JOURNAL OF MATERIALS SCIENCE **35** (2000) 4365–4372

Preparation of silicon carbide foams using polymeric precursor solutions

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A simple method was developed to produce silicon carbide foams using polysilane polymeric precursors. Polyurethane foams were immersed in polysilane precursor solutions to prepare pre-foams. Subsequently, these were heated in nitrogen at different temperatures in the range of 900°C to 1300°C. The silicon carbide foams produced in this manner showed well-defined open-cell structures and the struts in the foams were free of voids. The shrinkage which accompanies pyrolysis of the pre-foams was reduced by increasing the concentration of the polymeric precursor in the solutions. © *2000 Kluwer Academic Publishers*

1. Introduction

Ceramic foams have found many industrial applications as high temperature thermal insulation, hot gas particulate filters, hot metal filters, catalyst supports and cores in high temperature structural panels due to their favourable properties such as low density, low thermal conductivity, thermal stability, high specific strength and high resistance to chemical attack [1–5]. The most common process for producing ceramic foams is impregnation of polyurethane foams with a ceramic suspension followed by pyrolysis and pressureless sintering at elevated temperatures [3–7]. Conventionally, the suspension or the slurry is made up of ceramic particles, water and other additives which provide handling strength, preventing the collapse of the foam structure during polymer removal [5]. Fig. 1a shows the various steps involved in the procedure.

Alternative methods have also been developed to produce ceramic foams. These include chemical vapour deposition of ceramics on to a porous carbon skeleton [8], sol-gel processes that develop porosity during phase transformations and chemical reactions [9], siliciding carbon foams [10], a gel-cast foam process which combines the foaming of ceramic suspensions and *in-situ* polymerization [11], a replication process where polymer is injected into a porous substrate, such as sodium chloride which is removed later to produce carbon and silicon carbide foams [12–14] and co-blowing a solution containing a pre-ceramic polymer and polyurethane precursors [15]. Ceramic foams synthesized directly by pyrolyzing polymeric precursors is also being investigated by Bao *et al.* [16].

In the present paper, a simple method has been developed to produce silicon carbide (SiC) foams using polymeric precursor solutions. Several polysilanes have been synthesized and used as the polymeric precursors for SiC. These precursors are soluble in common solvents such as dichloromethane, tetrahydrofuran and toluene. Thus, SiC foams have been prepared by immersion of polyurethane foams in the precursor solution to form a polymeric precursor coated pre-foam. After drying, the pre-foam was subjected to firing at a high temperature to obtain a ceramic foam (Fig. 1b). Compared with the conventional polyurethane-ceramic slurry method (Fig. 1a) and other foaming methods reported, the main advantages of this process are the simplicity and ease of control of structure of the final product.

2. Experimental details

2.1. Synthesis of polysilanes

The polysilanes discussed in this paper were synthesized using alkali dechlorination of various combinations of chlorinated silane monomers in refluxing toluene/tetrahydrofuran with molten sodium as described previously [17–20]. Details of the various monomers used are summarized in Table I.

2.2. Preparation of pre-foams

A polyurethane (PU) sponge with open-cell sizes in the range of 400–800 μm was used in this work. The polysilanes were dissolved in dichloromethane to form polymeric precursor solutions. The concentration of polymer in the precursor solution can be adjusted by varying the amount of polymer dissolved. Typically, 0.8 g of polymer was dissolved in 2000 mm^3 of dichloromethane. The PU sponge was first cut into cubes of volume $\sim$1000 mm^3 and was then immersed in each precursor solution for about 2 hours. The samples were air-dried at room temperature overnight to obtain the pre-foams. These pre-foams were subsequently pyrolyzed in nitrogen.

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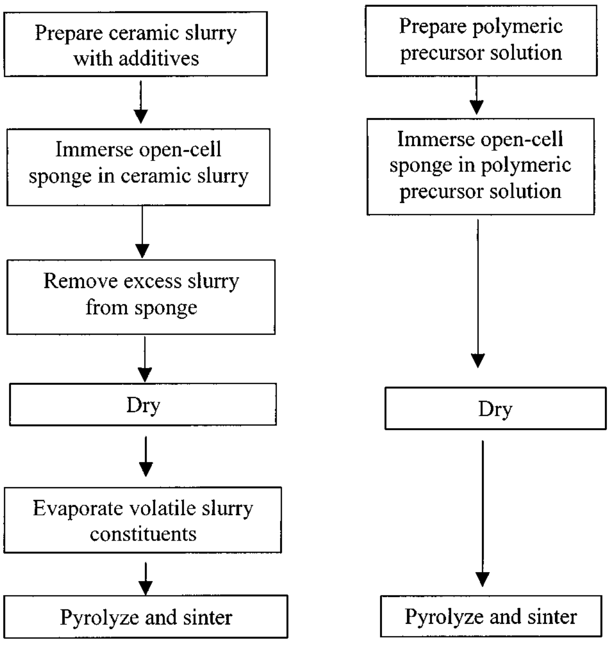
TABLE I Monomers used in the synthesis of polysilanes, f refers to functionality

Monomers	Formula	f	Abbreviations
Dichloromethyphenylsilane	$(CH_3)(C_6H_5)SiCl_2$	2	MP
Dichloromethylsilane	$(CH_3)HSiCl_2$	3	MH
Trichlorophenylsilane	$C_6H_5SiCl_3$	3	TCP
Dichloromethylvinylsilane	$(CH_3)(CH_2{=}CH)SiCl_2$	4	MVin



(a) (b)

Figure 1 Key stages involved in the production of ceramic foam using (a) the traditional polyurethane-ceramic slurry method and (b) the polymeric precursor solution method.

