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Conversion mechanism of polyborosilazane into silicon nitride-based ceramics

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The pyrolysis of polyborosilazane in anhydrous ammonia has been studied up to 1200 °C through the analysis of the gas phase and the characterization of the solid residue by elemental analyses, thermogravimetric analysis, Fourier transform-infrared analysis, X-ray photoelectron spectroscopy, X-ray diffraction and ^{29}Si cross-polarization/magic angle spinning-nuclear magnetic resonance. The pyrolysis mechanism involves four main steps: (1) below 400 °C, an evaporation of residual solvent and reaction with ammonia leading to an increase of nitrogen content; (2) from 400–600 °C, reaction with ammonia leading to an increase of nitrogen content and formation of preceramic polymer–ceramics intermediate solid with a three-dimensional network along with evolution of gaseous species; (3) from 600–800 °C, completion of loss of C–H functionalities and progress of formation of an amorphous ceramic, accompanied by evolution of CH_4 and H_2; (4) from 800–1200 °C, completion of formation of an amorphous hydrogenated Si–B–O–N solid composed of $SiN_{4-x}O_x (x=0,1,2,3)$ and $BN_{3-y}O_y$ $(y=0, 1)$, along with evolution of H_2

1. Introduction

There has been much interest in the use of organometallic polymers as precursors to high-performance ceramics such as silicon nitride [1–5] and silicon carbide [6–10]. Some of the potential advantages in the preparation of ceramic materials from these precursors include: (1) compositional homogeneity in the final products, (2) high-purity ceramic products with uniform microstructure, amorphous to microcrystalline, (3) the preparation of refractory ceramics at relatively low temperatures, and (4) the ability to form fibres, coatings and near-net-shape structures [11].

We have reported the production of high ceramic yield perhydropolysilazane which is an excellent precursor for high-purity silicon nitride fibres [1, 12–14]. Yokoyama *et al.* [15] suggested that this amorphous silicon nitride has either α-or β-Si_3N_4-like structures or a mixture of them. The conversion mechanism of perhydropolysilazane into ceramics has also been reported [16]. The pyrolysis mechanism involves three main steps. (1) Below 400 °C, evaporation of residual solvent is the main reason for the weight loss. The structure of the polymer does not change markedly. (2) From 400–600 °C, ammonia reacts with Si–H bonds in the polymer to build an Si–N three-dimensional network. The solid with polymer-like structure converts into a solid with Si_3N_4-like structure. (3) From 600–1000 °C, formation of hydrogenated solid is completed.

A novel polyborosilazane has been derived from perhydropolysilazane and trimethyl borate [17]. This polyborosilazane can be converted into amorphous Si–B–O–N ceramics without a curing process. However, the pyrolysis mechanism is not well known. The conversion mechanism of polyborosilazane into ceramics should be understood in order to prepare ceamic materials with desirable properties. This paper describes the conversion mechanism of polyborosilazane into ceramics in anhydrous ammonia.

2. Experimental procedure

2.1. Preceramic polymer synthesis

The polyborosilazane used in this study was obtained from perhydropolysilazane and trimethyl borate. Perhydropolysilazane was synthesized by ammonolysis of dichlorosilane-pyridine adduct followed by heat treatment at 160 °C in pyridine with ammonia. Perhydropolysilazane and trimethyl borate were mixed with pyridine to form a homogeneous solution (Si/B = 3 atomic ratio), which 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 (polyborosilazane, $M_n \approx 2400$ Da).

2.2. Pyrolysis

Prior to pyrolysis, the polymer was ground to a powder with a mean particle size of 4–8μm in a nitrogen atmosphere. Polymer samples were pyrolysed in a tube furnace (Nishimura Kogyo T-12S10). Initially, the furnace tube was flushed with anhydrous ammonia at room temperature. The polymer was pyrolysed by heating from room temperature to given temperatures

0022–2461

(ranging from 200–1200 °C) at a heating rate of 10 °C min^{-1}, holding at given temperatures for an additional 5 min, and finally furnace cooling to room temperature. All heating was completed under flowing anhydrous ammonia (1 nl min^{-1}).

2.3. Characterization

The analysis of the gaseous species resulting from the pyrolysis (200, 400, 600, 800 and 1000 °C) were performed either by gas chromatography (GC) (Hewlett Packard 5890A) or first collected in cooled traps (– 100 °C) and subsequently identified by gas chromatography/mass spectroscopy (GC/MS) (Jeol JMS-DS303).

