

A quasi-stoichiometric SiC-based experimental fibre obtained from a boron-doped polycarbosilane precursor

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A quasi-stoichiometric SiC-based fibre, has been prepared at a pyrolysis temperature of 1800 °C, from a boron-doped polycarbosilane precursor using an extrusion-chemical curing-pyrolysis procedure. The green fibre was rendered infusible by sequential curing with ozone and trimethylamine-borane adduct ($O_3/Me_3N: BH_3$). The fibre was characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy, electron energy loss spectroscopy and Raman spectroscopy.

1. Introduction

The development of Nicalon Si–C–O fibres (Nippon Carbon, Japan) by S. Yajima *et al.* [1] using a procedure successively comprising of: spinning of a molten polycarbosilane (PCS) precursor, curing with oxygen, and pyrolysis in an inert gas, represents a considerable breakthrough in the field of ceramic matrix composites (CMC). However, this kind of SiC-based fibre is metastable at high temperatures, due to the occurrence of an amorphous SiO_xC_y phase. The decomposition of the fibre begins at 1200 °C, with an evolution of CO and SiO. Therefore, the oxygen curing step has been replaced by electron beam irradiation in anaerobic conditions [2]; the thus-obtained fibre is referred to as Hi-Nicalon (an experimental fibre from Nippon Carbon). The decrease of the oxygen content to a level of ≈ 1 at % results in an increase in the thermal stability (the fibre being stable up to ≈ 1600 °C). In addition, the mechanical properties of the fibre have also been improved by decreasing its free carbon content. A quasi-stoichiometric fibre, referred to as Hi-Nicalon S with a Young's modulus of ≈ 400 GPa, has recently been prepared using a modified Yajima route whose details have not yet been disclosed [3, 4].

J. Lipowitz *et al.* have independently reported a chemical curing technique using a sequential NO_2/BCl_3 treatment [5]. The ceramic fibres obtained in this way, after pyrolysis for 1 h at 1800 °C under an argon flow, consisted of nearly pure SiC with a low oxygen content [6]. The introduction of boron into the green PCS fibre during the curing step appears to be the key step of this process. Although heating the PCS fibre at 1800 °C normally produces a significant decrease in their mechanical properties, such a ther-

mal treatment performed on PCS fibres cured with NO_2/BCl_3 does not reduce the tensile strength (which is still ≈ 2600 MPa for pyrolysis at 1800 °C), the fibres displaying a Young's modulus of ≈ 450 GPa at room temperature [7]. Other curing reagents such as BCl_3/NH_3 , NO/B_2H_6 and NO/BCl_3 have been proposed but they lead to Si-C(B) fibres with poorer mechanical properties [8].

The aim of this work was to produce and characterize an experimental Si–C(B) continuous fibre using the following approach:

- (i) synthesis of a novel boron-doped PCS precursor, from a polysilacarbosilane/triethylamine-borane ($Et_3N: BH_3$) mixture,
- (ii) spinning of the precursor in the molten state,
- (iii) sequential curing of the green monofilament with the couple $O_3/Me_3N: BH_3$,
- (iv) ceramization and physico-chemical characterization of the fibre.

2. Experimental procedure

2.1. Characterization

Fourier transform-infrared (FT-IR) spectra were recorded using a FT20 SXC Nicolet spectrometer operating in the transmission mode over the range of 400–4000 cm^{-1} , from pressed pellets made from a mixture of KBr powder and finely ground samples. Thermogravimetric analyses (TGA) were performed with a TGS2 Perkin Elmer analyser under a high purity argon flow (40 $ml\ min^{-1}$) at atmospheric pressure. The 10 mg samples were heated at a rate of 5 °C min^{-1} , between 40–950 °C. Size exclusion chromatography (SEC) was performed with a Waters

chromatograph equipped with UV and refractometer detectors (columns porosity: 4.0–10⁶ nm; eluent: THF 1 ml min⁻¹; calibration with polystyrene standards). The X-ray diffraction (XRD) study was performed with a Philips diffractometer (operated at 40 kV, 40 mA) using CuK α radiation (0.154 nm). The structure and composition of the fibres pyrolysed at 1800 °C were studied by transmission electron microscopy (TEM) (using a Philips CEM 30 ST microscope) and also electron energy loss spectroscopy (EELS) using a 666 PEELS Spectrometer from Gatan.

