

# Preparation of silicon carbide–silicon nitride composite foams from pre-ceramic polymers

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## Abstract

A new method of forming silicon carbide–silicon nitride composite foams is presented. These are prepared by immersing a polyurethane foam in a polysilane precursor solution mixed with  $\text{Si}_3\text{N}_4$  powder to form a pre-foam followed by heating it in nitrogen at  $> 900^\circ\text{C}$ . X-ray diffraction patterns indicate that a  $\text{SiC-Si}_3\text{N}_4$  composite was formed after sintering the ceramic foam at  $> 1500^\circ\text{C}$ . Micrographs show that most of these foams have well-defined open-cell structures and macro-defect free struts. The shrinkage is reduced considerably due to the addition of  $\text{Si}_3\text{N}_4$  particles. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Foams; Processing; Precursors-organic;  $\text{SiC-Si}_3\text{N}_4$

## 1. Introduction

Ceramic foams are finding increasing application due to their unique properties such as low density, low thermal conductivity, high temperature stability, low dielectric constant and high resistance to chemical attack.<sup>1–5</sup> The most common process for producing ceramic foams is the impregnation of polyurethane foams with slurries containing ceramic particles and appropriate binders followed by pyrolysis and pressureless sintering at elevated temperatures.<sup>3–6</sup> This involves coating and recoating a reticulated polymeric sponge with a ceramic slurry, removal of the polymer to form a ceramic skeleton followed by sintering. Ceramic foams produced by this method are of low strength and fracture toughness as very thin webs with coarse-cells of ceramic are normally left after the organic sponge is burned out, making them sensitive to structural stresses and limiting their structural applications.<sup>5,7</sup>

One of the most common ways to improve the mechanical properties of such foams is by the addition of fibers to the ceramic structure. Typically, about 1–5 wt% of fiber is added to either the ceramic slurry or the chemical mixture. Different fibers such as aluminosilicates, carbon, graphite, zirconia, silicon carbide and

alumina have been used to improve the strength of ceramic foams.<sup>8–11</sup> However, uniformly impregnating a polymeric sponge with a ceramic slurry containing fibers is difficult although various approaches such as applying a vacuum during infiltration and spraying the slurry onto the sponge have been used.<sup>5</sup>

Because of their potential high strength and toughness, silicon carbide–silicon nitride ( $\text{SiC-Si}_3\text{N}_4$ ) composites have recently received a great deal of attention as structural materials.<sup>12–15</sup> These composites are made conventionally from powder mixtures which require high amounts of sintering additives and a high sintering temperature and such a procedure gives rise to relatively large agglomerates and/or inclusions of one phase resulting in an inhomogeneous microstructure and poor mechanical properties of the composite.<sup>16</sup> The polymeric precursor route has been developed to improve the homogeneity of the microstructure of the  $\text{SiC-Si}_3\text{N}_4$  composites. It has been reported that this can be achieved by mixing  $\text{SiC}$  powders with polycarbosilazane-based  $\text{SiCN}$  precursor,<sup>17</sup> by mixing a polysilane  $\text{SiC}$  precursor in solution with  $\text{Si}_3\text{N}_4$  powder<sup>18</sup> or by pyrolyzing a single co-polysilane–silazane polymeric precursor.<sup>19</sup> Such methods improve homogeneity of the microstructure because preparation involves liquids and efficient mixing of the precursor with the powders.<sup>17–20</sup> The use of a polymeric precursor route to synthesize ceramic composites also offers processability at low

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temperature and the possibility to optimize processing to produce new composite materials by tailoring the composition and molecular structure of the polymers.<sup>15,21–24</sup>

The use of polymeric precursors for the preparation of ceramic foams is currently generating a great deal of interest.<sup>25–27</sup> Recently, a new method to produce ceramic foams using polymeric precursor solutions was developed.<sup>28</sup> Polyurethane foams were immersed in polymeric precursor solutions to form pre-foams followed by pyrolysis in nitrogen. The main advantages of this new approach are the simplicity and ease of control of structure of the final product. In the present study, this new process is exploited further to prepare SiC–Si<sub>3</sub>N<sub>4</sub> composite foams.

## 2. Experimental details

### 2.1. Synthesis and characterization of polysilane precursor

The polysilane precursor discussed in this paper was synthesized by the alkali dechlorination of a combination of chlorinated silane monomers in refluxing toluene/tetrahydrofuran with molten sodium as described previously.<sup>24,29</sup> Details of the various monomers used are summarized in Table 1.

#### 2.1.1. Preparation of SiC–Si<sub>3</sub>N<sub>4</sub> pre-foams

A polyurethane (PU) sponge with open-cells was used in this work. The polysilane precursor was dissolved in dichloromethane to form a polymeric precursor solution. Subsequently, Si<sub>3</sub>N<sub>4</sub> powder (supplied by the AME Division of Morgan Matroc, UK) was added into the solution. Typically, 0.4 g of polymer was dissolved in 2 ml of dichloromethane and then 0.1 g of Si<sub>3</sub>N<sub>4</sub> powder was added to this precursor solution. The proportion of Si<sub>3</sub>N<sub>4</sub> powder in the precursor was varied. The polyurethane sponge was first cut into 10 mm side cubes and was then immersed in the polymer/Si<sub>3</sub>N<sub>4</sub> powder suspension for about 2 h. The samples were air-dried overnight at the ambient temperature to obtain pre-foams. These were pyrolyzed subsequently in nitrogen. A SiC foam prepared from the polysilane precursor was also produced using the same method for comparison.

