JOURNAL OF MATERIALS SCIENCE **33** (1998) 2537–2549

Synthesis of beta silicon carbide powders using carbon coated fumed silica

RASIT KOC, SAI V. CATTAMANCHI
Department of Mechanical Engineering and Energy Processes, Southern Illinois University, Carbondale, IL 62901, USA
E-mail: kocr@siu.edu

The synthesis of beta silicon carbide (β-SiC) powders by carbothermic reduction of carbon coated silica and silica mixed with carbon black was investigated. The production of β-SiC powders by using carbon coated silica consists of two steps. The first step is to prepare the carbon coated silica precursor by coating fumed silica particles with carbon by pyrolytic cracking of a hydrocarbon gas (C_3H_6). This provides intimate contact between the reactants and yields a better distribution of carbon within the fumed silica. Fumed silica was also mechanically mixed with carbon black for comparison. Both starting mixtures were reacted in a tube furnace for 2 h at temperatures of 1300 °C to 1600 °C in 1 l min^{-1} flowing argon. The reaction products were characterized using weight loss data, X-ray diffraction (XRD), a BET surface area analyser, oxygen and free carbon analysis and transmission electron microscopy (TEM). The carbon coating process resulted in a more complete reaction, purer product and high yield SiC powders with very little agglomeration at temperatures of 1500 °C and 1600 °C. The β-SiC powders produced at 1600 °C for 2 h in argon gas flow have oxygen content of 0.3 wt %, a very fine particle size 0.1–0.3 μm and uniform shape.

1. Introduction

Silicon carbide (SiC) is a prominent material used in advanced ceramic applications with many superior properties such as high hardness and strength, excellent oxidation resistance, and high thermal conductivity [1]. The final properties of the sintered SiC material depend largely on the sintering method and the characteristics of the starting powder. In general, high densities in the sintered components require the use of submicrometre particles and chemically pure starting powders. A number of processes [2] exist for producing fine silicon carbide powders, and they can be classified into three categories: i) the direct carbonization of silicon metal, ii) the pyrolysis of silane compounds, and iii) the carbothermal reduction of SiO_2 with carbon in an inert atmosphere at temperatures above 1600 °C. Methods (i) and (ii) are capable of producing chemically high purity SiC powders. However, the high cost of the silicon source used in method (i) leads to a relatively expensive SiC product while the precursors used in method (ii) are hazardous and are also of high cost [3]. SiC powder is commercially produced primarily by method (iii), the reduction of SiO_2 by carbon in a temperature range between 1600–2100 °C as shown by reaction 1:

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \qquad (1)$$

This is an inexpensive process. Because the reactants exist as separate particles, the extent of this reaction is limited by the contact area between the reactants and the distribution of the carbon within the SiO_2. These limitations result in a product that contains unacceptable quantities of unreacted silica and carbon. The SiC powder produced has a relatively wide size range, due to grain growth and bonding together of the individual particulates during the reduction reaction and therefore requires subsequent milling. For this process, reaction time is typically very long (10–20 h), and heterogeneities due to diffusion gradients established during the reduction reaction.

It is also well known that the actual reaction mechanism in the carbothermal process proceeds through the subsequent reaction of gaseous silicon monoxide according to the following sequence:

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \qquad (2)$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \qquad (3)$$

For reaction 1, the Gibbs free energy change is positive up to about 1514 °C. In order to promote the overall reaction to occur at lower temperatures, CO has to be continuously removed from the system. However, the gaseous silicon monoxide formed together with the carbon monoxide has a high vapour pressure and tends to be swept away and lost from the reaction chamber unless reacted with carbon. Silicon monoxide loss results in a lowered SiC yield. Therefore, the intimate contact of carbon with SiO_2 and SiO is essential during the reactions for complete conversion of SiO_2 into SiC and for a high SiC yield.

The generation of SiO via reaction 2 requires temperatures above approximately 1754 °C for it to proceed under equilibrium conditions at atmospheric pressure. Since reaction 3 is favourable over the entire temperature range, a reduced CO partial pressure allows the overall reaction to occur at lower temperatures by improving the favourability of SiO generation via reaction 2. It should be noted that the reactants in reaction 2 are both solids. Weimer *et al.* [4] observed that reaction 2 is feasible only at points of direct contact between C and SiO_2 and hence it takes place during the initial period only. After the direct contact points are consumed, reaction 2 most likely ceases.

Klinger *et al.* [5] and Lee and Cutler [6] in their research on the formation of silicon carbide from rice hulls, proposed SiO generation to occur through dissociation of SiO_2 in the following manner:

$$SiO_2(s) = SiO(g) + 1/2O_2(g) \qquad (4)$$

$$C(s) + 1/2O_2 = CO(g) \qquad (5)$$

Further, Weimer *et al.* [4], Wei *et al.* [7] and Miller *et al.* [8] proposed the following reaction steps as rate limiting:

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) \qquad (6)$$

$$C(s) + CO_2(g) = 2CO(g) \qquad (7)$$

Since the formation of SiO is the rate limiting step, the mixing condition of two raw materials (silica and carbon) greatly influences the rate of reactions and the properties of the final product. Therefore, the intimate contact of carbon with SiO_2, SiO and CO_2 is required during the reduction in order for complete conversion of SiO_2 into SiC.

In the present work, the minimization of the rate limiting step is achieved by the carbon coating of silica particles. This provides intimate contact between carbon and silica and an even distribution of carbon among the silica particles. A detailed description of the carbon coating method and comparison with commercial processes are presented. The physical, chemical and crystalline nature of the produced powders and the effects of process variables are discussed.

2. Experimental procedure

2.1. Starting SiO_2 powders

The starting silica powders were a high surface area fumed SiO_2 from Cabot Corp. (Cabosil EH-5, Springfield, IL). The transmission electron microscopy (TEM) micrograph of the Cabosil EH-5 SiO_2 particles (Fig. 1) showed that it has an average particle size of 10 nm. These particles were in the form of three-dimensional chain-like, approximately 0.5–10 μm size agglomerates. Cabosil fumed silica is the purest commercially available amorphous silica. It contains at least 99.8% by weight silicon dioxide on an ignited weight basis.

2.2. Preparation of carbon coated precursors

The precursor powders were prepared using a rotating coating apparatus, consisting of a 10 cm internal diameter (i.d.) × 35 cm long stainless steel vessel used for preparing the pyrolytic carbon coated SiO_2 particles utilizing propylene (C_5H_6) as the coating gas. About 100 g of silica powder were placed in the vessel and the vessel was evacuated, purged with argon, and again

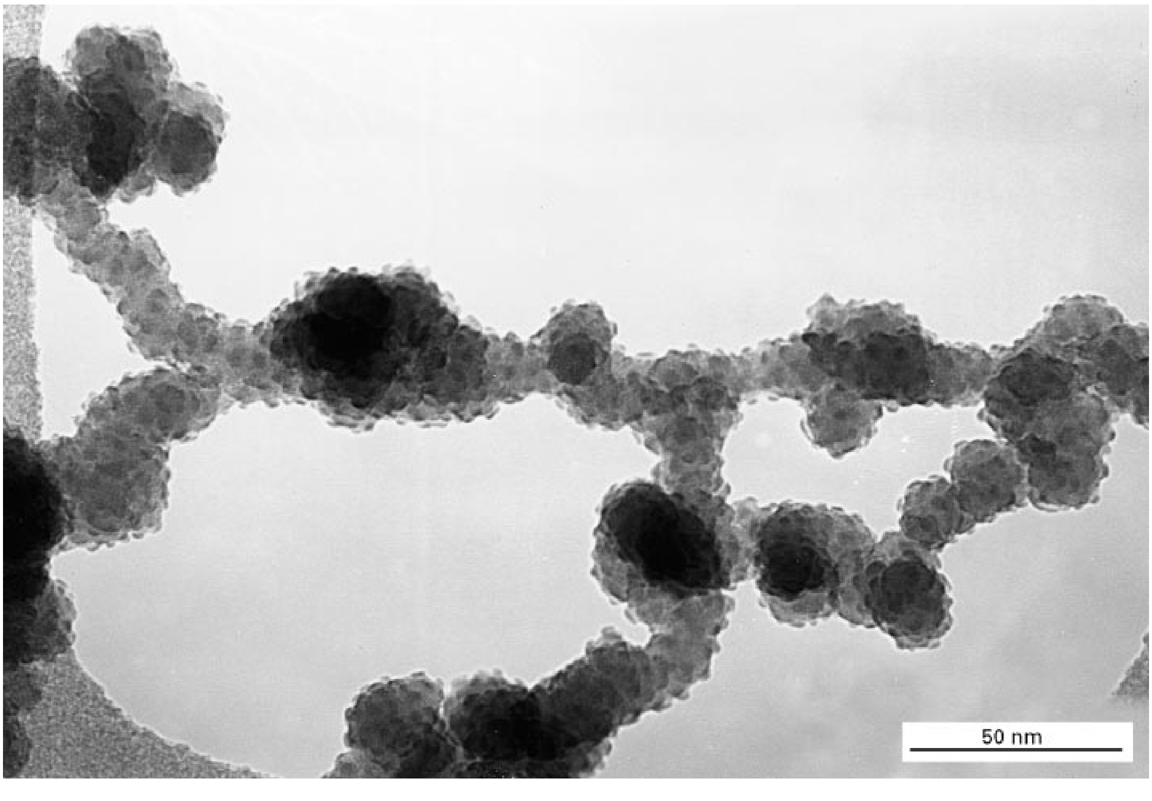

Figure 1 TEM micrograph of Cabosil EH-5 fumed silica.

