

A chemical vapor deposition method for the manufacture of silicon carbide tubes

Guo Ying Zhao, Ching Wen Zhu, Vithal Revankar and Vladimir Hlavacek
Laboratory for Ceramic and Reaction Engineering, Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260 (USA)

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Abstract

An investigation on the deposition of silicon carbide to manufacture silicon carbide tubes from thermal decomposition of CH_3SiCl_3 in a hydrogen atmosphere is presented. A thermodynamic analysis is carried out to obtain the optimum conditions for this operation. A detailed design of the reactors is described. Two critical problems in the operation of the deposition and the solutions are given. A method of carbon coating is used to eliminate the crack induced by the different expansion coefficients of the β -SiC coating and the graphite substrate. The problem of scaling up is discussed.

1. Introduction

A new class of processes with enormous technological flexibility and capability, so-called chemical vapor deposition (CVD), was developed and successfully applied in the last two decades. CVD is a unique way to deposit solid materials by using surface vapor chemical reactions. Even though the application of CVD in the electronics industry is extremely successful and certain technologies seem to be mature, there is still a lot of room for scientists to do research work in order to develop or improve the technologies and thereby to promote the application of ceramic materials.

The manufacture of high performance ceramic tubes is very complicated. Since the techniques and tooling that have been developed to produce these elements from "conventional" alloys are not easily applicable, several attempts were made in this field [1–4, 9–12].

Lloyd and Howard [1], from the British Ceramic Research Association, reported their research on the fabrication and properties of large-diameter tubes and coatings in pyrolytic silicon carbide. They heated the substrate by r.f. induction. Silicon carbide deposition was carried out by the thermal breakdown of methyl trichlorosilane at a surface heated to 1400 °C. It was pointed out that, due to cooling from the deposition temperature, large stresses arose in the coatings which often cracked when the restraint of the substrate was removed. These stresses might be caused partly from the differences in the thermal expansion between the substrate and the coating and partly from the expansion differences between silicon carbides of different

stoichiometries occurring in the bands with excess carbon material. Micro-cracking in the coating gave mechanical strengths considerably lower than those predicted from small specimens.

Later, Martin *et al.* [2] described the application of CVD to produce tungsten tubing by using electrical heating of the substrate and the reduction of WF_6 in a hydrogen atmosphere. Tungsten tubing of high purity might be made up to 4 ft in length and in various diameters and wall thicknesses. In the as-deposited form, this product was less costly than tubing produced by the more conventional routes of arc casting, electron beam melting, and powder metallurgy, followed by extrusion, drawing and annealing operations.

In order to investigate the application of refractory coatings in fusion reactor environments, Pierson *et al.* [3] described an experiment of the coating of graphite with TiB_2 by CVD using the H_2 reduction of BCl_3 and $TiCl_4$ at 925 °C and 1 atm. They successfully used r.f. induction to heat their graphite susceptor. The graphite they selected could be reasonably matched to the thermal expansion of TiB_2 , and eventually the cracking was eliminated.

In 1987, Sato and Tachikawa [4] did some research on the deposition of TiB_2 onto a mild steel substrate through the hydrogen reduction of $TiCl_4$ and BCl_3 , and found the optimum deposition conditions to make a deposit with good composition, hardness and morphology onto a mild steel substrate. They were as follows: temperature, 900 °C; source gas ratio, $TiCl_4:(TiCl_4 + BCl_3) = 0.3-0.4$, $Cl:H = 0.17-0.2$. The heating used was by a specially designed electrical heater. Nothing was reported concerning the possible cracking induced by the mismatching between the TiB_2 coating and the mild steel substrate during cooling.

In the Laboratory for Ceramic and Reaction Engineering in the State University of New York at Buffalo, a series of studies on CVD methods for the production of thick films have been conducted over a year. The purpose of the work is to investigate the possibility and the optimum procedure to manufacture tubing, optical domes and refractory crucibles using CVD methods.

This paper reports part of the above work. An investigation of the deposition of silicon carbide tubing from thermal decomposition of industrial grade CH_3SiCl_3 in a hydrogen atmosphere by using electrical heating is presented. A thermodynamic calculation was carried out to obtain the optimum conditions. Details of the reactors are described. Two critical problems in the operation of the deposition and their solutions are given. Finally, the feasibility of scaling up is discussed.

2. Theoretical considerations

The use of thermodynamic calculations is extremely valuable in analyzing the combination of condensed phases that will give the most stable deposit

during chemical deposition. The comparisons with actual results provide insights into the reaction mechanisms involved. Even though kinetic factors may cause deviation from thermodynamic expectation, such calculation provides at least an approximate basis for further probing by systematic experimentation.

Thermodynamic calculations, reported in this paper, were conducted using the NASA code [5] which was based on the minimization of Gibbs free energy. The specific heat, enthalpy, entropy and the enthalpy of formation of each species were taken from the *JANAF Thermochemical Tables* [6].

The calculation was specific for the $\text{CH}_3\text{SiCl}_3\text{-H}_2$ system; 64 gas species and four condensed phases (silicon, carbon, $\alpha\text{-SiC}$, $\beta\text{-SiC}$) were considered.

Figures 1(a)–1(d) show the calculation of the decomposition of CH_3SiCl_3 in a hydrogen atmosphere at atmospheric pressure. The calculation reveals the following.

(1) Even if hydrogen does not exist, $\beta\text{-SiC}$ starts forming at temperatures as low as 500 K. The molar concentration of SiC increases gradually under the conditions of Fig. 1(a). As the initial hydrogen concentration increases (Figs. 1(b)–1(d)), $\beta\text{-SiC}$ will reach its maximum value at 1300 K and stay at this value with further temperature increase.

(2) Solid carbon appears at lower H_2 ratios. When the initial hydrogen increases, solid carbon disappears when the $\text{H}_2\text{-to-CH}_3\text{SiCl}_3$ ratio is larger than 3.

