JOURNAL OF MATERIALS SCIENCE **24** (1989) 3756–3762

Reinforcement and antioxidizing of porous carbon by pulse CVI of SiC

KOHZO SUGIYAMA, EIJI YAMAMOTO
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

In order to reinforce and antioxidize porous carbon, chemical vapour infiltration (CVI) of SiC was investigated using a repetitive cycle of evacuation of vessel and instantaneous source-gas filling. From a source gas of 5% CH_3SiCl_3–H_2, a temperature range of 1273 to 1373 K was considered to be suitable to infiltrate SiC into a deep level, and surface deposition was enhanced at above 1373 K which led to pore blockage. With 3000 pulses, flexural strength was improved from 35 to about 90 MPa. Several specimens were exposed to air at 1573 K for 1070 h during which the specimens were cooled to room temperature between four and seven times. SiC felt was also obtained by oxidation of a carbon skelton after pulse CVI.

1. Introduction

The CVI (chemical vapour infiltration) process for fibre-reinforced composites such as carbon fibre–pyrolytic carbon matrix (C/C) [1–3], C/SiC [4–9], C/TiC [7, 10], C/TiB_2 or BCx [11], C/BN [7, 12], C/B_4C [13], SiC/SiC [4, 6, 14, 15], BN/BN [16], SiC/BN or Si_3N_4 [14] has been investigated during the last 15 years. Adhesion of matrix to fibre is excellent, however, there are two weak points in the CVI process; the long operation time of up to 500 h, and the residual porosity of up to 10 to 20%. Another CVI process has been reported [17, 18] which aimed to consolidate particles or densify porous materials, however, it also has the same disadvantages. In most CVD (Chemical Vapour Deposition) reactions, the volume of the product is larger than that of the reactant, therefore, fresh reactant gas has to permeate to a deep level against the outflowing stream of the product gas. This is one of the causes of the long operation time and relatively high residual porosity. Byrant [19] has proposed an unique process of "pulse CVD" in which pressure pulse is composed of evacuation of chamber, instantaneous charge of source gas, holding (reaction), and evacuation. The instantaneous charge of gas diminishes the non-uniformity of the gas composition along the length of reaction chamber, and leads to uniform structure, composition, and thickness. Pulse CVD has been rarely used in the CVD process, because of the complexity of the apparatus and of low deposition rate. However, if pulse CVD is applied to CVI process, that is to say "pulse CVI", the process may be markedly shortened, because the product gas in fine pore is removed in evacuation step. Such a pulse CVI method may be applied well to the later period of infiltration to fibre preform or of consolidation of particles and also to the full period of impregnation to porous materials. One of the authors of the present paper reported on the pulse CVI of TiN to porous carbon [20] as a model of pulse CVI. In the present paper, the conditions of pulse CVI of SiC to porous carbon were studied for the preparation of oxidation resistant or reinforced materials.

2. Experimental details

The apparatus for pulse CVI is shown in Fig. 1. The total volume of pipe, dead space and reaction zone was suppressed to be as small as 40 cm^3 for the objectives of high gas yield and short evacuation time. One to five substrates ($15 \times 10 \times 0.7\,mm^3$) were hung at the bottom of the tube which was sealed at one end. Purified hydrogen was bubbled through CH_3SiCl_3 (Tokyo Kasei > 98%), then, accumulated in a reservoir, from which the gas was fed to the reaction tube instantaneously through the electromagnetic valve. It took 0.05 sec to fill up the tube to 22.4 or 92.1 KPa. Then, the inlet electromagnetic valve was closed and the gas was held for a given time (hold-time; t_h) to allow SiC deposition. Thereafter, the outlet electromagnetic valve was opened to the vacuum system. It took 0.3 sec to evacuate from 92.1 to 3.9 KPa by a first pumping system, and then it took 0.7 sec from 3.9 to below 0.2 KPa by a second large pumping system. The deposition rate for apparent unit surface area was simply calculated from the weight increase assuming the concentration of the deposition. Three kinds of carbon were used as a substrate, whose specified

TABLE I Specific properties of carbon substrates

Substrates	Gross density ($g\,cm^{-3}$)	Specific resistivity ($\mu\Omega\,cm$)	Flexural strength ($kg\,cm^{-2}$)	Porosity (%)	Thermal expansion coefficent ($10^{-6}\,°C$)
CZR-1 Poco Co	1.62	1970	410	29	–
Specimen A Toyo Carbon	1.82	1225	445	16	4.26
Specimen B Toyo Carbon	0.42	37300	87	65	2.9

