Processing and microstructure of non-oxide ceramic fibres

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Abstract. Research and development efforts on high-temperature, oxidation-resistant fibres have increased over the past decade due to the demand for light-weight, stiff and strong composite materials in aerospace applications. Varieties of 'high-performance', continuous, non-oxide fibres with low-density, high tensile strength and tensile modulus have been developed either from organic precursors or via chemical vapour deposition for fabrication of ceramic matrix composites. Fibres derived from polymer precursors (e.g. Nicalon, Tyranno, HPZ) are small in diameter (compared to CVD monofilaments) and are ideally suited for ceramic composites. Processing, microstructural stability and mechanical properties of these newly developed SiC and Si₃N₄ base fibres are briefly reviewed in this paper.

Keywords. SiC; Si₃N₄; composites; organic/polymer precursors; curing; pyrolysis; chemical vapour deposition; microstructure; mechanical properties.

1. Introduction

Monolithic structural ceramics such as silicon carbide, silicon nitride and sialons are inherently brittle, and are highly sensitive to processing and surface (Griffith) flaws. To overcome the inherent brittleness, there has been intensive research activity for the development of 'highly-reliable' and 'damage-tolerant' ceramic matrix composites (CMCs) in the past decade. The first approach adopted was dispersion of particles, platelets or whiskers in a ceramic matrix with the objective of increasing fracture toughness (K_{IC}) two to three times of the matrix value. In these composites, apart from second phase morphology, thermal expansion mismatch and dispersoid-matrix interface, toughening mechanisms such as crack-deflection, crack-bridging and pull-out play an important role in the enhancement of fracture toughness.

The second approach is based on incorporation of high-strength, high-modulus, semi-continuous ceramic fibres in a brittle matrix, to give a 'graceful' failure in a service overload situation by transferring the load to the fibre via a weakly bonded fibre-matrix interface. In fibre reinforced ceramic matrix composites (FRCMCs), the pull-out of fibres in the crack-wake makes an important contribution to the enhancement of toughness. The pull-out is influenced by the properties of the fibres and by the sliding resistance of the interface. Parameters which dominate the micromechanical behaviour of interfaces are thermal expansion mismatch strain (ϵ), the critical strain energy release rate (fracture energy) for the interface relative to that for the fibre (G_i/G_f), and shear resistance of the interface (τ), after debonding. From the experimental and theoretical work, the following criteria have emerged. $G_i/G_f \leq 1/4$; $2 \leq \tau \leq 40$, $\epsilon \geq 3 \times 10^{-3}$ (Cao *et al* 1990; Evans 1990). An *in situ* carbon-rich layer formed in silicate matrices or a pre-synthesized layer deposited on the fibres prior to fabrication fulfils the above prerequisites.

For FRCMC fabrication, high-modulus oxidation resistant fibres with small-diameter are ideal. Small-diameter fibres are easily weavable to produce net-shape

fibre preforms that are subsequently infiltrated by a matrix. The high volume fraction of small-diameter fibres not only reduces the risk of introducing process-related flaws but also ensures that a sufficient number of fibres bridge the matrix microcracks, thereby greater applied strains for further matrix crack propagation. Another advantage of using a small-diameter fibre is that the fibre length required for full fibre-matrix load transfer is also small (Dicarlo 1989). Additionally, reinforcing fibres should be capable of retaining the structure, stiffness and strength under processing and service conditions i.e. $> 1000^{\circ}\text{C}$. Keeping these in view, a wide range of oxide and non-oxide ceramic fibres suitable for ceramic matrix reinforcement have been developed.

Carbon fibres offer a wide range of mechanical properties. However, they exhibit poor oxidation resistance. Although oxide fibres (e.g. Al_2O_3) are capable of withstanding higher temperatures, reactivity with silicate matrices and poor creep properties discouraged their use in high temperature ceramic composites. Fibres based on the compounds of SiC and Si_3N_4 have received greater attention due to their improved stability in oxidizing conditions and reduced reactivity during processing. Among various non-oxide fibres, the most developed systems are silicon carbide and silicon nitride. Compared to monofilaments, fibres developed from polymer base precursors are fine in diameter ($8\text{--}15\text{ }\mu\text{m}$) and are ideally suited for CMC fabrication. The production methods, microstructure and mechanical properties of various non-oxide fibres are reviewed in the following sections.

