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Preparation of gas-permeable SiC shape by pressure-pulsed chemical vapour infiltration into carbonized cotton-cloth preforms

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Carbonized cotton-fibre preforms were partially infiltrated with SiC by pressure-pulsed chemical vapour infiltration (CVI) from $SiCl_4$–CH_4–H_2. Fibrous carbon/SiC of 10 mm dia. and 20 mm long having the porosity of 83% was obtained after 15 000 pulses at 1150 °C. Pores of the sample after 10 000 pulses distributed below 100 μm (average pore size, 30 μm). Pressure drop of the sample after 15 000 pulses under the axial air-flow was 11 kPa at a face velocity of 1.1 m s^{-1}. On the samples after 15 000 pulses, 15% of preform-carbon were lost within 5 h by air oxidation at 1000 °C, and tensile strength along the axis reached 10 MPa, which was close to that before oxidation. In the case of the sample after 5000 pulses, tensile strength lowered significantly after oxidation, however, the strength was recovered by application of 4000 pulses of second CVI. © *1998 Chapman & Hall*

1. Introduction

Highly gas-permeable SiC shape is a promising material as a clean-up filter for diesel exhaust gas or coal combustion process, and also as a catalyst carrier for high-temperature use. In order to obtain a highly gas-permeable SiC shape, a thin wall structure is ideal, and chemical vapour infiltration (CVI) process is suitable 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, isothermal and isobaric CVI has the characteristic of obtaining a near-net-shaped product; however, it needs a long operation time because of slow gas diffusion [1–2]. Another process of forced CVI uses steep gradients of pressure and temperature along the preform thickness, and the operation time is remarkably shortened [3–4]. This process, however, requires the use of one holder per preform, and the shape of preforms is limited to cubic or cylindrical for homogeneous gas flow. Pressure-pulsed CVI (PCVI), which consists of sequential steps of evacuation of reaction vessel, instantaneous introduction of source gas, and holding to allow deposition (holding time), has the advantage to process many preforms of complex shape in a run with relatively short operation time [5–9].

During the preparation process of porous SiC shapes by CVI, SiC coated fibre has been obtained from ceramic–fibre preforms such as carbon fibres or Nextel fibres [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. The author of the present paper has investigated PCVI process to porous carbon plates, and reported that highly porous SiC shapes could be prepared [12]. Use of the carbonized cotton fibres as a source of the preforms may lead to the low cost preparation of fibrous SiC. In this study, partial densification process of carbonized cotton-cloth preforms with SiC was investigated using PCVI from $SiCl_4$– CH_4–H_2.

2. Experimental procedure

Carbonized cotton-cloth preforms were prepared as follows. Commercial cotton flannel, which has relatively random fibre orientation, was rolled tightly into column, put into a quartz tube, carbonized at 1000 °C in an Ar flow, and cut to 10 mm dia. and 20 mm long. Gross density and porosity of the carbonized preforms were 0.06 g cm^{-3} and 95%, respectively. Fig. 1 shows the main part of the PCVI apparatus. The source gas mixture of $SiCl_4$ (4%)–CH_4 (8%)–H_2 was flowed into a reservoir, and introduced instantaneously (within 0.1 s) to a reaction vessel up to 0.1 MPa, held here for 0.2–1.0 s to allow SiC deposition (holding time), and evacuated to below 0.7 kPa within 1.5 s.

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 initial porosity of preform, volume of SiC deposits and initial volume of pores in preform, respectively, and the density of SiC deposits was assumed to be 3.1 g cm^{-3}. Tensile and compressive strength along the axis and pressure drop in the axial air flow were measured at room temperature.