evacuated to a moderate vacuum level, using a rotary vacuum pump. Then the vessel was heated to 600 °C for 30 min, and filled with propylene gas until the pressure reached 2.5×10^5 Pa. Thermal cracking of propylene increased the internal vessel pressure to approximately 3.5×10^5 Pa upon initiation of the carbon coating. After 20 min the remaining gas was released and the vessel was filled with fresh propylene. After every third cycle the vessel was evacuated, purged with argon, and again evacuated before filling with propylene. The coating step was continued until 38.6 wt % of carbon was deposited, which required about thirty cycles. The amount of carbon in the precursor was determined by measuring the weight loss in the powder after the carbon coated precursor was exposed to air, at a temperature of 750 °C, for 4 h.

2.3. Preparation of SiO_2 and carbon black mixtures

Fumed SiO_2 and carbon black (Monarch 880, Cabot, Waltham, MA) samples were prepared by adding 61.4 g (61.4 wt %) of SiO_2 with 3.86 g (38.6 wt %) of carbon black (particle size = 16 nm, surface area of 220 m^2g^{-1}). The SiO_2 and carbon black mixtures were placed in a plastic container (i.d. = 5 cm, height = 7 cm) and milled with four polymethylcrylate balls for 6 h in a Spex (Model 8000 Mixer/Mill, Meutuchen, NJ) mixer.

2.4. Synthesis of SiC powders

The carbon coated fumed silica precursors and the fumed silica with carbon black mixtures were then synthesized in a tube furnace (Model CTF 17/75/300, Carbolite, Hope, Sheffield, UK) with an i.d. of 70 mm. Ten grams of a given sample for each temperature (1300, 1400, 1500 and 1600 °C) were placed in a graphite crucible (i.d. = 65 mm, length = 10 cm). The furnace was first evacuated before a flowing stream of argon at 1 l min^{-1} was supplied. The SiC powders were then produced by promoting a carbothermal reduction within the carbon coated silica and mixed silica and carbon black samples. The samples were synthesized at temperatures ranging from 1300 to 1600 °C for 2 h to investigate reaction mechanisms and determine an optimal reaction temperature. A heating rate of 4 °C min^{-1} and a cooling rate of 4 °C min^{-1} was used.

2.5. Characterization of powders

The starting materials, intermediate products and the reaction products were characterized using X-ray diffraction (XRD) (Model DMAX-B, Rigaku, Tokyo) with CuK_α radiation, a BET surface area analyser (Gemini 2360, Micromeritics, Norcross, GA), and transmission electron microscopy (TEM) (Model Fa 7100, Hitachi, Tokyo). Oxygen was analysed by infrared detection in a LECO R0416DR (St. Joseph, MI) induction furnace, while free carbon content was determined by heating the powders in air at 750 °C for 4 h.

3. Results and discussion

Fig. 2 shows a TEM micrograph of the carbon coated fumed silica precursors. The darker areas are silica

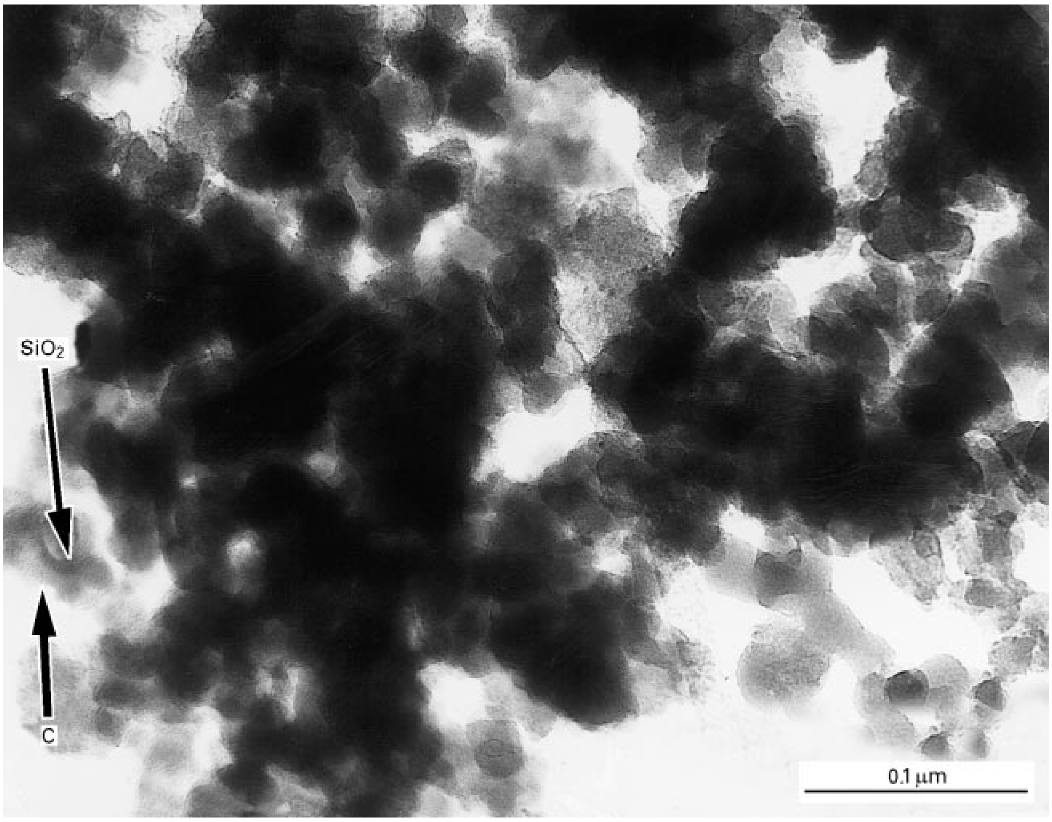

Figure 2 TEM micrograph of Cabosil EH-5 fumed silica coated with carbon.

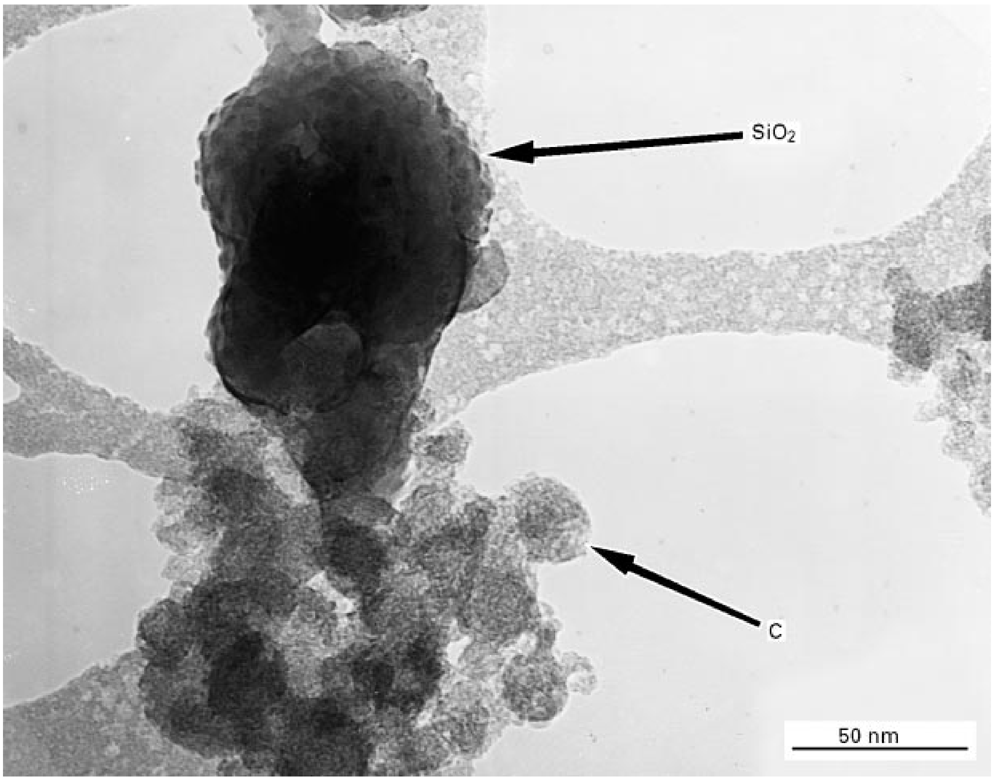

Figure 3 TEM micrograph of Cabosil EH-5 fumed silica mixed with carbon black.

particles and the lighter areas surrounding the darker areas are the carbon coating. As shown in Fig. 2, a uniform coating of pyrolytic, highly porous and low density carbon on silica is apparent. The BET surface area of the silica powder decreased from 310 to 260 $m^2 g^{-1}$. These results showed that a uniform, highly porous and low density carbon coating can be obtained at 600 °C on silica particles by using C_3H_6 gas. These precursors provide intimate contact between the reactants and results in a very low silicon monoxide loss. In addition, they are capable of producing high purity SiC particles at low temperatures, because the carbon source is a hydrocarbon gas. Therefore, impurities, such as iron, which is ordinarily found in commercial carbon material, are eliminated. The use of the precursor results in the production of submicrometre and uniform size SiC particles, because the agglomeration of the oxides of silicon is also inhibited by a carbon layer.

