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Pulse chemical vapour infiltration of SiC in porous carbon or SiC particulate preform using an r.f. heating system

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SiC was infiltrated into a porous carbon or an SiC particulate preform from a gaseous system of 6% CH_3SiCl_3–H_2 using a pulse chemical vapour infiltration apparatus and r.f. heating at 1273 to 1423 K. At 1273 K, the SiC matrix infiltrated the porous carbon initially to half the thickness of the substrate and finally over the full thickness. After 10 000 pulses, three-point flexural strength saturated at about 120 MPa. SiC particulate preform made from an average particle size of 4 μm was infiltrated by SiC. After 30 000 pulses at 1273 K, the flexural strength of the composite increased to 200 to 220 MPa.

1. Introduction

Chemical vapour infiltration (CVI) has received attention as a process for the preparation of fibre- or particulate-reinforced composites. In this process, a source gas is flowed through a fibre or particulate preform at high temperature, during which specific material is deposited as a matrix between the fibres or particles [1–10]. The bonding between the matrix and the preform is excellent; however, this process has two weak points, the long operation time and insufficient infiltration into fine pores. We have attempted CVI of TiN and SiC into porous carbon and of BN into Si_3N_4 particulate preforms using a pressure pulse ("pulse CVI") [11–13]. In the present paper, pulse CVI of SiC into porous carbon and SiC particulate preform by r.f. heating will be described. When the substrate is heated by r.f. induction, a cold source gas is introduced into vessel; therefore, deposition is expected to initiate from the deepest zone, where the temperature is the highest in the system.

2. Experimental procedure

The apparatus for pulse CVI of SiC is shown in Fig. 1a. Hydrogen was bubbled into an ice-cooled saturator of methyltrichlorosilane (CH_3SiCl_3; Tokyo Kasei Kogyo Co.), by which the concentration of CH_3SiCl_3 was kept at 6%. The gas mixture of CH_3SiCl_3–H_2 was held in a reservoir, from which source gas was filled instantaneously into a reaction vessel up to 0.92 atm via an electromagnetic valve in each pulse. Dead space was narrowed to 30 cm^3 by insertion of a bottom-sealed inner tube. Five plates

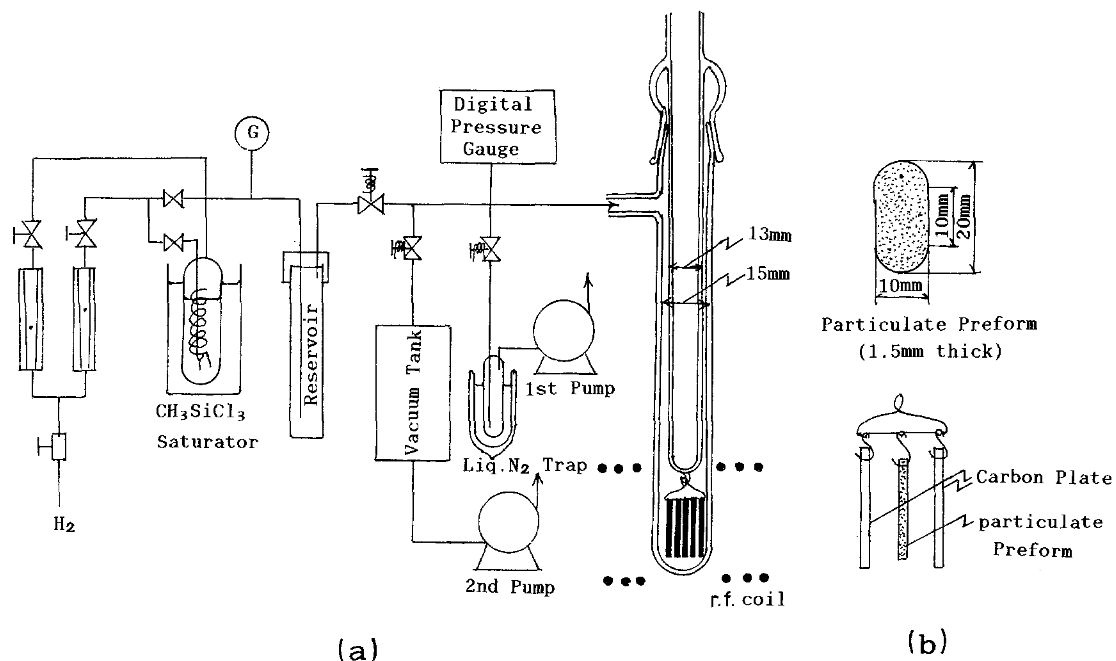


Figure 1 Apparatus for pulse CVI of SiC. (a) Apparatus, (b) oval-shaped SiC particulate preform and the setting arrangement.

