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Continuous SiC-based model monofilaments with a low free carbon content

Part II *From the pyrolysis of a novel copolymer precursor*

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Quasi stoichiometric model SiC monofilaments (C/Si atomic ratio ≈ 1.02) with still some free carbon (≈ 3 mol%) and residual oxygen have been produced from a novel copolymer precursor, itself prepared from methylphenyldichlorosilane and 2,4-dichloro-2,4-disilapentane. The continuous green fibre was melt spun at 230 °C, cured by electron-beam irradiation, and pyrolysed under argon at temperatures, T_p, in the range 1000–1600 °C. The fibre remained nanocrystalline at high temperature with the SiC grain size growing from 1.5 nm to 7.3 nm when T_p was raised from 1400 °C to 1600 °C. Its Young's modulus continuously increased as T_p was raised (with $E = 320$ GPa for $T_p = 1400$ °C), whereas its tensile strength at room temperature underwent a maximum for $T_p = 1200$ °C ($\sigma_R \approx 1850$ MPa for $L = 10$ mm and $d \approx 20$ μm).

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1. Introduction

Recent research on SiC/SiC composites and their constituents has suggested that an improved reinforcement for these composites, in terms of thermal stability, i.e. creep resistance, compatibility with the pyrocarbon interphase and SiC matrix, as well as oxidation resistance, is likely to be a SiC-based fibre, free from oxygen, and with a C/Si atomic ratio ≈ 1 [1–4].

Up to now, commercially available SiC-based fibres used in ceramic matrix composites (CMCs), including SiC/SiC composites, e.g. the Si–C–O Nicalon fibres (from Nippon Carbon, Japan), are produced from polycarbosilane (PCS) precursors, according to the Yajima route [5–7]. This route displays two important drawbacks. First, the fibres with an empirical formula close to $SiC_{1.55}H_{0.027}O_{0.326}$, contain a significant amount of oxygen. This oxygen, introduced during the curing step and present in an amorphous SiC_xO_y phases, is actually responsible for their metastability at high temperatures [8, 9]. Moreover these fibres also contain free carbon resulting from the incomplete loss of pendent methyl groups of the PCS during the pyrolysis step under an inert atmosphere. The formula of PCS derived from polydimethylsilane (PDMS) is close to $SiC_{1.77}H_{3.70}O_{0.035}$ [6, 7]. Oxygen-free fibres, e.g. Hi-Nicalon, are now available. They are produced, either via an oxygen-free physical (electron-beam) irradiation process of Yajima-type PCS precursor [10, 11] or via dry-spinning of solutions of infusible, high molecular weights PCSs [12]. However, these improved fibres still contain free carbon in large amounts [1, 3].

More recently, quasi stoichiometric experimental SiC fibres free from oxygen have been prepared from various precursors. A first approach consists of the release of both the excess carbon and oxygen from Si–C–O Yajima-type fibres (or related materials) as CO, by heat treatment at high temperature, typically 1800 °C. However, some sintering aid such as a boron derivative, has to be introduced into the fibre (e.g. during the curing step) to yield fibres of high strength [13]. Simultaneously, Takeda *et al.* [14] have reported the properties of a quasi stoichiometric SiC fibre prepared from PCS, according to a modified Yajima route without disclosing the details of the process.

Another approach to quasi stoichiometric SiC fibres starts from a preceramic polymer with a low C/Si atomic ratio. Such a strategy developed by Zhang *et al.* [15] uses mixtures of polymethylsilane (PMS), "$\text{-}\!\!\!\![(CH_3SiH)]\!\!\!\!\text{-}_n$" and appropriate spinning aids. On our part, we have involved for that purpose a copolymer whose composition has been chosen to yield a ceramic residue with a C/Si atomic ratio ≈ 1, after pyrolysis under an inert atmosphere [16].

