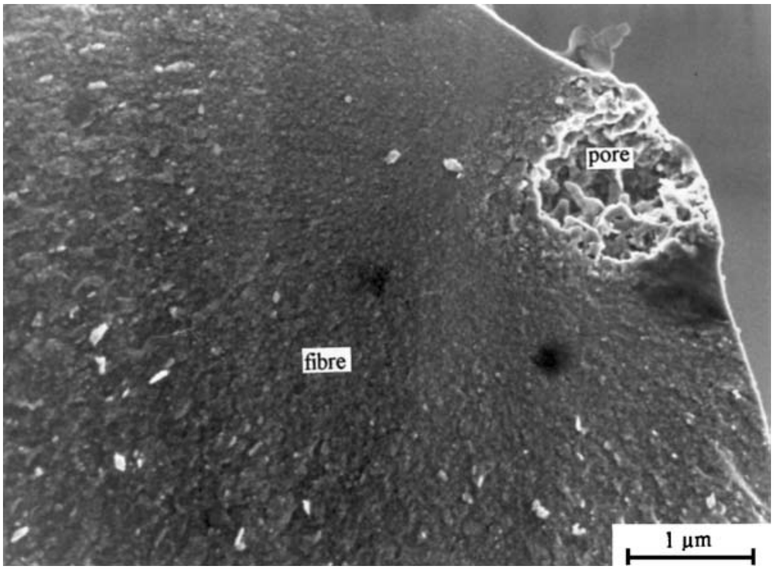

Figure 9 Hi-Nicalon fibre broken at 1400°C showing a large pore perhaps produced by oxidation of carbon.

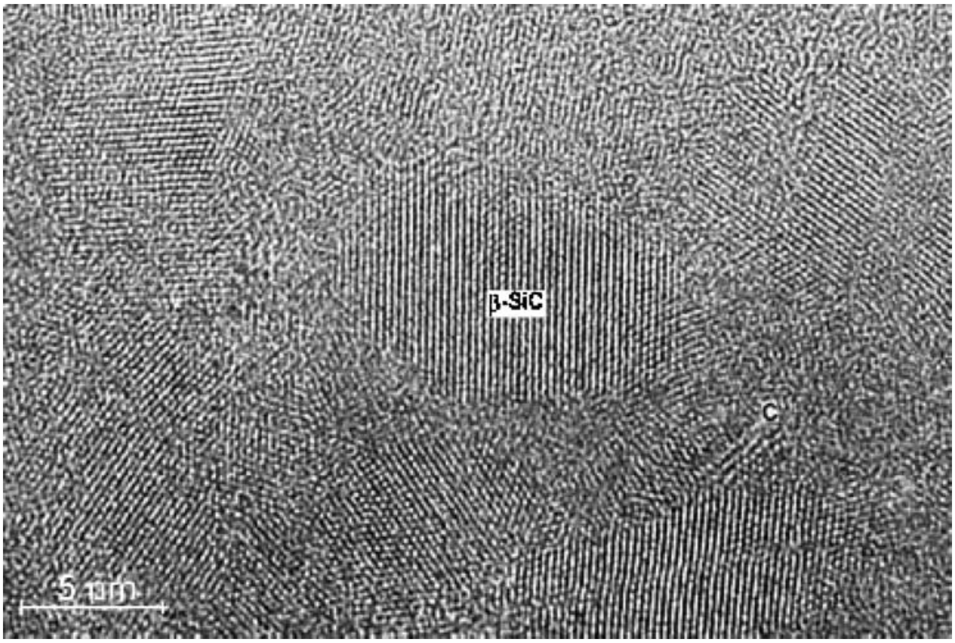

Figure 11 High Resolution Transmission Electron Microscopy image of a Hi-Nicalon fibre, showing β-SiC grains of about 10 nm, surrounded by poorly a organised Si–C phase, and turbostratic carbon [42].

