JOURNAL OF MATERIALS SCIENCE 28 (1993) 2632–2638

Si–C–N ceramics with a high microstructural stability elaborated from the pyrolysis of new polycarbosilazane precursors

Part II *Effect of oxygen–curing on properties of ex-PCSZ monofilaments*

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Si–C–N–O monofilaments were spun from a molten new polycarbosilazane (PCSZ) precursor, cured under oxygen within the temperature range 90–230 °C and submitted to a pyrolysis treatment in argon up to 1600 °C. The curing step was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA)and infrared (i.r.) analysis. The effect of the curing conditions on the weight loss, composition, structure and tensile properties was characterized after pyrolysis. The main reaction occurring during the curing step is the oxidation of Si–H bonds. The mechanical characteristics after pyrolysis have maximum values ($\sigma^R = 1850$ MPa and $E = 185$ GPa) for a curing temperature $\theta_R = 140$ °C, corresponding to an oxygen atomic concentration of 12%. The lowering of σ^R and E observed when $\theta_R \neq 140$ °C could be due to: (i) a tendency of the monofilaments to stick to one another during pyrolysis ($\theta_R < 140$ °C) and (ii) the evolution of gaseous oxygen-containing species during pyrolysis as well as an increase in Si–O bonds ($\theta_R > 140$ °C). The Si–C–N–O monofilaments remain amorphous up to 1400 °C whatever their oxygen concentration is.

1. Introduction

The potential of ceramic-matrix composites (CMCs) as materials for applications at high temperatures and under atmospheres containing oxygen is largely dependent on the performance of the fibres. In this field, the most commonly used fibres are those obtained from the pyrolysis of polycarbosilane precursors (ex-PCS fibres) [1]. Unfortunately, ex-PCS fibres undergo, beyond about 1100 °C, a decomposition process which results in a lowering of their failure tensile strength, thus limiting their reinforcing properties at high temperatures. It has been shown that Si–C–N ceramics produced from polycarbosilazane precursors exhibit improved microstructural stability [2]. Although there are several ex-PCSZ fibres in development, none as far as we know is available commercially at the present time.

The elaboration of a ceramic fibre from an organosilicon green fibre requires a curing step to retain the cylindrical fibre geometry during the high-temperature pyrolysis step. Three different curing processes are commonly used: (i) chemical curing [1–3], (ii) radio-or photo-curing [4–6], and (iii) thermal curing [7–8]; the former has been most frequently used for organosilicon polymeric fibres. The chemical-curing process of such fibres is based on treatments with wet air, oxygen, ozone or even sulphur vapours. Verbeek [9] in the early 1970s was among the first investigators to suggest that green organosilicon fibres could be made infusible by chemical curing. Hasegawa *et al.* [10] have applied the oxygen-curing process to green PCS fibres. It is this process which has been used, up to now, for the ex-PCS fibres (Nicalon fibres from Nippon Carbon Co. Ltd) available commercially. More recently, Penn *et al.* [11] have worked out a chemical-curing process for green PCSZ fibres, which is based on a treatment with water vapour and some of us [12] have established that green PCS fibres could be chemically cured by treatment with sulphur vapours.

The aim of the present contribution is to show the influence of the oxygen-curing conditions on the properties of monofilaments, spun from a new kind of PCSZ precursor, before and after the high-temperature pyrolysis step. This contribution is the continuation of Part I [13] which was devoted to the study of the organic/inorganic transition occurring in such a precursor when the temperature of pyrolysis, as well

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as the subsequent crystallization and decomposition processes, are increased.

2. Experimental procedure

2.1. Preparation of the green PCSZ monofilaments

The PCSZ precursor used in this study, was prepared by a two-step process, described in detail in Part I [13]. In the first step, a polysilasilazane (PSSZ) was prepared by adding dropwise both dimethyldichlorosilane and 1,3-dichloro 1,3 dimethyldisilazane in an equimolar ratio to a suspension of sodium in boiling toluene, under an argon amosphere. The clear mobile PSSZ was converted, in a second step, into PCSZ by heating in a fluidized sand bath at 400–425 °C. The material used in the present study was that referred to as PCSZ-II in Part I [13]. Its overall chemical composition corresponds to the formula $Si_1C_{1.22}N_{0.45}H_{4.2}O_{0.03}$ which shows that oxygen contamination has been maintained at a low level during processing. The average mass weight, $\bar{M}_w$, is of the order of 15200. The green PCSZ is meltable and can be dissolved in most common organic solvents. In the molten state, it exhibits rheological properties compatible with spinning.

The green PCSZ was spun with a laboratory scale apparatus equipped with a single spinneret in order to prepare a continuous monofilament. Mechanical stretching was applied to the green molten filament, through the take-up reel, in order to achieve a mean diameter of the order of 25 µm in the solid state.