In Part I [17] we reported attempts to decrease the free carbon content of ex-PCS fibres by performing

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the pyrolysis under a hydrogen atmosphere, because hydrogen favours the release of pendent methyl groups by forming methane. The aim of this paper is to report the preparation of a continuous, quasi stoichiometric SiC, model monofilament from a new precursor whose structure has been especially designed for this purpose, and to present some of its properties.

2. Experimental procedure

2.1. Synthesis of the precursor

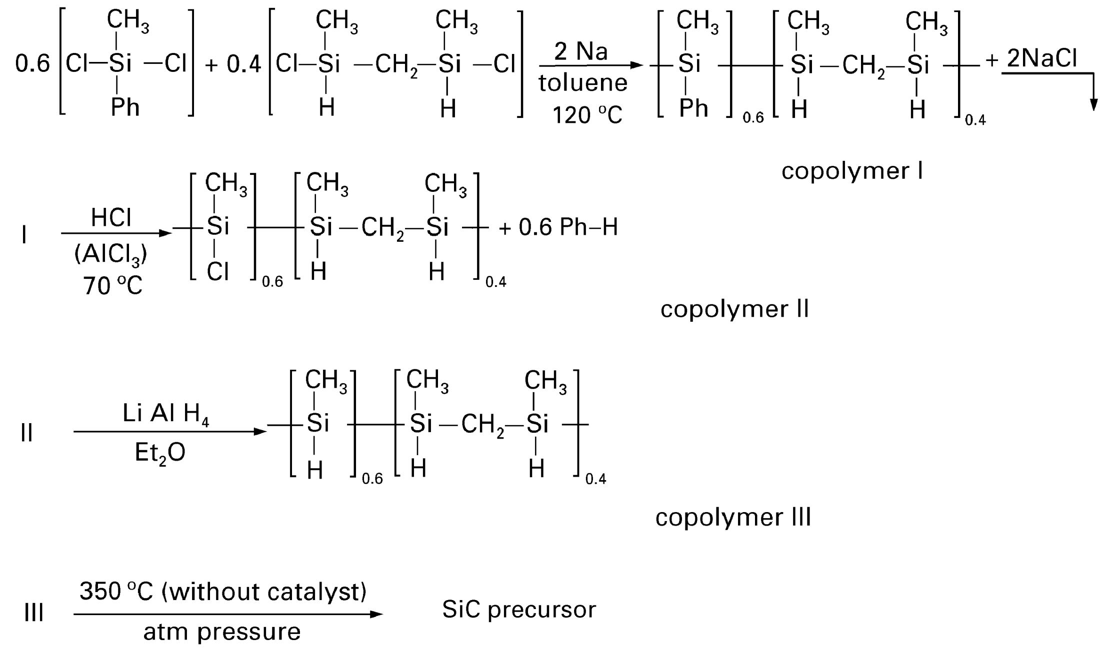
The precursor was prepared via a copolymer route which has been previously reported [16]. This precursor (referred to previously as P I [16]) is constituted with both Si–Si and Si–CH_2–Si units in its backbone. The main steps of its synthesis are briefly recalled here for the purpose of subsequent discussion. As shown in Scheme 1, the first step consisted of the polycondensation of 2,4-dichloro-2,4-disilapentane and methylphenyldichlorosilane in the presence of sodium, which yielded copolymer I. The second step, i.e. the replacement of the phenyl groups by chlorine atoms, was achieved by treating I with HCl in the presence of catalytic $AlCl_3$, yielding the chlorinated copolymer II. In a third step, the Si–Cl bonds were reduced with $LiAlH_4$, leading to the hydrogenated copolymer III. Because the ceramic yield of III is low, i.e. 14 wt % at 950 °C due to poor cross-linking, thermolysis of III was performed at 350 °C, under inert gas at atmospheric pressure and without a catalyst, yielding a convenient precursor (char yield 60%). The composition of the precursor, particularly its C/Si atomic ratio, can be controlled by varying the respective amounts of the two initial monomers. A molar proportion of 0.6 molar equivalent of methylphenyldichlorosilane and 0.4 molar equivalent of 2,4-dichloro-2,4-disilapentane, corresponding to a C/Si atomic ratio of 1.29 (instead of 1.77 for the Yajima PCS precursor), was selected to obtain quasi stoichiometric SiC-based ceramics upon pyrolysis under an inert atmosphere.

