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Preparation of high-temperature filter by pressure-pulsed chemical vapour infiltration of SiC into carbonized paper-fibre preforms

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SiC was partially infiltrated into three types of carbonized paper-fibre preforms using pressure-pulsed chemical vapour infiltration from $SiCl_4$(4%)–CH_4(4%)–H_2 at 1100 °C (A-type preforms, source fibres of filter paper; B_H- and B_L-type preforms, source fibres of recycled paper). The porosity of the preforms decreased linearly with the number of pulses. After 10 000 pulses, the porosity of A-, B_H- and B_L-type samples was 77, 78 and 85%, respectively. Average pore sizes of A-, B_H- and B_L-type samples after 10 000 pulses were about 5.0, 2.7 and 7.0 μm, respectively. On an A-type sample of 10 mm ϕ and 5 mm long after 10 000 pulses, pressure drop along the direction of axial air flow was 10 kPa at a face velocity of 0.8 m s^{-1}. The order of pressure drop was $B_H > A > B_L$. Flexural strength of A-type sample reached 10 MPa after 15 000 pulses. © *1998 Kluwer Academic Publishers*

1. Introduction

Gas-permeable SiC is a promising material for use as a high-temperature filter for diesel exhaust gas or for coal combustion processes; it can also be used as a catalyst carrier for high-temperature applications. In order to obtain a highly gas-permeable SiC shape, a thin wall structure is ideal: the chemical vapour infiltration (CVI) process is a suitable method to obtain such a structure, because the SiC films can be deposited on the wall of the micropores in the porous preforms. Among the CVI processes, three methods have been developed; isothermal and isobaric CVI (ICVI), forced CVI (FCVI) and pressure-pulsed CVI (PCVI). ICVI has the characteristic of producing a near-net-shape product [1, 2]. However, it needs a long operation time because of slow gas diffusion, and it is difficult to infiltrate the matrix uniformly. FCVI uses steep gradients of pressure and temperature along the preform thickness, and has the advantage of a short operation time [3, 4]. This process, however, requires the use of one holder per preform, and the shape of the preform is limited to a cube or cylinder for homogeneous gas flow. The PCVI process consists of three sequential steps: evacuation of the reaction vessel, instantaneous introduction of source gas, and holding to allow deposition (holding time). The PCVI process permits one to prepare many products with complex shapes in a run and in a relatively short time, e.g. 5–40 h [5–9]. This process also allows homogeneous infiltration of the matrix through the thickness of the preforms under suitable conditions, because of rapid penetration of the source gas throughout the preform.

It has been reported that a fibrous SiC shape was obtained from ceramic-fibre preforms, such as carbon fibres or Nextel fibres, using the CVI method [10, 11]. Fibrous SiC has the advantage of high thermal shock resistance because of the structural flexibility caused by point-to-point bonding of fibres. However, such ceramic-fibre preforms are expensive. It is expected that fibrous SiC can be prepared from carbon-fibre preforms by the successive steps of oxidation of the preform carbon after PCVI of SiC, and use of carbonized paper-fibres as a source of preforms may lead to low cost preparation of fibrous SiC. In this study, the partial densification process of carbonized paper-fibre preforms with SiC was investigated using PCVI from $SiCl_4$–CH_4–H_2.

2. Experimental procedure

Carbonized paper-fibre preforms were prepared as follows. Commercial cellulose fibres from filter paper or the fibres of recycled paper were disentangled and suspended in water at 100 °C, twisted, put into a glass tube, pressed, dried, carbonized at 1000 °C in Ar for 4 h, and cut to 8–9 mm ϕ and 5–15 mm long. Three types of columnar preforms were prepared, specific properties of which are shown in Table I. The initial porosity of the preforms was controlled by changing the pressure in the pressing step, where the pressures for A- and B_H-type preforms were about 0.7 MPa, and B_L-type preforms were shaped without pressure.