Fig. 3 shows a TEM micrograph of the SiO_2 mixed with carbon black. As shown in Fig. 3, the contact area between the silica and carbon black is inconsistent; therefore, there will be no immediate availability of carbon when SiO is generated during the reactions. Consequently, the reduction reactions will reverse and the resultant powders will have hard agglomerates with very low SiC yield.

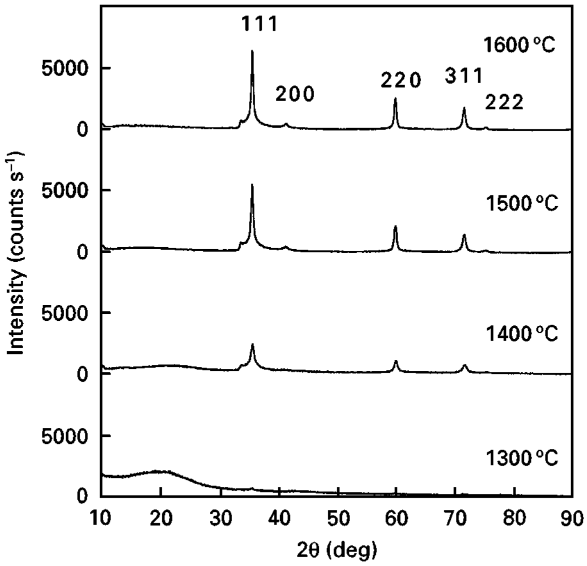

Figure 4 XRD results of reaction products from fumed silica mixed with carbon black and produced at 1300–1600 °C for 2 h in flowing argon.

3.1. Mixed Precursor

3.1.1. Reaction products at 1300 °C

X-ray diffraction (Fig. 4) of reaction products of mixed precursor at 1300 °C show no crystalline nature. From weight loss data (Fig. 5) it can be seen that the reaction did not go to completion at this temperature. The surface area of the products has decreased when compared to the unreacted precursor. When the surface area of the reacted products was measured after removing carbon (Fig. 6), it was very low compared to the products with carbon. Most of the surface area in the original product is due to unreacted carbon. Fig. 7 shows the TEM micrographs of the reaction products. In the absence of considerable silica conversion to form silicon carbide, silica particles have been

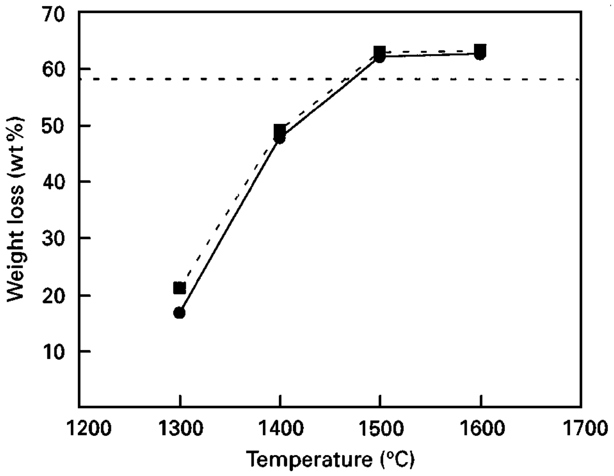

Figure 5 Weight loss versus temperature for coated (●) and mixed (■) fumed silica precursors (theoretical weight loss = 58.3 wt %).

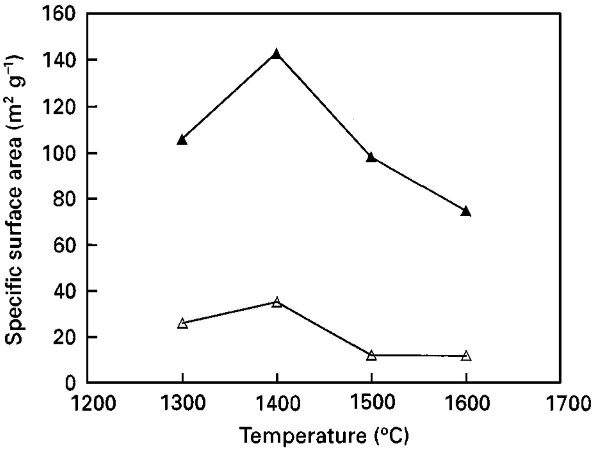

Figure 6 BET surface area versus temperature for mixed precursor before (▲) and after (△) carbon removal.

observed to fuse together to form very low surface area particles. Carbon particles (Fig. 8) have been observed to retain their morphology. Extensive examination of the high surface area particles did not reveal any visible traces of silicon carbide formation. However, substantial silicon loss from the system has been observed, indicating that the reaction proceeds via SiO(g) formation. Formation of SiO(g) proceeds, initially, through solid state reaction 2. Reaction 2 stops as the contact points are consumed. In view of extensive growth of silica particles, it is highly unlikely that reaction 4 can occur at this stage. It has been assumed that further SiO(g) generation proceeds through reaction 6.

3.1.2. Reaction products at 1400 °C

The basic difference that started to show in these reaction products when compared to those obtained at 1300° is the crystalline nature. The XRD patterns (Fig. 4) of the reaction products at this temperature show considerable formation of silicon carbide. The weight loss is much higher when compared to the reaction at 1300 °C. However, the weight loss did not cross the theoretical limit of 58.3 wt % for complete conversion. The reaction remained incomplete at this temperature also. Because of increased reaction and formation of silicon carbide, as denoted by weight loss and XRD, the free carbon (Fig. 9) and oxygen content (Fig. 10) were lower when compared to reaction

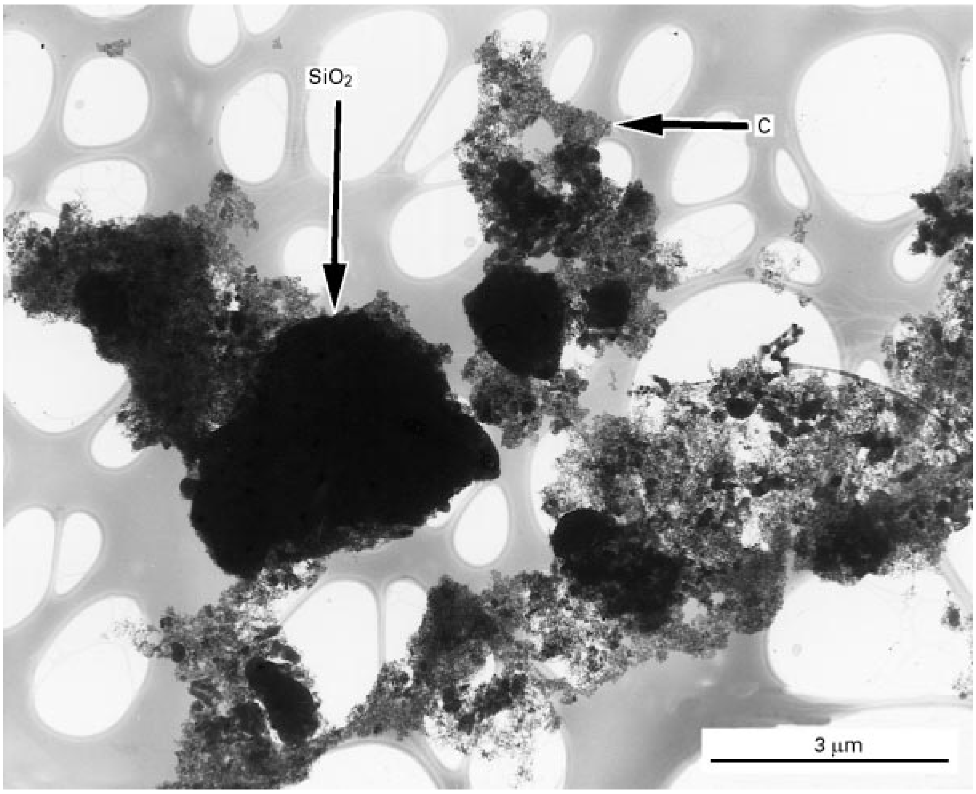

Figure 7 TEM micrograph of mixed precursor reaction product at 1300 °C for 2 h in flowing argon.