0022–2461/89 $03.00 + .12 © *1989 Chapman and Hall Ltd.*

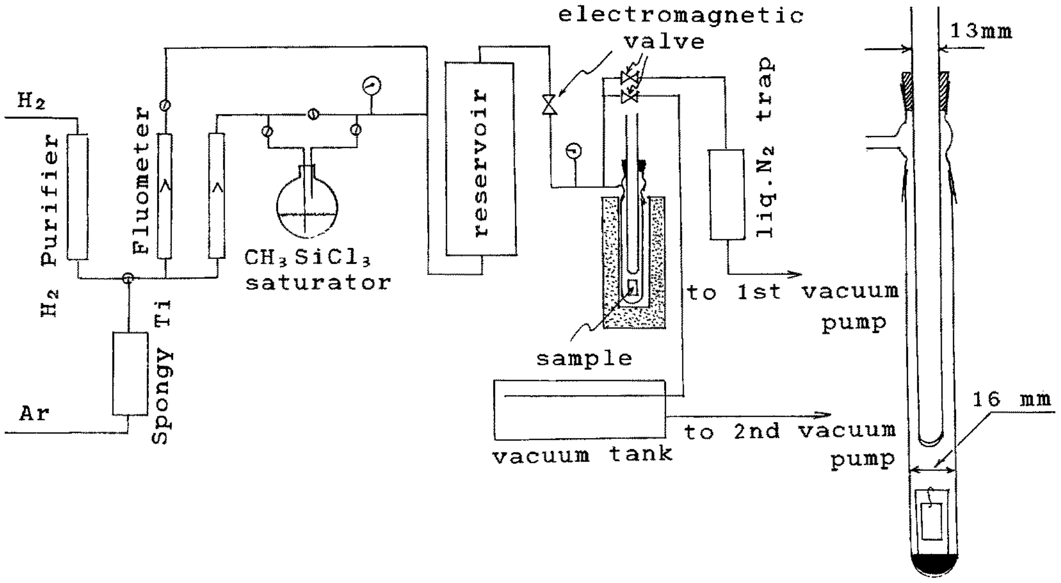

Figure 1 Apparatus for pulse CVI of SiC.

properties and the porosity distributions are shown in Table I and Fig. 2, respectively. CZR-1 was used mainly, which is characteristic in two points; narrow pore size distribution from 0.2 to 0.5 μm, and, 29% porosity with full open pore. Carbon A is dense but has similar thermal expansion coefficient to SiC. Carbon B has a very high porosity of 65%. Hitachi S-510 and Horiba EMAX-7050 were used for SEM observations and EPMA analysis, respectively.

3. Results and discussion

3.1. Relations between weight increase and hold-time

Fig. 3 shows the relationship between weight increase per pulse and hold time. Under 22.4 KPa and at 1673 K, the reaction had finished within half a second, however, at 1448 K, deposition proceeds with a hold time of up to 3 or 4 sec. Under 92.1 KPa, deposition rate increased about four times compared to that under 22.4 KPa, and at temperatures as low as 1373 K, it took more than 10 sec to finish the reaction. Fig. 4 shows the cross-sections at the half thickness of the substrate, that is 350 μm deep, and silicon-images of EPMA at the same area. From Fig. 4d, which was infiltrated at 1573 K, the silicon-image is not detectable, therefore, it is considered that SiC deposition rate is so high at this temperature that surface films are mainly formed, which block the inlet of the pores. On the contrary, a silicon-image can be clearly seen in Fig. 4c which was infiltrated at 1373 K. These results show that slow deposition is necessary for CVI to a deep level.

3.2. The effect of the concentration of CH_3SiCl_3

Fig. 5 shows the relation between the filling ratio and the concentration of CH_3SiCl_3 at 1173, 1273, 1373 and

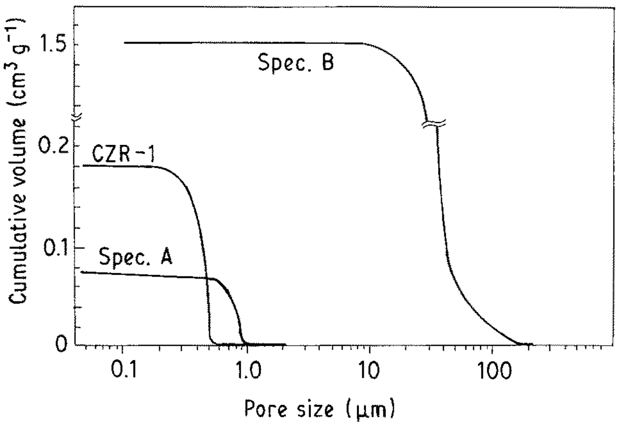

Figure 2 Pore distribution of three kinds of carbon.