Thermogravimetric analysis (TGA) was performed on the polymer up to 1000 °C at heating rate of 10 °C min^{-1} under flowing anhydrous ammonia (Rigaku TG8110D).

X-ray diffraction measurements were performed on the polymer and the pyrolysed samples using Cu$K\alpha$ radiation using an automated powder diffractometer equipped with a monochromater (Rigaku RINT 1400).

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

X-ray photoelectron spectroscopy (XPS) spectra were recorded with Mg$K\alpha$ (1253.6 eV) as the excitation source (Kratos XSAM-800). The analyses were performed, under a residual pressure less than 6.65×10^{-7} Pa, on the polymer and the pyrolysed samples. The sample was cleaned by argon ion bombardment (20 mA intensity, 3.5 kV energy) prior to XPS analysis. The XPS data recorded on the samples were calibrated utilizing the C ls binding energy in carbon (284.6 eV as a standard).

Infrared (IR) spectra were recorded on KBr pellets containing powder samples (Jeol JIR-5500). Elemental analyses for silicon, boron, nitrogen, carbon, oxygen and hydrogen were obtained for the polymer and the pyrolysed samples.

3. Results and discussion

3.1. Analysis of gaseous species

Pyrolysis of the polymer in NH_3 was examined by analysis of the volatile gases by GC. Fig. 1 shows the amount of H_2 and CH_4 as a function of temperature. Quantitative estimates of the amount of the gases are made by integration of the GC peak. H_2 is detected from all pyrolysis conditions but shows a peak at 400 °C; it is probably produced by the dissociation of Si–H and N–H functionalities during pyrolysis of polyborosilazane. CH_4 is detected from 400–800 °C. At 600 °C, a large amount of CH_4 is detected. CH_4 may result from abstraction of either hydrogen by a methyl radical or a CH_3 group by a hydrogen radical. Preliminary ESR experiments revealed that the polymer contains no detectable spin density, but the 600 °C pyrolysed sample contains a free spin density of 2×10^{16} spins g^{-1}, which increased to 6×10^{17} spins g^{-1} in 1200 °C pyrolysed sample. Another radical source could be NH_3 which dissociates to $H_2N\cdot$ and $H\cdot$ [18]. The detection of methane corroborates the participation of radical species in the pyrolysis of polyborosilazane.

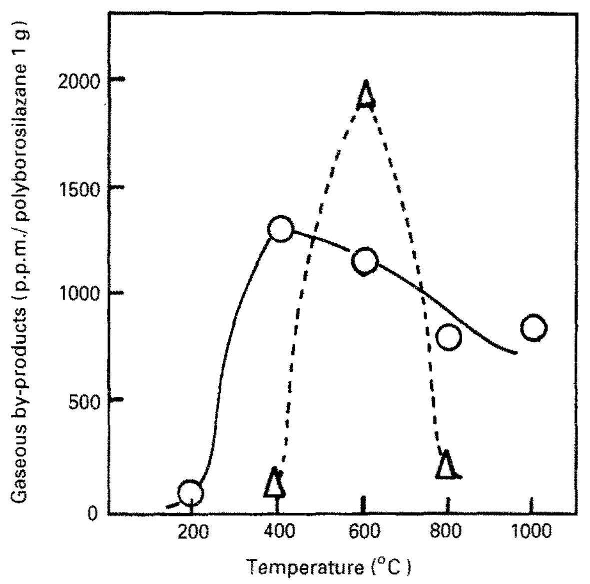

Figure 1 Gaseous species obtained from the pyrolysis of polyborosilazane in NH_3 as a function of temperature; (○) H_2, (△) CH_4.

Because NH_3 interfered with GC/MS measurement, GC/MS was performed for the volatile gases during pyrolysis in nitrogen. This information should assist in understanding the volatile gases during pyrolysis in NH_3. At 200 °C, a large amount of xylene, which is the residual solvent, and small amount of CH_3OH and low molecular weight silazane compound are observed. CH_3OH may be produced by elimination of the pendant methoxy groups during pyrolysis of the polymer. Fig. 2 shows the chromatogram and mass spectra recorded for the volatile gases at 400 °C, Borazine, trimethoxysilane, and CH_3OH are detected. Borazine is produced by loss of side groups of the polymer. Trimethoxysilane may result from a reaction of the polymer with either CH_3OH or methoxy radical. Above 600 °C, no volatile gas is observed because H_2 and CH_4 cannot be detected by GC/MS.