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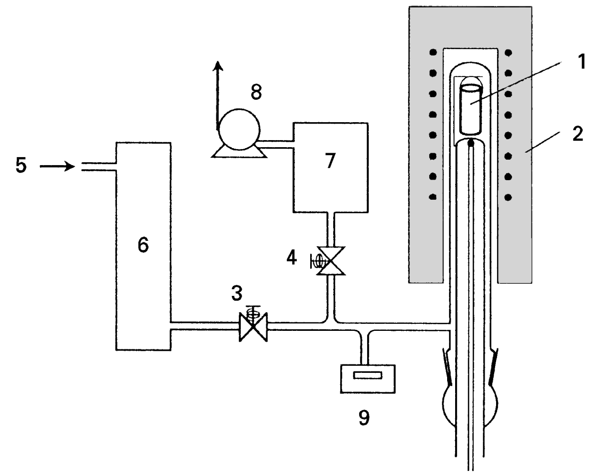

Figure 1 Main part of PCVI apparatus. 1, preform; 2, hot-wall furnace; 3, inlet valve; 4, outlet valve; 5, source gas; 6, reservoir; 7, vacuum tank; 8, vacuum pump; 9, pressure gauge.

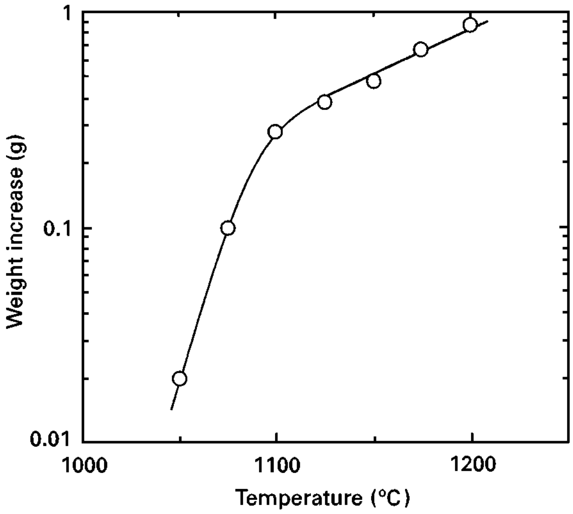

Figure 2 Temperature dependence of weight increase. Holding time, 1.0 s; number of pulses, 10 000.

Surface area was measured by the Brunauer–Emmett–Teller (BET) method. Pore size distribution was determined by bubble-point method according to ASTM standard F 316. In this method, the air pressures and the flow rates are measured for both a dry and fluid-wet sample (undecane was used for the fluid in 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 percentage of the pores that air passes through can be calculated, and the average pore size is determined by a pressure at which the wet sample flow is half of the dry sample flow.

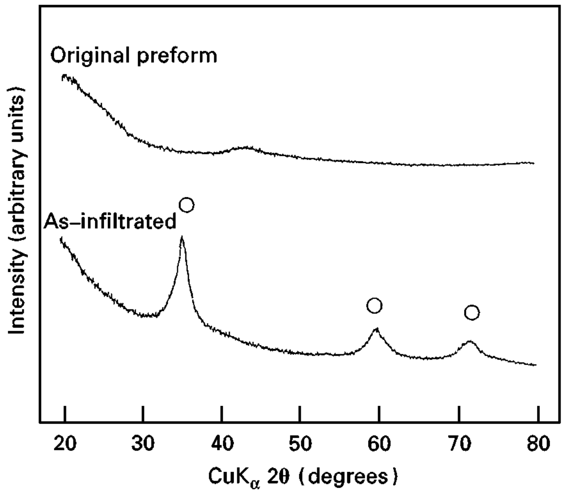

Figure 3 XRD patterns of the cross-sections of the original preform and the infiltrated samples. CVI temperature, 1150 °C; holding time, 0.3 s; and number of pulses, 10 000. (○) β-SiC.