(3) The solid phases that may appear, according to the equilibrium calculation, are SiC and carbon. This is a contradiction to the experimental result, *i.e.* where in certain cases solid silicon has appeared. From the above results we can conclude that, for temperatures higher than 1300 K and for the $\text{H}_2\text{:CH}_3\text{SiCl}_3$ ratio equal to 3–4, the optimum conditions are achieved for $\beta\text{-SiC}$ deposition.

3. Design of the system

Figure 2 is the schematic of the experimental set-up used to deposit a silicon carbide thick film. A.c. current at 220 V passes through a Variac in order to control the power; a transformer is connected with the Variac to regulate the voltage to the maximum value of 10 V. The electric current passes through a pair of water-cooled electrodes to heat a graphite tube which is mounted in a well-sealed reactor as a substrate. Before starting the experiment, argon is used to purge all gases from the system for 1 h. The experiment starts with the switching on of the electric heating. When the graphite substrate is heated to the temperature required, hydrogen is passed through the reactor. The reactant liquid CH_3SiCl_3 is heated to an assigned temperature. Finally, hydrogen passes through the reactant container and brings CH_3SiCl_3 vapor to the reactor. CH_3SiCl_3 decomposes on the graphite surface in the hydrogen atmosphere by the following chemical reaction:

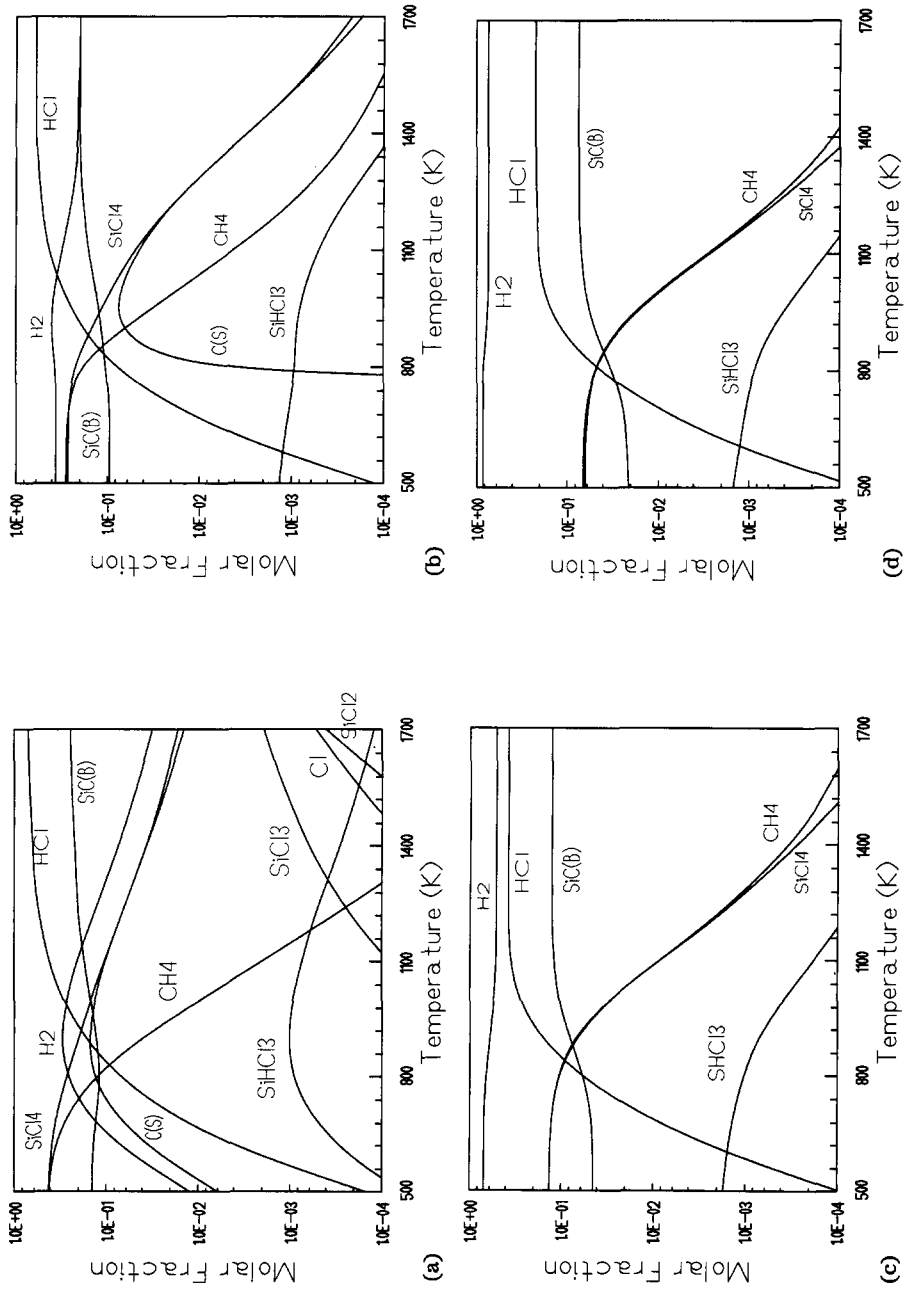


Fig. 1. Equilibrium calculated compositions of the CH_3SiCl_3 - H_2 system (CH_3SiCl_3 , 1 mol): (a) H_2 , 0.0 mol; (b) H_2 , 0.1 mol; (c) H_2 , 0.4 mol; (d) H_2 , 1.0 mol.