From the analysis of the volatile gas species, below 400 °C, the residual solvent is found to contribute significantly to the gas evolution. In the 400–600 °C range, where decomposition of the polymer mainly occurs, H_2, CH_4, borazine, trimethoxysilane, and CH_3OH are evolved. The gas evolved from 600–800 °C is composed of CH_4 and H_2. Above 800 °C, H_2 contributes mainly to the gas evolution. Decomposition of the polymer is characterized by decomposition of the side groups and chain scission.

The evolution temperature and the amount of low molecular weight silazane compounds from the polyborosilazane are quite different from those from perhydropolysilazane [16]. From polyborosilazane, a small amount of low molecular weight silazane compound can be detected only at 200 °C. From perhydropolysilazane, low molecular weight silazane

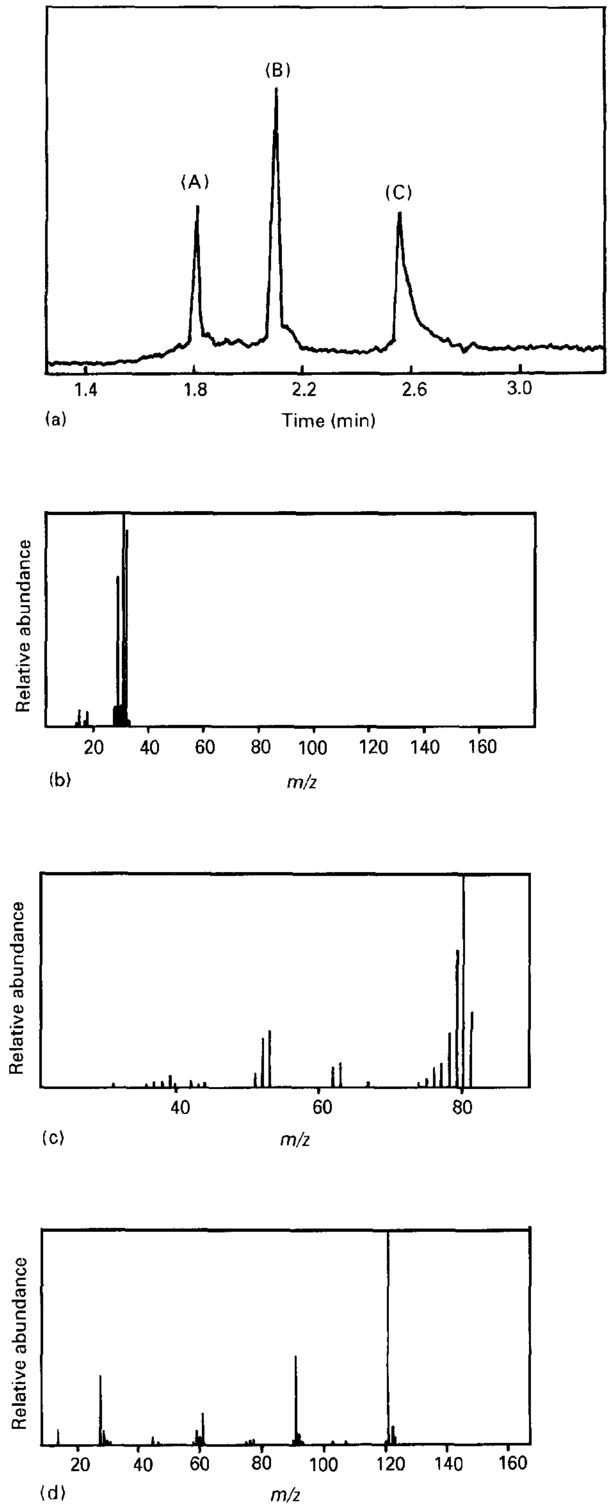

Figure 2 (a) Chromatograms of the gaseous species resulting from the pyrolysis of polyborosilazane at 400 °C. (b–d) Mass spectra of (b) 1, CH_3OH, (c) 2, borazine, and (d) 3, trimethoxysilane (m = ion mass, z = ion charge).

compounds contribute mainly to the gas evolution above 400 °C. The difference is attributed to the amount of the functional groups in the polymers. Presumably, low molecular weight silazane compounds in polyborosilazane react with functional groups to form a cross-linked structure. This reaction suppresses the evolution of low molecular weight silazane compounds from polyborosilazane above 400 °C.