2.2. Oxygen curing and high-temperature pyrolysis

The green continuous PCSZ monofilament, removed from the take-up reel, was cut as samples of length $L = 50$ mm and then chemically cured. The curing process was performed, under an oxygen/nitrogen atmosphere ($p(O_2) = 50$ kPa, $p(N_2) = 50$ kPa) at a temperature θ_R ranging from 80 to 230 °C. The PCSZ sample lengths were set in a silica boat within a laboratory tube of silica heated with an electrical furnace. Each sample was first progressively heated to θ_R (ramping rate: 5 °C h^{-1}) and maintained at θ_R for 1 h. It has been observed that θ_R should be higher than 90 °C (for $\theta_R < 90$ °C, the fibres had a tendency to stick together during the subsequent high-temperature pyrolysis step).

The pyrolysis step was performed under a pure argon atmosphere, according to a procedure described in Part I [13]. Each PCSZ fibre bundle was heated in two steps to a temperature θ_p and maintained at θ_p for 15 min [13].

2.3. Monofilament characterization

Thermogravimetric analyses (TGAs, Perkin-Elmer: TGS 2) were performed on PCSZ samples (mass: 10–30 mg) set in a platinum crucible, by two different procedures to simulate, at least to some extent, the curing (heating in air up to $\theta_R = 210$ °C at a ramping rate of 12 °C h^{-1}) and pyrolysis (heating in argon to $\theta_p = 950$ °C) of various PCSZ samples after curing at increasing θ_R values (at a ramping rate of 300 °C h^{-1}).

Infrared (i.r.) spectroscopy analyses (Nicolet FTIR-20 SXC) were performed in the Fourier transform mode (FTIR) on samples of cured PCSZ fibres. The samples were first ground, mixed with KBr powder (weight ratio: 1%) and finally pressed as pellets. As discussed below, the oxygen-curing process resulted in significant changes in the intensities of the i.r. absorption bands. At a given frequency ν, the absorption A of the i.r. beam by the sample is given by $A_\nu = \log(I_0/I)$ where I_0 and I are the intensities of the incident and transmitted beams, respectively. Assuming that the data obeyed the Beer-Lambert law, the product, A_ν, is equal to Kcl where K is the molar extinction coefficient, c the concentration and l the thickness of the pellet. Since, in the procedure used, c and l were not known with great accuracy, the data were used to calculate the ratio $R = A_{\nu(SiH)}/A_{\delta(SiCH_3)}$ in which $A_{\nu(SiH)}$ and $A_{\delta(SiCH_3)}$ are the areas of the absorption bands for ν(SiH) and δ($SiCH_3$), respectively. Since the area of the δ($SiCH_3$) absorption band was observed to remain almost constant during the oxygen-curing process, the ratio R was used to depict, semi-quantitatively, the variations of the ν(SiH) absorption band (i.e. the δ($SiCH_3$) absorption band was used as an internal reference).

Elemental chemical analyses were performed by electron-probe microanalysis (EPMA, CAMEBAX-75 from CAMECA), on polished cross-sections of the monofilaments, with two different monochromators (i.e. PET for the analysis of SiK_α and a multilayer of pseudo crystals PCI for CK_α; OK_α and NK_α) and pure SiC, BN and SiO_2 as standards.

Differential scanning calorimetry (DSC) analyses (METLER TA 300 DSC) were performed under air with a sample of 10 mg of PCSZ from room temperature up to 300 °C (temperature rate increase: 120 °C h^{-1}) in order to simulate, at least to some extent, the thermal phenomena taking place during the oxygen-curing of PCSZ.

X-ray diffraction analyses (XRDs) were performed on monofilaments which had first been oxygen-cured at $120 < \theta_R < 190$ °C and then heated at $1200 < \theta_p < 1600$ °C under argon. Each sample was ground and the powder was analysed with a diffractometer (CuK_α PHILIPS PW-1710 diffractometer control).

Finally, the monofilaments were tensile tested at room temperature with an apparatus similar to that described by Bunsell *et al.* [14]. For each θ_R, θ_p conditions, a batch of about 20 monofilaments was tested with a gauge length of $L = 10$ mm and the data were used to derive the mean ultimate tensile stress $\bar{\sigma}^R$ and the apparent Youngs' modulus E (defined as the slope of the stress/strain graph).