Table 1  
Monomers used in the synthesis of polysilanes

Monomer	Formula	F <sup>a</sup>	Abbreviations
Dichloromethylphenylsilane	(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )SiCl <sub>2</sub>	2	MP
Dichloromethylsilane	(CH <sub>3</sub> )HSiCl <sub>2</sub>	3	MH
Dichloromethylvinylsilane	(CH <sub>3</sub> )(CH <sub>2</sub> =CH)SiCl <sub>2</sub>	4	MVin

<sup>a</sup> Functionality.

### 2.2. Pyrolysis

The pre-foams were placed in an alumina boat and heated from the ambient temperature to 900°C at 1°C min<sup>-1</sup> in a tube furnace (Lenton Thermal Designs Ltd., Market Harborough, UK) in the presence of flowing nitrogen gas (flow rate approximately 250 ml min<sup>-1</sup>) followed by soaking at this temperature for 2 h. Subsequently, the furnace was switched off and allowed to cool to the ambient temperature. Some of the pyrolyzed samples were heated further in the tube furnace in the presence of flowing nitrogen gas (flow rate approximately 250 ml min<sup>-1</sup>). This heat treatment was started from the ambient temperature ending at different final temperatures (1100–1600°C) and the rate used was 2°C min<sup>-1</sup>. Heating was followed by soaking at this temperature for 2 h and then cooling to the ambient temperature at 2°C min<sup>-1</sup>. In each case, after cooling to the ambient temperature the weight change was measured to an accuracy of 0.001 g.

### 2.3. Characterization

The molecular weight of the polysilane was determined by gel permeation chromatography (GPC) carried out at RAPRA Technology Ltd., Shrewsbury, UK. GPC studies were calibrated using polystyrene standards with chloroform as the eluent. The flow rate used was 1.0 ml/min. The Fourier transform-infrared (FT-IR) spectrum of the polymeric precursor was obtained using a Nicolet 710 spectrometer. 1 mg of polymer was ground and mixed with 150 mg of dried KBr powder and pressed into a pellet. The spectrum was obtained in the wavenumber range of 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The pyrolytic yield from polysilane precursor, Si<sub>3</sub>N<sub>4</sub> powder, PU foam and pre-foams was measured by thermogravimetry. Samples were heated from the ambient temperature up to 900°C in flowing nitrogen (0.5 ml min<sup>-1</sup>) at 10°C min<sup>-1</sup> in a Hi-Res Modulated TGA 2950 thermogravimetric analyzer to determine the pyrolytic yield.

The particle size distribution of the Si<sub>3</sub>N<sub>4</sub> powder was measured by laser diffraction size analysis. A few milligrams of Si<sub>3</sub>N<sub>4</sub> powder were dispersed in water with two drops of proprietary dispersant. After keeping the suspension in an ultrasonic bath for 1 min, samples were pipetted into a sample dispersion unit and studied using a Mastersizer (Malvern Instruments Ltd, Malvern, UK).

X-ray diffraction (XRD) was carried out on the Si<sub>3</sub>N<sub>4</sub> powder (as received) and SiC–Si<sub>3</sub>N<sub>4</sub> ceramic foams after pyrolysis to various final temperatures (≥1100°C) in nitrogen. Samples for X-ray diffractometry were ground using an agate pestle and mortar. A modified Philips X-ray diffractometer with filtered CuK<sub>α</sub> radiation of wavelength 0.15418 nm was used (a graphite monochromator

removes  $K_{\beta}$  radiation). The voltage and current settings of the diffractometer were 40 kV and 30 mA, respectively. The scan range was from  $10^{\circ}$  to  $90^{\circ}$  with a step size of  $0.05^{\circ}$  and a scan speed of  $0.025^{\circ}\text{s}^{-1}$ . The samples were mounted on a glass slide using a double-sided tape.

The microstructures of the pyrolyzed products were investigated using a Cambridge S360 scanning electron microscope (SEM). Samples studied using the SEM were coated with gold.

### 3. Results and discussion

#### 3.1. Polymer synthesis and characterisation

The characteristics of the polysilane PS used as the SiC precursor are given in Table 2.

The FT-IR spectrum of PS is shown in Fig. 1. It exhibits characteristic C–H stretching between  $3100$  and  $2700\text{ cm}^{-1}$ . The peaks at  $3050$  and  $3067\text{ cm}^{-1}$  represent C–H stretching in the phenyl group. C–H stretching in

the methyl group is observed at  $2956$  and  $2894\text{ cm}^{-1}$ . Additional peaks at  $1406$  and  $1248\text{ cm}^{-1}$  are characteristic of the asymmetric and symmetric bending modes, respectively, of  $\text{CH}_3$  bonded to silicon. Three small peaks at  $1949$ ,  $1887$  and  $1815\text{ cm}^{-1}$  are attributed to the phenyl-Si vibration. The peaks at low wavenumbers of  $697\text{ cm}^{-1}$  for Si–C stretching and  $464\text{ cm}^{-1}$  for Si–Si are typical for these polysilanes.<sup>30–32</sup> Two characteristic peaks at  $1589$  and  $2081\text{ cm}^{-1}$ , where the vinyl group and the Si–H group occurs, are clearly present.<sup>21,33</sup>

