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Pulsed chemical vapour infiltration of SiC to three-dimensional carbon fibre preforms

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Three-dimensional carbon fibre preforms were infiltrated with silicon carbide from a gas system of CH_3SiCl_3–H_2 using a process of pressure pulsed chemical vapour infiltration. To infiltrate to a deep level, the temperature had to be lowered to 870–900 °C, and the hold time per pulse below 1.0 s. Three-dimensional carbon fibre preforms partly filled with SiC fine powder were compared with those without filler. The weight of the preforms increased linearly with increasing number of pulses up to 10^5 when no filler was present. However, the weight increase slowed down above 8×10^4 pulses when the filler was used. Preforms with and without SiC filler showed three-point flexural strengths of 160 and 80 MPa after CVI of 10^5 pulses, respectively. In order to improve the strength, a denser filling of SiC powder is necessary.

1. Introduction

Among the production processes of ceramic composites, chemical vapour infiltration (CVI) has the advantage of producing a product which has the same shape and size as the preform, and therefore expensive processings to final shape can be minimized. Naslain and co-workers [1–3] reported the CVI of TiC, BN, etc., to two-dimensional carbon fibre preforms; however, a very long operation time was necessary (2–3 weeks). On the other hand, Stinton and co-workers [4–6] reported a forced CVI process, which used steep temperature and pressure gradients, and under these conditions the operation time for CVI of SiC into SiC fibre preforms was decreased to 20 or 30 h; however, the shape of the preforms may be limited to cubic or cylindrical in order to allow the flow of the reactant gas through the preforms, and therefore expensive processings may be necessary to produce the final shape. Bryant [7] proposed a unique process of "pulsed chemical vapour deposition" in which sequential steps of evacuation of the vessel, instantaneous introduction of source gas, and holding to allow deposition, are repeated. The instantaneous introduction of fresh gas diminishes the non-uniform deposition along the long vessel. If this pulse CVD process is applied to CVI, called "pulsed CVI", thin pores or spaces between the filaments or the particles are filled by fresh gas at each pulse and the required matrix may be deposited in fine pores or spaces. We have reported the pulsed CVI of TiN, BN and SiC to porous carbon and Si_3N_4- and SiC-particulate preforms [8–11]. In present paper, a study on the pulsed CVI of SiC to three-dimensional carbon fibre preforms (3D-C/C) will be described.

2. Experimental procedure

2.1. Apparatus for pulsed CVI of SiC.

Fig. 1 shows the apparatus used for pulsed CVI of SiC. A part of the hydrogen stream was bubbled into ice-cooled methyltrichlorosilane (CH_3SiCl_3) and then accumulated, together with a separate stream of hydrogen, in a reservoir, from which gas was fed to the reaction vessel up to 760 torr in each pulse via an electromagnetic valve. Three to seven pieces of preform of 10×30 mm^2 rectangle and 1.0 or 0.6 mm thick were hung at the bottom of the vessel. The dead space in the vessel including that of the entry and exit paths was reduced to 50 cm^3 in order to shorten the evacuation time and to increase gas yield. After a given hold-time to allow deposition, gas was evacuated to below 1 torr using pumps 1 and 2 sequentially. The total time per pulse was only 1.1–2.0 s.

2.2. Preparation of fibre preforms

Two types of preform were prepared by the sequential steps shown in Fig. 2. Carbon fibre yarn with 3000 monofilaments (Toray M-40) was woven to two-dimensional cloths, and several sheets of cloth were stitched using another type of yarn, T-300 (Toray). Plyophen (Dainihon Ink, 5900) was used as a binder after dilution with ethanol to 20%, 40% and 60%. After curing at 150 °C for 1 h, the cross sections were observed, and 20% dilution was found to be the best for pulsed CVI because it gave the highest porosity. Some of the three-dimensional cloths were immersed into 20% plyophen–ethanol solution in which 4 μm SiC powder was suspended and an ultrasonic wave was passed through the solution. By this means, large

