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Synthesis of α-Silicon Nitride Powder from a Polymeric Precursor

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Abstract

Methylcyclosiloxanes and methylcyclosilazanes prepared using dichloromethylsilane have been reacted together to prepare a copolymer which was pyrolysed to give a ceramic powder. The copolymer was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infra-red spectroscopy (FT-IR). Thermogravimetric analysis of the pyrolysis process and reactions which could occur during conversion of the copolymer to the ceramic are discussed. The product, which was found to be amorphous, was also studied using FT-IR, crystallized by re-heating and characterized using FT-IR, X-ray techniques and scanning electron microscopy. It was identified as α-silicon nitride and its characteristics are compared with a conventionally prepared, widely used, commercially available grade of silicon nitride. The α-silicon nitride synthesised in the present work contains a wide range of particle morphologies, varying from needles (500 nm in length and 100 nm in width) to equiaxed agglomerates (200–500 nm in size with a substructure in the size range 50–120 nm).

1 Introduction

Strength retention at high temperature, high thermal shock, corrosion and wear resistance makes silicon nitride (Si_3N_4) a rapidly emerging engineering material, especially useful for structural applications such as components in advanced engines.[1,2] However, there are several difficulties that must be overcome before the full market potential of Si_3N_4 is realized. A major issue is the lack of suitable Si_3N_4 powder from which ceramic components can be fabricated. Currently, Si_3N_4 powders are manufactured by three main methods:[3]

(1) Nitridation of silicon: $3Si + 2N_2 \rightarrow Si_3N_4$.
(2) Ammonolysis (in the gas phase) of silicon tetrachloride: $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$.
(3) Carbothermic reduction of silicon dioxide $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$.

These conventional routes produce powders with the following drawbacks:[4]

(1) Lack of control over crystal structure, phase chemistry and impurity levels, resulting in glass formation at grain boundaries which drastically lower the strength of the materials, especially at high temperatures.
(2) A large average particle size, >1–10 μm, with some powder particles in the 20–100 μm range, thereby giving rise to poor sintering and large grains in the final microstructure.
(3) Irregular morphologies which reduce the packing efficiency during fabrication of components.
(4) A high degree of agglomeration which result in micro-defects in the final microstructure.

Some of the above-mentioned difficulties have been overcome by process modifications, e.g. the use of laser-driven, gas phase reactions which produces finer powders,[4] but it is increasingly acknowledged that chemical processing of ceramic materials could provide the stoichiometry, purity and microstructural control required.[5,6] One such processing method is the pyrolytic conversion of organometallic molecules and polymers to ceramics to produce powders, fibres, coatings and even ceramic artefacts,[7–10] as postulated by Chantrell and Popper[11] in 1964. However, it must be noted that this processing route produces amorphous Si_3N_4 and further heating is necessary to form a crystalline product.

Pioneering work on the synthesis of Si_3N_4 from polymeric precursors was carried out by Seyferth and coworkers[12] who reacted dichlorosilane (H_2SiCl_2), a potentially hazardous material, with NH_3 to produce silazane oil which, when pyrolysed in N_2 at 1150°C, produced α-Si_3N_4 with Si as

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an impurity. The yield obtained was approximately 70%wt. Subsequently, Seyferth and Wiseman[13] reported the use of dichloromethylsilane (CH_3SiHCl_2) which was reacted with NH_3 to produce polysilazanes and these were pyrolysed in N_2 at 1420°C to produce ceramics. However, the product was a mixture of Si_3N_4, silicon carbide (SiC) and C (yield of ceramics 80–85%wt.). Further work[14] on mixtures of CH_3SiHCl_2 and $CH_3(CH_2=CH)SiCl_2$, and CH_3SiHCl_2 and $CH_3(CH_2=CHCH_2)SiCl_2$, which were ammonolysed to prepare several polysilazanes and pyrolysed in Ar or N_2 at 1000°C, produced a slightly higher yield of ceramics (up to 86%wt.) but still contained a mixture of Si_3N_4 and SiC (about 68%wt. Si_3N_4). In fact, most investigations in this area of research report the preparation of several preceramic polymers which on pyrolysis produce Si_3N_4–SiC mixtures rather than Si_3N_4.[15] Improvement of the Si_3N_4 content was achieved by increasing the N content of the preceramic polymer, e.g. by using mixtures of CH_3SiHCl_2 and H_2SiCl_2 for ammonolysis,[14] and by pyrolysing the precursor in a reactive gas such as NH_3 rather than N_2 or Ar.[14] The first strategy seems to be case-specific as Seyferth and coworkers[14] have also used other types of commercially available $RSiCl_3$ compounds which were mixed with CH_3SiHCl_2, but, overall, there was no appreciable increase in the Si_3N_4 content. Pyrolysis in NH_3 produced Si_3N_4 with 0·29%wt. of C but the phase chemistry of the ceramic obtained is not discussed.

Many other subsequent investigations[16,17] used pyrolysis in NH_3 for the synthesis of nitrogen ceramics, mainly Si_3N_4. In particular, Blum and coworkers[16] give detailed chemical analyses of several ceramic products obtained using different polymers and these clearly indicate that pyrolysis in NH_3, compared with that in N_2, reduces the molar ratio of C by an order of magnitude. Yu and Mah[18] reported the use of a mixture of poly-siloxanes and polysilazanes to produce a 'living' polymer which can be pyrolysed in NH_3 at 1000°C to produce silicon oxynitride (Si_2ON_2). It is worth noting that if the 'living' polymer was pyrolysed in N_2 or Ar, the product obtained was a mixture of Si_3N_4 and SiC.[14] Laine and coworkers[19] report a dehydrocoupling reaction (with an Ru catalyst) to polymerise a silazane oligomer to give a high molecular weight ($\overline{M}_n > 8000$) precursor which can be pyrolysed in NH_3 to produce approximately 97%wt. pure Si_3N_4 with a >80%wt. yield.

