

Pressure-pulsed chemical vapour infiltration of SiC to porous carbon from a gas system SiCl₄–CH₄–H₂

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SiC matrix was deposited into porous carbon from a gas system SiCl₄–CH₄–H₂ in the temperature range 900–1200 °C using pressure-pulsed chemical vapour infiltration (PCVI) process. At 1000 °C, silicon single phase, a mixed phase of (Si + SiC), and SiC single phase, were detected by X-ray diffractions for specimens obtained with the reaction time per pulse of ~ 1, 2–3, and ~ 5 s, respectively. At 1100 °C, SiC single phase was obtained with a reaction time of only 0.3 s. Between 1050 and 1075 °C, deposition rate accelerated suddenly. The increase of SiCl₄ concentration increased the deposition rate linearly up to 4%–6%. The residual porosity decreased from 29% to 6% after 2 × 10⁴ pulses of CVI at 1100 °C, and the flexural strength was 110 MPa.

1. Introduction

A chemical vapour infiltration (CVI) process has been developed for matrix packing to fibre preforms of composites. Among the CVI processes, isothermal and isobaric CVI (ICVI) has the characteristic of obtaining a near net-shaped product; however, this needs a very long operation time, such as 2–3 weeks [1–3]. Another process of forced CVI (FCVI) uses steep gradients of pressure and temperature along the preform thickness, and the operation time is shortened to 20–40 h by the forced gas flow, but the characteristic of obtaining a near net-shape product is lost [4–6]. One of the present authors investigated a pressure-pulsed CVI (PCVI) process, which consists in sequential steps of evacuation of a reaction vessel, instantaneous introduction of a source gas, and holding to allow deposition (holding time) [7–11]. This process characteristically yields a near net-shaped product with short operation time, such as 40 h for 10⁵ pulses of CVI. As a source gas for SiC deposition, a gas system of methyltrichlorosilane (MTS)–H₂ has been frequently used; however, this source is expensive compared with SiCl₄–CH₄–H₂, and also elemental silicon is apt to codeposit with SiC at low deposition temperature, e.g. below 1000 °C. Although the silicon codeposition can be suppressed by temperature elevation up to 1100 °C, and the strength of the SiC deposits is also improved [12–14], the deposition rate of SiC from the system MTS–H₂ is accelerated above 900 °C; therefore, films are easily formed on the macro-surface, which blocks the gas penetration path to the deep levels of the preforms. The deposition temperature of SiC from the system SiCl₄–CH₄–H₂ is above 1000 °C, which is higher by 150–200 °C than that from MTS–H₂; therefore, suppression of silicon codeposi-

tion and improvement of flexural strength are expected to be caused by elevation of the deposition temperature. The present paper describes the conditions needed to obtain single-phase SiC deposits, and the relation between flexural strength and the number of pulses.

2. Experimental procedure

The source gas mixture of SiCl₄–CH₄–H₂ was reserved in a 2 l reservoir, and then introduced instantaneously to a 50 cm³ reaction vessel (Fig. 1) up to 0.1 MPa, and held here for 0.3–10 s to allow SiC deposition (holding time), and subsequently evacuated to below 0.7 kPa. The normal holding times and evacuation times were 0.5 and 1 s, respectively; therefore, one pulse requires 1.5 s, and 10⁴ pulses are processed for about 4.2 h. A porous carbon plate CZR-1 (Poco Graphite Co.) of 20 × 10 × 1 mm³ was hung at the top of the reaction vessel. The porosity of CZR-1 was 29% with fully open pores, and the pore size distribution was from 0.2–0.5 μm. Packing ratio (%) is defined as

(packing ratio %)

$$= \frac{(\text{volume of SiC after PCVI})}{(\text{volume of initial pore})} \times 100 \quad (1)$$

The phases of silicon and SiC in the deposits were detected by XRD; however, the existence of carbon phase could not be detected definitely. Flexural strength was measured by the three-point method at room temperature.