The precursor prepared under such conditions, is a fusible solid (with a softening temperature ≈ 190 °C), soluble in various solvents, including pentane and tetrahydrofuran. It is characterized by $\bar{M}_n \approx 1600$ and a polydispersity index, $I_p = 2.3$, and afforded a good ceramic yield at 950 °C under argon, 64%.

The ^{1}H n.m.r. spectra showed that the last step of the synthesis (i.e. the heat treatment at 350 °C) involved the reactive Si–H bonds, according to a common cross-linking mechanism in such polymers. Finally, the precursor appeared to be extremely sensitive to oxidation, as supported by the occurrence of a shoulder in the infrared spectrum at 1100 cm^{-1}, assigned to the Si–O valence vibration.

2.2. Preparation of model monofilaments

Continuous monofilaments were melt-spun in a dry glove-box filled with nitrogen, as previously described [17], in order to minimize contamination by oxygen (air) and/or moisture. Spinning was performed at 230 °C by applying a pressure of 6 MPa to the molten precursor forced to flow through a single-hole spinneret. The extruded monofilament was drawn down under the mechanical stretching resulting from the rotation of the take-up reel. Then, the green monofilaments were cured by electron-beam (EB) irradiation under anaerobic conditions at a temperature close to ambient [17]. The overall irradiation dose was 1000 Mrad. After EB irradiation, the cured fibre bundle was set in an alumina boat in a glove-box and transferred to a prepyrolysis silica glass furnace directly fitted to the glove-box in order to minimize contamination by oxygen and moisture (EB-cured organosilicon fibres very likely contain free radicals which are extremely sensitive to oxidation, as reported by Okamura *et al.* [10]). To trap these free radicals, a treatment (12 h at 400 °C under argon atmosphere) was applied to the as-cured fibres, before prepyrolysis. Then the fibres were heated up to 1000 °C under argon (heating rate



Scheme 1.

1 °C min^{-1}; isothermal plateau of 1 h at 1000 °C). Finally, the prepyrolysed fibres, which were no longer sensitive to oxidation, were further heated up to T_p with $1000 < T_p \leqslant 1600$ °C, as reported in Part I [17].

2.3. Characterization of the fibres

The elemental composition of the fibres was determined by electron probe microanalysis (EPMA), using SiC and SiO_2 standards. The remaining hydrogen was not determined. Free carbon, when present as a minor phase, was characterized by Raman spectroscopy (laser wavelength = 514.5 nm, source power = 150 mW). The X-ray diffraction (XRD) spectra (CuK_α, Phillips diffractometer control) of monofilament samples placed on a silica plate, were recorded. The apparent average grain size of the β-SiC crystalline phase was calculated from the width of the (1 1 1) diffraction peak at mid-height, according to the Scherrer equation.

The failure stress and Young's modulus were measured through tensile tests performed on single-filament samples (gauge length $L = 10$ mm) [18]. More details on the fibre characterization methods have been given in Part I [17].

Finally, the change in morphology occurring during the pyrolysis of the fibres, was studied by scanning electron microscopy (SEM) (Jeol 840 A).

3. Results

3.1. Composition and structure

The chemical composition of the fibre coming from the precursor prepared according to scheme 1 (C/Si atomic ratio = 1.29), then cured by electron-beam irradiation, and finally pyrolysed under argon at $T_p = 1400$ °C, is given in Table I. The data show that the C/Si atomic ratio is close to unity (namely 1.02), i.e. that the fibre is quasi stoichiometric. The fibre also contains a noticeable amount of oxygen (3.9 at %) despite the efforts to minimize oxygen contamination. Assuming that oxygen is bonded to silicon as SiO_2 and the silicon carbide phase is stoichiometric SiC, the amount of free carbon derived from EPMA data would be only 2.9 mol %.