2.2. Preparation of the ceramic monofilaments

The precursor was prepared using a route that has been previously reported [9]. The process involves two steps: (i) the partial conversion of polydimethylsilane (PDMS) into a polysilacarbosilane (PSCS) under pressure (treatment in autoclave at 470 °C) and (ii) the thermolysis at 350 °C under atmospheric pressure of a mixture of PSCS/Et₃N: BH₃ in the molar ratio 10:1.

The precursor was melt-spun in a nitrogen atmosphere dry glove-box at a temperature of 150 °C, with a laboratory-scale apparatus equipped with a single spinneret. This set up allows us to prepare a continuous monofilament of 20 μ m in diameter. The green fibres were cured under an ozone–oxygen flow at atmospheric pressure and heated at 100 °C for 4 h. Then, the fibres were exposed to Me₃N: BH₃ diluted in an argon flow at 180 °C for 6 h. The cured filaments were placed in a silica boat, transferred to an electrical furnace that was directly connected to the glove-box, and pyrolysed for 1 h at 1000 °C with the heating rate being 60 °C h⁻¹. The fibres were finally treated for 1 h at 1800 °C (with a heating rate of 30 °C min⁻¹) in a graphite crucible that was heated with a radio-frequency coil inductor, at a pressure of 100 kPa under a high purity argon flow.

2.3. Preparation of TEM samples

Three techniques can be used to prepare samples of ceramic fibres for TEM analysis: (i) ultramicrotomy with a diamond knife, (ii) ion-beam etching, which often leads to compositional changes in the sample and (iii) fracturation. The last two techniques have been used in this work.

Table I gives a comparison of the elemental compositions of samples of Nicalon NLM 202 fibres obtained from; (a) conventional bulk analyses (b) EELS analysis on sample prepared by a fracturation technique and (c) ion-beam etching. It is clearly apparent that the fracturation method gives results that are in agreement with the average of measurements reported by various authors, and also with the composition given by the manufacturer.

Conversely, ion-beam etching induces O and Ar ion implantation during the argon etching of the sample.

Thus, samples were prepared using a splinter technique, which is a fracturation technique adapted for hard brittle materials such as fibres [12]. Overlapping

TABLE I Quantitative analysis results for Nicalon NLM 202 fibres. (a) Average results from various authors taken from reference [10], (b) EELS on fractured sample [11], and (c) EELS after ion beam etching [11]

Source	(a)	(b)	(c)
Si (at %)	36	36 (4)	33 (3)
C (at %)	49	47 (5)	28 (3)
O (at %)	15	17 (3)	27 (3)
Ar (at %)	–	–	2 (1)

5 mm pieces of fibre were placed between two planes of silicon carbide (or alumina). Thumb pressure was sufficient to break the fibres with a grinding sound. Finally, a copper grid coated with a holey carbon film was rubbed on to splinters in order to stick them onto the film. This simple and chemically safe technique was thought to be well adapted to the study of the samples provided that the splinters have a recognizable shape.

3. Results and discussion

3.1. Characterization of the precursor

The precursor was characterized by IR spectroscopy, SEC and TGA. The observed IR absorption bands corresponded to those previously reported [13,14]. The characteristic absorptions of Si–CH₂–Si groups are observed at 1350 cm⁻¹ (δ_{CH_2}) and 1027 cm⁻¹ (ν_{CH_2}). The Si–H stretching band is present at 2100 cm⁻¹ as well as the absorption bands of the aliphatic groups, ν_{CH_2} and ν_{CH_3} at 2800–3000 cm⁻¹ (Fig. 1). The average molecular mass is $\overline{M}_n = 1640$, with a polydispersity index $I_p = 1.8$. The ceramic yield at 950 °C is about 54%. The softening temperature, measured on a Kofler hot bench, is about 120 °C.

3.2. Characterization of the filaments

3.2.1. SEM characterization

Examination of the failure surface of the filaments pyrolysed at 1000 °C under argon reveals that the material is amorphous (Fig. 2a). Conversely, examination of the failure surface of the fibre pyrolysed at 1800 °C for 1 h, reveals an important crystallization state and the presence of an outer layer more or less bonded to the surface of the fibre (Fig. 2b).