2.3. Pyrolysis

The pre-foams were placed in an alumina boat and heated from the ambient temperature to 900°C at 1°C min^{-1} in a tube furnace (Lenton Thermal Designs Ltd., Market Harborough, UK) in the presence of flowing nitrogen gas (flow rate approximately 2.50×10^5 mm^3 min^{-1}) followed by soaking at this temperature for 2 hours. Subsequently, the furnace was switched off and allowed to cool to room temperature. Some of the pyrolyzed samples were heated further in the tube furance in the presence of flowing nitrogen gas (flow rate approximately 2.50×10^5 mm^3 min^{-1}) from the ambient temperature to different final temperatures (1100°C to 1300°C) at 2°C min^{-1} followed by soaking at this temperature for 2 hours and then cooling to room temperature at 2°C min^{-1}.

2.4. Characterization

The molecular weights of the polysilanes were 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 1000 mm^3 min^{-1}. Fourier transform-infrared (FT-IR) spectra of as-synthesized polymer samples were obtained using a Nicolet 710 spectrometer. 1 mg of each polymer was ground and mixed with 150 mg of dried KBr powder and pressed into a pellet. Spectra were obtained in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

The pyrolytic yield from each polymer was measured by thermogravimetry. Samples were heated from the ambient temperature up to 900°C in flowing nitrogen (500 mm^3 min^{-1}) at 10°C min^{-1} in a Hi-Res Modulated TGA 2950 Thermogravimetric Analyzer to determine the pyrolytic yield.

X-ray diffraction (XRD) was carried out on the polysilanes after heating to various final temperatures ($\geq$900°C) in nitrogen. Samples for X-ray diffractometry were ground using an agate pestle and mortar. A modified Philips X-ray diffractometer with filtered Cu Kα radiation of wavelength 0.15418 nm was used (a graphite monochrometer removes Kβ radiation). The voltage and current settings of the diffractometer were 40 kV and 30 mA, respectively. The scan range was from 10° to 90° with a step size of 0.05° and a scan speed of 0.025° s^{-1}.

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 characterization

Polysilanes were prepared with different monomers as shown in Table I. Each reaction leads to the production of three different polymer fractions, i.e. insoluble solid (IS), soluble solid (SS) and soluble liquid (SL). The soluble solid (SS) is used as the SiC precursor. The yields and molecular weights of the polysilanes prepared in the present work are given in Table II.

As an example, a typical FT-IR spectrum of terpolysilane (PS4) is shown in Fig. 2. It exhibits characteristic C-H stretching between 3100 and 2700 cm^{-1}. The peaks at 3050 and 3067 cm^{-1} represent C-H stretching in the phenyl group. Methyl group stretching is observed at 2956 and 2894 cm^{-1}. Additional peaks at 1406 and 1248 cm^{-1} are characteristic of the asymmetric and symmetric bending modes, respectively, of CH_3 bonded to silicon. Three small peaks at 1949, 1887 and 1815 cm^{-1} are attributed to the

TABLE II Details of monomer(s) used in the synthesis, polymer yield, molecular weight and pyrolytic yield of each polymer

Polymer	Monomer(s) used (mol %)	Polymer yield (wt %)	Molecular weight ($\bar{M}_w$)	Pyrolytic yield (wt %)
PS1	MP = 100	43	7680	23.6
PS2	MP/MVin/MH = 60/20/20	38	12000	53.2
PS3	MP/MVin/MH = 50/25/25	30	7530	54.3
PS4	MP/MVin/TCP = 60/20/20	60	7650	56.0
PS5	MP/MVin/TCP = 50/25/25	57	8210	60.0