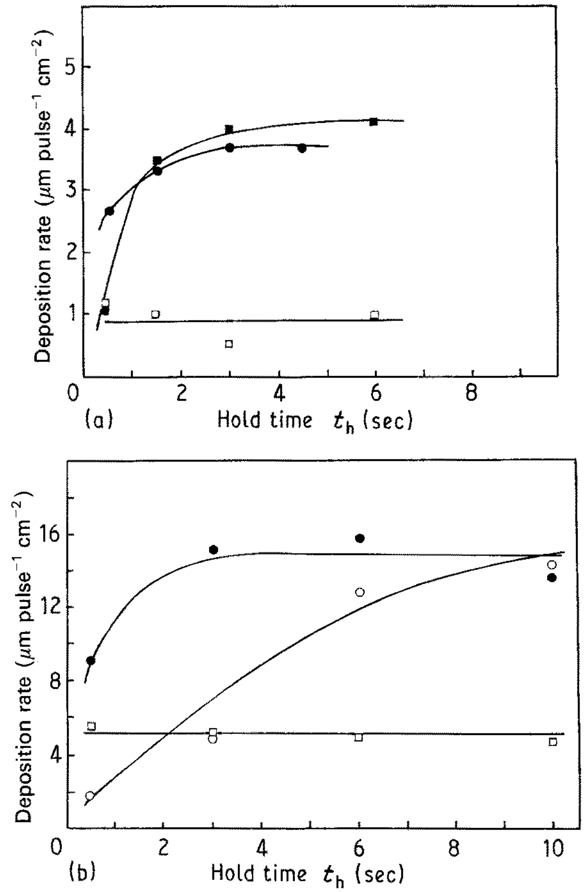

Figure 3 Relations between hold-time and weight increase Substrate CZR-1, 5% CH_3SiCl_3-95% H_2, 1000 pulse (a) 22.4 KPa, (b) 92.1 KPa, (■ 1448 K, ● 1573 K, □ 1673 K, ○ 1373 K).