3.2.2. XRD characterization

The XRD pattern shows that the fibres consist essentially of β -SiC (the α -SiC peak that occurs at diffraction angle of 34.22° is very weak).

The width of the β -SiC (111) reflection (measured at mid peak height) is about 0.7° which is close to the measurement limit of the apparatus. Only its widening should be used in the Scherrer formula ($t = 0.9\lambda/B\cos\theta$, where $B^2 = B_{\text{mes}}^2 - B_{\text{app}}^2$, t is the size of the crystals, λ is the wavelength, B is the widening of the peak in radians and θ is the Bragg angle) [15]. Thus the crystals size cannot be measured in this way, but is presumably over 0.1 μ m (usual limit of this method).

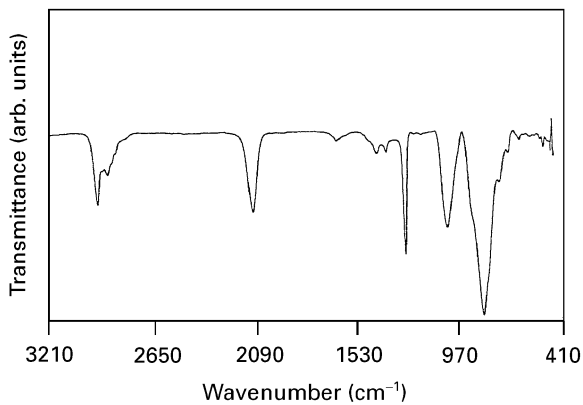


Figure 1 IR spectrum of the precursor.

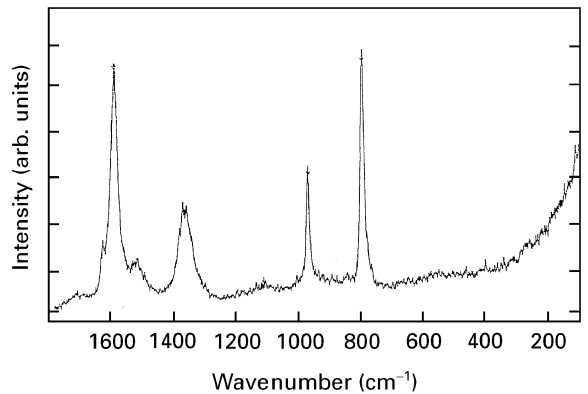


Figure 3 Raman spectrum of fibre pyrolysed under argon atmosphere at 1800 °C.

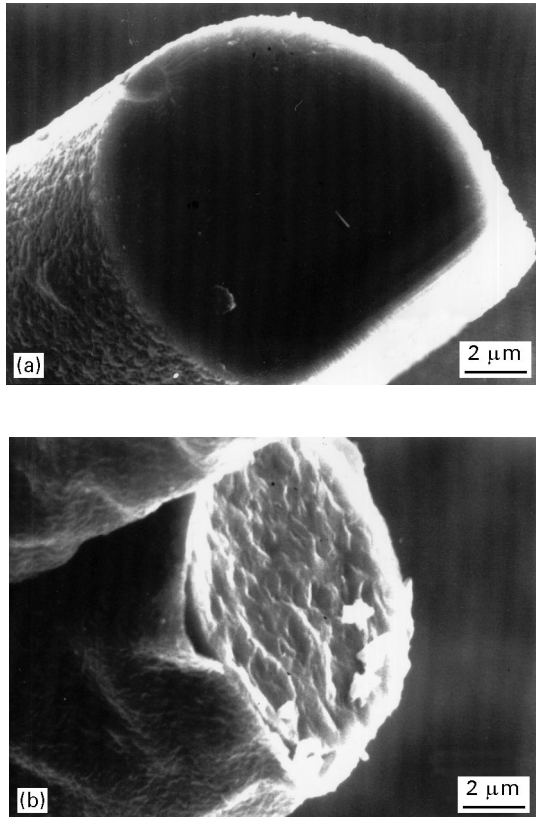


Figure 2 Failure surface and surface morphology of; (a) fibre pyrolysed at 1000 °C and (b) fibre pyrolysed at 1800 °C.

