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Pressure-pulsed chemical vapour infiltration of TiN to SiC particulate preforms

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SiC particulate preforms were infiltrated by TiN matrix from a gas mixture of $TiCl_4$ (5%), nitrogen (30%) and hydrogen using a repeating pressure pulse between 760 and about 1 torr. SiC particle sizes of 5 and 20 μm were used. For matrix packing into deep level, optimum temperature was determined between 800 and 850 °C, and the maximum packing ratio reached 67% after 4×10^4 pulses at 850 °C. The increase of $TiCl_4$ concentration to 10% resulted in higher deposition rate and packing ratio. The decrease of nitrogen concentration led to slower deposition, that is, a similar effect to temperature lowering. The maximum flexural strength measured was 140 MPa.

1. Introduction

Among the chemical vapour infiltration processes (CVI), two processes are well known, that is, ICVI and FCVI. The former CVI process is operated under an isothermal and isobaric condition, and a near net-shape product can be obtained, but this process needs a long operation time [1–3]. On the contrary, the latter CVI process applies steep gradients of pressure and temperature between upper and lower surfaces of preform, therefore, the operation is shortened to 20–40 h, but loses the characteristic of near net shape [4–6]. However, pressure pulsed CVI (PCVI) has a characteristic that fresh source gas can be introduced to deep levels of preforms through fine pores possibly submicrometre thick, and furthermore, the infiltration initiates from the deepest zone if the reaction temperature is kept suitably low and the reaction time per pulse is held considerably short. The PCVI process consists of repeating steps of evacuation of the vessel, instantaneous introduction of fresh source gas, and holding to allow deposition (holding time). The PCVI process can be applied to fibrous, particulate and porous preforms, and the matrix may be selected from chemically vapour-depositable materials [7–11]. In this paper, various factors which affect the infiltration of TiN into SiC particulate preforms will be described. The deposition of TiN from the system $TiCl_4$–N_2–H_2 takes place above 750 °C, and the deposition rate accelerates above 900 °C [12]. Dense packing of the matrix by PCVI to deep levels of preforms is severely affected by the deposition rate; therefore, TiN is suitable as a model matrix for PCVI.

2. Experimental procedure

A hydrogen stream was bubbled into the $TiCl_4$ saturator, and was accumulated in a reservoir kept near 760 torr (1 torr = 133.322 Pa) together with separate streams of hydrogen and nitrogen. Unless otherwise mentioned, the concentrations of $TiCl_4$ and nitrogen were controlled at 5% and 30%, respectively. A reaction vessel (Fig. 1) was inserted into the upside-down furnace in order to suppress the preheating of flow-in gas, and the total volume of the dead space of the reaction zone and those of inlet and outlet pipes was narrowed to 30 cm^3 for short evacuation time and high gas yield. The source gas in the reservoir was instantaneously introduced to the vessel up to 760 torr via a magnetic valve (< 0.1 s), and the gas was held there for up to 2 s for deposition (holding time); then the gas in the vessel was evacuated to about 1 torr using two pumps (< 1 s), sequentially.

Particulate preforms were prepared from SiC powder (Showa Denko Co.). The average particle size used was either about 5 or 20 μm. The powder was pressed to 10 mm × 20 mm oval shapes, 0.9 or 1.8 mm thick, with the addition of a small amount of water and starch, and baked at 900 °C for 6 h in a nitrogen flow. The preforms had about 50% porosity. The packing ratio in this paper is defined as

$$\text{(packing ratio \%)} = \frac{\text{(volume of TiN after infiltration)}}{\text{(initial volume of pores)}} \times 100 \quad (1)$$

3. Results and discussion

3.1. Effect of deposition temperature on packing ratio

When the holding time and thickness of the preform were kept at 1 s and 0.9 mm, respectively, a relation between weight increase after 10^4 pulses and deposition temperature was obtained as shown in Fig. 2.