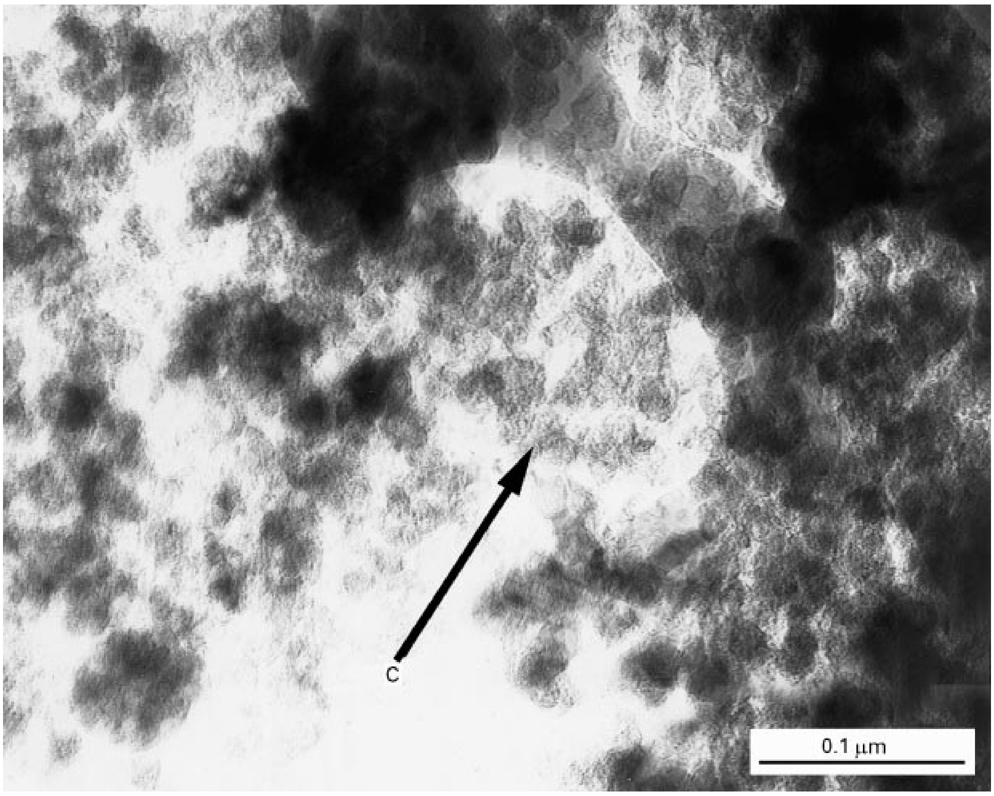

Figure 8 TEM micrograph of mixed precursor reaction product at 1300 °C for 2 h in flowing argon (lower magnification).

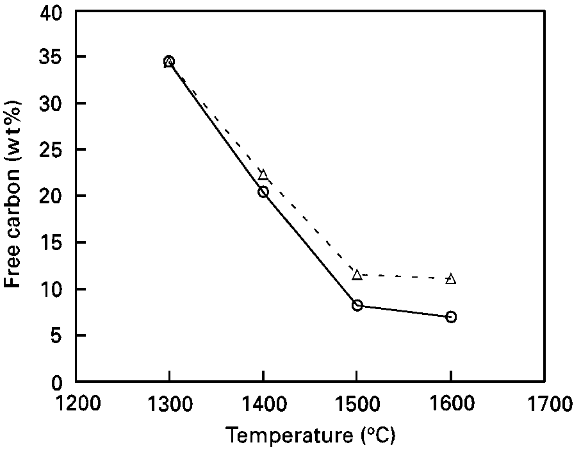

Figure 9 Free carbon content versus temperature for coated (○) and mixed (△) precursors reaction products.

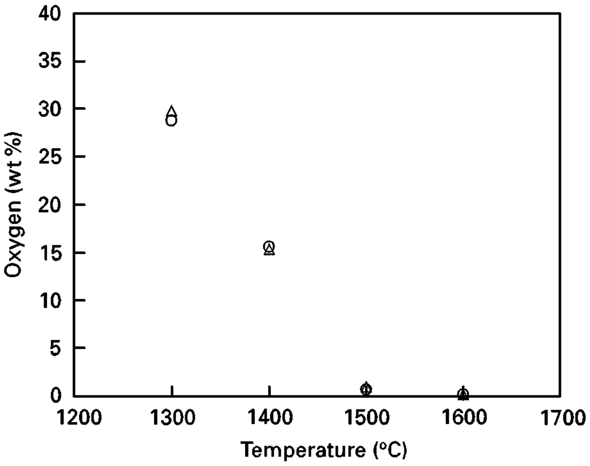

Figure 10 Oxygen content versus temperature for coated (△) and mixed (○) precursors reaction products.

products at 1300 °C. In contrast to the idea that surface area of the particles should decrease with increase in temperature, the surface area of the reaction products increased with increase in reaction temperature. Even when carbon has been removed the surface area of the reaction products was higher when compared to the corresponding value at 1300 °C. TEM micrographs in Figs 11 and 12 show the reaction products with and without carbon. Fusing of silica particles is still observed at this temperature, however, the size of the fused particles is smaller when compared to those seen at 1300 °C and have a smoother appearance. Fusing of silica particles occurs in the heating stage and, as a result of the gas-solid reaction 6, silica is gradually consumed. The improved conversion resulted in smaller silica particles. The morphology of the silicon carbide is very much like that of carbon. Each of the carbon particles have transformed to silicon carbide particles. However, extensive necking of formed SiC particles has been observed after the carbon has been removed. This suggests that the SiO(g) and carbon reaction (reaction 3) starts at the carbon neck areas where the chemical potential of atoms is highest. This resulted in silicon carbide powders that showed the morphology of carbon with an agglomerate structure (Fig. 12) similar to that of carbon in the initial precursor (Fig. 3). Further, some of the particles have coalesced to form larger

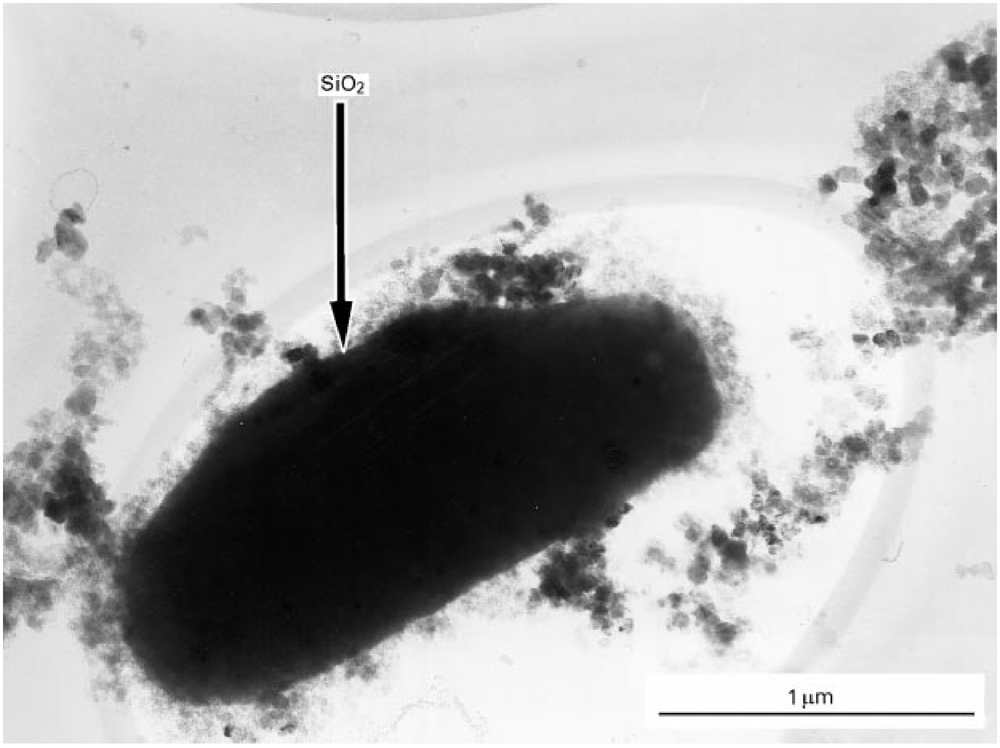

Figure 11 TEM micrograph of mixed precursor reaction product at 1400 °C for 2 h in flowing argon (unreacted silica particles).