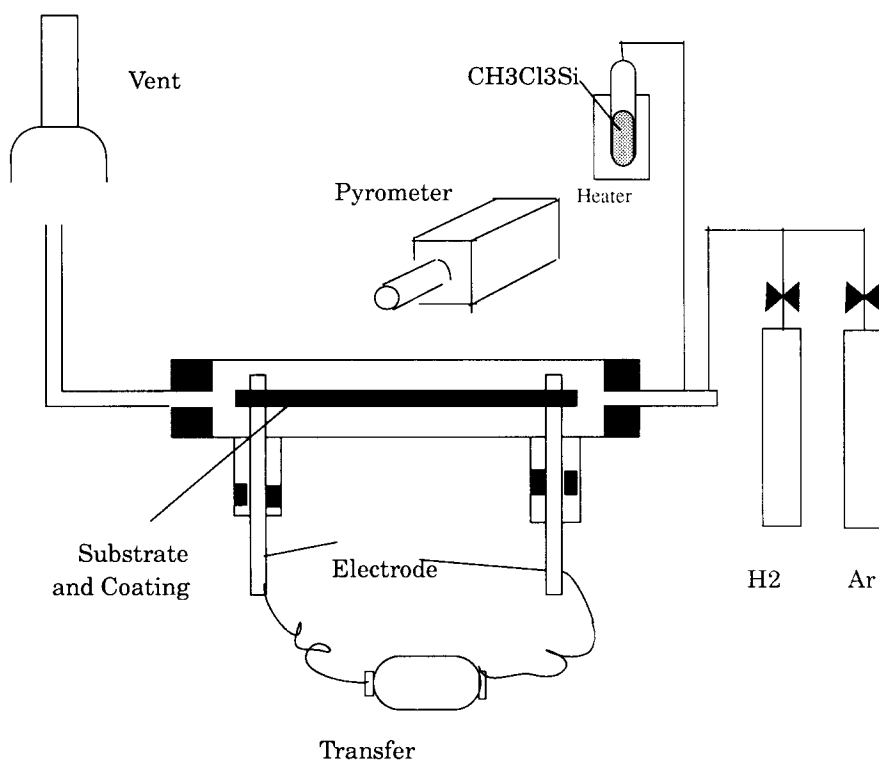
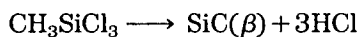


Fig. 2. The schematic of the experimental set-up.



and the resultant β -SiC deposits on the graphite surface.

During the experimental operations we continuously modified the various parts of the reactor system. This resulted in the following optimum design.

3.1. Substrate

As shown by the thermodynamic calculations discussed in the last section, the minimum value of the favorable temperature of the substrate for the deposition of silicon carbide should be above 1100°C . In order to simplify our system, we decided to select a substrate which can also be used as a heating element. It is well known that the substances which can be used as the electrical heating elements are copper, nickel alloys, iron-based alloys, refractory metals such as platinum, molybdenum, tantalum, tungsten, graphite, silicon carbide and TiB_2 . Table 1 lists the related properties of the above substances. Obviously, the operating temperatures of copper, nickel alloys and iron-based alloys are too low for them to be used as the substrates for the deposition of silicon carbide tubes; and the refractory metals are too expensive for this purpose. As far as silicon carbide is concerned, its resistance is so high that a very high voltage electrical power supply would be required. Also, it is difficult and expensive to make a silicon carbide substrate with a suitable shape.

TABLE 1
Electrical and thermal properties of some possible substrates [13]

Material	Operating temperature (°C)	Resistivity at 20 °C ($\times 10^8 \Omega \text{ m}$)	Temperature coefficient of resistivity	Linear expansion coefficient ($\times 10^4 \text{ }^\circ\text{C}^{-1}$)
Copper	350	1.72		0.161
Nickel alloys	1050–1250	108–124	6.24×10^{-5}	0.13
Iron-based alloys	1050–1300	134–145	$(4.7\text{--}12) \times 10^{-5}$	0.11
Refractory metals (Pt, Mo, Ta, W)	1300–2500	10–20	$(2.5\text{--}5.9) \times 10^{-3}$	0.0646
Graphite	3000	1000	-2.7×10^{-4}	0.03–0.077
Silicon carbide	1600	1.1×10^5	-2.63×10^{-4}	0.0568
TiB ₂	–	–		0.055

Fortunately, the only option – graphite – is a very good substrate for our purpose. This is because of the following.

(1) It is a material with an operating temperature sufficiently high for use as a substrate.

(2) Even though its resistance is very high, one can heat it easily to a temperature high enough for silicon carbide deposition.

(3) Moreover, in comparison with other substances, it is a very cheap material, so it will make things easy when the scale of this technology is increased.

(4) The most outstanding characteristic of graphite is its expansion coefficient which can be chosen to match that of β -SiC. This is extremely important during the cooling process as discussed in the later part of this paper.

3.2. Reactor

The reactor is the most important part for this project because it is the place where CVD proceeds. Three reactors were designed for operations. The first one is a small quartz tube, placed horizontally, with the dimensions $L=11$ in, $D=1.2$ in, $L_s=4$ in and $D_s=0.4$ in. The second one is a large quartz tube, also placed horizontally, with the dimensions $L=19$ in, $D=2$ in, $L_s=10.5$ in and $D_s=0.75$ in. Finally, a large stainless steel vertical reactor with a water cooling jacket was used. Its dimensions are $L=20$ in, $D=2$ in, $L_s=12$ in and $D_s=0.75$ in, where L and D are the length and diameter of the reactor respectively; L_s and D_s are the length and diameter of the substrate respectively.

Figure 3 shows the layout of the whole system. The advantage of the quartz tube is that the temperatures at every point on the mandrel can be measured and the phenomena taking place inside the reactor can be observed. The advantage of a stainless steel tube is that it is very easy to clean and very sturdy.

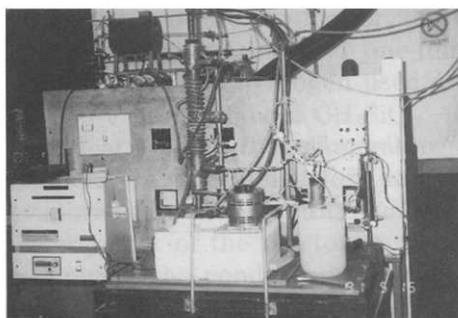


Fig. 3. A photograph of the vertical CVD reactor system.