3.2.3. Raman spectroscopy

The Raman spectrum shows two fine absorption bands at 793 and 966 cm^{-1} , indicating the presence of crystalline β -SiC (Fig. 3). Additionally, the diffuse peaks at 1590 and 1360 cm^{-1} are assigned to organized and non-organized carbon respectively. The fact that carbon is detected by Raman spectroscopy does not necessarily mean that it is present in significant amounts, since the detection limit of Raman spectroscopy for carbon is known to be very low.

3.2.4. TEM and EELS characterization

A D-shaped splinter is shown in Fig. 4. The curvature of its right side locates the original fibre surface and allows estimation of the depth along the thinner left

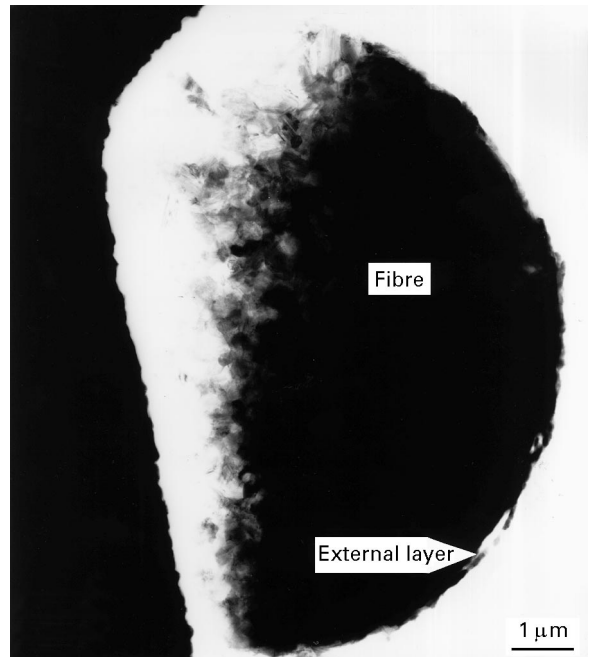


Figure 4 Quasi-stoichiometric 1800 °C-pyrolysed SiC fibre; a fibre splinter.

side. The core of the fibre consists of 0.3–1 μm β -SiC crystals. Such a crystallite size justifies the use of the Scherrer formula to analyse the XRD results. Some of these crystals can be found defect free over several hundreds of nm (Fig. 5), but most of them have stacking and twinning faults (α -components), as revealed by bright field and 111-centred dark field TEM images (Fig. 6(a and b)).

An external 0.2 μm thick layer, partially unstuck or just removed, can be seen along the right surface of the splinter, it is clearly the layer previously observed by SEM, that has somehow been removed from where it has been broken by the fracturing. Enlargement of an unstuck portion (Fig. 7) shows 0.1 μm crystals surrounded by other sheet-like crystals. Microdiffraction could allow the identification of all these crystals only if one could differentiate hexagonal boron nitride from graphite (the occurrence of these two phases being equally probable). However, the similarity of the (0002) interplanar spacings (0.335 nm for graphite and 0.333 nm for h-BN) means that both electron