#### 3.2. Conversion to ceramic foams

The thermogravimetric traces of the polysilane,  $\text{Si}_3\text{N}_4$  powder, PU foam and the pre-foam are shown in Fig. 2. The thermal decomposition of the PU foam starts at about  $200^{\circ}\text{C}$  and nearly 95 wt% of the material is lost by  $420^{\circ}\text{C}$ . In fact, PU foam is almost fully pyrolyzed at  $500^{\circ}\text{C}$ . On the other hand, there is no appreciable weight loss occurring in  $\text{Si}_3\text{N}_4$  powder below  $900^{\circ}\text{C}$ . In the case of PS, the pyrolysis process takes place in three

Table 2  
Details of monomers used in the synthesis, polymer yield, molecular weight and pyrolytic yield of the polymeric precursor

Polymer	Monomers used (mol %)	Polymer yield (wt %)	Molecular weight ( $\bar{m}_w$ )	Pyrolytic yield (wt%)
PS	MP/MVin/MH = 60/20/20	38.0	12000	53.2

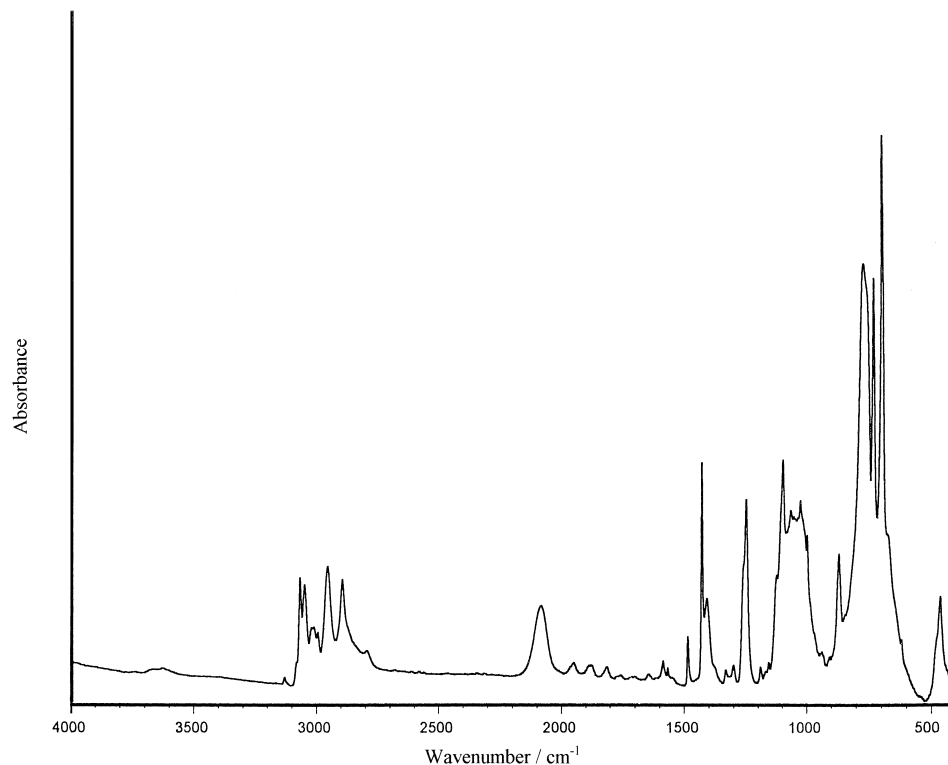


Fig. 1. FT-IR spectrum of polysilane precursor PS.

consecutive stages. In the first stage (up to 300°C), a very slow rate of weight loss of less than 2% occurs and this is characteristic of high molecular weight polymers. In the second stage (300–700°C), a major weight loss takes place, due to the decomposition and re-arrangement of the polymeric precursor and small molecules consisting mainly of methane and hydrogen are evolved.<sup>21</sup> In the third and final stage of pyrolysis (above 700°C), a further weight loss of about 2% occurs as the samples are heated to 900°C. The pre-foam shows a similar thermogravimetric trace to PS. The major weight loss occurs in the temperature range 300–700°C.

Previous research<sup>24</sup> showed that the pyrolytic yield is very dependent on the composition of the polymers. The polysilanes with reactive groups such as hydro-silane (Si–H) and vinyl (CH<sub>2</sub>=CH) give better pyrolytic yields, as cross-linked structures are formed during the pyrolysis due to the thermal cross-linking capability of these reactive groups.<sup>34–37</sup> Such cross-link formation will allow the materials to maintain its formed shape during pyrolysis because the melting of the polymeric precursors is hindered<sup>27</sup> and this is critical in preventing the collapse of the ceramic foams during pyrolysis. Thus, all ceramic foams processed in this work maintained