2. Fibres derived from organic precursors

Although the conversion of organometallic polymers to covalent solids was known for a long time (Chantrell and Popper 1965; Popper 1967), only in the recent past, this process has gained prominence for the production of fine ceramic powders, coatings and fibres (Yajima 1980; Rice 1983; Wynne and Rice 1984; Wei *et al* 1984). Some potential advantages of preparing inorganic materials via organic precursors are (i) improved compositional homogeneity in the final product due to mixing of elemental components on the molecular and atomic levels, (ii) high-purity ceramic products with uniform non-crystalline/microcrystalline microstructures, (iii) ability to produce high surface area powder of controlled morphology, (iv) preparation of refractory ceramics at exceptionally low temperatures and (v) some compositions which cannot be obtained in traditional route can be prepared using organometallic polymers. Precursor materials used for the development of ceramic fibres/coatings should possess properties such as high molecular weight to reduce volatilization, tractability (meltability, malleability or solubility) to form any desired shape before final curing, polymeric structure that is branched or containing cages/rings to decrease the polymer skeleton degradation, presence of latent chemical reactivity for thermo-setting/curing and low organic functional group content to increase ceramic yield and low residual free carbon/carbides.

Carbon fibres with high tensile strength were successfully produced by controlled processing of polyacrylonitrile (PAN) precursor (Morley 1987). A similar approach led to the development of fibres with constitution of Si and C or N. In particular, polysilane or polycarbosilane (PCS) precursors to SiC and polysilazane precursors to silicon nitride are emerging as potential starting materials for the development of high-strength, high-modulus continuous fibres.

Figure 1. Various steps involved in the preparation of ceramic fibres from polymer precursors.

For obtaining continuous ceramic fibres, a preceramic organosilicon polymer is synthesized, purified, spun and cross-linked (curing and pyrolysis) to obtain an inorganic microcrystalline structure with good mechanical properties (figure 1). Each step is dictated by several important factors that will affect final fibre properties. Utmost care has to be taken in purifying the polymer to remove impurities and particulates, which can become the strength-limiting critical flaws in the ceramic fibre. The final properties also depend on the type of spinning viz. wet, dry or melt spinning (Lipowitz 1991). Fibres must be well cured to prevent any inter-fibre fusion during process. Fibre tows, consisting of several hundred individual fine fibres are treated with a sizing agent to minimize abrasion damage during curing (chemical, thermal or irradiation) process. In curing, fibre is converted to a highly cross-linked, infusible material. Finally, by pyrolysing, volatile materials are lost and an inorganic ceramic material is developed.

2.1 Polymer precursors for SiC ceramic fibres

2.1a Polycarbosilane (PCS): An extensive work carried out by Yajima and co-workers on the development of SiC fibres has revolutionized the field of composites. Various polycarbosilane precursors synthesized to obtain better ceramic yield and tensile properties are listed in table 1. At infancy stages, polycarbosilane was prepared from dodecamethylcyclohexasilane (PC-D) (figure 2). This method was technically difficult, expensive and time-consuming and therefore, in an improved method, polycarbosilane was derived from polydimethylsilane (PC-A). Later this process was also abandoned due to usage of an autoclave. Subsequently another method was developed by polymerizing polydimethylsilane under nitrogen flow (PC-N). Further, this process can also be accelerated by small additions of polyborodiphenylsiloxane (PC-B). PC-N and PC-B fibres (table 1) (figure 2) are now being manufactured by Nippon Carbon Co., Tokyo, under the trade name 'Nicalon'. These fibres are currently available for the development of polymer, metal and ceramic matrix composites.

2.1b Polysilanes: Methylchloropolysilane is synthesized by redistribution of Si-Cl and Si-Si bonds. Mixed disilanes are catalytically rearranged with tetrabutyl phosphonium chloride to produce methylchloropolysilane preceramic polymer (Baney and Gaul 1982; Baney 1984).

2.1c Polysilastyrene: Polysilastyrene is developed from a combination of dimethyldichlorosilane and phenylmethyldichlorosilane with the addition of sodium metal in a hydrocarbon solvent such as toluene (Mazdiyani *et al* 1978; West *et al* 1983; West 1984). Absorption of an ultraviolet light (300–350 nm) by solid polysilastyrene

Table 1. Organic precursors for SiC ceramic fibres.

