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Development of Si–B–O–N fibres from polyborosilazane

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A polyborosilazane, which is a precursor of ceramic fibre, was synthesized from perhydropolysilazane and trimethyl borate. The polyborosilazane was dry-spun and then pyrolysed to produce amorphous Si–B–O–N fibre. The Si–B–O–N fibre retained its high tensile strength to higher temperatures (about 1600 °C). The fibre has a density of 2.4 g cm^{-3}, tensile strength of 2.5 GPa and an elastic modulus of 180 GPa.

1. Introduction

High-performance ceramics such as silicon nitride and silicon carbide can be prepared by pyrolysis of various organometallic polymers. The main advantage in the preparation of ceramic materials from these precursors is the ability to prepare ceramic shapes (e.g. fibres, films) which are difficult to achieve by conventional powder processing techniques. High-purity Si–N fibre has been synthesized from perhydropolysilazane [1]. $Si_xN_yC_z$ fibre [2] and Si–N–C fibre [3] have been derived from polycarbosilazane and hydridopolysilazane, respectively. Both Si–C–O fibre [4] and Si–N–O fibre [5] have been synthesized from polycarbosilane and Si–Ti–C–O fibre [6] has been derived from polytitanocarbosilane. However, these ceramic fibres have a weak point: the mechanical properties deteriorate at high temperature.

A novel polyborosilazane has been derived from perhydropolysilazane and trimethyl borate [7]. This polyborosilazane can be converted into amorphous Si–B–O–N ceramics by pyrolysis without a curing process. Using this polymer, a new Si–B–O–N fibre with high tensile strength and excellent heat resistance has been synthesized by pyrolysis of dry-spun polyborosilazane fibre. This paper describes the synthesis and the mechanical properties of Si–B–O–N fibre, and also the pyrolysis process of the polyborosilazane fibre.

2. Experimental procedure

2.1. Preceramic polymer synthesis

Polyborosilazane was produced by the reaction of perhydropolysilazane with trimethyl borate. Perhydropolysilazane was synthesized by ammonolysis of dichlorosilane–pyridine adduct [8] followed by heat treatment at 120 °C in pyridine with ammonia. In a typical reaction, perhydropolysilazane and trimethyl borate were mixed with pyridine to form a homogeneous solution (Si/B = 3 atomic ratio). The solution was heated in an autoclave at 120 °C for 3 h with stirring. After cooling to ambient temperature, dry *o*-xylene was added to the reaction mixture and the solvent was removed by distillation at 50 °C under 5–7 mm Hg to give a white powder. This powder (polyborosilazane) was found to be soluble in toluene, tetrahydrofuran and chloroform. Polyborosilazane had a number average molecular weight of 2100. This polymer did not melt in nitrogen up to 500 °C. The yield of product was typically > 95% of theory, based upon the starting perhydropolysilazane. For reference, perhydropolysilazane with $M_n = 2200$ was prepared under the same conditions as polyborosilazane without the addition of trimethyl borate.

2.2. Fibre spinning

Polymer solutions were filtered to remove insoluble material and concentrated to develop appropriate rheological characteristics for the spinning operation. Polymer fibres (polyborosilazane and perhydropolysilazane) were continuously prepared by dry spinning at about 60 °C. With proper drawdown of the viscous polymer solution during extrusion from the spinneret, fibres with diameters of 10–15 μm were produced. A drum on a variable speed motor was used for fibre take-up.

2.3. Pyrolysis

Fibres (120 mm in length) were pyrolysed in an Al_2O_3 tube furnace (Model F-1201, Nishimura Kogyo, Tokyo, Japan) under flowing anhydrous ammonia at 5 °C min^{-1} to temperatures ranging from 200–1200 °C, with 1 h hold at those temperatures (referred to as NH_3-pyrolysed fibre). The pyrolysed fibres were subsequently annealed for 1 h under flowing nitrogen at temperatures ranging from 1300–1800 °C (referred to as nitrogen-annealed fibre) in a carbon furnace (Model HG-010, Nikkato, Osaka, Japan).

Polyborosilazane fibre was pyrolysed without ammonia pretreatment at 1500 °C for 1 h in nitrogen (referred to as 1500 °C nitrogen-pyrolysed fibre) to

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compare the chemical and mechanical properties with those of ammonia-pretreated fibres.

2.4. Characterization

Molecular weight distributions were measured with a gel permeation chromatography (GPC) system (Model 801-SC, 830-RI, JASCO, Tokyo, Japan) using chloroform as solvent. Molecular weights quoted are based on polystyrene standards.

Infrared spectra (IR) were recorded of KBr pellets containing powder samples (Model JIR-5500, Jeol, Tokyo, Japan). A ^{1}H nuclear magnetic resonance spectrum (NMR) (Model EX-400, JEOL) was recorded of the polymer in $CDCl_3$ solution at room temperature. Elemental analyses for silicon, boron, oxygen, nitrogen, carbon and hydrogen were obtained for the polymer, pyrolysed and annealed fibres.