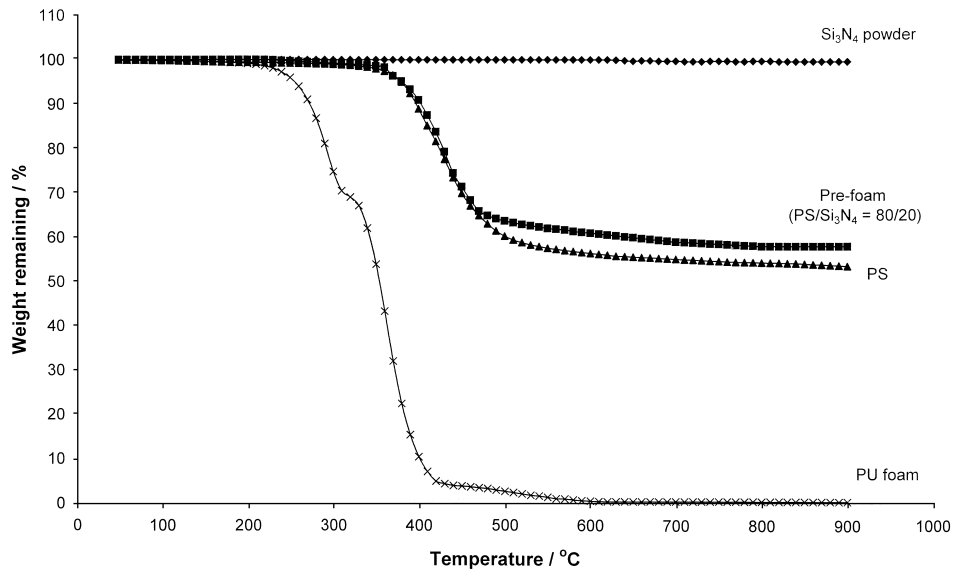


Fig. 2. Thermogravimetric traces of polyurethane foam (PU), Si<sub>3</sub>N<sub>4</sub> powder, polysilane precursor (PS) and pre-foam (PS/Si<sub>3</sub>N<sub>4</sub> = 80/20 wt%).

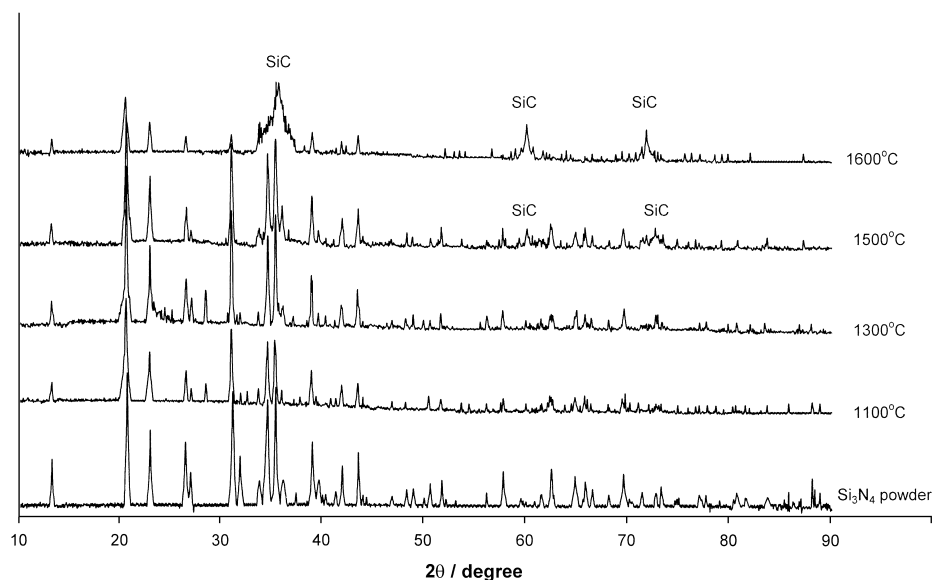


Fig. 3. XRD patterns of Si<sub>3</sub>N<sub>4</sub> powder and ceramic foam made from PS/Si<sub>3</sub>N<sub>4</sub> (80/20 wt%) after heating to different temperatures in the range 1100–1600°C.

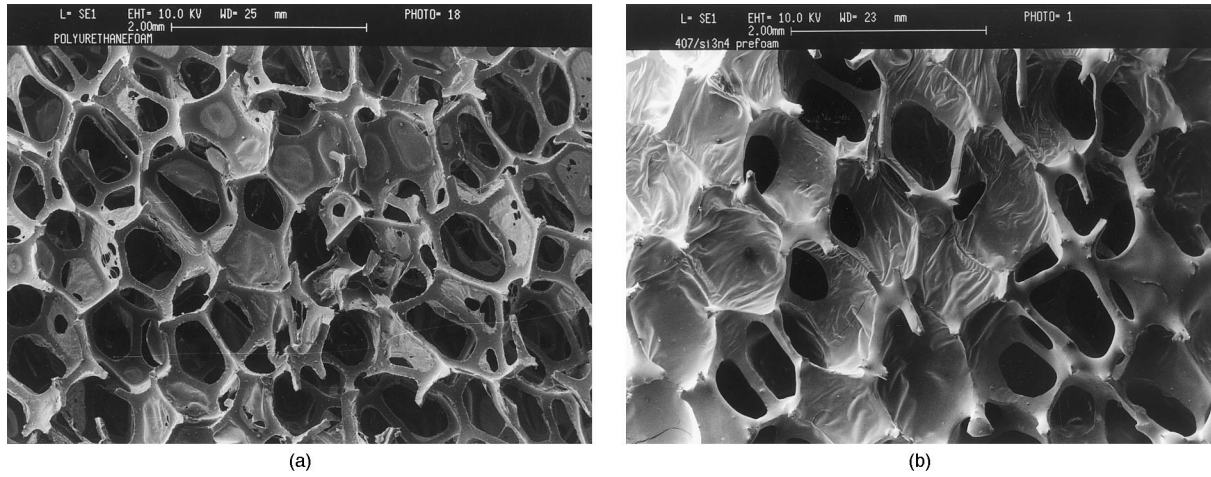


Fig. 4. Scanning electron micrographs of (a) polyurethane foam (PU) and (b) pre-foam with PS/Si<sub>3</sub>N<sub>4</sub> = 80/20 wt%.