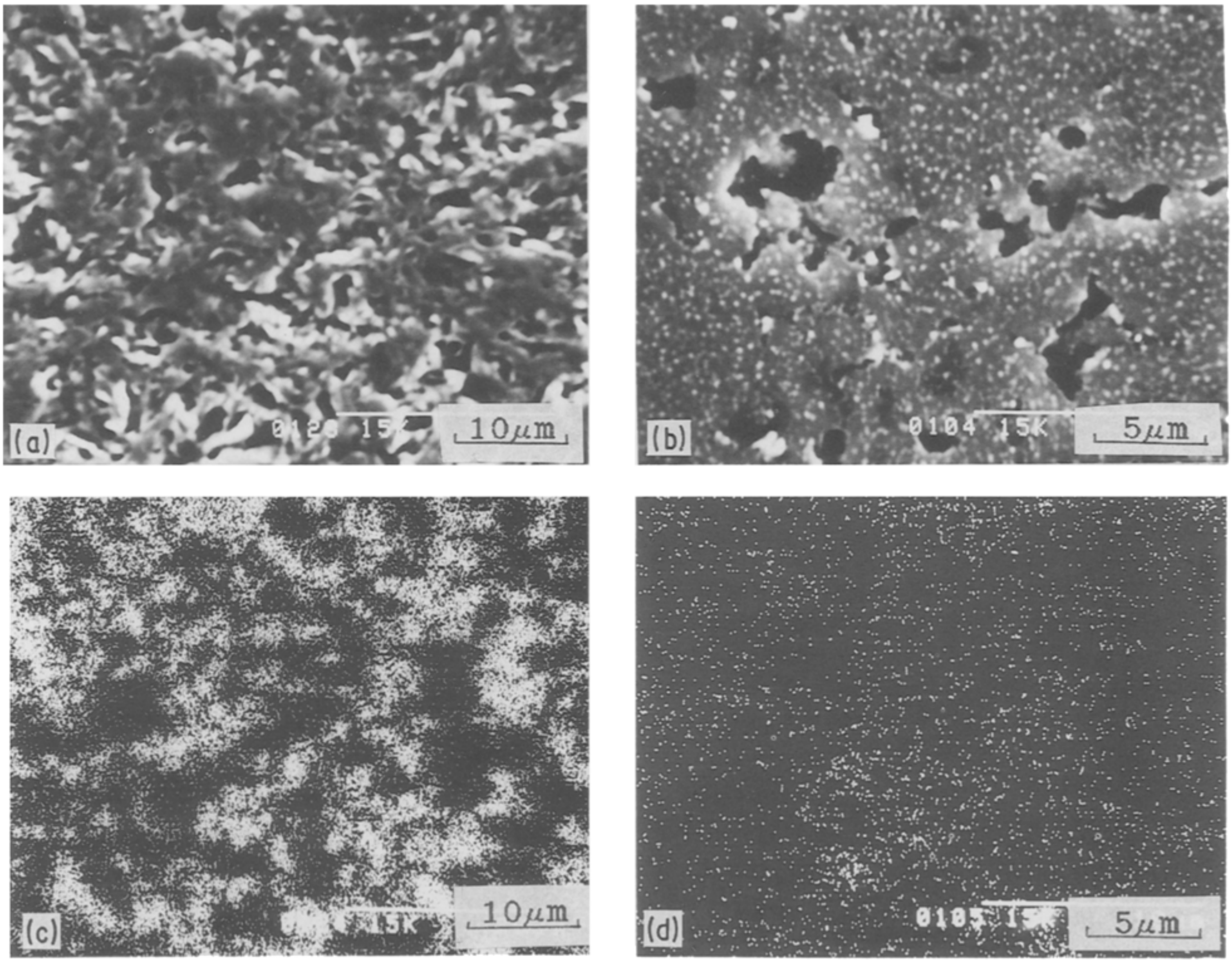

Figure 4 (a, b) SEM and (c, d) EPMA Si images of cross-sections at a depth of 350 μm from surface. Substrate CZR-1, 5% CH_3SiCl_3, 1000 pulse, hold time 0.5 sec, 92.1 KPa. Pulse CVI temperature; (a, c) 1373 K (ΔW 6.0 mg), (b, d) 1573 K (ΔW 14.9 mg).

1573 K. The filling ratio (f) was estimated by

$$f = \frac{V_f}{V_p} = \frac{(\Delta W/3.12 - hA)}{V_p}$$

in which V_p and V_f refer the initial pore volume and filled volume, respectively, and ΔW, h and A refer to the total weight increase, thickness of the surface layer and apparent surface area of specimen, respectively. The density of SiC was assumed to be 3.12 g cm^{-3}. At 1173 K, the filling ratio increased linearly with the increase of CH_3SiCl_3 concentration. On the contrary, the filling ratios saturate at 9% and 3% at temperatures of 1273 and 1373 K, respectively. After 3000 pulses of CVI, the filling ratios attained 50% at 1273 and 1373 K, however, the ratio remained below 30% at 1573 K.

3.3. Surface morphology of deposits

The surface morphology is shown in Fig. 6. At 1673 K, pyramidal cones were found (Fig. 6a), and at 1573 K fine grains developed on primary grains, and the surface film stopped the pores with below 1000 pulses

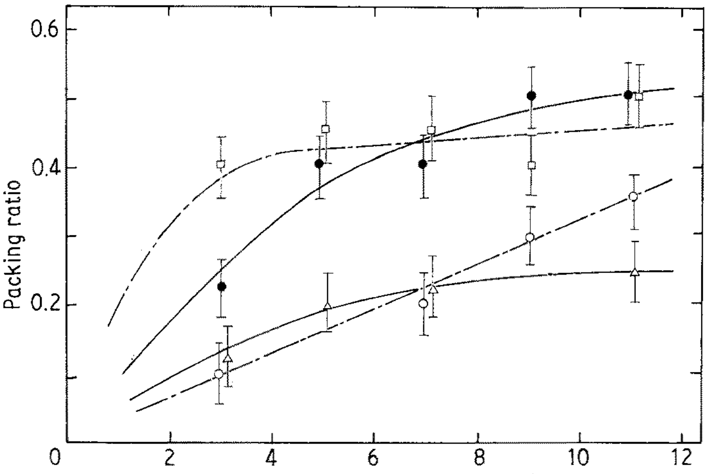

Figure 5 Affect of CH_3SiCl_3 concentration on packing ratio. Substrate CZR-1, hold-time 2 sec, 3000 pulse, 92.1 KPa (● 1273 K, □ 1373 K, ○ 1173 K, △ 1573 K).