3.2. Preceramic polymer–ceramics transition

The results of the elemental analyses performed on polymer and pyrolysed samples are given in Table I. The empirical ratios of polymer and pyrolysed samples are $SiB_{0.36}N_{0.99}O_{0.42}C_{0.40}H_{4.86}$, $SiB_{0.35}N_{0.93}O_{0.43}C_{0.19}H_{4.02}$(200 °C), $SiB_{0.37}N_{1.16}O_{0.43}C_{0.15}H_{1.40}$ (400 °C), $SiB_{0.37}N_{1.32}O_{0.40}C_{0.07}H_{1.30}$(600 °C) and $SiB_{0.39}N_{1.22}O_{0.40}C_{0.04}H_{1.15}$(800 °C), $SiB_{0.38}N_{1.21}O_{0.38}C_{0.03}H_{0.68}$(1200 °C), respectively. As can be seen from these results the Si/B atomic ratio is almost the same in the polymer as it is in its pyrolysed samples. From 200–600 °C, the nitrogen content increases. The value of Si/N in the 600 °C pyrolysed sample is revealed to be close to that of silicon nitride. The oxygen and boron contents are almost the same in the polymer as they are in its pyrolysed samples. Analysis of the gaseous species shows an evolution of oxygen-containing gases (CH_3OH and trimethoxysilane) and boron-containing gas (borazine) during the pyrolysis. However, elemental analyses reveal that the amount of those gases is small. The carbon content decreases during the pyrolysis. The gaseous species which are formed during the pyrolysis should be mainly carbon-based molecules. Several reports described the use of NH_3 during the pyrolysis of preceramic polymers to reduce carbon, and the reaction mechanisms have been proposed [18–21]. The use of NH_3 during the pyrolysis of polyborosilazane results in nitridation and elimination of carbon. Presumably, elimination of carbon occurs by the attack of the hydrogen radical on carbon.

The TGA curve of polyborosilazane in an NH_3 atmosphere is shown in Fig. 3. Three regions are apparent in the TGA curve. The first region, below 400 °C, shows a weight loss of nearly 12%. Analysis of gaseous species and results of elemental analyses suggest that the weight loss in the first region results mainly from the loss of residual solvent. The second region, from 400–600 °C, shows a weight gain of 3%. The increase of nitrogen content suggests the nitridation. The nitridation of polyborosilazane will proceed by dehydrogenation of Si–H bonds in the polymer with NH_3. Weight gain in TGA was not detected for polyborosilazane in a previous report [17]. The deficiency of nitrogen for polyborosilazane in this study is due to the conditions of synthesis of the starting perhydropolysilazane. Analysis of the gaseous species indicates that the decomposition of the polymer mainly occurs in this second region. The weight loss due to the decomposition is compensated with the weight gain of the nitridation. The third region, from 600–1000 °C, shows a slight weight loss of 2%. Elemental analyses indicate a slight loss of nitrogen and carbon. Analysis of the gaseous species at 800 °C shows an evolution of CH_4, but low molecular weight silazane compounds cannot be detected. The ceramic yield for the white powder obtained at 1000 °C is about 90%.

The conversion from polymer to ceramics was investigated by the changes in i.r. spectra of the solid samples with increased pyrolysis temperature (Fig. 4). Absorptions of the polymer sample at 3400 and 1200 cm^{-1} indicate the presence of N–H groups, at

TABLE I Elemental analyses of polyborosilazane and its pyrolysed samples

Sample	Composition (wt %)					
	Si	N	B	O	C	H
Polyborosilazane	44.90	22.30	6.40	10.90	7.70	7.80
200 °C pyrolysed sample	48.10	22.70	6.60	11.80	3.90	6.90
400 °C pyrolysed sample	48.00	27.80	7.00	11.70	3.10	2.40
600 °C pyrolysed sample	47.40	31.30	6.90	10.70	1.50	2.20
800 °C pyrolysed sample	48.80	29.80	7.40	11.10	0.80	2.00
1200 °C pyrolysed sample	49.70	30.10	7.50	10.80	0.70	1.20