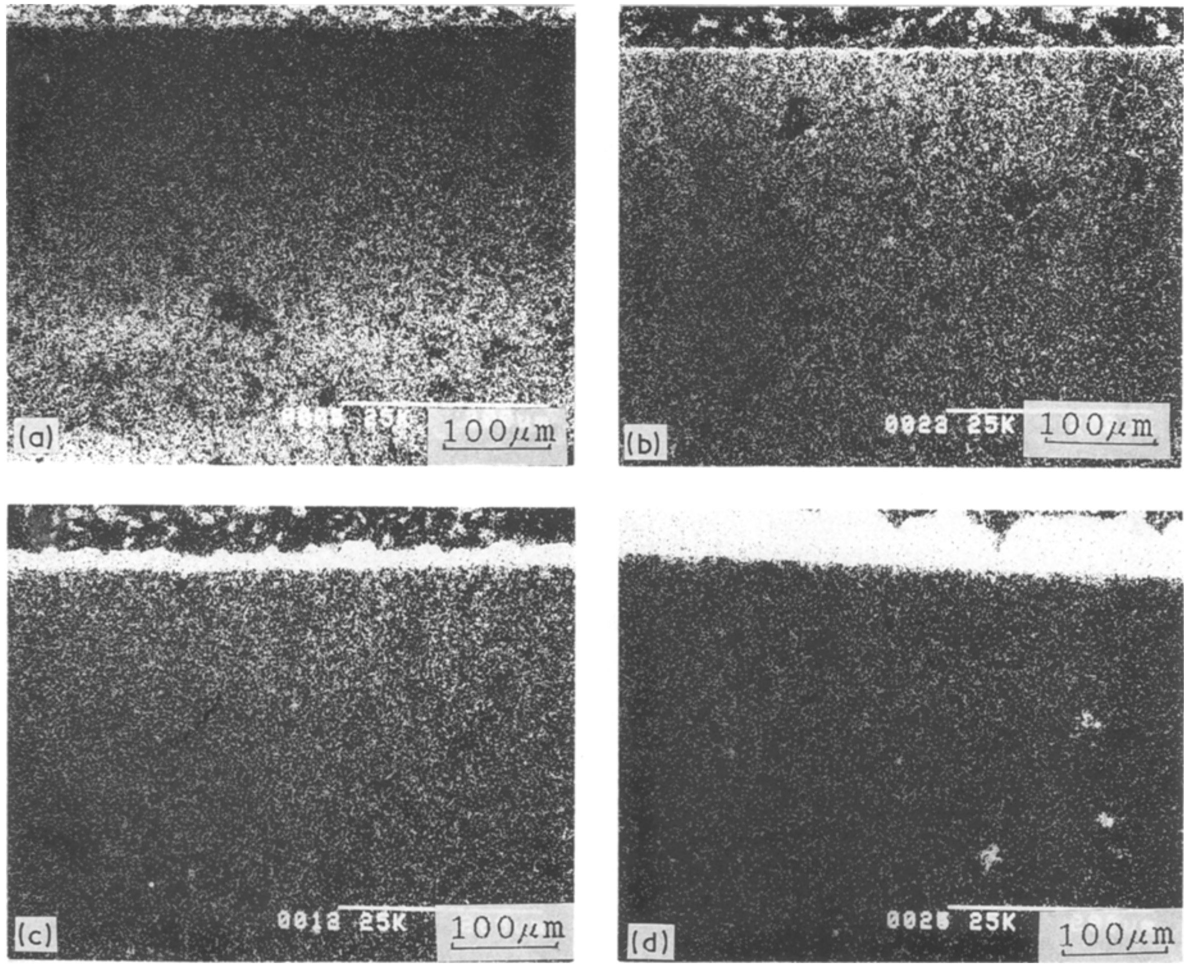


Figure 2 EPMA silicon images of the cross-section after 3000 pulses of CVI. CVI temperature: (a) 1273 K, (b) 1373 K, (c) 1473 K, (d) 1573 K.

of porous carbon (Poco Co.; average pore diameter 0.2 to 0.5 μm, total pore volume 29%) of 10 mm × 20 mm × 0.7 mm were hung from the bottom hook of the inner tube. In the case of SiC particulate preform, SiC powder (Showa Denko Co., average particle sizes 4 and 50 μm), added with a minute amount of starch, was pressed into oval shapes as shown in Fib. 1b, and baked at 1273 K in a nitrogen gas flow for 6 h. These SiC particulate preforms contained 0.4 wt % free carbon, and had a porosity of 45% to 50% and 42% to 48% for the particle sizes 4 and 50 μm, respectively. The particulate preform was hung from the bottom hook of the inner tube, and two carbon plates were also hung in the front of and at the back of the preform, as shown in Fig. 1b. An r.f. coil (400 kHz) was wound as shown in Fig. 1a, and the temperature of the central plate or preform was measured from the side using an optical pyrometer. After a holding time of 1 sec under 0.92 atm, the system was evacuated sequentially by two vacuum pumps; it took 2 sec to evacuate to below 200 Pa. This sequence of steps (gas filling, holding to allow infiltration and evacuation) was repeated by a programmed number of pulses. Hitachi S 510, Horiba EMAX 1700 and Marusho 9004 were used for SEM observation, electron probe X-ray microanalysis and measurement of flexural strength, respectively.