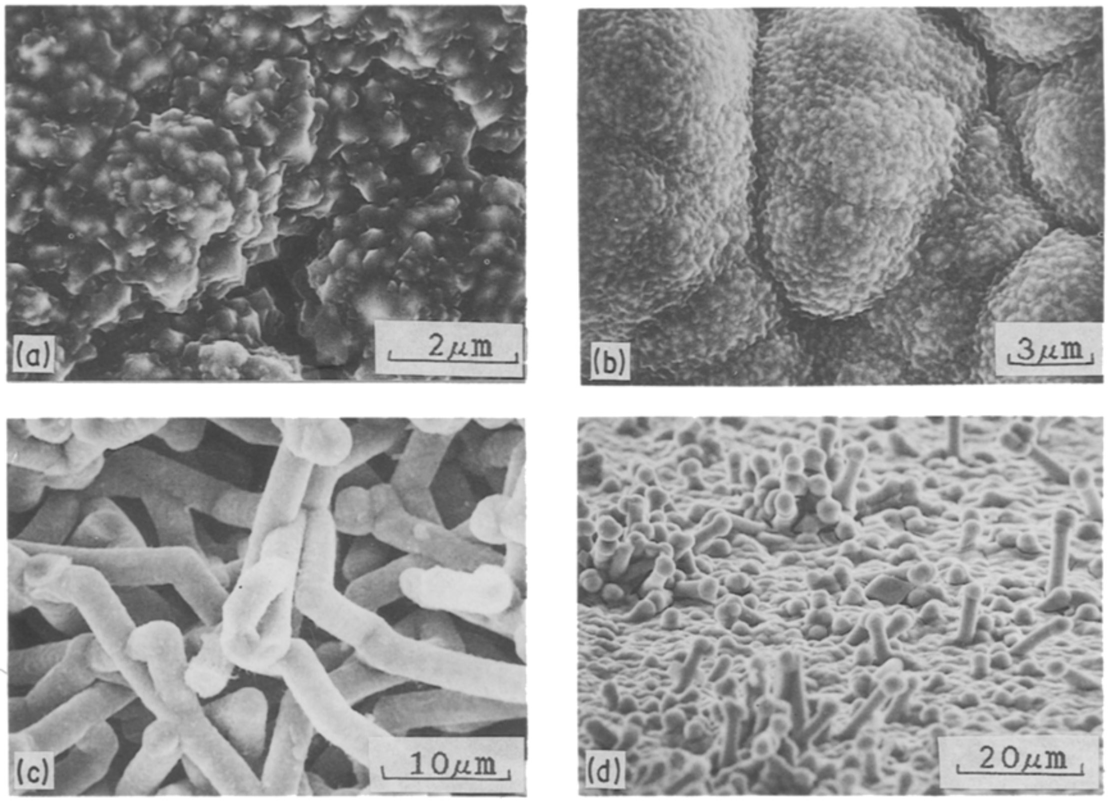

Figure 6 Morphology of surface deposits. Substrate CZR-1, 5% CH_3SiCl_3, (a, b, d) pulse CVI, (c) flow CVD. (a) 1673 K, hold time 3 sec, 92.1 KPa, 1000 pulse, ΔW 17.7 mg, (b) 1573 K, hold time 10 sec, 92.1 KPa, 1000 pulse, ΔW 45.6 mg, (c) 1573 K, 92.1 KPa, 1 h, ΔW 59.5 mg, (d) 1448 K, hold time 10 sec, 92.1 KPa, 1000 pulse, ΔW 37.4 mg.

(Fig. 6b). Under a conventional flow CVD at 1300° C, nodules were apt to grow, as can be seen in Fig. 6c. In pulse CVI, nucleation is enhanced by highly supersaturated gas arrival in each pulse, thus, nodules are markedly suppressed.

3.4. Uniformity of deposits among the five substrates

The most striking advantage of pulse CVD is uniform deposition irrespective of substrate position. When five substrates were hung with a clearance of 1 mm, the weight increase per pulse at various temperatures is shown in Fig. 7, in which the position numbers 1 and 5 refer to the nearest positions to the inner wall of the vessel, and the number 3 refers to that of the central one. Slight non-uniformity of the weight increase among the substrates can be seen. At high temperatures, fast deposition to the inner wall of vessel decreases the source gas concentration more near the wall than at the central position, thus leading to convex distribution. On the contrary, the temperature distribution is the dominant factor to deposition at low temperature, therefore, the substrates near the wall of the vessel exhibit higher weight increase than those at the central position, which leads to concave distribution as shown in Fig. 7.

3.5. The relations between pulse CVI conditions and three point flexural strength

Fig. 8 shows the relations between three-point flexural strength at room temperature and the number of pulses. At 1573 K, surface deposition became dominant above 1000 pulses but the increase of the

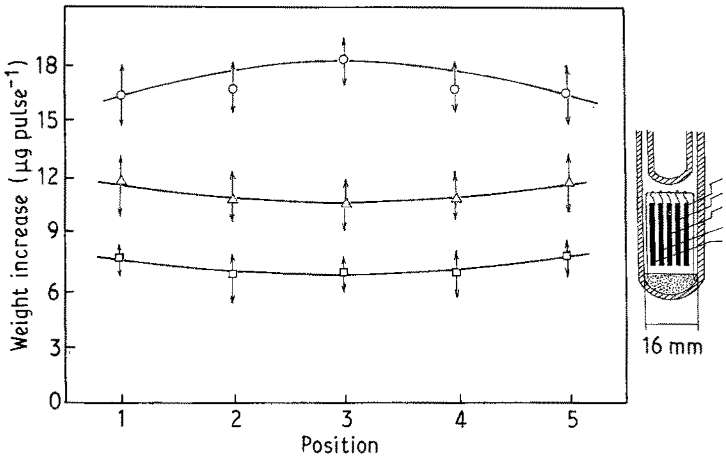

Figure 7 Distribution of weight increase among five substrates. Substrate CZR-1, hold time 2 sec, 5% CH_3SiCl_3, 92.1 KPa, 1000 pulses. (○ 1573 K, △ 1273 K, □ 1173 K).