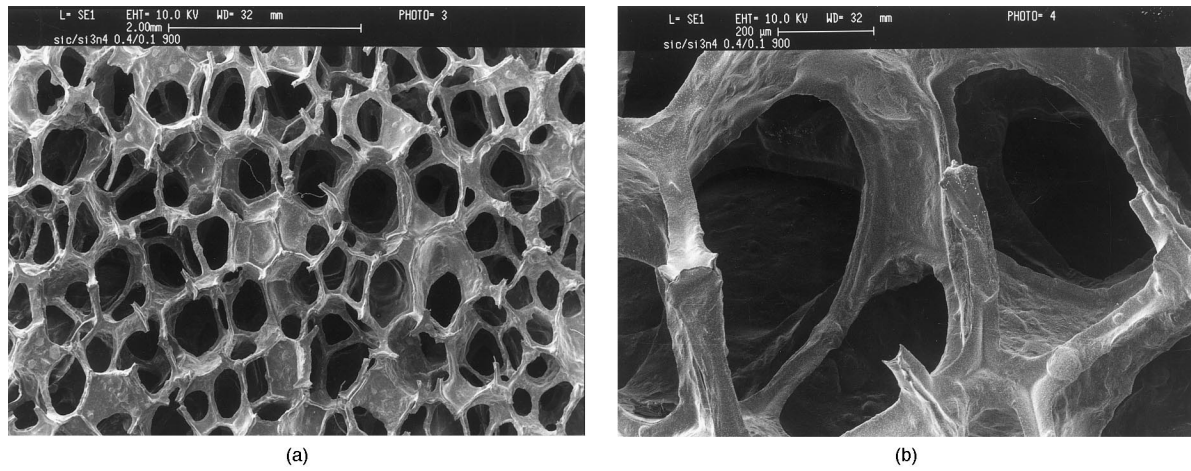


Fig. 5. Scanning electron micrographs showing (a) the open-cell structure and (b) the strut structure of a SiC-Si<sub>3</sub>N<sub>4</sub> foam produced from PS/Si<sub>3</sub>N<sub>4</sub> (80/20 wt%) after pyrolysis at 900°C.

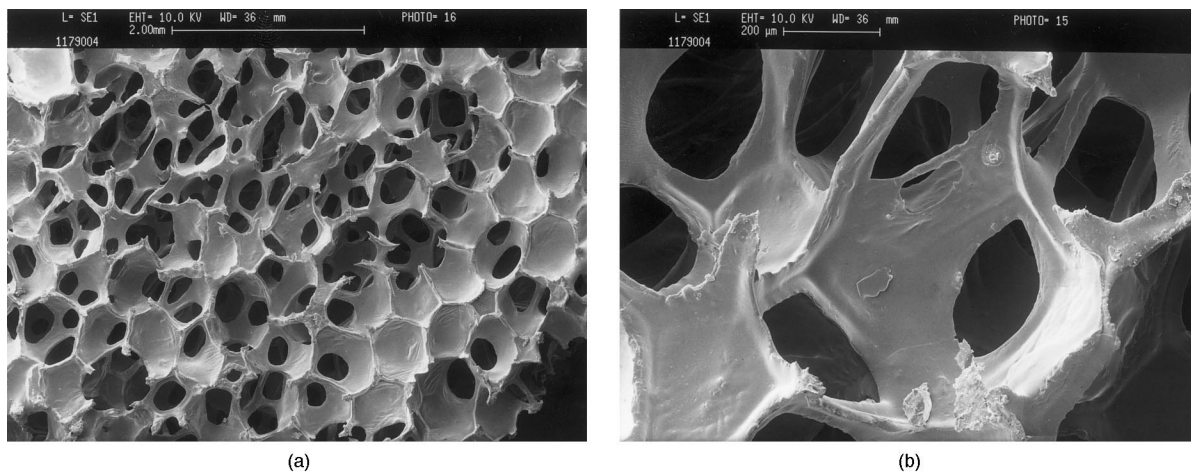


Fig. 6. Scanning electron micrographs showing (a) the open-cell structure and (b) the strut structure of corresponding SiC foam produced from PS after pyrolysis at 900°C.