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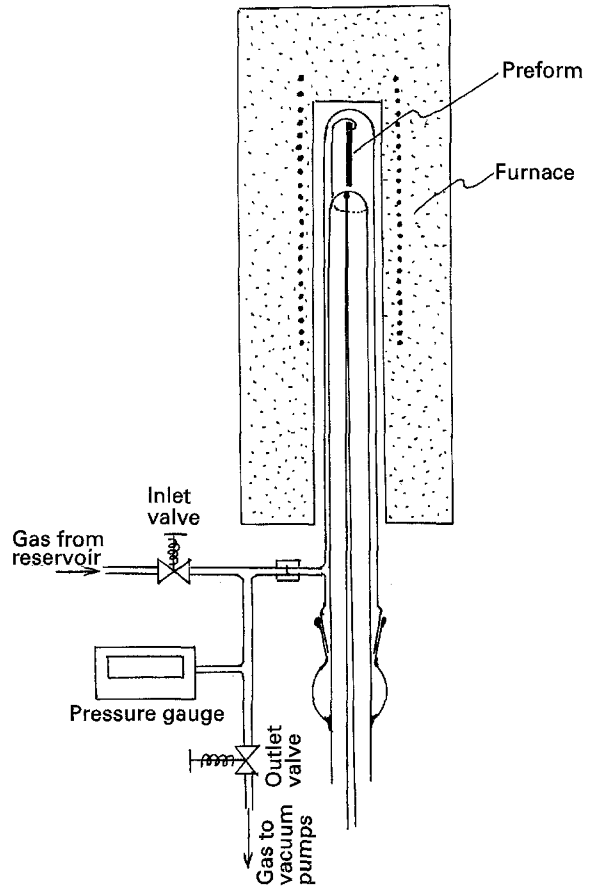

Figure 1 Reaction vessel and upside-down furnace.

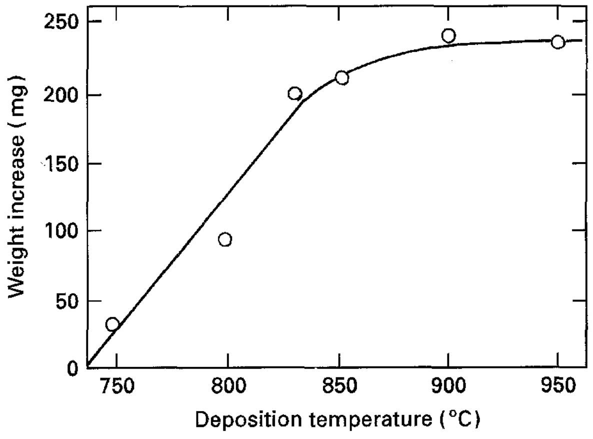

Figure 2 Dependence of weight increase on deposition temperature, after 10^4 pulses, holding time of 1 s, and $TiCl_4$ = 5%.

The weight increases linearly with increasing temperature up to 850 °C, and saturates above 900 °C. The packing ratio versus the number of pulses is plotted in Fig. 3 for preforms 1.8 mm thick. The curves of 850 and 830 °C saturate above 3×10^4 pulses with packing ratios of 48% and 52%, respectively, if the initial porosity is assumed to be 50%. At 800 °C, the packing ratio curve saturates above 5×10^4 pulses with the ratio of 54%. Fig. 4 shows SEM images and line analysis of EPMA-Ti of the cross-sections after 2×10^4 pulses at 900 °C. At such a high temperature, TiN deposits mainly near and on the surface, therefore, TiN films at deep level are thin and the line analysis of EPMA-Ti shows a high peak near the surface. With the acceleration of the reaction rate above 900 °C [12], the reactant is fully exhausted during a holding time of 1 s, and the curve saturates from deficiency of source gas. To avoid the formation of a surface film which blocks the gas-penetration path into deep levels, lowering of the temperature below 900 °C is necessary.

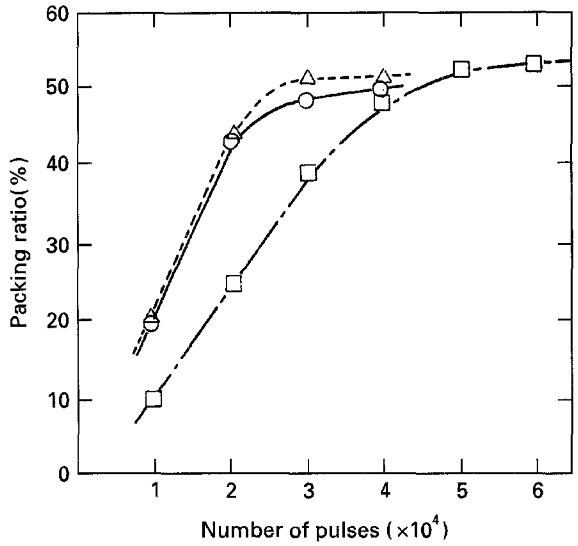

Figure 3 Relationship between packing ratio and number of pulses: thickness of preform 1.8 mm, holding time 1 s, $TiCl_4$ = 5%. (○) 850 °C, (△) 830 °C, (□) 800 °C.