Table IV. The microstructure can be seen to have consisted of areas of well ordered SiC surrounded by Si and C atoms which were not completely crystallized into β-SiC grains. The Hi-Nicalon fibre contained a higher ratio of carbon atoms to silicon atoms than in the first generation fibres as the absence of oxygen did not allow the excess carbon to be oxidized. The free carbon can be seen in Fig. 11 and was composed of 4 to 10 distorted layers with some aggregates measuring up to 5 nm. The small amount of oxygen in these fibres was presumed to be present at the SiC/SiC boundaries. The Hi-Nicalon fibre would be composed by weight of 85% SiC, 11% C and 4% of $SiC_{0.86}O_{0.29}$ if the oxicarbide phase is taken to be composed of $SiO_xC_{1-x/2}$ with three carbon atoms to every one oxygen atom. It was calculated that the non-crystallized SiC in the Hi-Nicalon fibre represented around 26% by weight of the fibre [46]. The absence of a significant amount of oxygen removed the amorphous phase present in the first generation fibres and allowed larger SiC grains to form at the higher manufacturing temperature used. Their size however was limited by the excess free carbon in the fibre. This microstructure explains the observed increase in Young's modulus of these fibres when compared to first generation fibres, as can be seen from Table IV.

The microstructure of the Tyranno LOX-E fibres was very similar to that of the first generation Tyranno LOX-M fibres with SiC grains having a mean size of approximately 2 nm, although some larger grains up to 5 nm were seen. The free carbon aggregates were around 1–3 nm and, as with the first generation Tyranno fibres, no Ti compounds were found indicating that the grains must be separated by a Si–C–Ti–O phase.

It became clear, therefore, that the oxygen content was the key factor in controlling the microstructures and ultimately the mechanical properties of the polymer derived SiC fibres. The oxygen cured, first generation fibres, the Nicalon 200 and Tyranno LOX-M fibres, possessed similar grain sizes, of about 2 nm, and properties. However the Hi-Nicalon and Tyranno LOX-E fibres had distinctly different microstructures and showed different behaviours. The reduction in oxygen content to 5 wt.% in the Tyranno LOX-E fibre did not produce a significant change when compared to the first generation fibres however the Hi-Nicalon with only 0.5 wt.% can be seen to be a very different fibre.

Although bulk SiC can be used to 1600°C, the oxygen rich SiC fibres became too brittle to be handled when heated above 1500°C and were reduced to a powder at 1800°C by the degradation of the silicon oxicarbide intergranular phase [47]. Thermodynamic analyses have shown that the solid solution $SiC_\alpha O_\beta$, coexisting with SiO_2 and C, were unstable above 1150°C in an inert atmosphere [48]. Its decomposition produced CO and SiO and free carbon. The SiO gas reacted with the free carbon to give SiC and CO [23]. The absence of an oxicarbide intergranular phase in the Hi-Nicalon fibre clearly helped its high temperature stability and the larger percentage of crystalline SiC accounted for its higher Young's modulus when compared to the first generation fibres and the still oxygen rich Tyranno LOX-E fibre.

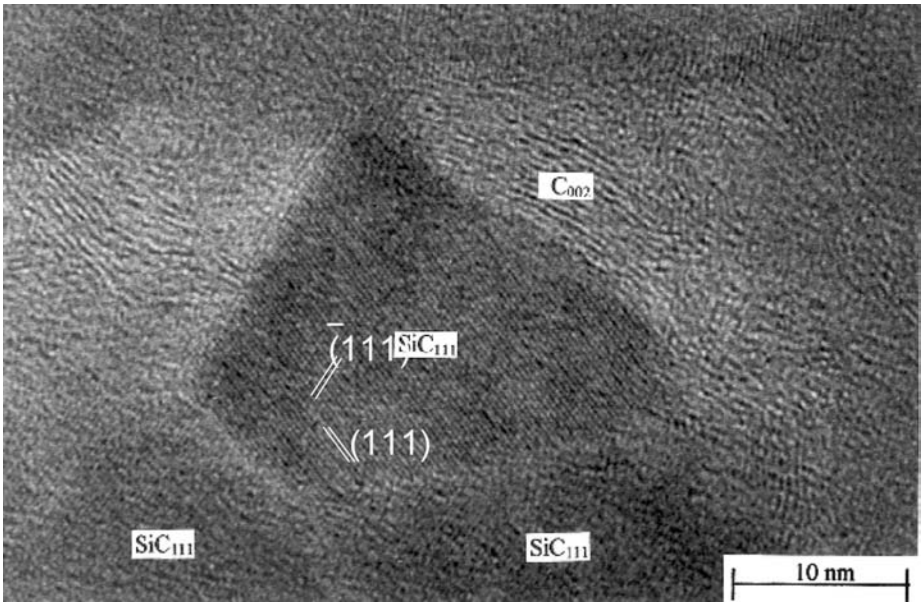

Figure 12 Microstructure of the Hi-Nicalon fibre after heat treatment at 1450°C for one hour in argon [42].