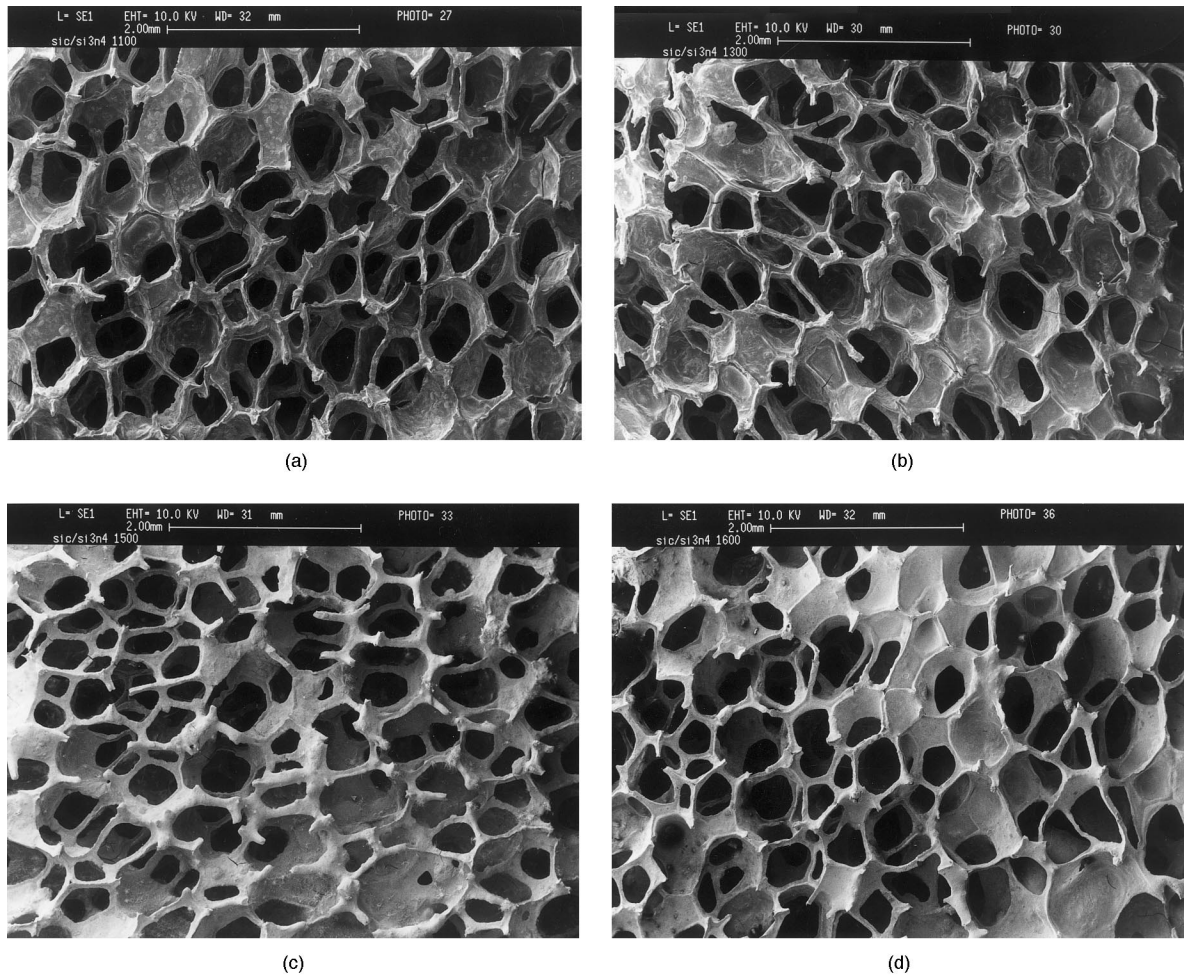


Fig. 7. Scanning electron micrographs of ceramic foams produced from PS/Si<sub>3</sub>N<sub>4</sub> (80/20 wt%) after heat treatment at (a) 1100°C, (b) 1300°C, (c) 1500°C and (d) 1600°C.

their original shapes very well during the conversion from polymer to ceramic.

Mastersizer analysis shows that the Si<sub>3</sub>N<sub>4</sub> powder contained particles in the size range 0.1–4.0 μm. The XRD patterns of the Si<sub>3</sub>N<sub>4</sub> powder and ceramic foams heated to ≥1100°C are shown Fig. 3. The XRD patterns of the ceramic foams are very similar to that of Si<sub>3</sub>N<sub>4</sub> powder until 1300°C. Three characteristic peaks

at  $2\theta = 36^\circ$ ,  $61^\circ$ , and  $72^\circ$  corresponding to the (111), (220), and (311) planes of β-SiC, respectively,<sup>36,37</sup> are observed at 1500°C with the forming of the SiC–Si<sub>3</sub>N<sub>4</sub> composite foam. This suggests that SiC remains amorphous after heating in nitrogen up to 1300°C, and then gradually crystallizes as the temperature is increased. However, as the temperature increases to 1600°C, the XRD pattern shows prominent peaks at  $2\theta = 36^\circ$ ,  $61^\circ$ , and  $72^\circ$  corresponding to β-SiC, mainly due to the residual carbon reacting with the Si<sub>3</sub>N<sub>4</sub> according to the reaction.<sup>38</sup>

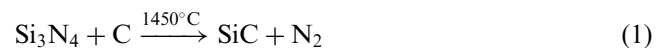


Table 3

Linear<sup>a</sup> and volume<sup>b</sup> shrinkage on pyrolysis of pre-foams (PS/Si<sub>3</sub>N<sub>4</sub>=20/80 wt%) at different temperatures<sup>c</sup>

Temperature/°C	ΔX%	ΔY%	ΔZ%	ΔV%
900	26.5	25.8	26.7	60.4
1100	27.0	26.8	27.1	61.1
1300	27.7	27.4	28.1	62.2
1500	30.5	29.8	31.3	66.1
1600	33.9	33.1	34.4	71.0

<sup>a</sup>  $\Delta L\% = 100 \times (L_{\text{pre-foam}} - L_{\text{ceramic foam}}) / L_{\text{pre-foam}}$ .

