ELSEVIER

Ceramics International 29 (2003) 69–75

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

The effects of starting precursors on the carbothermal synthesis of SiC powders

Yung-Jen Lin*, Chia-Ping Tsang

Department of Materials Engineering, Tatung University, 40 Chung-san North Road, Section 3, 10454, Taipei, Taiwan

Received 26 March 2002; received in revised form 29 April 2002; accepted 5 June 2002

Abstract

Two kinds of SiO_2: colloidal silica (L) and quartz (Q), are mixed with two kinds of carbon sources: acetylene carbon black powder (C) and phenolic resin (P), to study the effects of the starting precursors on the carbothermal synthesis of SiC. β-SiC starts to form at 1300 °C for 4 h of heat treatment and becomes the only crystalline phase at 1500 °C for 4 h of heat treatment, regardless of the starting SiO_2 and carbon sources. The characteristics of the synthesized SiC particles strongly depend on the characteristics of the carbon sources. The carbon sources also affect the stability of SiO_2 structures. In samples containing carbon black powder, whether it is amorphous silica or quartz, the SiO_2 transforms into cristobalite at synthesis temperature. In contrast, in samples containing pyrolyzed carbon from phenolic resin, the SiO_2 reacted with carbon in its original crystal forms. The structural difference in SiO_2 may affect the synthesis of SiC powders. Our results indicate that the amorphous silica could result in higher residual carbon than quartz. In addition, the SiC particles in the samples with amorphous silica appear to be more resistant to partial sintering than those in the sample with quartz.

Keywords: A. Powder; D. SiC; Carbothermal synthesis

1. Introduction

In choosing reinforcement for ceramic composites, SiC is definitely among the best. It exhibits attractive properties such as high modulus, high strength, good corrosion/oxidation resistance and good high-temperature strength. Ceramics reinforced with SiC shows better mechanical properties than its monolithic counterparts [1–2]. Furthermore, when the sizes of the SiC reinforcement are in the nanometer range, these so-called nanocomposites demonstrate further improvements in the microstructures and various properties [3–10]. Consequently, economical and efficient synthesis routes for nanometer-sized SiC powders become more important than ever.

The methods of synthesizing SiC powders include direct carbonization of Si metals, CVD from silane, sol-gel of silicon alkoxides and carbothermal reduction of SiO_2. In terms of economy and efficiency, the carbothermal reduction is the best choice. It involves inexpensive silicon dioxide and carbon (or carbon precursors) as the starting materials. These starting materials react to form β-SiC at temperatures as low as ~1200 °C and the yield of β-SiC increases with increasing synthesis temperatures [11–13]. In the carbothermal reduction of SiO_2, the commonly accepted mechanism of SiC formation is the gas–solid reaction between $SiO_{(g)}$ and $C_{(s)}$ [14,15]. The $SiO_{(g)}$ is an intermediate product when SiO_2 is in contact with and reduced by carbon. Hence, the extent of SiC formation is affected by the contact area and degree of mixing between SiO_2 and carbon [11,16]. It is generally agreed that the starting carbon is the decisive constituent in the carbothermal synthesis of SiC. The carbon was shown to substantially influence the rate of reaction and the morphology and size of the synthesized SiC [13,14,17]. Nevertheless, whether the starting SiO_2 also plays a role is not clearly demonstrated.

In this research, we synthesized β-SiC from two different sources of SiO_2 and carbon as the starting materials hoping to illustrate the relative importance of the starting carbon and SiO_2. The SiO_2 sources are colloidal silica dispersed in water (Ludox®) and quartz powder. The carbon sources are commercially available acetylene carbon black powder and active carbon powder, which

---

* Corresponding author. Tel.: +886-2-2586-6040; fax: +886-2-2593-6897.

E-mail address: yjlin@ttu.edu.tw (Y.-J. Lin).

0272-8842/02/$22.00 © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.
PII: S0272-8842(02)00091-3

is a product from the decomposition of phenolic resin. Because of the differences in the particle sizes and/or crystal structures of SiO_2 and carbon, the reaction of SiC formation would show differences. These differences could reveal the effects of the starting constituents on the carbothermal synthesis of SiC.