Only a few investigations indicate the phase chemistry of the Si_3N_4 prepared and the product has been mainly a mixture of α-Si_3N_4 and β-Si_3N_4. Burns and Chandra[20] have reported the pyrolysis of several cross-linked polycarbosilanes, polysilanes and polysilazanes in N_2 or NH_3 at 1200°C to produce amorphous Si_3N_4 with a yield of 81–93%wt. but the crystallized product contained only 56%wt. α-Si_3N_4. Schwab and coworkers[21] have also used polysilazanes to produce Si_3N_4 fibres but the product contained a mixture of α-Si_3N_4 and β-Si_3N_4. Recently, Funayama and coworkers[22] used a polyborosilane but pyrolysis in NH_3 and subsequent crystallization in N_2 produced a mixture of α-Si_3N_4 and β-Si_3N_4. Interrante and coworkers[23] report the preparation of α-Si_3N_4 and free C as the main products of pyrolysis of silicon tetradiethylamide produced by condensation polymerisation but no further details are given.

Reports of investigations on the synthesis of ceramics by the pyrolysis of polymeric precursors suffer from the fact that information on polymer synthesis, pyrolysis reactions and the phase and powder characteristics of the ceramic produced are not presented together. In the present work we pyrolyse a copolymer, prepared from methylcyclosiloxanes and methylcyclosilazanes, which have been produced using dichloromethylsilane (CH_3SiHCl_2), in N_2 to synthesise amorphous Si_3N_4 which is heat treated to form crystalline α-Si_3N_4. The copolymer used is a precursor which is suitable for the synthesis of several nitrogen ceramics, as discussed above. Reactions which can occur during pyrolysis are discussed and the resulting crystalline Si_3N_4 powder synthesised is characterized and compared with a conventionally prepared, commercially available grade of Si_3N_4.

2 Experimental Details

2.1 Starting materials

CH_3SiHCl_2 was obtained from Aldrich Chemical Co. (Poole, UK). The middle cut from the distillation of CH_3SiHCl_2 over Mg metal under dry N_2 was used to prepare methylcyclosiloxanes by hydrolysis and methylcyclosilazanes by ammonolysis. Details of these methods and products have been fully described earlier.[24,25]

2.2 Copolymerization

The reaction conditions and procedure described below have been deduced from a detailed investigation on the copolymerization of methylcyclosiloxanes and methylcyclosilazanes.[26] Methylcyclosiloxanes (0·5 g) were added to a THF solution of the methylcyclosilazanes (90 ml, containing 1 g of the silazanes) in a round bottom flask containing a magnetic stirrer. The catalyst/initiator, KH (0·05 g) was added and the reaction was carried out at

60°C for approximately 30 h. Chloromethylsilane (0·2 ml) was injected into the flask to terminate the reaction and about 3 min later a white precipitate appeared. The system was stirred for 3 h and then left for 5 h. Subsequently, the solution was taken in a dry flask and the solvent was evaporated under high vacuum. A redissolvable white solid (the copolymer) was thus obtained.

2.3 Pyrolysis

The copolymer was placed in an alumina holder and pyrolysed in a tube furnace (Lenton Thermal Designs Ltd., Market Harborough, UK) in the presence of flowing N_2 (flow rate approximately 250 ml min^{-1}). The furnace tube was at 120°C when the copolymer was inserted (to minimize any effects of moisture) and heating to 1000°C was carried out at 100°C h^{-1} followed by soaking at this temperature for 2 h. Subsequently, the furnace was switched off and allowed to cool to room temperature. The copolymer was also pyrolysed in a Perkin-Elmer TG2 thermogravimetric balance under similar conditions but at a faster heating rate (20°C min^{-1}).

2.4 Crystallization

The residue after pyrolysis was ground to a fine powder using a mortar and pestle and pressed into a disc shape, (8 mm diameter and a few mm thick). It was encapsulated in a commercially available sub-micrometer size silicon oxynitride powder (supplied by Mandoval Ltd., Surrey, UK) and further pressed to produce a thicker disc which was heated in the tube furnace used for pyrolysis in the presence of flowing N_2 (flow rate approximately 200 ml min^{-1}) to 1600°C at 60°C h^{-1}, soaked at this temperature for 2 h and subsequently cooled to room temperature at 60°C h^{-1}. This encapsulation was carried out to prevent the pyrolytic residue from reacting with any O_2 present in the N_2 during heat treatment at high temperature. Subsequently, the 8 mm disc was separated carefully from the thicker disc and characterized as described below. Crystallization experiments were also carried out at other temperatures (< 1600°C) using a similar temperature ramp.

2.5 X-ray and microscopical characterization

The crystallized ceramic powder and a commercially available Grade LC12 Si_3N_4 powder (supplied by Hermann C. Starck Berlin, Goslar, Germany) were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). For the last technique the samples were sputter coated with gold before examination to avoid charging effects.

2.6 FT-IR spectroscopy

A sample of the solution (mentioned in Section 2.2) was taken before the solvent evaporated and used for FT-IR spectroscopy. It was placed on a KBr disc and the solvent was allowed to evaporate under dry N_2. A Nicolet 710 FT-IR spectrometer was used to obtain a spectrum in the range 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}. The pyrolytic residue, the crystallized ceramic powder and LC12 Si_3N_4 powder were also investigated using a Nicplan FT-IR microscope to obtain the FT-IR spectrum in the range 4000 cm^{-1} to 600 cm^{-1} with a resolution of 4 cm^{-1}.

2.7 ^{1}H NMR spectroscopy

A JEOL FX200 spectrometer was used and a 10%wt./vol. solution of the copolymer in $CDCl_3$ was studied at 200 MHz. A delay time of 6–10 s was used to ensure that the proton signals were completely relaxed between pulses. Tetramethylsilane (TMS) was used as the internal reference.