Nuclear magnetic resonance with cross polarization–magic angle spinning (CP/MAS–NMR) spectra were recorded on an MSL-300 Bruker spectrometer. A ^{1}H 90° pulse of 4.5 µs, a contact time 3 ms and a delay between pulses of 10 s were used for ^{29}Si NMR spectra measurements performed on 1300 °C nitrogen-annealed Si–B–O–N and Si_3N_4 fibres.

X-ray diffraction (XRD) measurements were performed on the nitrogen-annealed fibres with CuK_α radiation using an automated powder diffractometer equipped with a monochromator (Model RINT 1400, Rigaku, Tokyo, Japan). Thermogravimetric analysis (TGA) was performed on the polymer fibre up to 1200 °C under flowing anhydrous ammonia (Model TG8110D, Rigaku).

The apparent density of ceramic fibres was measured using a short length in a density gradient column. The high- and low-density solvents used were bromoform was carbon tetrachloride, respectively, covering a density range 1.60–2.89 g cm^{-3}.

The mechanical properties, tensile strength and elastic modulus, of single-filament ceramic fibres were carried out with a universal testing machine (Model AG-2000C, Shimazu, Kyoto, Japan) and a 5 kg load cell at a crosshead speed of 0.5 mm min^{-1} and a chart speed of 200 mm min^{-1}. The procedure was based on ASTM test method D-3379-75. The cross-sectional area of the fibre was calculated from a scanning electron micrograph of the fracture ends which were captured in a toluene-soluble grease which was subsequently removed.

Samples for transmission electron microscopy (TEM) analysis were prepared by mounting ground samples on a thin copper mesh which was previously coated with a thin layer of carbon. An electron microscope (Model JEM-3010, Jeol) operating at 300 kV was used for bright-field imaging and for selected-area electron diffraction.

3. Results and discussion

During heating the mixture of perhydropolysilazane and trimethyl borate, the formation of B–N and Si–O bonds occurs. The bondings between perhydropolysilazane and trimethyl borate are mainly via B–N bonds. The formation of Si–O bonds are due to the reaction of Si–H bonds of perhydropolysilazane with CH_3OH, which is the by-product of the reaction between perhydropolysilazane and trimethyl borate [7]. GPC of the polymer showed a number average molecular weight, M_n, of 2100 and a weight average molecular weight, M_w, of 9000 (Fig. 1). A ^{1}H NMR spectrum of the polymer showed peaks centred at 4.8, 4.6, 4.3, 3.5, and 1.4 p.p.m, corresponding to SiH/SiH_2 [9], $HSiON_2$, SiH_3 [9], OCH_3, and NH [9], respectively (Fig. 2). Polyborosilazane is a polymer consisting mainly of structural units of $HSiN_3$, H_2SiN_2, H_3SiN, $HSiON_2$, $NB(OCH_3)_2$, and $NB(OCH_3)N$ [7].

With proper drawdown of the viscous polymer solution, fibres with a diameter of 10–15 µm are readily produced. The TGA curve of the polyborosilazane fibre is shown in Fig. 3; the curve indicates that the weight loss starts around 100 °C and is completed around 1100 °C in an ammonia atmosphere. Three regions are apparent in the curve. The first region below 200 °C results from the loss of residual solvent and the second region, from 400–800 °C, is thought to correspond to the breaking of organic bonds with the

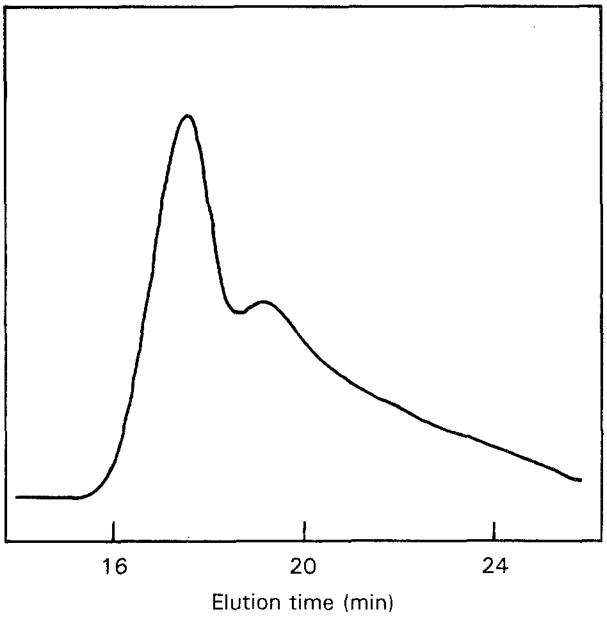

Figure 1 GPC of polyborosilazane.