2. Experimental procedures

Two types of silica and two types of carbon sources were used in the experiments: colloidal silica (Ludox®) and quartz as the silica sources; acetylene carbon black and phenolic resin as the sources of carbon. The characteristics of these sources are listed in Table 1. Four combinations of silica and carbon were made, namely, colloidal silica (Ludox®) + carbon black (LC), quartz + carbon black (QC), colloidal silica + phenolic resin (LP), and quartz + phenolic resin (QP).

The carbothermal synthesis of SiC can be described as $SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)}$. Therefore, the molar ratio of silica and carbon was fixed to 1:3 in the preparation of each combination. Before the preparation of powder mixtures, the carbon content of phenolic resin and the silica content of Ludox® were determined first. The carbon content of phenolic resin was determined by drying and pyrolyzing the resin at 1000 °C for 2 h in flowing Ar (80 ml/min). The yield of the pyrolyzed carbon was ~50 wt.%. The silica content of Ludox® is 40 wt.% according to the manufacturer's data.

After being properly weighed, LC and QC samples were mixed in ethanol and ball-milled for 20 h with 3Y-TZP balls. LP and QP samples were mixed in ethanol with a magnetic stirrer for 1 h. After mixing, the slurries were dried under IR lamp and ground to pass 80-mesh of sieves. The dried powder mixtures were placed in covered alumina crucibles and synthesized in a tube furnace between 1300 and 1500 °C for 4 h with a heating rate of 10 °C/min under flowing Ar (80 ml/min) and furnace cooling. For samples containing phenolic resin (LP and QP), a burnout stage at 1000 °C for 2 h was included on the way of heating to the desired temperatures. The choice of burnout temperature was determined by FTIR analyzes of LP mixtures after heating at various temperatures between 300 and 1000 °C. The results indicated that the phenolic resin would completely decompose into carbon at 1000 °C.

Characterizations included weight loss after syntheses and X-ray diffraction (XRD; D-5000, Siemens, Karlsruhe, Germany) for the structural evolution. Residual carbon in the synthesized powder was determined by thermogravimetric analysis (TGA; SDT-2960 Simultaneous DSC-TGA, TA Instruments, Inc., New Castle, DE) in flowing air (100 ml/min). The densities of powders were measured with a pycnometer (Multipycnometer, Quantachrome, Boynton Beach, FL) using He as the medium. The particle sizes were measured by the laser diffraction technique (Mastersizer E, Malvern Instruments, Ltd., Worcestershire, UK) while the crystallite sizes of the powders were estimated from the (220) peaks of XRD patterns using the Scherrer formula [18]. The powders were also observed in scanning electron microscope (SEM; JSM 5600, Jeol, Tokyo, Japan) and transmission electron microscope (TEM; H-7100, Hitachi, Tokyo, Japan) after suitable conductive coatings.

3. Results and discussions

Since the carbothermal reduction of $SiO_{2(s)}$ involves gaseous product (CO), weight loss accompanies the reaction. If the reaction is completed and SiC is formed, the weight should remain about the same, or even increase if SiC is oxidized. Hence, monitoring of weight change after synthesis could reveal the extent of SiC formation. Fig. 1 is the remaining weight of each combination after synthesized at various temperatures. As the synthesis temperatures increase, weights decrease with similar rates for each combination. After heating at around 1500 °C for 4 h, the remaining weights reach the theoretical values. Further increase in the synthesizing temperature only slightly decreases the remaining weights. Hence, 1500 °C/4 h appears to be the proper condition for the synthesis of SiC.

The choice of 1500 °C as the proper synthesizing temperature is justified by the XRD analyses for the phase evolution. Fig. 2 (a–d) are XRD patterns of the powders from each combination synthesized at various

Table 1
Characteristics of starting materials

Starting materials	Characteristics (manufacturers' data)
Ludox (colloidal SiO_2)[a]	40 wt.%, water suspension, particle size: 20–24 nm
Quartz (SiO_2)[b]	Purity: 99.5%, average particle size: 7.75 μm
Acetylene carbon black[b]	Purity: 99.99%, average particle size: 42 nm
Phenolic (phenol–formaldehyde) resin[c]	Resol type (in methanol), solid content: 78%

[a] AS 40, Dupont, Wilmington, DE, USA.

