GAS FLOW SIMULATION OF CHEMICAL VAPOUR INFILTRATION IN A VERTICAL HOT-WALL REACTOR

M. SASAKI, A. OHKUBO and T. HIRAI

*Institute for Materials Research, Tohoku University,
Katahira 2-1-1, Sendai 980, Japan*

ABSTRACT

Deposition of silicon carbide (SiC) into two types of capillaries (1.5 mm dia. x 6 mm depth, 1.0 mm dia. x 4 mm depth) has been attempted by a vertical hot-wall-type chemical vapour infiltration (CVI) process using an $\text{SiCl}_4\text{-CH}_4\text{-H}_2$ system. Dependence of the deposition temperature (T_{dep}) and the total gas pressure (P_{tot}) on the thickness distribution of SiC in the two types of the capillaries (parallel and perpendicular to the gas stream) was studied. Activation energy of the deposition of SiC was 42 kJ/mol in the T_{dep} range of 1673 to 1773 K, and 167 kJ/mol in the T_{dep} range of 1573 to 1673 K. The most suitable CVI condition was a T_{dep} below 1673 K accompanied by the reaction-rate controlled process. The uniformity of the film thickness obtained at P_{tot} below 0.13 kPa was lower than that obtained at P_{tot} below 13 kPa. The lower the P_{tot} and the closer the deposition was to the capillary entrance, the higher the vorticity in the two types of capillaries became. The film thickness at the capillary entrance increased coincident with the increase in vorticity. Vorticity in the capillaries perpendicular to the gas stream was higher than that parallel to the gas stream. In the diffusion-rate controlled process ($T_{\text{dep}} > 1673$ K), in which decreasing P_{tot} was accompanied by increasing vorticity, film thickness uniformity in the capillary decreased. Results of the CVI experiments and the gas flow simulation suggest that lower vorticity under reaction-rate controlled conditions is important for obtaining uniformity of SiC thickness in the capillaries.

1. INTRODUCTION

Chemical vapour infiltration (CVI) is widely used in the fabrication of fiber-reinforced ceramic composites /1-8/. CVI process can be classified into three main types, an isothermal process /1-4/, a temperature gradient process /5-7/ and a pressure gradient process /8/. Regarding practical applications of ceramic composites, the isothermal CVI process is favourable for manufacturing larger and complex-shaped ceramic composites. Basic research including kinetic study and local gas flow simulation is necessary to extend the applicability of this process.

Use of C/C composites is anticipated because of their higher strength ratio and elasticity at high temperatures, although C/C composites are not highly oxidation resistant. An oxidation resistant coating on the C/C

composite is indispensable for use in high temperature oxidation atmosphere. Naslain et al. /9/ reported CVI of SiC into the C/C composite using a CH_3SiCl_3 (MTS)- H_2 system. However, the deposition rate of SiC is very low (several μmhr^{-1}). Lackey et al. reported CVI experiments in which the MTS flow rate was $50 \text{ mm}^3 \text{ min}^{-1}$ and the H_2 /MTS molar ratio was 10 at a T_{dep} of 1473 K and a P_{tot} of 100 kPa /10/. Sugiyama et al. /11/ investigated pulse-CVI of SiC into the porous carbon substrate using an MTS- H_2 system at a T_{dep} of 1448 K in which the P_{tot} was from 79 to 1.3 kPa. Not many research concerning the isothermal CVI of SiC with gas flows under steady-gas flow conditions has not been attempted.

On the other hand, the present authors have previously reported the influence of the rate-limiting process, a geometrical feature of the CVI hot-zone and the bulk gas flow condition on the CVI process /12/. Local gas flow simulation in the capillaries, however, had not been investigated.

This work describes the importance of local gas flow on the CVI process as shown by CVI experiments and the calculations.

2. EXPERIMENTAL

A vertical hot-wall CVI reactor was used for the experiments in an SiCl_4 - CH_4 - H_2 system. A graphite heater (I.D. 40 mm x 75 mm length) set on the graphite substrate (30 mm dia. x 10 mm length) was heated by the inductive-heating method.

Figure 1 illustrates the CVI hot-zone. The graphite substrate has two types of capillaries (1.5 mm dia. x 6 mm depth, 1.0 mm dia. x 4 mm depth) both parallel and perpendicular to the gas stream. CVI experimental conditions are shown in Table I. The H_2 , SiCl_4 and CH_4 gas flow rates were kept constant. Deposition temperature (T_{dep}) varied from 1573 to 1773 K, and total gas pressure (P_{tot}) varied from 0.13 to 13 kPa. SiC thickness was measured by optical microscopy and scanning electron microscopy.

Table I. CVI conditions.