Notation	PCS is obtained from any other precursor	References
PC-TMS	Tetramethylsilane (TMS) by heat condensation at 700°C	Fritz <i>et al</i> (1965)
PC-D	Dodecamethylcyclohexasilane (DMCHS) which is obtained by conversion of dimethyldichlorosilane (DMDCS) with the addition of lithium	Yajima <i>et al</i> (1975, 1976a)
PC-A	Polydimethylsilane (PDS) which is derived from dimethyldichlorosilane (DMDCS) using autoclave	Yajima <i>et al</i> (1976b), Yajima (1983), Hasegawa and Okamura (1986), Hasegawa <i>et al</i> (1980)
PC-N	Polydimethylsilane (PCS) using reflex condenser (without autoclave)	Yajima <i>et al</i> (1976c, 1978b)
PC-B	Polydimethylsilane (PDS); additionally Polyborodiphenylsiloxane (PBDPSO) is added	Yajima <i>et al</i> (1977a,b, 1978a) Ichikawa <i>et al</i> (1986)
—	Polysilastyrene (dimethyl dichlorosilane + phenylmethyldichlorosilane)	West (1984), West <i>et al</i> (1983)
—	Silicon – carbon bond forming reactions of vinylic or chloromethyl silanes	Schilling <i>et al</i> (1983)
—	Dehydrocoupling of MeSiH ₃ to obtain polymethylsilane	Zhang <i>et al</i> (1991)
—	Polysilanes	Baney (1984), Carlsson <i>et al</i> (1990)
—	Commercial polycarbosilane	Soraru <i>et al</i> (1990)

Figure 2. Processing routes for selected non-oxide ceramic fibres obtained from various polymer precursors.

in an inert atmosphere leads to cross-linking by decrease in weight and the polymer becomes rigid.

2.1d Polytitanocarbosilane (PTC): Polytitanocarbosilane is synthesized using a mixture of polydimethylsilane, polyborodiphenylsiloxane and titanium alkoxide (Yajima *et al* 1981; Song *et al* 1988; Yamamura *et al* 1988) (figure 2). They are heated to 340°C under nitrogen atmosphere for 12 h to obtain polytitanocarbosilane precursor. The polymer is concentrated and Si-Ti-C-O fibre is produced by melt-spinning at

$\sim 270^\circ\text{C}$. During the above process, the cleavage of Si–Si bonds in polydimethylsilane, formation of Si–H and Si–CH₂–Si bonds, condensation of Si–H bonds and cross-linking by the titanium compound occur simultaneously (Yamamura 1984). Alternatively, polytitanocarbosilane can also be obtained by the reaction of polycarbosilane (PC-B in table 1) with titanium tetrabutoxide at $\sim 200^\circ\text{C}$ (Okamura *et al* 1985). Fibres derived from PTC are currently produced by Ube Industries Ltd., Tokyo, under the trade name 'Tyranno'.

2.2 Polymer precursors for Si₃N₄ ceramic fibres

Silicon (oxy) nitride fibres are prepared from a wide variety of precursors such as polycarbosilane, poly (di) silazane, polysilane, etc. (table 2). The common method for silazane synthesis is the ammonolysis of halosilanes. The presence of Si–CH₃ groups in polysilazanes consistently results in small proportion of SiC along with Si₃N₄ after pyrolysis (Penn *et al* 1982). Similarly, oxygen is induced in the nitridation of polycarbosilane during oxidation curing (Okamura *et al* 1988b). The fibres produced by fibermic (Rhone–Poulenc, France) or HPZ (Dow Corning, USA) contain small concentrations of oxygen and carbon. Relatively oxygen/carbon free fibres with Si₃N₄ constitution can be obtained by electron/neutron irradiation curing of polycarbosilanes (Okamura *et al* 1987a).

2.3 Conversion of polymer precursors to ceramic fibre

2.3a Oxidation curing and pyrolysis: Polycarbosilane is melt spun into fibres at 290–310°C in a nitrogen atmosphere. These fibres are oxidation-cured at 190°C in air to cross-link polycarbosilane molecules; depending on curing conditions, properties of SiC fibres vary (Ichikawa *et al* 1987). Using various techniques such as IR spectroscopy

Table 2. Organic precursors for Si₃N₄ base ceramic fibres.

Investigators	Precursor/Preparative method
Verbeek (1974)	Polysilazanes obtained from alkylchlorosilane and alkylamines
Penn <i>et al</i> (1982)	Polysilazane prepared from tris (N-methylamino) methylsilane
Okamura (1987), Okamura <i>et al</i> (1988)	Nitridation of polycarbosilane*
Baney (1984)	Polydisilylazane by reaction of mixed disilanes with hexamethyldisilazane
Seyferth and Wiseman (1984)	Polysilazane by the reaction of chlorosilane with ammonia and dichloromethane
Wills <i>et al</i> (1983)	Polysilanes/polysilazanes
Legrow <i>et al</i> (1987)	Hydridopolysilazane by the reaction of trichlorosilane and hexamethyldisilazane
Blum <i>et al</i> (1989)	Various polysilazanes
Schmidt <i>et al</i> (1990)	Vinylc polysilane
Yokoyama <i>et al</i> (1991)	Perhydropolysilazane by ammonolysis of chlorosilane + 2 pyridine

* Produced by Toa Nenryo Kogyo K. K., Tokyo, Japan.

