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Chemical vapor deposition of C on SiO_2 and subsequent carbothermal reduction for the synthesis of nanocrystalline SiC particles/whiskers

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ABSTRACT

This study investigates chemical vapor deposition of C from CH_4 on particulate SiO_2 and subsequent carbothermal conversion of the resultant composite particles to SiC powders. Mass measurements, HR-TEM, SEM and XRD were used to characterize the products at various stages of the processes. It was found that oxide particles gained mass rapidly at 1300 K under CH_4 atmosphere owing to enhanced C uptake. Pyrolytic carbon layers 5–8 nm thick were deposited on SiO_2 particles. The coated powders with high C loadings (40–42.6 wt.% C) were converted to SiC under Ar flow in a temperature range of 1700–1800 K. Almost pure SiC powders containing a mixture of particles and whiskers of ~100 nm were synthesized at 1750 K for 45 min and at 1800 K for 30 min using the starting powder with 40 wt.%C. Whisker diameter increased with the C content of the coated powder. It was proposed that SiC whisker was grown by a vapor–solid mechanism. Equilibrium thermodynamic analysis by the method of minimization of Gibbs' free energy predicted the reaction pathways to SiC and to the product species in the Si–O–C–Ar system. This study demonstrated that either C shell-SiO_2 core powders or SiC powders could be synthesized rapidly in the same reactor.

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1. Introduction

Because silicon carbide (SiC) has a high melting point, good oxidation resistance, high thermal stability and high hardness, it has been exploited in many areas including abrasives, varistors, armor, catalyst supports. SiC particles or whiskers are incorporated into metallic and ceramic matrices as a reinforcement component to produce advanced composites.

SiC powder is commercially produced by Acheson process which involves carbothermal reduction of SiO_2 by C at 1873–2373 K [1]. It, however, requires high temperatures and long reaction times because of sluggish reaction rates between separate precursors leading to coarse powders. Subsequent prolonged milling reduces powder particle size, but it introduces impurities into SiC. Since demands for nanosized ceramic powders have increased due to improved properties (such as better densification, higher hardness and lower wear rate) in the products produced from them [2], numerous processes have been developed for the synthesis of the materials. The approaches [3–10] for SiC essentially focus on the use of precursors which provide close contact between the reactants to enhance SiC formation reactions at low temperatures. Saito et al. [3] synthesized SiC whiskers with a mean diameter of 500 nm by vapor phase reactions between SiO and CO without catalyst, while Kennedy and North [4] obtained SiC particles by reaction of gaseous SiO with particulate carbon. Koc and Cattamanchi [5] used C_3H_6 (propylene) and silica to produce fine SiC particles of 100–300 nm. They reported that silica particles were coated with carbon by thermal cracking of the hydrocarbon at elevated pressure and at 873 K. It was also stated that thirty cycles, each lasting ~20 min, were necessary to achieve the amount of carbon required for subsequent carbothermal conversion of SiO_2 to SiC, which was carried out in a separate vessel. Multicycle C coating process and the use of a different reactor for the carbothermal reduction seem to limit mass production of the powder. Recently, fine SiC powders have been synthesized by other techniques such as thermal plasma [6], direct reaction between silicon and carbon [7], combustion synthesis [8], high-energy ball-milling [9] and mechanically activated carbothermic reduction [10]. These approaches, however, involve complex, time consuming processes or high cost precursors.

Carbon shell–silicon oxide core composite powders have received considerable attention for tribological applications [11]. Recently, Vital et al. [12] produced C–SiO_2 nanocomposite particles with carbon loading of maximum 14 wt. % by flame synthesis and studied their carbothermal conversion to SiC. Extra carbon was, however, needed to complete the carbothermal reduction at 1773 K within 2 h. Hence, it is worthy of studying carbon coating processes using different techniques and precursors for possible alternative routes to carbon encapsulated SiO_2 particle synthesis.

It appears that a fast, simple and economical process for producing C–SiO_2 composite powders with high carbon loading and fine SiC powders is presently needed. The current study shows that both powders can be synthesized in the same reactor within a short time by allowing CH_4 flow during heating to 1300 K and by switching to Ar flow at higher temperatures. We used CH_4 (natural gas) as a carbon source

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because it is relatively cheap and abundant. Hence, the process described here has inherent advantages including a simple flexible synthesis procedure, low cost carbon source and short reaction time, providing a sound rationale for massive productions of either C–SiO_2 nanocomposite powders or nanocrystalline SiC powders. Consequently, the present work was undertaken to establish optimal conditions for the syntheses of these materials by chemical vapor deposition of C on SiO_2 particles from CH_4 and by carbothermal conversion of the C coated powders to SiC.

2. Experimental procedures

The experimental set-up used for the present study essentially consists of a hot-wall tubular (20 mm in diameter) alumina furnace equipped with SiC heating elements and gas flow meters. The chemicals used were SiO_2 (99.5%) powder (Sigma-Aldrich), high purity argon (99.999%) and methane (99.5%). Particle size of the SiO_2 powder was reported to be 10–20 nm by the producer. The alumina boat with gas entrance side cut to allow smooth gas flow was loaded with the powder. The boat was placed at the hot zone of the furnace. Prior to the experiments, the oxide powder was held at 373 K in an oven for moisture removal. In order to determine the extent of the reactions, mass measurements before and after the experiments were carried out by a calibrated electronic balance (Sartorius BP110S) with a sensitivity of $\pm 10^{-4}$ g. Change in mass was calculated using the equation of $(m - m_o)/m_o \times 100$, where m is the mass at temperature T or time t and m_o is the starting mass of the sample.

