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

Part I: *From the pyrolysis of a polycarbosilane precursor under an atmosphere of hydrogen*

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Pyrolysis of a Yajima-type polycarbosilane (PCS) has been performed under an atmosphere of hydrogen on both bulk samples and model monofilaments up to 1000 °C, in order to reduce the free carbon content of the resulting ceramics. The organic/inorganic transition occurs within the 400–800 °C temperature range, with mainly an evolution of CH_4. At 1000 °C, it yields an hydrogenated amorphous ceramic with a C/Si atomic ratio and a free carbon content significantly lower than for its counterpart obtained under inert atmosphere (namely, 1.18 and 9 at% versus 1.72 and 27 at%). Hydrogen is thought to favour the release of the pendent methyl groups of the PCS via demethanation radical reactions. Continuous model filaments were produced via the melt spinning of the PCS, electron beam curing, pyrolysis under hydrogen up to 1000 °C, and a final heat treatment under argon up to 1600 °C. The ceramic fibres exhibit a C/Si atomic ratio of 1.10, a free carbon content of ≈ 8 at%, a Young's modulus of 260–300 GPa and a tensile failure stress of 2100 MPa. Their thermal stability is limited to 1400 °C due to some oxygen contamination during the process.

1. Introduction

The only weavable SiC-based fibres which have been used up to now as reinforcement in ceramic matrix composites (CMCs), i.e. the Si–C–O (Nicalon, from Nippon Carbon, Japan) and Si–C–Ti–O (Tyranno, from Ube Industries, Japan) fibres, are produced from polycarbosilane (PCS) or polytitanocarbosilane (PTCS) precursors, according to the Yajima method. In this method, the precursors are prepared from polydimethylsilane (PDMS) by insertion of CH_2-groups in the PDMS backbone via the Kumada rearrangement, which is performed thermally with or without a catalyst [1–8]. As an example, the most commonly used PCS is prepared by heating PDMS in an autoclave at a temperature of ≈ 470 °C without catalyst. It is a branched polymer with an empirical formula close to $SiC_{1.77}O_{0.03}H_{3.70}$ [1, 5–8]. In the Yajima route, PCSs are melt-spun, the green fibre being then cured by oxidation in air and pyrolysed under inert atmosphere at about 1200 °C. Its final composition corresponds to the empirical formula $SiC_{1.55}H_{0.027}O_{0.326}$, showing that the fibre contains significant amounts of oxygen and free carbon [5]. It consists of a dispersion of SiC-nanocrystals and sp^2 carbon clusters in an amorphous matrix of silicon oxycarbide [10–12]. Such a complex microstructure is metastable at high temperatures. Beyond about 1100 °C, the amorphous silicon oxycarbide phase decomposes with an evolution of CO (and SiO), a coarsening of the SiC nanocrystals and a decrease in the failure strength of the fibre [9, 12].

Several attempts have been made recently to reduce (or even suppress) the occurrence of oxygen and free carbon in SiC-based fibres in order to increase their microstructural stability at high temperatures. Radiation curing of Yajima-type PCSs under anaerobic conditions [13, 15] or dry spinning of soluble but infusible PCSs of high molecular weights [16] have led to oxygen-free fibres, which still contain significant amounts of free carbon. More recently, quasi-stoichiometric SiC fibres free of oxygen have been produced from Yajima-type PCSs [17] or novel precursors [18–20], but very few details have been given on their processing.

The aim of the present study, whose results are presented as two companion articles, was to explore two routes which seemed promising for the production of SiC-based fibres with low oxygen and free carbon contents. This paper concerns the pyrolysis of a radiation cured fibre (from Yajima-type PCS

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precursor) in an atmosphere of hydrogen supposed to favour the abstraction of the methyl pendent groups. The second paper [21], is based on the use of a novel copolymer precursor [22] whose composition has been tailored to yield ceramics with a C/Si ratio close to 1 upon pyrolysis.

2. Experimental procedure

2.1. Materials

Bulk ceramic samples and continuous monofilaments were prepared from a commercial PCS (from Nippon Carbon, Japan). This precursor was elaborated according to the Yajima route, i.e. by thermal rearrangement of a PDMS polymer in an autoclave [1, 5, 8]. According to Okamura [5], such PCSs display an oxygen content of about 1 wt % and correspond to an empirical formula close to $SiC_{1.77}H_{3.70}O_{0.035}$ (Table I), which differs significantly from that of polysilapropylene (PSP), $\mathrm{-\!\!\!\![(MeSiH)\text{–}CH_2]\!\!\!\!-}_n$, the ideal chain polymer resulting from the simple insertion of methylene groups in the Si–Si backbone of PDMS, namely SiC_2H_6. This difference has been assigned to the branched character of Yajima-type PCSs [5–7]. The PCS which has been used here was a yellowish solid at room temperature, with a number-average molecular weight, $\bar{M}_n \approx 1530$, a polydispersity index, $I_p = 2.7$ and a softening point $T_s \approx 300\,^\circ C$. The molecular weight distribution of the as-received PCS has been slightly adjusted, in order to remove the low and high molecular weight species ($\bar{M}_n \approx 1160$, $I_p = 1.3$) and thus to improve its spinnability in the molten state [23]. A continuous filament was melt spun at $\approx 280\,^\circ C$ in a dry glove box filled with nitrogen. Spinning was performed with a laboratory scale extrusion apparatus equipped with a single hole spinneret (diameter of the extrusion hole: 300 μm), by applying a pressure of about 6 MPa of nitrogen on the molten PCS. The monofilament was drawn down to a diameter of ≈ 20 μm, the mechanical stretching being applied to the filament via the take-up reel.