3 Results and Discussion

3.1 Copolymer

The molar ratio of Si–$\underline{H}$: N–$\underline{H}$: Si–C$\underline{H}_3$ of the copolymer (from Fig. 1(a)) is equal to 1 : 1·2 : 7·6. We have shown previously[26] that the reaction between methylcyclosiloxanes and methylcyclosilazanes result in a block copolymer dominated by silazane blocks and therefore it is reasonable to compare the ^{1}H NMR spectrum of the copolymer with that of methylcyclosilazanes used in the copolymerization reaction (Fig. 1(b)). The molar ratio of Si–$\underline{H}$: N–$\underline{H}$: Si–C$\underline{H}_3$ of the methylcyclosilazanes (Fig. 1(b)) is 1 : 1 : 3·2. Therefore, it can be concluded that the copolymer contains a much higher concentration of Si–C$\underline{H}_3$ groups. Also, comparison of Figs 1(a) and 1(b) shows that the peaks in the former (copolymer) are broader, indicating the complex nature of its chemical structure.

The FT-IR spectra also show the same trends. The relative intensities of Si–CH_3, Si–H and N–H bands of the copolymer (Fig. 2(a)) are compared with similar bands in the reactant methylcyclosilazanes (Fig. 2(b)). Clearly, the relative intensity of the Si–CH_3 bands in the copolymer have increased in comparison with the Si–H and N–H bands. Fig. 2(a) also indicates the presence of Si–NH_2 groups in the copolymer (3450 cm^{-1} for NH_2 stretching and 1540 cm^{-1} for NH_2 deformation, respectively).

3.2 Pyrolytic residue

The pyrolysis of the copolymer results in approximately 70%wt. of residue (Fig. 3). Pyrolysis of

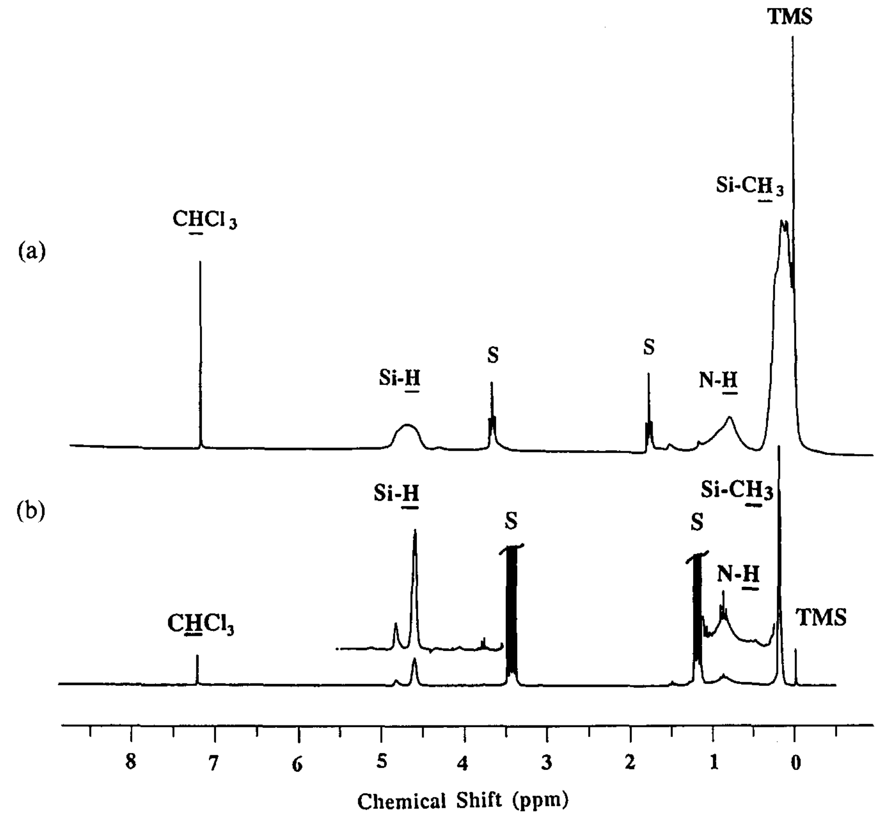
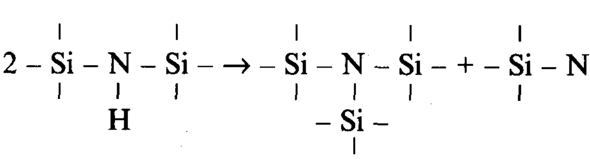


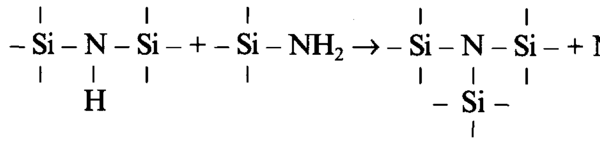
Fig. 1. ^{1}H NMR spectra of (a) the copolymer and (b) the methylcyclosilazanes used to prepare the copolymer (after Refs 25 and 26). TMS and S refer to tetramethylsilane and solvents respectively.

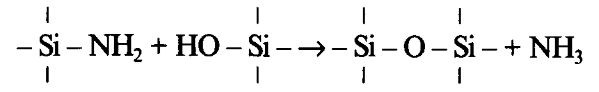
larger quantities in the tube furnace also resulted in the same yield. The residue contained 11·20%wt. C, 21·90%wt. N, and H was not detected (chemical analysis performed using a CHN Elemental Analyser, Carlo Erba, Italy. Chemical analysis to assess Si was not carried out, hence the O content is not reported here). XRD does not show any peaks and therefore the residue is amorphous. The FT-IR spectrum of the residue (Fig. 4(a)) shows the characteristics of Si_3N_4.