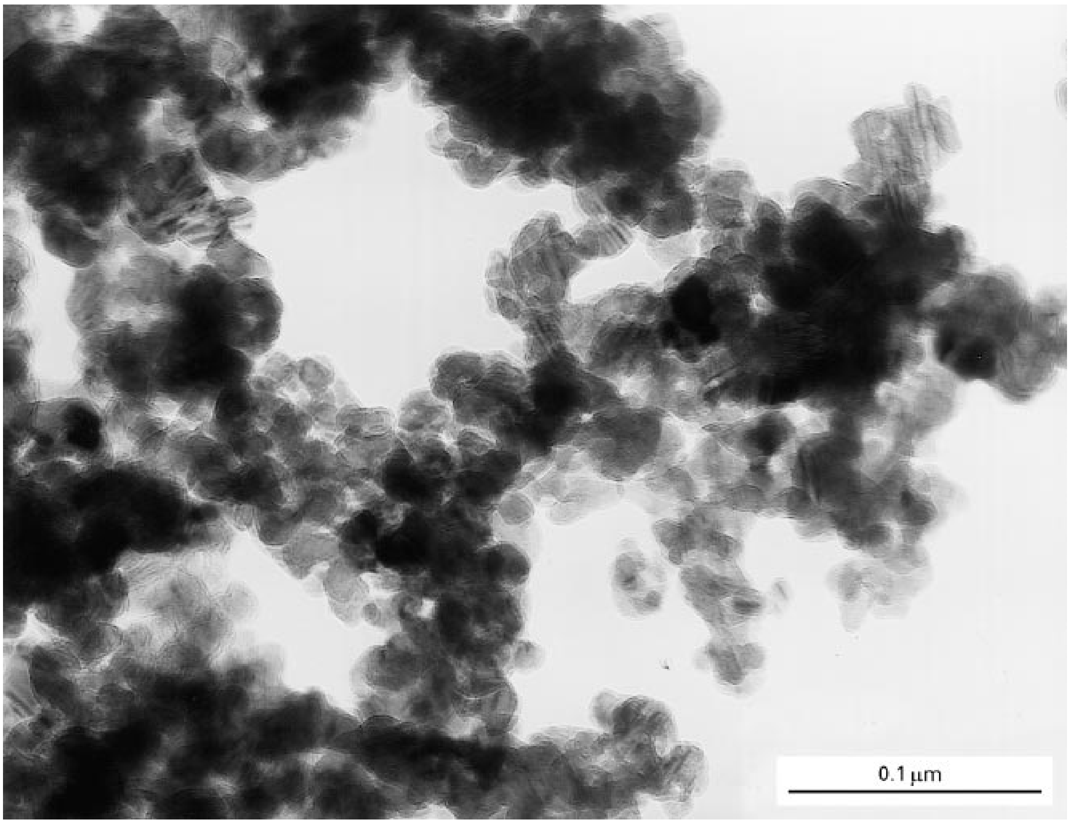

Figure 12 TEM micrograph of mixed precursor reaction product at 1400 °C for 2 h in flowing argon (SiC particles).

polycrystalline particles. Since the individual crystallites still resemble carbon, surface diffusion has been assumed to be responsible for the polycrystalline nature.

3.1.3. Reaction products at 1500 °C and 1600 °C

Complete conversion of silica has occurred at these temperatures. X-ray diffraction patterns (see Fig. 4)

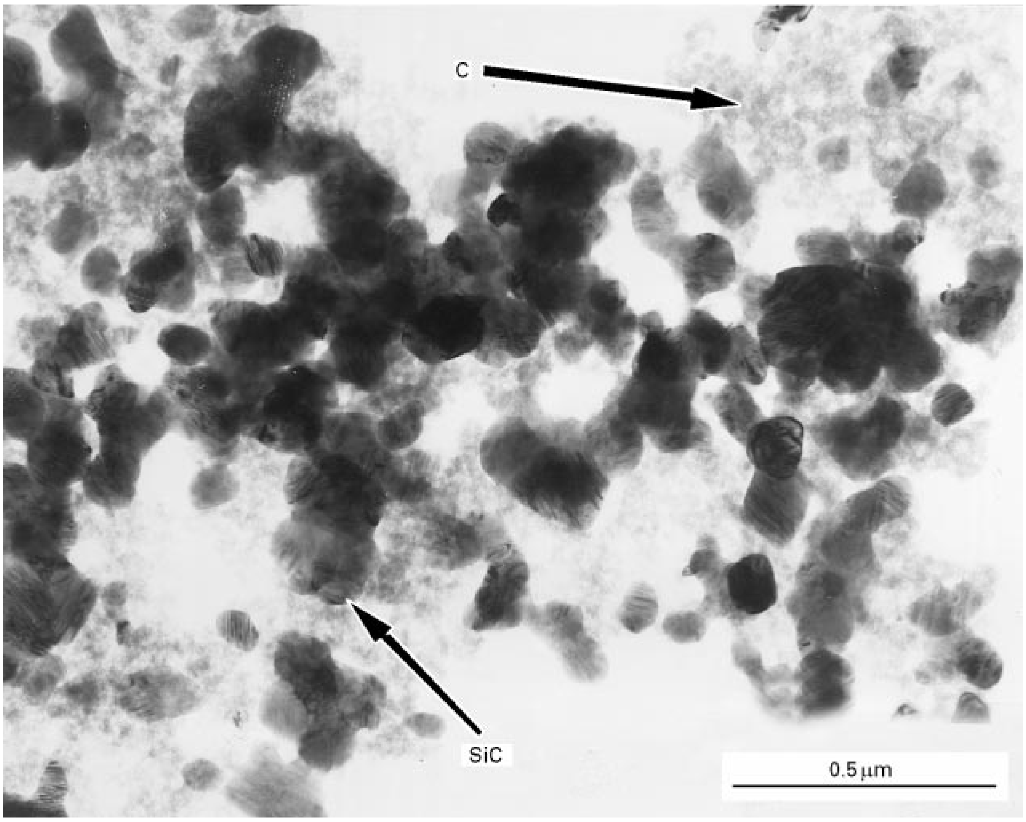

Figure 13 TEM micrograph of mixed precursor reaction product at 1500 °C for 2 h in flowing argon.

show sharp and well defined peaks. Weight loss is over the theoretical value and in spite of the temperature difference in these two products there is negligible difference in the weight loss (Fig. 5). This suggests that the mechanism of formation of silicon carbide at 1600 °C is predominantly the same as that at 1500 °C. Moreover, the difference in the amount of free carbon in the two reaction products is very small (Fig. 9). This indicates that the rate of SiO, and thus the SiC, formation is similar at both these temperatures. SiO(g) generation occurs predominantly through reaction 6. The size of the SiC particles produced at these temperatures is quite similar. The powders produced at 1600 °C are slightly lower surface area than those produced at 1500 °C. Oxygen content in these two reaction products was found to be very low; 0.3 wt % at 1600 °C and 0.7 wt % at 1500 °C. Such low content and the minor difference in the values reflects that whatever oxygen present is not in the form of silica particles, is associated with the surface of the silicon carbide particles.

Figs 13 and 14 show the TEM micrographs of silicon carbide powders produced at 1500 °C and 1600 °C, respectively. The size of most of the SiC particles is in multiples of the size of the carbon used in the precursor. However, the SiC produced at 1400 °C is in relation to the size of the carbon used. The basic difference between these two sets of reaction products is temperature. However, considering only the 1500 °C and 1600 °C products, the temperature difference did not affect the particle size at these temperatures to the extent to which it affected the reaction products at 1400 °C and 1500 °C. This difference seems to depend not only on temperature but also on SiO generation and subsequent formation of SiC. Kevorkijan *et al.* [9] proposed several routes of coalescence and growth in SiC particles: (i) direct formation of SiC agglomerates from agglomerated particles of carbon black, (ii) formation of polycrystalline aggregates of SiC which bond subsequently into strong agglomerates, (iii) formation of individual SiC crystallites which coalesce into aggregates and agglomerates, and (iv) at higher temperature, aggregates and agglomerates transform into monocrystalline particles by bulk diffusion.

At low SiO generation formation and growth of SiC seem to occur through route (i). When SiO generation is sufficiently fast, i.e. at temperatures of 1500 °C and 1600 °C, formation and growth of SiC, however, seem to proceed in the following order: (1) formation of individual crystallites which coalesce into primary aggregates, (2) groups of such primary aggregates coalesce to larger secondary aggregates or form agglomerates and simultaneous transformation of primary aggregates into monocrystalline particles by bulk diffusion. The formation of monocrystalline particles is driven by the size of the individual crystallites in aggregates at a particular reaction temperature for a constant time of reaction. Probable higher bulk diffusion in powders produced at 1600 °C when compared to the powders produced at 1500 °C did not affect the particle size of the 1600 °C SiC powder because the transformed monocrystalline particles are of larger size and retard further growth.