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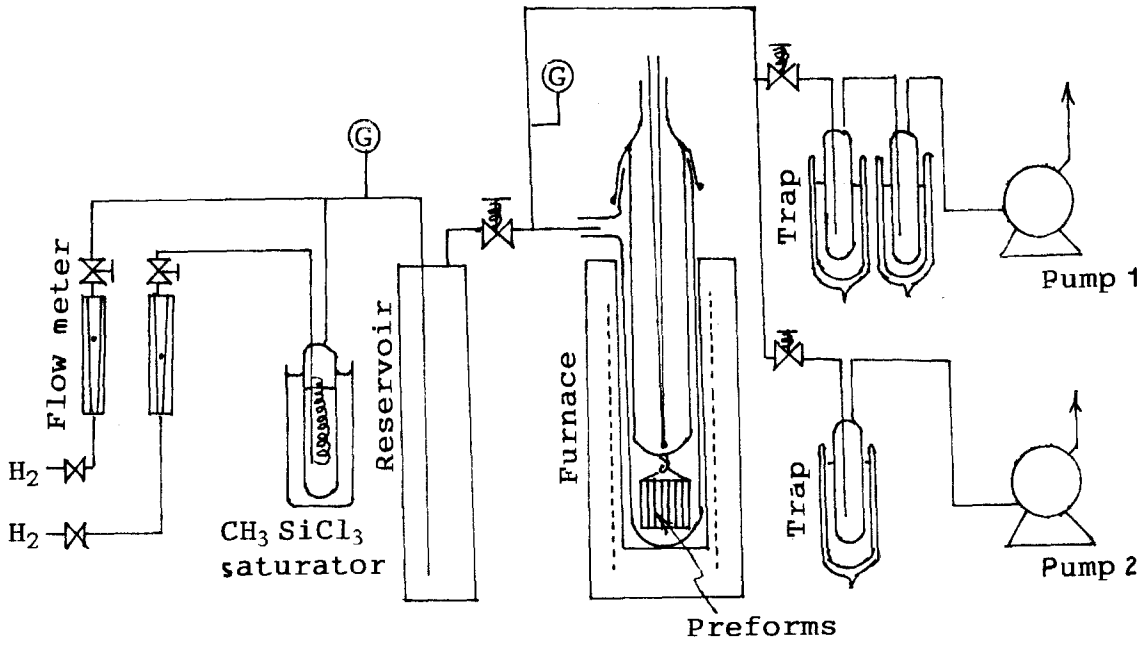

Figure 1 Apparatus for pulsed CVI of SiC to 3D-C/C preforms.

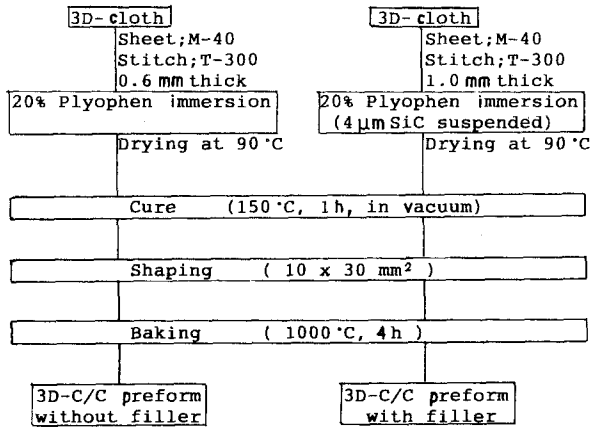

Figure 2 Preparation steps of preforms.

weaving spaces in the three-dimensional cloths were half filled with SiC powder. Then, the cloths with SiC filler were cured, shaped and baked.

3. Results and discussion

3.1. Effects of temperature and position of preforms

Fig. 3a–c show the cross-sections after 1000–1200 pulses of CVI at 1300, 1200 and 1100 °C, respectively. Thick coatings on the macrosurface can be seen at these high temperatures, and a thin layer had formed even at 1100 °C. Fig. 3d shows the cross-section after 8500 pulses at 1000 °C, and thick films had also formed with the increasing number of pulses, even at 1000 °C. Therefore, the temperature was lowered to 900 °C. Fig. 4a–d show the cross-sections of preforms after 32 070 pulses set at various positions. In this case, seven preforms without SiC filler were hung close to each other. From the photographs, no marked difference of infiltration can be seen between the different setting positions.

3.2. Relations between the weight increase and the number of pulses

The weight increase with the increase of the number of pulses is plotted in Fig. 5. In the case of the preforms without SiC filler, the weight increased linearly with increasing number of pulses up to 10^5. On the other hand, the gradient of the weight increase curve of the preforms with SiC filler decreased above 8×10^4 pulses. These differences in the weight increase curves are attributed to whether or not films on the macrosurface are partially formed and this situation can be seen from the figures in the following section.

3.3. Cross-sectional appearance in relation to the number of pulses

Cross-sections of preforms without SiC filler after 32 070, 64 400 and 99 800 pulses at 900 °C and with a hold-time of 1 s are shown in Figs 6–8, respectively. The numbered windows in the low-magnifiecation photographs (top) are shown highly magnified in the lower photographs. From the magnified photographs, thin films on the macrosurface, which block gas penetration, could not be seen in all cases. These infiltration profiles are in agreement with the behaviour of the weight increase curve in Fig. 5.

For preforms with SiC filler, progression of infiltration can be seen from Figs 9–11 which were obtained at 870 °C and with a hold-time of 0.6 s after 3×10^4, 7×10^4 and 10^5 pulses, respectively. Although no surface film was formed after 3×10^4 pulses (Fig. 9) which is similar to the situation in Fig. 6, microcracks were clearly seen. Filling of SiC powder into the large spaces between the carbon fibre yarns produces bonding between carbon yarns and the SiC matrix in a short time. As a result of bonding, the preform is rendered very rigid, therefore, the thermal stress which is generated during the cooling process leads to microcracks. However, these microcracks are considerably repaired during the following CVI process, as can be