[b] Strem Chemicals, Newburyport, MA, USA.

[c] PF-650, Chung-chun Plastics Co. Ltd., Hsinchu, Taiwan.

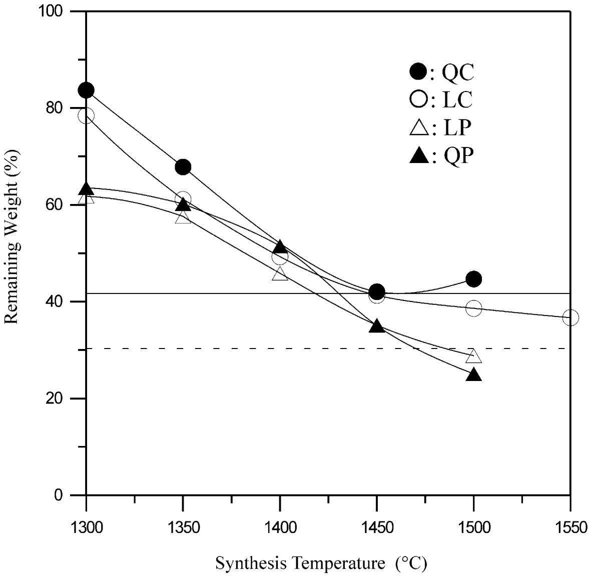

Fig. 1. Remaining weights (%) of each combination after synthesized at various temperatures for 4 h. Theoretical remaining weights are indicated by two horizontal lines: solid line for QC and LC; dash line for LP and QP.

temperatures. The XRD patterns show that SiC starts to form at 1300 °C for 4 h of heat treatment and becomes the only crystalline phase at 1500 °C for 4 h of heat treatment, regardless of the starting SiO_2 and carbon sources. The synthesized SiC is cubic β-SiC with stacking faults, which are revealed by the shoulders near the XRD peak at $2\theta \sim 36°$ [19,20].

However, between 1300 and 1450 °C, different combinations exhibit different phase evolution of SiO_2. The SiO_2 in the samples containing pyrolyzed carbon from the decomposition of phenolic resin (LP and QP) appears to be more stable against the transformation into cristobalite. The colloidal silica crystallized into cristobalite in LC, but remains amorphous in LP systems. Similarly, cristobalite, rather than quartz, was the prevailing silicate phase at 1400 °C/4 h in QC, but only a little cristobalite is formed from quartz at 1450 °C/4 h in QP system. Consequently, the type of carbon source affects the crystal structures of SiO_2 during synthesis. In samples containing carbon black powder, whether the SiO_2 source is amorphous silica or quartz, the carbothermal reaction is, in effect, a reaction between cristobalite and carbon black. In contrast, in samples containing pyrolyzed carbon (from phenolic resin), the SiO_2 reacted with carbon in its original crystal forms (amorphous silica or quartz).

After synthesizing at 1500 °C for 4 h, the characteristics of the powders are listed in Table 2. The color of the powders from LC and QP samples is greenish gray while the powder of LP sample is dark gray and the powder of QC sample is nearly black. When these powders were heated to 1000 °C in flowing air and their weights were monitored with a thermogravimetric analyzer, they showed different weight changes, see Fig. 3. The LC and QP samples had slight weight increase due to oxidation of SiC. In contrast, the LP and QC samples exhibited significant weight loss at about 500 and 600 °C, respectively, before the weight increased at higher temperatures. It was also noted that all the samples after 1000 °C in air (after TGA analyses) became greenish gray in the color.

In addition to TGA analyses, the synthesized powders were heated in air at 600 or 800 °C for 1 h. All the powders became greenish gray in the color and the densities of the powders also increased. The density increments were relatively large in the QC and LP samples, which were also subjected to obvious color change (see Table 2). From the TGA weight loss, color change and density increase after heating in air, it is concluded that significant amount of residual carbon existed in QC and LP samples. Since the ratio of silica and carbon is the same in each sample, the residual carbon implied lower yields of SiC in QC and LP samples. Table 2 also lists the crystallite size and particle size of each sample. The crystallite sizes are ~35–40 nm except the LP sample, which is ~25 nm. However, the average particle size (measured by the laser diffraction technique) in samples containing phenolic resin is much larger than the samples with carbon black. This indicates severe agglomeration in samples with phenolic resin.