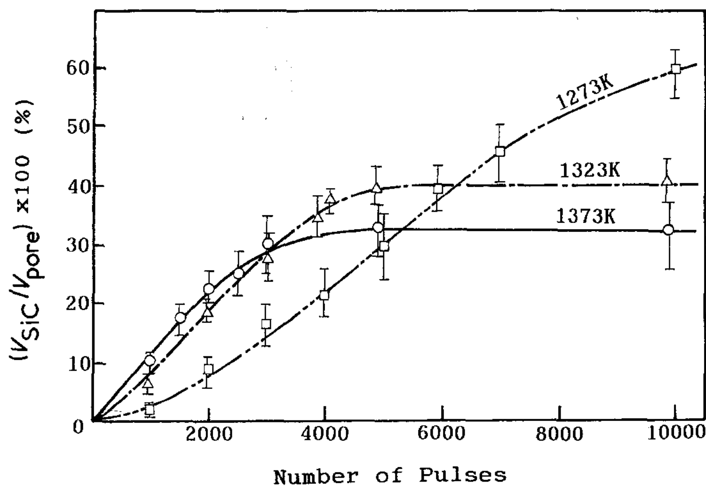


Figure 3 Relations between the number of pulses and the packing ratio (V_{SiC}/V_{pore}).

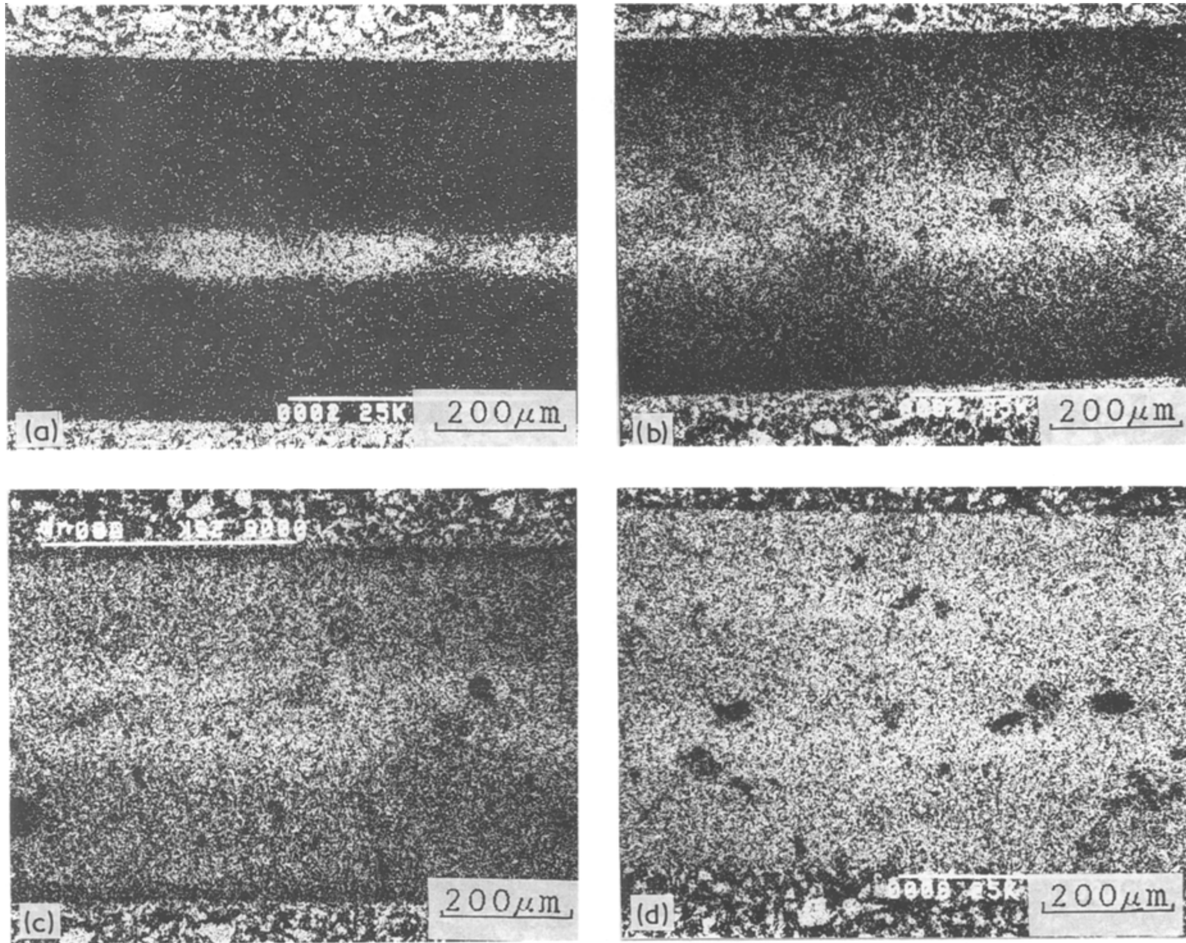


Figure 4 EPMA silicon images of the cross-section after CVI at 1273 K. Number of pulses: (a) 1000, (b) 3000, (c) 5000, (d) 10 000.