The occurrence of some free carbon in the fibres is also supported by their Raman spectra (Fig. 1). Owing to its low detection limit for carbon, Raman spectroscopy has been often used to characterize SiC-based fibres [19–21]. The spectra of the fibres exhibit the two characteristic bands (respectively at ≈ 1600 and ≈ 1350 cm^{-1}) of poorly organized sp^2 carbon. As T_p is raised from 1200 °C to 1400 °C, these peaks become better separated. Additionally, the spectra display broad and weak bands at ≈ 400 and ≈ 800 cm^{-1}, assigned to amorphous or poorly crystallized silicon carbide. For $T_p = 1600$ °C, crystallization of the SiC-phase occurs as evidenced by two sharp peaks which appear at 968 and 792 cm^{-1}, assigned to SiC (Fig. 2). For $T_p = 1200$ °C,the fibre is amorphous on the basis of its XRD pattern (Fig. 3). As T_p is progressively raised, the crystallization of the SiC phase occurs, the apparent SiC crystal size (determined by the Scherrer equation) being ≈ 1.5 nm for $T_p = 1400$ °C and still only 7.3 nm for $T_p = 1600$ °C.

The variations of the tensile strength, σ_R, and Young's modulus, E, as a function of T_p, are shown in

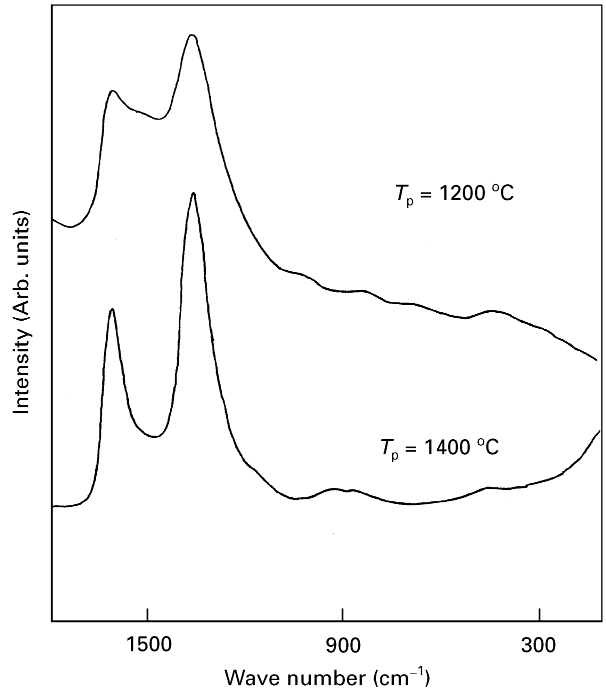


Figure 1 Raman spectra of fibres pyrolysed under argon at $T_p = 1200$ and 1400 °C .

TABLE I Chemical composition of various SiC-based fibres with a low oxygen content resulting from the pyrolysis of organosilicon precursors

Precursors	T_p (°C)	Pyrolysis atm	Elemental composition (at %)				Free C (mol %)	C/Si atomic ratio	Ref.
			Si	C	O	H			
1. Novel copolymer	1400	Argon	47.6	48.5	3.9	ND	2.9	1.02	present work
2. Yajima-type PCS	1400	Hydrogen	44.6	51.0	4.4	ND	9	1.14	[17]
3. Yajima-type PCS	≈1400	Argon	39	58	3	ND	20.5	1.49	[22]
4. Yajima-type PCS	1000	Inert	42.0	55.0	0.8	2.1	13.4	1.31	[23]
5. Yajima-type PCS[a]	–	Inert	41.0	58.1	0.9	ND	17.6	1.42	[24]
6. High $\bar{M}_n$ PCS[b]	–	Argon	31.7	56.7	1.8	< 8.0	25.9	1.79	[12]
7. High $\bar{M}_n$ PCS[b]	–	–	48.1	51.8	< 0.1	ND	3.7	1.08	[25]
8. PMS-polymer[c]	1000	Argon	48.4	51.6	ND	ND	3.2	1.07	[15]

[a] Hi-Nicalon from Nippon Carbon.
[b] Infusible soluble PCS + additive.
[c] Plus spinning additive.