The filament was then cured by electron beam irradiation under anaerobic conditions according to a technique which has been reported elsewhere [23]. The skein of fibre was first removed from the take-up reel and cut into lengths of 200 mm. These bundles were set in metal containers which were sealed in the glove box. The containers were irradiated (experiments carried out at CARIC, Orsay) at room temperature (water cooling), the overall dose being of the order of 1000 Mrad. After irradiation, the containers were reopened in the glove box. Each bundle was set in an alumina boat, and from there transferred to a pyrolysis furnace equipped with a silica glass tube directly fitted to the glove-box in order to minimize contamination by oxygen and moisture.

A prepyrolysis to 1000 °C was performed under flowing N55 hydrogen or, for purpose of comparison, under flowing N56 argon or N55 helium at atmospheric pressure, with a heating rate of $1\,^\circ C\,min^{-1}$ and an isothermal plateau of 1 h at 1000 °C. After such a treatment, the filament was no longer sensitive to oxygen or moisture and could be handled in the open air. Additional heat treatments were applied to some samples (set in a graphite crucible) up to 1600 °C under flowing argon at atmospheric pressure [24]. The samples were heated at a rate of $30\,^\circ C\,min^{-1}$ up to a temperature T_p ($1000 < T_p < 1600\,^\circ C$), held at T_p for 1 h and cooled to room temperature.

TABLE I Chemical compositions and fomulas of PSP, Yajima-type PCS and related fibres [5]

Material	Chemical composition (wt %)				Formula
	Si	C	H	O	
PSP	48.29	41.31	10.40	–	SiC_2H6
PC-A-470(1)	48.2	39.9	6.85	0.81	$SiC_{1.77}H_{3.70}O_{0.035}$
Fibre[a]	44.4	31.0	5.30	5.11	$SiC_{1.63}H_{3.34}O_{0.201}$
Si–C–O[b]	51.3	34.1	0.05	9.55	$SiC_{1.55}H_{0.027}O_{0.326}$

[a] cured in air from PC-A-470 (1).
[b] Fibre (1) pyrolysed at $\approx 1200\,^\circ C$ in inert atmosphere.

2.2. Characterization

Chemical analysis was performed by electron probe microanalysis (EPMA, Camebax, from Cameca, Paris) for silicon (SiK_α), carbon (CK_α), and oxygen (OK_α) on polished cross-sections of fragments of bulk ceramics or filaments embedded in an epoxy resin. Although hydrogen was assumed to be present in small amounts (see Table I) in the materials treated at low T_p (typically 1000 °C), it could not be analysed by EPMA and was neglected. EPMA characterization was performed with a pentaerythritol (PET) monochromator for Si and with a W/Si multilayer for C and O. Conventional procedures and SiC and SiO_2 standards were used to derive the elemental concentrations from the SiK_α, CK_α and OK_α line intensities.

The gas evolution during the prepyrolysis (the organometallic/ceramic conversion) was qualitatively studied by mass-spectrometry with a single focalization spectrometer (VG Micromass 16F) equipped with a data treatment system.

The pyrolytic residues, i.e. fragments of bulk ceramics or fragments of filaments, were reduced in a fine powder and characterized by X-ray diffraction (D 5000 from Siemens) (CuK_α wavelength, $\lambda = 0.154$ nm). The average apparent size of the β-SiC crystals, $L_{1\,1\,1}$, was calculated from the Scherrer formula

$$L_{1\,1\,1} = K\lambda/(D\cos\theta) \qquad (1)$$

where K is a correction factor equal to 0.9, λ the X-ray wavelength ($\lambda = 0.154$ nm), D the width at midheight of the 1 1 1 reflexion of β-SiC, and θ the Bragg angle (θ: 17.8° for β-SiC 1 1 1).

The Raman spectra of the pyrolytic residues were recorded with a spectrometer (OMARS 89 from Dilor) coupled to an ionized argon laser (from Spectra Physics) (source power: 150 mW; wavelength $\lambda = 514.5$ nm; slit width: $3\,cm^{-1}$).

The tensile strength of the monofilaments were tested at room temperature with an apparatus and a procedure which have been previously described [25].

For each value of T_p, about 20 single fibre specimens were tested at a gauge length $L = 10$ mm. The failure stress was calculated from the load at failure and from the actual diameter, previously measured on each specimen by laser interferometry. Finally, the Young's modulus of the fibre was calculated from the slope of the stress–strain curve at the origin, taking into account the machine compliance and assuming a linear relationship up to the failure [25]. The failure surfaces of the filaments were observed by scanning electron microscopy (840 A SEM from Jeol, Japan) when possible.