3.2. Effect of $TiCl_4$ concentration

Mass transport in the vapour phase is very slow compared with that in solution or solid, therefore, an increase of reactant concentration is desirable to accelerate the infiltration rate. Fig. 5 shows the effect of $TiCl_4$ concentration. With twice the increase of $TiCl_4$ concentration (10%), both packing rate and final packing ratio increase, and the latter reaches 65% after 4.2×10^4 pulses of CVI at 850 °C (Fig. 5). However, troublesome problems arose with increasing $TiCl_4$ concentration.

3.3. Dependence of infiltration on holding time

Holding time is an important factor, particularly at high temperature, where reaction rate is high; therefore, gas in the dead space of the vessel fully reacts to deposit on the macrosurface. Fig. 6 shows the relation between packing ratio and number of pulses in relation to holding time. At 850 °C, packing curves of holding times of 0.5, 1.0 and 2.0 s fall on a curve, indicating that the reaction has finished within 0.5 s at this temperature. On the other hand, lowering the temperature to 800 °C leads to a very slow deposition; therefore, a long holding time of 2 s can be allowed without the formation of surface films. Fig. 7 shows SEM images and line analyses of EPMA-Ti of the cross-sections after 5×10^4 pulses of CVI at 800 °C and a holding time of 2 s. The EPMA-Ti line analysis shows a nearly constant distribution along the thickness.