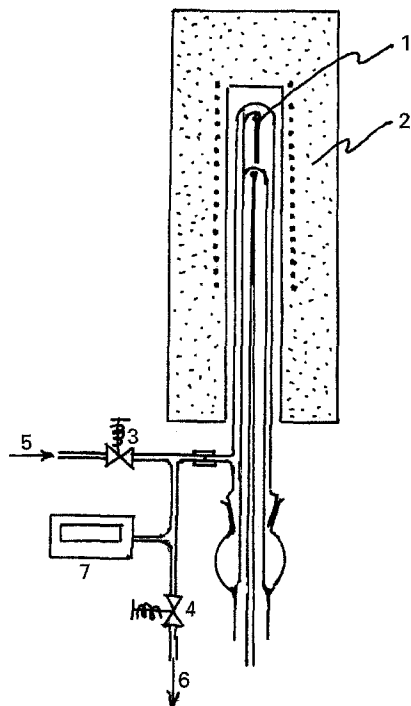


Figure 1 Reaction vessel. 1, preform; 2, furnace; 3, inlet valve; 4, outlet valve; 5, gas from reservoir; 6, to vacuum pump; 7, pressure gauge.

3. Results and discussion

3.1. Effects of temperature and holding time on weight increase and phase relation

Fig. 2 shows the relationship between weight increase after 3000 pulses and holding time with deposition temperature. Here, both concentrations of SiCl_4 and CH_4 were kept at 2%. Below 1050°C , weight increase begins above a holding time of 2 s, which is supposed to be the induction period for the formation of active precursors, such as SiH_2Cl_2 , SiHCl_3 , or SiCl_2 [15–17]. However, above 1075°C , no induction period could be seen for a holding time over 0.3 s. This fact may be caused by the acceleration of precursor formation. Above 1075°C , weight increase curves saturate above a certain holding time, i.e. above 5, 2, and 0.5 s for the temperatures of 1075, 1100, and 1200°C , respectively. The weight increase at the saturation zone decreases with increasing temperature. This result means that the higher the deposition temperature, the faster is the deposition rate on the inner wall of the vessel before reaching the gas to preform zone. An

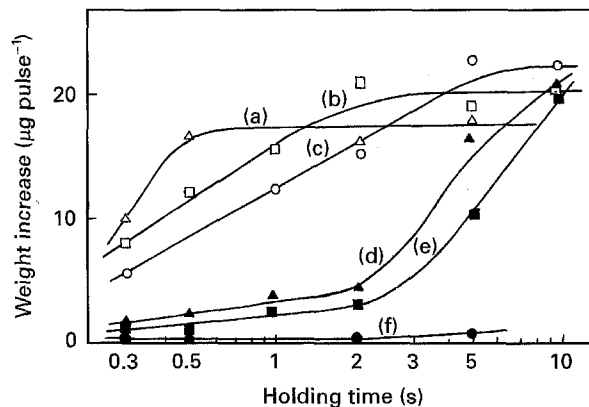


Figure 2 Relation between weight increase and holding time, for SiCl_4 2%, CH_4 2%. Temperature: (a) 1200°C , (b) 1100°C , (c) 1075°C , (d) 1050°C , (e) 1000°C , (f) 900°C .

interesting phase change of deposits occurs in the temperature range 1000 – 1100°C . Table I shows the phase relation with temperature and holding time. At 1000°C , single-phase silicon is deposited up to a holding time of 1 s, then (Si + SiC) mixed phase is deposited up to 3 s, and SiC single phase can be obtained above a holding time of 5 s. At 1050°C , (Si + SiC) mixed phase is deposited up to 2 s, and SiC single phase above 3 s. Above 1100°C , SiC single phase is deposited even if the holding time is as short as 0.3 s. In the PCVI process, the source gas at room temperature is instantaneously introduced into the vessel and also into the pores of preforms without sufficient preheating time; therefore, the near-surface zone of preforms is cooled at the moment of gas introduction, and this transient temperature change causes the onset of infiltration to deep levels of the preforms [7], and also elemental silicon deposition, which is apt to be formed at low temperature. In the case of long holding times at low temperature (1000°C), the temperature of the cooled specimen recovers to the normal temperature after several seconds; therefore, very small silicon nuclei, which were deposited early in the holding time, react with CH_4 directly or with adsorbed carbon atom to form SiC. In any case, it was found that the requisite conditions to obtain a single-phase SiC were not only deposition temperature but also holding time in the PCVI process. Fig. 3 shows scanning electron micrographs of ruptured sections of the samples infiltrated at various temperatures under the conditions as in Fig. 2, except for a fixed holding time of 2 s. Surface