3. Results and discussion

3.1. Effect of temperature and holding time on weight increase and uniformity of SiC infiltration

Temperature dependence of weight increase after 10 000 pulses is shown in Fig. 2. The deposits increase with the temperature elevation, because the reaction rate becomes fast. Below 1075 °C, weight increase is significantly low, which may be caused by the rapid decrease of the formation rate of the active precursors, such as SiH_2Cl_2, $SiHCl_3$, or $SiCl_2$ [13–14] ; therefore, it takes long operation time for the desired infiltration of SiC, and furthermore, it is supposed that silicon codeposits with SiC under short holding time [13]. On the other hand, above 1175 °C, films on macrosurface of the preform are formed at early stage of PCVI, and block the gas penetration to deep level. Therefore, suitable temperature range is considered to be between 1075 and 1150 °C in the present preforms. Fig. 3 shows the X-ray diffraction (XRD) patterns from the cross-section of the original carbonized preform and the sample infiltrated at 1150 °C after 10 000 pulses with a holding time of 0.3 s. Only broad peaks assigned to β-SiC are observed on the infiltrated sample.

Fig. 4 shows the scanning electron microscope (SEM) images of the ruptured cross-section of the sample obtained at 1150 °C after 5000 pulses with a holding time of 0.3 s. Fig. 4a and c show the images at centre of the sample, and Fig. 4b shows that near the surface. Low-magnification photograph (Fig. 4a) shows that the present sample consists of the continuous fibres of about 7 μm in diameter. From Fig. 4b and c, it is observed that SiC thin films deposit around the carbonized cotton fibres. Thickness of SiC films is about 1.5 μm in both photographs. Change of the thickness of SiC films from the centre to the surface of the sample is shown in Fig. 5. In the case of holding time of 0.5 s, SiC films at centre of the preform is thicker than that near surface, because the surface of the preform is cooled by the source gas, which is introduced into the vessel without sufficient preheating in the PCVI process. In the case of the holding time below 0.3 s,

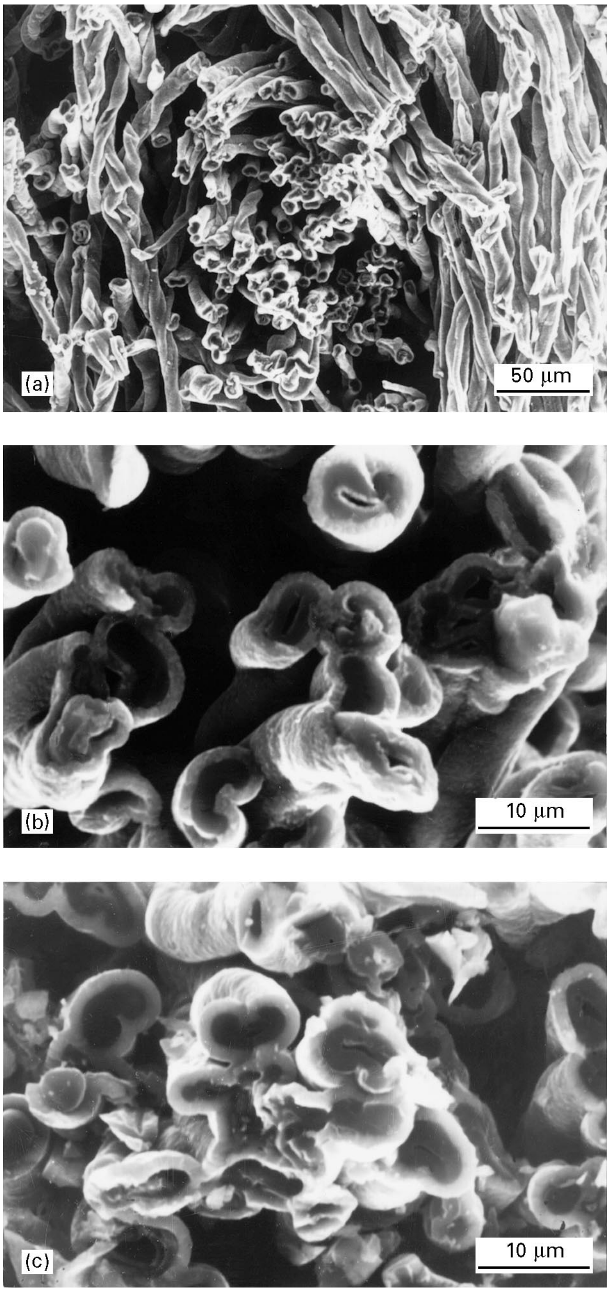

Figure 4 SEM images of the cross-section of the sample obtained at 1150 °C after 5000 pulses with a holding time of 0.3 s. (a), (c) show the images at centre of the sample; and (b) shows that near surface.