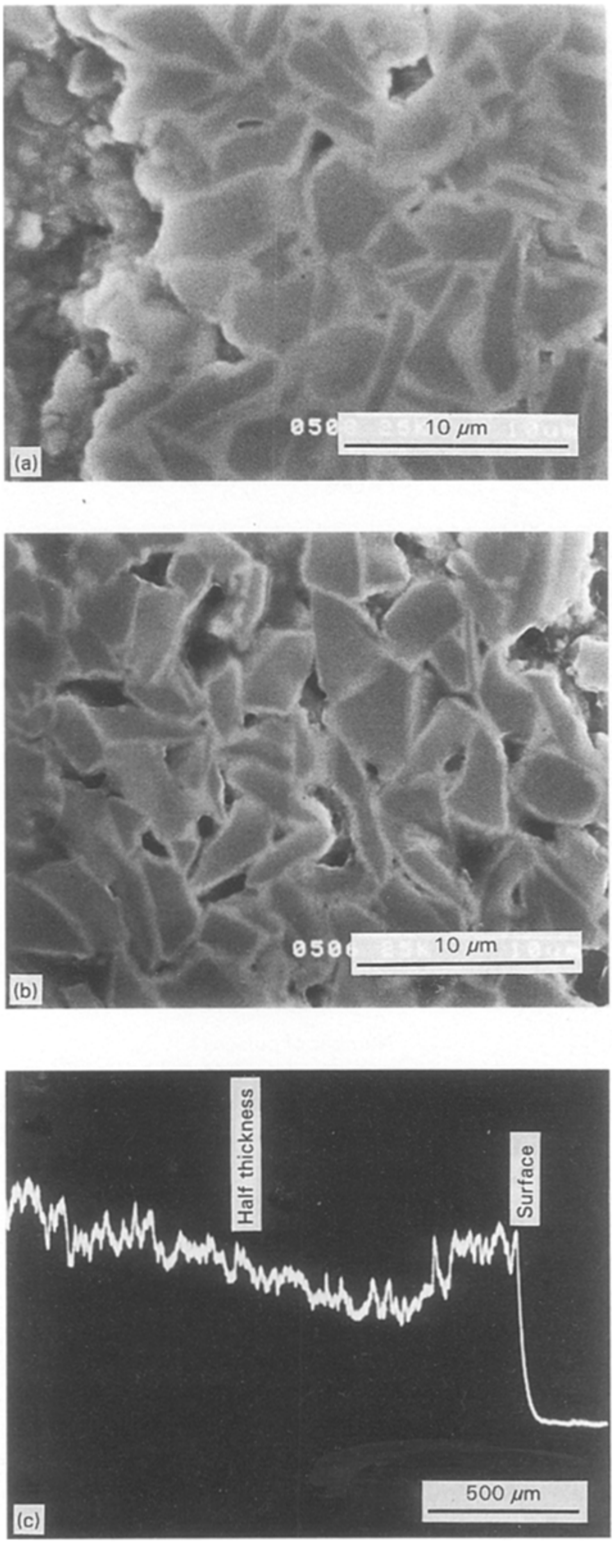

Figure 4 (a, b) SEM images and (c) EPMA line analysis (Ti) of the cross-section after 2×10^4 pulses at 900 °C. Thickness of preform 1.8 mm, holding time 1 s, $TiCl_4 = 5\%$. (a) Near surface, (b) 900 μm deep, (c) EPMA-Ti line analysis along the thickness.

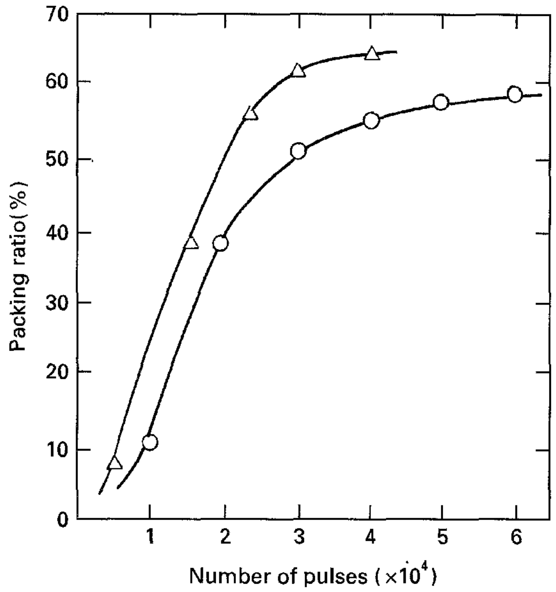

Figure 5 Effect of $TiCl_4$ concentration. 850 °C, thickness of preform 0.9 mm, holding time 1 s. $TiCl_4$: (○) 5%, (△) 10%.

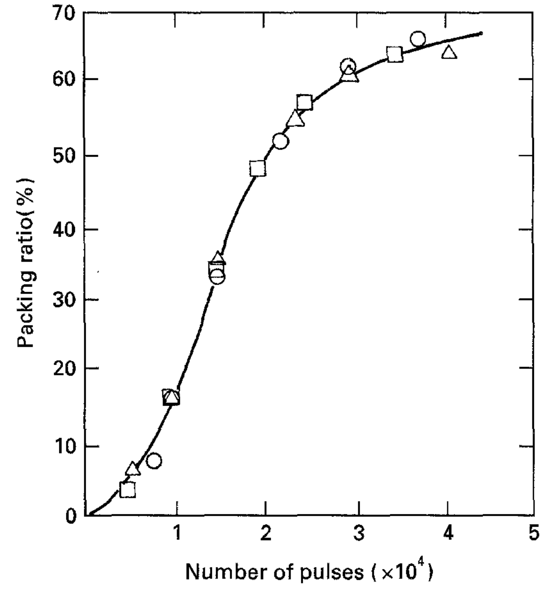

Figure 6 Effect of holding time on packing ratio. 850 °C, thickness of preform 0.9 mm, $TiCl_4 = 5\%$. Holding time: (○) 0.5 s, (△) 1.0 s, (□) 2.0 s.

3.4. Effect of nitrogen concentration

Nitrogen concentration considerably affects the deposition rate of TiN. Fig. 8 shows the relation between weight increase after 10^4 pulses and nitrogen concentration. The maximum deposition takes place at about 35% N_2 ($TiCl_4$ 5%, H_2 60%). The increase of packing ratio with increase of the number of pulses is shown in Fig. 9 using two levels of nitrogen concentration. The curve of 5% nitrogen concentration shows a considerably slower deposition compared with that of 30%, but the final packing ratio is greater than in the case of 30%. From these results, decrease of the nitrogen concentration is seen to have a similar effect to that of lowering the temperature, that is, slow deposition.