The thermogravimetric trace (Fig. 3) indicates that pyrolysis takes place mainly in two stages. The first occurs between approximately 120 and 440°C when about 20%wt. is lost. This is followed by an approximately 10%wt. loss between 440 and 900°C which takes place at a slower rate. The shape of the TGA curve and the %wt. of residue left did not change significantly with variations in the rate of heating, suggesting that cross-linking during pyrolysis is quite fast compared with the thermal degradation of (vinyl SiHNH)$_x$ (MeSiHNH)$_y$ polymers studied by Bahloul *et al.*[27] In a previous paper[28] we used thermogravimetric-Fourier transform infra-red spectroscopy (TG-FTIR) to suggest reactions that take place when a copolymer, very similar to the one used in the work discussed here, is pyrolysed in N_2. However, the resulting ceramic was not identified at that time[28] and we were unable to fully justify the entire scheme of reactions. We can now propose, using the results of the present work, a full scheme of reactions as described below.

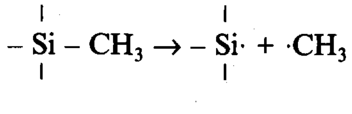
The first stage of weight loss is largely transamination, similar to that occurring during the pyrolysis of polymers of silazanes,[27,29,30] resulting in the formation of the –Si–N–Si– structure according to reaction 1. In addition, –Si–NH$_2$ and HO–Si– groups are removed according to Reactions 2 and 3, respectively.


$$2-\overset{|}{\underset{|}{\mathrm{Si}}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}-\underset{\underset{\underset{|}{-\mathrm{Si}-}}{|}}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-+-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{NH_2} \quad (1)$$


$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-+-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{NH_2}\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}-\underset{\underset{\underset{|}{-\mathrm{Si}-}}{|}}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-+\mathrm{NH_3} \quad (2)$$


$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{NH_2}+\mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}-\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-+\mathrm{NH_3} \quad (3)$$

These reactions are accompanied by the release of NH_3 as shown by TG-FTIR studies.[28] The second stage of weight loss is accompanied by the evolution of CH_4, as indicated by TG-FTIR studies,[28] and this can occur due to reactions 5 and 6. The $\cdot CH_3$ can be produced initially by Reaction 4.


$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{CH_3}\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}\cdot+\cdot\mathrm{CH_3} \quad (4)$$

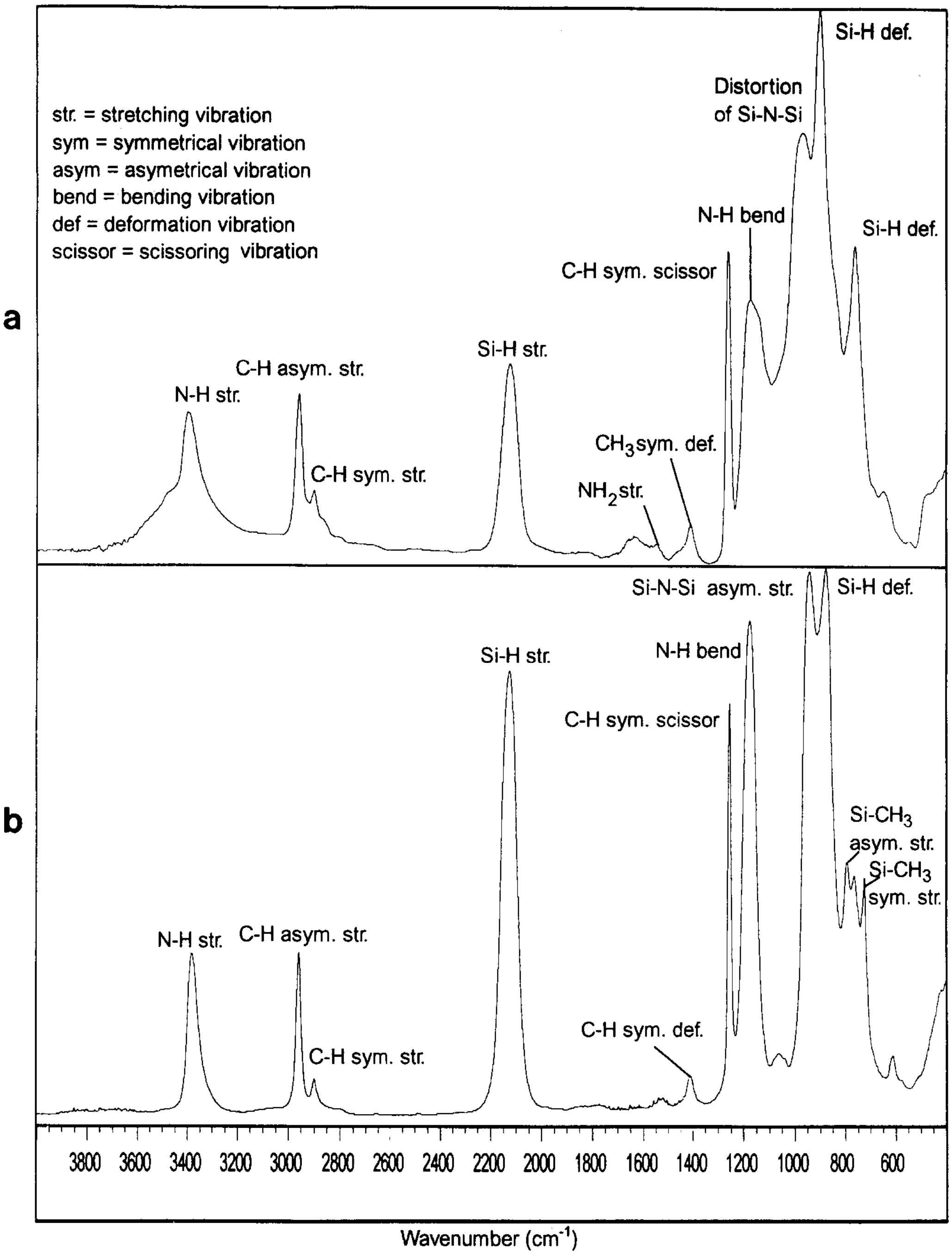
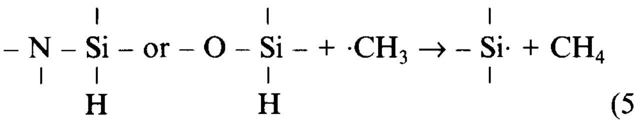
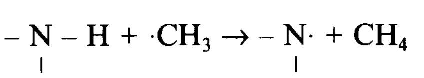


Fig. 2. FT-IR spectra of (a) the copolymer and (b) the methylcyclosilazanes used to prepare the copolymer (after Refs 25 and 26).