3. Results

3.1. Bulk ceramics

Samples (typically ≈ 500 mg) of the as-received PCS were set in an alumina boat, prepyrolyzed up to 1000 °C (ramp: 1 °C min^{-1}), held at this temperature for 1 h, and cooled to room temperature. The experiments were performed under inert gas or hydrogen, the overall weight loss being 60 and 52%, respectively. Some of the samples were further heat-treated up to 1600 °C, as mentioned in the previous section. The chemical composition of the pyrolytic residues at $T_p = 1000$ °C, neglecting hydrogen, is shown in Table II. The data show that both pyrolytic residues are C-rich, with respect to stoichiometric SiC. However, the pyrolytic residue obtained upon pyrolysis under hydrogen contains much less carbon than that resulting from the pyrolysis under argon. Furthermore, the oxygen content, namely 2 at %, is relatively low and similar for both materials. Assuming that oxygen is present as SiO_2 and that the remaining silicon is present as stoichiometric silicon carbide, the amount of free carbon can be calculated. The results of the calculations clearly show that replacing argon by hydrogen, all the other pyrolysis parameters being constant, reduces significantly the percentage of free carbon in the pyrolytic residues, i.e. from 27 to 9 at %.

TABLE II Chemical composition of the pyrolytic residues of PCS. (The last column gives the amount of free carbon calculated from EPMA data, assuming that oxygen is present as SiO_2 and SiC is stoichiometric)

Pyrolysis atmosphere	Si (at %)	C (at %)	O (at %)	Free Carbon (at %)
Hydrogen	45	53	2	9
Argon	36	62	2	27

The gaseous species formed during the PCS pyrolysis were characterized by mass spectrometry. Under inert atmospheres (argon or helium), the main gaseous species are hydrogen and methane (Figs 1 and 2). Hydrocarbons with higher molecular weights, namely ethane, ethylene and acetylene, are also formed in minor amounts, as shown by pyrolysis experiments performed under helium (to avoid overlap between the mass of argon and those of the hydrocarbons). The gas evolution occurs between 500 and 800 °C, as previously reported [3, 5, 8], with a maximum at about 650 °C. When the pyrolysis is performed under hydrogen, the only gaseous species which is observed by mass spectroscopy is methane (hydrogen may also be formed but its formation could not be ascertained since it is the carrier gas). Furthermore, the evolution curve of methane is shifted towards lower temperatures by about 100 °C, i.e. the evolution of CH_4 begins at about 400 °C (rather than 500 °C under argon) and its maximum occurs at ≈ 600 °C (Fig. 2). All these results clearly demonstrate that the release of CH_4 from the PCS preceramic polymer is easier when the pyrolysis is performed under hydrogen.

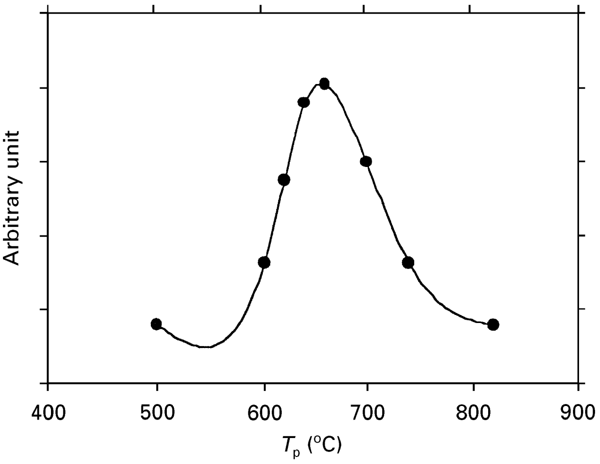


Figure 1 Evolution of hydrogen during the pyrolysis of PCS under an atmosphere of argon, as assessed by mass spectroscopy analysis.

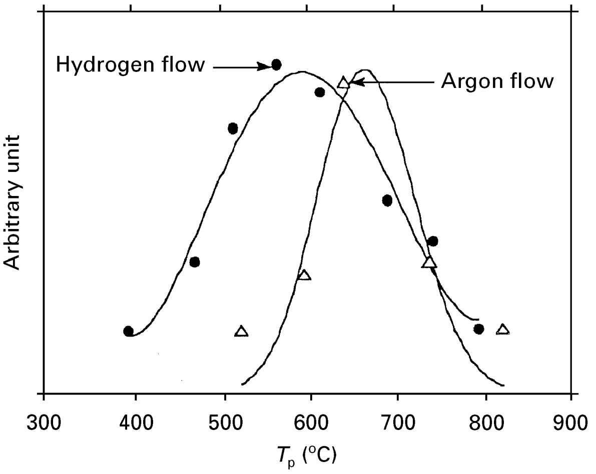


Figure 2 Evolution of methane during the pyrolysis of PCS under argon or hydrogen atmospheres, as assessed by mass spectroscopy analysis.

The residue resulting from the pyrolysis under an atmosphere of hydrogen remains amorphous up to about 1000 °C (Fig. 3). As it could be expected from the pyrolysis conditions, it still contains significant amounts of hydrogen, mainly bonded to aliphatic or aromatic carbons, as clearly shown by its i.r.-spectrum (Fig. 4 and Table III). Conversely, such bonds are virtually absent from the pyrolytic residue obtained upon pyrolysis under argon. Crystallization becomes apparent at ≈ 1200 °C with the formation of nano sized β-SiC crystals. When T_p is further increased,

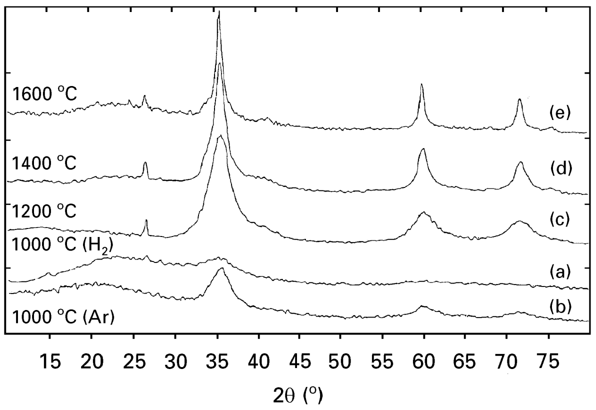


Figure 3 XRD patterns of ceramics residues resulting from the pyrolysis of PCS under hydrogen (a) and argon (b) at 1000 °C and from annealing treatments under argon at 1200–1600 °C ((c) to (e)).