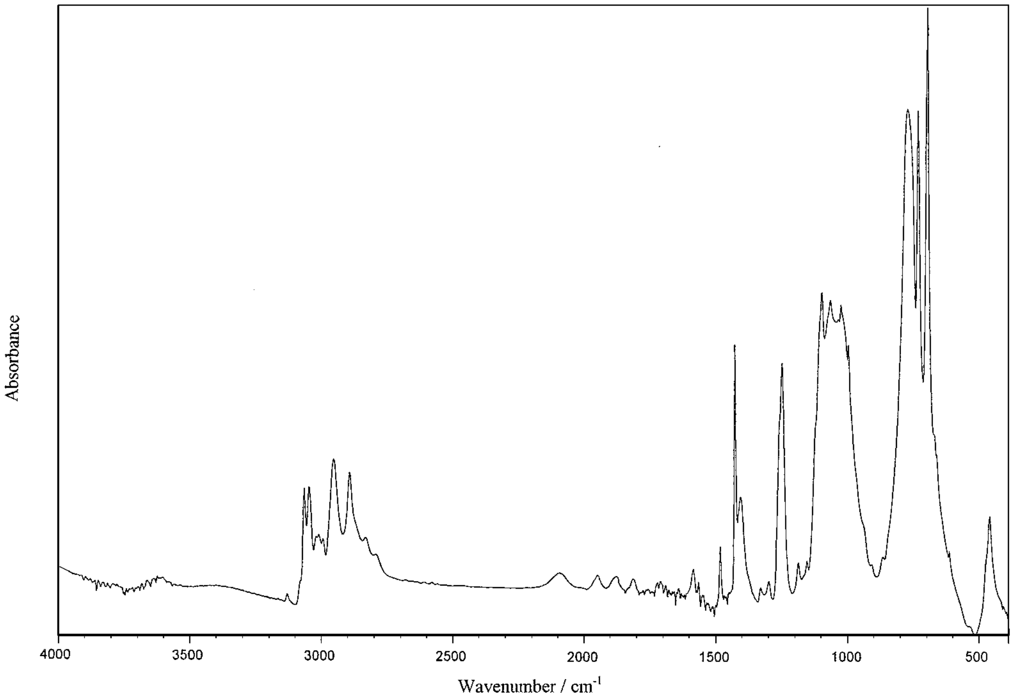


Figure 2 FT-IR spectrum of polysilane PS4.

phenyl-Si vibration. The peaks at low wavenumbers of 697 cm^{-1} for Si-C stretching and 464 cm^{-1} for Si-Si are typical for these polysilanes [21–23]. A characteristic peak at 1589 cm^{-1}, where the vinyl group occurs, is clearly present [24, 25]. The appearance of a Si-H stretching peak around 2100 cm^{-1} implies that there were some hydrosilane groups formed in the polymers during polymerization [18].

3.2. Conversion to ceramic foams

The thermogravimetric traces of the polysilanes and polyurethane foam are shown in Fig. 3 and the pyrolytic yield of each polysilane is given in Table II. It is noteworthy that thermal decomposition of the PU foam starts at about 200°C and nearly 95 wt% of the material is lost by 420°C. In fact, PU foam is almost fully pyrolyzed at 500°C. On the other hand, in the case of the polysilane SiC precursors, the pyrolysis process takes place in three 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 polymers and small molecules consisting mainly of methane and hydrogen are evolved [25]. 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.

It is apparent that the pyrolytic yield is very dependent on the composition of the polymers. Ter-polymers (PS2-PS5) give better pyrolytic yields, compared with

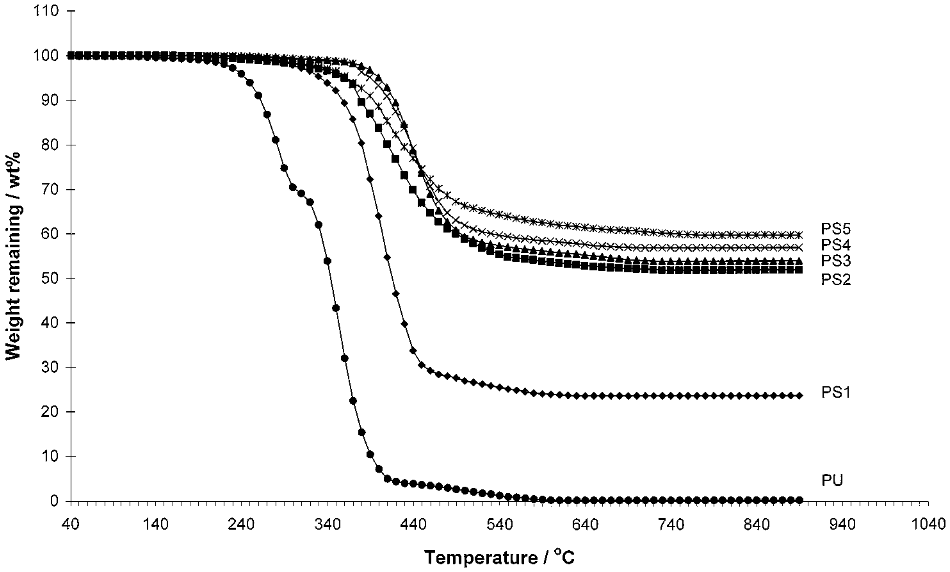


Figure 3 Thermogravimetric traces of polyurethane foam and polymeric precursors PS1-PS5.

the homopolymer P1. This can be attributed to the cross-linked structures formed during pyrolysis due to the thermal cross-linking capability of hydrosilane (Si-H) and vinyl ($CH_2{=}CH$) groups in the polymeric precursors and the branched structures generated during polymerization due to the addition of trichlorophenylsilane monomer [24–29]. Such cross-link formation will allow the material to maintain its original morphology during pyrolysis because the melting of the polymeric precursors is hindered [16] and this is critical in preventing the collapse of the ceramic foams during pyrolysis, as is the case in the PS1 pre-foam. All other polysilane precursor coated pre-foams maintained their original shapes very well during conversion to the ceramic.