Figure 3. Gas evolution and tensile strength during conversion of thermal oxidation curing of polycarbosilane (after Okamura 1987; Hasegawa and Okamura 1983).

copy, UV, X-ray, Raman spectroscopy, magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy etc the following steps are identified in conversion of polycarbosilane to SiC fibre (Hasegawa and Okamura 1983; Taki *et al* 1989):

- (I) The weight loss due to evaporation of low molecular weight components and increment in the molecular weight (figure 3).
- (II) Molecular weight increases by dehydrogenation and dehydrocarbonation condensation.
- (III) Side chain decomposition by dehydrogenation and demethanation and the beginning of the inorganic structure starting with the formation of Si-C and C-C bonds.
- (IV) Formation of amorphous SiC.
- (V) Formation of β SiC with further dehydrogenation, the product containing excess carbon and silica.
- (VI) Crystal growth of crystalline β SiC with a decrease in Si-O bonds due to reaction with excess carbon.

In PCS, the transition from amorphous to crystalline occurs approximately at 1000°C (Soraru *et al* 1990) although the crystallization becomes distinctly visible at 1200°C. Beyond 1200°C, free carbon dispersed in fibre reacts with oxygen and forms CO. Following various progressive structural readjustments, the fibre gains strength till 1200°C and beyond that the strength decreases drastically due to evolution of CO (figure 3).

Polytitanocarbosilane precursor is more easily spinnable than polycarbosilane. PTC fibre is cured in air at 170°C at a heating rate of 150°C/h. Cured fibre is finally treated in the temperature range of 800–1500°C in a stream of nitrogen to obtain maximum strength.

Silicon (oxy) nitride fibres are obtained from the nitridation of cured polycarbosilane. On the other hand, silazane fibres are spun in an inert atmosphere (to avoid oxygen) followed by curing treatment in a multi-functional chlorosilane. Finally, fibres are pyrolysed at 1200°C in a high pure nitrogen atmosphere (Legrow *et al* 1987).

2.3b Electron/neutron irradiation curing: At higher temperature (> 1300°C), the tensile strength of SiC/Si₃N₄ fibres decreases rapidly due to CO gas evaluation (reaction of C and O takes place within the fibre). In order to improve the elevated temperature properties of SiC/Si₃N₄ fibres, an oxygen-free curing process viz. electron/neutron irradiation curing has been studied. Doses of electron (15 MGy) or neutron (9×10^{24} n/m²) irradiation increased the density and mechanical properties of the fibre (Okamura *et al* 1987a, b, 1988a; Matsuzawa *et al* 1988). The curing mechanism during irradiation process is found to be the breakage of Si-H and C-H bonds and the formation of Si-C, Si-Si and Si-N bonds (Taki *et al* 1988).

Radial distribution function (RDF) curves for different SiC fibres subjected to oxidation curing and irradiation treatment are compared in figure 4a. The atomic arrangement of the nearest neighbours remains unchanged while the second nearest neighbour is slightly ordered in irradiated fibres; number of second neighbours are larger in neutron-irradiated SiC fibres. Similarly, in electron-irradiated Si-N fibres, depending on radiation intensity and post heat-treatment, the structure varied from amorphous to α Si₃N₄ (Okamura *et al* 1988b) (figure 4b).

Figure 4. (A) Radial distribution functions of SiC fibres (a) untreated amorphous SiC fibre, (b) heat treated at 1200°C and (c) neutron irradiated (9×10^{24} n/m²) (after Matsuzawa *et al* 1988) and (B) radial distribution functions of Si₃N₄ fibres obtained by heat treatment of 15 MGy electron irradiation cured fibres at 1200, 1300 and 1400°C (after Okamura *et al* 1988b).

2.4 Fibre microstructure

Among various preceramic precursors synthesized, fibres derived from polycarbosilane, polytitanocarbosilane and hydridopolysilazane have been commercialized (table 3). Both Nicalon and Tyranno fibres have similar carbon and silicon levels, but Tyranno additionally contains 2–4 wt% titanium (figure 5), which is claimed to improve fibre high-temperature properties. Though the fibre chemistry is anticipated to be uniform throughout the structure in these fibres, there are deviations from bulk to the surface. For instance, in Nicalon fibres, oxygen enrichment and Si deficiency have been detected on the fibre surface (Macey *et al* 1984; Porte and Sartre 1989). Similarly, the HPZ fibres display a surface layer of $\sim 0.5\ \mu\text{m}$ thickness which is richer in oxygen as compared to the uniform distribution of Si, N, C, O in the interior (Sawyer *et al* 1987).