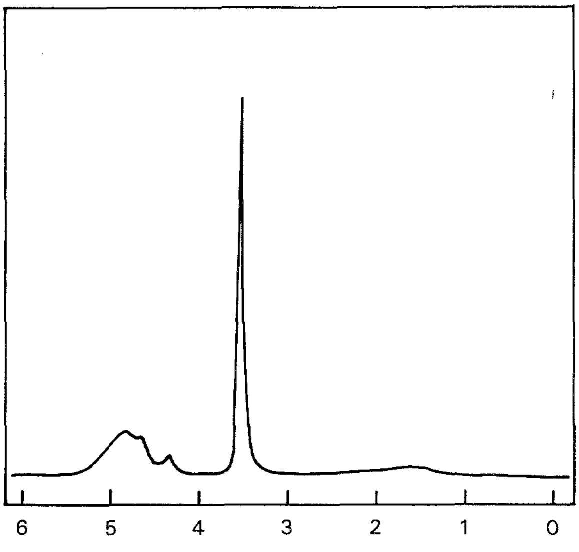

Figure 2 ^{1}H NMR spectrum of polyborosilazane.

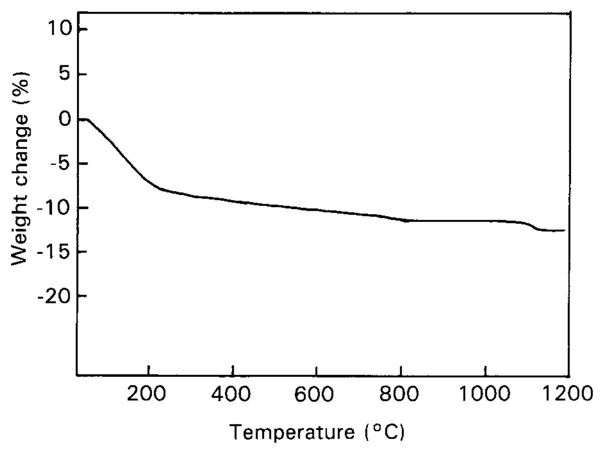

Figure 3 TGA of polyborosilazane fibre (NH_3 flow 100 $cm^3 min^{-1}$; heating rate 5 °C min^{-1}).

formation of gaseous species. The conversion of the polyborosilazane fibre into the inorganic compound is completed around 800 °C. The third region, around 1100 °C, may be due to evolution of hydrogen (Table I).

We have detected evolution of hydrogen by GC/MS at this temperature. The weight loss of TGA is inconsistent with the decrease of hydrogen by the elemental analysis. The reason might be either the experimental error of the elemental analysis or evolution of other gaseous species which we could not detect. However, evolution of hydrogen is the main reason of the weight loss.

The results of the elemental analyses of polyborosilazane, 800 °C NH_3-pyrolysed, 1500 °C nitrogen-annealed, 1800 °C nitrogen-annealed and 1500 °C nitrogen-pyrolysed (without ammonia pretreatment) fibres are shown in Table I. The Si/B atomic ratio is almost the same in the polymer as it is in its pyrolysed and annealed fibres. The 1500 °C nitrogen-pyrolysed fibre contains about 5 wt% carbon; however, the 1500 °C nitrogen-annealed fibre contains only 0.2 wt% carbon. The carbon content reflects the colour of the fibre. The 1500 °C nitrogen-pyrolysed fibre is black and ammonia pretreated fibres are white in colour. Ammonia pretreatment contributes to decreasing carbon content.

The infrared spectra of the 200, 400, 600 and 800 °C NH_3-pyrolysed polyborosilazane fibres are shown in Fig. 4. Upon pyrolysis, the absorption bands between 2800 and 3100 cm^{-1} (C–H) [10] in the fibre virtually disappear. These changes reflect the loss of carbon and hydrogen in the polymer fibre during the pyrolysis (Table I). The conversion of the polymer fibre into the inorganic compound is brought to completion about 800 °C. This result is in good agreement with that observed in TGA.

^{29}Si CP/MAS-NMR spectra of 1300 °C nitrogen-annealed Si–B–O–N and Si_3N_4 fibres are shown in Fig. 5. Si_3N_4 fibre shows a peak at − 46 p.p.m. assigned to amorphous Si_3N_4 [11]. Si–B–O–N fibre shows a main peak at − 46 p.p.m. Broad tails of the peak may correspond to resonance of some silicon oxynitride species at approximately − 50 and − 60 p.p.m.

Fig. 6 shows XRD patterns of 1500, 1700 and 1800 °C nitrogen-annealed Si–B–O–N fibres. XRD patterns of 1500 and 1700 °C nitrogen-annealed fibres are very broad and indicate the amorphous state. The XRD pattern of 1800 °C nitrogen-annealed fibre shows the crystalline α- and β-Si_3N_4. But BN cannot be observed.