Fig. 4(a–e) are TEM micrographs of the starting carbon black powders and the synthesized SiC powders after being heated in air to remove the residual carbon.

Table 2
Characteristics of the powders synthesized at 1500 °C for 4 h

Sample notation	Color		Density (g/cm^3)		Average particle size[b] (μm)	Crystallite size[c] (nm)
	As synthesized	After carbon removal	As synthesized	After carbon removal[a]		
LC	Greenish gray	Greenish gray	2.77	2.83	0.61	34
LP	Dark gray	Greenish gray	2.89	3.09	6.77	25
QC	Nearly black	Greenish gray	2.53	2.93	0.39	39
QP	Greenish gray	Greenish gray	2.68	2.76	1.30	38

[a] All powders except QC sample were heat-treated at 600 °C for 1h in air. QC powder was heat-treated at 800 °C for 1 h in air.

[b] Measured by the laser diffraction technique.

[c] Measured from XRD peak broadening.

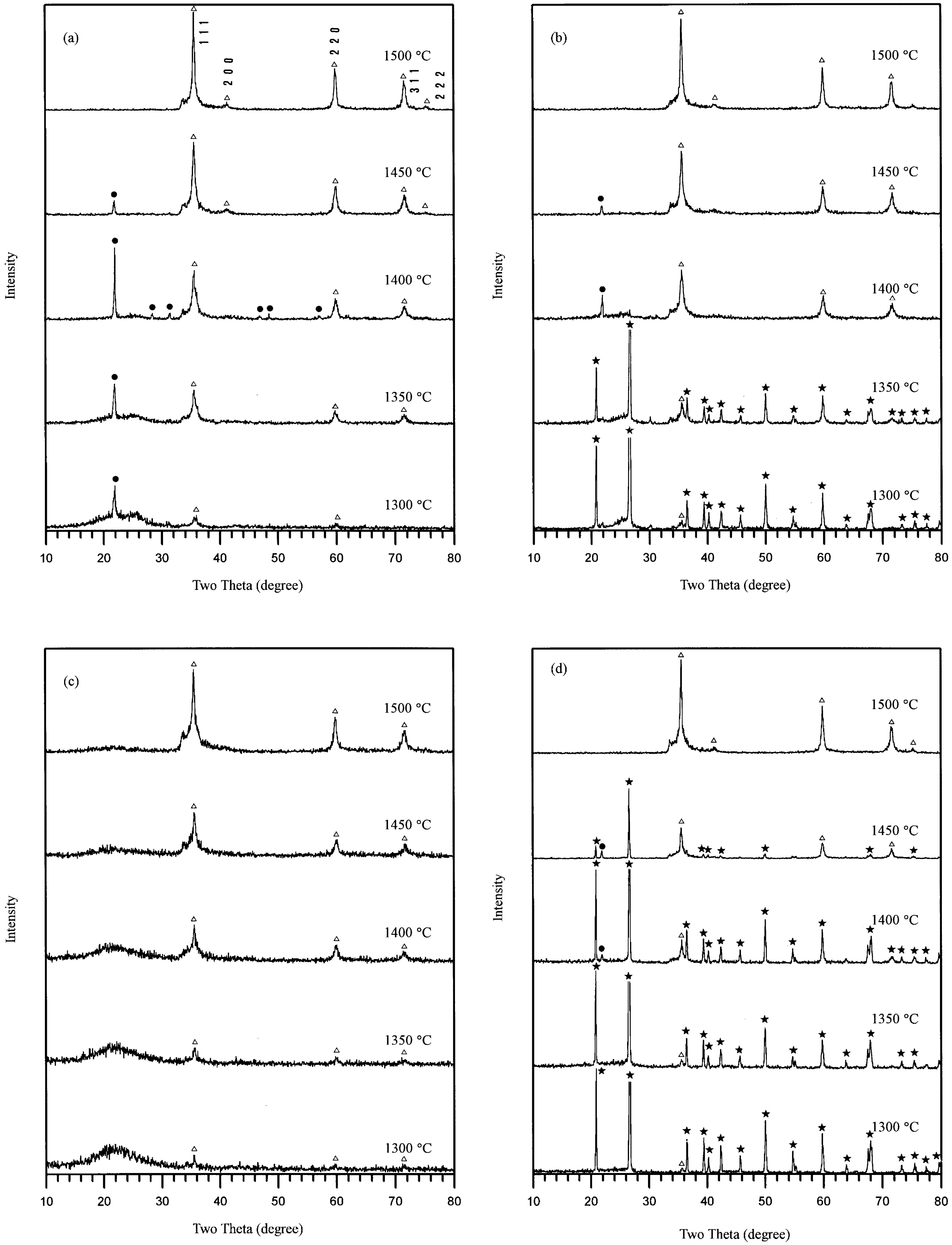

Fig. 2. XRD patterns of the powders from each system synthesized at various temperatures for 4 h. (a) Colloidal silica + carbon black (LC), (b) quartz + carbon black (QC), (c) colloidal silica + phenolic resin (LP), (d) quartz + phenolic resin (QP). (△:β-SiC; ●:cristobalite; ★:quartz).

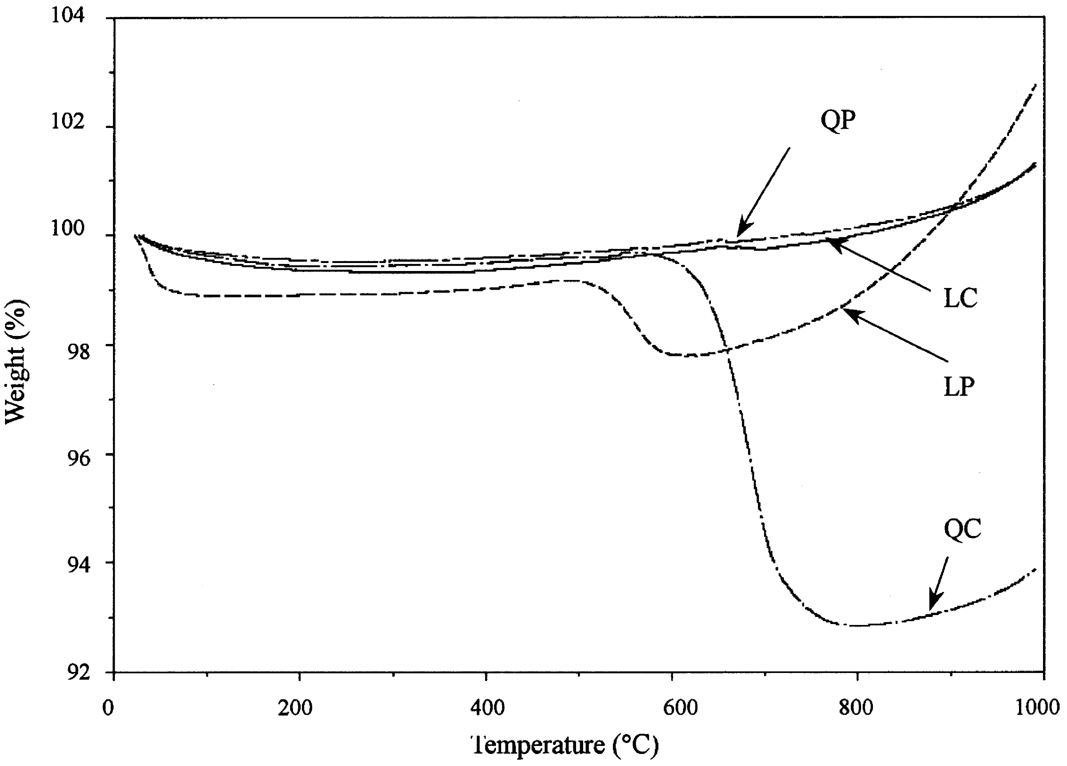

Fig. 3. TGA curves of the powders synthesized at 1500 °C for 4 h. (10 °C/min heating rate to 1000 °C in flowing air.).

The LC and QC powders are both discrete and equiaxed. Their particle sizes in the TEM micrographs are consistent with the crystallite sizes measured from XRD patterns (Table 2). The SiC particles synthesized from LC and QC are similar with the carbon black powder in the morphology as well as in the particle size.