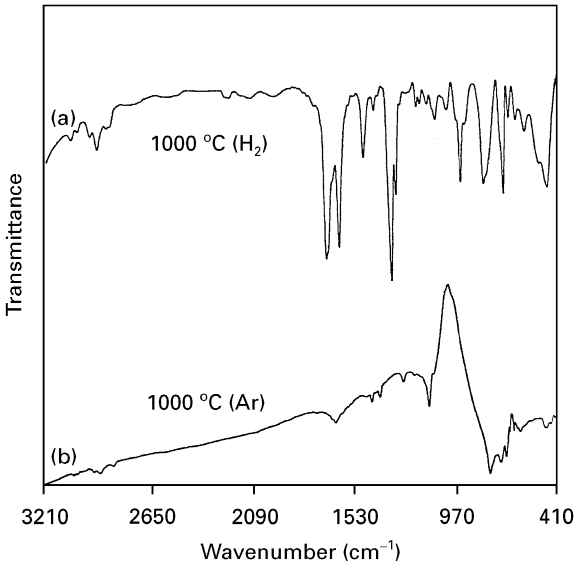


Figure 4 Infrared spectra of ceramic residues resulting from the pyrolysis of bulk PCS under hydrogen (a) and argon (b) at 1000 °C.

TABLE III Main absorption bands observed in the i.r. spectrum of the pyrolytic residue of bulk PCS samples at $T_p = 1000$ °C and under an atmosphere of hydrogen

Wave number (cm^{-1})	I	Assignment	Wave number (cm^{-1})	I	Assignment
3200–3000	w	ν^aC-Har^b	1080	w	νSi–O
3000–2800	m	νC-Hal^c	1004	w	δCCCar
1600	s	νC$=$C$_{ar}$	940	m	γ^dC-Har
1450	m	δ^eC-Har	815	m	νSi–C (β-SiC)
1350	s	δC-Har	707	m	τ^fCC$_{ar}$
1290	m	νC = Car	674	m	γC-Har
1176	w	δC-Har	630	m	δCCC$_{ar}$
1153	w	δC-Har	580	m	δCCC$_{ar}$
			460	m	δSi–O + τCCar

I, intensity; s, strong; m, medium; w, weak.
[a] stretching.
[b] aromatic.
[c] aliphatic.
[d] out of plane bending.
[e] in plane bending.
[f] torsion.

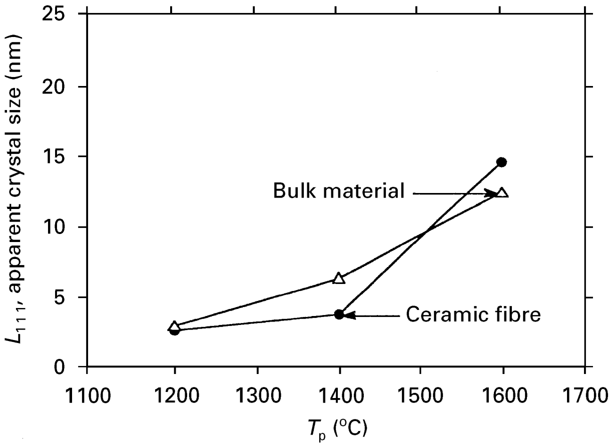


Figure 5 Variations of the apparent crystal size (as assessed by XRD) of SiC as-function of the pyrolysis temperature, in ex-PCS ceramics treated under an atmosphere of hydrogen.