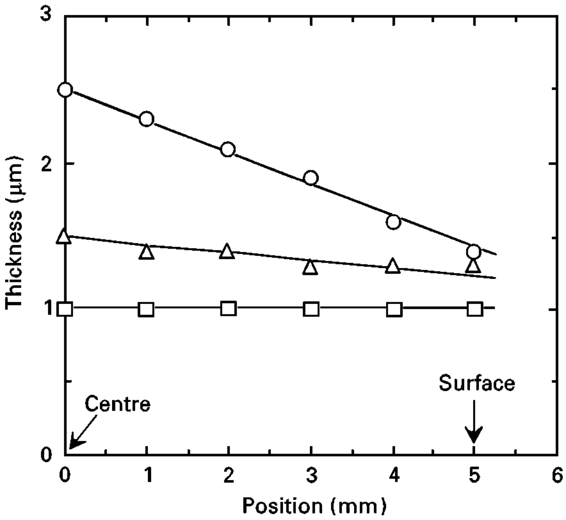

Figure 5 Change of the thickness of SiC films from centre to surface with various holding times. CVI temperature, 1150 °C, number of pulses, 5000. (○) 0.5 s; (△) 0.3 s; (□) 0.2 s.

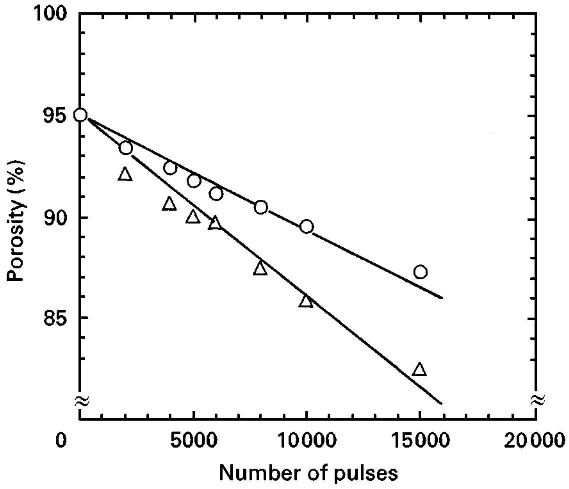

Figure 6 Dependence of porosity on number of pulses at various temperatures with a holding time of 0.3 s. (○) 1100 °C; (△) 1150 °C.

however, SiC deposits almost uniformly through the preform depth, the reason of which is now open to further investigation.

3.2. Effect of number of pulses on porosity, pore size distribution, and pressure drop

Fig. 6 shows the dependence of the residual porosity on number of pulses. The porosity of the sample decreases linearly with number of pulses up to 15 000 pulses, as SiC is infiltrated into the preform. At 1150 °C with holding time of 0.3 s, the porosity becomes about 83% (gross density of 0.45 g cm^{-3}) after 15 000 pulses. Decreasing rate of the porosity becomes slow with lowering the temperature, reflecting the deposition rate.

Pore size distribution of the sample obtained at 1150 °C after 10 000 pulses with a holding time of 0.3 s is shown in Fig. 7. Maximum pore size is about 100 μm, and average pore size is about 30 μm. Maximum pore size is in similar range to that reported for porous SiC filter by Kowbel *et al.* [10]; however, average pore size of present study is about 20–30 μm smaller. The preforms in the present study were prepared by rolling the cotton cloths into columns; therefore, it is supposed that the distribution at relatively large pore size above 50 μm is resulted from the gaps between the cloth layers.