Fig. 1 shows the apparatus for the PCVI of SiC. The source gas mixture of $SiCl_4$(4%)–CH_4(4%)–H_2 flowed into a reservoir, introduced instantaneously (within 0.1 s) to a reaction vessel up to 0.1 MPa, held here for 0.4 s to allow SiC deposition (holding time), and

TABLE I Size, porosity and average pore size of preforms

Type	Source paper for preform fibres	Size (mm)	Porosity (%)	Average pore size (μm)
A	Filter paper	$9\phi \times 5-15$	88	6
B_H	Recycled paper	$9\phi \times 15$	87	4
B_L	Recycled paper	$8\phi \times 15$	95	8

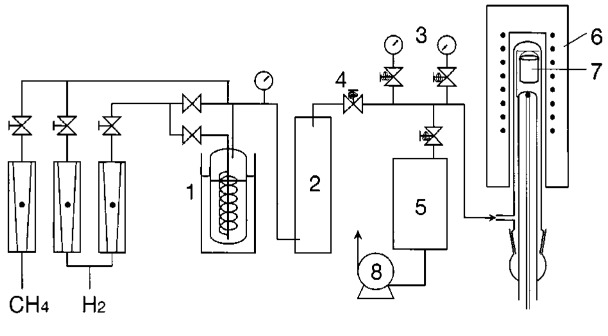

Figure 1 Apparatus for pressure-pulsed CVI of SiC: 1, $SiCl_4$ saturator; 2, reservoir; 3, pressure gauge; 4, electromagnetic valve; 5, vacuum tank; 6, furnace; 7, preform; 8, vacuum pump.

evacuated to below 0.7 kPa within 1.5 s. The CVI temperature was kept at 1100 °C. The oxidation step of the as-infiltrated samples was carried out in an air flow at 1000 °C for 5 h.

Residual porosity, R(%), of the sample was calculated from the following equation

$$R = R_0[1 - (V_{SiC}/V_0)]$$

where R_0, V_{SiC} and V_0 are the initial porosity of the preform, and the volume of SiC deposits and the initial volume of pores in the preform, respectively; and the densities of SiC deposits and carbon were assumed to be 3.1 and 1.8 g cm^{-3}, respectively.

Pore size distribution was determined by the bubble-point method according to ASTM F316. In this method, the air pressures and the flow rates are measured for both a dry and a fluid-wet sample (undecane was used as the fluid in the present measurement). The air flows through the wet sample when the applied air pressure exceeds the capillary attraction of the fluid into the pore, where the pressure is inversely proportional to the pore size. By comparing the air flow rates of both the wet and the dry samples at the same pressure, the volume percentage of the pores that air passes through can be calculated, and the average pore size is also determined by the pressure at which the wet sample flow is half of the dry sample flow.

Pressure drop was determined by measuring the air pressures under varying air flow rates through the dry columnar sample in an axial direction at room temperature.

Flexural strength was measured by the three-point bending test at room temperature, using specimens $3 \times 10 \times 2$ mm^3 in size, which were cut from the columnar sample.

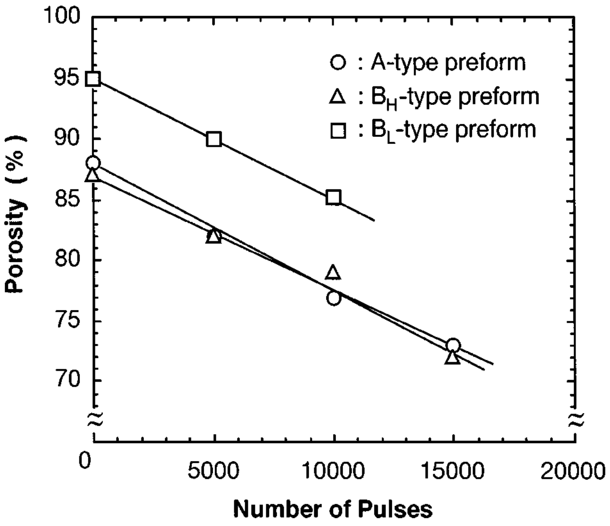

Figure 2 Dependence of porosity on number of pulses. Sample size: A- and B_H-type, 9 mm ϕ and 15 mm long; B_L-type, 8 mm ϕ and 15 mm long.