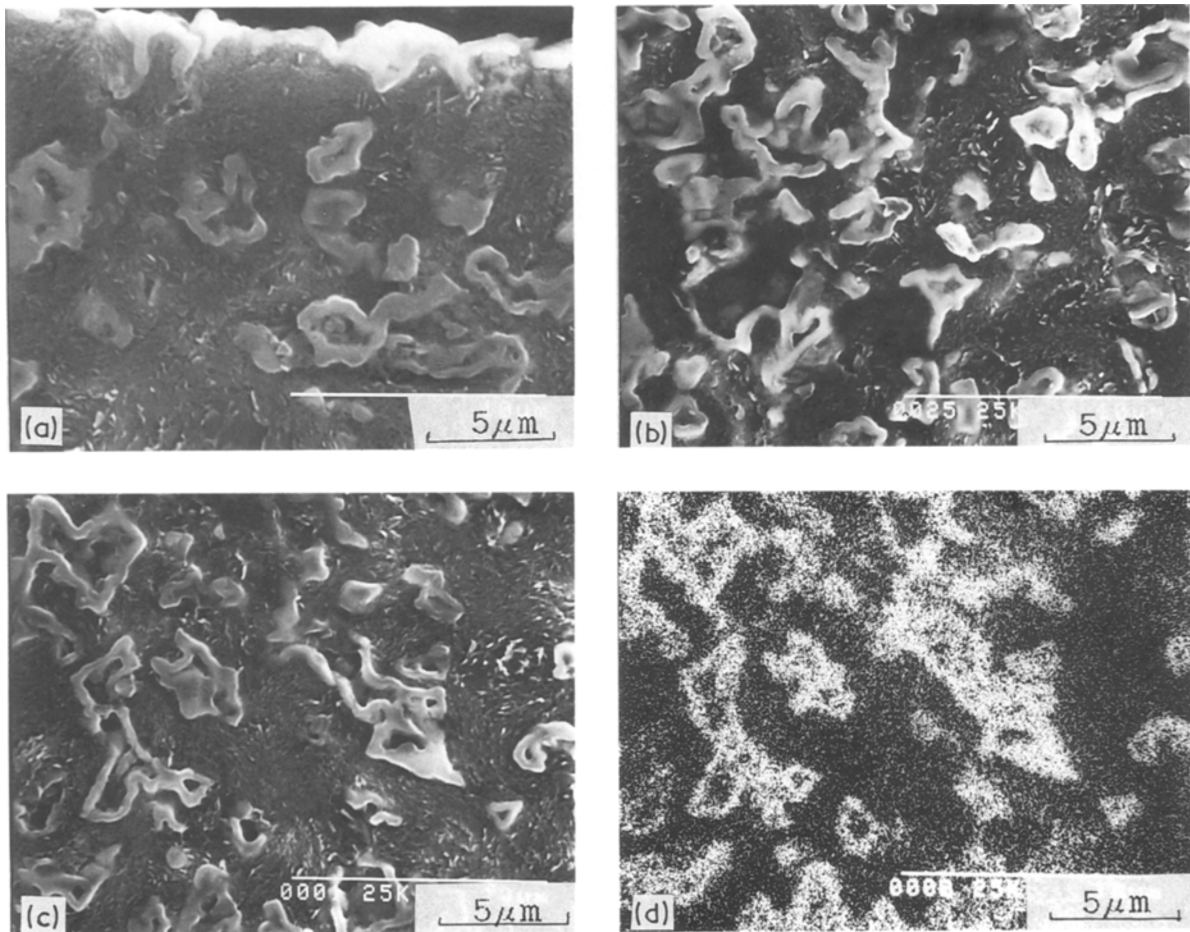


Figure 5 (a to c) Scanning electron micrographs and (d) EPMA silicon image of the cross-section after 10 000 pulses of CVI at 1273 K. Depths from surface: (a) 20 μm, (b) 200 μm, (c, d) 300 μm.