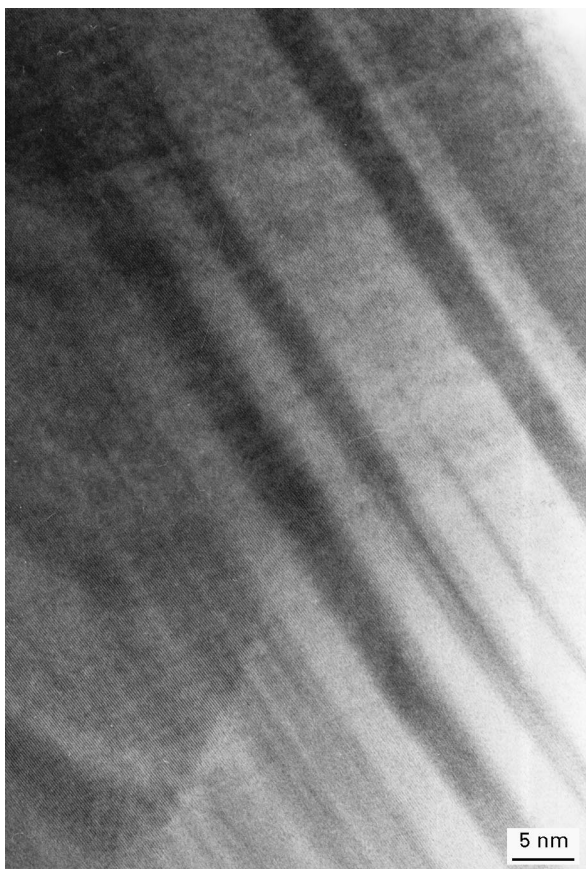


Figure 5 Quasi-stoichiometric 1800°C-pyrolysed SiC fibre; SiC-(111) lattice fringes.

diffraction and high-resolution TEM techniques are inappropriate techniques to solve this problem [16].

The compositions of the core and external layer have been assessed by EELS. Spectra have been recorded from the core (Fig. 8) and from the skin of the fibre (Fig. 9), with acquisition parameters chosen to obtain quantitative information (the collection semiangle, β is 14.8 mrad, the convergence semi-angle, α is less than 1.73 mrad, the entrance diaphragm of the spectrometer, Φ_{SP} is 1 mm and the image mode, magnification is 39000 \times). Provided that the sample is homogeneous over a 70 nm-diameter zone, and especially in its centre, quantitative analysis can be done (the analysed zone is 26 nm, i.e. 1/39000 mm in diameter, but it extends to 70 nm for the O_K edge because of the chromatic aberration of the microscope [17]). The cross-section ratio $\sigma_{SiL_{2,3}}/\sigma_{CK}$ was measured separately in the same optical configuration on SiC powder crushed and deposited on a copper grid coated with a holey carbon film. The average of twelve measurements is: $\sigma_{SiL_{2,3}}/\sigma_{CK}=11.6$ with a standard deviation of 9%. Quantitative analysis results are summarized in Table II.

The average composition of the core of the fibre is Si:C=52:48 at % (C/Si=0.93 \pm 0.1), therefore the fibre can be considered as approximately stoichiometric. As the oxygen K edge was unobserved, it can be confidently stated that the oxygen content is less than 2 at %. Similarly, the boron K edge and nitrogen K edge were unobserved. Analyses on both sides of the external layer show the presence of free carbon (100%)



Figure 6 Quasi-stoichiometric 1800°C-pyrolysed SiC fibre; (a) bright field image and (b); dark field image, SiC-(111) reflection.

in a graphitic or turbostratic form (sp^2 hybridization). Inside the layer, analysis gives a composition of Si:C=40:60 at % which is compatible with a superposition of SiC and free carbon in a proportion SiC:C_{free}=80:20 mol %. The occurrence of free

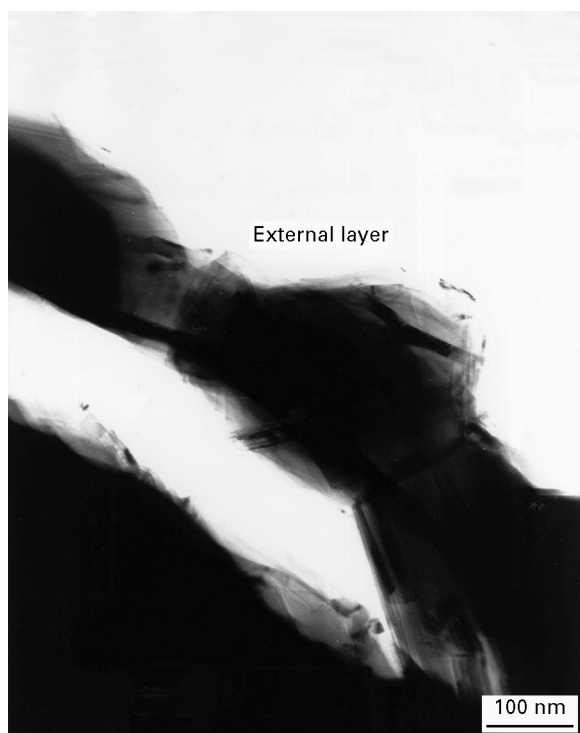


Figure 7 Quasi-stoichiometric 1800 °C-pyrolysed SiC fibre; external layer.