Heating Hi-Nicalon fibres in air above 800°C produced a weight gain indicating oxidation of the fibre [49] and from 1200°C a double layer consisting of crystallized silica and amorphous silica covered the surface of the fibre. At this temperature, the amorphous silica nearest the fibre surface was devitrified and converted to cristobalite [44]. At 1400°C, the layer was completely devitrified and was cracked when observed at room temperature due to shrinkage associated with a phase change in the cristobalite at 270°C. The pores, mentioned earlier, between the silica coating and the fibre were due to bubble formation which is observed with SiC polycrystals, which contain carbon inclusions, during oxidation in air but is not seen in SiC single crystals [50]. The growth of the silica layer is more rapid with the Hi-Nicalon fibre than that seen with bulk SiC but the layer does play a passive role in inducing a parabolic rate law up to 1400°C. Above this temperature, the oxide layer no longer provides a protective sheath. The oxidation of the Tyranno LOX-E fibre was more complex and did not strictly follow a parabolic law above 1100°C [51].

Heating Hi-Nicalon fibres in flowing CO up to 1200°C produced no change in the microstructure or properties of the fibre when measured at room temperature. There was some grain growth and some loss of strength above 1300°C. When heated for five hours to 1500°C in flowing argon all strength was lost but room temperature strength was retained after ten hours under the same heating conditions but under flowing CO [52, 53]. This was due to the suppression by the CO atmosphere on the thermal decomposition of the SiC_xO_y phase.

The description and image of the microstructure, shown in Fig. 11 of the Hi-Nicalon fibre suggested that the structure could be made to evolve further by heat treatment. Grain growth was seen to begin at 1300°C which, as Table III shows, was the approximate temperature during fibre manufacture. At 1400°C, the grains ranged in size from 10 to 40 nm and from 10 to 70 nm at 1500°C. The grain growth was not impeded in this fibre by a non-stoichiometric oxygen rich phase, as in the other fibres considered so far. This permitted the grains to grow and develop facets by consuming the less well ordered regions which surrounded the grains, as can be seen in Fig. 12. The free carbon can be seen to have become organised parallel to the SiC grain facets forming cages around the grains and eventually limiting their growth.

The consequence of these changes was that the fibre became stiffer, with Young's moduli being measured up to 295 GPa and the fibre showed lower creep rates. The stress exponent for the creep of Hi-Nicalon fibres was between 2 and 3 between 1000°C and 1450°C [54].

The Tyranno ZE fibre, which shared some characteristics with the Hi-Nicalon fibre, consisted of β-SiC grains of 3 to 4 nm and free carbon aggregates comparable to that seen in the Hi-Nicalon fibre. Crystallisation of ZrO_2 was seen at the SiO_2/SiC interface after heat treatment of the fibre at 1400°C for 24 h. It is not clear if this fibre is commercially available.

6. Third generation small diameter SiC fibres

A major driving force for the development of the small diameter SiC fibres has been the need of the gas turbine generator industry for materials able to withstand higher temperatures than nickel based alloys which are limited to a maximum temperature of 1150°C. The development of ceramic matrix composites based on the small diameter SiC fibres embedded in a SiC matrix held out this promise from the early 1980s however those composites based on first generation fibres did not meet all the high temperature requirements. Improvements in the high temperature stability of the fibres were therefore desired and calls were made from the mid 1980s for the development of more stoichiometric fibres which would be stable in air up to 1400°C. The fibres needed to be based on truly sintered SiC. The approach taken by the two Japanese fibre manufacturers to meet this challenge has been to extend their technology based on an understanding of the processes controlling the behaviour of the first and second generation fibres.

Ube Industries further developed their control of the chemistry of the precursor polymer and grafted another metal, aluminium, by reaction of aluminium acetylacetonate with PCS. The role of the aluminium is to help in cross-linking the precursor fibres and also play the part of a sintering agent [55, 56]. The fibre contains up to 2 wt.% of aluminium. The precursor fibre is cured by oxidation, pyrolysed in two steps, first to allow oxide phases to decompose and to allow the outgassing of CO during heating above 1200°C and then, in the second step, the Al sintering aid allows the SiC grains to sinter at temperatures above 1600°C and up to 1800°C. These fibres are designated Tyranno SA fibres and two versions have been made available: Tyranno SA1 and Tyranno SA3.