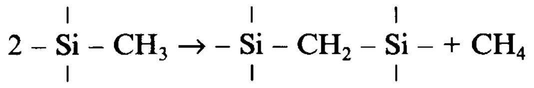


$$-\underset{|}{\mathrm{N}}-\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{Si}}}}-\text{or}-\mathrm{O}-\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{Si}}}}-+\cdot\mathrm{CH_3}\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}\cdot+\mathrm{CH_4}\tag{5}$$



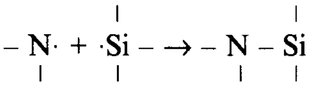
$$-\underset{|}{\mathrm{N}}-\mathrm{H}+\cdot\mathrm{CH_3}\rightarrow-\underset{|}{\mathrm{N}}\cdot+\mathrm{CH_4}\tag{6}$$

Reaction 7 can also produce CH_4 and $-Si-CH_2-Si-$ groups which have been detected in a recent study where silicon oxynitride was synthesised from a preceramic polymer.[31]



$$2-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{CH_3}\rightarrow-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{CH_2}-\overset{|}{\underset{|}{\mathrm{Si}}}-+\mathrm{CH_4}\tag{7}$$

The products of Reactions 5 and 6 will enable Reaction 8 to take place forming –Si–N–networks.



$$-\underset{|}{\mathrm{N}}\cdot+\cdot\overset{|}{\underset{|}{\mathrm{Si}}}-\rightarrow-\underset{|}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-\tag{8}$$

The decomposition of the copolymer can also result in the formation of free C.[32] At higher temperatures (>850°C) C reduces the –Si–O–Si– groups, which are present in the polymer or are formed in reaction 3, eliminating oxygen in the residue and producing both CO and CO_2. In fact in our previous work,[28] TG-FTIR analysis showed that the relative intensities of the CO and CO_2 peaks increased between 850 and 980°C. If the C content available is sufficiently high most of the O should

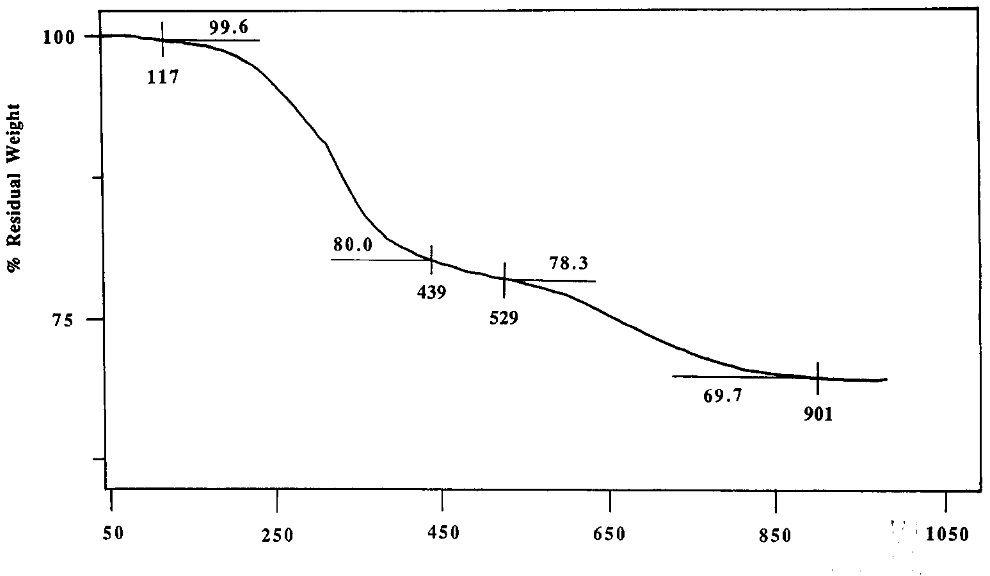


Fig. 3. Thermogram for the degradation of the copolymer in N_2 at a heating rate of 20°C per minute.

be removed and Si_3N_4 with residual O and C is produced as in the present work. The presence of a lower C:O ratio at higher temperatures (>850°C) during pyrolysis will result in a –Si–O–N– ceramic (silicon oxynitride) as observed recently.[31] This confirms the important role C would play during pyrolysis, especially during the final stages of pyrolysis.[33] However, the C content can be controlled by changing the pyrolysis atmosphere.[31]

3.3 Crystalline ceramic

The FT-IR spectra of the crystalline product (Fig. 4(b)) and LC12 Si_3N_4 (Fig. 4(c)) both show the characteristic peak of α-Si_3N_4 at approximately 1100 cm^{-1}. It is well known that Si_3N_4 synthesised from polymeric precursors are amorphous and when heated above 1200°C undergo a diffusion controlled transformation to the crystalline form.[34] In the present work, XRD of the pyrolysis residue heated to various temperatures first showed peaks