3. Results

3.1. TGA and DSC data

The weight increase occuring, as θ_R is progressively raised, during the curing treatment in air of an as-prepared PCSZ sample is shown in Fig. 1. The weight

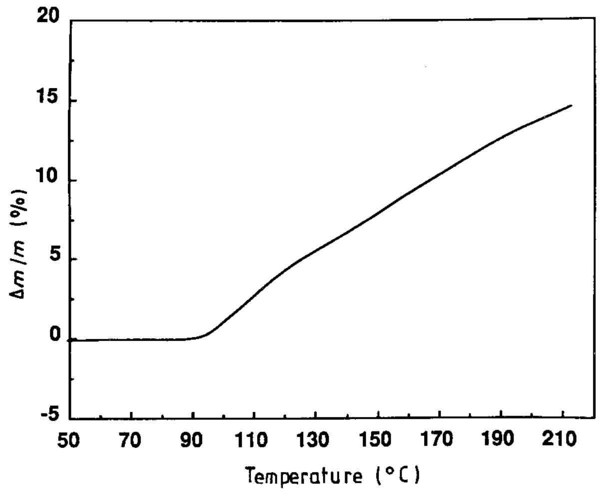

Figure 1 Weight increase of a PCSZ sample during a curing treatment under air.

increase starts at about $\theta_R = 90\,°C$ at a rate which first increases with θ_R; then, i.e. for $\theta_R > 110\,°C$, the weight increase rate remains constant. At the end of the curing treatment, i.e. for $\theta_R = 210\,°C$, the overall weight increase of the sample is about 14%.

TGA experiments have also been used to study the variations of the ceramic yield, defined as $1 - \Delta m/m$ (where $\Delta m/m$ is the weight loss occurring during a pyrolysis treatment performed at 950 °C), as a function of the oxygen-curing temperature θ_R. As shown in Fig. 2, the ceramic yield increases rapidly when θ_R is raised from 80 to 140 °C, then a plateau is observed (corresponding to a ceramic yield of about 88%). Finally, the TGA curves recorded for PCSZ samples cured in air at increasing θ_R are shown in Fig. 3. As θ_R is increased (i.e. as the PCSZ is more severely cured: (i) the beginning of the organic/inorganic transition is shifted to a higher temperature, and (ii) the ceramic yield at 950 °C is raised (with a limit close to 88% as already mentioned).

From the DSC curve recorded during the curing under air of a PCSZ sample (Fig. 4), at a temperature increase rate of $120\,°C\,h^{-1}$, it clearly appears that an exothermic phenomenon takes place between 110 and 230 °C.

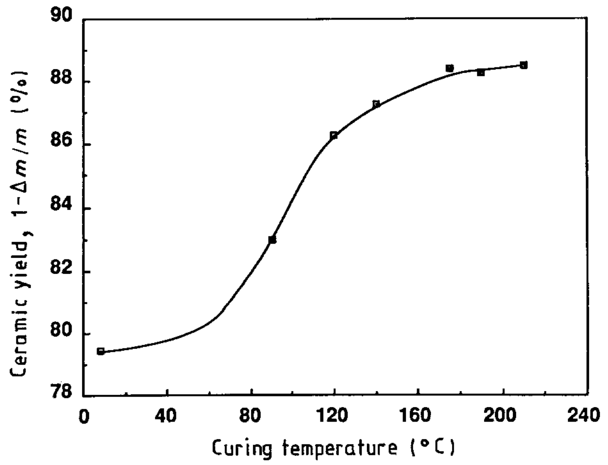

Figure 2 Variations of the ceramic yield $(1 - \Delta m/m)$ of a PCSZ precursor at 950 °C, as a function of the temperature θ_R of the curing treatment.

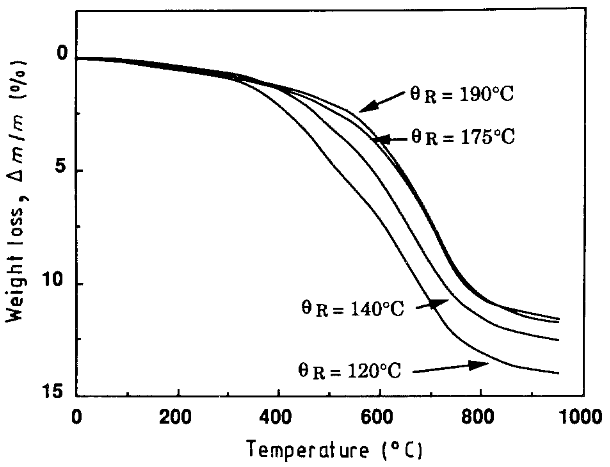

Figure 3 TGA curves of PCSZ samples cured under air at increasing θ_R temperatures.

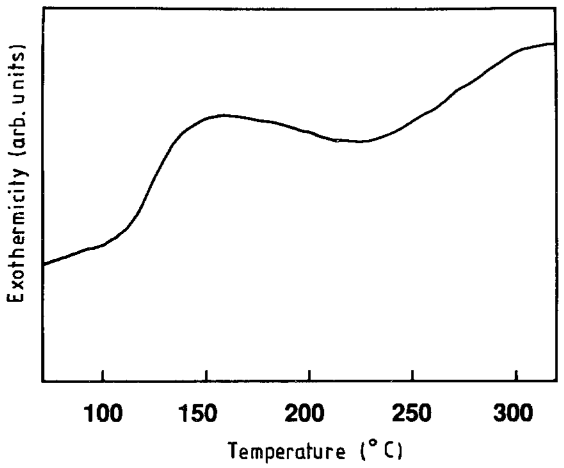

Figure 4 Evolution of heat (DSC) occurring during the curing under air of a PCSZ sample.