The American company Dow Corning, which had long been studying the production of small diameter ceramic fibres, partly with US government funding, extended the approach adopted by Ube Industries to make the Tyranno LOX-M fibre and, from PTC produced fibres, diffused boron into them as a sintering aid [57]. In this way degradation of the oxicarbide phase at high temperature is controlled and catastrophic grain growth and associated porosity, as occurred with the previous oxygen rich fibres, is avoided. The precursor fibre can then be heated to around 1400°C so that the excess carbon and oxygen are lost as volatile species and then sintered at a higher temperature, as for the Tyranno SA fibre, to yield a polycrystalline, near-stoichiometric, SiC fibre called Sylramic fibre. This fibre is now produced by a company called ATK COI Ceramics which, in collaboration with researchers at NASA Glenn, has improved on the original Sylramic fibre by removing the boron from the fibre surface by further heating in a nitrogen containing gas [58]. This latter fibre is called Sylramic-iBN and it is claimed that it shows reduced creep and increased oxidation resistance together with a BN rich surface [59].

Nippon Carbon saw that to achieve near stoichiometry the excess carbon in the Hi-Nicalon fibre had to be reduced. The radiation cured precursor route taken by Nippon Carbon to make the Hi-Nicalon fibre was used as an intermediary step to producing a near stoichiometric SiC fibre without the use of sintering aids. The Hi-Nicalon fibre was further heated to around 1500°C in a hydrogen rich atmosphere to reduce the excess carbon from a C/Si ratio of 1.39 to 1.05 for the near stoichiometric fibre, which was called Hi-Nicalon-Type-S [60].

Some details of manufacture and the elemental composition of these third generation fibres are given in Table III.

Laboratory produced near-stoichiometric SiC fibres which have been produced from high-molecular-weight PCS by a process involving dry spinning of the precursor concentrated polymer solutions. It is reported that the as-spun fibres were dried and subsequently subjected to heat treatments inducing carbothermal reduction reactions at elevated temperatures in the range of s1400°C to 1600°C during which the excess carbon was eliminated from the fibre by reaction with the siliceous phase [18]. The fibres were then subsequently sintered at or above 1750°C in an inert atmosphere. Boron additions, of typically around 1 wt.%, were used as a sintering aid. The properties of these fibres were very similar to those of the commercialised third generation fibres [61].

7. Mechanical behaviour of third generation SiC fibres

The third generation fibres exhibit properties which are much closer to those of bulk SiC than either of the two earlier generations. In particular their Young's moduli and thermal conductivities are considerably increased, as can be seen from Table IV, for which some data has been quoted from [59], which summarises the properties of fibres of all three generations. The third generation fibres retain their strengths and moduli up to at least 1300°C, as shown in Fig. 13 for the Tyranno SA3 fibre. The strength and modulus of the Hi-Nicalon-Type-S fibre remain steady up to 1400°C. The values of breaking stresses, shown in Fig. 13, should not be taken as absolute as they depend on the testing method and gauge lengths used (250 mm in this case as compared to 25 mm for the results given in Table IV) but rather Fig. 13 should be seen as showing relative values of fibre strengths at the different temperatures. Fig. 14 illustrates this last point as the strength of these fibres is very gauge-length dependent. The tests at high temperature are often carried out with grips outside the furnace which means that the fibre specimen is much longer than the 25 mm which is usually used for tests at room temperature. As there is a greater probability of a large defect occurring, with increasing lengths, the mean strength of the fibres falls. This is clearly shown in Fig. 14 for three types of third generation fibre but is also seen with the earlier produced fibres. Comparable data have not been published for the Sylramic family of fibres. The improved stability of the Tyranno SA3 fibre compared to the Tyranno SA1 can be clearly seen. Improvements have also been reported for the Sylramic fibre in, what the present authors take to be