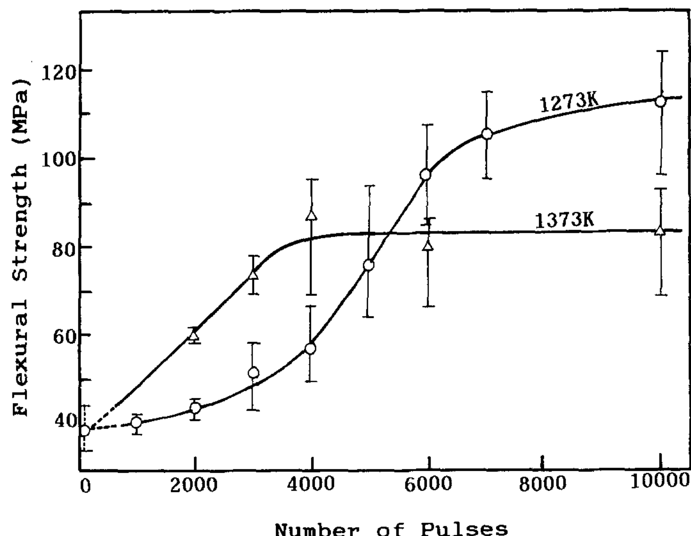


Figure 6 Dependence of three-point flexural strength on the number of pulses.

3. Results and discussion

3.1. Pulse CVI of SiC into porous carbon

Fig. 2 shows the EPMA silicon images of the cross-section after 3000 pulses of CVI at 1273 to 1573 K. At 1573 K, a thick surface film was found, but infiltration into carbon could not be found. Although infiltration of SiC is clearly seen in images of those infiltrated at 1373 and 1473 K, the existence of SiC surface films suggests difficulty of further infiltration. On the other hand, infiltration proceeds only at the deep level at 1273 K, and the reason may be attributed to the slow deposition rate at this temperature and instantaneous introduction of the cold gas which cools the substrate surface to below the deposition temperature. The relationships between the number of pulses and the ratio of the volume of infiltrated SiC (V_{SiC}) to that of initial pore (V_{pore}) are shown in Fig. 3, where the volume of infiltrated SiC was roughly estimated from the weight increase subtracted by that of the surface film, using the scanning electron micrograph of the cross section, and the density of SiC was assumed to be 3.21 g cm^{-3}. At 1373 K, a packing ratio (V_{SiC}/V_{pore}) saturates above 3000 pulses where surface films initiate to block the pore entrance. On the other hand, the ratio increases with the number of pulses up to 10 000 pulses at 1273 K.

Fig. 4 shows the EPMA silicon images of the cross-section after CVI of 1000, 3000, 5000 and 10 000 pulses at 1273 K. As expected, the cold source gas cools the substrate in each pulse; therefore, SiC deposition initiates at the hottest position in the system with r.f. heating and of cold gas introduction. Electrical resistance decreases with deposition of SiC, which spreads the hot zone from the half thickness to the surface. After 10 000 pulses of CVI, uniform deposition of SiC can be seen over the full thickness of the substrate. Figs 5a to c show scanning electron micrographs of the cross-section at various depths after 10 000 pulses of CVI at 1273 K. Although the packing is not yet sufficient, the uniformity over the thickness is fairly good.

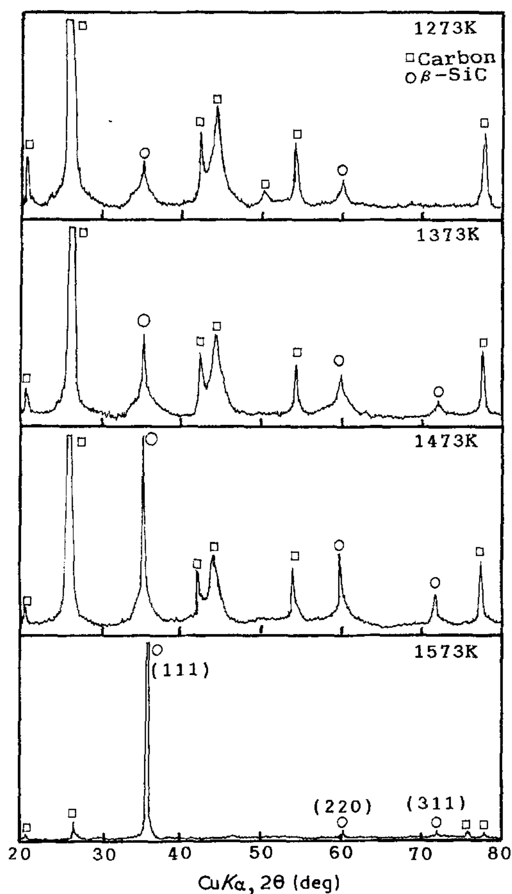


Figure 7 X-ray diffraction diagrams of deposits after 3000 pulses of CVI.