The reactor assembly consists of five parts: a water-cooled stainless steel outer chamber; water-cooled electrodes; seals; observation windows; and inlet and outlet lines.

The water-cooled stainless steel outer chamber has a water-cooled coil on its wall. By adjusting the coil distance, we are able to keep the inside substrate temperature uniform. We also used differential cooling at different regions by dividing and bifurcating the coil. The two ends of the reactor were sealed with a special kind of rubber. This has special significance in our operation because, during the heating and cooling processes, it can accommodate the expansion of the electrode and the substrate. The observation windows were mounted on the wall of the reactor to record the temperatures through an infrared pyrometer. This observation directly helped us to eliminate the temperature gradient. Inlet and outlet lines were heated to eliminate any condensation of the reactants.

3.3. *Electrodes*

Design of electrodes is an important problem which was realized at the initial stage of the experiments. This was crucial when the scale of the experiment was increased. Four types of electrodes were tried, varying from the air cooled to the water cooled. The one currently in use works perfectly. It is shown in Fig. 4. The electrode is a water-cooled tube. A stainless steel tube fitting connects the graphite substrate with the electrode. One side of this connection is a tight fitting. It acts as a good contact for the electricity to pass through. Another side of the fitting is a thread, which connects the electrode. The reason why stainless steel fittings are used is because the operating temperature of stainless steel is high, up to 1100 °C, as shown in Table 1 and its thermal conductivity is not as high as that of copper. Thus the end which connects with the graphite substrate can be held at high temperature without melting even if its other end is connected with the water-cooled electrode. The electrical current sometimes reaches 550 A. This is a very serious condition; however, the electrodes manufactured according to this design work very well. We have kept very good connection between the substrate and the electrodes and also maintained uniform

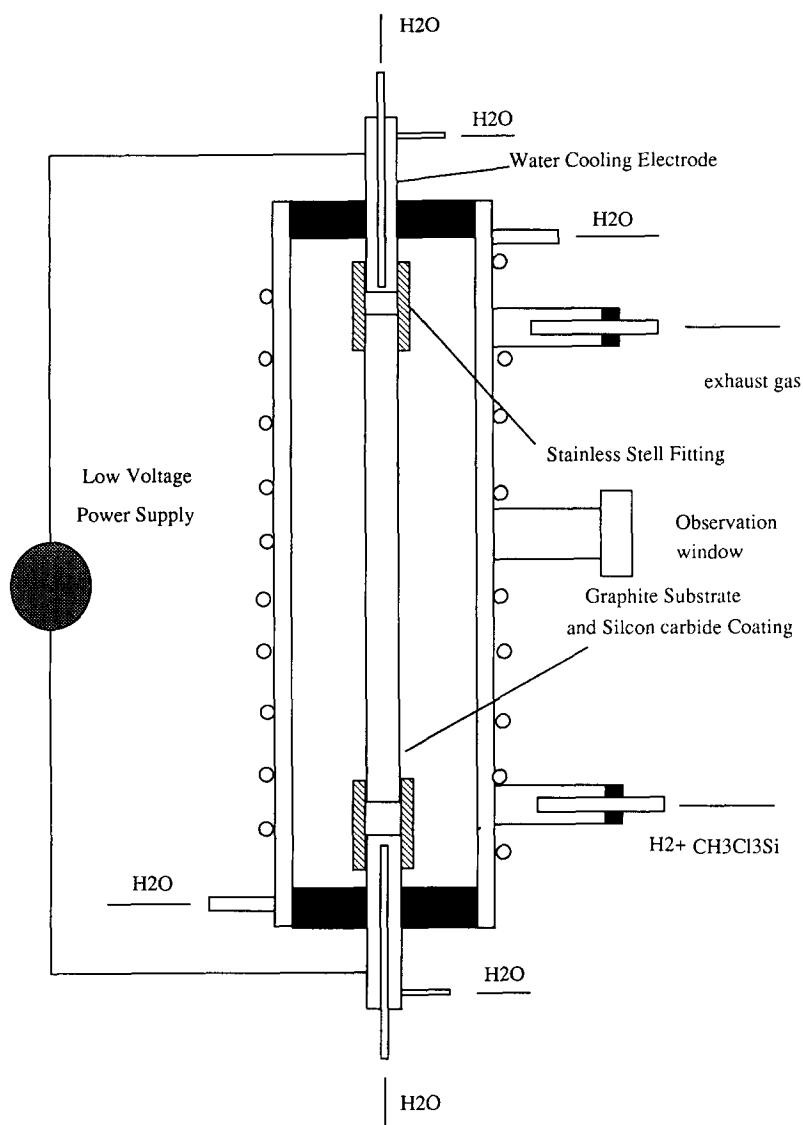


Fig. 4. Schematic of a recently designed electrode.

temperature distribution on the substrate because the heat loss from the two ends of the substrate is not very large.

4. Experimental details

The substrate temperature was held between 900 and 1250 °C, and was measured by an infrared pyrometer. The flow rate of H₂ could be changed from 0.2 to 0.4 l min⁻¹. The CH₃SiCl₃ was evaporated by passing the hydrogen gas through the evaporator. By controlling the hydrogen flow rate and the

temperature of the evaporator, the flow rate of CH_3SiCl_3 can be adjusted to between one-sixteenth and one-third of the hydrogen flow rate. Both the CH_3SiCl_3 and the hydrogen used are industrial grade (hydrogen, extra dry, 99.950% purity, Linde; CH_3SiCl_3 , industrial grade 97.000% purity, Aldrich Chemical). When the temperature of the evaporator is higher than room temperature, the tubing for the transportation of CH_3SiCl_3 vapor from the evaporator to the reactor must be heated, and the cooling water for the water jacket of the reactor must be held at a certain temperature in order to prevent the condensation of CH_3SiCl_3 which would otherwise block the tubing or condense in the reactor.