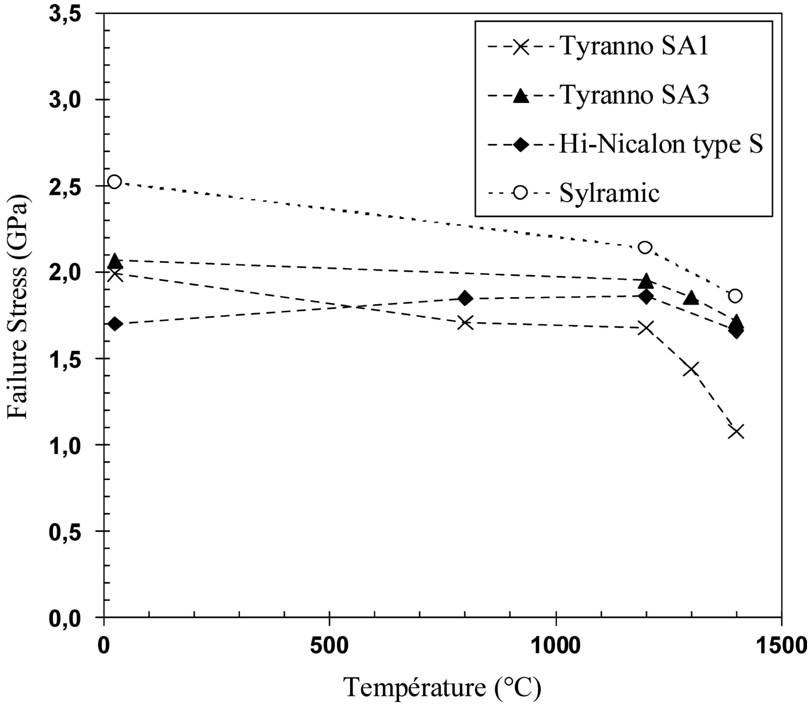

Figure 13 Strength as a function of temperature for third generation fibres with a 250 mm gauge length.

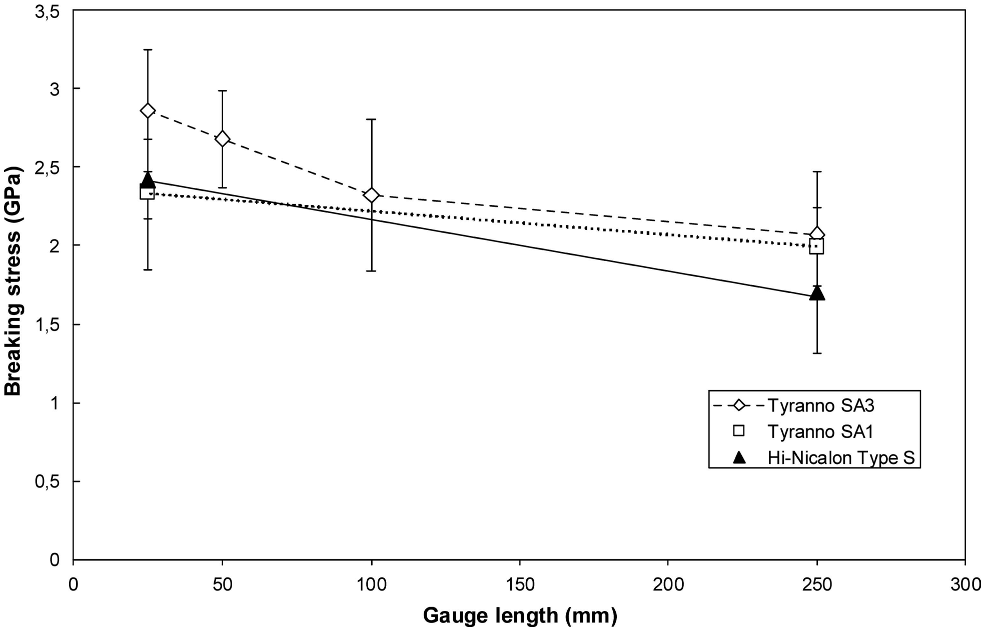

Figure 14 Length dependence of the strength of third generation SiC fibres.

an early form of the Sylramic-iBN fibre. This latter fibre is said to retain its strength, after exposure to high temperatures and then tested at room temperature, better than the Hi-Nicalon-Type-S [62].

The latest generation of fibres which are described as being near stoichiometric show a marked change in fracture morphology when compared to earlier generations. Fig. 15 shows the fracture morphology of a Tyranno SA1 fibre. The fibre had a diameter of 10 μm. The fracture surface can be seen to be markedly granular, in sharp contrast to the earlier fibres. The SiC grains in the Tyranno SA1 fibre were around 200 nm in size. Despite the claim of near stoichiometry, there was free carbon in the fibre and its concentration increased near the centre of the fibre, indicating incomplete removal during sintering. The Sylramic fibre also showed a granular fracture