Table II. As reported for other fibres prepared from organosilicon polymers, the Young's modulus progressively increases as T_p is raised, whereas the tensile strength exhibits a maximum for $T_p = 1200\,^{\circ}C$. Additionally, the value of the Young's modulus, e.g. for $T_p = 1400\,^{\circ}C$, is much higher (namely ≈ 300 GPa) than that reported for fibres containing a large amount of free carbon. Finally, the maximum value of σ_R is moderate, namely 1850 MPa, partly due to the relatively large diameter of the fibre (22 μm). No attempt was made to optimize the processing conditions.

The failure surface of the fibre remains smooth for $T_p = 1200$ and $1400\,^{\circ}C$ (Fig. 4a, b) is in good agreement with the amorphous (or poorly crystalline) state of the fibre (Fig. 3). Conversely, for $T_p \geqslant 1400\,^{\circ}C$, the failure surface clearly shows the polycrystalline nature of the fibre (Fig. 4c), which corroborates the conclusions drawn from Raman spectroscopy (Fig. 2) and XRD (Fig. 3) data.

4. Discussion

4.1. Composition of the fibre

Neglecting hydrogen, which can be assumed to be present only in a very small amount in the fibre pyrolysed at 1400 °C under argon, the EPMA data given in Table I clearly show that the fibre prepared in the

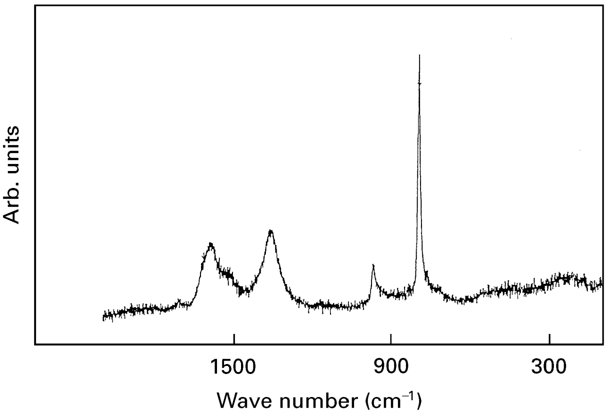


Figure 2 Raman spectrum of fibre pyrolysed under an argon atmosphere at 1600 °C.