3.5. Relationship between particle size and packing ratios

Up to now, 5 μm SiC powder has been used for the preparation of preforms. Fig. 10 shows cross-sections and EPMA-Ti line analysis of a 20 μm particulate preform after 1.1×10^5 pulses at 800 °C. The initial porosities of the particulate preforms of 5 and 20 μm powder are both about 50%, therefore, it is considered

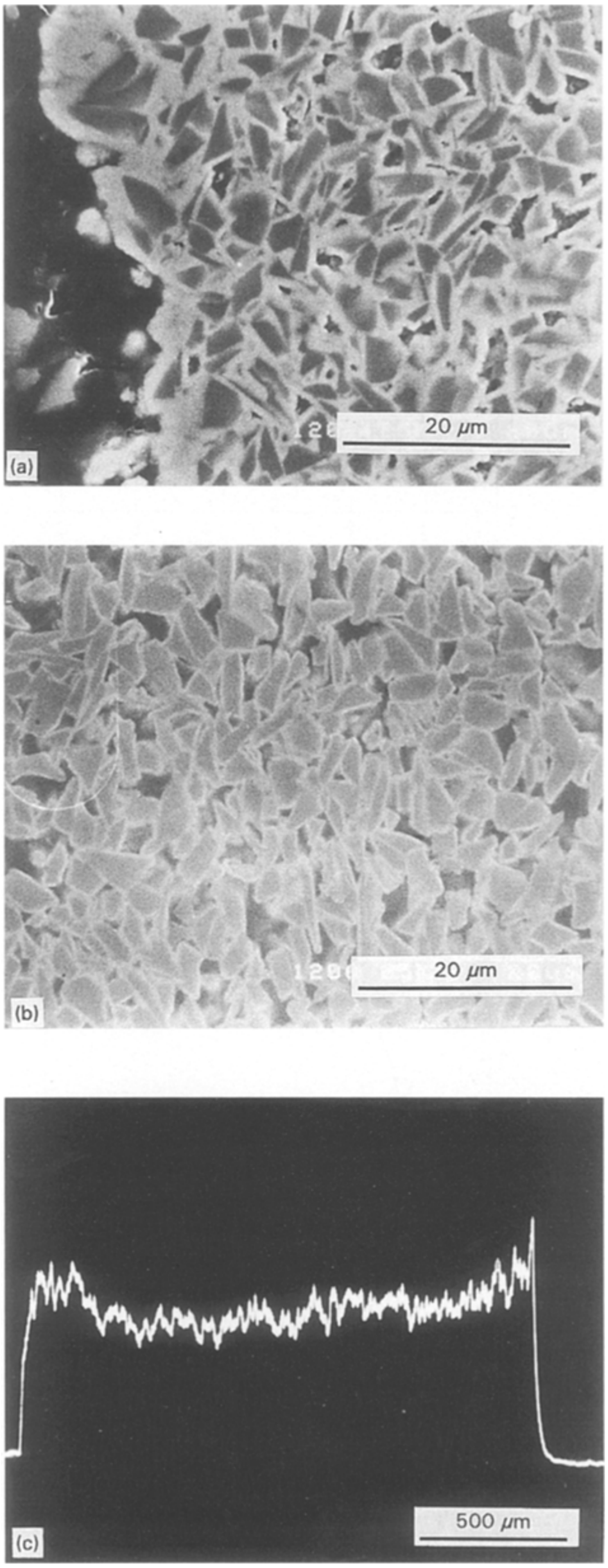

Figure 7 (a, b) Scanning electron micrographs and (c) EPMA-Ti line analysis along the thickness. 800 °C, 5×10^4 pulses, thickness of preform 1.8 mm, holding time 2 s, $TiCl_4$ = 5%. (a) Near surface, (b) 500 µm deep.

that the 20 µm preform has larger pores than those in the 5 µm preform. As was expected, larger pores can be seen on the cross-section even near the surface (Fig. 10), and the EPMA line analysis shows a rough distribution across the thickness. A preform in which 5 µm powder sheet was sandwiched by 20 µm powder