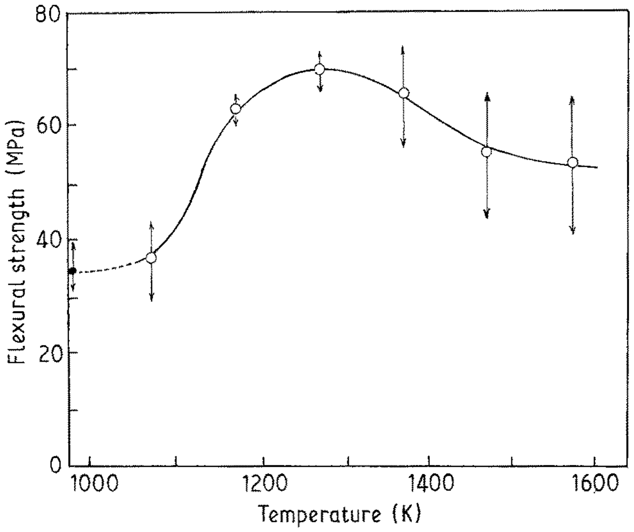

Figure 8 Relation between pulse CVI temperature and flexural strength. Substrate CZR-1, 5% CH_3SiCl_3, hold time 2 sec, 92.1 KPa, 3000 pulse.

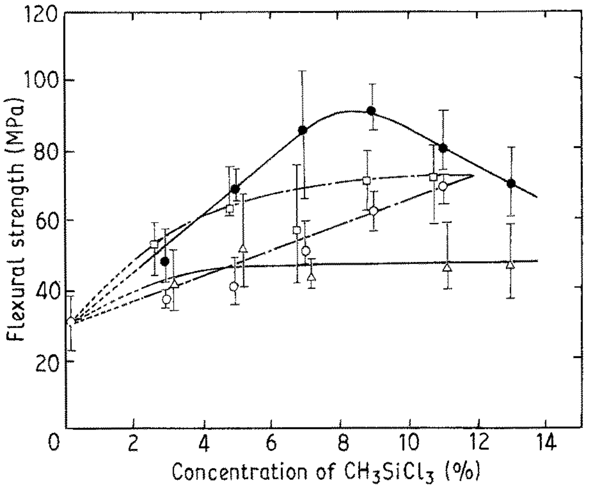

Figure 9 Affect of CH_3SiCl_3 concentration on flexural strength. Substrate CZR-1, hold time 2 sec, 92.1 KPa, 3000 pulse. (● 1273 K, □ 1373 K, ○ 1173 K, △ 1573 K).

thickness of the surface film did not increase the strength effectively, thus the strength saturated above 2000 pulses. On the contrary, at low temperature as 1173 K, flexural strength increased with pulses but only with slow rate. Therefore, there is an optimum temperature as 1273 K as can be seen in Fig. 8.

Fig. 9 shows the affect of CH_3SiCl_3 concentration on the flexural strength. The highest strength of 90 MPa was measured on the specimen filled from 7 to 9% CH_3SiCl_3 at 1273 K. The strength corresponds to about 2.5 times comparing with that of original carbon.

3.6. Oxidation resistivity

After pulse CVI, the atmosphere was changed to continuous argon flow, and furnace was slowly cooled to room temperature. Then the SiC-infiltrated substrates were weighed and reheated in an air flow, however, all substrates were oxidized at below 1273 K, probably caused by fine cracks formed during cooling process. Fig. 10 shows the ruptured cross-sections after oxidation. It can be clearly seen that SiC had been infiltrated over the whole thickness. Such a method of preparation of SiC-felt was not intended, but is interesting because of easy preparation.

In order to improve the oxidation resistivity, the atmosphere of pulse CVI was changed from reactant gas to continuous air flow just after the pulse CVI, and the substrate surface was oxidized for 24 h at the same temperature, and thereafter cooled to room temperature. The preoxidized substrates exhibited considerably high oxidation resistivity to air oxidation when reheated at 1573 K. It is supposed that the silica film seals the cracks formed during the cooling process. Samples were cooled, weighed and reheated to 1573 K several times. In Fig. 11, open circles show the cooling