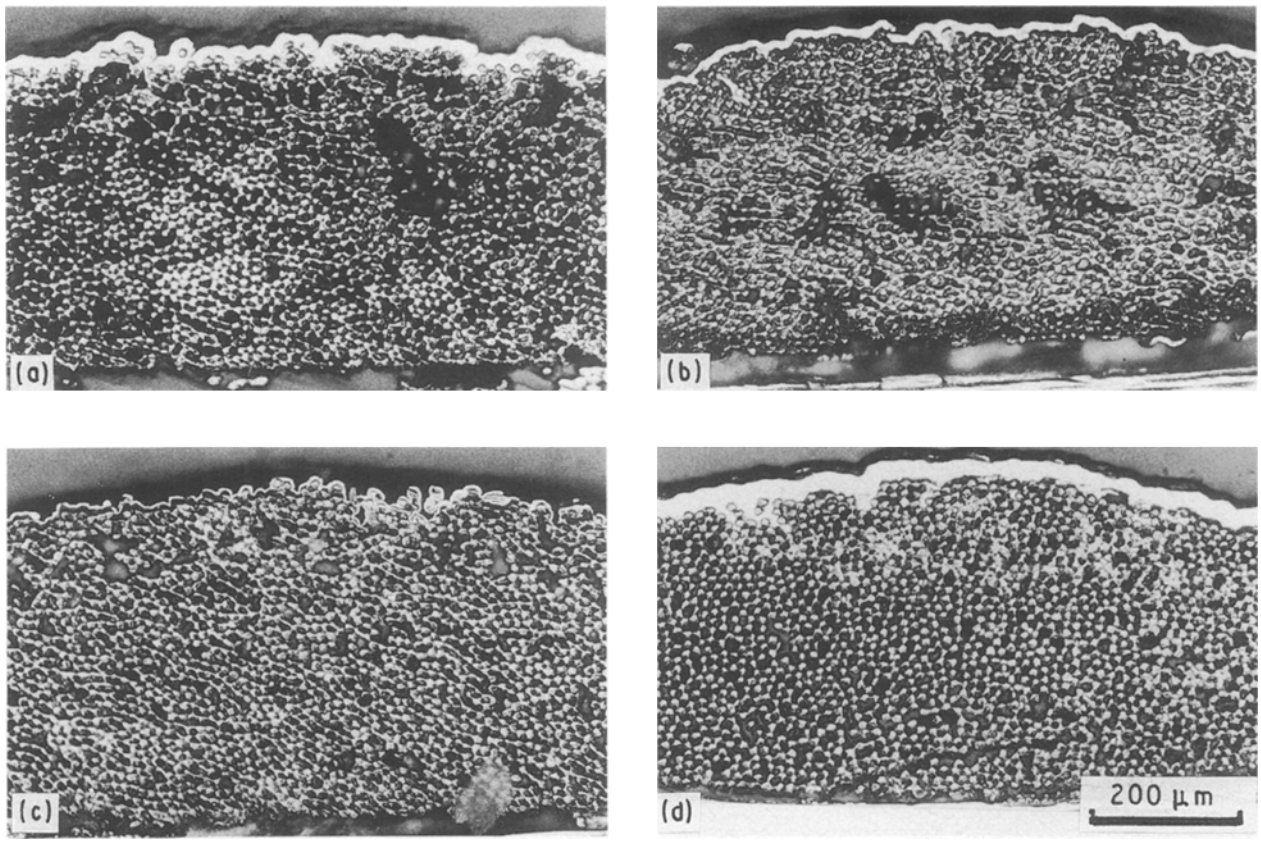

Figure 3 Dependence of infiltration on the deposition temperature and number of pulses. (a) 1300 °C, TMS 7%, hold-time 0.7 s, 1000 pulses, (b) 1200 °C, TMS 7%, hold-time 3.5 s, 1200 pulses, (c) 1100 °C, TMS 7%, hold-time 2.5 s, 1200 pulses, (d) 1000 °C, TMS 4.5%, hold-time 2.5 s, 8500 pulses.