The density of 1500 °C nitrogen-annealed Si–B–O–N fibre as measured using a density gradient column (2.40 g cm^{-3}) is about 15% lower than the density of 2.8–2.9 g cm^{-3} calculated using densities of SiO_2 glass, graphite and crystalline Si_3N_4, BN and SiC, which are the rule-of-mixture components. Rule-of-mixture components were calculated as reported [12] by assigning all oxygen to silicon as SiO_2, all boron to nitrogen as BN, then all nitrogen to silicon as Si_3N_4, then all silicon to carbon as SiC; excess carbon or silicon, if any, is considered to be in the elemental standard state. The gradient column density of 2.40 g cm^{-3} is similar to the helium pycnometry density of 2.38 g cm^{-3}. Nevertheless, methods of densifying to > 2.77 g cm^{-3} without compositional change or crystallization have been found. It is assumed that appreciable free volume is present in the ceramics. Free volume may result from loss of gases during pyrolysis (up to 800 °C). The average void diameter was calculated from the small-angle X-ray scattering results and found to be about 1.7 nm. This value is close to the value reported for other polymer-derived ceramic fibres [13]. The density of 1500 °C nitrogen-pyrolysed fibre (2.52 g cm^{-3}) was found to be about 5% higher than that of ammonia-pretreated fibre. Ammonia pretreatment will not only reduce carbon content but also generate free volume in the ceramics. The reason why ammonia-pretreated fibre has a lower density than that of ammonia-untreated fibre is not clear, but a similar phenomenon was reported for Si–N–O fibre [5].

TABLE I Elemental analysis of polyborosilazane and pyrolysed fibres

Sample	Compositions (wt%)					
	Si	N	B	O	C	H
Polyborsilazane fibre	46.00	24.70	6.30	10.30	6.20	6.50
200 °C NH_3-pyrolysed fibre	47.60	25.00	6.90	11.30	3.20	6.00
800 °C NH_3-pyrolysed fibre	46.30	33.90	7.10	11.40	0.20	1.10
1500 °C N_2-annealed fibre	46.70	33.20	7.20	11.80	0.20	0.90
1800 °C N_2-annealed fibre	49.70	42.50	7.30	0.30	0.20	ND
1500 °C N_2-pyrolysed fibre (without NH_3 pretreatment)	48.20	28.70	7.10	10.40	4.80	0.80