3. Results and discussion

3.1. Effect of number of pulses on porosity and pore size distribution

Fig. 2 shows the dependence of the residual porosity of the samples obtained from the three types of preforms on the number of pulses. The porosity of the A-type sample decreases linearly when the number of pulses increases up to 15 000, as SiC is infiltrated into the preform. After 10 000 and 15 000 pulses, the porosity becomes 77 and 73%, respectively. The porosity of B_H-type reaches about 78% after 10 000 pulses, which is close to that of the A-type. The porosity of the B_L-type after 10 000 pulses is about 85%, which is higher than that of B_H-type, reflecting the high initial porosity of the B_L-type preform. The rate of decrease of the porosity is similar in every sample. In Fig. 3, X-ray diffraction (XRD) patterns from the cross-sections of the original A-type preform and the sample after infiltration of 15 000 pulses are shown. Only broad peaks assigned to β-SiC are observed on the infiltrated sample. Fig. 4

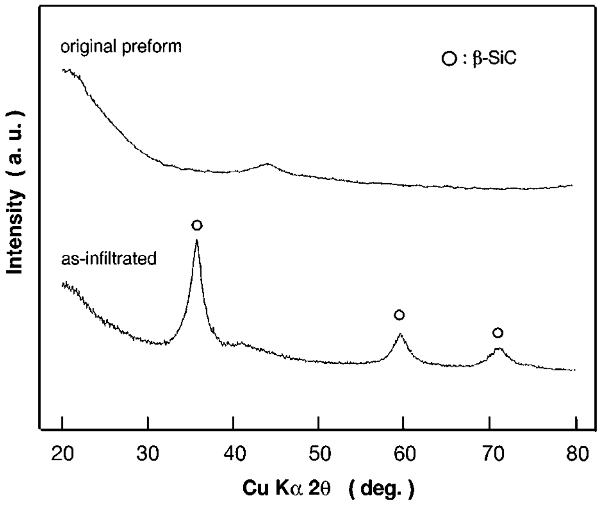

Figure 3 XRD patterns of the cross-sections of the original A-type preform and the infiltrated sample after 15 000 pulses.