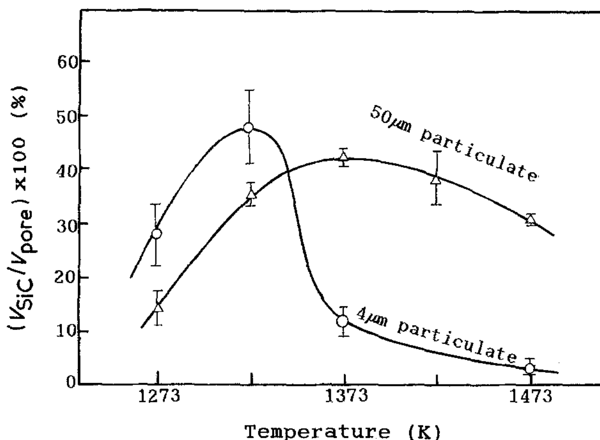


Figure 8 Dependence of packing ratio and flexural strength on deposition temperature after 10 000 pulses of CVI.

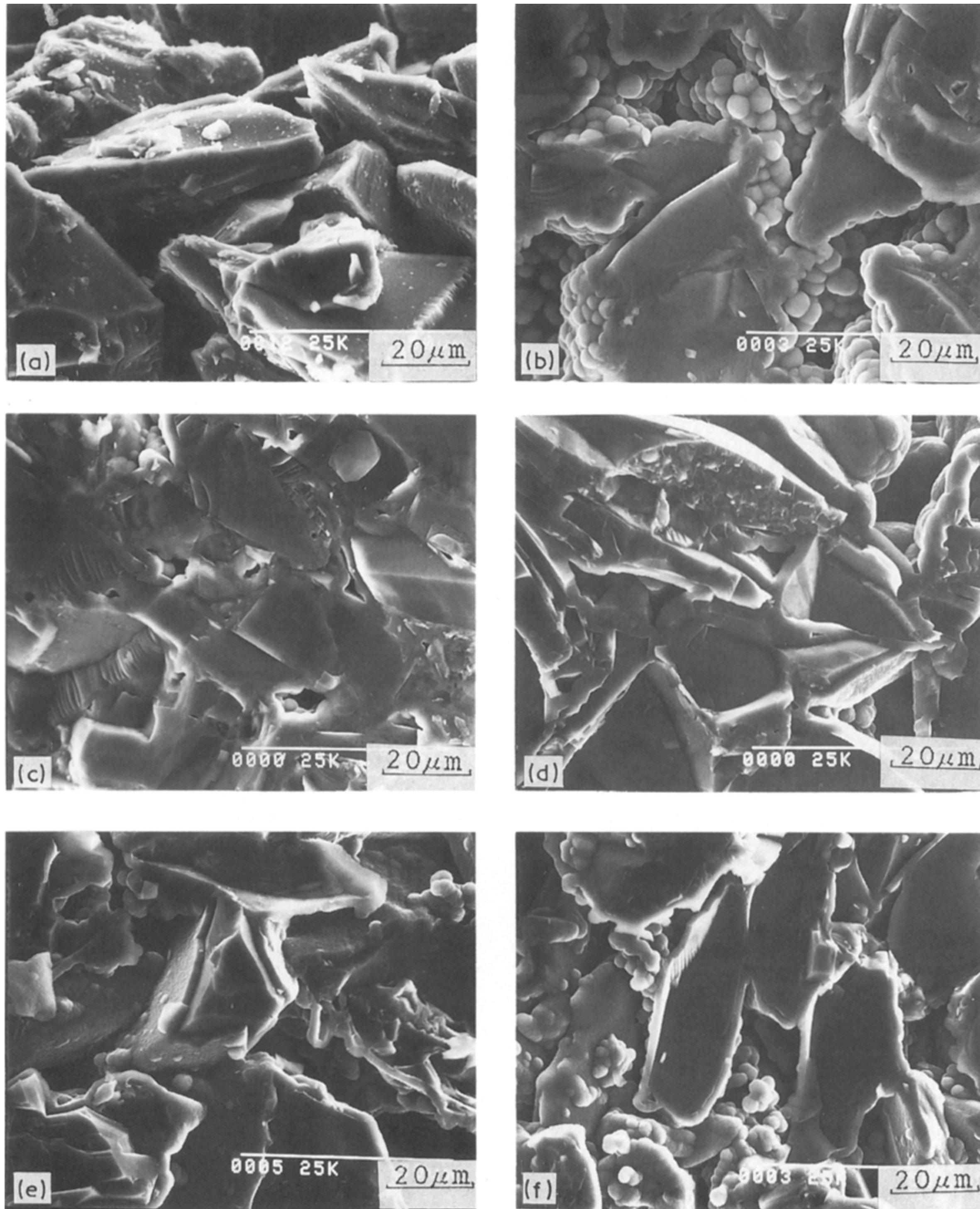


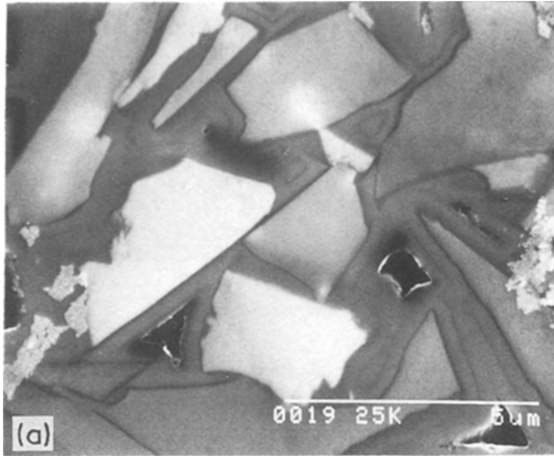
Figure 9 Ruptured sections at various depths infiltrated into 50 μm particulate preform. (a to c) 1273 K, 20 000 pulses; (d to f) 1473 K, 10 000 pulses. Depths from surface (μm): (a) 25, (b) 500, (c) 700, (d) 25, (e) 200, (f) 700.

The dependence of three-point flexural strength at room temperature on the number of pulses is shown in Fig. 6. The strength of the substrates infiltrated at 1373 K saturates above 4000 pulses; however, in those infiltrated at 1273 K it increases sigmoidally with the number of pulses, and reaches about three times the strength of the original substrate after 10 000 pulses. The above results suggest that the strength is increased effectively with deposition into the pores, but not with the thickening of the surface films.

In Fig. 7, X-ray diffraction diagrams of the deposits are shown. The peaks of β-SiC sharpen with increasing of deposition temperature, and also the peaks of the carbon substrate are weakened with thickening of the surface films of SiC.