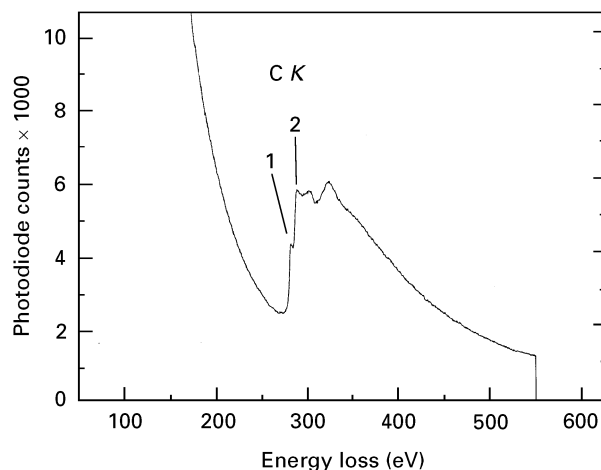


Figure 9 EELS spectrum recorded from a tape-like crystal in the external side of the superficial layer (pyrolysis temperature 1800 °C).

carbon near the fibre surface is consistent with the Raman absorption bands at 1590 and 1360 cm^{-1} . The free carbon could be a result of a decomposition of SiC that is limited to the fibre surface (possibly enhanced by some active oxidation due to traces of residual oxygen in the pyrolysis atmosphere).

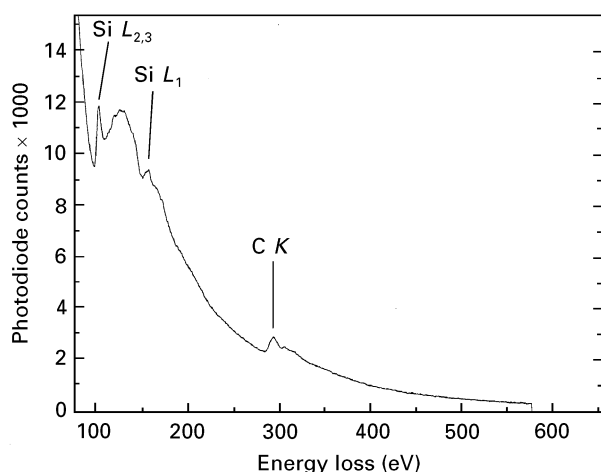


Figure 8 EELS spectrum recorded from the core of a fibre pyrolysed at 1800 °C.

4. Conclusions

A quasi-stoichiometric, experimental Si-C fibre has been produced by the melt spinning, sequential curing with $\text{O}_3/\text{Me}_3\text{N}:\text{BH}_3$, and pyrolysis at 1800 °C under a high purity argon flow, of a polycarbosilane doped with boron. The synthesis of this precursor comprises of: (i) a controlled thermolysis of polydimethylsilane in an autoclave which yields a polysilacarbosilane, PSCS; and (ii) thermal treatment of this oligomer at atmospheric pressure in the presence of the triethylamine-borane adduct.

The monofilaments keep their fibrous morphology when treated at 1800 °C. The oxygen introduced during the curing process is eliminated, leading to a quasi-stoichiometric SiC core with large crystallites (0.3–1 μm) and a surface enriched in carbon.

TABLE II EELS quantitative analysis results. Estimated accuracies are about a tenth of the atomic percentages (oxygen, nitrogen and boron *K* edges were not observable).

Analysed zone	Estimated depth (nm)	Silicon (at %)	Carbon (at %)	C/Si atomic ratio (estimated error)
Core	7300	52.4	47.6	0.908 (0.1)
Core	7300	52.0	48.0	0.924 (0.1)
Core	4500	49.7	50.3	1.011 (0.1)
Core	4500	52.8	47.2	0.892 (0.1)
Average		51.7	48.3	0.934 (0.1)
Standard deviation (%)		2.2	2.2	
Interfacial side	300	0.0	100.0	∞
Layer	100	39.6	60.4	1.527 (0.15)
External side	20	0.0	100.0	∞

Studies on the mechanisms of the curing step, and on its influence on the fibre composition at various pyrolysis temperatures are in progress.

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