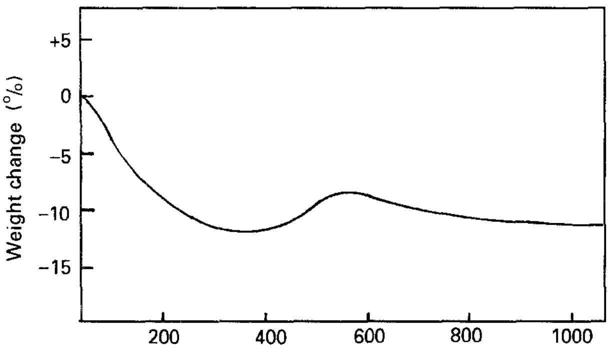

Figure 3 TGA of polyborosilazane (ammonia flow 100 cm^3 min^{-1}; heating rate 10 °C min^{-1}.

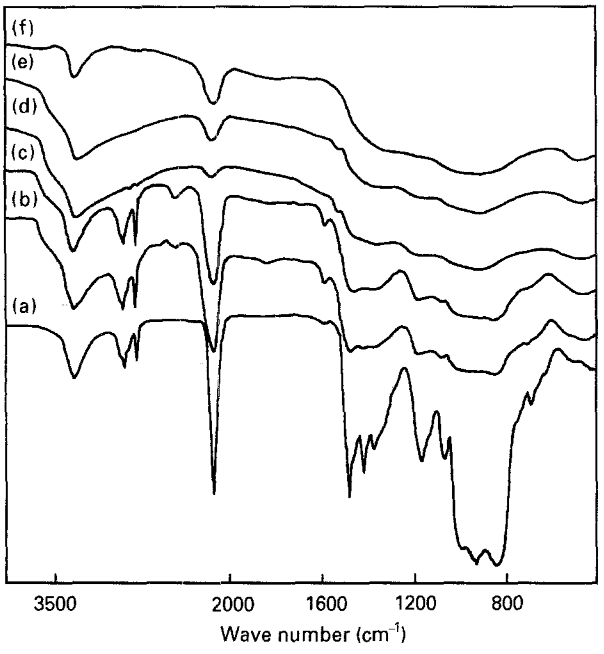

Figure 4 FT-IR spectra of (a) untreated, (b) 200 °C pyrolysed, (c) 400 °C pyrolysed, (d) 600 °C pyrolysed, (e) 800 °C pyrolysed, and (f) 1200 °C pyrolysed polyborosilazane.

2800 cm^{-1} are ascribed to C–H bonds, at 1480 cm^{-1} to B–N bonds, at 1420 and 1380 cm^{-1} to B–O bonds, at 1100 cm^{-1} to Si–O bonds, and at 2100 cm^{-1} indicate the presence of Si–H groups, whereas the strong broad band at 800–1000 cm^{-1} indicates Si–N–Si moieties [17]. The polymer consists mainly of structural units of $HSiN_3$, H_2SiN_2, H_3SiN, $HSi(OCH_3)N_2$, $NB(OCH_3)_2$, and $NB(OCH_3)N$ [17]. On heating polyborosilazane to 600 °C, there is a decrease in the intensity of C–H bonds (2800 cm^{-1}) and of Si–H bonds (2100 cm^{-1}). The decrease in the intensity of Si–H bonds is due to the reaction of Si–H bonds with NH_3. The spectrum of the 800 °C pyrolysed sample indicates that most of the C–H functionalities of the polymer are lost on heating to 800 °C. The band at 2100 cm^{-1} increases in intensity with increased pyrolysis temperature from 600–800 °C. The increase in the intensity of the Si–H bonds may be due to the release of NH_3. From the elemental analyses, a slight decrease of the nitrogen content of the 800 °C pyrolysed sample compared with that of the 600 °C pyrolysed sample suggests this mechanism. The band at 2500 cm^{-1} in the 200 and 400 °C pyrolysed samples may be attributed to B–H bonds which may be formed by abstraction of hydrogen by boron radical. The boron radical may be produced by elimination of pendant methoxy groups. From analysis of gaseous species at 200 and 400 °C, evolution of methoxy-containing gases (CH_3OH and trimethoxysilane) suggests the elimination of methoxy groups. This B–H bond disappears at 600 °C, presumably by forming B–N bonds. The spectrum of the 1200 °C pyrolysed sample still exhibits the presence of N–H, Si–H, B–N, B–O and Si–N bonds. The absence of resolved features in the 800–1000 cm^{-1} band has been attributed to the amorphous nature of silicon nitride [22, 23]. This spectrum indicates that the 1200 °C pyrolysed sample is an amorphous hydrogenated silicon nitride containing B–N and B–O bonds.