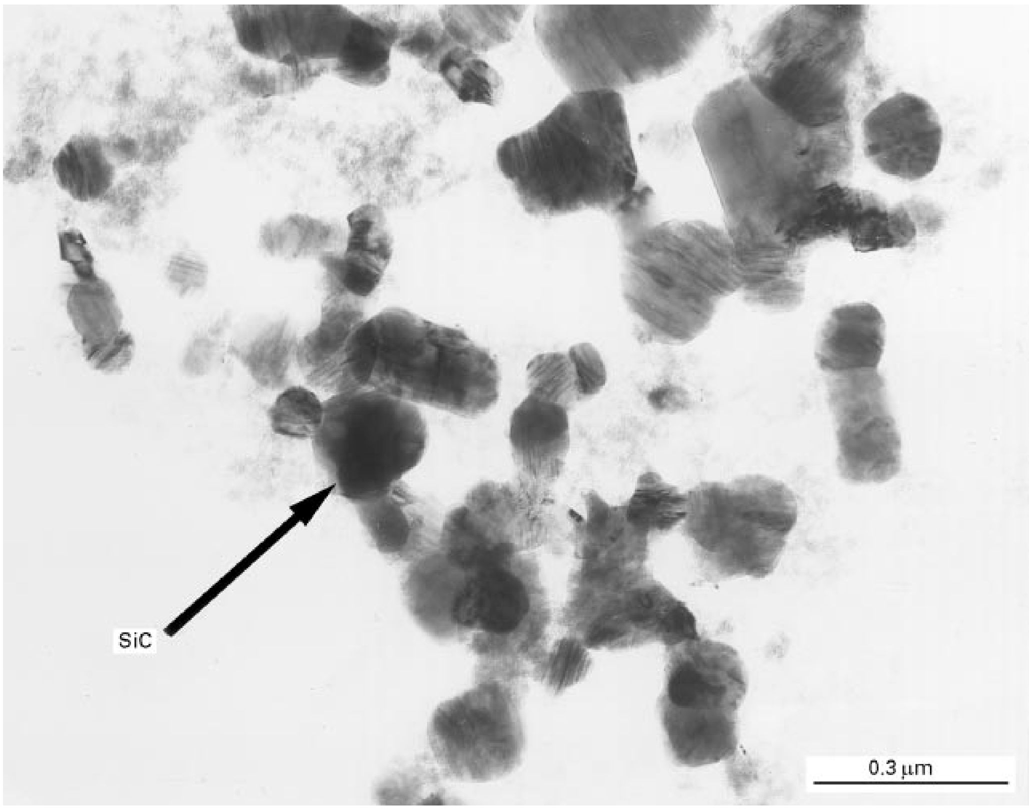

Figure 14 TEM micrograph of mixed precursor reaction product at 1600 °C for 2 h in flowing argon.

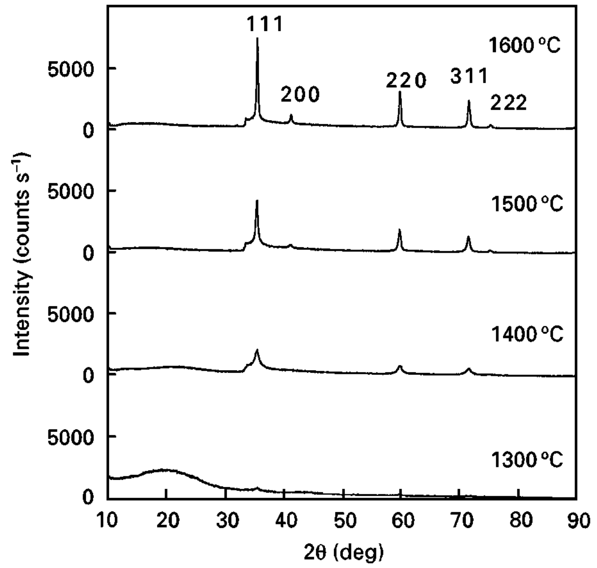

Figure 15 XRD results of reaction products from fumed silica coated with carbon and produced at 1300–1600 °C for 2 h in flowing argon.

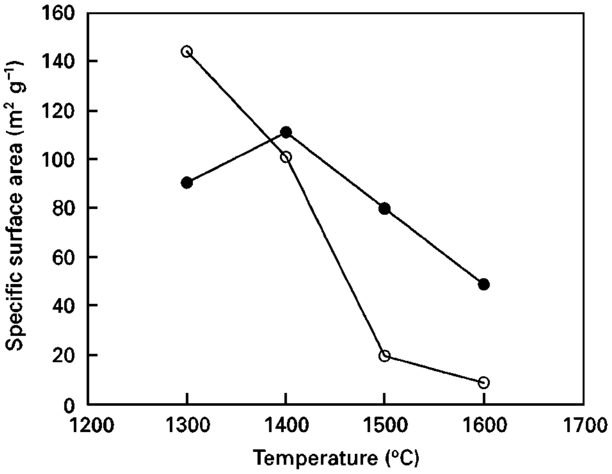

Figure 16 BET surface area versus temperature for coated precursor before (●) and after (△) carbon removal.

3.2. Coated precursor

3.2.1. Reaction products at 1300 °C

The XRD pattern in Fig. 15 shows very little formation of SiC. The weight loss is appreciably less, when compared to the same data of the mixed precursor at this temperature (Fig. 5). While the amount of free carbon (Fig. 9) is the same as that in the mixed precursor, the amount of silica (Fig. 10) left in the system is more than that found in the reaction products of the mixed precursor at this temperature. Fig. 16 shows the surface area of the reaction products of coated precursor with and without carbon. In contrast to the mixed precursor, the surface area of the powders of the coated precursor without carbon is greater than the surface area of the products with carbon. As discussed earlier, carbon is deposited over the silica particles and results in a reduction in surface area of the silica particles. At this temperature, as seen from TEM (Fig. 17), the coating has not broken up completely due to carbothermal reduction. Thus, when the carbon is removed the surface area of the reaction products appears to be higher because of silica which is of higher surface area and which constitutes the majority

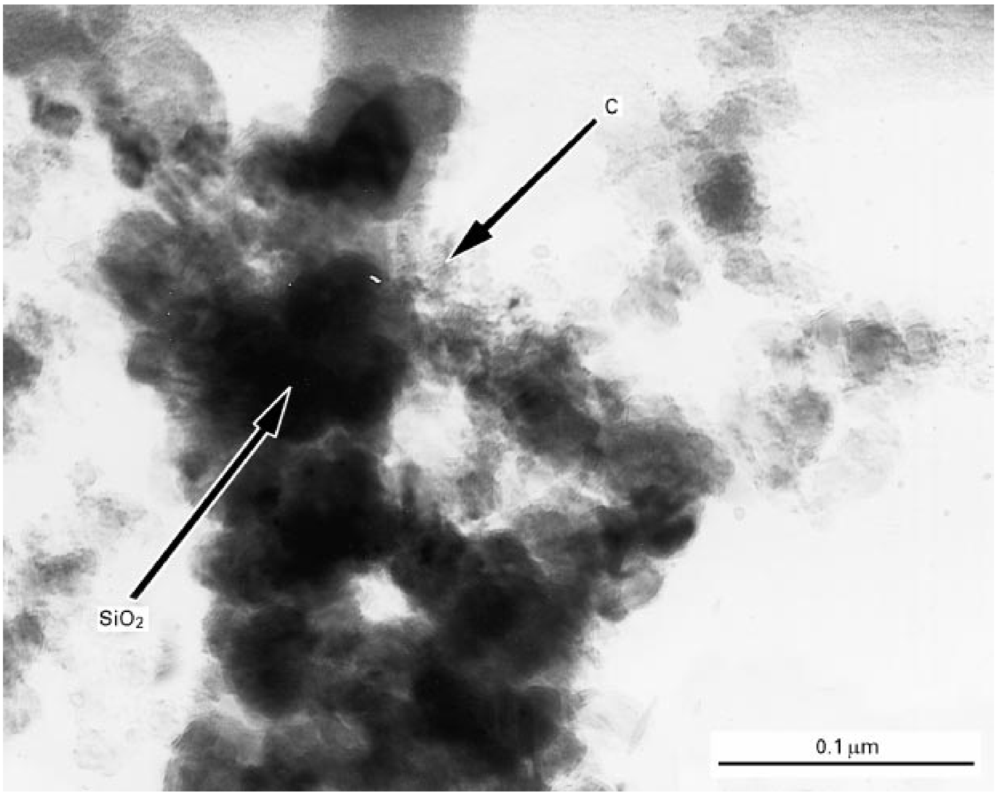

Figure 17 TEM micrograph of coated precursor reaction product at 1300 °C for 2 h in flowing argon (carbon coating).