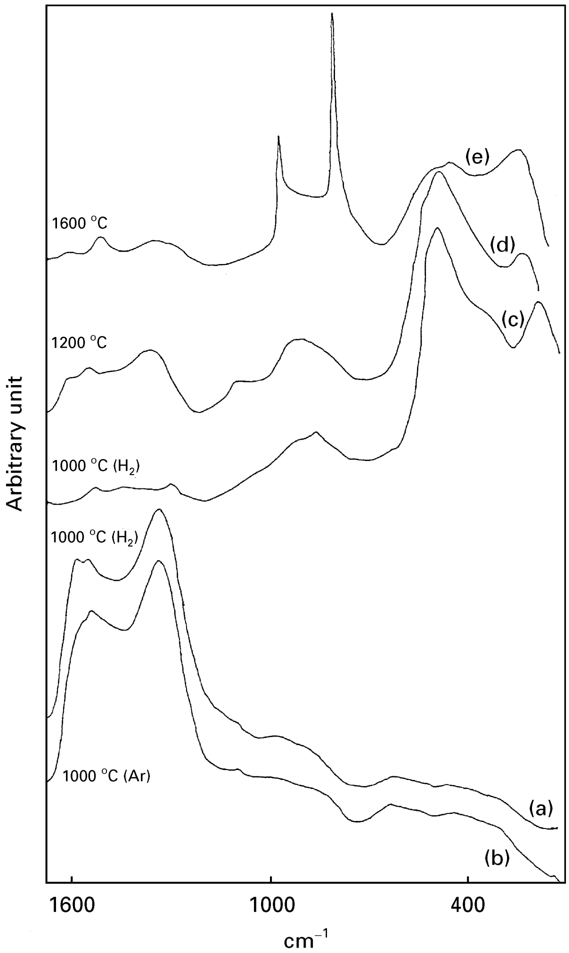


Figure 6 Raman spectra of ceramic residues resulting from the pyrolysis of bulk PCS under hydrogen (a) and argon (b) at 1000 °C, and from the pyrolysis of monofilaments under hydrogen at 1000 °C, (c) and under argon at 1200 °C (d) and 1600 °C (e).

growth of the SiC crystals takes place, the apparent grain size increasing from 3 nm for $T_p = 1200$ °C to 12.5 nm for $T_p = 1600$ °C (Fig. 5). Raman spectra clearly demonstrate the occurrence of free carbon (Fig. 6, absorption bands at 1330 and 1560 cm^{-1}), corroborating the EPMA data (Table II).

3.2. Model monofilaments

The chemical composition of the monofilaments prepyrolyzed under hydrogen and heat-treated at increasing T_p-values, is shown in Table IV. As already

TABLE IV Chemical composition of ex-PCS fibres pyrolysed under hydrogen at various temperatures. (The last column gives the amount of free carbon calculated from EPMA data assuming that oxygen is present as SiO_2 and SiC is stoichiometric)

Temperature of pyrolysis (°C)	Si (at %)	C (at %)	O (at %)	Free carbon (at %)
1000	45.0	50.7	4.3	8
1200	45.7	50.2	4.1	7
1400	44.6	51.0	4.4	9
1600	46.7	52.5	0.8	6

TABLE V Mechanical properties at room temperature of ex-PCS monofilaments pyrolysed under hydrogen at various temperatures

T_p(°C)	d(μm)	E(GPa)	σ^R(MPa)
1000	20	225	1360
1200	20	260	1730
1200	11.4	260	2100
1400	20	300	1450
1400	11.4	290	1750
1600	20	110	370

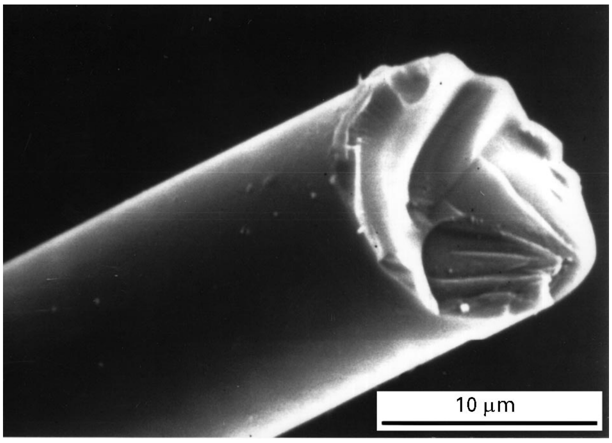


Figure 7 Failure surface and surface morphology of an ex-PCS monofilament prepyrolysed under hydrogen up to 1000 °C and further heat treated at 1400 °C.

observed for the bulk specimens, the monofilaments are C- rich, the amount of excess carbon being similar (≈ 8 at %). But they contain more residual oxygen (4 at % instead of 2 at %), at least up to $T_p = 1400$ °C, and despite the care taken in the experimental procedure to minimize contamination (particularly during the E-beam irradiation and pyrolysis steps).

The monofilaments remain amorphous up to $T_p \approx 1000$ °C. Crystallization becomes apparent from the XRD-spectra beyond 1200 °C, with an apparent SiC crystal size increasing from 2.7 nm at $T_p = 1200$ °C to 14.9 nm at $T_p = 1600$ °C. Crystal growth is slower in the monofilaments than in the bulk specimens up to 1400 °C, the L_{111} values at this temperature being 3.9 and 6 nm, respectively (Fig. 5). Beyond $T_p = 1400$ °C, the SiC crystals grow more rapidly.

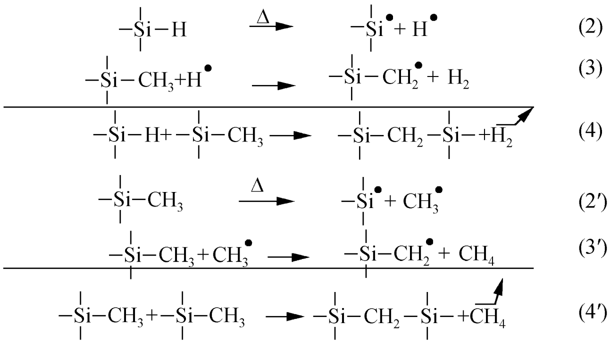
The tensile failure stress and Young's modulus were measured at room temperature on two monofilament gauges of different diameters, namely 11.4 and 20 μm, after pyrolysis under hydrogen up to 1000 °C and heat treatment at various temperatures up to 1600 °C. The data listed in Table V suggests the following remarks. First, the Young's modulus regularly increases as T_p is raised to 1400 °C, with a value at this temperature (300 GPa) which is about 50% higher than that of Si–C–O Nicalon fibres (typically 200 GPa), but still lower than the Young's modulus of stoichiometric SiC fibres (≈ 400 GPa). Second, the tensile failure stress undergoes a maximum for $T_p \approx 1200$ °C, which is observed to increase when the filament diameter decreases, as expected for ceramic fibres. Finally, both the Young's modulus and the tensile failure stress dramatically decrease for $T_p > 1400$ °C, i.e. when the crystal size is large enough and surface defects are formed (Fig. 7).