The XRD patterns of the residues heated to over 900°C showed that the polysilanes synthesized produced SiC on pyrolysis. Taking PS2 as an example, XRD results (Fig. 4) suggest that the residues obtained after heating in nitrogen were amorphous up to 1100°C, and then gradually crystallized as the temperature was

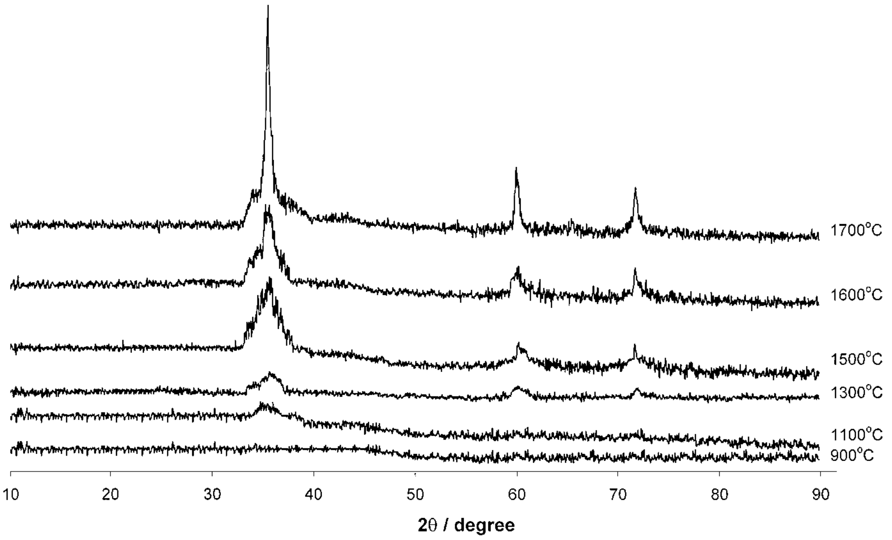


Figure 4 XRD patterns of ceramics derived from polysilane PS4 after heating to different temperatures in the range of 900°C−1700°C.

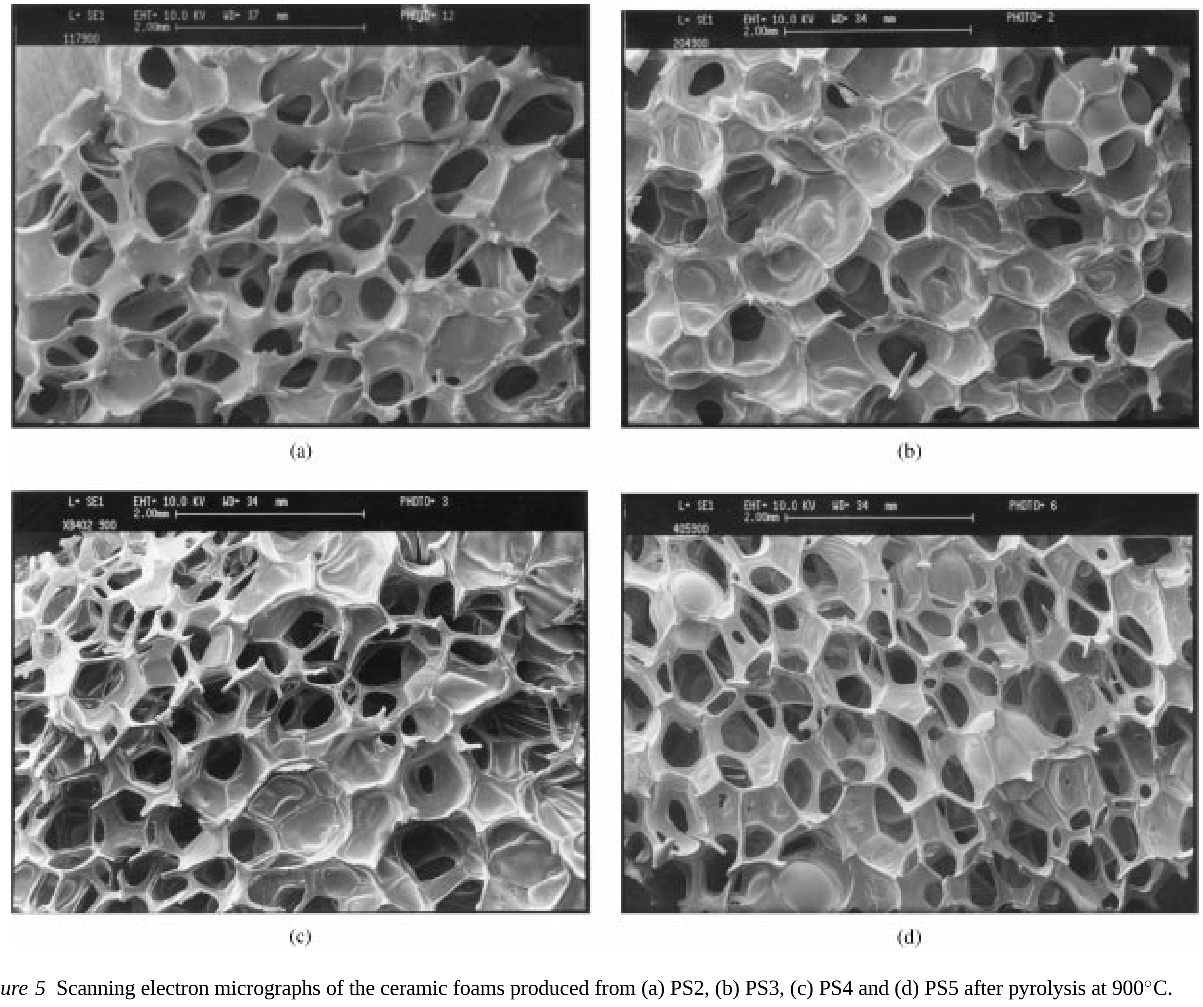
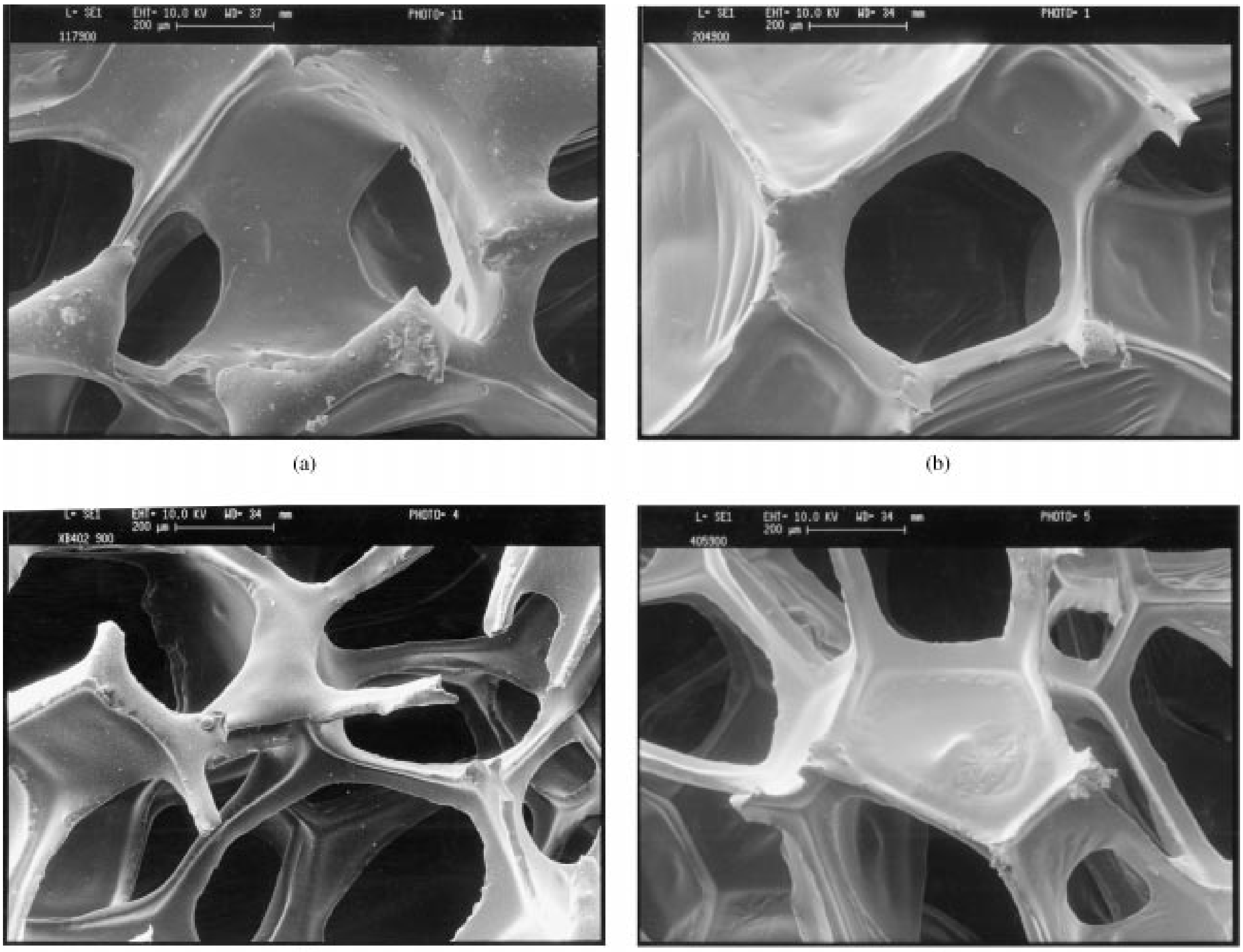