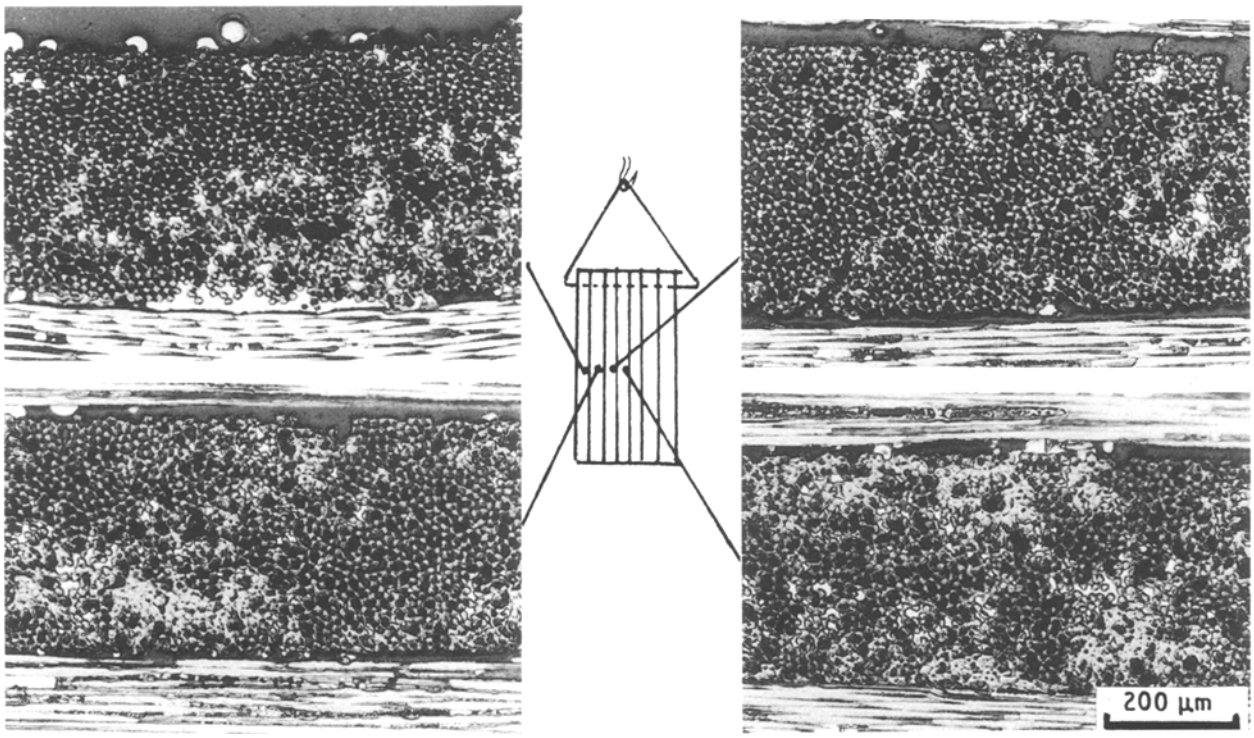

Figure 4 Effect of setting positions on infiltration (without SiC filler). 900 °C, TMS 4.5%, hold-time 1 s, 32 070 pulses.

seen in Fig. 11. After 7×10^4 pulses, surface films had formed imperfectly, not only on the macrosurface, but also on the microsurface of the filled SiC powder piles (Fig. 10, position 3). This situation explains the decrease in the gradient of the weight increase curve above 8×10^4 pulses in Fig. 5. Above 10^5 pulses, films on the macrosurface grew further, and highly magnified SEM images and electron probe microanalysis

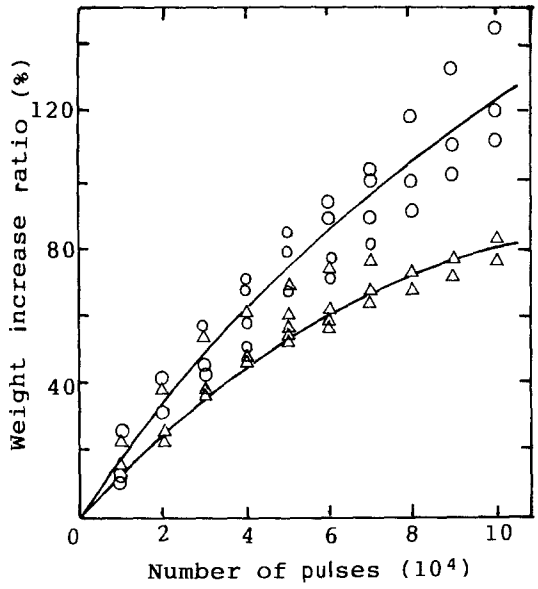

Figure 5 Relationship between weight increase and number of pulses (○) without SiC filler, 900 °C, TMS 4.5%, hold-time 1 s, (△) with SiC filler, 870 °C, TMS 4.5%, hold-time 0.6 s.

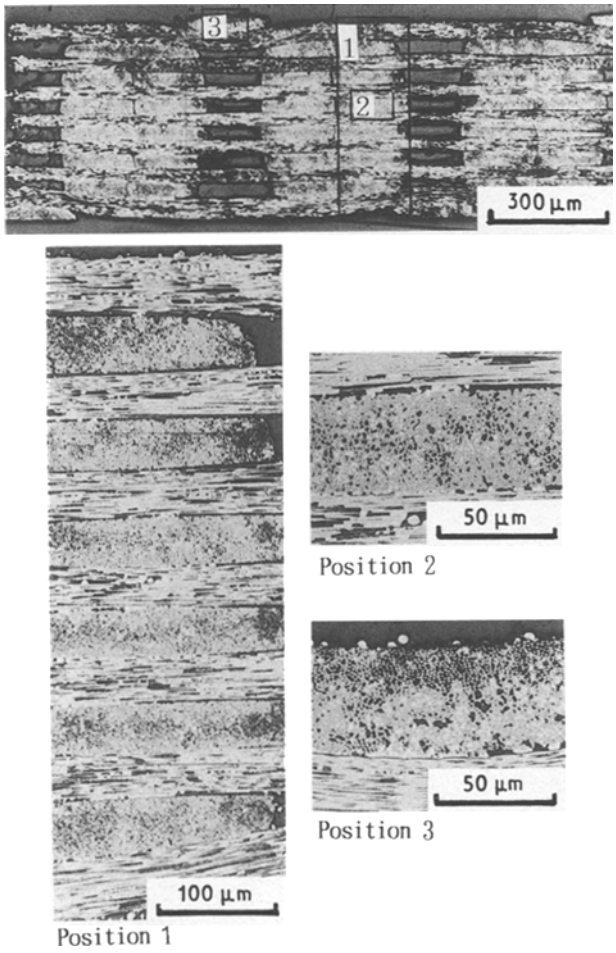

Figure 6 Cross-sectional appearance of a preform without SiC filler after 32 070 pulses of CVI at 900 °C, TMS 4.5%, hold-time 1 s.