<sup>b</sup>  $\Delta V\% = 100 \times (V_{\text{pre-foam}} - V_{\text{ceramic foam}}) / V_{\text{pre-foam}}$ .

<sup>c</sup> X, Y, and Z refer to length, width and height, respectively, of the cubic foam.

### 3.3. Structure and shrinkage

The structures of the polyurethane foam and polysilane/Si<sub>3</sub>N<sub>4</sub> pre-foam are shown in Fig. 4. The PU foam shows a reticular structure with cell size in the

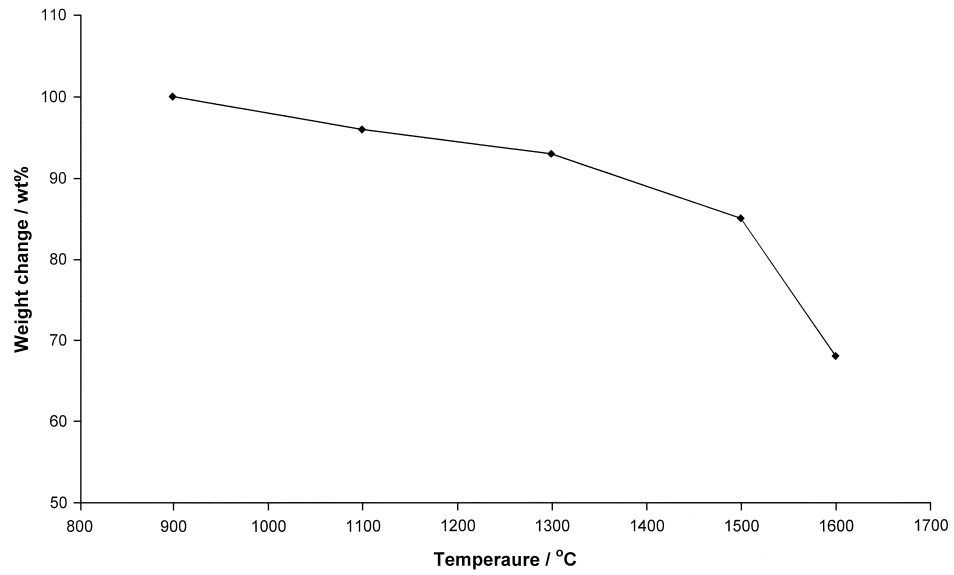
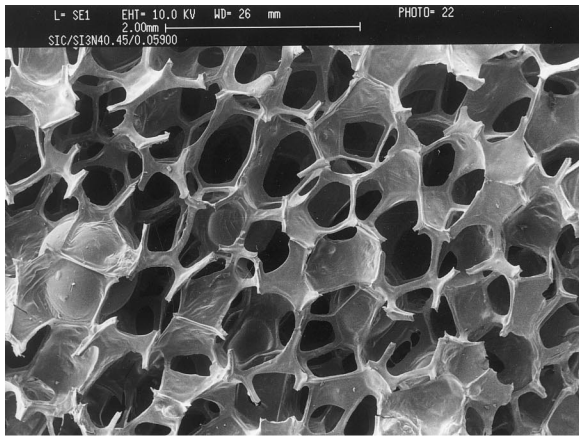
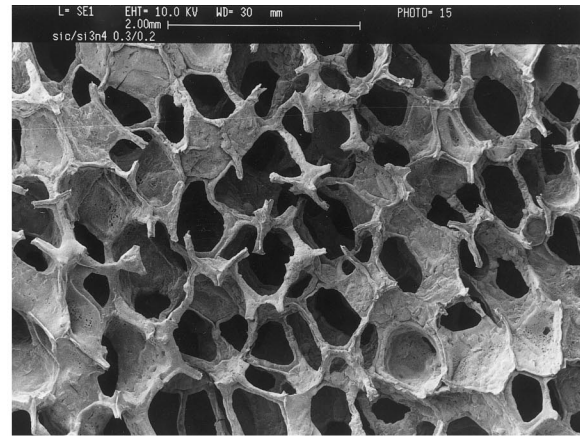


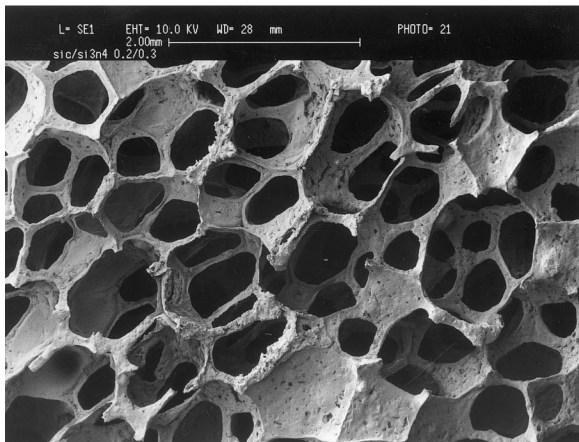
Fig. 8. Weight change in SiC-Si<sub>3</sub>N<sub>4</sub> foams produced from PS/Si<sub>3</sub>N<sub>4</sub> (80/20 wt%) as a function of temperature.