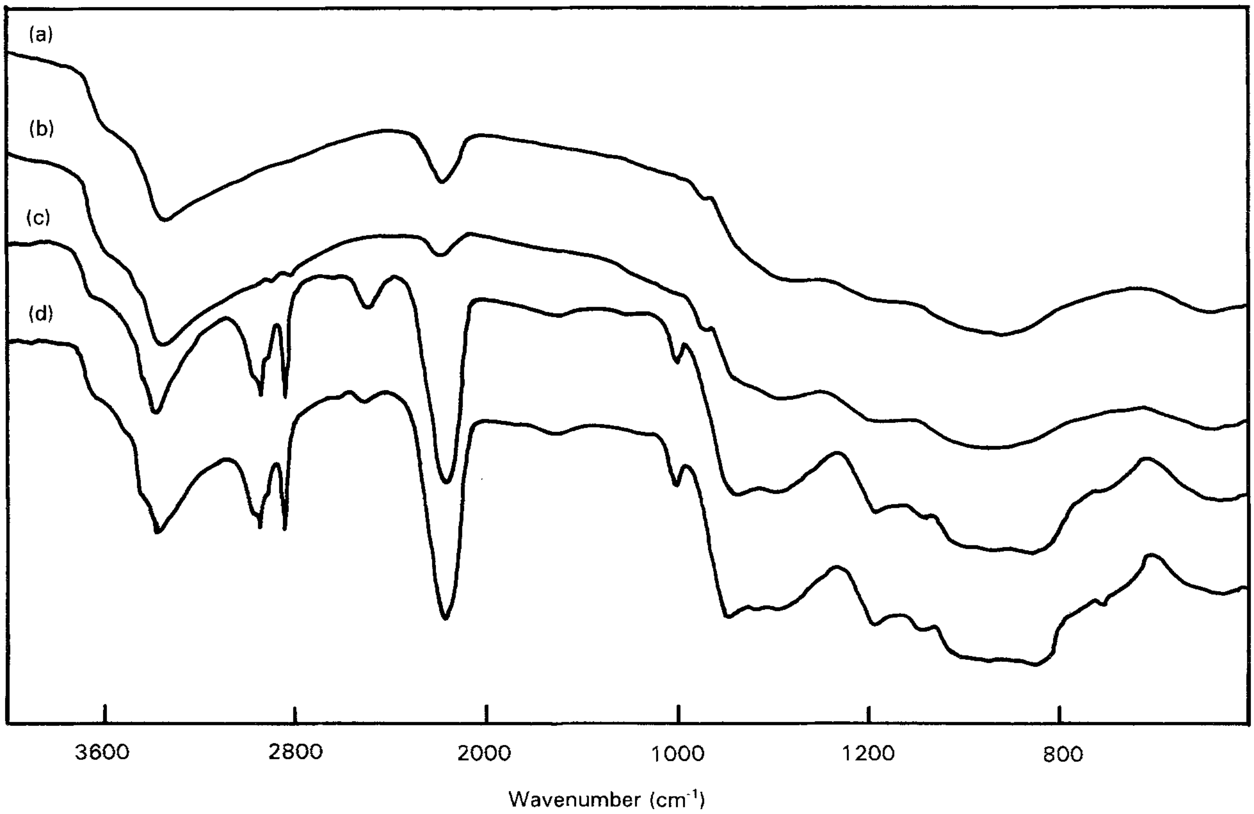

Figure 4 FT–IR spectra of (a) 800 °C, (b) 600 °C, (c) 400 °C and (d) 200 °C NH_3-pyrolysed polyborosilazane fibres.

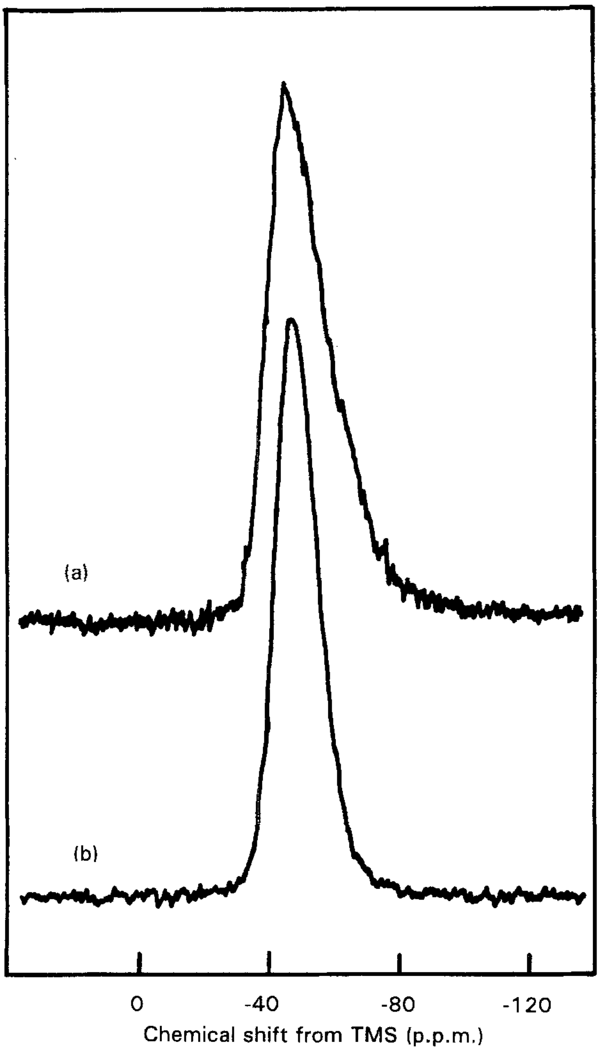

Figure 5 ^{29}Si CP/MAS–NMR spectra of 1300 °C nitrogen-annealed (a) Si–B–O–N fibre and (b) Si_3N_4 fibre.

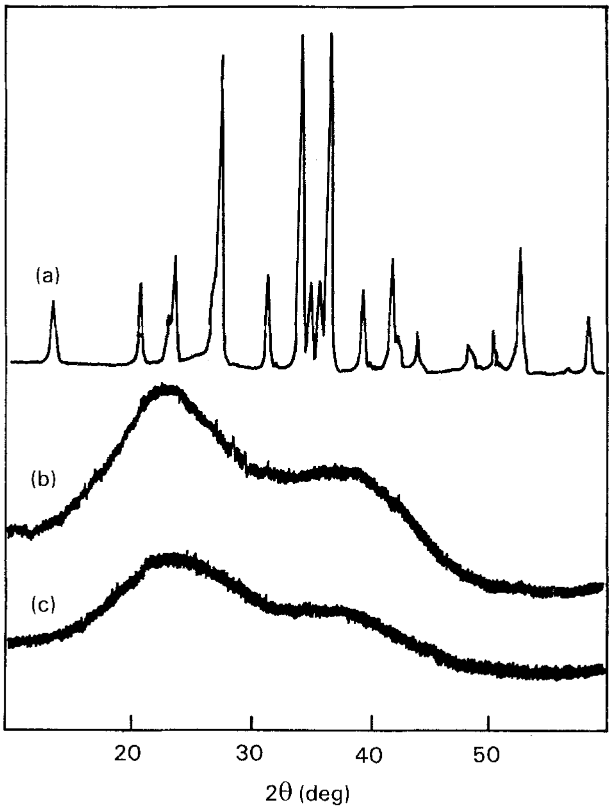

Figure 6 XRD patterns of (a) 1800 °C, (b) 1700 °C and (c) 1500 °C nitrogen-annealed Si–B–O–N fibres.