The conversion of polyborosilazane was also monitored by the changes in the ^{29}Si CP/MAS–NMR spectra as a function of temperature (Fig. 5). The polymer sample exhibits two peaks, attributed to $HSiN_3/H_2SiN_2$ (-37 p.p.m). and H_3SiN (-51 p.p.m.). On heating to 400 °C, the intensity of the peak at -51 p.p.m.) assigned to SiH_3N units, decreases. At 600 °C, the peak due to $HSiN_3/H_2SiN_2$ (-37 p.p.m.) broadens and shifts to -41 p.p.m. These phenomena and the results of elemental analyses and TGA, indicate that up to 600 °C, the reaction between NH_3 and Si–H bonds in the polymer leads to the building of an Si–N three-dimensional network. But the solid obtained in this temperature range is thought to be a preceramic polymer–ceramics intermediate. From 600–1200 °C, the position of the broad peak shifts towards a value corresponding to amorphous Si_3N_4 phase (-46 p.p.m) [24]. From 600–1200 °C, the

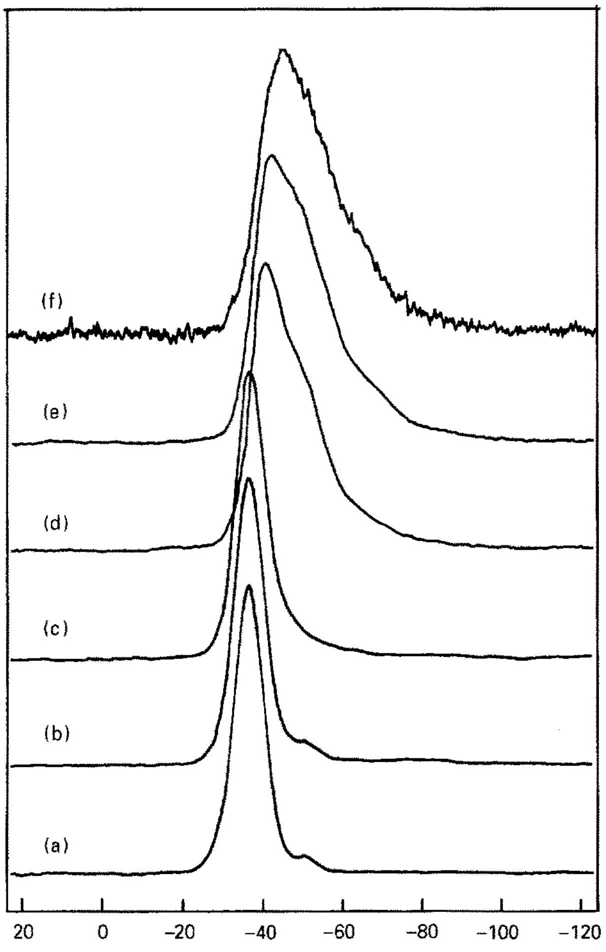

Figure 5 ^{29}Si CP/MAS-NMR spectra of (a) untreated, (b) 200 °C pyrolysed, (c) 400 °C pyrolysed, (d) 600 °C pyrolysed, (e) 800 °C pyrolysed, and (f) 1200 °C pyrolysed polyborosilazane.