3.2. I.r. spectroscopy analysis

The i.r. spectra recorded for both spun green PCSZ monofilament and oxygen-cured monofilaments are shown in Fig. 5. Both monofilaments exhibit characteristic absorption bands which have been assigned to partly cross-linked PCSZ polymers (see Part I [13]) and particularly: a ν(Si–H) absorption band at about 2100 cm^{-1}, a $\delta(Si–CH_3)$ absorption band at 1260 cm^{-1}, and two absorption bands at 1045 and 1350 cm^{-1}, $\delta(Si–CH_2–Si)$ and ω $(Si–CH_2–Si)$, respectively.

It clearly appears that the only absorption band which undergoes a significant change in intensity during the curing process, namely a decrease, is ν(Si–H). Thus, $\delta(Si–CH_3)$, whose intensity remains almost unchanged, as already discussed, was chosen as an internal standard and the variations of the ratio $I = A\nu(Si–H)/A\delta(Si–CH_3)$ were calculated as a function of θ_R to follow the consumption of the Si–H bonds during the oxygen-curing process. From the graph shown in Fig. 6, it appears that the curing process becomes noticeable at about $\theta_R = 120\,°C$ then

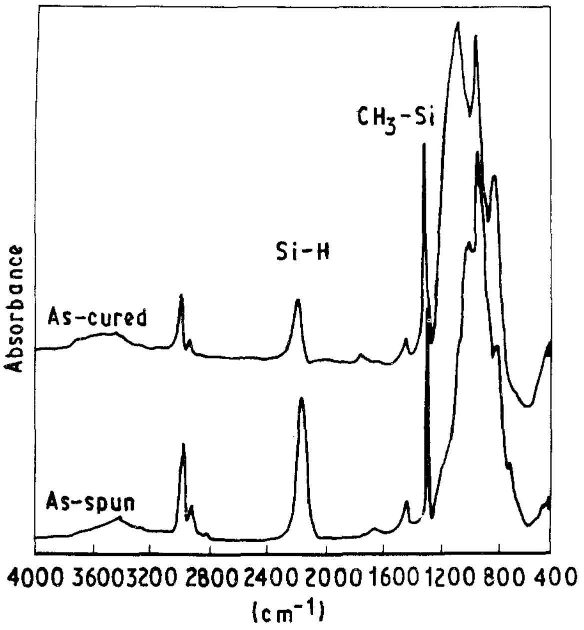

Figure 5 I.r. spectra of as-spun and as-oxygen-cured PCSZ monofilaments (θ_R = 190 °C).

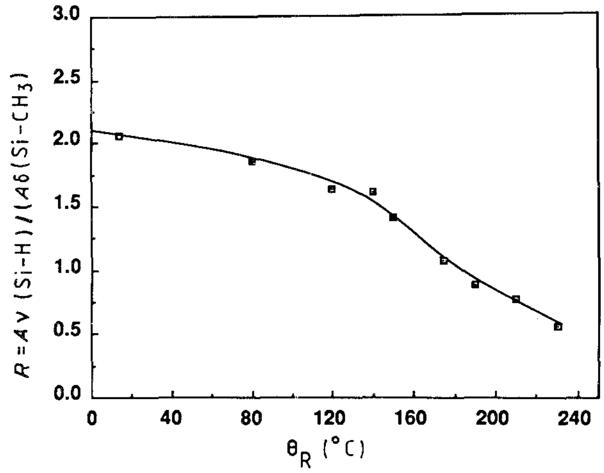

Figure 6 Variations of the $I = A(\nu\ (\text{Si–H})/A\delta\ (\text{Si–CH}_3)$ ratio as a function of θ_R during the oxygen curing of a PCSZ monofilament.

its rate increases whilst finally slowing down for $\theta_R > 220$ °C.

3.3. Elemental analysis

The variations of the elemental composition (as established by EPMA) of the pyrolytic residues at 1200 °C of PCSZ monofilaments, as a function of the oxygen-curing temperature, are shown in Fig. 7. The oxygen concentration increases from 11.5 to 28.5 at % as θ_R is progressively raised from 120 to 230 °C. Moreover, the analyses performed on monofilaments with different diameters have shown that oxygen is uniformly distributed within the cross-section for all values of θ_R.