TABLE I Effect of temperature and holding time on the crystal phase of deposits from XRD detection: SiCl_4 2%, CH_4 2%, after 3000 pulses, SiC; β -SiC

Temperature ($^\circ\text{C}$)	Holding time(s)						
	0.3	0.5	1	2	3	5	
900	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	
1000	Si	Si	Si	Si + SiC	Si + SiC	SiC	
1050	Si + SiC	Si + SiC	Si + SiC	Si + SiC	SiC	SiC	
1075	Si + SiC	SiC	SiC	–	–	–	
1100	SiC	SiC	–	–	–	–	
1200	SiC	SiC	–	–	–	–	

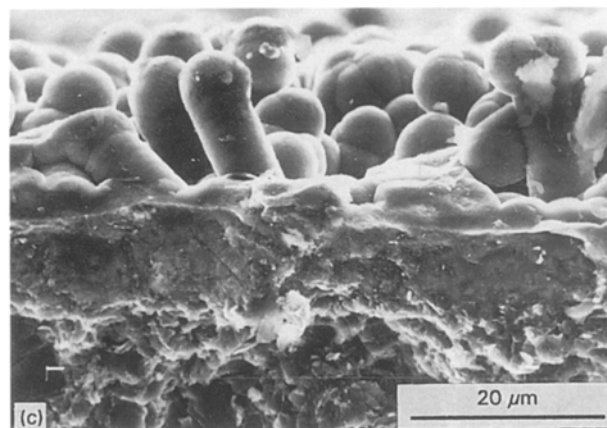
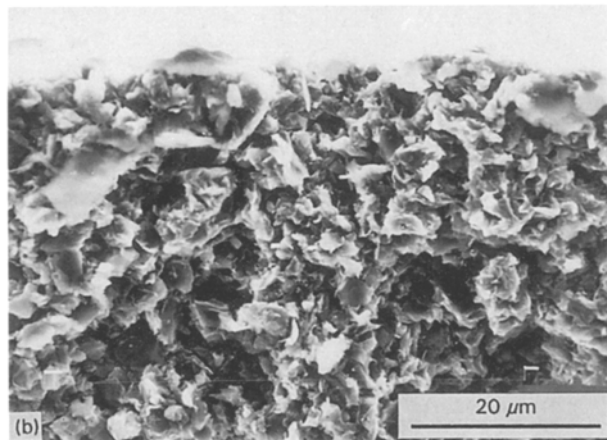
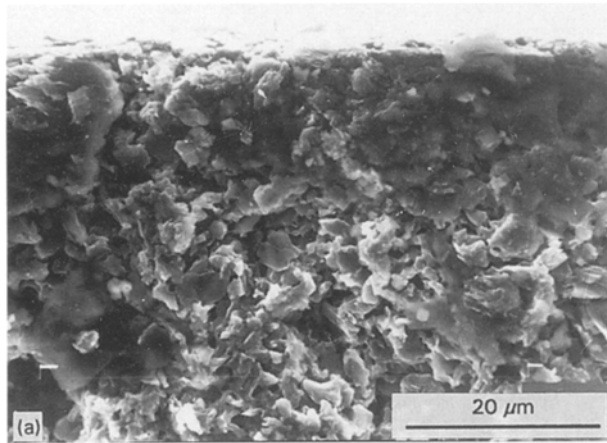


Figure 3 SEM images of ruptured sections, for SiCl₄ 2%, CH₄ 2%, holding time 2 s, after 3000 pulses. CVI temperature: (a) 1050 °C, (b) 1100 °C, (c) 1200 °C.

films cannot be seen on the cross-sections except for that obtained at 1200 °C, on the surface of which thick polycrystalline films have grown even after 3000 pulses.