After many test experiments, very thick silicon carbide coating could be produced on the graphite substrate tubing. The length of the deposition could reach 25 cm, the diameter varied from 5 mm to 2.5 cm depending upon the size of the substrate used, and the thickness varied from 20 μm to 3 mm depending upon the operating time and operating temperature and reactant flow rates. Figure 5 shows one of the tubes produced in our laboratory. Two serious problems were discovered, as follows.

The first was cracking. The deposition surface of SiC was fairly smooth. After grinding, some microcracks appeared. In Fig. 5, the top part of the tubing is the surface formed without grinding, the lower part is ground, and the microcracks are obvious on the ground surface. Figure 6 shows a magnified picture of these microcracks. There are two kinds of cracking: (1) most of the cracks are circumferential hair-line cracks; (2) few of them are in the radial direction. Cracks are, in general, seen in tube areas where the coating appearance is less regular and often of a slightly darker color.

The second problem relates to the deposition conditions. It is very critical to find the right conditions for the deposition. Chi *et al.* [7] carried out a very careful investigation on the morphologies of SiC deposited by the thermal decomposition of CH_3SiCl_3 . The morphologies of the deposits were found to vary with the substrate temperature, chamber pressure and gas composition. In our case, the pressure is always equal to 1 atm, so the effective parameters are the substrate temperature and gas composition. As discussed above, the ratio $\text{H}_2:\text{CH}_3\text{SiCl}_3$ in the experiments is larger than 4, and the temperature

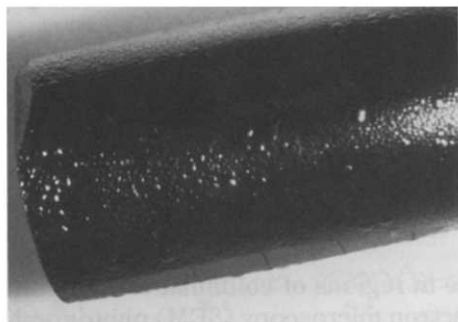


Fig. 5. One of the tubes made at the first stage of the investigation.

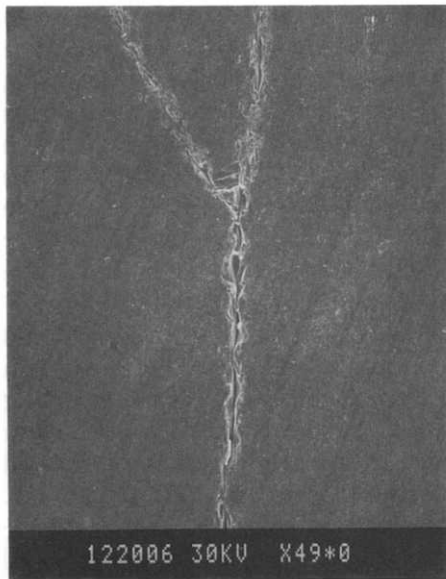
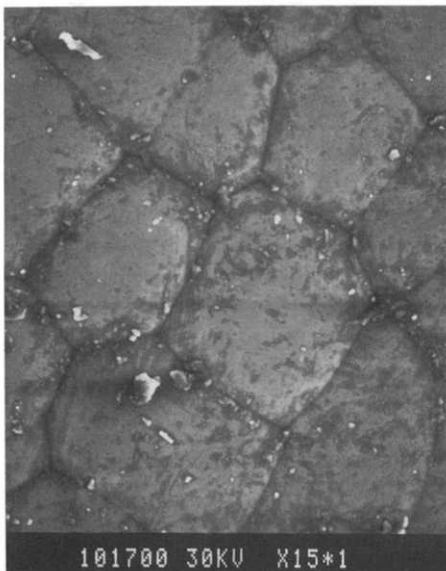
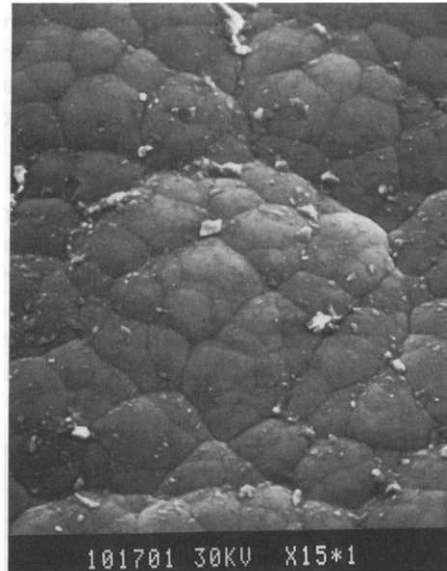


Fig. 6. A magnified photograph of cracked silicon carbide tubing (magnification, $\times 33$).



(a)



(b)