Deposition temperature, T_{dep} (K);	1573 to 1773
Total gas pressure, P_{tot} (kPa);	0.13 to 13
Gas flow rate ($10^{-6} \text{ m}^3 \text{ sec}^{-1}$)	
SiCl_4 ;	1.7
CH_4 ;	1.3
H_2 ;	5.0
Deposition time, t_{dep} (ks);	10.8

Fig.1. Geometrical diagram of the CVI hot zone, $d=40 \text{ mm}$; $L=75 \text{ mm}$; $\phi=30 \text{ mm}$; $e=10 \text{ mm}$; (1) heater; (2) substrate with 2 types of capillaries: A and B, capillary (1.5 mm dia x 6 mm length); C and D, capillary (1.9 mm dia x 4 mm length)

3. RESULTS AND DISCUSSION

3.1. Thickness profiles of the SiC film in the capillaries

Figures 2 and 3 show that variation in the thickness distribution of SiC in capillaries "A" and "B" was accompanied by variation of the T_{dep} from 1573 to 1773 K and variation of the P_{tot} from 0.13 to 13 kPa.

Measurement of the SiC thickness in capillaries "A" and "B" showed that the closer the site of deposition to the capillary entrance, the higher the thickness became at the relatively higher T_{dep} (1723-1773 K) under all P_{tot} conditions (0.13-13 kPa). The reason for the high level of thickness distribution is thought to be due to the diffusion-rate controlled process at higher T_{dep} , and SiC formation is thought to be controlled by the concentration of the source gas. On the other hand, the dependence of the deposition temperature on the thickness distribution is lower in the T_{dep} range of 1573 to 1723 K, and the dependence of the thickness distribution on P_{tot} is also higher in this range.

Fig.2. Thickness distribution of SiC in the capillaries A (a) and B (b).

Fig.3. Thickness distribution of SiC in the capillaries A (a) and B (b).

Figures 4 and 5 show the effect of P_{tot} on the thickness distribution in capillaries "A" and "B" at T_{dep} of 1773 and 1623 K. Figure 4 demonstrates the independence of the thickness distribution on P_{tot} at a T_{dep} of 1773 K. This result shows that a T_{dep} of 1773 K is not suitable for CVI conditions. In this case, CVI parallel to the gas stream is better than CVI perpendicular to the gas stream. Figure 5 shows the effect of P_{tot} on SiC thickness distribution in capillaries "A" and "B" under reaction-rate controlled conditions (T_{dep} = 1623 K). The

uniformity of the thickness is high at a T_{dep} of 1623 K and a P_{tot} of 13 kPa. This tendency is thought to be due to the reaction-rate controlled process. A T_{dep} of 1623 K and a P_{tot} of 0.13 kPa are not good conditions for CVI in contrast with the same T_{dep} and a P_{tot} of 13 kPa as mentioned above.

Gas flow simulation was attempted under viscous flow conditions. Calculated temperature distribution in the CVI hot-zone at the P_{tot} of 13 kPa is shown in Fig. 6. Temperature uniformity around the substrate within 10 mm was very high. This result shows that this CVI experiment was conducted under isothermal conditions.

Fig.4.Effect of total gas pressure (P_{tot}) on the SiC thickness distribution in the capillaries A (a) and B (b).

Fig.5.Effect of total gas pressure (P_{tot}) on the SiC thickness distribution in the capillaries A (a) and B (b).

Fig.6.Temperature profile in the CVI hot zone at $P_{tot} = 13\text{ kPa}$ ($T_{dep} =$ (a)1573 K; (b)1623 K; (c)1773 K).

3.2. Dependence of total gas pressure on the flow rate and vorticity

Figure 7 shows the calculated stream lines in the CVI hot-zone at a T_{dep} of 1573 K. With a decrease in the P_{tot} , the distance between stream lines became narrower and the flow rate and the flow rate distribution increased with decreasing P_{tot} as shown by calculation of the flow rate distribution using the stream function. This calculated result shows the flow rate distribution around the substrate and the heater.

Fig.7. Stream line in the CVI hot zone at $T_{\text{dep}}=1573$ K ($\text{m}^2\text{sec}^{-1}$; P_{tot} : (a) 0.13 kPa; (b) 1.3 kPa; (c) 13 kPa).

Fig.8. Dependence of the infiltration depth on T_{dep} and P_{tot} (Δ 0.13 kPa; $\circ$ 1.3 kPa; $\square$ 13 kPa) open circle: perpendicular to the gas stream, closed circle: parallel to the gas stream.

Figure 8 demonstrates the dependence of the infiltration depth on T_{dep} and P_{tot} . The infiltration depth (D_{50}) is defined as the place in which the thickness fell to a level fifty percent lower than that at the entrance. These results show that the conditions at lower T_{dep} (<1623 K) and higher P_{tot} (≥ 13 kPa) are suitable for CVI.