4. Discussion

4.1. Influence of the atmosphere in PCS pyrolysis

The results which have been presented in Section 3 demonstrate the strong influence of the atmosphere on the pyrolysis mechanism of a Yajima-type PCS and thus on the chemical composition of the pyrolytic residue. In the Yajima route, the pyrolysis of branched PCSs has always been reported to be performed under inert atmosphere [1–5].

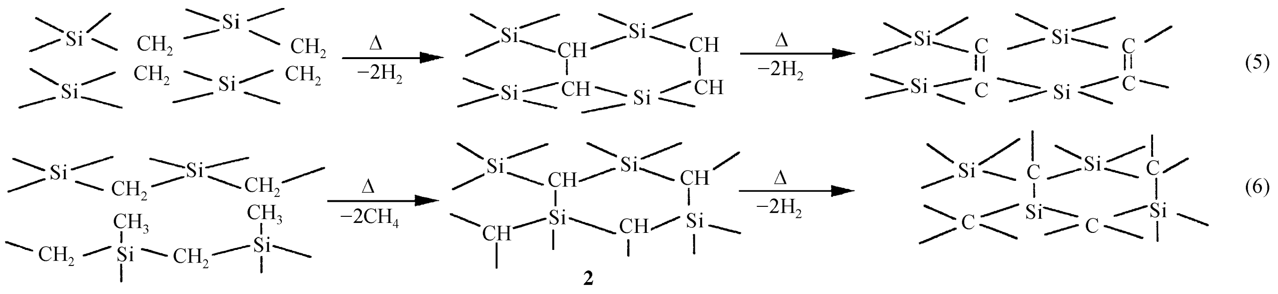
On the basis of i.r.-spectroscopy and gas evolution analysis data, Hasegawa and Okamura [3] have suggested that the organometallic/inorganic transition which takes place under inert atmosphere within the temperature range 550–800 °C, also reported by Bouillon *et al.* [24] or Chollon *et al.* [23] and observed in the present work, may occur according to radical reactions (scheme **1**). Their mechanism first assumes thermal cleavage of the relatively weak Si–H and Si–CH_3 bonds, in the low portion of the 550–800 °C temperature range (Equations 2 and 2′). Then, the free radicals which have been formed react with C–H bonds and with each other to form Si–CH_2–Si groups, with an evolution of hydrogen and methane (Equations 3, 4, 3′ and 4′). As temperature is raised, i.e. in the high portion of the



$$-\text{Si}-\text{H} \xrightarrow{\Delta} -\text{Si}^{\bullet} + \text{H}^{\bullet} \qquad (2)$$
$$-\text{Si}-\text{CH}_3 + \text{H}^{\bullet} \longrightarrow -\text{Si}-\text{CH}_2^{\bullet} + \text{H}_2 \qquad (3)$$
$$-\text{Si}-\text{H} + -\text{Si}-\text{CH}_3 \longrightarrow -\text{Si}-\text{CH}_2-\text{Si}- + \text{H}_2\uparrow \qquad (4)$$
$$-\text{Si}-\text{CH}_3 \xrightarrow{\Delta} -\text{Si}^{\bullet} + \text{CH}_3^{\bullet} \qquad (2')$$
$$-\text{Si}-\text{CH}_3 + \text{CH}_3^{\bullet} \longrightarrow -\text{Si}-\text{CH}_2^{\bullet} + \text{CH}_4 \qquad (3')$$
$$-\text{Si}-\text{CH}_3 + -\text{Si}-\text{CH}_3 \longrightarrow -\text{Si}-\text{CH}_2-\text{Si}- + \text{CH}_4\uparrow \qquad (4')$$

1

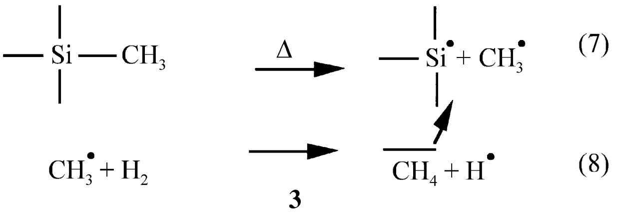
Scheme **1** Formation of Si–CH_2–Si bonds with an evolution of both H_2, and CH_4, via a radical mechanism, during the organometallic/inorganic transition in PCS, according to Hasegawa and Okamura [3].



Scheme **2** Formation of a three-dimensional Si–C network that may also contain C–C bonds via a combination of demethanation and dehydrogenation reactions involving the CH_2 groups of the PCS backbone, during the organometallic/inorganic transition in PCS, according to Hasegawa and Okamura [3].