Fig. 7 shows the tensile strength of the Si–B–O–N fibres obtained by pyrolysing polyborosilazane fibre in the temperature range 200–1200 °C in NH_3 followed by annealing at 1500 °C in nitrogen. The maximum value of tensile strength is obtained from 800 °C NH_3-pyrolysed fibre. The decrease of the mechanical

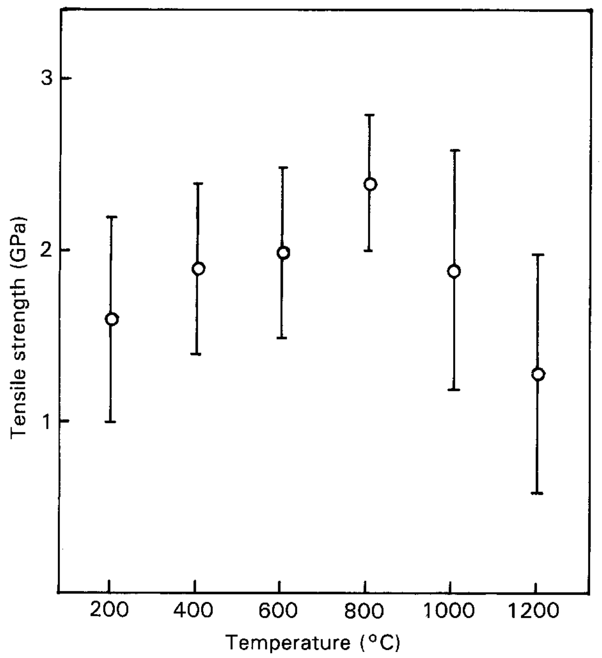

Figure 7 Tensile strength of Si–B–O–N fibre as a function of pyrolysing temperature in NH_3 (subsequently annealed at 1500 °C in nitrogen).

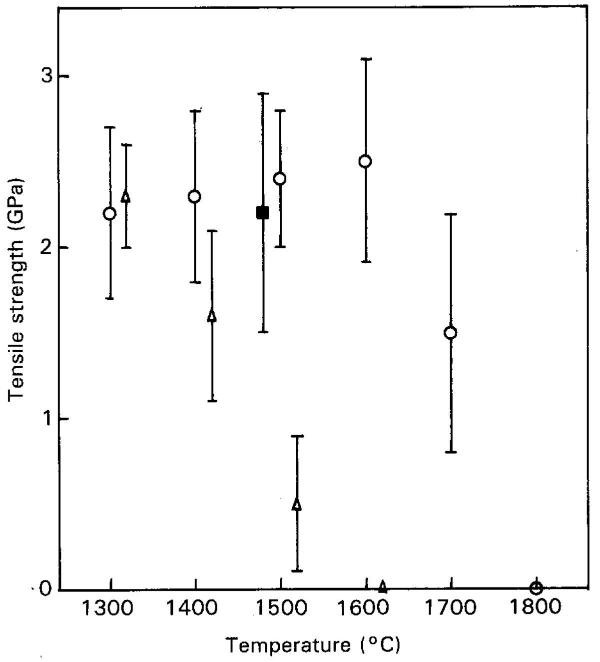

Figure 8 Tensile strength of (○) Si–B–O–N fibre and (△) Si_3N_4 fibre as a function of annealing temperature in nitrogen (previously pyrolysed at 800 °C in NH_3) and (■) of 1500 °C nitrogen-pyrolysed fibre.

properties is considered to be due to the crystallization of amorphous Si_3N_4. Pyrolysing polyborosilazane fibre at > 1000 °C in anhydrous ammonia may accelerate the crystallization. Fig. 8 shows the tensile strength of the Si–B–O–N fibres obtained by annealing of the 800 °C NH_3-pyrolysed fibre in the temperature range 1300–1800 °C in nitrogen. For reference, the tensile strength of Si_3N_4 fibres obtained from the 800 °C NH_3-pyrolysed perhydropolysilazane fibre and 1500 °C nitrogen-pyrolysed fibre are shown together in this figure. Fig. 9 shows the elastic modulus of these fibres. The tensile strength of these fibres increases with heat-treatment temperature. The Si–B–O–N fibre and Si_3N_4 fibre have maximum values at 1600 and 1300 °C, respectively. The 1800 °C nitrogen-annealed Si–B–O–N fibre and 1600 °C nitrogen-annealed Si_3N_4 fibre were too brittle to measure. The degradation of the tensile strength may be due to the crystallization of amorphous Si_3N_4. This result is consistent with the XRD results. The characteristic feature of Si–B–O–N fibre derived from polyborosilazane is that the annealing temperature that gives the maximum mechanical property is shifted to 300 °C higher than that of Si_3N_4 fibre. Boron in Si–B–O–N fibre is thought to retard the crystallization of amorphous Si_3N_4. Amorphous BN may inhibit