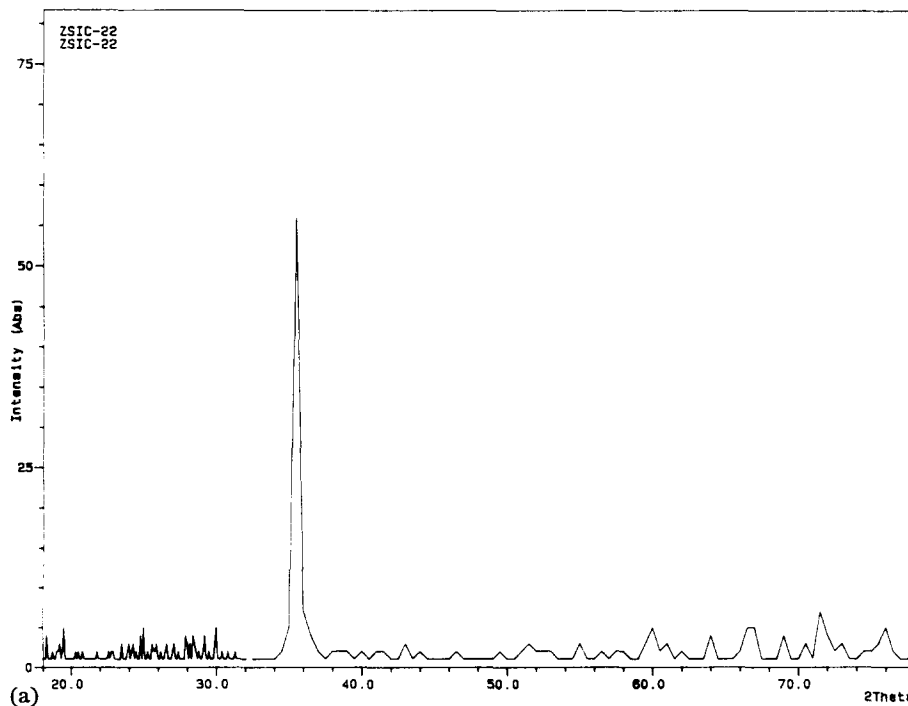
Fig. 7. SEM pictures of the surface morphology of the deposited silicon carbide (magnification, $\times 100$).

lower than $1250\text{ }^{\circ}\text{C}$, so the operations are in regions of columnar and smooth deposition. Figure 7 shows a scanning electron microscopy (SEM) photograph of the deposition which reveals the surface morphologies of the deposited

silicon carbide. Figure 8 shows typical X-ray diffraction patterns of the deposition. Almost all the X-ray diffractions show a sharp peak at $2\theta = 36^\circ$, and the density is around 97.0% of the theoretical density of silicon carbide.

It is possible to avoid microcracks by coating a carbon film on the substrate before deposition. A similar operation was carried out for boron fiber deposition [8]. However, it was very difficult to produce a carbon coating on graphite at the beginning. More than five methods were tried, but none of them worked. CVD of $\text{CH}_4\text{-CCl}_4\text{-C}_6\text{H}_6$ to yield an intermediate "spongy" carbon layer was tried. Since there is a large temperature gradient on the substrate, this process failed to produce a uniform coating. This temperature gradient gave a pronounced effect because the carbon is deposited at low temperature. Active charcoal was dispersed in alcohol and the resultant paste was coated on the substrate. This process was carried out several times to achieve a thicker coating. For each coating, the drying process took several minutes. However, under the operating conditions, this process failed due to the formation of microcracks when the coating reached a certain thickness.

Eventually we used a cellulose-based glue to paste carbon powders on the substrate. The main points of this method are: (1) a very thin layer of carbon powders can be coated every time; immediately after the glue is dried, the coating must be heated in order to evaporate most of the glue used; (2) before the graphite substrate with a thick carbon coating is used for SiC deposition, it must be heated to the temperature for SiC coating in



(a) Fig. 8.

(continued)