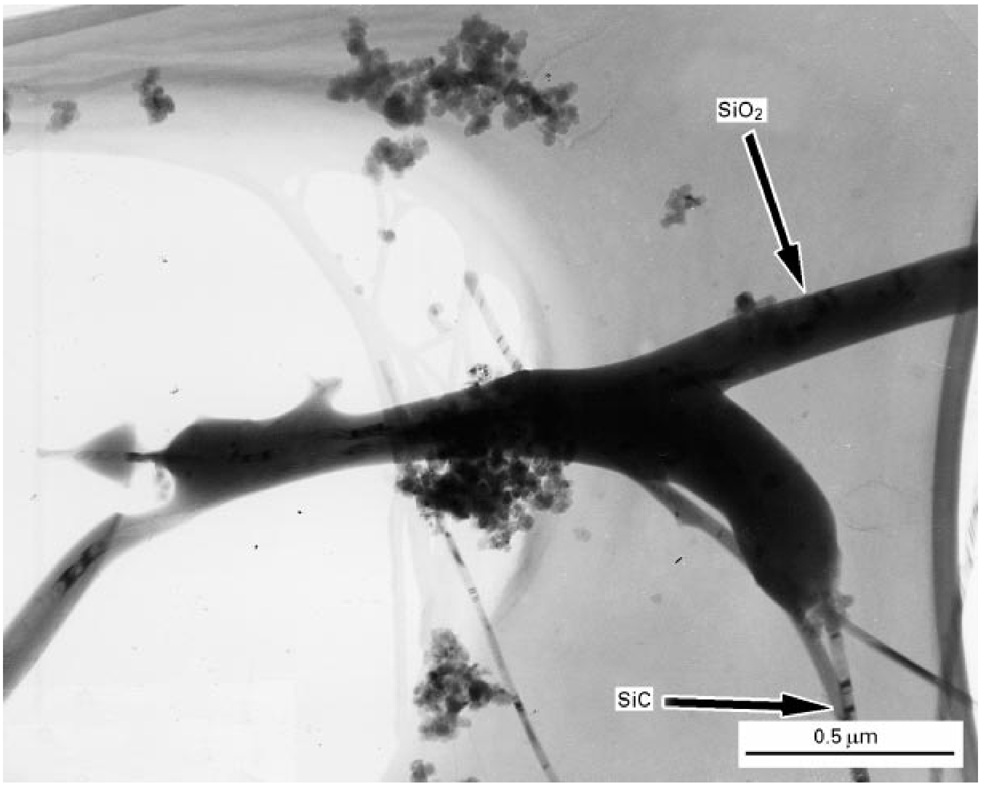

Figure 18 TEM micrograph of coated precursor reaction product at 1300 °C for 2 h in flowing argon (unreacted silica containing SiC based whiskers).

of the reaction products. Moreover, carbon coating inhibited fusing of silica to form larger particles, as is seen in the case of the mixed precursor. The TEM micrographs (Fig. 18), however, show long and bent fibres of amorphous SiO_2 and few SiC whiskers which might have been the reason for the spongy nature of the powders produced. Observing the morphology, the formation of these SiC whiskers with pockets of silica covering them is believed to occur due to the reaction:

$$3SiO(g) + CO(g) = SiC(s) + 2SiO_2(s) \qquad (8)$$

The interaction between SiO(g) and CO(g) is increased by the intimate contact arising from carbon coating which contains these reactants in the reaction mixture. This behaviour is not observed in the mixed precursor since such intimate contact is not present in the mixed precursor. The low weight loss and occurrence of reaction 8 suggests that most of the SiO(g) is generated by the solid–solid reaction 2. At this temperature, very fine SiC particles are formed with little or no agglomeration. Sizes of the formed SiC particles depend on the availability of SiO(g). Agglomeration is inhibited by the presence of unreacted carbon, which is very high.

3.2.2. Reaction products at 1400 °C

The gas-solid reaction 6 is enhanced at this temperature and, as a result, higher conversion of silica has been observed. Surface area (Fig. 16) and TEM (Fig. 19) data indicate break up of the carbon coating at this temperature. Accordingly, very few SiO_2 and SiC whiskers are seen at this temperature. As the temperature of the reaction is increased, solid–solid reaction 2 seems to proceed instantaneously and the increased rate of reaction 6 resulted in the break up of the carbon coating. As a result, fusing of silica particles is observed to a small extent, however, it is limited by the simultaneous reduction by CO(g). The morphology of SiC formed at this temperature is shown in Fig. 19.

3.2.3. Reaction products at 1500 °C and 1600 °C

Complete conversion of silica has been observed at this temperature. XRD data show the formation of β-SiC. However, the peaks for 1500 °C are observed to be broader than the peaks for 1600 °C (see Fig. 15). The weight loss (Fig. 5) and free carbon contents (Fig. 9) are similar at both these temperatures. In relation to the mixed precursor, the reaction proceeded identically at both these temperatures. However, in contrast to the mixed precursor, there is significant difference in the surface area of the SiC produced at these two temperatures. According to Greskovich and Rosolowski [10], surface diffusion may be responsible for the observed surface area reduction in SiC particles at temperatures below 1500 °C during sintering. Kevorkijan *et al.* [9], suggest that growth of SiC particles occurs primarily by bulk diffusion at temperatures above 1500 °C. The present results are in agreement to the results of Greskovich and Rosolowski [10] and Kevorkijan *et al.* [9]. Carbon in the precursor is of very fine size and is in the form of a coating. These carbon particles crystallize into SiC throughout the reaction mixture depending on the availability of SiO(g). Once crystallization occurs, the growth proceeds through surface and/or volume diffusion mechanisms. Figs 20 and 21 show TEM micrographs of SiC produced at 1500 °C and 1600 °C, respectively. The SiC produced at 1500 °C primarily grows by surface diffusion. A large reduction in surface area of the SiC produced is observed at temperatures of 1600 °C owing to the dominance of bulk diffusion. These results indicate that the particle size and growth of SiC derived from coated precursor is influenced to a large extent by the temperature of the reaction.

The major difference between the coated precursor and mixed precursor is seen in the SiC yield. For the same compositions of the precursor, higher free carbon contents are found in the mixed precursor while

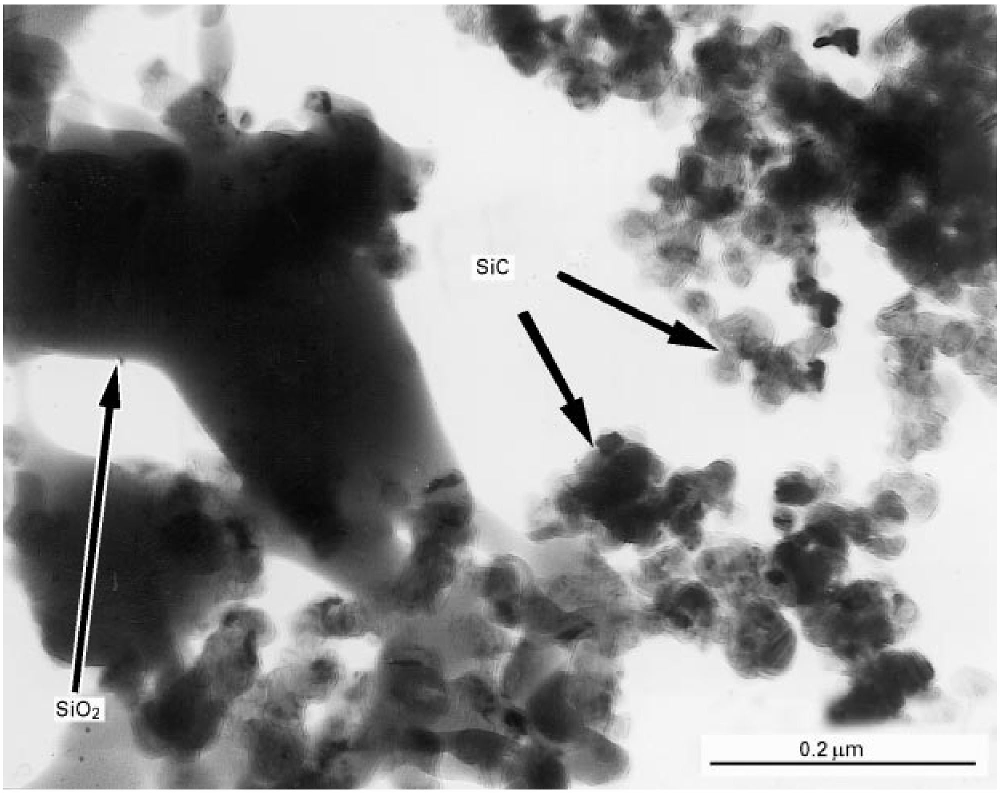

Figure 19 TEM micrograph of coated precursor reaction product at 1400 °C for 2 h in flowing argon.