Fig. 8 shows the relation between number of pulses and pressure drop along the axial air flow on the sample obtained at 1150 °C with a holding time of 0.3 s. Pressure drop increases with number of pulses, because of the decrease of pore sizes. Pressure drop at the face velocity of 1.1 m s^{-1} is about 9.5 kPa and 11 kPa after 10 000 and 15 000 pulses, respectively. These values are in similar range to those reported for porous SiC filters [10–11]. Suitable number of pulses

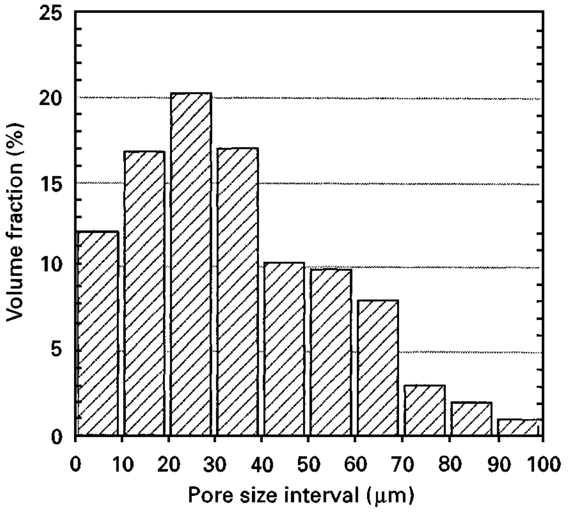

Figure 7 Pore size distribution of the sample obtained at 1150 °C after 10 000 pulses with a holding time of 0.3 s.

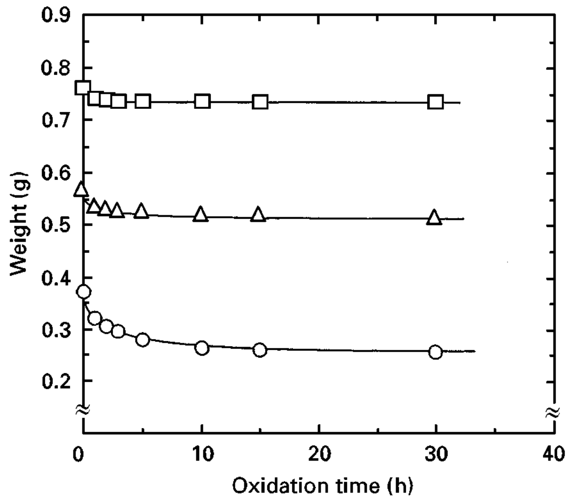

Figure 9 Weight change during oxidation at 1000 °C in air. CVI temperature, 1150 °C; holding time, 0.3 s. (□) 15 000 pulses; (△) 10 000 pulses; (○) 5000 pulses.

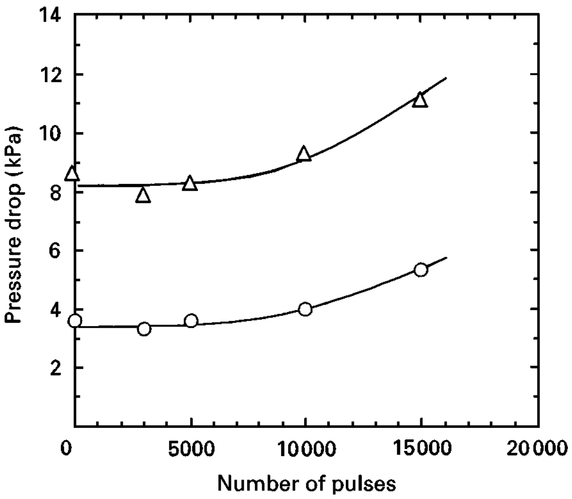

Figure 8 Relation between number of pulses and pressure drop along the axial air-flow. CVI temperature, 1150 °C; holding time, 0.3 s. Face velocity: (△) 1.1 m s^{-1}; (○) 0.5 m s^{-1}.