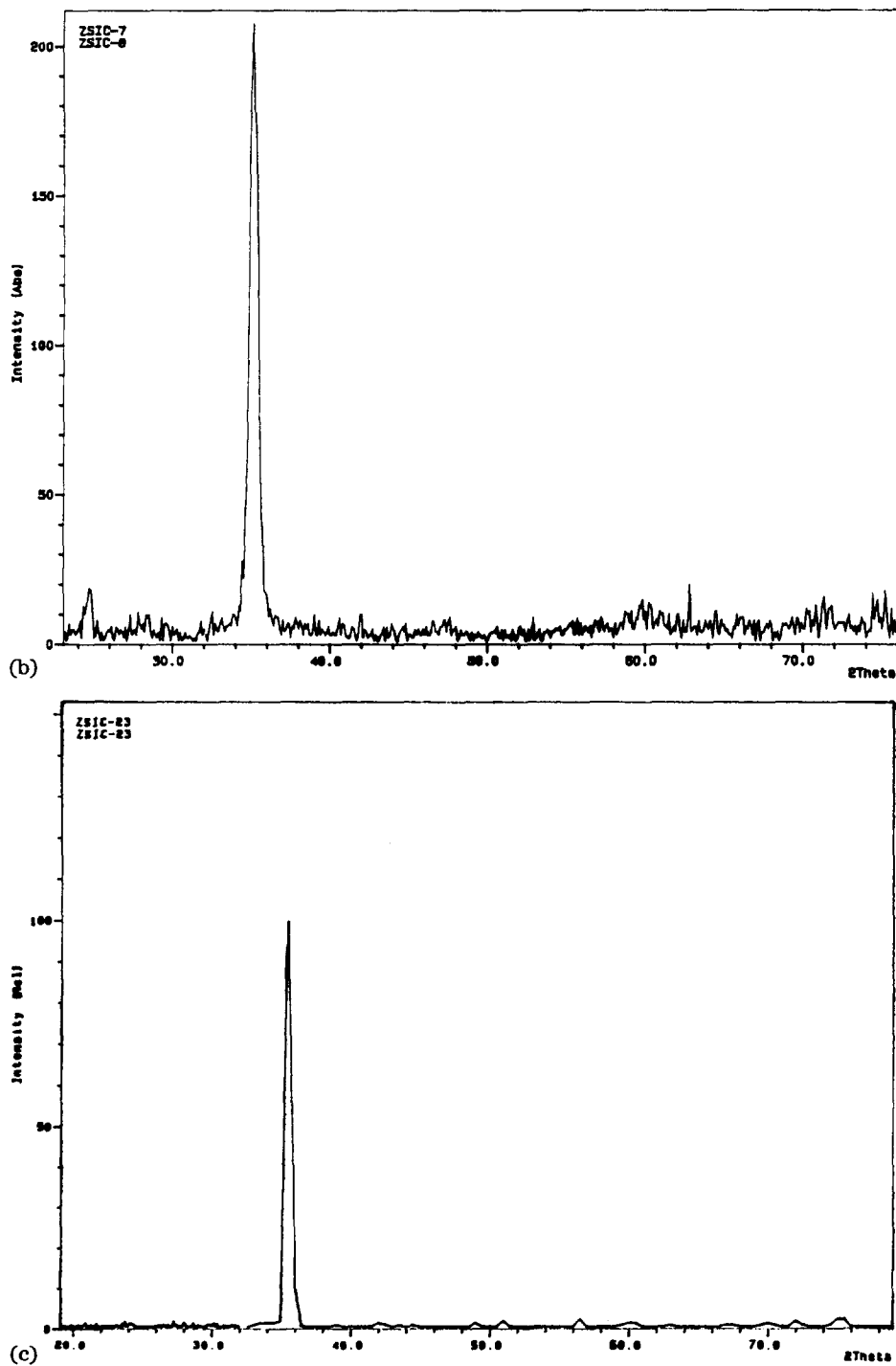


Fig. 8. Typical X-ray diffraction patterns of the deposition (Stoe powder diffraction system): (a) June 3, 1991; (b) June 4, 1991; (c) November 21, 1990.

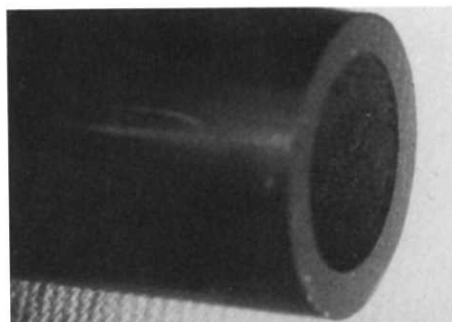
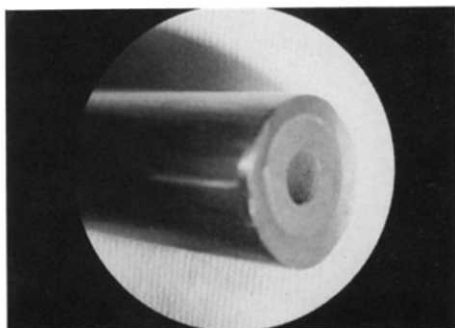


Fig. 9. A photograph of the graphite substrate, carbon film coating and the deposited silicon carbide (48% actual size).

Fig. 10. A photograph of deposited silicon carbide with the substrate removed.

an argon atmosphere to evaporate the remainder of the glue. It seems that this method works perfectly. Not only a thin film of carbon about $5\ \mu\text{m}$ but also a thick film up to $1\ \text{mm}$ can be coated. Using graphite tubing with a thin layer coating of carbon powders, an SiC tubing without microcracks was produced. When the diameter of the substrate increases, the carbon layer can be thinner. Figure 9 shows a photograph of a sample of the deposition. Here the graphite substrate and the carbon film were not removed, so both can be seen with the deposited silicon carbide. Figure 10 is another sample of a silicon carbide deposition where the graphite and carbon film were removed. Figure 11 shows three SEM pictures of silicon carbide depositions without cracks. Figure 11(a) is one end cross-section of the sample of Fig. 9. Figure 11(b) is one end of the sample of Fig. 10. Figure 11(c) is an SEM picture of the cylindrical surface of the sample in Fig. 10. These three pictures give us some idea about the carbon coating method.

5. Scaling up

It seems that, for small substrates, it is very easy to control the gas composition and the surface temperature on the substrate. However, for substrates with large diameters and lengths it is very difficult to do so, because non-uniform deposition and some microcracks are induced. In order to scale up the system, two problems must be solved: (1) to maintain a uniform and constant temperature on the whole surface of the substrate; (2) to maintain a uniform concentration of reactants on the deposition surface. Using the reactor shown in Fig. 3, solutions to these problems are being sought.

6. Conclusion

A technology for the deposition of silicon carbide tubing from thermal decomposition of CH_3SiCl_3 in a hydrogen atmosphere using electrical heating