Figure 5 Scanning electron micrographs of the ceramic foams produced from (a) PS2, (b) PS3, (c) PS4 and (d) PS5 after pyrolysis at 900°C.

increased. Three characteristic peaks were observed in the crystallized materials at $2\theta = 36°$, $61°$, and $72°$, which correspond to the (111), (220), and (311) planes of β-SiC, respectively [30, 31].

3.3. Structure and shrinkage

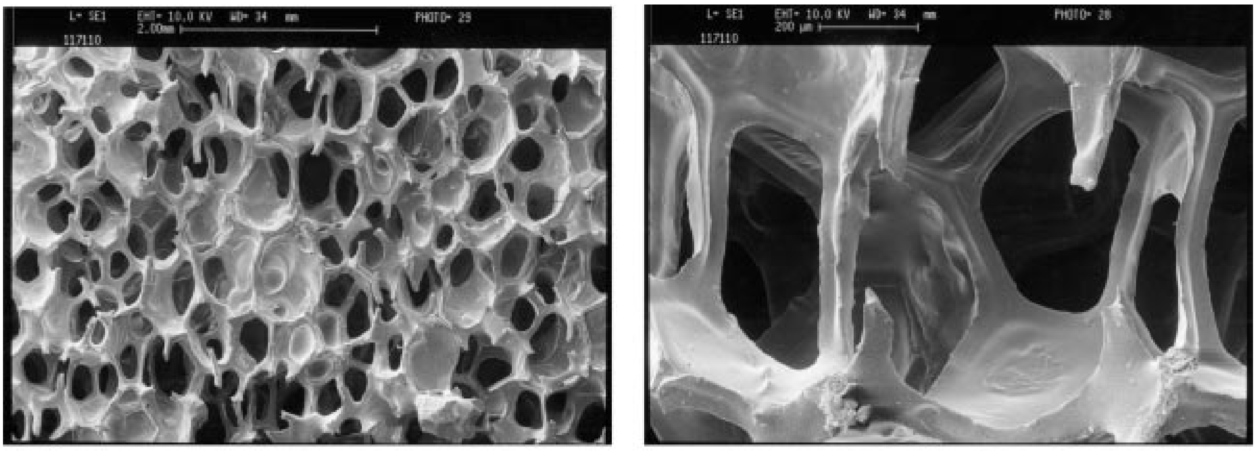
The structures of the ceramic foams prepared by pyrolysis of the pre-foams made using polymer PS2-PS5 to 900°C are shown in Fig. 5. These micrographs reveal that these foams consist of a three-dimensional array of struts and a well-defined open-cell structure with cell sizes between 400 μm and 800 μm. The cell windows vary in size from 200 μm to 500 μm. Some of the cell windows are covered with a thin ceramic membrane. As discussed above, the PU foam starts to thermally decompose from about 200°C and is almost fully pyrolyzed at 500°C (Fig. 3). Hence these foams are self-supporting and retain the shape during the later stage of pyrolysis from polymer to ceramic in the temperature



(a) (b)

(c) (d)

Figure 6 Scanning electron micrographs of strut structures of (a) PS2, (b) PS3, (c) PS4 and (d) PS5 after pyrolysis at 900°C.



(a) (b)

Figure 7 Scanning electron micrographs showing (a) the open-cell structure and (b) the strut structure of a SiC foam produced from PS2 after heat treatment at 1100°C.

range 500°C–700°C. It indicates that the polymeric precursors form a homogeneous and continuous structure within the polyurethane template. Struts of these foams do not contain any voids (Fig. 6).

These pyrolyzed foams were further heat-treated to 1100°C and 1300°C in nitrogen to investigate the effect of higher temperatures on the structure of these foams. Micrographs of a SiC foam prepared from PS2, as an example, are shown in Figs 7 and 8. The results indicate that there are no obvious changes in the morphology of the ceramic foams after heat treatment at a higher temperature. However, more shrinkage takes place with the increase of temperature (Table III), due to the loss of free carbon and crystallization of the SiC [20].

The influence of the concentration of the pre-ceramic polymer solution on the structure of the ceramic foams was also investigated. As shown in Figs 9 and 10, taking PS2 as an example, with the increase of concentration,

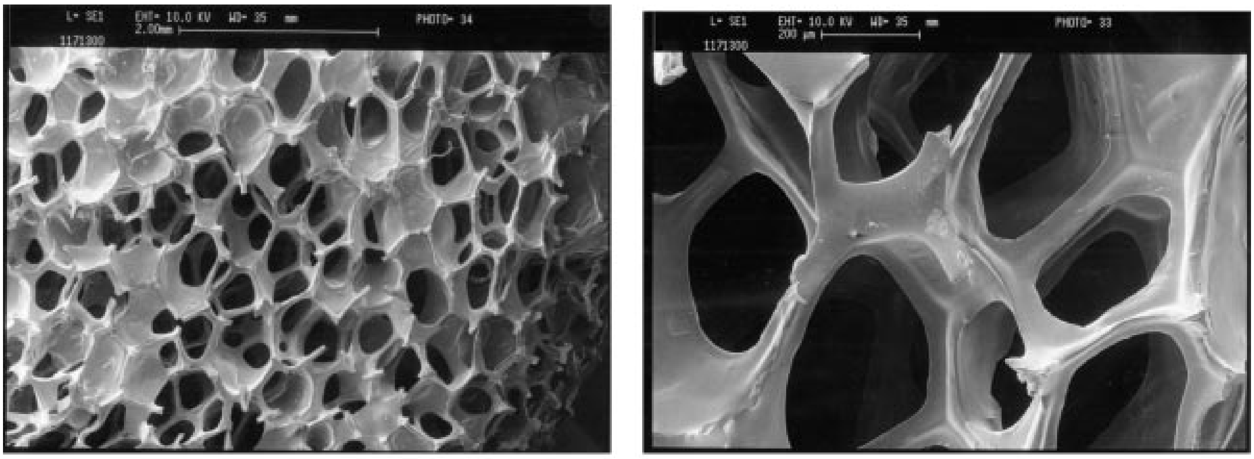

(a) (b)

Figure 8 Scanning electron micrographs showing (a) the open-cell structure and (b) the strut structure a SiC foam produced from PS2 after heat treatment at 1300°C.