(EPMA) silicon images of positions 2 and 3 on the low magnification photograph in Fig. 11 are shown again in Fig. 12. Position 2 is near the macrosurface, and is the cross-section of stitching yarn S-300, which has

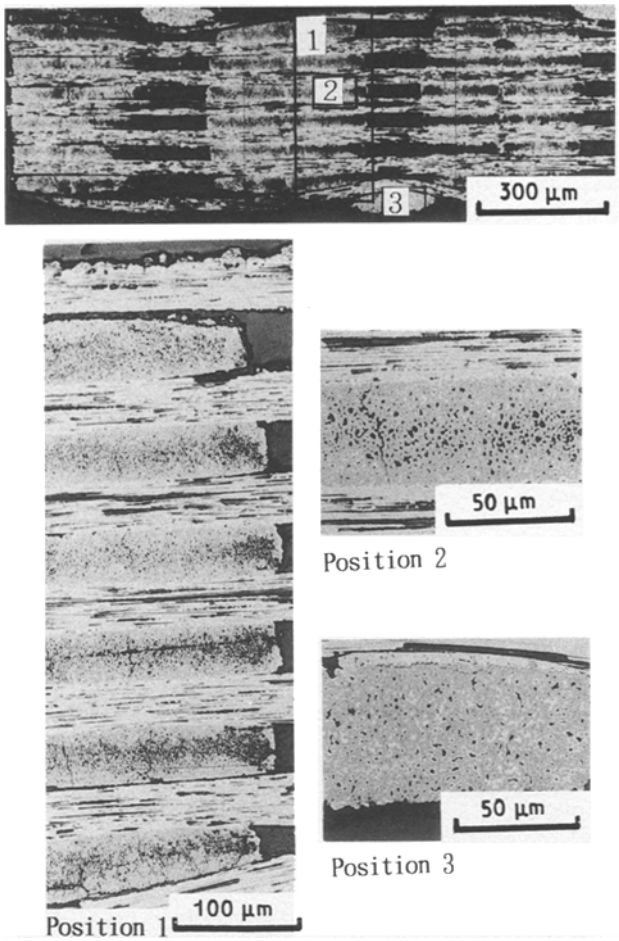

Figure 7 Cross-sectional appearance of a preform without SiC filler after 64 400 pulses of CVI at 900 °C, TMS 4.5%, hold-time 1 s.

considerable spaces between the monofilaments, therefore, infiltration is satisfactory. On the other hand, position 3 is at a deep level; furthermore, the position consisted of M-40 yarn which is densely bonded by coked resin. Although the source gas could hardly flow through the spaces between the filaments, the EPMA Si image shows considerable infiltration into the yarn. To improve the infiltration rate into the M-40 yarn, preliminary washing-out of the resin between the filaments is necessary.

3.4. Flexural strength

Load–strain curves of the infiltrated 3D-C/C preforms, were constructed using a span of 20 mm at room temperature, and the three-point flexural strength, S, was calculated from

$$S = 3Pl/2BD^2 \quad (1)$$

where P, l, B and D are the maximum load, span length, width and thickness of the preform. The load–strain curves are shown in Fig. 13. The effect of SiC filler can be seen after 3×10^4 pulses of CVI. Without filler, the form of the curve is that of a non-rigid body; on the other hand, the curve with filler shows that of a rigid body. From the tailing curves over the peaks, a loose adhesion can be supposed between the carbon filament and SiC matrix after 10^5