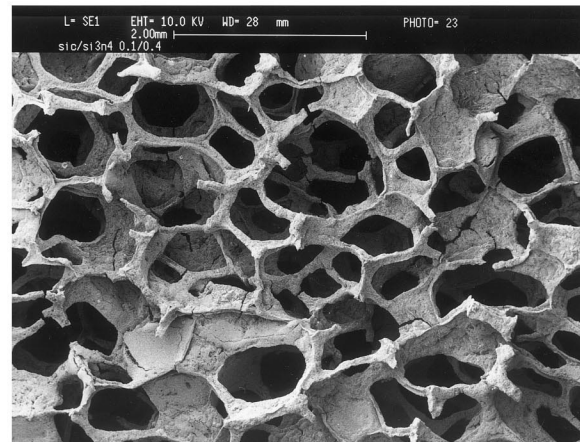
(a)



(b)



(c)



(d)

Fig. 9. (a) Scanning electron micrographs of pyrolyzed ceramic foams (900°C) produced with different PS/Si<sub>3</sub>N<sub>4</sub> formulations (wt%), (a) 90/10, (b) 60/40, (c) 40/60 and (d) 20/80.

Table 4  
Linear<sup>a</sup> and volume<sup>b</sup> shrinkage on pyrolysis of pre-foams with different proportions of Si<sub>3</sub>N<sub>4</sub> in the composite at 900°C<sup>c</sup>

Si <sub>3</sub> N <sub>4</sub> powder in PS/Si <sub>3</sub> N <sub>4</sub> (wt%)	ΔX%	ΔY%	ΔZ%	ΔV%
0	32.0	31.7	33.9	69.3
10	31.4	30.8	31.6	67.5
20	26.5	25.8	26.8	60.4
40	20.3	19.8	20.9	49.6
60	7.5	7.4	7.6	20.9
80	5.4	5.3	5.8	15.3

$$^a \Delta L\% = 100 \times (L_{\text{pre-foam}} - L_{\text{ceramic foam}}) / L_{\text{pre-foam}}$$

$$^b \Delta V\% = 100 \times (V_{\text{pre-foam}} - V_{\text{ceramic foam}}) / V_{\text{pre-foam}}$$

<sup>c</sup> X, Y, and Z refer to length, width and height, respectively, of the cubic foam.

range of 500–800 μm (Fig. 4a). The pre-foam displays a similar reticular structure, but quite a large proportion of cells are covered by thin membranes (Fig. 4b). These thin membranes are burned out almost completely during pyrolysis to 900°C as shown in Fig. 5. The micrograph shown in Fig. 5a reveals that the foams consist of a three-dimensional array of struts and a well-defined open-cell structure with cell sizes between 600 and 900 μm. The cell window size varies from 300 to 600 μm. Struts of the ceramic foam do not contain any voids and are rather densified (Fig. 5b). A similar structure is observed in SiC foam produced by this method (Fig. 6).

These pyrolyzed foams were heat-treated further in nitrogen in the temperature range 1100–1600°C to investigate the effect of higher temperatures on their structure. Micrographs of the ceramic foams after heat treatment at different temperature are shown in Fig. 7. The results indicate that there are no significant changes in the overall structural features of the foams after heat treatment at higher temperatures. However, more shrinkage takes place with the increase of the temperature, particularly at ≥1500°C (Table 3), probably due to the loss of free carbon, crystallization of the ceramics and the release of nitrogen gas because of the reaction between silicon nitride and free carbon as shown in Eq. (1).<sup>38,39</sup> The latter is supported by the fact that the weight loss of the foam increases with temperature with a steep change between 1400 and 1500°C (Fig. 8).

The influence of the percentage of Si<sub>3</sub>N<sub>4</sub> in the pre-ceramic polymer solution on the structure and shrinkage of the ceramic foams was also investigated. As shown in Fig. 9, with the increase of the Si<sub>3</sub>N<sub>4</sub> content, the overall structure of ceramic foams remains similar but some cracks and voids are observed in the foam structure, probably due to the aggregation of Si<sub>3</sub>N<sub>4</sub> particles. However, it is also noteworthy that the shrinkage of the ceramic foams is reduced considerably with the increase of the Si<sub>3</sub>N<sub>4</sub> content in the composite foams (Table 4).

A more detailed scanning electron microscopy based structural evaluation of SiC and SiC–Si<sub>3</sub>N<sub>4</sub> foams prepared using this route has been completed recently.<sup>40</sup>

The results show that struts of the foams are free from holes in the centre. The strut surfaces also do not show any cracks at the right level of Si<sub>3</sub>N<sub>4</sub> addition. These defects are usually observed in the foams made using ceramic slurries.

#### 4. Conclusions

A new process was developed to produce SiC–Si<sub>3</sub>N<sub>4</sub> composite foam by immersing a polyurethane foam in a polysilane precursor solution containing silicon nitride powder to form a pre-foam followed by heating in nitrogen. The polymeric precursor was converted to SiC and SiC–Si<sub>3</sub>N<sub>4</sub> composite foams were thus prepared. Most of the ceramic composite foams produced by this method showed well-defined open-cell structures and macro defect-free struts. With the increase of the increase of temperature from 900 to 1600°C, there were no significant structural changes but increase of weight loss and shrinkage were observed. The shrinkage of the foams was reduced with the increase of the silicon nitride content in the composites, but some cracks in the foam structure were observed at high percentages of Si<sub>3</sub>N<sub>4</sub>.

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