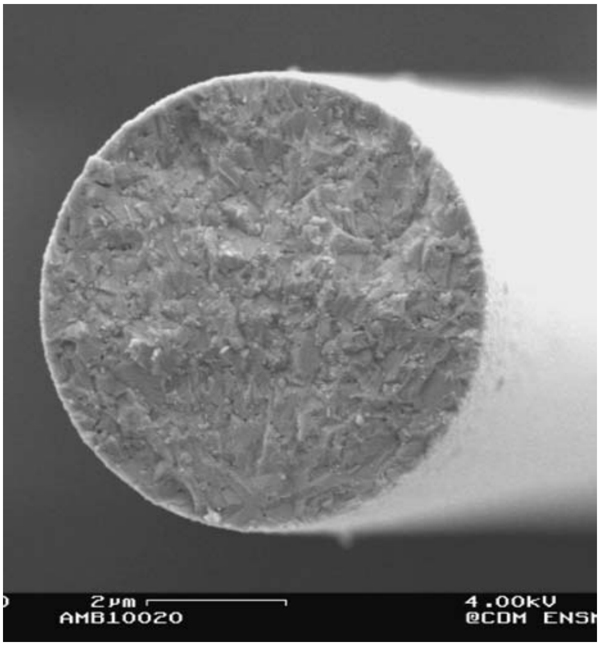

Figure 15 Fracture morphology of a Tyranno SA1 fibre.

surface with SiC grains of around 100 nm with smaller grains of TiB_2 at triple points, identified by TEM studies. The Hi-Nicalon-Type-S fibre had a fracture surface which was noticeably less granular in appearance that the other two near stoichiometric fibres due to a smaller average grain size of around 50 nm, as shown in Fig. 16. An elastic fracture mechanics analysis of fibre failure using the Griffith principle shows that grain sizes have to be over 100 nm in size to control failure stress but below this size the strength is limited to a maximum of 3 GPa due to processing defects but also because the carbon rich surface blunts the effects of surface flaws. If the carbon is removed the strength falls up to 20% [59]. The differences in grain size are attributable to differences in manufacturing temperatures, as can be seen in Table III. Creep behaviour of the third generation fibres also shows considerable improvements when compared to the earlier generations. Figs.17 and 18 show the strain rates of third generation fibres tested at 1300°C and 1400°C respectively. The fibres showed creep rates of the order of 10^{-8} s^{-1} at 1400°C [63]. The creep resistance of the Hi-Nicalon-Type-S fibre can be seen to be greater than the Tyranno SA3 and Sylramic fibres. The smaller grain size in the Hi-Nicalon-Type-S fibre could, however, be expected to increase sensitivity to creep. This is further discussed below.

These results show that the Hi-Nicalon-Type-S fibre crept at a lower rate than those fibres which contained a sintering aid by one order of magnitude. Creep rates are reduced in Sylramic after heating (annealing) near to their production temperatures. No increase in grain size is observed, in this latter fibre, but the behaviour is thought to be due to the elimination of boron from grain boundaries.

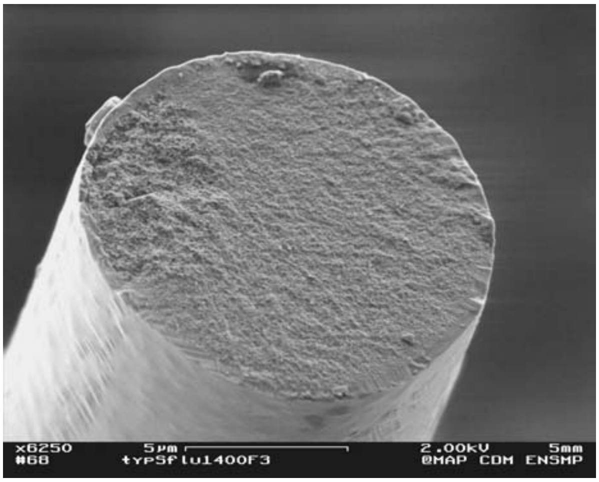

Figure 16 Fracture morphology of a Hi-Nicalon Type-S fibre broken at 1400°C.

It is claimed that an early form of the Sylramic-iBN fibre, denoted as Sylramic (1,2) crept at an even lower rate, as can be seen from Fig. 18. These latter results have been extracted from a NASA document [62] for purposes of comparison but unfortunately the present authors have found no other data in the literature and none from a source independent from the manufacturers so as to corroborate these values.