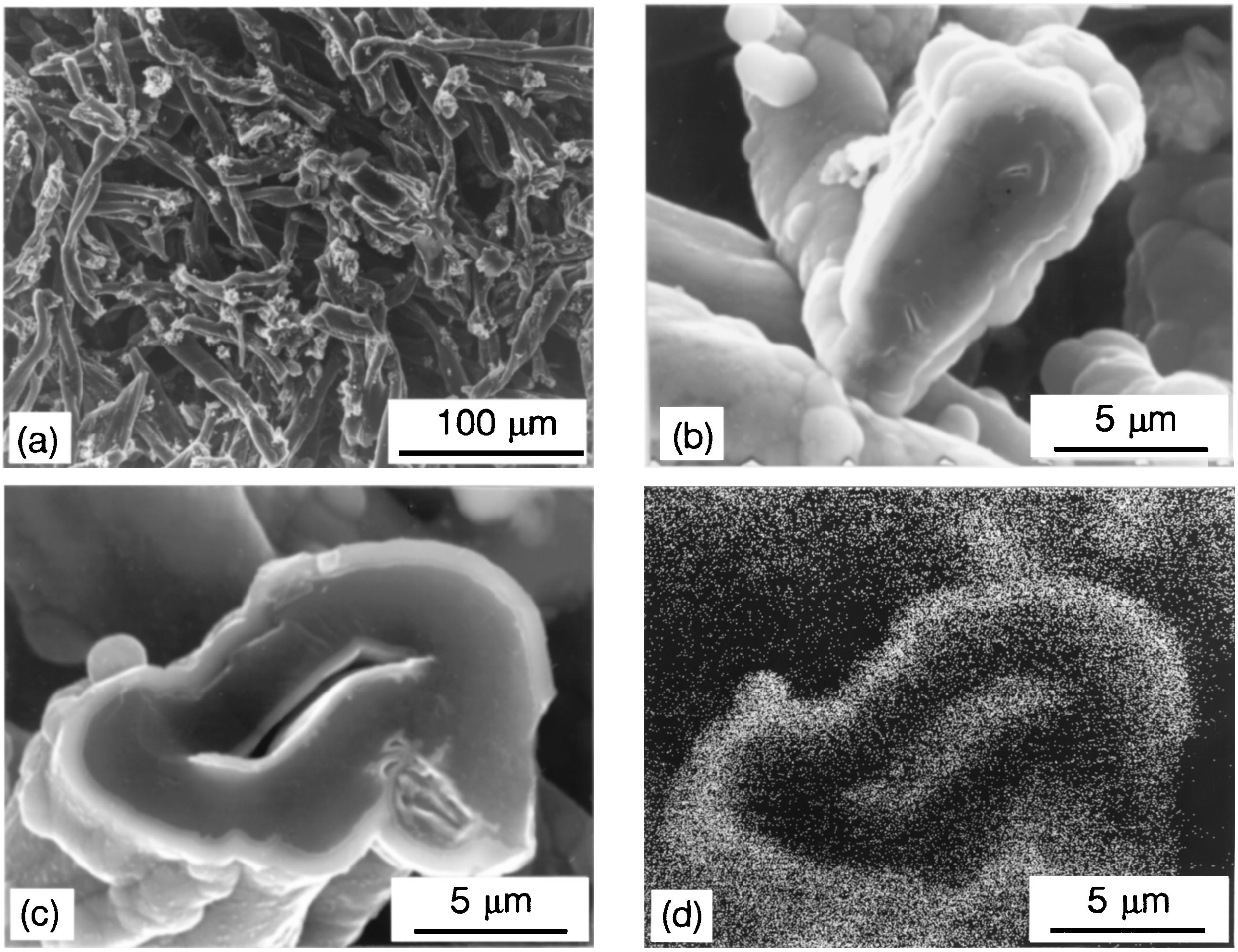

Figure 4 SEM and EPMA Si images of the cross-section of the sample after 15 000 pulses: (a) and (b) show the images at the centre of the sample, and (c) shows that near the surface; (d) shows the EPMA Si image of (c).

shows the images observed by scanning electron microscopy (SEM) and the Si electron probe microanalysis (EPMA) image of the cross-section of the A-type sample after 15 000 pulses. Fig. 4a, b shows the images at the centre of the sample, Fig. 4c shows the sample near the surface, and Fig. 4d shows the EPMA Si image of Fig. 4c. Fig. 4a shows that the present sample consists of fibres about 5–10 μm in diameter. From Fig. 4b–d, it is found that SiC thin films were deposited on the carbonized fibres, and the thickness of SiC films is about 1 μm in Fig. 4b and c.

Fig. 5 shows the effect of the number of pulses on the average and maximum pore sizes of A-type sample. Both the average and maximum pore sizes decrease with the number of pulses, reflecting thickening of SiC films on the carbonized fibres. The average pore size after 5000 and 15 000 pulses is about 6 and 4 μm, respectively. In Fig. 6, pore size distributions of three types of samples after 10 000 pulses are shown. The pores of the A-type sample are below 22 μm (average pore size, 5 μm). Maximum pore size and average pore size of B_H-type are 10 and 2.7 μm, respectively, which are lower than those of A-type in agreement with the initial pore sizes of these preforms. The length of the source fibres of the A-type preform (fibres for filter paper) is between 70–150 μm. However, it is supposed that the B_H-type preform, the source of which is fibres of recycled paper, includes shorter fibres, which may pack large clearance, and therefore, lower the pore size. On the other hand, the pore size distribution of the B_L-type sample shifts to larger range (average pore size, 7 μm), because the pressure in the B_L-type preform preparation step is lower than that for the B_H-type preform.

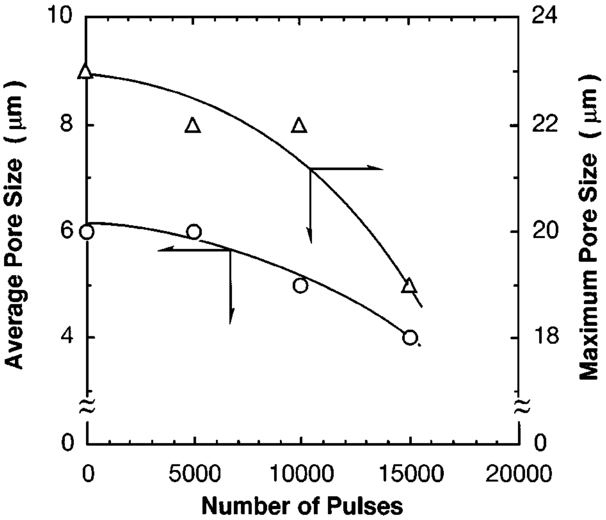

Figure 5 Dependence of average and maximum pore size of A-type sample on the number of pulses (sample size: 9 mm ϕ and 15 mm long).