3.2. Pulse CVI of SiC into SiC particulate preform

The oval-shaped preforms were infiltrated by SiC. Fig. 8 shows the dependence of packing ratio (V_{SiC}/V_{pore}) and flexural strength on the deposition temperature after 10 000 pulses. One of the difficulties of CVI is the low mass-transport because of the low density of the source in the gaseous phase. Therefore, packing into coarse particulate substrate requires a long time. In other words, the maximum packing temperature is



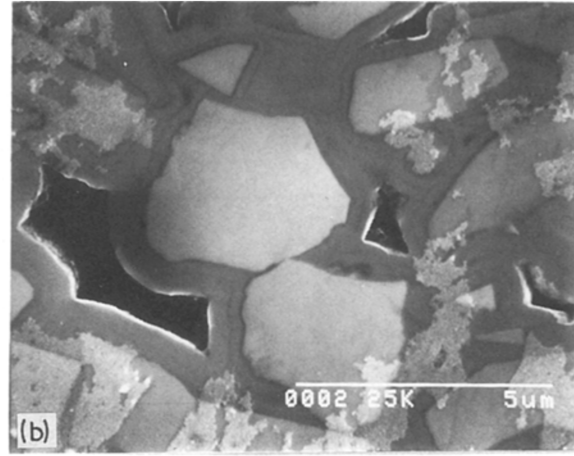


Figure 10 Cross-sections at various depths after 30 000 pulses of CVI into 4 μm particulate substrate at 1273 K. Depths (μm): (a) 100, (b) 300, (c) 500.

supposed to move to a value higher than that for fine particulate preform under a constant number of pulses. In Fig. 8, maximum packing temperatures for the preforms of 4 and 50 μm sized particles can be seen at 1323 and 1373 K, respectively. The flexural strength of these substrates also had maxima at 1323 and 1373 to 1423 K, respectively.