8. Compositions and microstructures of third generation fibres

The Hi-Nicalon-Type-S fibre shows the greatest strength and modulus retention at high temperatures of those fibres tested and reported in the open literature, although the makers of the Sylramic-iBN fibre claim greatest strength retention when tested at room temperature after over one thousand hours at high temperatures [59]. The presence of a small amount of free carbon in the Hi-Nicalon Type-S fibre is said, by Nippon Carbon, to be deliberate as it serves to limit grain growth and explains why the size of SiC grains in this fibre is limited to around 50 nm. This may help explain the good strength retention of the fibres tested at room temperature after exposure in argon for ten hours at temperatures up to 1600°C [64]. The absence of a grain growth limiting mechanism, as in a pure stoichiometric polycrystalline SiC fibre, could lead to an explosive growth of the grains and a catastrophic fall in strength. The presence of sintering aids in the Tyranno SA and Sylramic fibres may explain why, even with larger grain sizes than those in the Hi-Nicalon-Type-S fibre, they creep at faster rates. The aluminium and boron in these fibres may explain their slightly earlier fall in strength and faster creep rates at temperatures of 1300°C and above. The removal of the boron from the surface of the Sylramic fibre is said to improve its creep properties which suggests that those elements used to favour sintering also

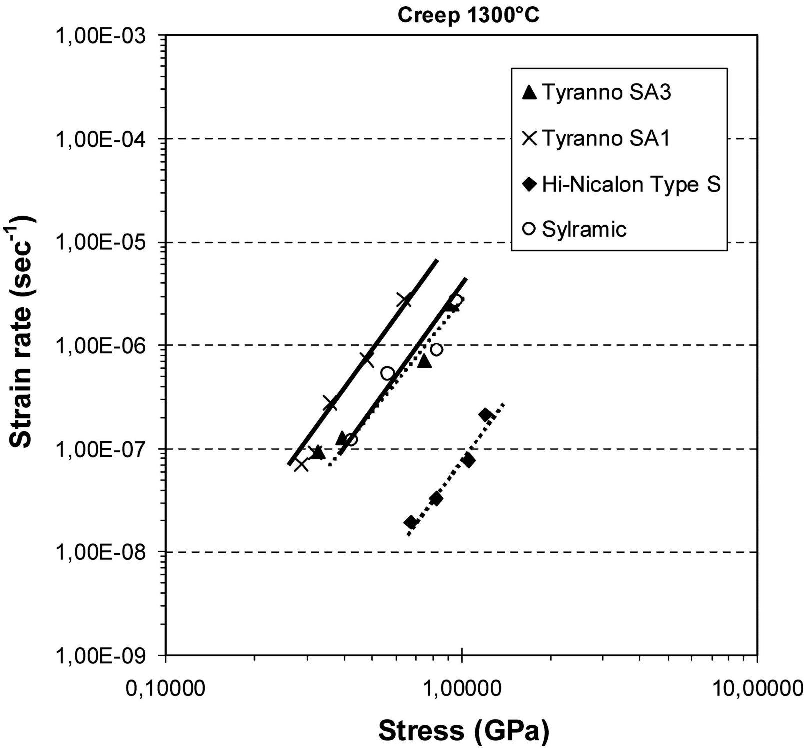

Figure 17 Strain rates of four third-generation fibres at 1300°C.