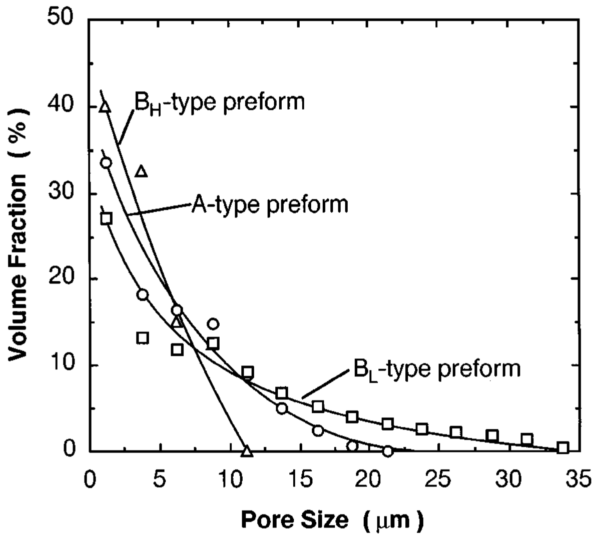

Figure 6 Pore size distributions of three types of samples after 10 000 pulses (sample size: A- and B_H-type, 9 mm ϕ and 15 mm long; B_L-type, 8 mm ϕ and 15 mm long).

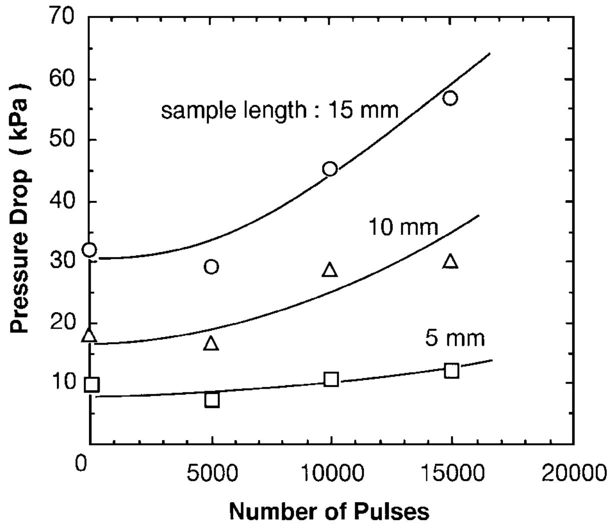

Figure 7 Relation between number of pulses and pressure drop along the direction of axial air-flow (preform, type A; sample diameter, 9 mm ϕ; face velocity, 0.8 m s^{-1}).

Thus, the pore size of the sample can be controlled by changing the kind of source fibre or the preparation condition of the preform.

3.2. Effect of number of pulses on pressure drop

Fig. 7 shows the relation between number of pulses and pressure drops of A-type samples with various axial lengths, where air passes along the axis of the sample at a face velocity of 0.8 m s^{-1}. Pressure drop increases with the number of pulses, and with increasing sample length. For instance, pressure drops after 5000 pulses are about 28 kPa for a sample 15 mm long and 7 kPa for a sample 5 mm long. On 5 mm long sample, pressure drops after 10 000 and 15 000 pulses are about 10 and 12 kPa, which are in a range similar to the reported values for porous SiC filters [10, 11]. A suitable number of pulses to obtain a highly gas-permeable SiC shape

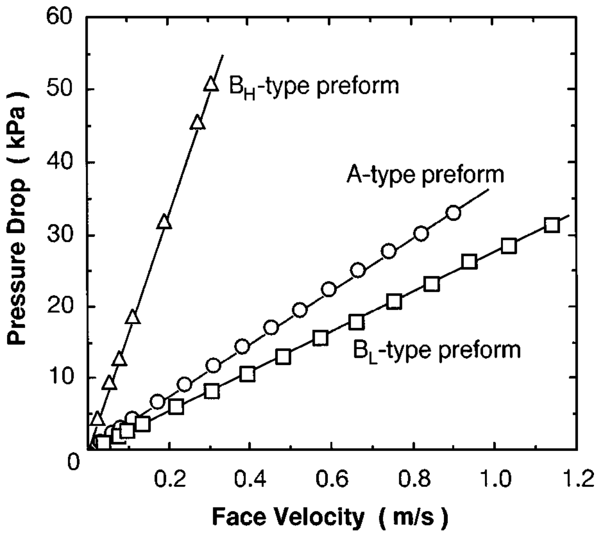

Figure 8 Pressure drops of three types of samples after 5000 pulses (sample size: A- and B_H-type, 9 mm ϕ and 15 mm long; B_L-type, 8 mm ϕ and 15 mm long).

is considered to be below 15 000 pulses for an A-type sample below 5 mm in length.