In contrast, the LP and QP powders look different. The LP powders are equiaxed and are much smaller than the other powders while the QP powders are elongated and have about the same particle size as that of LC and QC samples. Nevertheless, the larger particle size and elongated particle morphology of the QP sample is likely the result of partial sintering of small SiC crystallites. Thus, the SiC powders synthesized from phenolic resin have smaller crystallites (before sintering of the crystallites occurs) than those synthesized from carbon black powders. This is because the pyrolyzed phenolic resin could result in smaller carbon particles than acetylene carbon black. According to the gas–solid reactions of SiC formation,

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)};$$

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)}$$

the synthesized SiC are strongly dependent of the carbon source [14]. Hence, smaller size of phenolic carbon results in smaller SiC crystallites.

Yet, the characteristics of SiO_2 also play a role. Although the synthesized SiC appears to be the same in LC and QC samples, different SiC powder characteristics exist between LP and QP samples. In the starting powder mixtures, the differences between colloidal silica and quartz lie in the particle sizes and crystal structures. However, in LC and QC samples at synthesizing temperature, the XRD revealed that both colloidal silica and quartz have transformed into cristobalite. But in LP and QP samples, the colloidal silica remained amorphous and quartz remained as quartz.

Since the difference between colloidal silica and quartz in LC and QC samples lies solely in the particle size, the difference between using colloidal silica and quartz in LC and QC systems would only affect the rate of $SiO_{(g)}$ formation from the reduction of SiO_2 (the smaller particle size of colloidal SiO_2, the higher SiO_2/carbon contact area to enhance the SiO formation). Therefore, the reaction rate and the yield of SiC are higher in LC than in QC samples. On the other hand, both size and structural differences exist between amorphous silica in LP and quartz in QP samples. This seems to complicate the situations. Our results indicate that the amorphous silica in LP sample results in lower yields of SiC than quartz in QP sample even though the size of colloidal silica is much smaller than that of quartz. In addition, the SiC particles in LP sample (with amorphous silica) appear to be more resistant to partial sintering than those in QP sample. Although the crystal