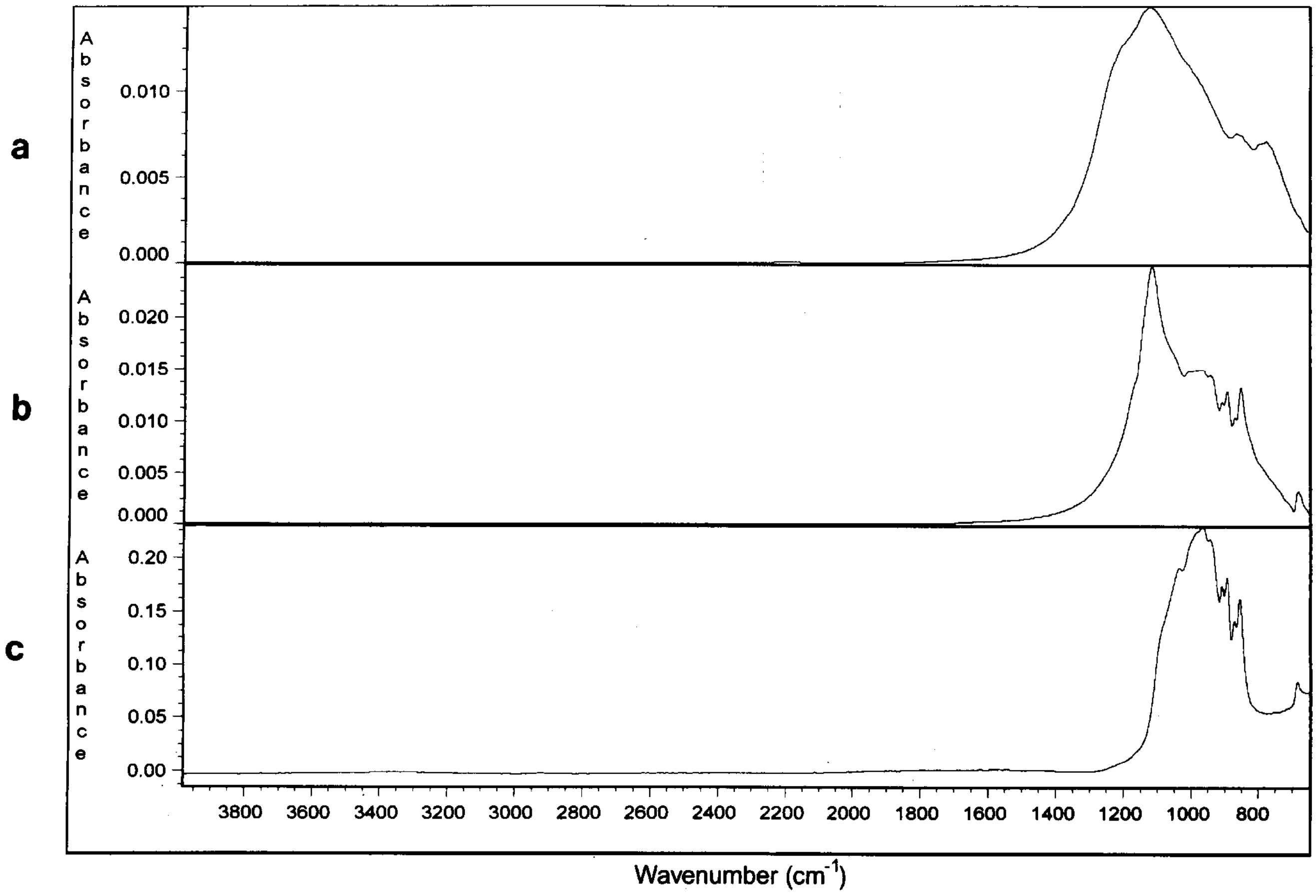


Fig. 4. FT-IR spectrum of (a) the pyrolytic residue, (b) the crystallised Si_3N_4 synthesised in the present work and (c) LC12 Si_3N_4.