A large number of characterization techniques (IR, UV, X-ray, electron microscopy, Raman and MAS-NMR spectroscopy, XPS, etc.) have been employed to study chemical bonding and microstructure of polymer derived fibres (Yajima 1985; Legrow *et al* 1987; Sasaki *et al* 1987; Song *et al* 1988; Hasegawa 1989). SiC and Si_3N_4 base fibres contain Si–O, Si–C and Si–N chemical bonds as revealed by infrared spectroscopy. X-ray photoelectron spectroscopy (XPS) of Nicalon fibre reveals a large Si 2p

Figure 5. (a) SEM micrographs of SiC (Tyranno) fibres and accompanying EDX analysis and (b) TiC precipitates in heat treated fibres at $> 1300^\circ\text{C}$.

Table 3. Properties of various commercial ceramic fibres.

Fibre	Constituents	Preceramic polymer/processing method	Diameter (μm)	Density (g/cm^3)	Typical tensile strength (GPa)	Typical elastic modulus (GPa)	Proposed maximum use (Temp. $^{\circ}\text{C}$)
<i>Polymer derived fibres</i>							
Nicalon	Si:C:O:H 1:1.46:0.36:0.03	Polycarbosilane	10-20	2.5	2.60	190	~ 1200
Nippon Carbon Co, Japan	Si:Ti:C:O	Polytitanocarbosilane	8-12	2.5	2.75	190	~ 1300
Tyranno	1:0.04:1.32:0.96						
Ube Industries, Japan	Si:N:C:O	Hydridopolysilazane	10-15	2.8	2.80	190	~ 1400
HPZ	1:0.49:0.18:0.07						
Dow Corning Corp., USA	Si:C:O	Polycarbosilane	10-15	2.5	3.30	300	~ 1200
Si ₃ N ₄ (TNSN)							
Toa Nenryo Kogyo K.K., Japan							
<i>CVD fibres</i>							
SiC Monofilaments, SSC-6	SiC/C	Chemical vapour deposition of SiC/C on a carbon core	142	3.0	3.4	410	1300
Avco Speciality materials, USA							
Sigma	SiC/C	Chemical vapour deposition of SiC/C on a 'W' core	100	3.4	3.4	410	1200
Berghaf, Germany							
BP, UK

Figure 6. ^{29}Si and ^{13}C MAS-NMR spectra obtained from commercial SiC and Si_3N_4 fibres. ^{13}C spectrum of Nicalon fibres is taken from Lipowitz's work.

peak, which is attributed to mixed chemical bonding of carbon and oxygen (Porte and Sartre 1989). Further insight about structural details has been obtained using MAS-NMR spectroscopy (Legrow *et al* 1987; Lipowitz *et al* 1987; Murthy *et al* 1989; Taki *et al* 1989; Lewis *et al* 1990). ^{29}Si MAS-NMR spectra obtained from as-prepared fibres are shown in figure 6. Nicalon and Tyranno fibres exhibit mixed tetrahedra coordinations with silicon, oxygen and carbon ($\text{SiO}_x\text{C}_{4-x}$; $0 < x < 4$); the higher oxygen and titanium dispersion in Tyranno fibres increases the structural disorder (figure 6b). HPZ fibres show a peak at -47 ppm based on SiN_4 coordination with asymmetric broadening towards SiC_4 polytypic structure, indicative of mixed coordinations ($\text{SiN}_a\text{C}_b\text{O}_c$; $a + b + c = 4$) (figure 6c).

The excess free carbon which is produced during the course of organic-inorganic transformation is dispersed uniformly within the structure (Yajima *et al* 1979). Free carbon in the fibre is disorganized, polyaromatic (sp^2 bonded), and turbostratic in nature and is spread over to several nanometers (~ 6 nm) in the polyaromatic plane (a-axis) (Lipowitz 1991). The presence of free carbon (as graphite microcrystals) has also been confirmed by several authors (figure 6d) (Day *et al* 1989; Laffon *et al* 1989; Maniette and Oberlin 1989). The number of colonies and size keeps growing as the temperature increases and graphite fills the interstices between SiO_2 or SiC . Graphite precipitates, besides holding SiC together, also suppress the growth and coale-

Figure 7. Model microstructure of SiC (Nicalon) fibre. (after Laffon *et al* 1989).

science of SiC microcrystals. Based on various structural details, a two-dimensional model has been proposed for Nicalon fibre (Laffon *et al* 1989) (figure 7). In addition to different phases, a pore phase has also been identified in Si–C–O and Si–N–C–O fibres. The porosity appears to be globular in shape and the pore size varies depending on pyrolysis temperature (Chaim *et al* 1988; Lipowitz *et al* 1990).