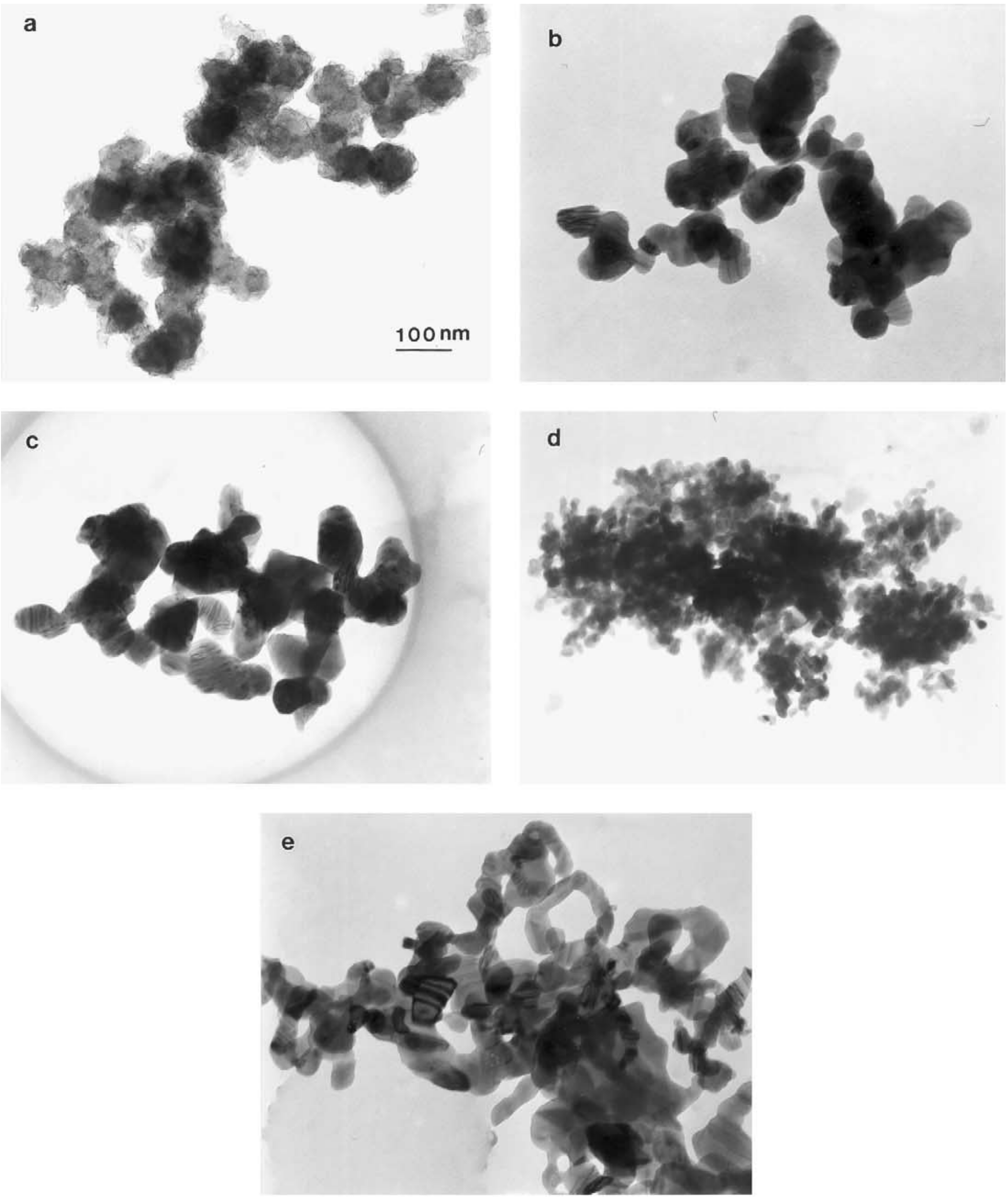

Fig. 4. TEM micrographs of carbon black powder and SiC powders synthesized from each combination at 1500 °C for 4 h. (a) Carbon black powder, (b) powders from LC, (c) powders from QC, (d) powders from LP, and (e) powders from QP. (All micrographs are of the same magnification.)

structure of SiO_2 affects the synthesis process of SiC and its powder characteristics, it should be noted that the phase stability of SiO_2 is influenced by the type of carbon source in the samples.

Under SEM investigations, it is noted that there also exist whiskers (or fibers) of SiC in all the four combinations; see Fig. 5 for an example. The formation of SiC whisker/fiber could not be explained by the gas–solid reaction of $SiO_{(g)}$ and $C_{(s)}$. It is more likely that the whisker/fiber formed via $SiO_{(g)}$ and $CO_{(g)}$ gas-gas reaction such that the morphology of the SiC could be totally independent of the morphology of carbon sources. The reactions could proceed as follows:[11]

$$SiO_{2(s)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)}$$

$$SiO_{(g)} + 3CO_{(g)} \rightarrow SiC_{(s)} + 2CO_{2(g)}$$

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)}$$

Therefore, both gas–solid and gas–gas reactions occur in the syntheses of SiC from carbothermal reduction of silica. Nevertheless, the gas–solid reaction is dominant in the temperature range of 1300–1500 °C.

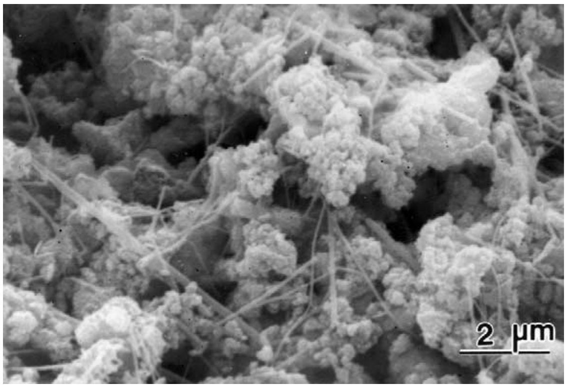

Fig. 5. SEM micrograph of SiC powders synthesized from LP sample at 1500 °C for 4 h. (Note SiC whiskers/fibers are present.)

4. Summary

Two kinds of SiO_2: colloidal silica (L) and quartz (Q), are mixed with two kinds of carbon sources: acetylene carbon black powder (C) and phenolic resin (P), to study the effects of the starting precursors on the carbothermal synthesis of SiC. The results show that all combinations react nearly completely to form β-SiC powders after heating at 1500 °C for 4 h. However, residual carbon exists in QC and LP samples.