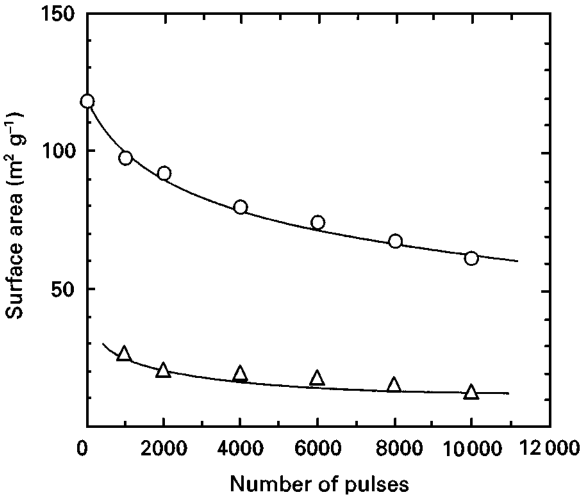

Figure 10 Relation between number of pulses and surface area of as-infiltrated sample (○) and after air oxidation (△). CVI temperature, 1150 °C; holding time, 0.3 s, oxidation temperature, 1000 °C; and oxidation time, 5 h.

to obtain a highly gas-permeable SiC shape is considered to be below 15 000 pulses under present conditions.

3.3. Changes of weight, surface area and strength during air-oxidation

The oxidation test was carried out in an air flow at 1000 °C. Weight changes of the samples infiltrated at 1150 °C with a holding time of 0.3 s are shown in Fig. 9. Weight of the sample after 5000 pulses decreases mainly within first 10 h, and the weight loss after 30 h is about 0.11 g, which corresponds to a loss of 86% of carbon preform (weight of preform was about 0.13 g). Weight loss after long oxidation decreases with the increase of number of pulses, and reaches about 0.02 g (i.e. 15% carbon loss) on the sample after 15 000 pulses.

Fig. 10 shows the relation between number of pulses and surface area of as-infiltrated sample and after oxidation for 5 h. Surface area of as-infiltrated sample decreases with the increase of number of pulses from 120 m^2 g^{-1} of original preform, and reaches 60 m^2 g^{-1} after 10 000 pulses. This means that the microscopically rough surface of the carbonized cotton fibres is smoothed as the fibres are coated with SiC thin films. Surface area after oxidation is lower than that before oxidation. It is supposed that the surface of the SiC films becomes more smooth by the formation of SiO_2 thin films.

Fig. 11 shows the relation between number of pulses and tensile and compressive strength of as-infiltrated sample and after oxidation for 5 h. Both of tensile and compressive strength of as-infiltrated sample increases linearly with number of pulses, reflecting the decrease of the porosity, as shown in Fig. 6. The strength after oxidation is lower than that before oxidation because of the loss of the preform-carbon. Below 5000 pulses, the strengths before and after oxidation separate widely, which means that SiC films have cracks formed