3.4. Crystal structure of ex-PCSZ monofilaments

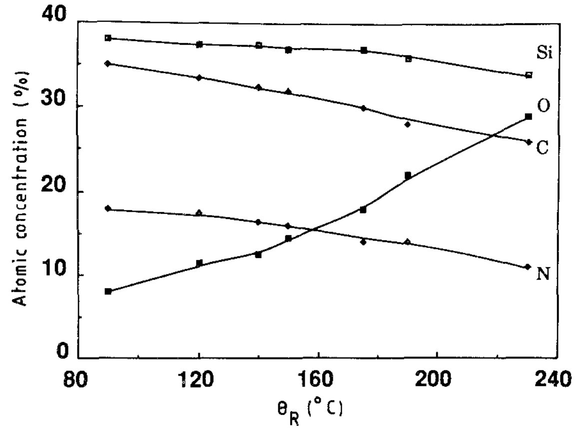

Figure 7 Variations of the elemental chemical composition of PCSZ monofilaments after pyrolysis at 1200 °C, as a function of the oxygen-curing temperature θ_R.

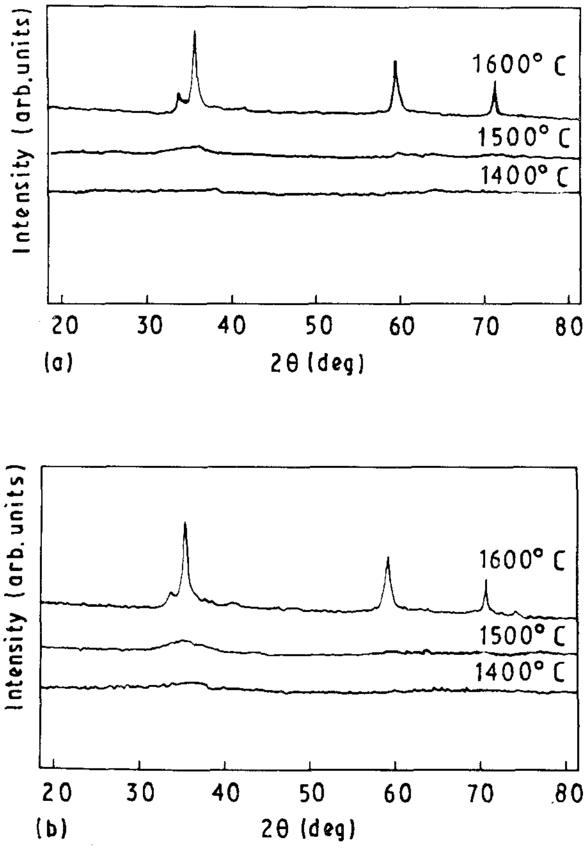

Figure 8 XRD patterns of ex-PCSZ Si–C–N–O filaments cured under an oxygen/nitrogen mixture pyrolysed at increasing temperatures under an argon atmosphere: (a) θ_R = 190 °C and (b) θ_R = 140 °C.

As shown in Fig. 8, the diffraction patterns of monofilaments, cured under oxygen/nitrogen at 140 and 190 °C (oxygen concentrations of 14 and 22 at %, respectively) and then pyrolysed, do not exhibit any significant diffraction peaks for $\theta_p \leq 1400$ °C. Thus, ex-PCSZ monofilaments consist of an amorphous silicon oxycarbonitride, a feature which has been confirmed by TEM analyses [15]. However, for $\theta_p = 1600$ °C and for both the curing conditions here considered, diffraction peaks assigned to the (1 1 1), (2 2 0) and (3 1 1) planes of β-SiC are observed as well as other weak peaks which have been tentatively assigned to a mixture of hexagonal polytypes of SiC.

3.5. Tensile testing at room temperature

The variations of the Young's modulus, E, and ultimate failure stress, σ^R, measured at room temperature for monofilaments pyrolysed at 1200 °C as a function of θ_R, are shown in Fig. 9. Both E and σ^R have maxima ($E = 185$ GPa and $\sigma^R = 1850$ MPa) for $\theta_R = 140\,°C$.

Furthermore, the cross-section of the monofilament measured at room temperature after pyrolysis ($\theta_p = 1200\,°C$) is observed (Fig. 10a) to increase as θ_R is progressively raised (it is equal to 255 μm^2 and 330 μm^2 for $\theta_R = 120$ and 230 °C, respectively). As shown in Fig. 10b, there is a linear relationship between the monofilament cross-section and the oxygen concentration.