The characteristics of the synthesized SiC particles strongly depend on the characteristics of the carbon sources. The SiC particles synthesized from LC and QC samples are similar with the carbon black powder in the morphology (discrete and equiaxed) as well as in the particle size ($\sim$40 nm). Similarly, the "primary" particles from LP and QP samples are small ($<$25 nm) due to the small size of the pyrolyzed carbon from phenolic resin. However, in the QP sample, the small crystallites could undergo partial sintering and result in elongated particles with the size about the same as that of LC and QC.

The carbon sources also affect the stability of SiO_2 structures. In samples containing carbon black powder, whether it is amorphous silica or quartz, the SiO_2 transforms into cristobalite. The carbothermal reaction is, in effect, a reaction between cristobalite and carbon black. In contrast, in samples containing pyrolyzed carbon (from phenolic resin), the SiO_2 reacts with carbon in its original crystal forms.

The structural difference in SiO_2 may affect the synthesis of SiC powders. Our results indicate that the amorphous silica (in LP system) could result in higher residual carbon than quartz (in QP system.) In addition, the SiC particles in the samples with amorphous silica (LP system) appear to be more resistant to partial sintering than those in the sample with quartz (QP system).

Acknowledgements

This work was financially supported by the National Science Council, Taiwan, Republic of China under Grant No. NSC 89-2216-E-036-015.

References

[1] H.R. Rezaie, W.M. Rainforth, W.E. Lee, J. Eur. Ceram. Soc. 19 (9) (1999) 1777.

[2] G-J. Zhang, Z-Y. Deng, N. Kondo, J-F. Yang, T. Ohji, J. Am. Ceram. Soc. 83 (9) (2000) 2330.

[3] K. Niihara, J. Ceram. Soc. Jpn. 99 (10) (1991) 974.

[4] M. Sternitzke, J. Eur. Ceram. Soc. 17 (9) (1997) 1061.

[5] J. Zhao, L.C. Stearns, M.P. Harmer, H.M. Chan, G.A. Miller, R.E. Cook, J. Am. Ceram. Soc. 76 (2) (1993) 503.

[6] L. Wang, H.Z. Gao, J.K. Guo, Ceram. Int. 26 (4) (2000) 391.

[7] N. Bamba, Y.-H. Choa, T. Sekino, K. Niihara, J. Eur. Ceram. Soc. 18 (1998) 693.

[8] N. Bamba, Y.-H. Choa, T. Sekino, K. Niihara, Solid State Ionics 111 (1998) 171.

[9] D.S. Cheong, K.-T. Hwang, C.-S. Kim, J. Am. Ceram. Soc. 82 (4) (1996) 981.

[10] T. Ohji, Y.-K. Jeong, Y.-H. Choa, K. Niihara, J. Am. Ceram. Soc. 81 (6) (1998) 1453.

[11] R. Koc, S.V. Cattamanchi, J. Mater. Sci. 33 (1998) 2537.

[12] J. Wang, I. Risa, T. Takayuki, Energy and Fuel 14 (5) (2000) 1108.

[13] C.Y. Chen, C.I. Lin, S.H. Chen, Br. Ceram. Trans 99 (2) (2000) 57.

[14] A.W. Weimer, K.J. Nilsen, G.A. Cochran, R.P. Roach, AIChE J. 39 (3) (1993) 493.

[15] H.-P. Martin, R. Ecke, E. Muller, J. Eur. Ceram. Soc. 18 (1998) 1737.

[16] S.-H. Chen, C.-I. Lin, J. Mater. Sci. Lett. 16 (1997) 702.

[17] F.J. Narciso-Romero, F. Rodriguez-Reinoso, M.A. Diez, Carbon 37 (1999) 1771.

[18] B.D. Cullity, Elements of X-Ray Diffraction, second ed, Addison-Wesley, MA 1973 (Chapter 3).

[19] H.-P. Martin, R. Ecke, E. Muller, J. Eur. Ceram. Soc. 18 (1998) 1737.

[20] W-S. Seo, K. Koumoto, J. Am. Ceram. Soc. 79 (7) (1996) 1777.