3.3. Relationship between vorticity and infiltration depth

Generally "vorticity" defines as a degree of self-rotating velocity in a local flow accompanied with a distribution of gas flow velocity. Figure 9 shows the calculated vorticity in the capillaries at T_{dep} of 1573 K. The ratios of the capillary depth to diameters of about 1.0 mm and 1.5 mm (conversion depth) for diameters of about 1.0 mm and 1.5 mm agree well with each other. These results are supported by our previous experiments /12/. Vorticity increases with decreasing P_{tot} and decreasing depth from the capillary entrance as shown in Fig. 9. Figure 10 demonstrates the relationship between the vorticity and the infiltration depth. Vorticity becomes lower at a P_{tot} of 13 kPa in the T_{dep} range of 1573 to 1773 K. Vorticity in a capillary entrance increased with decreasing P_{tot} . Source gas diffusion makes difficult under relatively high P_{tot} . These calculated results suggest that the lower vorticity resulting from higher P_{tot} and the lower T_{dep} due to the reaction-rate controlled condition are important in CVI processing.

Fig.9. Vorticity in the capillary at $T_{dep}=1573$ K: (A) and (D) perpendicular to the gas stream; (B) and (C) parallel to the gas stream; (A) and (B) are 1.5 mm diameter, (C) and (D) are 1.0 mm diameter (P_{tot} : 0.13 kPa; 1.3 kPa; 13 kPa).

Fig.10. Dependence of the infiltration depth on the vorticity (T_{dep} : (—) 1573 K; (---) 1623 K; (- - -) 1723 K; (....) 1773 K, P_{tot} : (Δ , $\blacktriangle$) 0.13 kPa; ($\circ$, $\bullet$) 1.3 kPa; ($\square$, $\blacksquare$) 13 kPa, open circle: perpendicular to the gas stream, closed circle: parallel to the gas stream).

4. CONCLUSIONS

CVI experiments on deposition of SiC into capillaries perpendicular to the gas stream (capillaries "A" and "D") and parallel to the gas stream (capillaries "B" and "C"), and related gas flow simulation yielded the following conclusions:

- (1) The rate-limiting process is thought to be due to diffusion-control at T_{dep} of 1673 to 1773 K and to reaction-controlled at T_{dep} of 1573 to 1673 K in the whole P_{tot} range of 0.13 to 13 kPa.
- (2) CVI into capillary "B" parallel to the gas stream is easier than CVI into capillary "A" perpendicular to the gas stream.
- (3) The thickness uniformity increased with increasing P_{tot} from 0.13 to 13 kPa at a lower T_{dep} of 1623 K.
- (4) Suitable CVI conditions for SiC deposition into the capillaries both parallel and perpendicular to the gas stream are lower T_{dep} (<1623 K) and higher P_{tot} ($\geq$ 13 kPa).
- (5) Flow rate distribution and vorticity increased with decreasing P_{tot} and the distance from the capillary entrance.

REFERENCES

- /1/ MORIN D., J. Less-Common Met., 47(1976)207.
- /2/ NEWKIRKL R., RILEY R.E., SHIEINBERGH H., VALENCIA F.A. and WALLACE T.C., Proc. 7th Conf. Chemical Vapor Deposition, eds. T.O. Sedgwick and H. Lydtin (Electrochem. Soc., Pennington, 1979), p.515.
- /3/ HERAUD L.H., CHRISTIN F., NASLAIN R. and HAGENMULLER P., Proc. 8th Conf. Chemical Vapor Deposition, eds. J.M. Blocher, Jr. and G.E. Vuillard (Electrochem. Soc., Pennington, 1981), p.782.
- /4/ FITZER E., HEGEN D. and STROHMEIER H., Proc. 7th Conf. Chemical Vapor Deposition, eds. T.O. Sedgwick and H. Lydtin (Electrochem. Soc., Pennington, 1979), p.525.
- /5/ CAPUTO A.J. and LACKEY W.J., Ceram. Eng. Sci. Proc., 5(1984)654.
- /6/ THEIS Jr. J.D., Proc. 3th Conf. Chemical Vapor Deposition, eds. F.A. Glaski (Electrochem. Soc., Pennington, 1972), p.561.
- /7/ GEBHARDT J.J., Proc. 4th Conf. Chemical Vapor Deposition, eds. G.F. Wakefield and J.M. Blocher (Electrochem. Soc., Pennington, 1973), p.460.
- /8/ SUGIYAMA K. and NAKAMURA T., J. Mat. Sci. Lett., 6(1987) 331.
- /9/ HERAUD L.H., CHRISTIN F., NASLAIN R. and HAGENMULLER P., Proc. 8th Conf. Chemical Vapor Deposition, eds. J.M. Blocher, Jr. and G.E. Vuillard (Electrochem. Soc., Pennington, 1981), p.782.
- /10/ CAPUTO A.J. and LACKEY W.J., Ceram. Eng. Sci. Proc., 5(1984)654.
- /11/ SUGIYAMA K. and YAMAMOTO E., Proc. 10th Conf. Chemical Vapor Deposition, eds. G.W. Cullen and J.M. Blocher, Jr. (Electrochem. Soc., Pennington, 1987), p.1041.
- /12/ SASAKI M., OHKUBO A., SUZUKI T. and HIRAI T., J. Mat. Res., submitted.