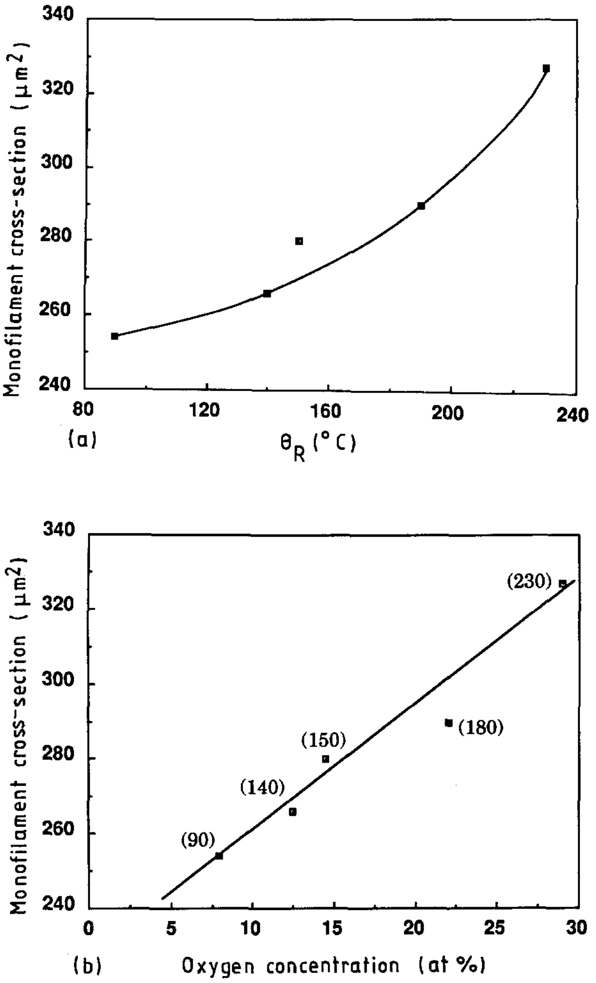

Figure 10 Variations of the monofilament cross-section measured after pyrolysis at 1200 °C as a function of: (a) the curing temperature and (b) the oxygen concentration (θ_R is shown in brackets, for each data point).

4. Discussion

The exothermicity observed by DSC (Fig. 4) during the curing under air of green PCSZ filaments occurs within the same temperature range (i.e. 110–230 °C) where both a decrease in intensity of the ν(Si–H) i.r. absorption band (Figs. 5, 6) and a weight increase (Fig. 1) occur. On the basis of this correlation, one could conclude that the main chemical reaction responsible for the curing process was the oxidation of the Si–H bonds by oxygen. However, and as already reported previously by Taki and coworkers [16, 17], oxidation of the Si–CH_3 bonds resulting in Si–O–C bridges could be also involved. The fact that the intensity of the δ(Si–CH_3) i.r. absorption band remains almost unchanged (Figs 5, 6) during the curing process supports the assumption that this second oxidation mechanism is not very important.

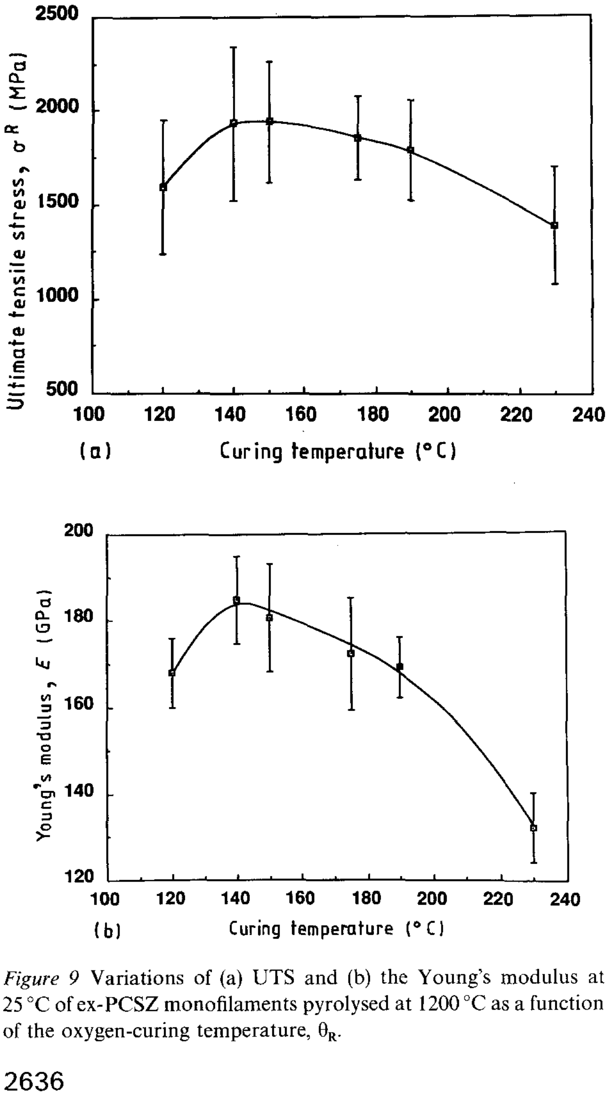

Figure 9 Variations of (a) UTS and (b) the Young's modulus at 25 °C of ex-PCSZ monofilaments pyrolysed at 1200 °C as a function of the oxygen-curing temperature, θ_R.

The width of the DSC exothermic peak (Fig. 4) could have two origins. It could be due to the facts that the Si–H bonds are more or less accessible to oxygen owing to steric effects and/or the Si–H bonds do not have exactly the same reactivity owing to the different surroundings of silicon, as shown in Fig. 11. This assumption is supported by the results of a study by Hasegawa [18] showing that the Si–H bonds from the $SiHC_{2-x}Si_x$ sites react with oxygen at a lower temperature than those from the SiC_3H sites.