In Fig. 9, ruptured sections at various depths of the 50 μm particulate substrates are shown after 20 000 pulses at 1273 K (Figs 9a to c) and after 10 000 pulses at 1423 K (Figs 9d to f). At 1273 K, deposition takes place at deep levels but not near the surface. On the other hand, deposition can be seen not only at the deep level but also near the surface at 1423 K. Fig. 10 shows the cross-sections at various depths after 30 000 pulses of CVI to a 4 μm particulate substrate at 1273 K. The cross-sections were polished, oxidized in air flow at 1573 K for 2 h, and etched in hydrofluoric acid. Considerable deposition occurs in the pores between the particles near the surface, but at deeper levels (500 μm) many pores remain unfilled. After 30 000 pulses of CVI, a surface film is formed to block the pores, and thus leading to insufficient packing at deep levels. Another reason for insufficient packing is thought to be the highly irregular shape of the particles, which stops the gas penetration.

Fig. 11 shows the relationship between the packing ratio (V_{SiC}/V_{pore}) and the number of pulses in connection with the particle size and deposition temperature. At 1373 K, the packing ratios saturate above 5000 and 10 000 pulses for 4 and 50 μm particles, respectively. At 1273 K, however, the packing continues linearly up to 40 000 pulses for 50 μm particle, although it is saturated above 30 000 pulses for 4 μm particles. From these results, it is considered that the lower temperature is favourable for a higher packing ratio irrespective of particle size.

Fig. 12 shows the relations between the flexural strength and the number of pulses. In accordance with the saturation of packing ratio above 30 000 pulses

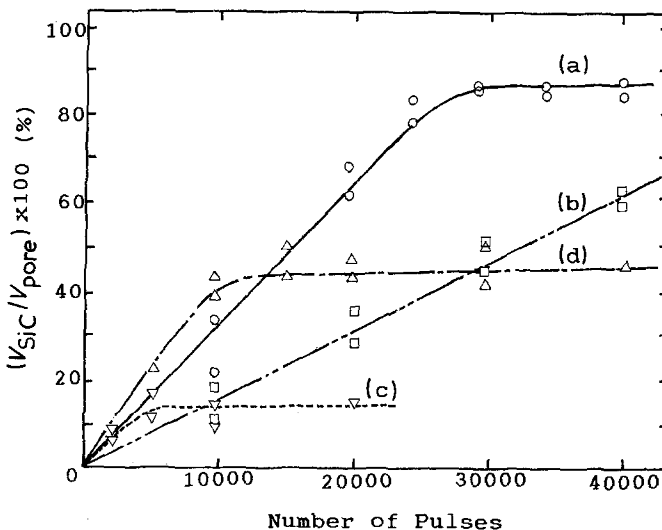


Figure 11 Relationship between the packing ratio and the number of pulses. (a) 1273 K, 4 μm particles, (b) 1273 K, 50 μm particles, (c) 1373 K, 4 μm particles, (d) 1373 K, 50 μm particles.

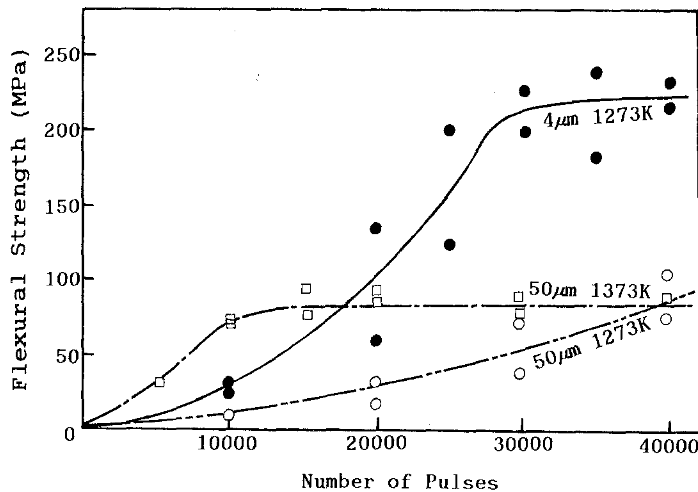


Figure 12 Dependence of flexural strength on the number of pulses.

(Fig. 11a), the strength also saturates at 200 to 220 MPa above a similar number of pulses. To increase the strength further, a selection of the particle shapes and a suitable particle size distribution from fine at the half thickness to coarse near the surface, may be required.

4. Conclusions

The effects of r.f. heating on the distribution of deposits in the pulse CVI process were examined using porous carbon and SiC particulate preform as substrates and SiC as a matrix. The following conclusions were drawn.

1. The most favourable temperature was thought to be 1273 K.

2. Porous carbon was infiltrated from the half-thickness zone.

3. Flexural strength of porous carbon was increased three-fold after 10 000 pulses of CVI.

4. The flexural strength of the SiC particulate preform (particle size 4 μm) reached 200 to 220 MPa after 30 000 pulses of CVI.

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