2.5 Microstructural stability and its influence on mechanical properties

Fibres derived from organic precursors exhibit exceptionally high tensile strength and elastic modulus (table 3; figure 8). The higher tensile properties are attributed to a microcrystalline structure, although the exact relation between the two is not fully understood. However, properties are found to be dependent on the impurities and flaws (internal or surface) created during the spinning process. For instance, the properties of Si–C–O and Si–O–N–C are controlled by the amount of oxygen present within the fibre (Sawyer *et al* 1987; Okamura *et al* 1988a). Oxygen cured Nicalon fibres contain > 10 wt% oxygen and exhibit inferior properties compared to electron/neutron irradiated fibres with lower oxygen content (3–4%). Fast irradiation not only reduces the retained oxygen but also improves the density of the fibre and hence its properties (figure 9) (Matsuzawa *et al* 1988; Okamura *et al* 1988a).

The thermal stability of these fibres has been measured by tensile strength retention after annealing in vacuum, argon, nitrogen and air (Mah *et al* 1984; Simon and Bunsell 1984a; Yamamura *et al* 1987; Jaskowiak and Dicarlio 1989; Pysher *et al* 1989; Kim and Moorhead 1991); generally, properties of all the fibres decrease with increase in temperature. High temperature structural degradation of silicon oxycarbide fibres

Figure 8. Fast fracture tensile strength and elastic moduli for Nicalon, Tyranno and HPZ fibres (after Lipowitz 1991).

Figure 9. (A) Density and crystalline size of heat heated and neutron irradiated fibres (Matsuzawa *et al* 1988), (B) tensile strength of heat-treated, and neutron irradiated fibres (after Matsuzawa *et al* 1988) and (C) comparison of heat-treated and electron irradiated fibres (after Okamura *et al* 1988a).

occurs by CO loss followed by progressive segregation of C and O to their respective tetrahedra (SiC_4 and SiO_4) with an accompanying increase in long range order. The ultimate structure is a microcrystalline mixture of β SiC and SiO_2 (cristobalite) (Murthy *et al* 1989). Due to the transition from short range order (nanocrystalline) to long range order (β SiC), fibre fracture changes from glassy to granular. In vacuum or inert atmospheres oxygen is lost as SiO and CO, leaving microporous β SiC crystalline fibres of low strength (< 0.4 GPa). In nitrogen atmosphere, the surface undergoes nitridation and the out-diffusion of gases becomes sluggish. In Tyranno, uniformly dispersed titanium reacts with free carbon and precipitates as TiC (figure 5). Further, creep properties of the fibres are also controlled by the change that occurs in the fibre viz. SiC grain growth and SiO_2 , SiO and CO formation (Simon and Bunsell 1984b).

3. SiC monofilaments via chemical vapour deposition

In the early stages of development, SiC monofilaments were produced by deposition of SiC onto a tungsten core ($\sim 12\ \mu\text{m}$ in diam.). In the as-prepared state, these fibres possess high tensile strength (3.45 GPa), however, the strength rapidly decreases as temperature approaches 1000°C . The strength degradation is mainly attributed to the reaction between tungsten and deposited SiC. Although, the reaction between tungsten core and the substrate is limited during deposition of SiC sheath, the reaction layer (W_5Si_3 and W_2C) thickness increases by consuming all the tungsten core and induces brittleness to the fibre (Crane and Krukoni 1975; Wawner 1988). To overcome the detrimental reaction between the core and the SiC substrate, tungsten was later replaced by carbon fibre. These improved fibres with 'C' core are produced by AVCO speciality materials, USA and are available for preparation of various composite materials (Prewo and Brennan 1980; Anderson and Warren 1984; Buljan and Sarin 1987; Jansson *et al* 1991; Scott *et al* 1991).

3.1 Production

A vertical glass chamber with mercury seals at both ends is used with inlet and exit ports for introducing and removing reactant gases and products respectively (figure 10). Carbon fibre is pulled continuously through the chamber and heated electrically with DC current. Monofilaments are produced by thermal decomposition of various silanes (methyl trichlorosilane and methylchlorosilane), hydrogen, propane and argon. The kinetics of SiC deposition are complicated and sensitive to deposition

Figure 10. Schematic diagram of a reactor used to produce SiC monofilaments (Martineau *et al* 1984).

pressure, flow, temperature, etc. While it is possible to obtain single phase of SiC, sometimes, traces of carbon and silicon are also deposited due to changes in the proportion of gas mixtures (Chin *et al* 1977; Kingon *et al* 1983; Martineau *et al* 1984). Additionally, variation of fibre resistance along the reactor length as SiC is being deposited, this generates a temperature gradient (figure 10) and influences the deposition and microstructure.