Assuming that oxidation of Si–H bonds is the main reaction mechanism during the oxygen-curing of

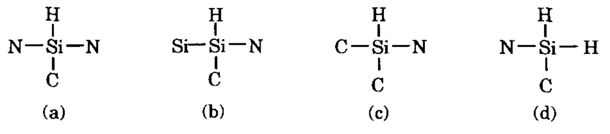

Figure 11 Some atomic surroundings in PCSZ for a silicon atom bonded to an hydrogen atom (schematic).

green PCSZ-monofilaments, the following interpretation is proposed:

$$2\mathrm{SiH} + \mathrm{O}_2 \rightarrow \mathrm{Si{-}O{-}Si} + \mathrm{H_2O} \qquad (1)$$

The actual detailed mechanism is undoubtedly more complex and might involve the formation of free radicals, as previously suggested by Hasegawa [18] for the related oxygen-curing of PCS:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\bullet + \mathrm{H}\bullet \qquad (2)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\bullet + \mathrm{O}_2 \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-O}\bullet \qquad (3)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-O}\bullet + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-OH} + -\overset{|}{\underset{|}{\mathrm{Si}}}\bullet \qquad (4)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-OH} + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} \rightarrow 2-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH} + \mathrm{H_2O} \qquad (5)$$

$$2\ -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-}\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \qquad (6)$$

However, as the curing temperature is low, the homolytic cleavage of Si–H bonds is not likely. On the other hand, as previously reported by other authors [19] this transformation, is better viewed as proceeding by direct oxidation of the Si–H bonds as depicted in Reactions (7–11).

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} + \mathrm{O}_2 \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-OH} \qquad (7)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-OH} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O}\bullet + \mathrm{OH}\bullet \qquad (8)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O}\bullet + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH} + \bullet\overset{|}{\underset{|}{\mathrm{Si}}}- \qquad (9)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\bullet + \mathrm{O}_2 \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-O}\bullet \qquad (10)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-O}\bullet + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O-OH} + \bullet\overset{|}{\underset{|}{\mathrm{Si}}}- \qquad (11)$$

The cross-linking steps could then occur by Reactions (4–6).

The variation of the ceramic yield at 950 °C as a function of the curing temperature (Fig. 2) could be related to the fact that some parts of the polymer which are eliminated as low-boiling-point oligomers during pyrolysis are more tightly bonded when they are integrated to the three-dimensional network, i.e. when the curing conditions are more severe [19, 20]. During the oxygen-curing of PCSZ monofilaments Si–O–Si bridges, known to be very strong, are formed rendering the polymer insoluble and unmeltable. Therefore, as the number of Si–O–Si bridges increase, the organic/inorganic transition, observed as a weight loss, is shifted towards higher temperatures. Furthermore, the linear relationship between the cross-sectional area of the pyrolysed monofilaments and the oxygen concentration is likely to be solely related to the oxygen absorption by green monofilaments during the curing process (since the ceramic yield is not significantly changed).

As mentioned in Section 3.4, ex-PCSZ monofilaments are amorphous, whatever their oxygen concentration, as long as $\theta_p < 1400\,^\circ\mathrm{C}$. On the basis of this important result, which is in contrast with those previously reported for ex-PCS fibres [20], oxygen could be assumed to be bonded to silicon atoms within a quaternary amorphous structure as $\mathrm{SiC}_x\mathrm{N}_y\mathrm{O}_z$, which is more stable with respect to temperature than the related amorphous $\mathrm{SiC}_x\mathrm{O}_y$ which is present in some ex-PCS fibres. It is only when $\theta_p > 1400\,^\circ\mathrm{C}$ that a decomposition process takes place in a significant manner resulting in an evolution of nitrogen and the formation of SiC crystals.

For $\theta_R \leq 120\,^\circ\mathrm{C}$, the degree of cross-linking of the PCSZ polymer is low and: (i) defects are observed at the surface of the monofilaments, as shown in Fig. 12, which might be responsible for the low ultimate tensile stress (UTS) σ^R values (i.e. 1500 MPa, Fig. 9a), and (ii) a significant internal porosity appears, possibly related to the evolution of gaseous species arising from the functional groups at the polymer end-chain or pendant groups, which might explain the low values of the Young's modulus (i.e. 160 GPa, Fig. 9b).

For $\theta_R = 140\,^\circ\mathrm{C}$ and an oxygen concentration of 12 at %, a maximum is observed for both the failure strength and stiffness of the monofilaments after pyrolysis at 1200 °C ($\sigma_R = 1850$ MPa and $E = 185$ GPa). For $\theta_R > 140\,^\circ\mathrm{C}$, the oxygen concentration continues to increase (e.g. for $\theta_R = 230\,^\circ\mathrm{C}$, it is equal to 28 at %) and, simultaneously, a significant lowering of the mechanical characteristics is observed (e.g. for $\theta_R = 230\,^\circ\mathrm{C}$, $\sigma^R = 1350$ MPa and $E = 130$ GPa). The decrease of the stiffness could be related to the fact that the number of Si–O bonds increases with respect to those of Si–C bonds as θ_R is raised, with the value of the Young's modulus going towards that of silica (i.e.