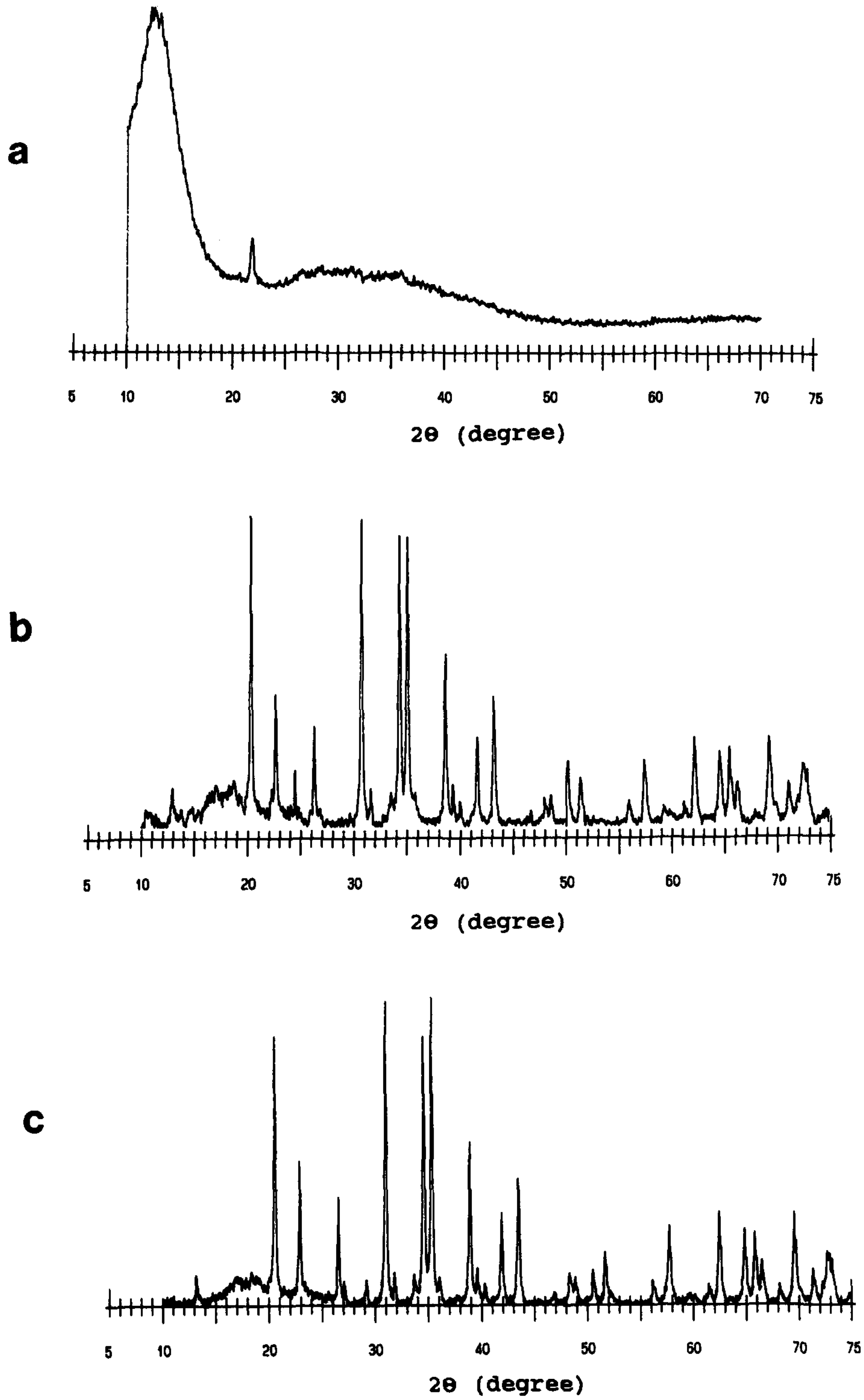


Fig. 5. X-ray diffraction pattern of (a) the pyrolytic residue heated to 1400°C for 5 h, (b) crystallised Si_3N_4 sample synthesised (heated to 1600°C for 2 h) in the present work and (c) LC12 Si_3N_4. A Philips X-ray diffractometer (CuKα radiation of wavelength 0·154 nm and a Ni filter) was used. The step size and scan speed were 0·021° and 0·005° s^{-1} for (a), 0·021° and 0·02° s^{-1} for (b) and 0·01025° and 0·005° s^{-1} for (c).

in the sample heated to 1400°C for 5 h (Fig. 5(a)). Therefore, the crystallization temperature required in the present work was much higher. XRD results of the crystallised product† (after heating to 1600°C for 2 h) are shown in Fig. 5(b). The peaks in Fig. 5(b) correspond to α-Si_3N_4. β-Si_3N_4 and Si were not detected but the diffraction trace shows that some residual C is present. In comparison, LC12 Si_3N_4 was predominantly α-Si_3N_4 containing β-Si_3N_4 and cubic silicon (Fig. 5(c)). The α/β ratio influences sintering behaviour[35] and a high value, as in the powder synthesised in the present work, is a pre-requisite for high technology applications.[36,37]

XPS results of the two samples of Si_3N_4 are shown in Figs 6(a) and (b) where the similarity of

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†Recent TEM studies, not reported here, show that complete conversion to the crystalline product was achieved.

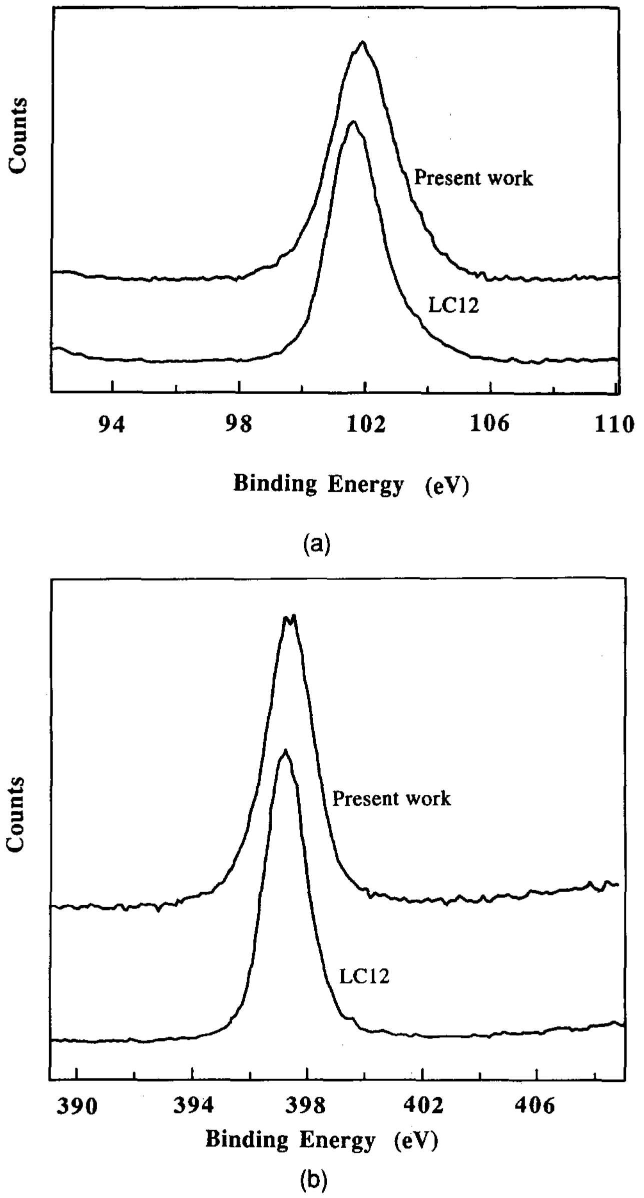

Fig. 6. XPS spectra of the crystallised Si_3N_4 synthesised in the present work and LC12 Si_3N_4 for: (a) Si_{2p} (b) N_{1s}.