formation of an amorphous hydrogenated solid is completed. The broad tail of the peak becomes apparent at 600 °C and may correspond to resonance of some silicon oxynitride species [2]. The number of Si–O bonds increases from 400–600 °C. The oxygen content of the 600 °C pyrolysed sample is close to that of the polymer. The increase of Si–O linkages cannot be explained by the oxygen accumulated during the pyrolysis step or the measurement procedure. Si–O bonds result from intermolecular or intramolecular cross-linking. The formation seems to follow Equation 1 or 2

$$\text{Si-H} + \text{Si-OCH}_3 = \text{Si-O-Si} + \text{CH}_4 \quad (1)$$

$$\text{Si-H} + \text{B-OCH}_3 = \text{Si-O-B} + \text{CH}_4 \quad (2)$$

The ceramic obtained from polyborosilazane is composed of a three-dimensional network of Si–O–Si and Si–O–B as well as Si–N–Si. The deconvolution of the spectrum of the 1200 °C pyrolysed sample reveals that the peak is composed of four components centred at − 46, − 50, − 60, and − 80 p.p.m. Three peaks centred at − 50, − 60, and − 80 p.p.m. are due to the presence of SiN_3O, SiN_2O_2, and $SiNO_3$, respectively. However, there is no peak around − 100 p.p.m. which is due to SiO_4 [25].

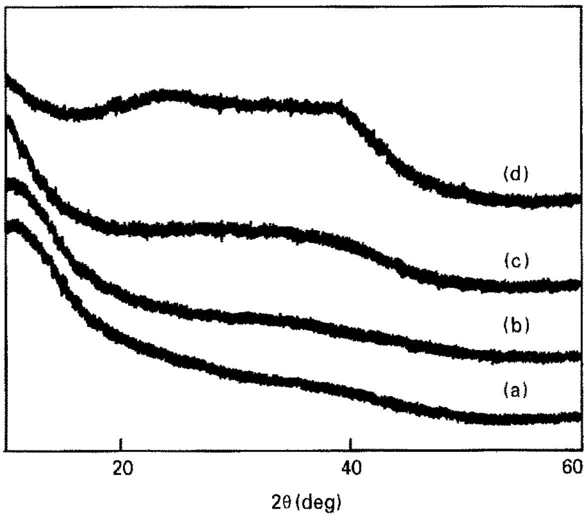

Figure 6 X-ray powder diffraction patterns of (a) untreated, (b) 400 °C pyrolysed, (c) 600 °C pyrolysed, and (d) 1200 °C pyrolysed polyborosilazane.

Fig. 6 shows the X-ray diffraction patterns of the polymer and the pyrolysed samples. In the 600 and 1200 °C pyrolysed samples, a very broad peak at about $2\theta = 20°–40°$ is observed. This broad peak is attributed to the amorphous nature of silicon nitride, which is not apparent in the polymer and 400 °C pyrolysed sample. This result suggests that the Si–N structure is built from 400–600 °C and the formation is completed from 600–1200 °C.

The organic–ceramic transition of the polymer is also monitored by XPS. All samples are made of silicon, boron, nitrogen, and oxygen. A semiquantitative analysis of the chemical bonds is possible by using the deconvolution of the Si 2p and B 1s peaks of the high-resolution spectra. The Si 2p and B 1s peaks of the 200 °C pyrolysed sample are illustrated in Fig. 7. The Si 2p peak can be analysed on the basis of three components: the first at 101.4 eV is assigned to Si–N bonds [26]; the second at 103.5 eV is assigned to Si–O bonds [27]; and the third at an intermediate energy of 102.1 eV could be assigned to silicon atoms bound to both nitrogen and oxygen. The B 1s peak consists of four components. The first, at about 189.5 eV, is assigned to the BN_3 component [28], whereas the second at 194.2 eV is assigned to the BO_3 component. The third at 191.5 eV and the fourth component at 193.0 eV are observed between those corresponding to BN_3 and BO_3 components. These are assigned to ternary species (BN_2O, BNO_2). A semiquantitative analysis of the chemical bonds in the materials at different steps of the pyrolysis is given in Table II. It appears that there are large amounts of Si (N, O) and BN_2O in polyborosilazane. From 200–400 °C, components of Si (N, O) and BN_2O decrease and components of SiN and BN_3 increase. This result is in good agreement with the result of elemental analyses that the nitrogen content increases above 200 °C. The pyrolytic residue at 1200 °C still contains a high percentage of oxygen. Ceramics from polyborosilazane is mainly made of SiN and BN_3.