3.2 Microstructure

AVCO SiC monofilaments produced via CVD are large in diameter ($\sim 142\ \mu\text{m}$). Initially, a pyrolytic graphite ($\sim 1\ \mu\text{m}$) is deposited onto the carbon core of $33\ \mu\text{m}$ (a) to improve the surface for SiC deposition and (b) to make the carbon fibre diameter uniform so that constant resistance is obtained during heating of the substrate. Following pyrolytic graphite, a sheath of SiC is deposited in a columnar crystal morphology (figure 11). The sheath consists of mainly β SiC grains extending in the radial direction with $\langle 111 \rangle$ preferred orientation (Wawner *et al* 1983; Nutt and Wawner 1985). The columnar grains within the sheath vary in size (40–50 nm near the substrate and 90–100 nm at the surface). Such a variation in grain size is attributed to the temperature difference within the production chamber. High supersaturation generally results in a high nucleation density (i.e. fine grains), whereas low saturation gives rise to coarse grain structure (Wawner *et al* 1983). MAS-NMR studies on the monofilaments revealed that the SiC is mainly β SiC (3c) with other polytypic forms such as 6H and 15R (figure 11) (Lewis *et al* 1990; Murthy *et al* 1990). Besides SiC, small amounts of free silicon were also detected in the microstructure (Brun and Borom 1989). Further, the fibre is coated with twin layers of amorphous carbon (by varying the ratio of SiC to C) towards the surface and the thickness can be varied to meet specific applications. The outer carbon-rich layer is claimed to heal micro-cracks on the SiC and also acts as a low-cohesion layer at the fibre-matrix interface in ceramic matrix composites. Similarly, Si_3N_4 fibres using C or W core can be produced using Si_4Cl and NH_3 reactant combination.

3.3 Properties

In the as-prepared condition, fibres display very high tensile strength ($\sim 4\ \text{GPa}$) and tensile modulus ($\sim 400\ \text{GPa}$) (Siemers *et al* 1988). However, tensile strength decreases drastically beyond 1200°C , both in oxidative and protective atmospheres (figure 12) (Dicarlo 1985). The poor performance of monofilaments at elevated temperatures is attributed to residual silicon which coexists with β SiC (Dicarlo 1986; Brun and Borom 1989). At still higher temperatures ($> 1400^\circ\text{C}$), fibres degrade because of SiO, CO evolution coupled with precipitation of impurities present within the fibre (Johnson *et al* 1988).

The creep properties were also found to be poor due to the presence of free silicon (Dicarlo 1985, 1986). A prior thermal heat-treatment above 1400°C was suggested to improve the creep properties of CVD fibres. It is believed that free silicon present in the grain boundaries will evaporate as SiO, thereby increasing viscosity of the grain boundary film and improving the resistance to grain boundary sliding (Dicarlo 1986).

Although SiC monofilaments are stable up to 1200°C , the large fibre diameter and

Figure 11. AVCO SiC monofilament (SCS-6) with EDX and MAS-NMR analyses.

Figure 12. Strength retention of AVCO SiC fibre in (a) argon/nitrogen and (b) oxygen environments (after 15 min exposure) (after Dicarlo 1985).

poor creep resistance are major limitations during fabrication and performance of CMCs respectively.

4. SiC fibres by other methods

4.1 *Controlled in situ reaction of carbon (fibre) and silicon*

Attempts have been made to convert carbon fibres into silicon carbide fibres by depositing free silicon (via CVD) on to a carbon fibre and controlling the *in situ* reaction between Si and C. Two mechanisms are proposed for conversion of C + Si to SiC (Pampuch *et al* 1987). (a) Formation of a SiC reaction layer on the C fibre surface and further growth of SiC via out-diffusion of carbon through the reaction layer to react with outside Si. The diffusion of C through SiC reaction layer is much faster than in-diffusion of Si through SiC shell and hence the reaction is expected to be self-sustaining and (b) SiC precipitation from the supersaturated liquid of C in liquid silicon. This mechanism seems to be faster compared to the former because of higher diffusivity in the liquid phase. SiC which has initially formed is porous in nature (figure 13) and encourages the out-diffusion of C through the shell. The solution formation of C in Si is endothermic in nature while precipitation of SiC from C + Si solution is exothermic. The temperature at the C + Si/SiC interface oscillates resulting in successive zones of poor and rich carbon regions with reference to C. Hence,

Figure 13. SiC fibres obtained via *in situ* reaction of carbon fibres and silicon.

control over the overall reaction kinetics and densification of SiC fibre to near theoretical value are essential for successful production of SiC fibres.