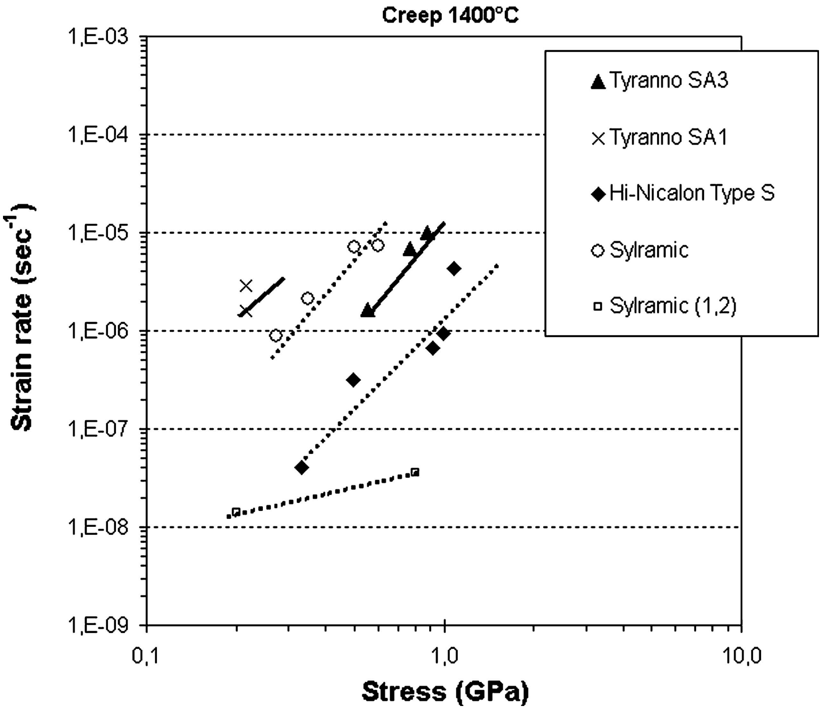

Figure 18 Strain rates of four third-generation fibres at 1400°C.

favour creep at high temperatures. This implies that the removal of the aluminium from the SA fibres would increase their thermal stability. The results shown in Fig. 18 suggesting that the Sylramic-iBN fibre creeps at a lower rate, if corroborated, indicate that the larger grain sizes in this fibre compared to the Hi-Nicalon-Type-S fibre, due to a higher manufacturing temperature, may be responsible. This leaves open the possibility of improving the creep behaviour of the Hi-Nicalon-Type–S fibre by further heat treatment. An alternative explanation would be that an intergranular phase, so far undetected, in the fibre increases the creep rate of the fibre over what could be achieved.

The first type of third generation fibre produced by Ube Industries seems to have suffered from incomplete elimination of the Si–O–C amorphous phase created by the cross-linking by oxygen of the precursor used. The Tyranno SA3 is of a smaller diameter, which generally is a means of increasing fibre strength but in this case allows more complete pyrolysis of the fibre. The results are improved thermal resistance and a lowered creep rate of the fibre when compared to its earlier version.

Although the electron irradiated fibres from Nippon Carbon show the greatest retention of strength at high temperature, of those fibres for which data are published, it must be recognized that the process is costly. The oxygen cross-linking process used to make the first generation of fibres has been shown to be a viable and less costly method for producing near stoichiometric fibres by the addition of sintering aids.

Data for ceramic matrix composites based on Sylramic-iBN fibres indicate that their creep rates are similar to those found for similar composite specimens reinforced with the Hi-Nicalon-Type-S fibres. This can be taken as an indication that the Sylramic-iBN fibres possess similar or even better creep characteristics than the Hi-Nicalon-Type-S, as is hinted at in Fig. 18 and the producers clearly believe that further progress can be made [65].

The most stable form of silicon carbide fibres will, however, be ultimately limited by oxidation, however, observations suggest that all the third generation fibres show considerable resistance to degradation by this process even at 1300°C in air.

9. Conclusions

The development of silicon carbide fibres with diameters of 15 μm or less has been stimulated by end users needs for fibres which show the characteristics of stoichiometric silicon carbide at high temperatures. The requirement was for fibres which would remain stable up to 1400°C in air. The first generation of fibres showed that filaments based on silicon carbide could be produced but it needed the efforts of research teams in a number of countries and the technology of the fibre manufacturers to improve the characteristics. These first generation fibres were limited to maximum temperatures of around 1000°C above which the fibres crept and ultimately decomposed. It was only when the vital role of oxygen in the fibre was recognised, which allowed an amorphous phase to be created that the step towards making a second generation of fibres could be made. The use of electron irradiation for cross-linking the precursor fibres enabled the oxygen content to be controlled but only in those fibres which did not contain other species which contained oxygen. Chemical stability and creep resistance became the main aims of the research and much effort was put into understanding the mechanisms involved in each. The third generation of fibres to be produced were nearly stoichiometric in composition with the microstructure of granular silicon carbide and Young's moduli which were close to that of bulk silicon carbide. The creep and strength retention at high temperatures of the third generation of fibres approach those of bulk silicon carbide. Even though improvements to the fibres can be expected to be made it is clear that, after a sustained effort over more thirty years, the third generation of small diameter SiC fibres now possesses characteristics which are close to being optimised and which are those required by industry. This has been possible through a fundamental understanding of the material science controlling the behaviour of this class of filaments.

Acknowledgements

The authors wish to acknowledge the contributions of a considerable number of research students and two colleagues, M-H. Berger and D. Ormston, at the Ecole des Mines de Paris in obtaining some of the results and images presented in this paper. They also thank O. Adam for her assistance in the preparation of the manuscript.

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