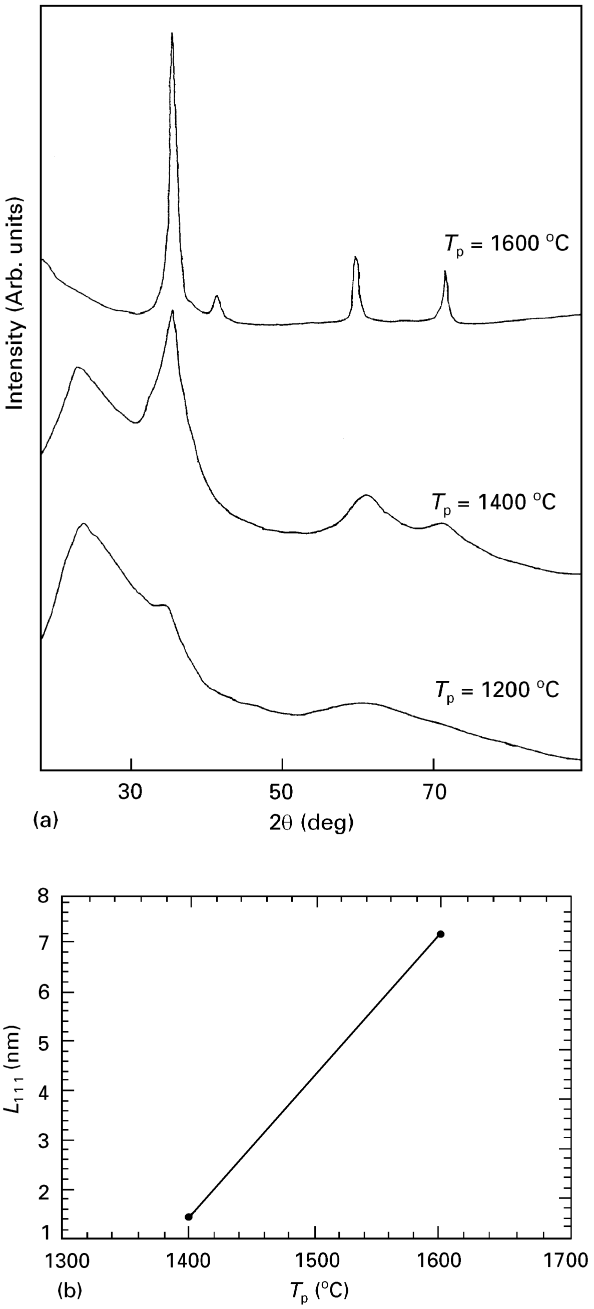


Figure 3 (a) XRD patterns (CuK_α) of fibres pyrolysed under argon at various temperatures. (b) The apparent L_{111} SiC crystal size.

TABLE II Properties of various SiC fibres with a low oxygen content

Precursors	T_p (°C)	Free carbon[a] (mol %)	ρ (g cm^{-3})	Mechanical properties at 25 °C		Reference
				E (GPa)	σ^R (MPa)	
1. Novel copolymer	1000	–		250	1300[b]	Present work
	1200	–		300	1850	Present work
	1400	2.9		320	1600	Present work
2. Yajima-type PCS	1000	8		225	1360[c]	[17]
	1200	7		260	1700–2100	[17]
	1400	9		290–300	1450–1750	[17]
3. Yajima-type PCS	1000	18.5	2.73	220	1480[d]	[3]
	1200	18.5		243	1620	[3]
	1400	20.5		260	1690	[3]

[a] Free carbon was calculated, assuming that oxygen is present as SiO_2 on a first approximation, and that the remaining silicon is present as stoichiometric silicon carbide.

[b] $L = 10$ mm; $d = 22$ μm.

[c] $L = 10$ mm; $d = 11–20$ μm.

[d] $L = 10$ mm; $d \approx 15$ μm.