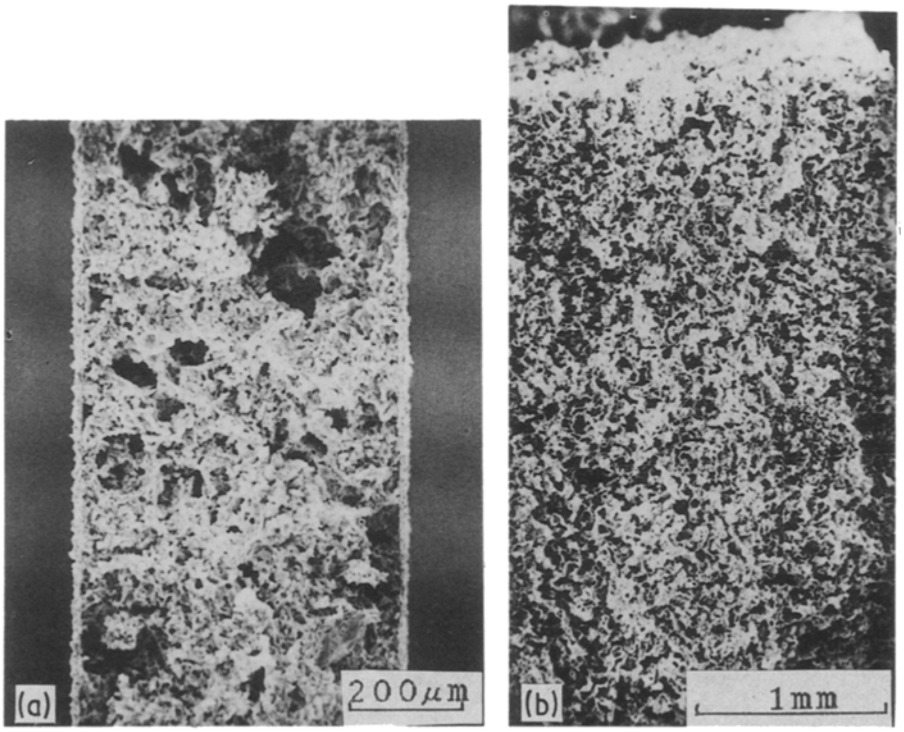

Figure 10 Cross-sections after air-oxidation. (a) CZR-1, CVI conditions; 1473 K, 5% CH_3SiCl_3, hold time 2 sec, 92.1 KPa, 1500 pulse, ΔW 38 mg, (b) Spec. **B** carbon, CVI conditions; 1448 K, 5% CH_3SiCl_3, hold time 1.5 sec, 92.1 KPa, 1000 pulse, ΔW 62 mg.

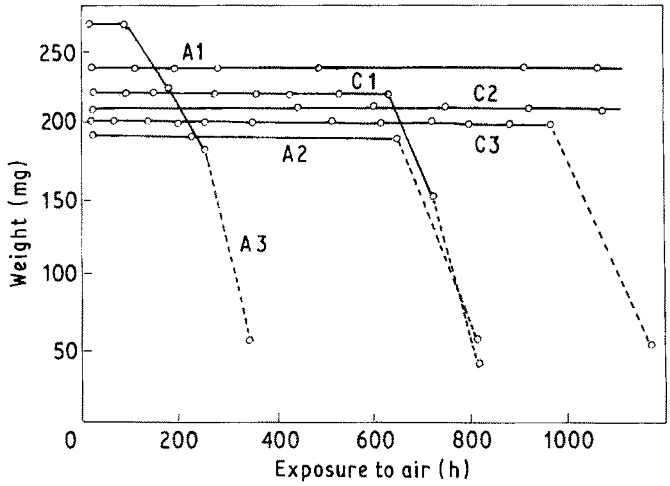

Figure 11 Air oxidation test at 1573 K. A; Spec. A carbon, C; CZR-1. Notation; First step/second step. Numerals are written in the order of; temperature (K) hold time (sec), number of pulse. A1; 1523, 1, 1000/1573, 1, 500, A2; 1448, 1, 1000/1573, 1, 500, A3; 1573, 1, 1500/none, C1; 1448, 1, 1000/none, C2; 1523, 1, 2000/none, C3; 1448, 1, 1000/1573, 1, 500.

points. Among a number of samples, a few samples resisted over 1000 h. Oxidation resistance at 1573 K is severe condition at this point, but this figure shows the possibility of obtaining the materials in any way.

The surface and the cross-section after air oxidation test for 1070 h are shown in Figs 12a and 12b, respectively. Fine cracks can be seen on the surface, probably formed during the heating–cooling cycles. From the ruptured cross-section, two silica layers can be seen, among which underside one has regrown after the upper layer had peeled off. This sample was cooled six times during the oxidation test, therefore, it is supposed that a silica layer resists two or three cooling cycles and carbon oxidation initiates when the front of the cracks reaches the SiC–carbon interface.

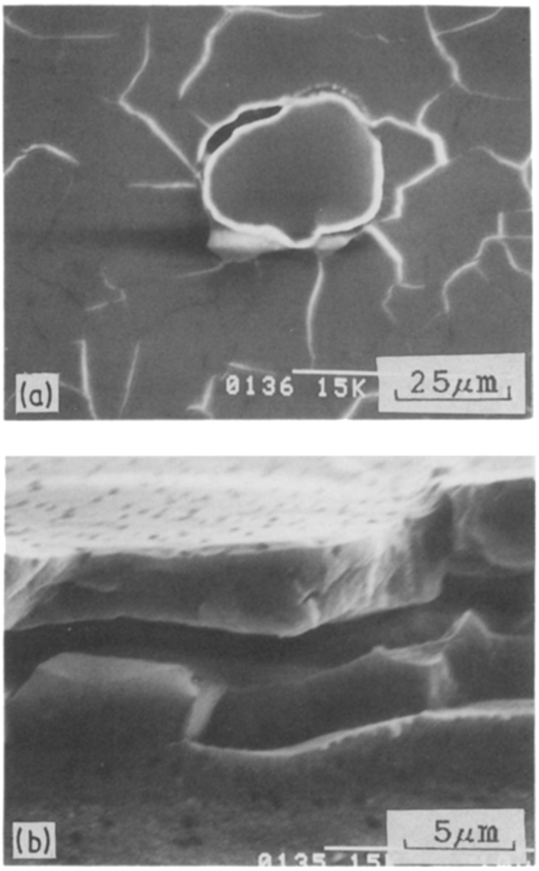

Figure 12 Appearance of (a) surface and (b) cross-section after oxidation test at 1573 K for 1070 h. Sample; C2 in Fig. 11.