TABLE II Effect of SiCl₄ and CH₄ concentrations on the crystal phase of deposits from XRD detection: CH₄/SiCl₄ molar ratio 1 or 2, holding time 2 s, after 3000 pulses, SiC, β-SiC

Temperature (°C)	CH ₄ /SiCl ₄ ratio	SiCl ₄ concentration (%)			
		2	4	6	8
1050	1	Si + SiC	Si + SiC	Si + SiC	SiC
	2	Si + SiC	Si + SiC	Si + SiC	SiC
1075	1	Si + SiC	SiC	SiC	SiC
	2	Si + SiC	SiC	SiC	SiC

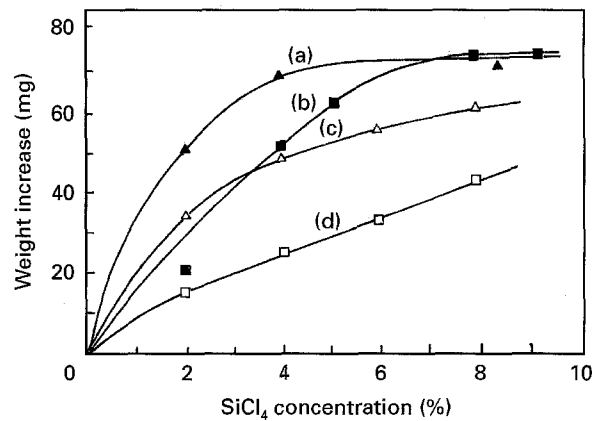


Figure 4 Effect of SiCl₄ concentration and CH₄/SiCl₄ ratio on deposition rate; holding time 2 s. CVI temperature: (a, b) 1075 °C, (c, d) 1050 °C. CH₄/SiCl₄ molar ratio: (a, c) 2, (b, d) 1.

3.2. Effect of concentrations of SiCl₄ and CH₄ on weight increase and phase relation

In the previous section, the concentrations of SiCl₄ and CH₄ were both kept at 2%. Here, the molar ratio of CH₄/SiCl₄ was changed to 1 or 2, and the SiCl₄ concentration was changed from 2% to 9.5%. At 1050 and 1075 °C, the relation between weight increase and SiCl₄ concentration was obtained as shown in Fig. 4. The weight increase for the CH₄/SiCl₄ ratio of 2 is larger than that for the ratio of 1. SiC single phase was obtained from gas mixtures in which the SiCl₄ concentration was above 8% at 1050 °C and above 4% at 1075 °C, irrespective of whether the CH₄/SiCl₄ ratio was 1 or 2 (Table II). Another experiment showed that the pyrolysis of CH₄ was accelerated by the addition of an inert gas, such as argon or nitrogen; therefore, single-phase SiC deposition at high concentrations of SiCl₄ and CH₄ may be caused by a fall in the concentration of hydrogen, i.e. by acceleration of CH₄ pyrolysis. When the SiCl₄ concentration was fixed at 4% and the CH₄/SiCl₄ ratio was varied from 1–5, single-phase SiC was detected at the ratio of 3, and a weakening of the SiC peak in the XRD patterns by carbon deposits was observed at a ratio of 5 (Table III).