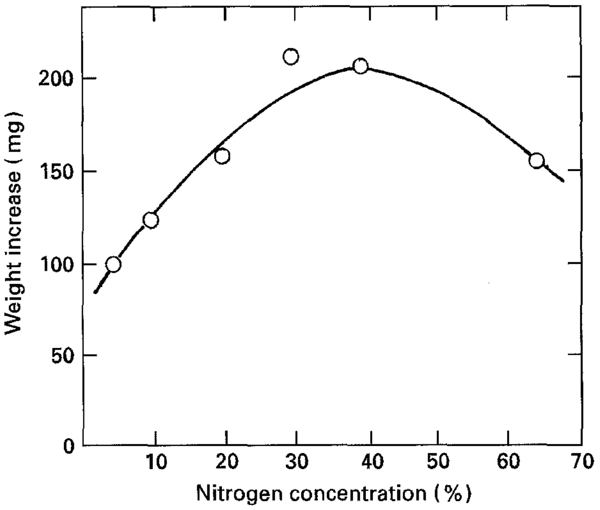

Figure 8 Dependence of deposition rate on nitrogen concentration. 850 °C, 10^4 pulses, thickness of preform 1.8 mm, holding time 1 s. $TiCl_4$ = 5%.

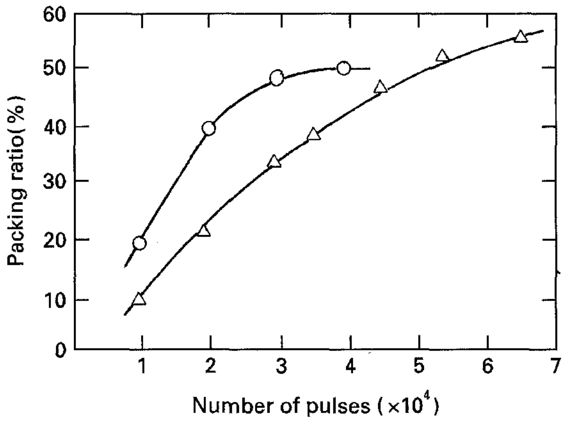

Figure 9 Relations between packing ratio and number of pulses under low nitrogen concentration. (○) 30%, (△) 5%.

sheets was infiltrated, resulting in poor packing, in particular into the inner sheet of 5 µm powder.

3.6. X-ray diffraction diagrams

Irrespective of deposition temperature, concentrations of $TiCl_4$ and N_2, and holding time, all diagrams obtained by surface diffraction had peaks of TiN at the same angles as those of JCPDS (ASTM) data, and also with similar intensity ratios to JCPDS data, although the peaks were somewhat diffuse in the case of low-temperature deposition.

3.7. Three-point flexural strength

Three-point flexural strength for as CVI samples without surface polishing was measured at room temperature, with a span of 10 mm. Fig. 11 shows the relation between flexural strength and number of pulses. The reproducibility was very poor. The best result was only 140 MPa. To improve the strength, a higher packing ratio has to be attained. However, another problem is the microcracks formed owing to the difference in the thermal expansion coefficients between TiN ($9.35 \times 10^{-6}\,^{\circ}C^{-1}$) and β-SiC