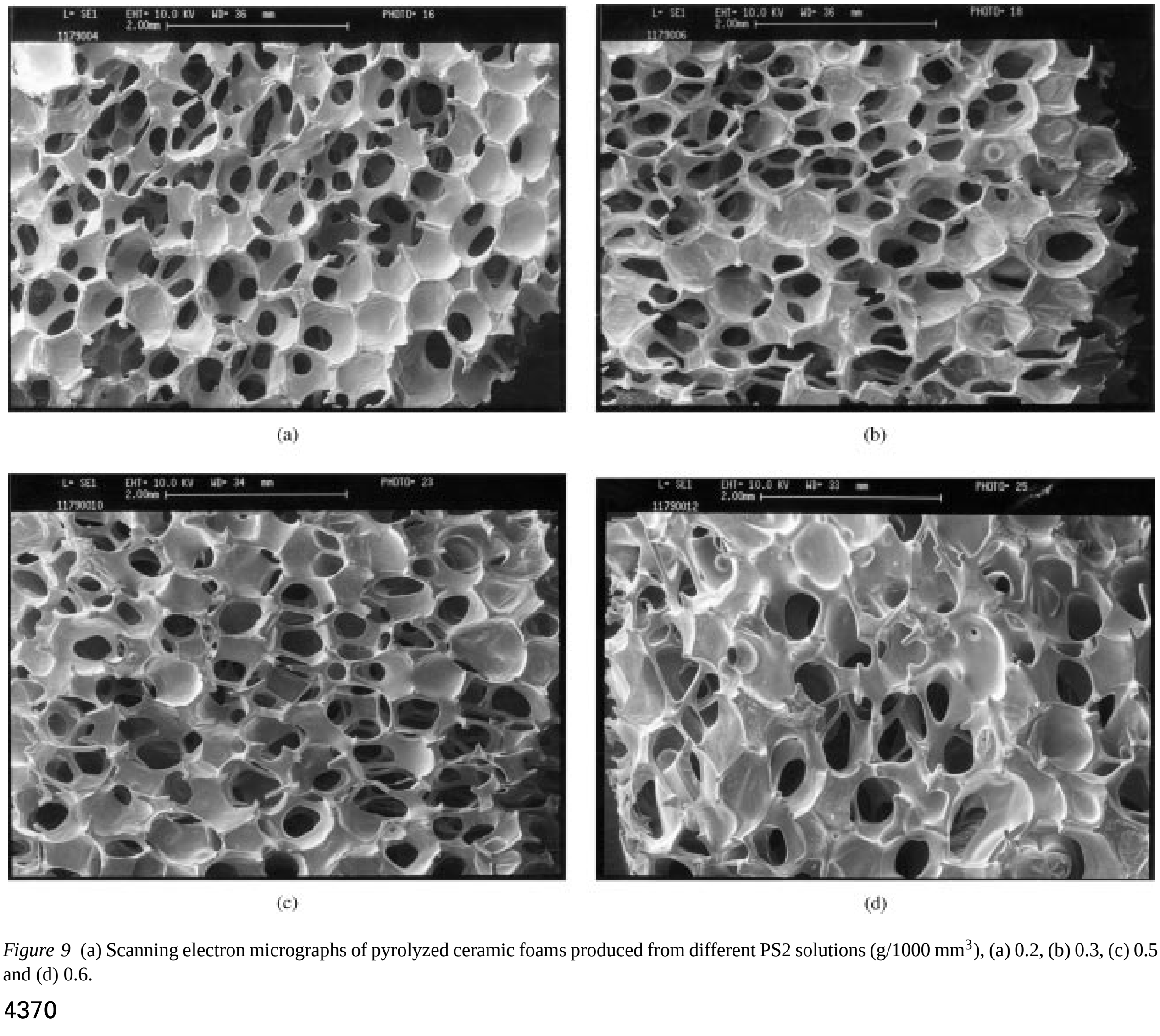
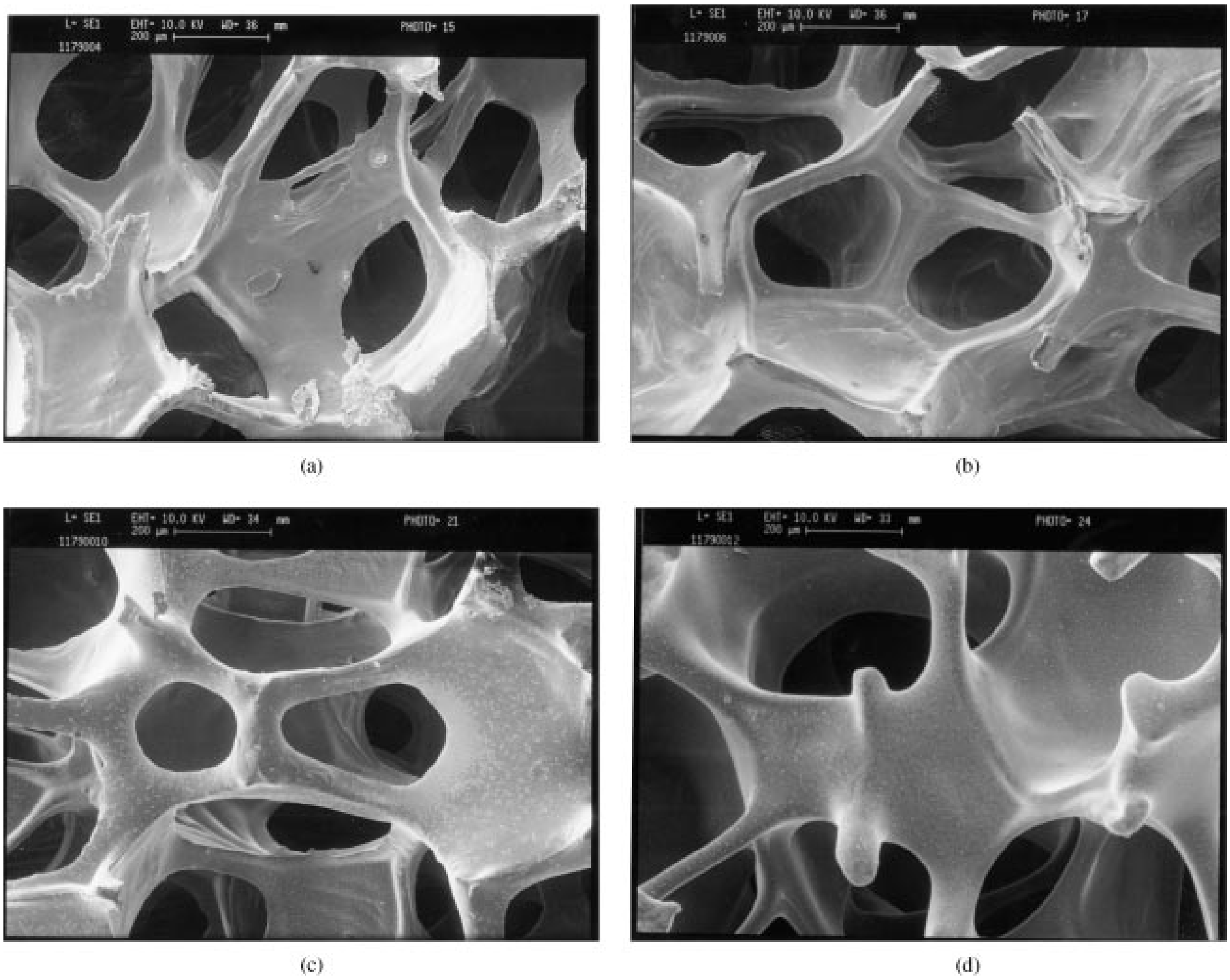