550–800 °C temperature range, a three-dimensional network with some C = C bonds is built through new demethanation and dehydrogenation reactions involving now the methylene groups of the $Si–CH_2–Si$ PCS backbone (scheme **2**). The occurrence of C = C bonds in the amorphous pyrolytic residue (i.e. at $800 < T_p < 1000$ °C) might be responsible for the formation of free carbon as basic structural units (BSUs) when crystallization starts at higher temperatures [3, 10, 26]. When the pyrolysis of PCS is performed under an inert atmosphere, the demethanation, i.e. the formation of CH_4 from pendent methyl groups, is only partial resulting in pyrolytic residues of PCSs which always contain an excess of carbon, with respect to the SiC stoichiometry. When T_p is high enough, this carbon excess, (≈ 30 at % in the present work for $T_p = 1000$ °C), is present as clusters of free carbon [10].

Conversely, when the pyrolysis of PCS is performed under an atmosphere of hydrogen, demethanation reactions are favoured whereas dehydrogenation reactions are unfavoured, within a temperature range which is now slightly shifted towards the low temperatures, i.e. 400–800 °C (Fig. 2). Furthermore, as suggested by the i.r. spectrum (Fig. 4 and Table III), the amorphous pyrolytic residue remains much more hydrogenated. Although the pyrolytic mechanism of Yajima-type PCSs in hydrogen is still unknown, demethanation could occurr according to the radical mechanism depicted in scheme **3**.



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As temperature is raised, the formation of the three-dimensional SiC network through reactions involving the methylene groups of $Si–CH_2–Si$ bonds, might occur preferably Equation 6 rather than according to Equation 5. As a result, the amorphous pyrolytic residue at $T_p = 1000$ °C is thought to contain less C = C bonds (since demethanation in hydrogen is more effective) but more C–H or/and Si–H groups, yielding at still higher temperatures a ceramic residue with less free carbon.

Under the conditions used in the present work, the pyrolytic residue still contains some free carbon, as demonstrated by EPMA and Raman spectroscopy data, typically 8–9 at % (instead of 27 at % for pyrolysis performed in argon), which corresponds to a C/Si atomic ratio of ≈1.15 (Tables II and IV). The question which now arises is: could this free carbon content be further reduced and how? Theoretically, the total demethanation of Yajima-type PCSs, i.e. the total abstraction of the pendent methyl groups, should yield stoichiometric silicon carbide (since the C/Si atomic ratio in the PCS backbone is 1, assuming a total Kumada rearrangement). This could be possibly achieved via prolonged pyrolysis under hydrogen within a temperature range (tentatively, 400–600 °C) where demethanation involves mechanisms as shown in scheme **3**. The use of activated hydrogen could also be envisaged. Finally, it is worthy of note that pyrolysis under NH_3 and even under hydrogen has been used to prepare Si_3N_4 or Si–C–N ceramics without free carbon, from preceramic polymers [7, 27].

4.2. Oxygen contamination

If one assumes that the Yajima-type PCS used in the present work had an initial oxygen content of 0.81 wt % (Table I) and that oxygen remains entrapped in the material for $T_p = 1000$ °C, the oxygen percentage in the pyrolytic residue should be 1.76 wt % for an overall weight loss of 52% (Section 3.1). This value is close to that actually measured by EPMA, i.e. 2 at % or 1.79 wt % (Table II). Under such assumptions, it thus appears that almost no additional oxygen contamination has occurred during the pyrolysis of bulk PCS samples.

Conversely, the EPMA data listed in Table IV show that the oxygen content of the monofilaments produced from the same starting material is more than twice that of the bulk ceramics for $T_p \leqslant 1400$ °C. This additional oxygen contamination may have two origins. First, the monofilaments display a higher specific surface area and should be more sensitive to oxidation. Second, after electron beam irradiation, free radicals remain entrapped in the fibres, as demonstrated by Okamura *et al.* [13]. These free radicals were reported to be stable at room temperature, but very sensitive towards oxygen and moisture. They can be eliminated by annealing before pyrolysis. However, such a treatment was not applied in the present work.

Finally, the majority of the entrapped oxygen is eliminated when $T_p > 1400\,^\circ C$, the residual oxygen content for $T_p = 1600\,^\circ C$ being only 0.8 at % or 0.65 wt % (Table IV). This decrease in the residual oxygen content for $T_p > 1400\,^\circ C$, also reported for oxygen-cured PCS, is thought to be related to the almost complete decomposition of the ternary silicon oxycarbide phase SiC_xO_y (in which oxygen is entrapped) with an evolution of CO and SiO [9, 24]. Okamura *et al.* have previously reported residual oxygen content less than 0.5 wt % for fibres prepared from the same kind of PCS precursor, but at $T_p = 1200\,^\circ C$ only [13]. However, such fibres have been submitted to an annealing treatment at 800 °C under vacuum, before the temperature was further raised to 1200 °C under argon. These results emphasize once again the influence of the pyrolysis atmosphere on the ceramic residue composition, in terms of free carbon content and oxygen contamination.

4.3. Structure and microstructure

The residue resulting from the pyrolysis under hydrogen of Yajima-type PCS at $T_p = 1000\,^\circ C$ is amorphous (Fig. 3). Furthermore, it contains a significant amount of hydrogen, as ascertained by the i.r. spectrum (Table III and Fig. 4). Thus, it should be regarded as an amorphous hydrogenated Si–C three-dimensional network with some excess carbon. Soraru *et al.* have proposed a structural model (see Fig. 6 in ref. [26]) to depict the amorphous residue of the pyrolysis of a Yajima-type PCS at 840 °C under an inert atmosphere. Such a model could still be valid here, provided more hydrogen is introduced in the structure (e.g. as C–H bonds). The number of C–C or C=C bonds should be less (since the excess carbon is lower) and the network should be more open.