Table 1. Summary of XPS results of Si_3N_4 powders. The published binding energy values for Si_{2p} and N_{1s} for Si_3N_4 are 101·9 eV and 397·7 eV, respectively. The area under each curve (given below) is after charge correcting all spectra relative to the C_{1s} peak

	Peak Identity	*Binding Energy (eV)*	*Area*	*Atomic%*
Present work	Si_{2p}	101·9	10·08	32
	N_{1s}	397·5	10·82	34
	O_{1s}	532·4	7·84	25
	C_{1s}	284·6	2·85	9
LC12	Si_{2p}	101·6	15·09	33
	N_{1s}	397·3	18·49	40
	O_{1s}	532·3	8·96	19
	C_{1s}	284·6	3·51	8

the band shape suggest that they exhibit similar chemical binding. Using a full spectrum scan, a summary of all bands present in the two samples are given in Table 1. Both samples contain C and O impurities but the powder prepared in the present work contains a slightly higher level of O. The latter feature is beneficial for sintering[38,39] but the presence of C is not helpful as it can remove O during sintering.[35]

Figure 7 shows that a wide range of particle morphologies, varying from needles to equiaxed lumps, are present in the Si_3N_4 synthesised from the copolymer. The needles are approximately 500 nm in length and 100 nm in width. The lumps are agglomerates, having diameters in the range 200–500 nm. The sub-structure in the agglomerates are in the range 50–120 nm. The particle characteristics of the LC12 Si_3N_4 are well documented.[40] The particles are in the size range 150–1500 nm with a median particle size of 500 nm and these particles are equiaxed in shape and

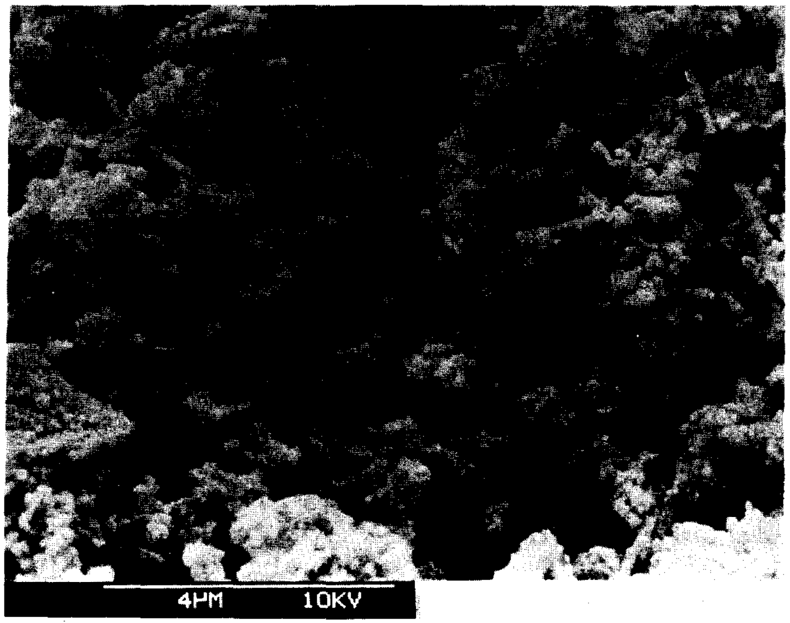

Fig. 7. A scanning electron micrograph of the Si_3N_4 powder in the crystalline form synthesised in the present investigation. A very wide range of particle morphologies is seen. The micrograph was taken using secondary electrons at 10 kV.

appear to be agglomerated to a lesser extent. Clearly, the mixed morphology of the Si_3N_4 prepared using the polymeric precursor indicates that by suitably varying and controlling the pyrolysis and crystallization heat treatments of the amorphous product various particle morphologies can be developed. Strutt *et al.*[41] have synthesised polymerized preceramic nanosized Si_3N_4 by laser irradiation of metalorganic precursors. A near spherical Si_3N_4 powder with a bimodal size distribution corresponding to median diameters of 45 nm and 120 nm was produced and the larger size was thought to be agglomerates. However, the yield of the ceramic powder from the metalorganic powder was about 54%wt. Our yield was approximately 70%wt., typical from the pyrolysis of preceramic polymers in N_2 but higher yields are reported for Si_3N_4 produced by pyrolysis of polymeric precursors in NH_3[14].

4 Conclusions

Crystalline Si_3N_4 powder has been synthesised from a copolymer prepared from methylcylosiloxanes and methylcyclosilazanes.

The complex structure of the copolymer contains a higher concentration of $Si{-}CH_3$ groups, compared with the reactants. Weight loss in the copolymer occurs mainly in two stages. Between 120 and 440°C the most likely reactions produce $-Si-N-Si-$, $-Si-NH_2$ and $-Si-O-Si-$ groups and NH_3, which results in about a 20% wt. loss. In the second stage, between 440 and 900°C during which about a 10%wt. loss occurs, release of CH_4 is accompanied by the formation of $-Si\cdot$ and $-N\cdot$ groups. These groups react to produce the $-Si-N-$ structure and hence Si_3N_4. However, the C:O ratio at temperatures $>850°C$ is a crucial factor in determining the type of ceramic product. A high C:O ratio supports the formation of Si_3N_4.

The product is amorphous and has been crystallised by heat treatment and identified as α-Si_3N_4 containing 9 atomic% of carbon and 25 atomic% of oxygen. The α-Si_3N_4, crystals produced have a wide range of morphologies ranging between 500 nm × 100 nm size needles to 200–500 nm size agglomerates containing 50–120 nm size particles. Comparison of the Si_3N_4 thus produced with conventional, commercially available LC12 Si_3N_4, shows that the former is superior in that it does not contain undesirable β-Si_3N_4 and is free from coarse particles (>1 μm). Also it has slightly higher oxygen which will aid sintering. However, the LC12 particles are predominantly equiaxed in shape and agglomerated to a lesser extent.

The results of the present investigation show clearly that both the pyrolysis and crystallization process conditions are related closely to the characteristics of the final product. Changes in these process variables seem to determine the type of Si_3N_4 produced. In fact, it should be possible to produce Si_3N_4 with a certain predetermined morphology (needles or equiaxed particles) and this could be of vital importance in the preparation of ceramic composites.

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