3.3. Effect of the number of pulses on packing ratio and flexural strength

The relation between number of pulses and packing ratio is shown in Fig. 5, where holding time, and the concentrations of SiCl₄ and CH₄ were kept at 2 s, 4% and 4%, respectively. At 1150 °C, the packing ratio curve decreased in gradient above 5 × 10³ pulses,

TABLE III Effect of $\text{CH}_4/\text{SiCl}_4$ molar ratio on the crystal phase of deposits from XRD detection: 1050 °C, SiCl_4 4%, holding time 2 s, after 3000 pulses, SiC, β -SiC

	$\text{CH}_4/\text{SiCl}_4$ molar ratio			
	1	2	3	5
Phases of deposits	Si + SiC	Si + SiC	SiC	C + SiC

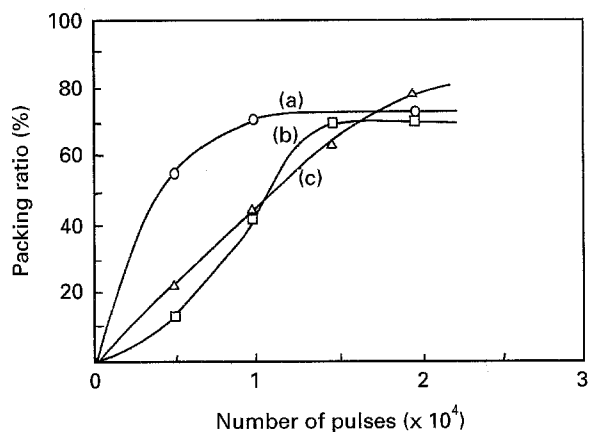


Figure 5 Relation between packing ratio and number of pulses, for SiCl_4 4%, CH_4 4%, holding time 2 s. CVI temperature: (a) 1150 °C, (b) 1075 °C, (c) 1100 °C.

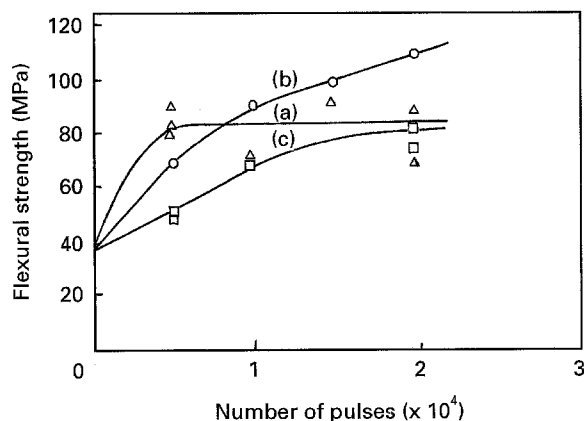


Figure 6 Relation between flexural strength and number of pulses, for SiCl_4 4%, CH_4 4%, holding time 2 s. CVI temperature: (a) 1150 °C, (b) 1100 °C, (c) 1075 °C.

and saturated above 10^4 pulses at the packing ratio of 70%; however, at 1100 °C the curve increased even after 2×10^4 pulses and reached the ratio of 78%, which is equivalent to the residual porosity of 6.4% ($0.29 \times (100 - 78)$). These results on packing ratios reflect the three-point flexural strength, as shown in Fig. 6. The flexural strengths of specimens obtained at 1150, 1100 and 1075 °C reach 80, 110 and 80 MPa after 2×10^4 pulses. In the case of PCVI of SiC particulate [7] or Tyranno fibre (Si-Ti-C-O) [18] preforms, the flexural strength exceeded 220 MPa; however, the porous carbon skeleton in the present experiment was weak, with a strength of 37 MPa, and the carbon volume was about 71%;