4. Conclusions

Pulse CVI of SiC to porous carbon was examined, and the following conclusions were obtained;

(1) Operation time per pulse was shortened to 1.5 to 3 sec by using dual evacuation system.

(2) Optimum temperature of SiC infiltration to deep level was about 1273 K.

(3) Air-oxidation just after the pulse CVI at the same temperature improved the oxidation resistivity at 1573 K in an air flow.

(4) Removing of carbon skelton after pulse CVI by air oxidation left an SiC felt.

(5) The flexural strength increased about 2.5 times by 3000 pulses of SiC CVI at 1273 K.

References

1. B. DACIC and S. MARINKOVIC, *High Temperatures-High Pressures* **13** (1981) 185.
2. J. D. THEIS, Jr, Proceedings 3rd International Conference CVD, (Amer. Nuclear Soc., 1972) 561.
3. H. O. PIERSON and J. F. SMATANA, Proceedings 2nd International Conference CVD, (The Electro-chem Soc., NJ, 1970) 487.
4. H. TAWIL, LARRY D. BENTSEEN, S. BASKARAN and D. P. H. HASSELMAN, *J. Mater. Sci.* **20** (1985) 3201.
5. J. W. WARREN, *Ceram. Eng. Sci. Proc.* **6** (1985) 684.
6. L. H. HERAUD, F. CHRISTIN, R. NASLAIN and P. HAGENMULLER, Proceedings 8th International Conference CVD, (The Electro-chem Soc., NJ, 1981) 782.
7. R. NASLAIN, J. M. QUENISSET, J. Y. ROSSIGNOL, H. HANNACHE, P. LAMIEQ, J. J. CHAURY, L. HERAUD and F. CHRISTIN, 5th International Conference on Composite Materials, (The Electro-chem Soc., NJ, 1985) 499.
8. J. C. WITHERS, Proceedings 2nd International Conference CVD, (The Electro-chem Soc., NJ, 1972) 507.
9. W. V. KOTLENSKY, D. H. LEEDS, K. R. CARNAHAN, R. W. KIGER, P. R. DOMPSEY and P. PARTIN, Proceedings 2nd International Conference CVD, (The Electro-chem Soc., NJ, 1972) 574.
10. J. Y. ROSSIGNOL, F. LANGLAIS, R. NASLAIN, Proceedings 9th International Conference CVD, (The Electro-chem Soc., NJ, 1984) 596.
11. L. R. NEWKIRK, R. E. RILEY, H. SEINBERG, F. A. VALENCIA, T. C. WALLACE, Proceedings 7th International Conference CVD, (The Electro-chem Soc., NJ, 1977) 515.
12. H. HANNACHE, J. M. QUENISSET, R. NASLAIN and H. HERAUD, *J. Mater. Sci.* **19** (1984) 202.
13. H. HANNACHE, F. LANGLAIS and R. NASLAIN, Proceedings 5th European Conference CVD, edited by

J.-O. Carlson and J. Lindström (Uppsata Univ., Uppsala, 1985) 219.

14. A. J. CAPUTO, W. J. LACKEY and D. P. STINTON, *Ceram. Eng. Sci. Proc.* **6** (1985) 694.
15. H. H. MOELLER, W. G. LONG, A. J. CAPUTO and R. A. LOWDEN, *Sample Quarterly,* **4** (1986) 1.
16. J. J. GEBHARDT, Proceedings 4th International Conference CVD, (1973) 460.
17. W. H. PFEIFER, W. J. WILSON, N. M. GRIESENAUER, M. F. BROWNING and J. M. BLOCHER Jr, Proceedings 2nd International Conference CVD, (The Electro-chem Soc., NJ, 1970) 463.
18. E. FITZER, D. HEGEN, H. STROHMEIER, Proceedings 7th International Conference CVD, (The Electro-chem Soc., NJ, 1977) 525.
19. W. A. BRYANT, *J. Cryst. Growth* **35** (The Electro-chem Soc., NJ, 1976) 257.
20. K. SUGIYAMA and T. NAKAMURA, *J. Mater. Sci. Lett.* **6** (1987) 331.

Received 26 July 1988
and accepted 4 January 1989