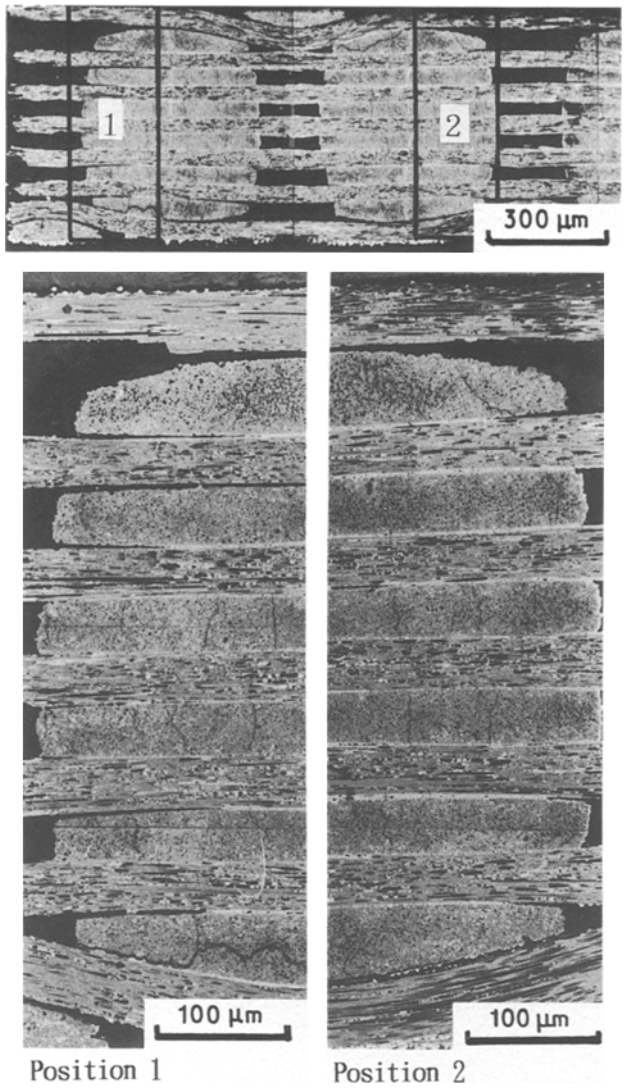

Figure 8 Cross-sectional appearance of a preform without SiC filler after 99 800 pulses of CVI at 900 °C, TMS 4.5%, hold-time 1 s.

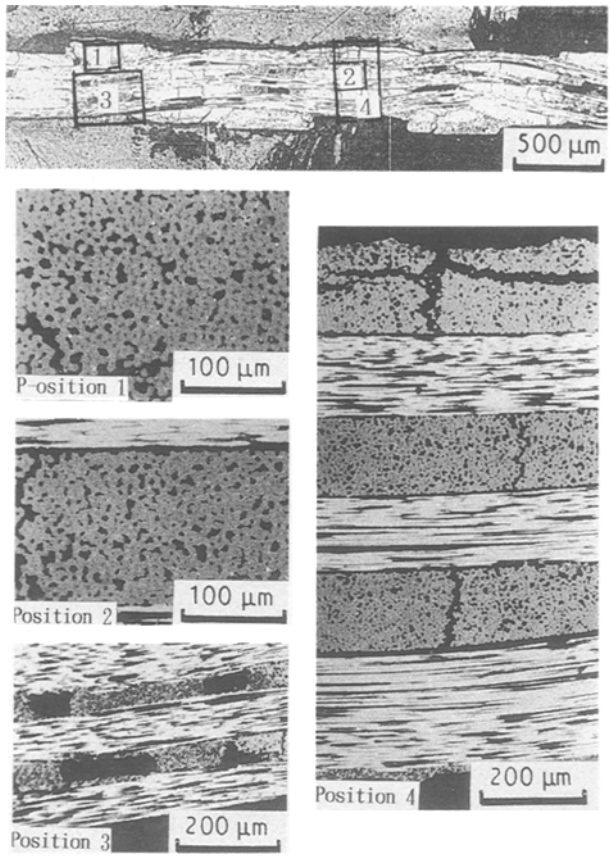

Figure 9 Cross-sectional appearance of a preform with SiC filler after 3×10^4 pulses of CVI at 870 °C, TMS 4.5%, hold-time 0.6 s.

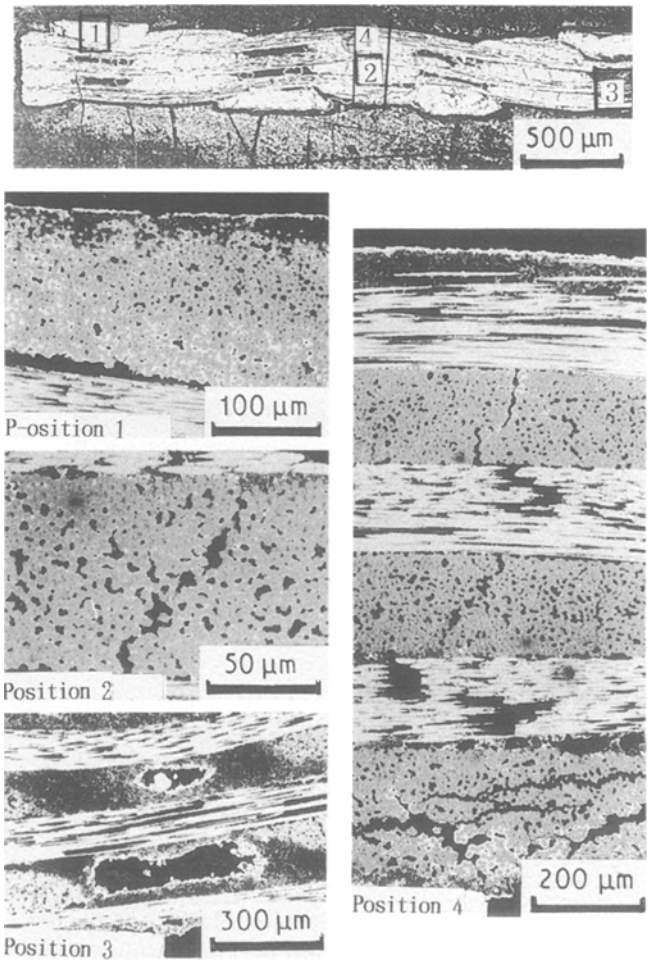

Figure 10 Cross-sectional appearance of a preform with SiC filler after 7×10^4 pulses of CVI at 870 °C, TMS 4.5%, hold-time 0.6 s.