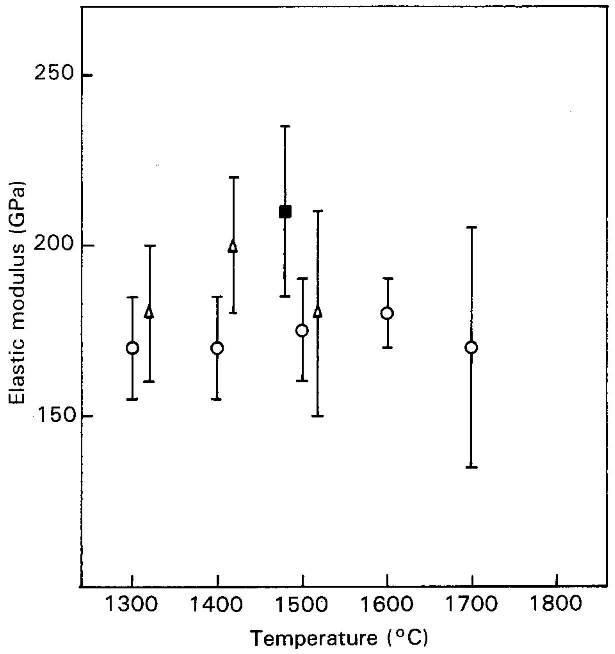

Figure 9 Elastic modulus of (○) Si–B–O–N and (△) Si_3N_4 fibre as a function of annealing temperature in nitrogen (previously pyrolysed at 800 °C in NH_3) and (■) of 1500 °C nitrogen-pyrolysed fibre.

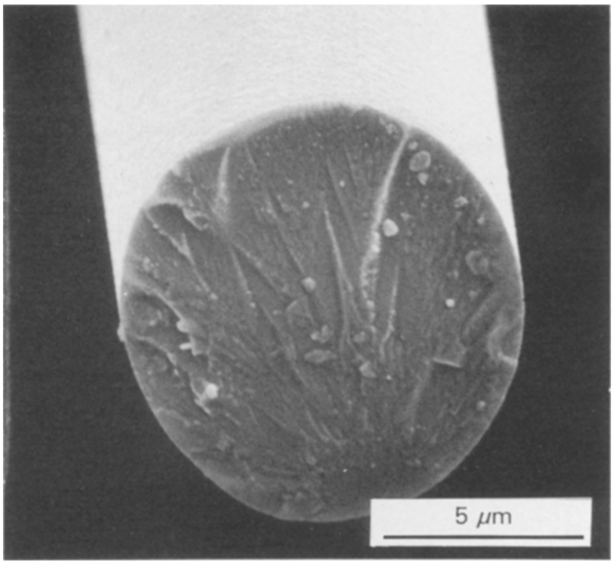

Figure 10 Fracture surface of 1500 °C nitrogen-annealed Si–B–O–N fibre.