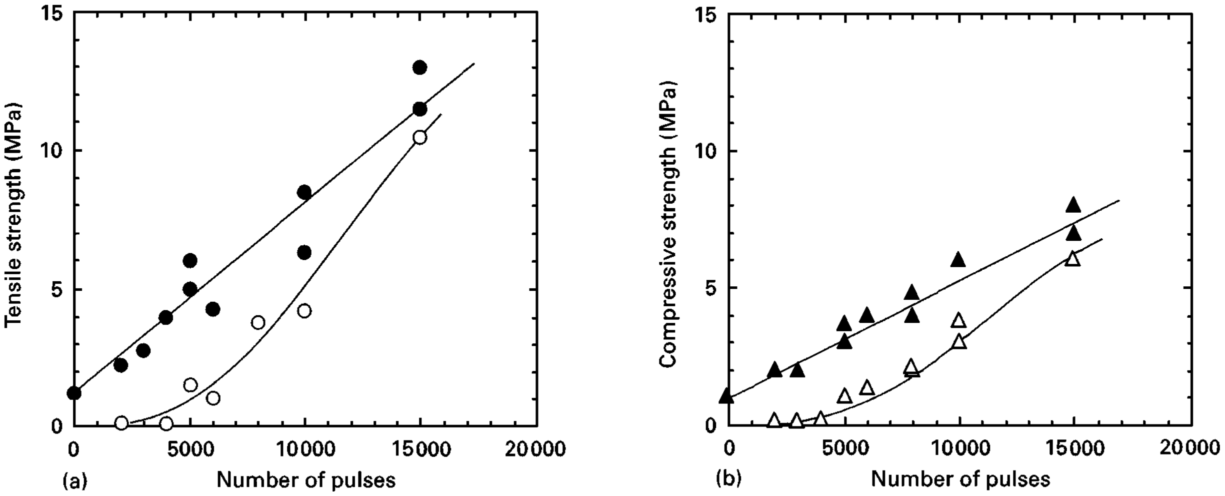

Figure 11 Relation between number of pulses and (a) tensile and (b) compressive strength along the axis of as-infiltrated (closed symbols) sample and after oxidation (open symbols). CVI temperature, 1150 °C; holding time, 0.3 s, oxidation temperature, 1000 °C; and oxidation time, 5 h.

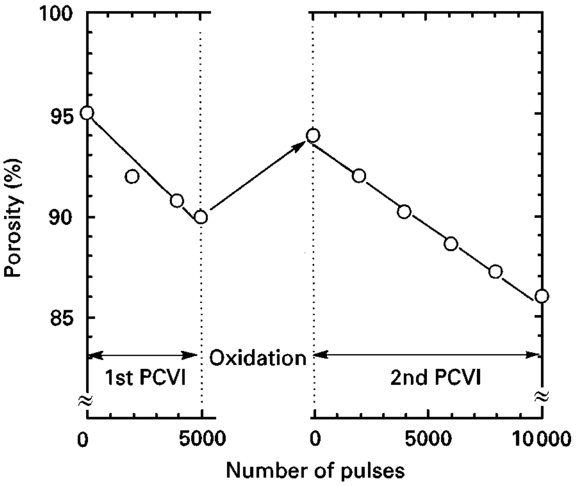

Figure 12 Dependence of porosity on number of pulses during processing. CVI temperature, 1150 °C; holding time, 0.3 s, oxidation temperature, 1000 °C; and oxidation time, 10 h.

during the cooling process. Above 8000 pulses, the strength curve after oxidation approaches that before oxidation, reflecting an increase of the residual carbon preform. Tensile and compressive strength after 15 000 pulses are 10 and 6 MPa after oxidation, respectively.

3.4. Second processing of PCVI after oxidation

As mentioned above, in the case of insufficient number of pulses, the strength decreases by oxidation. However, the free-standing shape retains the size and dimension after oxidation, therefore, second processing of PCVI into SiC skeleton may improve the strength [12]. Fig. 12 shows the dependence of porosity on number of pulses during the sequential processes consisted of first PCVI, air oxidation and second PCVI. After 5000 pulses of first PCVI, the porosity decreases from 95 to 90%; however, it increases to 94% after oxidation because of the loss of the preform carbon. The porosity decreases again by the application of second PCVI, and reaches 90 and 86% after 4000 and 10 000 pulses, respectively. Fig. 13 shows the SEM images of the cross-section of the sample after oxidation (a) and 2nd PCVI (b). From Fig. 13a, it is found that SiC fibres have the capillary-like structure which