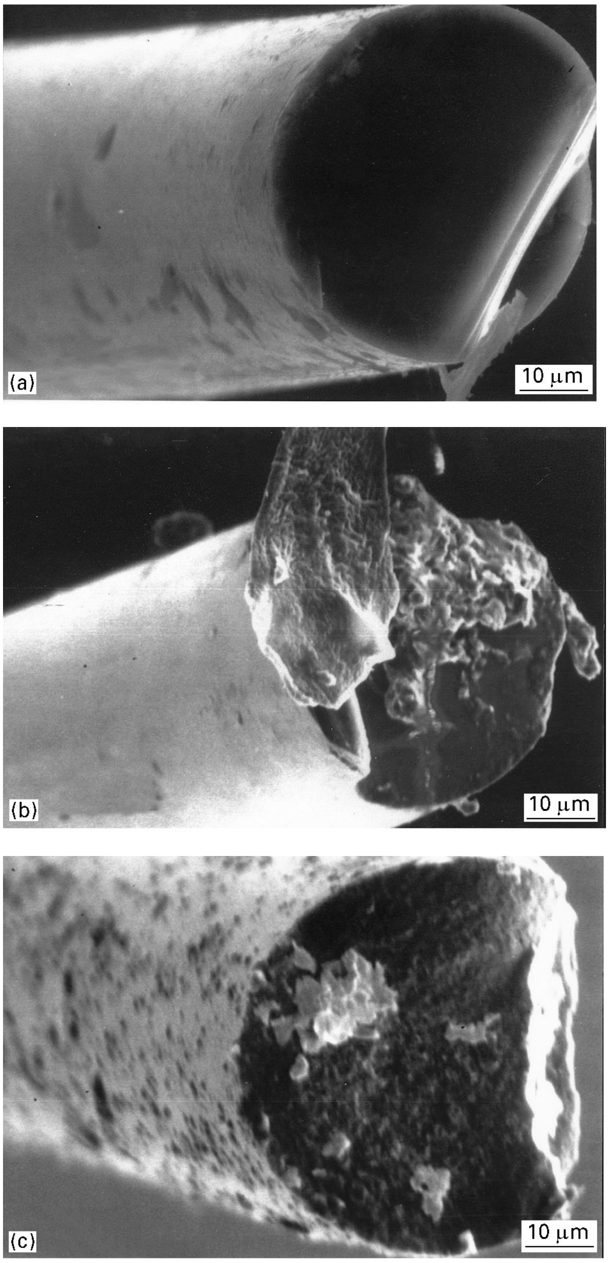


Figure 4 Scanning election micrographs of the failure surface of fibres treated at increasing temperatures: (a) $T_p = 1200\,^\circ\mathrm{C}$; (b) $T_p = 1400\,^\circ\mathrm{C}$, and (c) $T_p = 1600\,^\circ\mathrm{C}$.

present work is close to stoichiometric composition (C/Si atomic ratio ≈ 1.02) but that it contains a noticeable amount of oxygen (≈ 3.9 at %) as pointed out above. As qualitatively ascertained by Raman spectroscopy (Fig. 2), all the fibres prepared under an inert atmosphere from EB-cured Yajima-type precursors (materials 3–5 in Table I) display a free-carbon content ranging from 14–20 mol %. The C/Si atomic ratio in the fibre prepared here (C/Si ≈ 1.02) and the free-carbon content (2.9 mol %) are much lower than those reported for the fibre produced under a hydrogen atmosphere from a Yajima-type PCS (C/Si atomic ratio ≈ 1.14 and 9 mol % free carbon), as shown in Table I (materials 1 and 2).

Low-oxygen content SiC-based fibres have also been prepared by dry-spinning solutions of high molecular weight infusible PCSs containing spinning additives (material 6 in Table I) [12]. The high C/Si atomic ratio (1.79) and high free-carbon content (≈ 29 mol %) could be explained by (i) the nature of the spinning aids, namely vinylpolysilazane and polyisobutylene, and (ii) the fact that the pyrolysis of the green fibre was performed under an inert atmosphere which does not permit a complete release of the methyl pendent groups. More recently the process has been successfully modified to yield a nearly stoichiometric fibre (material 7 in Table I), but the spinning and pyrolysis conditions have not yet been disclosed [25].

Quasi stoichiometric SiC fibres have also been produced via the pyrolysis under argon of polymethylsilane (PMS) in which the C/Si atomic ratio = 1. However, because under such pyrolysis conditions some demethanation occurs that would lead to ceramic fibres with free silicon, spinning aids (containing presumably among others carbon-rich species) were added to increase the C/Si atomic ratio in the spun precursor [15].

Finally, a quasi stoichiometric SiC fibre, referred to as Hi-Nicalon S (an experimental product from Nippon Carbon) has been very recently produced from a Yajima-type PCS by modifying the pyrolysis conditions. However, these conditions have not yet been disclosed [14]. Thus it appears that there are now several potential routes to quasi stoichiometric SiC fibres which differ from one another mainly by the composition of the precursor (and/or the spinning aids) and the pyrolysis conditions (including the nature of the pyrolysis atmosphere). Our work (Parts I and II) gives examples of both approaches.