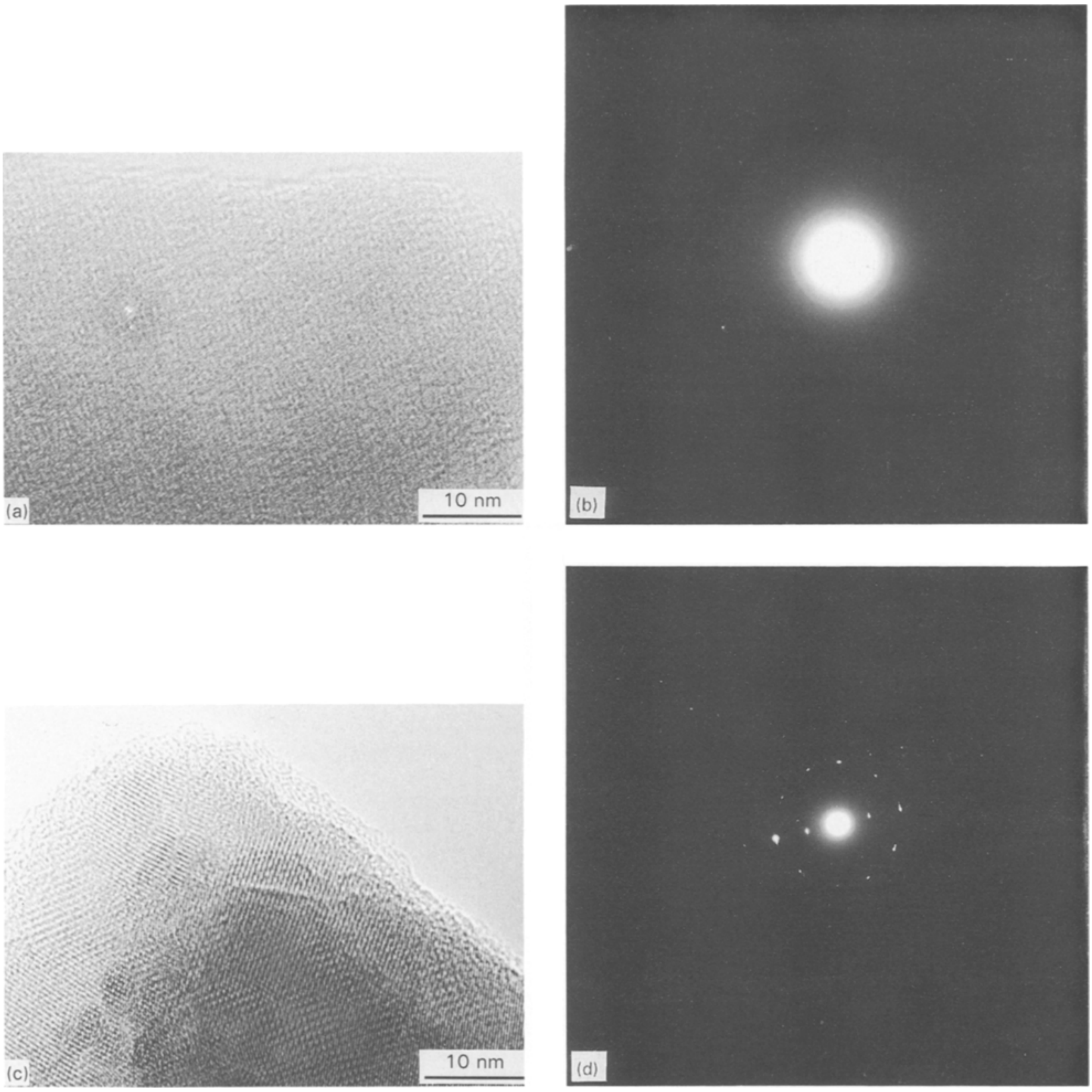

Figure 11 (a, c) TEM bright-field micrographs and (b, d) electron diffraction patterns of (a, b) Si–B–O–N fibre and (c, d) Si_3N_4 fibre (1500 °C nitrogen-annealed).

the material transport that occurs during the amorphous-to-crystalline transformation. The 1500 °C nitrogen-pyrolysed fibre has higher elastic modulus than that of 1500 °C nitrogen-annealed Si–B–O–N fibre. This reflects the density of these fibres.

The Si–B–O–N fibres exhibit the classical tensile fracture behaviour of brittle materials and follow the Griffith equation for tensile strength. From SEM fractography, the predominant strength-limiting critical flaws that are surrounded by a fracture mirror are internal defects and spinning-induced or mechanical damage-induced surface defects. The fracture mirror is surrounded by a region of mist and hackle (Fig. 10).

High-resolution electron micrographs of 1500 °C nitrogen-annealed Si–B–O–N fibre and Si_3N_4 fibre are shown in Fig. 11a and c, respectively. In Fig. 11b and d, the lattice image and electron diffraction pattern corresponding to α-Si_3N_4 are observed in all areas and its size is 15–20 nm. The Si_3N_4 fibre is in the α-Si_3N_4 microcrystalline state. No lattice image can be observed in the Si–B–O–N fibre (Fig. 11a). The Si–B–O–N fibre is considered to be in the amorphous state consisting of silicon, boron, nitrogen and oxygen. It is clear from these results that the Si–B–O–N fibre retains the amorphous state up to 1500 °C but that the Si_3N_4 fibre is a uniform dispersion of α-Si_3N_4 microcrystallites at this temperature. These crystallinities reflect the tensile strength of 1500 °C nitrogen-annealed Si–B–O–N fibre and Si_3N_4 fibre.

4. Conclusion

Polyborosilazane polymer has been synthesized, dry spun, and pyrolysed to produce Si–B–O–N ceramic fibre with high tensile strength and excellent thermal stability. Pyrolysis of polyborosilazane fibre is completed around 800 °C. The annealing temperature that gives the maximum mechanical properties in producing Si–B–O–N fibre (1600 °C) has shifted to a higher temperature than that of Si_3N_4 fibre (1300 °C). This shift may be attributed to the retention of the amorphous state in the Si–B–O–N fibre at the higher temperature in comparison with that of Si_3N_4 fibre. Density and porosity measurements show that the ceramic fibre is not fully dense, but contains ≈ 15 vol % fine porosity or free volume. Fibres exhibit classical brittle failure. Tensile strength up to 2.5 GPa and elastic modulus up to 180 GPa have been obtained for these fibres that range from 8–12 μm in diameter.

Pyrolysis of polyborosilazane fibre in NH_3 reduces the carbon content in the ceramics and gives a ceramic fibre white in colour. Without ammonia pretreatment, black Si–B–O–N fibre containing about 5 wt % carbon and having a density of $2.52\ g\ cm^{-3}$, can be produced. This ammonia-untreated fibre has higher elastic modulus than that of ammonia-pretreated fibre. The chemical and mechanical properties of Si–B–O–N fibre are affected by the pyrolysis conditions.

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