Fig. 8 shows the relation between the face velocity and pressure drops of three types of samples after 5000 pulses. The pressure drop is almost proportional to the face velocity for every sample. At the same face velocity, pressure drops of the three samples are in the order of $B_L < A < B_H$, reflecting the respective pore sizes.

3.3. Effect of number of pulses on flexural strength

Fig. 9 shows the dependence of flexural strength on the number of pulses. Flexural strength increases linearly with the number of pulses, reflecting the decrease of porosity as shown in Fig. 2. After 15 000 pulses, a strength of about 10 MPa is obtained for the A-type sample having a porosity of 73%. Kowbel *et al.* [10] have reported that a strength of 45 MPa was obtained for fibrous SiC having a porosity of 55%, which was

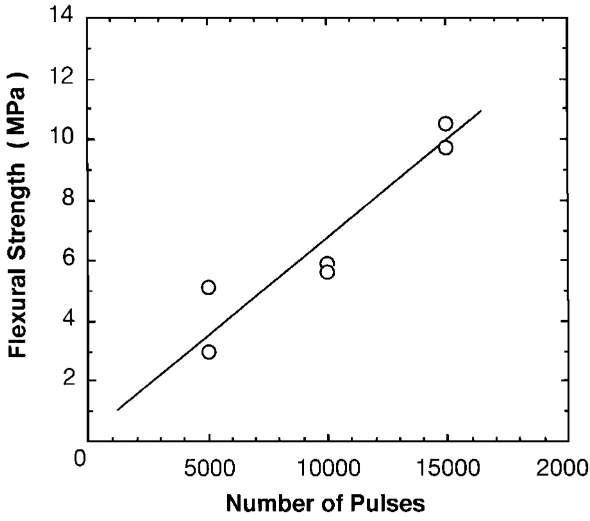

Figure 9 Dependence of flexural strength of A-type sample on number of pulses.

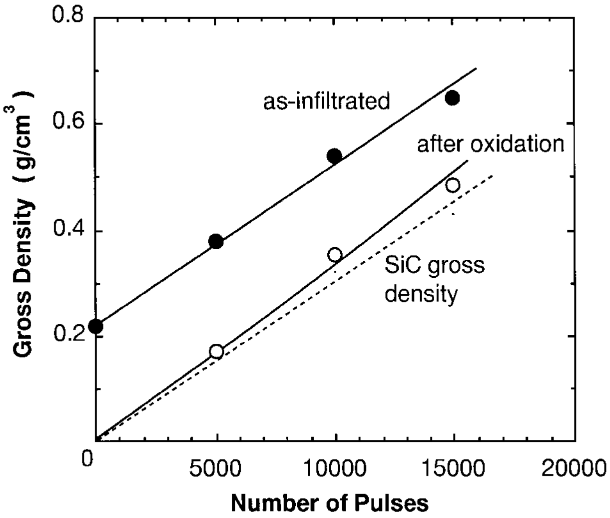

Figure 10 Relation between number of pulses and gross density of as-infiltrated A-type samples and after air-oxidation at 1000 °C for 5 h (the broken line shows the gross density of SiC deposits only).

prepared by chemical vapour reaction (i.e. the conversion process of carbon-fibre preform to SiC), followed by CVI with SiC. However, the strength decreased to about 11–18 MPa upon increasing porosity to 68–73% [10]. The strength of the present sample after 15 000 pulses is somewhat weaker than that of Kowbel *et al.*'s.

3.4. Changes of gross density and flexural strength during air-oxidation

The oxidation test was carried out in an air flow at 1000 °C for 5 h using A-type samples. Fig. 10 shows the change of gross density with the number of pulses. In the figure, the broken line shows the gross density of the SiC deposits only, which is calculated by subtracting the gross density of the preform from that of the as-infiltrated sample. The gross density of the as-infiltrated sample increases linearly with the number of pulses, reflecting infiltration of SiC. The density curve after oxidation is nearly close to the broken line, which indicates that carbonized fibres are almost totally lost by oxidation. It is suggested that preform carbon is oxidized by air diffusion through microcracks in SiC films formed during the cooling process. However, the free-standing shape retained the pre-oxidation size and dimension. In Fig. 11, SEM images of the cross-section after oxidation are shown. Fig. 11b is a high-magnification image of Fig. 11a. From Fig. 11a, it is found that the sample after oxidation retains the fibrous structure. In Fig. 11b, SiC fibres are seen to have a hollow structure, which results from loss of the carbon-fibre core.