(a) (b) (c) (d)

Figure 9 (a) Scanning electron micrographs of pyrolyzed ceramic foams produced from different PS2 solutions (g/1000 mm^3), (a) 0.2, (b) 0.3, (c) 0.5 and (d) 0.6.



(a) (b)

(c) (d)

Figure 10 (a) Scanning electron micrographs of the strut structures of pyrolyzed ceramic foams produced from different PS2 solutions (g/1000 mm^3), (a) 0.2, (b) 0.3, (c) 0.5 and (d) 0.6.

TABLE III Linear[a] and volume[b] shrinkage on heating pre-foams (PS2) at different temperatures. X, Y and Z refer to length, width and height, respectively, of the cubic foam

Temperature/°C	$\Delta X\%$	$\Delta Y\%$	$\Delta Z\%$	$\Delta V\%$
900	22.4	20.0	23.5	52.5
1100	24.0	24.2	25.2	56.9
1300	32.2	31.7	33.0	67.8

[a] $\Delta L\% = 100 \times (L_{\text{pre-foam}} - L_{\text{ceramic foam}})/L_{\text{pre-foam}}$.
[b] $\Delta V\% = 100 \times (V_{\text{pre-foam}} - V_{\text{ceramic foam}})/V_{\text{pre-foam}}$.

TABLE IV Linear[a] and volume[b] shrinkage on pyrolysis of pre-foams prepared using different concentrations of PS2. X, Y and Z refer to length, width and height, respectively, of the cubic foam

Concentration (g/1000mm^3)	$\Delta X\%$	$\Delta Y\%$	$\Delta Z\%$	$\Delta V\%$
0.2	32.0	31.7	33.9	69.3
0.3	24.8	23.3	26.0	57.4
0.4	22.4	20.0	23.5	52.5
0.5	19.2	18.3	20.0	47.2
0.6	15.2	14.2	16.5	39.2

[a] $\Delta L\% = 100 \times (L_{\text{pre-foam}} - L_{\text{ceramic foam}})/L_{\text{pre-foam}}$.
[b] $\Delta V\% = 100 \times (V_{\text{pre-foam}} - V_{\text{ceramic foam}})/V_{\text{pre-foam}}$.

the overall structure of ceramic foams remains similar but an increase in the thickness of the struts is observed. Also more cell windows are covered with thin ceramic membranes.

Linear and volume shrinkage of the ceramic foam samples prepared from PS2 precursor solutions of different concentrations were measured and these data are reported in Table IV. It is noteworthy that with the increase of concentration of precursor in the solution, the shrinkage of the ceramic foams is reduced and appears to be fairly isotropic. These are favourable characteristics when considering the production of foamed ceramic parts.

4. Conclusions

Silicon carbide foams have been prepared successfully by immersing polyurethane foam in polymeric precursor solutions to form pre-foams followed by heating in nitrogen. The polymeric precursors were thus converted to silicon carbide. The silicon carbide foams produced by this method showed well-defined open-cell structures and void-free struts. With increasing concentration of the polysilanes in the precursor solutions, the shrinkage of the foams was reduced without changing significantly the structure of the foams.

Acknowledgements

The authors wish to thank the Government of Pakistan for partial support of this work via a PhD scholarship to Mr. Nangrejo. Part of this work was done at the Institute of Polymer Technology & Materials Engineering in Loughborough University. Mr. F. Page and Mr. J. S. Bates are thanked for help in electron microscopy. The support of Dr. D. H. Ross and Mr. T. J. Atkinson in resolving technical matters are acknowledged.

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Received 7 July
and accepted 22 September 1999