pulses with SiC filler. Fig. 14 shows the relation between flexural strength and number of pulses. Without SiC filler, the increase in strength is very slow and is only 80 MPa after 10^5 pulses. This result may be attributed to the poor bonding between the carbon yarns because of large volume of spaces in the initial preforms. Pulsed CVI is not suitable for filling a matrix into large spaces. On the other hand, the strength of the preform with SiC filler increases with increasing number of pulses, and reaches 160 MPa after 10^5 pulses. The strength continues to increase even after 10^5 pulses. The total net operation time of 10^5 pulses was 40 h. To improve the strength, denser filling of SiC powder into the large spaces is necessary, and the best way is supposed to be by filling with powder during the stitching process. Fig. 15 shows the ruptured surface of the preform with SiC filler after 10^5 pulses of CVI. Loose adhesion between carbon filament and SiC matrix can be seen.

4. Conclusion

Pressure-pulsed chemical vapour infiltration of SiC into three-dimensional carbon/carbon preforms were

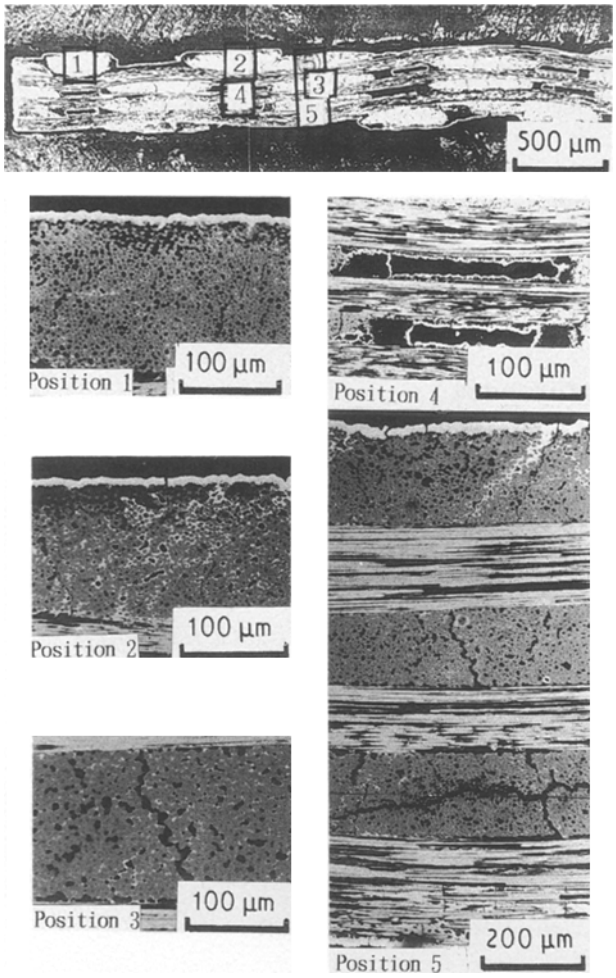

Figure 11 Cross-sectional appearance of a preform with SiC filler after 10^5 pulses at 870 °C, TMS 4.5%, hold-time 0.6 s.

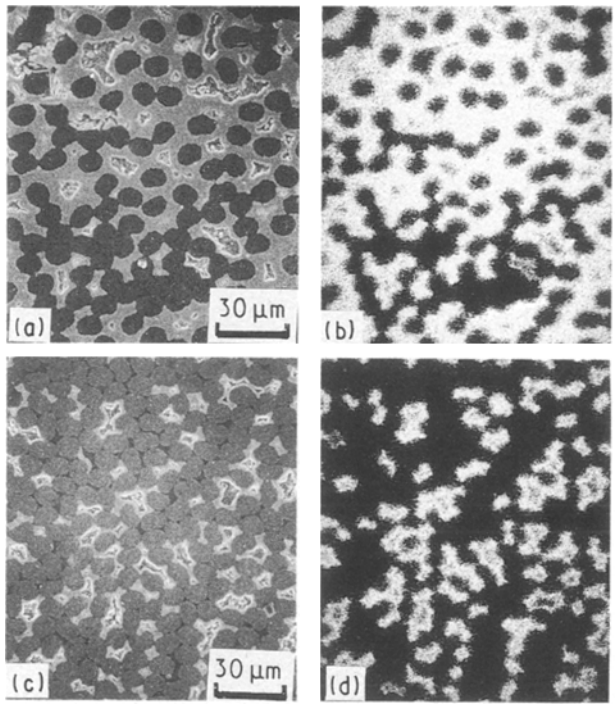

Figure 12 (a, c) Magnified scanning electron micrographs and (b, d) EPMA images of the positions 2 and 3, respectively in Fig. 11.

investigated using a system of methyltrichlorosilane–hydrogen in the temperature range 800–1300 °C. The results are summarized as follows.

1. To infiltrate to a deep level avoiding the growth of a surface film, the temperature had to be lowered to 870–900 °C, and the reaction time (hold-time) per pulse had to be kept below 1.0 s.