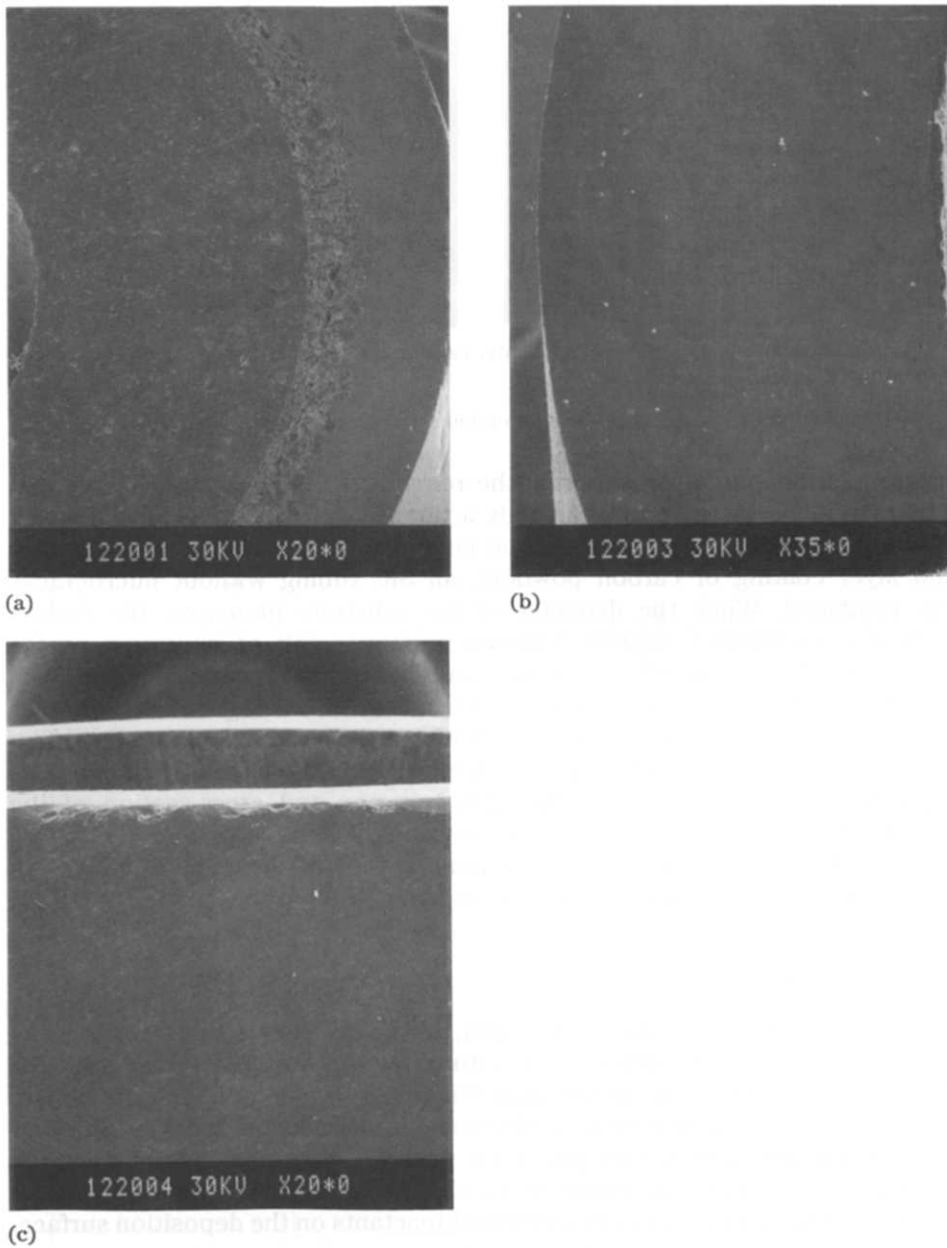


Fig. 11. SEM pictures of silicon carbide deposition with magnifications of (a) $\times 13$, (b) $\times 23$ and (c) $\times 13$.

is presented. The thermodynamic calculations give the optimum conditions for this procedure at atmospheric pressure: the surface deposition temperature of the substrate should be higher than $1100\text{ }^{\circ}\text{C}$, and the $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio

should be higher than 4. The detailed structure of the reactors used was described. Two critical problems in the operation of the deposition and their solutions were given. A method of carbon coating is used to eliminate the cracks induced by the different expansion coefficients of SiC coating and graphite substrate. Problems in scaling up were discussed.

References

- 1 D. E. Lloyd and V. C. Howard, The fabrication and properties of large-diameter tubes and coating in pyrolytic silicon carbide, in P. Popper (ed.), *Proc. 4th Symp. on Special Ceramics*, British Ceramic Research Association, Academic Press, London, 1967.
- 2 W. R. Martin, R. L. Heestand, R. E. McDonald and G. A. Reimann, Application of chemical vapor deposition to production of tungsten tubing, *Proc. Conf. on Chemical Vapor Deposition of Refractory Metal, Alloys, Compound, Gatlinburg, TN*, A. C. Schaffhauser (ed.), American Nuclear Society, Hinsdale, IL, 1967, p. 304.
- 3 H. O. Pierson, E. Randich and D. M. Mattox, The chemical vapor deposition of TiB₂ on graphite, *J. Less-Common Met.*, 67 (1979) 380.
- 4 T. Sato and T. Tachikawa, Formation of TiB₂ on a mild steel substrate by the CVD method, *Denki Kagaku*, 55 (10) (1987) 766.
- 5 S. Gordon and B. J. McBride (eds.), Computer program for complex chemical equilibrium compositions, rocket performance, incident and reflected shocks and Chapman–Jouguet detonations, *NASA SP-273*, NASA, Lewis Research Center, Cleveland, OH, 1976.
- 6 D. R. Stull and H. Prophet (eds.), *JANAF Thermochemical Tables*, 2nd edn., U.S. National Bureau of Standards, Washington, DC, 1971.
- 7 J. Chi, P. K. Gantzel and R. G. Undson, The substance of chemical-vapor-deposited silicon carbide, *Thin Solid Films*, 40 (1977) 57.
- 8 H. O. Pierson and A. W. Mullendore, Thick boride coatings by chemical vapor deposition, *Thin Solid Films*, 95 (1982) 99.
- 9 W. Abrams, A. Garg, S. Gonnella, J. Harding, R. Kaplan and R. Tuffaias, Large refractory metal free-standing shapes, *Proc. Conf. on Chemical Vapor Deposition of Refractory Metal, Alloys, Compound, Gatlinburg, TN*, A. C. Schaffhauser (ed.), American Nuclear Society, Hinsdale, IL, 1967, p. 293.
- 10 R. L. Gentiman, B. A. Dibenedetto, R. W. Tustison and J. Pappis, Chemical vapor deposition of ceramics for infrared windows, in H. O. Pierson (ed.), *Chemical Vapor Deposited Coatings*, American Ceramics Society, Westervill, OH, 1981, p. 46.
- 11 K. Hashimoto, K. Miura, T. Masuda, M. Tota, H. Sawai and M. Kawase, Growth kinetics of polycrystalline by thermal chemical vapor deposition method, *J. Electrochem. Soc.*, 137 (3) (1990) 1000.
- 12 V. I. Krukonis, Chemical vapor deposition of boron filament, in V. I. Matkovich (ed.), *Boron and Refractory Borides*, Springer, Berlin, 1977, p. 517.
- 13 R. H. Perry, D. W. Green and J. O. Maloney (eds.), *Chemical Engineering Handbook*, 6th edn., McGraw-Hill, New York, NY, 1973.