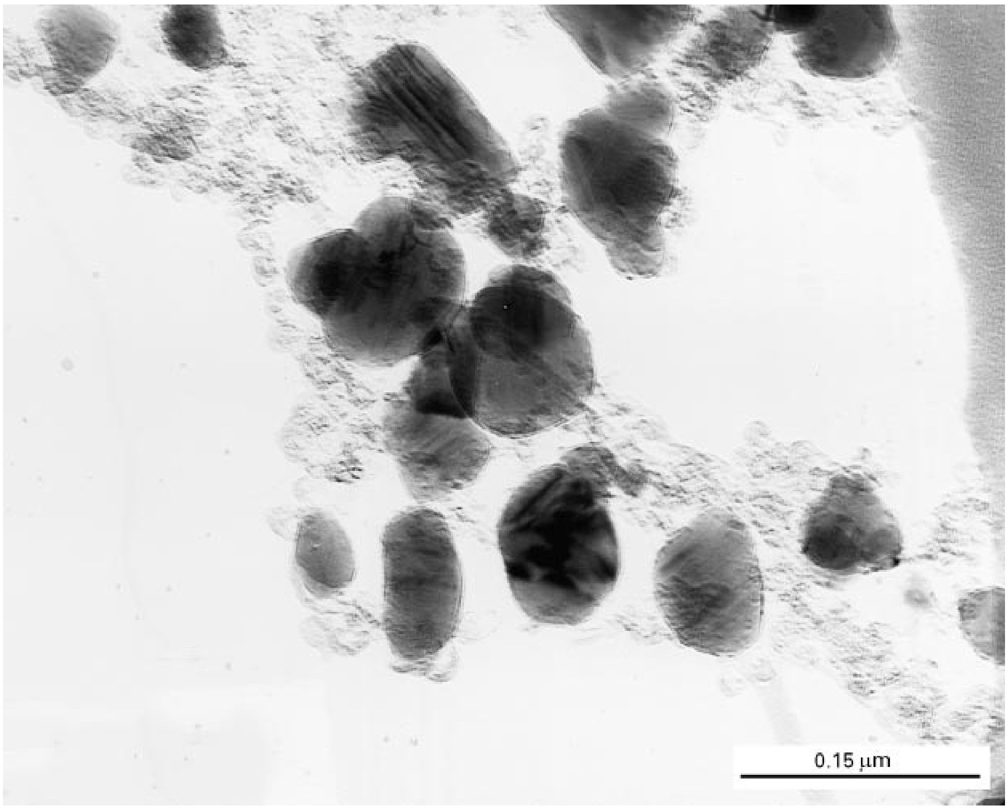

Figure 20 TEM micrograph of coated precursor reaction product at 1500 °C for 2 h in flowing argon.

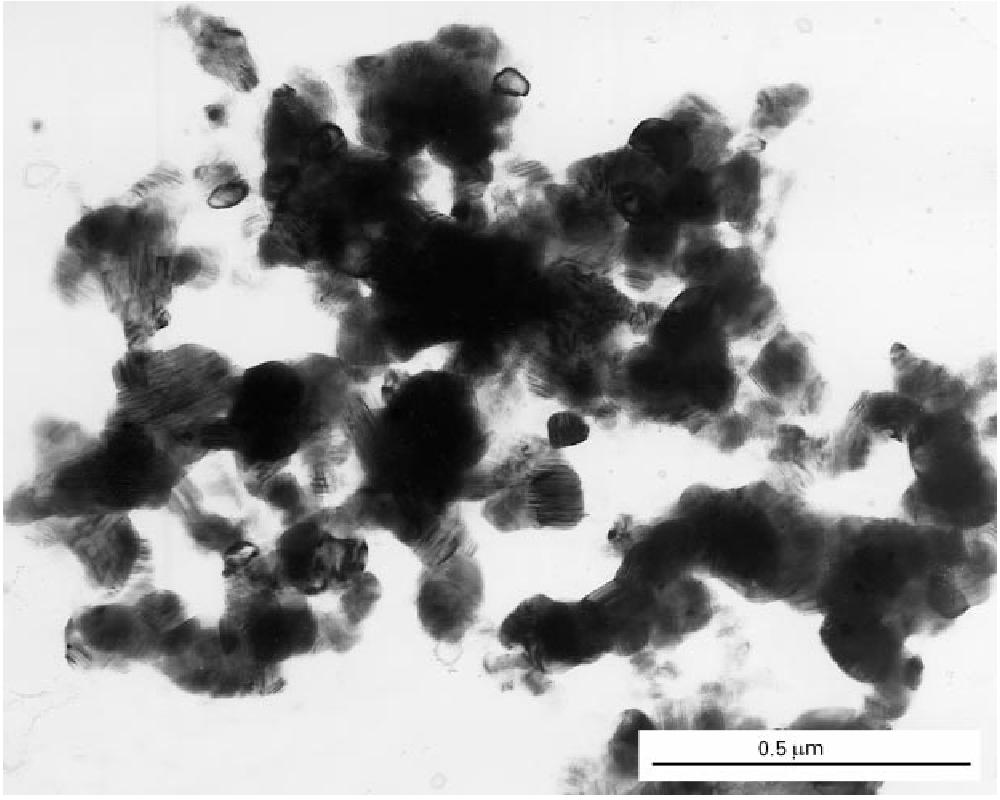

Figure 21 TEM micrograph of coated precursor reaction product at 1600 °C for 2 h in flowing argon.

the oxygen content in the products remained the same. This implies that a higher loss of SiO(g) occurs in the reaction of mixed precursor. This can be attributed to both the quality of mixing and the nature of the carbon used. Uniform dispersion of carbon in the mixture would result in the capturing of SiO(g) as it is generated, thereby reducing the loss of SiO(g). The fine nature of the carbon in the coated precursor would also have resulted in faster conversion of carbon into SiC. If the time of reaction is less, reduced loss of

SiO(g) in the sweep gas can be concluded. However, this needs to be confirmed by kinetic studies.

4. Conclusions

The carbon coating process is capable of producing high quality SiC powders suitable for making ceramic materials and composites. When reacted at 1600 °C for 2 h in flowing argon atmosphere, the carbon coated fumed silica resulted in β-SiC powders that showed: fine particle size (0.1–0.3 μm), oxygen content of 0.3 wt %, uniform particle shape and loose agglomeration between particles. This process is patented [11] and received an R&D 100 award in 1995 [12].

Both precursors showed similar behaviour for the formation of SiC particles. Reaction at high temperatures proceeds, most likely, through reduction of SiO_2 by gaseous CO. However, the quality of mixing affects the reaction path at low temperatures. TEM investigations indicate that SiC forms on carbon particles, but the growth of the SiC particles depends strongly on the reaction temperature and initial carbon particle size for a constant reaction time. At higher temperatures, although SiC forms on carbon particles, the size of the SiC particles is much larger than the size of the carbon particles used. It is suggested that particle size depends on the growing SiC aggregate size. Using carbon coated fumed silica, instead of a simple mixture of silica and carbon black, not only influences the reaction path, but also affects the loss of SiO(g) from the system.

Acknowledgement

This research was sponsored by the U.S. Department of Energy, Office of Industrial Technologies, as part of the Advanced Industrial Materials Program, under contract DE-AC05-840R21400 with Lockheed Martin Energy Systems, Inc.

References

1. V. D. KRISTIC, *J. Am. Ceram. Soc.* **75** (1992) 170.
2. T. HASE and H. SUZIKI, *Yogyo KyokaiShi*, **86** (1978) 541.
3. D. P. STINTON, T. M. BESMANN and R. A. LOWDEN, *Am. Ceram. Soc. Bull.* **67** (1988) 350.
4. A. W. WEIMER, K. J. NILSEN, G. A. COCHRAN and R. P. ROACH, *AIChE*, J. **39** (1993) 493.
5. N. KLINGER, E. L. STRAUSS and K. L. KOMAREK, *J. Am. Ceram. Soc.* **49** (1966) 369.
6. J. G. LEE and I. B. CUTLER, *J. Am. Ceram. Soc. Bull.* **54** (1975) 195.
7. G. C. WEI, C. R. KENNEDY and L. A. HARRIS, *ibid.* **63** (1984) 1054.
8. P. D. MILLER, J. G. LEE and I. B. CUTLER, *J. Am. Ceram. Soc.* **62** (1979) 147.
9. V. M. KEVORKIJAN, M. KOMAC and D. KOLAR, *J. Mater. Sci.* **27** (1992) 2705.
10. C. GRESKOVICH and J. H. ROSOLOWSKI, *J. Am. Ceram. Soc.* **59** (1976) 336.
11. G. GLATZMIER and R. KOC, US Patent 5 324 494 (1994).
12. R. KOC, G. GLATZMIER, K. SCHOLL, M. ANSELMO and J. SIBOLD, *R&D Mag.* **37** (1995) 58.

Received 4 September 1997
and accepted 13 February 1998