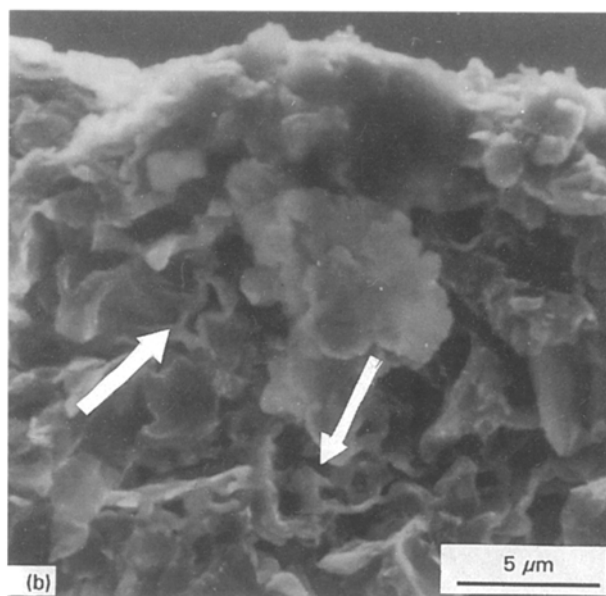
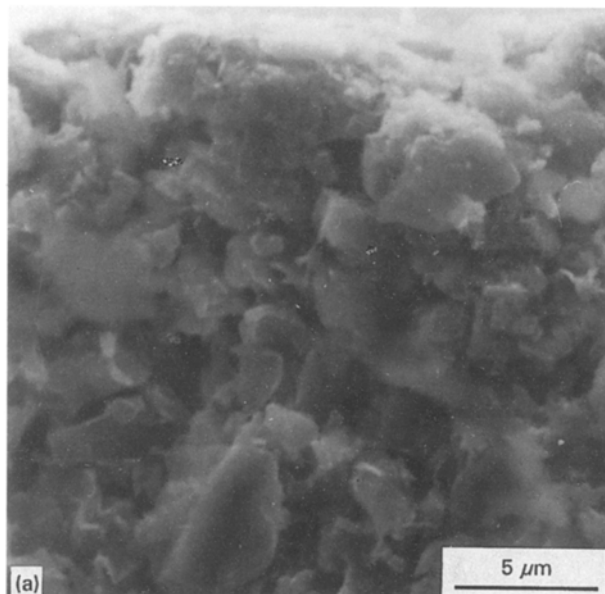


Figure 7 SEM images of ruptured sections, after 10000 pulses, SiCl_4 4%, CH_4 4%, holding time 2 s. CVI temperature: (a) 1075 °C, (b) 1100 °C. Arrows indicate extruds of SiC from the pores.

therefore, rupture takes place mainly at the porous carbon skeleton.

Fig. 7 shows the ruptured sections after 10^4 pulses of CVI at 1075 and 1100 °C. At 1075 °C, packing of the matrix is low; therefore, the appearance is similar to that of the original porous carbon. On the other hand, the specimen obtained at 1100 °C shows a narrowing of pores and SiC extrudes from each pore.

4. Conclusion

In pressure-pulsed chemical vapour infiltration (PCVI) of SiC into porous carbon, the system $\text{SiCl}_4\text{-CH}_4\text{-H}_2$ was investigated with the objectives of obtaining single-phase SiC deposits from a less-expensive source gas and at higher deposition temperature than that of the methyltrichlorosilane system (MTS)- H_2 . The deposition rate suddenly accelerated between 1050 and 1075 °C. Below 1050 °C, there was induction period of

more than 2 s; however, the period disappeared above 1075 °C. Another finding was the change of phase constitution with holding time; i.e. at 1000 °C the phases of the deposits changed from silicon, to (Si + SiC), and to SiC with holding times of ~ 1, 2–3, and ~ 5 s. Similarly, at 1050 °C, phases also changed from (Si + SiC) to SiC with holding times of ~ 2, and ~ 3 s, respectively. Above 1100 °C, single-phase SiC was deposited above a holding time of 0.3 s. These results suggest the deposition process to be silicon deposition, followed by reaction with carbon to form SiC. However, the fact that the increase in molar ratio, CH₄/SiCl₄ of the source gas from 1 to 2 increased the SiC deposition rate, shows that carbon also has a secondary effect on SiC deposition. After 2 × 10⁴ pulses of CVI into porous carbon at 1100 °C, residual porosity decreased to about 6.4%, and the flexural strength reached 110 MPa, about three times that of the original porous carbon.

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