The crystallization of the amorphous residue resulting from the pyrolysis of the PCS under hydrogen becomes apparent at about 1200 °C (Fig. 3), whereas it has been reported to start at ≈ 1000 °C when pyrolysis is performed under argon (see Fig. 9 in ref. [26]). This delay is probably related to its hydrogenated character, the occurrence of numerous C–H bonds impeding the development of the three-dimensional network of Si–C sp^3 bonds which characterizes the β-SiC structure. The crystallization rate remains relatively slow, the mean SiC grain size being still less than 15 nm after a heat treatment at 1600 °C for 1 h (Fig. 5). Finally, the pyrolytic residue of PCS also contains free carbon, as ascertained by the Raman spectrum (Fig. 6), which is poorly organized and probably present in its turbostratic form.

The monofilaments consist of a mixture of three phases for a high enough T_p value, i.e. $1200 < T_p < 1400\,^\circ C$, on the basis of EPMA, Raman and XRD data: (i) β-SiC nanocrystals (the main phase); (ii) a small amount of poorly organized free carbon, as already mentioned; and (iii) a still noticeable amount of the amorphous ternary SiC_xO_y phase related to oxygen contamination, as discussed in Section 4.2. Below 1400 °C, the growth rate of the SiC crystals is lower than in the bulk specimens (see Fig. 5), presumably due to the higher amount of SiC_xO_y (which is known to impede the growth of the SiC phase, as long at it is thermally stable). Conversely, beyond 1400 °C, the SiC_xO_y phase decomposes with an evolution of various gaseous species (e.g. CO and SiO) with the result that the SiC growth rate is accelerated. However, even at $T_p = 1600\,^\circ C$ and for $t = 1$ h, the SiC grain size remains limited, owing to the impeding effect of free carbon, known to be located around the SiC-crystals [23].

4.4. Mechanical properties

Although preliminary, the results of the mechanical tests performed on the monofilaments studied in the present work (Table V) can be used to compare their mechanical behaviour with that of their counterparts prepared under argon, which have been recently reported by Chollon *et al.* [23]. As expected, the main difference lies in the value of the Young's modulus. The monofilaments pyrolysed in hydrogen up to 1000 °C and further heat-treated in argon at 1400 °C (free carbon: ≈ 9 at %) display a Young modulus of 300 GPa, whereas those pyrolysed and heat-treated in argon (free carbon: ≈ 19.5 at %) exhibit a Young's modulus of only 260 GPa for the same T_p value $= 1400\,^\circ C$ [23]. This difference is explained by the fact that poorly organized carbon has a very low stiffness (typically, $E \approx 50$ GPa). Its occurrence in SiC-based fibres significantly lowers their stiffness. This effect also explains that the Young's modulus of the monofilaments prepared in the present work is still noticeably lower than that of quasi-stoichiometric fibres prepared at 1300 °C from the same kind of precursor, i.e. ≈ 400 GPa, as recently reported by Takeda *et al.* [17].

The tensile failure stress of ceramic fibres is controlled by their population of flaws, thus by their processing conditions. As shown in Table V, its variation as a function of T_p undergoes a maximum for $T_p \approx 1200\,^\circ C$, as already reported for Si–C–O fibres prepared according to the Yajima route [2, 5, 8, 23]. Such a behaviour is obviously related to the occurrence of the metastable SiC_xO_y phase in the monofilaments and thus to the oxygen contamination. When SiC_xO_y decomposes with an evolution of gaseous species (CO and SiO), pores and surface defects are formed which act as flaws (Fig. 7), explaining the dramatic decrease in both the Young's modulus and the tensile failure stress for $T_p > 1400\,^\circ C$. It is noteworthy that under such conditions, oxygen cured Si–C–O fibres are so weak that they cannot be tested.

5. Conclusions

From the results of experiments performed on Yajima-type PCS preceramic precursors presented and discussed in Sections 3 and 4, the following conclusions can be drawn:

1. The use of an atmosphere of hydrogen instead of an inert gas during the pyrolysis of PCS is a simple, efficient way to reduce the free carbon content of the resulting ceramics. With a ramp of $1\,^\circ C\,min^{-1}$ and

a plateau of 1 h at $T_p = 1000\,^\circ\mathrm{C}$, the ceramics display a C/Si at. ratio of 1.18 and a free carbon content of 9 at % when pyrolysed under hydrogen (versus 1.72 and 27 at % under argon). Still lower values could be achieved by decreasing the ramp or introducing plateaus within the temperature range 400–700 °C.

2. The mechanism responsible for the decrease of the free carbon content is the release of the pendent methyl groups which is favoured in an atmosphere of hydrogen and may occur via radical reaction in the temperature range 400–700 °C.

3. The pyrolytic residue at $T_p = 1000\,^\circ\mathrm{C}$ is an amorphous Si–C solid much more hydrogenated than its counterpart obtained under inert atmosphere. Hydrogen is released by further heat treatment.

4. Continuous model monofilaments, with C/Si at = 1.10 and 7 at % free carbon, have been prepared according to melt spinning, electron beam irradiation, and pyrolysis under hydrogen. They exhibit a Young's modulus of 260–300 GPa and a tensile failure stress up to 2100 MPa. Their thermal stability is limited to 1400 °C owing to some oxygen contamination during processing.

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