Table I shows that both our model monofilaments contain noticeable amounts of oxygen (3–4 at %) despite our efforts to limit this pollution. This residual oxygen is detrimental to the high-temperature stability and mechanical properties of Si–C fibres [3]. This contamination is due to the fact our polymer is very sensitive to oxidation, because in addition to the Si–Si linkages, it contains more Si–H bonds than usual, because of the decrease in the carbon content involves the presence of more (easily oxidizable) Si–H bonds. Moreover, the electron-beam irradiation process would involve the formation of organosilicon radicals very sensitive to oxidation [10].

Oxygen contamination could be reduced by an improved optimization of the experimental procedure. After controlling the oxygen content, the approach to SiC fibres proposed here could be of great interest because it allows the preparation of stoichiometric SiC fibres without spinning aids and without pyrolysis under a hydrogen atmosphere.

4.2. Properties of the fibre

Although the presence of residual oxygen may somewhat alter the properties of the monofilaments, some good trends are apparent from the results presented in Section 3, which are in good agreement with the conclusions previously drawn for quasi stoichiometric SiC fibres. First, the fibres still display a fine grain microstructure after 1 h annealing at 1400 °C with an apparent SiC grain size (≈ 1.5 nm) similar to that of the high-strength Nicalon NLM grade known to be no longer stable at such a temperature. Even at 1600 °C, the grain growth remains limited ($\approx$ 7 nm). These results suggest that the small amount of residual free carbon (C/Si atomic ratio ≈ 1.02) may be sufficient to prevent the grain growth of the SiC phase. Unfortunately, the fact that some silicon oxycarbide (which is known to play the same role in the Nicalon fibre) is also present would not allow one to define precisely the minimum percentage of free carbon (if there is any) which is necessary to prevent the SiC grain growth. As expected, the Young's modulus of the fibre (320 GPa), is significantly higher than that ($\approx$ 250 GPa) of low oxygen content fibres (e.g. materials 3–5 in Table I) prepared from Yajima-type PCSs and which contain 14–20 mol % free-carbon [3]. However, it is also much lower than the Young's moduli which have been recently reported for other quasi stoichiometric SiC fibres [13, 14]. This difference may have two origins: (i) the fibre prepared in the present work still contains minor phases (free carbon and silicon oxycarbide) of low stiffness; (ii) it may also display some residual nanoporosity because it has not been treated by very high temperatures and it does not contain sintering aids (e.g. boron compounds).

Finally, our experimental monofilament does not display an extremely high tensile strength ($\sigma_R = 1850$ MPa for $T_p = 1200$ °C) and additionally, it undergoes a maximum for a relatively low T_p value ($T_p \approx 1200$ °C). The low maximum value of σ_R results from the relatively large diameter of the samples (22 μm) and no attempt has been made to optimize the processing. The decrease in tensile strength observed when T_p is raised beyond 1200 °C is probably related to the decomposition/reduction of the residual silicon oxycarbide phase (and hence to oxygen contamination) resulting in the formation of new flaws in the bulk and at the fibre surface (Fig. 4c).

5. Conclusions

1. A copolymer approach based on the use of 2,4-dichloro-2,4-disilapentane and methylphenyldichlorosilane monomers is a convenient route to SiC-based materials, because this method allows a good control of the chemical composition of the precursor, and the ceramic.

2. By selecting the relative amounts of the two monomers, namely 0.6 mol methylphenyldichlorosilane for 0.4 mol 2,4-dichloro-2,4-disilapentane, a new precursor has been produced whose pyrolysis, at 1200–1400 °C under an atmosphere of argon, after an electron-beam irradiation step, yields a quasi stoichiometric SiC-fibre (C/Si atomic ratio ≈ 1.02) with very little free-carbon despite the presence of residual oxygen.

3. The fibre remains nanocrystalline up to $T_p \approx 1400$ °C (SiC grain size 1.5 nm). It displays at room temperature a Young's modulus of 320 GPa and a tensile strength of 1.6–1.8 GPa.

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