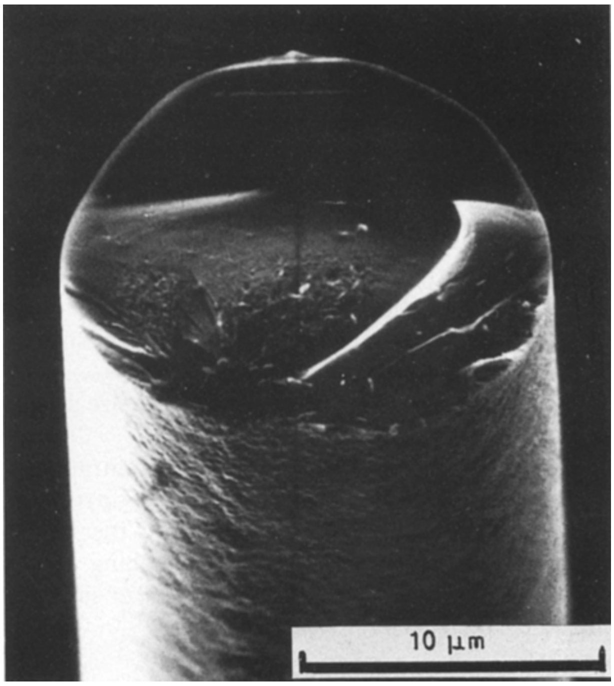

Figure 12 Surface defects observed for ex-PCSZ monofilaments pyrolysed at 1200 °C when the curing temperature is too low (i.e. $\theta_R \leq 120\,^\circ\mathrm{C}$).

about 75 GPa). The lowering of the failure strength might be explained by the occurrence of large size defects located both near the surface of the monofilaments and in the bulk, and resulting from the evolution of gases during the pyrolysis. This gas evolution was observed to be more and more abundant as the oxygen concentration and therefore θ_R were high [22].

The above results are consistent with those previously published by Ichikawa *et al.* [23, 24] for oxygen-cured ex-PCS fibres. In fact, the highest UTS value measured in the present work for ex-PCSZ monofilaments is observed for an oxygen concentration of about 12 at %, which is also that reported by Ichikawa *et al.* for ex-PCS fibres. We suggest that the lowering of E and σ^R observed for both materials beyond this oxygen concentration limit, could be explained on the basis of the same mechanisms: (i) an increase of the Si–O bonds with respect to those of Si–C, in the ceramic materials obtained after pyrolysis, having a softening effect; and (ii) an evolution of gases, producing large-size defects after pyrolysis which is enhanced at high oxygen concentrations and results in low UTS values. However, it should be mentioned that the relative variations of both σ^R and E with the curing conditions are less pronounced for the ex-PCSZ monofilaments studied here than for the ex-PCS fibres studied by Ichikawa *et al.* [24]. This important difference could be related to the fact that ex-PCS fibres exhibit a change in the crystallization state beyond about 1200 °C which is dependent on the oxygen concentration whereas ex-PCSZ monofilaments remain amorphous up to about 1400 °C independently of the oxygen concentration (possibly due to the occurrence of Si–N bonds).

5. Conclusion

Si–C–N–O monofilaments remaining amorphous up to 1400 °C have been obtained by spinning molten new PCSZ precursors, oxygen curing and pyrolysis under argon. Curing, which occurs in the temperature range 120–210 °C, is thought to result in the oxidation of the Si–H bonds.

The failure strength and stiffness of the monofilaments, obtained after pyrolysis at 1200 °C, exhibit maxima ($\sigma^R = 1850$ MPa and $E = 185$ GPa) for a curing temperature $\theta_R = 140\,^\circ\text{C}$ corresponding to an oxygen concentration of about 12 at %.

For $\theta_R < 140\,^\circ\text{C}$, the monofilaments tend to stick to one another during the pyrolysis step due to too low a degree of cross-linking. The resulting large size defects yield low UTS values.

For $\theta_R > 140\,^\circ\text{C}$, the high oxygen concentration is responsible for an evolution of gases during pyrolysis, causing large size defects and lowering the failure strength, on the one hand, and a softening of the ceramics whose stiffness approaches that of silica on the other hand.

Acknowledgements

This research was done within a national programme supported by CNRS, the Direction des Recherches et des Etudes Techniques (DRET), Rhône-Poulenc (RP) and Société Européenne de Propulsion (SEP). The authors acknowledge the participation of P. Olry from SEP for valuable discussions.

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Received 1 May
and accepted 21 September 1992