TABLE II Semiquantitative XPS analysis of the chemical bonds (%) at different steps of pyrolysis of polyborosilazane

Sample	Si 2P peak			B 1s peak			
	Si–N	Si(N, O)	Si–O	BN_3	BN_2O	BNO_2	BO_3
Polyborosilazane	15	65	20	15	40	30	15
200 °C pyrolysed sample	20	65	15	15	45	30	10
400 °C pyrolysed sample	70	20	10	60	15	15	10
600 °C pyrolysed sample	75	20	5	65	20	10	5
800 °C pyrolysed sample	80	15	5	70	20	10	0
1200 °C pyrolysed sample	80	15	5	80	20	0	0

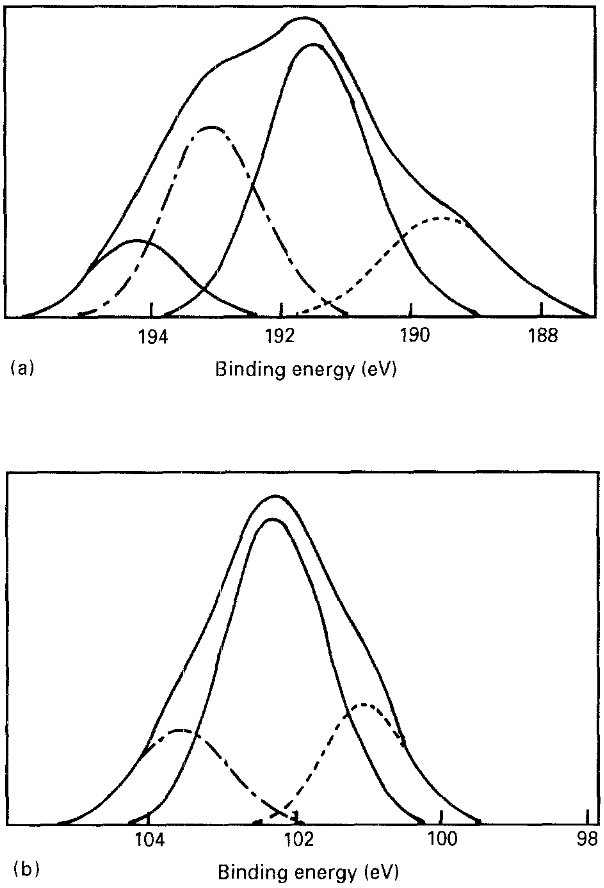

Figure 7 XPS spectra of 200 °C pyrolysed polyborosilazane: (a)B'1s, (b) Si'2p.

By considering the results of FT–IR, ^{29}Si CP/MAS–NMR and XPS measurements, the ceramic obtained at 1200 °C is made of $SiN_{4-x}O_x$ ($x = 0, 1, 2, 3$) and $BN_{3-y}O_y$ ($y = 0, 1$). Each unit is cross-linked through a three-dimensional network of Si–N–Si, Si–N–B, Si–O–Si, Si–O–B, B–N–B, and B–O–B.

4. Conclusion

Pyrolysis of polyborosilazane in anhydrous ammonia has been studied through the analysis of the gas phase and the characterization of the solid residue by elemental analyses, TGA, FT–IR, XRD, ^{29}Si CP/MAS–NMR, and XPS. The pyrolysis mechanism involves four main steps. (1) Below 400 °C, residual solvent contributes significantly to the gas evolution. SiH_3N units in the polymer decreases and the nitrogen content increases via the reaction between Si–H bonds and NH_3. The formation of B–H bonds occurs, which may be due to elimination of pendant methoxy groups. Silicon and boron environments change to nitrogen-rich conditions. (2) In the 400–600 °C range, nitridation and the main polymer–ceramic transition take place. The polymer–ceramic transition is characterized by decomposition of the side groups and chain scission, along with the formation of a three-dimensional network of Si–O–Si and Si–O–B as well as Si–N–Si and evolution of gaseous species. (3) From 600–800 °C, most of the C–H functionalities are lost and the formation of the three-dimensional network continues, accompanied by evolution of CH_4 and H_2. (4) Above 800 °C, consolidation of the Si_3N_4 network proceeds, along with evolution of H_2. The ceramic obtained at 1200 °C is an amorphous hydrogenated solid composed of $SiN_{4-x}O_x$ ($x = 0, 1, 2, 3$) and $BN_{3-y}O_y$ ($y = 0, 1$).

The pyrolysis mechanism of polyborosilazane is more complicated than that of perhydropolysilazane, because polyborosilazane contains OCH_3 functionalities in addition to Si–H and N–H. The information obtained from this study should assist in the preparation of a continuous fibre with desirable physical properties.

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