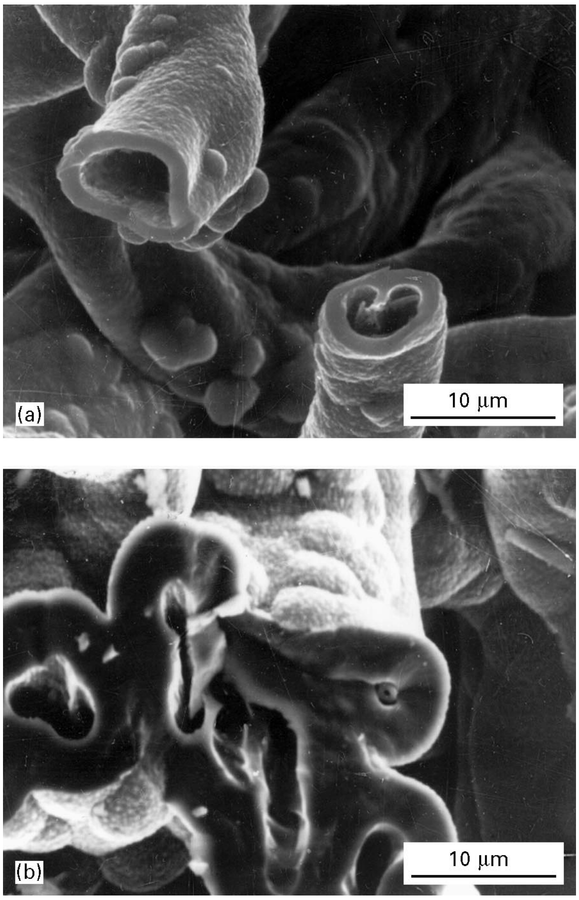

Figure 13 SEM images of the cross-section of the sample after oxidation (a) and second PCVI (b). Condition during processes: (a) first PCVI at 1150 °C after 5000 pulses with holding time of 0.3 s/air-oxidation at 1000 °C for 10 h; (b) first PCVI at 1150 °C after 5000 pulses with holding time of 0.3 s/air-oxidation at 1000 °C for 10 h/ second PCVI at 1150 °C after 10 000 pulses with holding time of 0.3 s.

TABLE I Change of pressure drop and tensile strength during processing

	Pressure drop[a] (kPa)	Tensile strength (MPa)
After first PCVI[b]	8.0	5.5
After oxidation	7.8	1.2
After second PCVI[c]	9.5	5.0

[a] Face velocity, 1.1 m s^{-1}.

[b] Temperature, 1150 °C; holding time, 0.3 s; number of pulses, 5000.

[c] Temperature, 1150 °C; holding time, 0.3 s; number of pulses, 4000.

results from the loss of the carbon-fibre core. In Fig. 13b, it is observed that SiC fibres become thick and are connected to each other by application of second PCVI. Table I shows the change of pressure drop and tensile strength during the processing. Pressure drop after oxidation is close to that before oxidation, which indicate that the pores between the fibres in the sample retain the size and geometry after oxidation. Pressure drop increases after 4000 pulses of second PCVI because of the decrease of the pore size. Tensile strength decreases after oxidation by the loss of the carbon core, however, by the application of second PCVI, the strength almost recovers the value before oxidation.

4. Conclusions

Preparation process of porous SiC shape was investigated using pressure-pulsed chemical vapour infiltration of SiC from $SiCl_4$–CH_4–H_2 into carbonized cotton fibre preforms. The following results were obtained.

1. Below 1075 °C, weight increase became significantly low, whereas, above 1175 °C, films on macrosurface of the preform were formed at early stage of PCVI. Suitable temperature range was considered to be between 1075–1150 °C on the present preforms.
2. In the case of the holding time below 0.3 s, SiC deposits almost uniformly in thickness along the preform depth.
3. The porosity of the sample decreased linearly with number of pulses. After 15 000 pulses at 1150 °C with a holding time of 0.3 s, the porosity was about 83%.
4. On the sample obtained at 1150 °C after 10 000 pulses with a holding time of 0.3 s, maximum and average pore size were about 100 and 30 μm, respectively. Pressure drops of the sample after 10 000 and 15 000 pulses were 9.5 and 11 kPa at the face velocity of 1.1 m s^{-1}, respectively. Surface area was 60 m^2 g^{-1} after 10 000 pulses.
5. Weight loss was found during the air-oxidation at 1000 °C. On the sample after 15 000 pulses, weight loss was about 0.02 g (i.e. 15% preform-carbon loss). Tensile and compressive strength after oxidation were 10 and 6 MPa, respectively, which was close to the strength before oxidation.
6. On the sample after 5000 pulses, tensile strength was significantly lowered after oxidation. However, by the application of a second PCVI processing after oxidation, the strength recovered the value before oxidation.

Acknowledgements

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