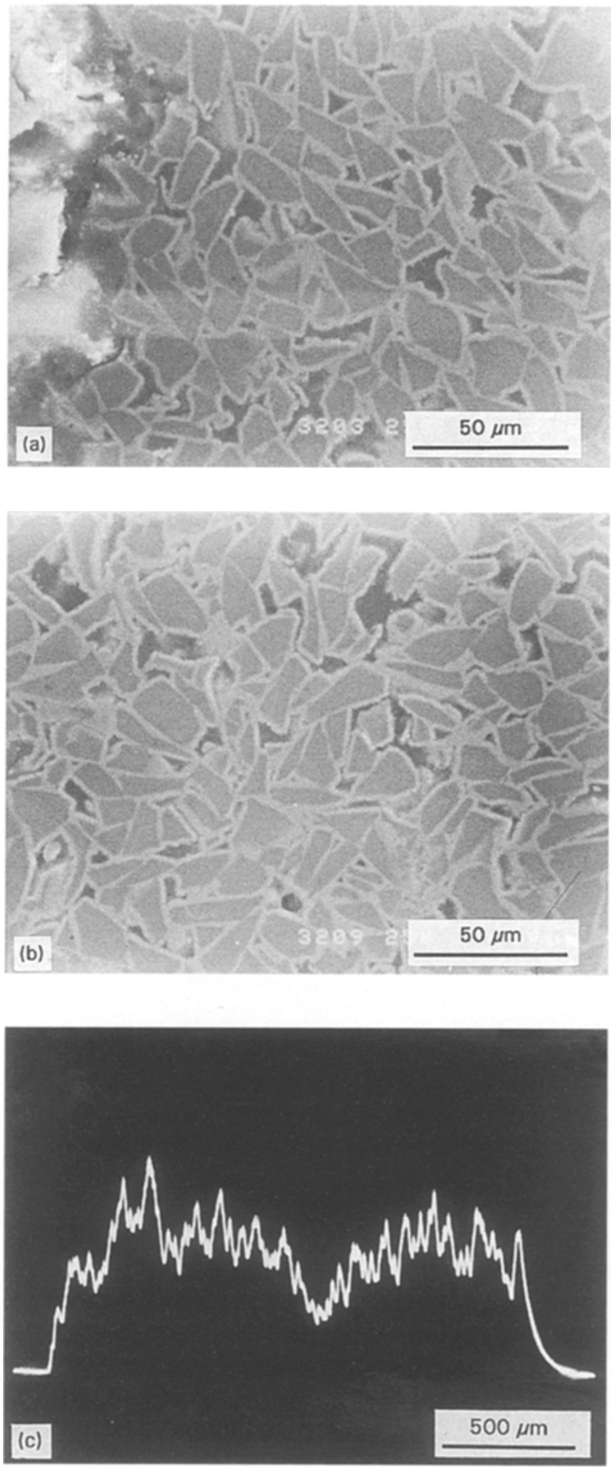

Figure 10 (a, b) Scanning electron micrographs and (c) EPMA-Ti line analysis of cross-section after 1.1×10^5 pulses. Particle size of SiC 20 μm, 800 °C, thickness of preform 1.8 mm, holding time 1 s, $TiCl_4 = 5\%$. (a) Near surface, (b) 800 μm deep, (c) full thickness.

($4.7 \times 10^{-6}\,°C^{-1}$) [13]. In many cases, fracture runs along the large pores which were apt to be formed at positions close to the irregular powder, such as thin but long. Therefore, the use of the more spherical powder of SiC may improve the strength.

4. Conclusion

In PCVI of TiN to SiC particulate preforms, a suitable deposition temperature was determined between 800 and 850 °C. Above 900 °C, deposition took place mainly on or near the surface. The use of a high concentration of $TiCl_4$ resulted in an increase of deposition rate and final packing ratio. Nitrogen concentration affected deposition rate. The maximum rate was obtained at 35%. A decrease of deposition rate with decreasing nitrogen concentration had a similar effect to lowering the temperature. At 800 °C, packing to deep levels proceeded without the formation of surface films up to 5×10^4 pulses, even with a long holding time of 2 s. The maximum three-point flexural strength was only 140 MPa, because of low final-packing ratio and microcracks formed owing to the difference in the thermal expansion coefficients of TiN and SiC.

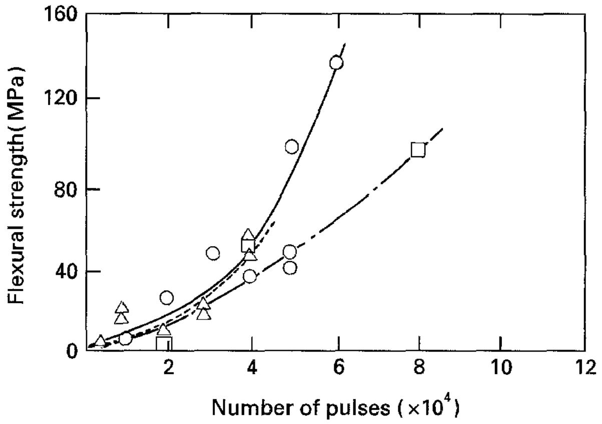

Figure 11 Relations between flexural strength and number of pulses. $TiCl_4 = 5\%$, holding time 1 s. SiC/temperature/thickness: (○) 5 μm, 850 °C, 0.9 mm; (△) 5 μm, 850 °C, 1.8 mm; (□) 20 μm, 800 °C, 1.8 mm.

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