4.2 Extrusion of fine ceramic powders followed by sintering

Fine ceramic powder (submicron or nanometer size) is mixed with appropriate sintering aids and binder and the admixture is extruded through a nozzle. Stoichiometric or near-stoichiometric powders used in this method are expected to give better properties, especially at higher temperatures ($> 1200^{\circ}\text{C}$). The extruded filament is subsequently sintered at elevated temperatures to obtain desired mechanical properties. The major limitation is the diameter of the fibre, which is larger ($\sim 70\ \mu\text{m}$) as compared to polymer derived fibres. Residual porosity is a strength-limiting factor in these fibres (figure 14) and attempts are under way to improve the fibre strength.

5. New developments

Oxygen-induced degradation of fibre structure and fibre-matrix interface microstructure is a major obstacle in the development of FRCMC. To improve the stability of existing fibres and interfaces, presynthesized multiple surface coatings of varying thicknesses ($0.25\text{--}2.0\ \mu\text{m}$) are given on as-prepared fibres. The primary layer is a layered structure (Van der wall type) with low-cohesion and low shear stress (τ) coupled with stability and non-reactivity at elevated temperatures. The second layer

Figure 14. SiC fibre obtained by extrusion of fine powder followed by high temperature sintering; in a magnified view, residual porosity is clearly visible.

is essentially a refractory coating to protect the low-cohesion layer and fibre during processing and performance. Sometimes, a third coating may be necessary if the second layer is incompatible with matrix chemistry. Carbon or boron nitride and SiC are emerging as the potential coating materials for primary and secondary layers respectively (Bender *et al* 1986; Lowden *et al* 1988). A combination of porous SiC

(CVD) followed by $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$ (sol-gel) has also proved to be successful in deflecting the crack efficiently at the fibre-matrix interfaces (Sheppard 1992).

Currently available yarn-based, non-crystalline SiC and Si_3N_4 fibres exhibit microstructural instabilities beyond 1200°C , with poor mechanical properties. Therefore, there is an immediate need for the development of fibres which can retain strength up to 1400°C . MERC, Dow corning and Carborundum (USA) are trying to develop a new class of silicon carbide fibres which are expected to exhibit improved properties up to 1600°C . Several Japanese research organizations have also joined in the effort by developing B-N and Si-B-N fibres, which are also targeted for CMC applications (Sheppard 1992).

6. Summary

(I) Although many organosilicon polymers have been explored for the development of SiC and Si_3N_4 fibres, only polycarbosilane, polytitanocarbosilane and polysilazane have emerged as potential starting materials for the production of continuous silicon (oxy) carbide (Nicalon), Si-Ti-C-O (Tyranno) and silicon (oxycarbo) nitride (HPZ) fibres respectively. Of these, silicon (oxy) carbide is the most extensively studied system.

(II) Both, curing and pyrolysis play an important role in the evolution of microstructure and mechanical properties of polymer derived fibres. In these fibres, polymer-to-ceramic conversion takes place in various steps; with progressive structural readjustments, fibre gains strength up to a critical point and beyond, strength decreases drastically due to coarsening of the structure and CO gas evolution.

(III) All the polymer derived ceramic fibres exhibit mixed tetrahedra coordinations with Si, O, C and N. Excess free carbon in these fibres is dispersed uniformly in the microstructure as graphite microcrystallites. In addition to different phases present, a pore phase has also been identified.

(IV) Fibres from organic precursors exhibit very high tensile properties. However, the stability (structural and mechanical) of these fibres is poor beyond 1000°C . At higher temperatures, the mixed C and O coordinations are progressively replaced by segregated SiC_4 and SiO_4 tetrahedra. In vacuum or inert atmosphere, oxygen within the fibre reacts with Si and C and escapes as SiO and CO respectively, leaving behind a microporous crystalline fibre.

(V) SiC monofilaments prepared via chemical vapour deposition are larger in diameter ($\sim 142\text{ }\mu\text{m}$) and possess good mechanical properties. However, the performance of these fibres is limited up to $\sim 1200^\circ\text{C}$ due to residual silica present along with βSiC . Traces of silica affect the creep properties and a prior thermal heat-treatment $> 1400^\circ\text{C}$ believed to improve the creep resistance.

(VI) Attempts have also been made to produce SiC fibres by other methods such as (i) conversion of carbon fibres to SiC, via reaction C and Si (deposited on the surface) and (ii) extrusion of fine powders. However, these methods are yet to be perfected.

(VII) Presently available non-oxide ceramic fibres have a limited temperature capability (up to 1000°C) and there is a need to develop fibres which can retain good strength above 1400°C . On the one hand, currently available yarn base fibre performance is extended by giving multi-layer coatings and on the other hand, new non-oxide fibres are being developed for high-temperature applications.

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