In Table II, the porosity and flexural strength of the as-infiltrated sample before and after oxidation are shown. The porosity increases after oxidation due to the loss of preform-carbon, and flexural strength decreases to 3.0–3.5 MPa, which is about one-third of the value before oxidation. It has been reported in a previous paper on partial PCVI of SiC into porous carbon plates that strength recovery is possible by second PCVI after oxidation [9]. On the present sample, it is expected that the strength after oxidation may be improved by second PCVI into the SiC skeleton.

TABLE II Porosity and flexural strength of as-infiltrated sample before and after oxidation

	Porosity (%)	Flexural strength (MPa)
As-infiltrated[a]	73	9.7–10.5
After oxidation	82	3.0–3.5

[a] Number of pulses, 15 000; preform, type A.

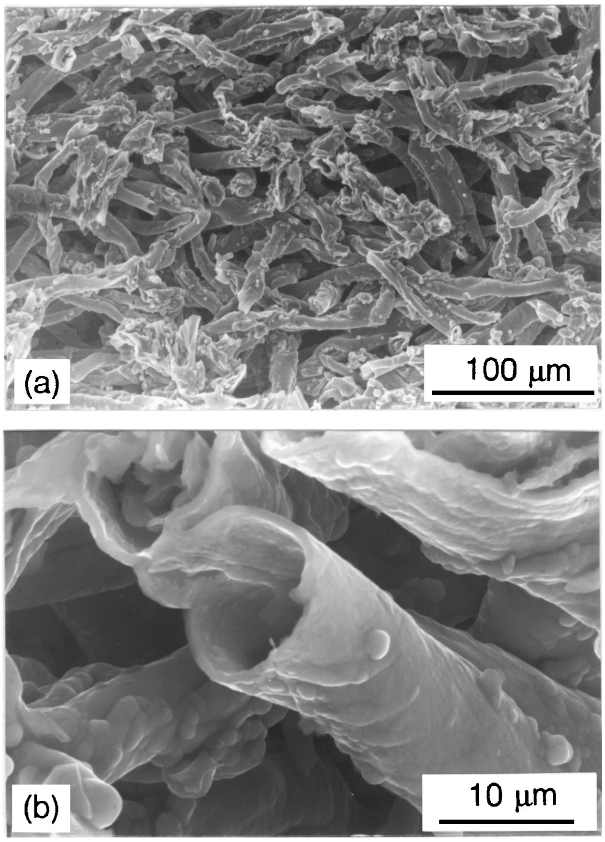

Figure 11 SEM images of the cross-section of the A-type sample after oxidation; number of pulses, 15 000: (b) shows a high-magnification image of (a).

4. Conclusions

The partial densification process of SiC by pressure-pulsed chemical vapour infiltration of SiC from $SiCl_4$ (4%)–CH_4(4%)–H_2 at 1100 °C with a holding time of 0.4 s was investigated using three types of carbonized paper-fibre preforms (A-type preform: source fibres of filter paper, porosity 88%; B_H- and B_L-type preforms: source fibres of recycled paper, porosities of 87 and 95%, respectively). The following results were obtained.

1. Porosity decreased linearly with the number of pulses. After 10 000 pulses, the porosities of A-, B_H- and B_L-type samples were 77, 78 and 85%, respectively.
2. Maximum and average pore sizes of an A-type sample of 10 mm ϕ and 15 mm long after 10 000 pulses were about 22 and 5 μm, respectively. Increase of number of pulses resulted in a shift of the pore size distribution towards lower values. Average pore sizes

of B_H- and B_H-type samples were about 2.7 and 7 μm, respectively.

3. On an A-type sample of 10 mm ϕ and 5 mm long after 10 000 pulses, pressure drop along the direction of axial air flow was 10 kPa at a face velocity of 0.8 m s^{-1}. The order of pressure drop was $B_H > A > B_L$.

4. Flexural strength increased linearly with the number of pulses, reflecting decrease of the porosity and the pore size. After 15 000 pulses, the strength of the A-type sample reached 10 MPa.

5. Preform carbon in the sample after 15 000 pulses was lost during air-oxidation at 1000 °C for 5 h. However, the free-standing shape retained the pre-oxidation dimension and fibrous structure.

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