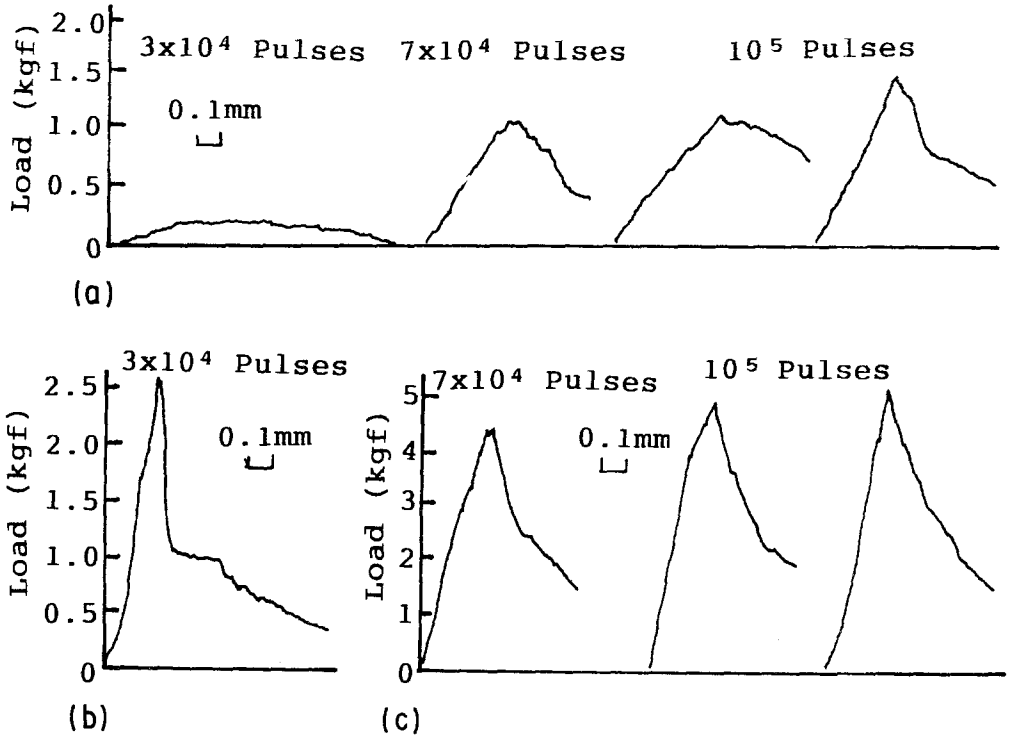

Figure 13 Stress–strain curves during the three-point flexural strength testing, (a) without filler, $10 \times 30 \times 0.6$ mm^3, (b, c) with filler, $10 \times 30 \times 1.0$ mm^3.

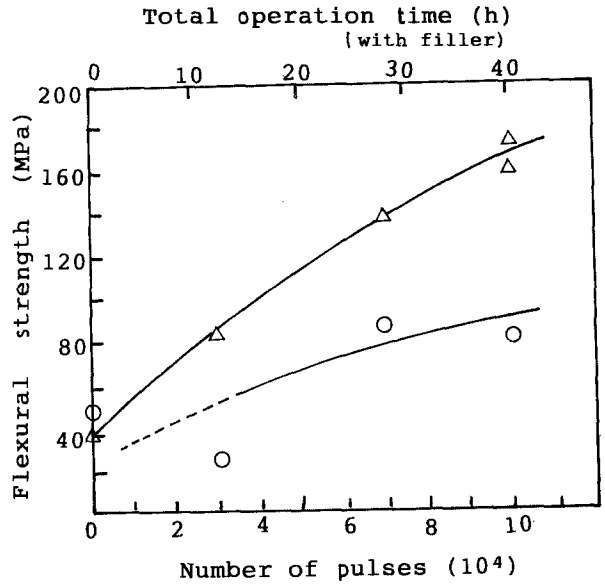

Figure 14 Relationship between flexural strength and number of pulses (○) without filler, (△) with filler.

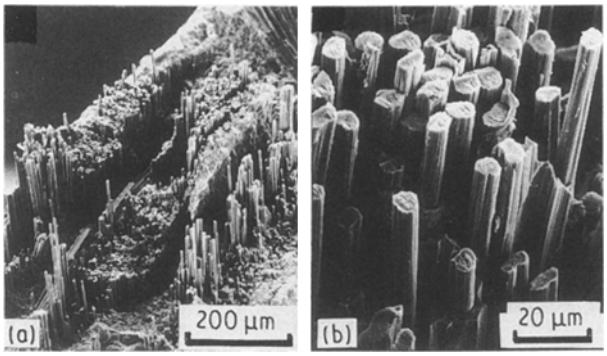

Figure 15 (a) Low and (b) high magnification views of the ruptured section. 870 °C, TMS 4.5%, hold-time 0.6 s, preform with SiC filler, after 10^5 pulses.

2. On the surface of preforms without SiC filler, no film was deposited even after 10^5 pulses. In the case of preforms with SiC filler, SiC films were partially formed on the surface above 7×10^4 pulses.

3. The three-point flexural strength at room temperature reached 160 and 80 MPa after 10^5 pulses for preforms with and without SiC filler, respectively. To improve the strength, a denser packing of SiC filler into the large spaces in the preforms is necessary.

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