The oxide powder of ~10^{-3} mol (~60 mg) was exposed to CH_4 flow (40 cm^3/min) during heating at a rate of 25 K/min to the temperatures of 700–1300 K for the chemical vapor deposition of C on SiO_2. At 1300 K, the powders were isothermally held for various periods of time. Carbon content of the coated samples was determined by burning it off in air at 900 K for ~10 min. In order to synthesize SiC, the C coated powders (~100 mg) were heated further to the target temperatures between 1700 and 1800 K at a rate of 40 K/min under Ar flow (250 cm^3/min). Duration of isothermal period was varied up to 180, 45 and 30 min for 1700, 1750 and 1800 K, respectively. The products were cooled under Ar atmosphere.

Morphology of the coated particles was examined by a High Resolution Transmission Electron Microscope (JEOL 2100 LaB_6 HR-TEM). For this examination, the product was mixed with ethanol with the help of an ultrasonic generator and the mixture was then dropped on the TEM grid. A Field Emission Gun Scanning Electron Microscope (JEOL 6335 FEG-SEM) was used to examine morphologies of the powders after carbothermal reaction. Mean sizes (diameters) of particles and whiskers were calculated from at least 50 measurements using the FEG-SEM images. A parafocusing X-ray diffractometer (RIGAKU D/Max-2200 XRD) equipped with a Cu radiation tube and a monochrometer was used for the phase analysis. The crystallite size of the β-SiC phase in the products was also calculated from the X-ray diffraction peak profile of the (111) crystallographic plane using the Scherrer formula:

$$t = \frac{\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the wavelength of Cu K_α radiation (0.15418 nm), θ is the diffraction angle, t is the crystallite size and β is the full breadth of the diffraction peak at half-maximum intensity, which was corrected for instrumental broadening (~0.2°).

3. Results and discussion

3.1. Chemical vapor deposition of C on particulate SiO_2

Fig. 1 displays the non-isothermal variation of the sample mass heated to the temperatures up to 1300 K under CH_4 flow. Initial mass change during heating is observed to be slightly below zero, suggesting that there is oxide loss. The samples slowly gain mass with temperature increasing to 1200 K due to carbon uptake. The color of the products changed progressively from white at 800 K to black at 1200 K. The mass change increases rapidly to the level of 54% during heating to a higher temperature of 1300 K. The inset in Fig. 1 reveals that the change in sample mass rises to 80% within isothermal holding time of 5 min at 1300 K. This result indicates that CH_4 is pyrolyzed significantly at the temperature.

It appears that carbon mass gain is masked by mass loss at temperatures > 800 K. Hence, the figure does not yield directly carbon content of the products. Consequently, carbon was burned off in air to determine its content in the coated product by a simple calculation using the mass of the coated powder and the residual mass. Carbon concentrations in the products at 1300 K for isothermal holding periods of 0, 1, 2.5 and 5 min were measured to be 40, 42.6, 47.7 and 50.6 wt.%, respectively. The loss of oxide was estimated from the residual mass after C burning. It was found to increase from ~3 wt.% at 800 K (no carbon deposition observed at this temperature) to ~7.7 wt.% of the initial SiO_2 mass at 1300 K. Oxide loss during coating process may take place via the following overall reaction:

$$SiO_{2(s)} + CH_{4(g)} \rightarrow SiO_{(g)} + CO_{(g)} + 2H_{2(g)} \quad (2)$$

Fig. 2 shows the X-ray diffraction patterns of the original SiO_2 powder and the product obtained in CH_4 atmosphere at 1300 K. As seen from pattern (a), the oxide powder exhibits of a broad diffraction peak at $2\theta \approx 22.3°$ ($d_{101} = 0.399$ nm) whose intensity and diffraction angle match those of the published line pattern of SiO_2 phase ($d_{101} = 0.404$ nm) [13]. The XRD pattern of the product with carbon content of 42.6% clearly shows the presence of pyrolytic carbon along with SiO_2. The interplanar spacing of the (002) major peak of the carbon at $2\theta = 26.31°$ was calculated to be 0.339 nm, close to the standard value of 0.3375 nm [13]. HR-TEM images of the product are displayed at various magnifications in Fig. 3a and b. They clearly reveal that the powder is comprised of SiO_2 core–C shell morphology. The oxide particles of 50–80 nm were coated with pyrolytic carbon layer 5–8 nm thick. The higher magnification image shown in Fig. 3b displays that pyrolytic carbon coating consists of basal planes parallel to each other within small crystallites. The interplanar spacing of the planes shown in the image was measured to be ~0.34 nm, which agrees well with the XRD data.

3.2. Carbothermal conversion of C shell–SiO_2 nanocomposite particles

Equilibrium thermodynamic analysis by the method of minimization of the Gibbs' free energy of a system [14] is a useful tool to predict

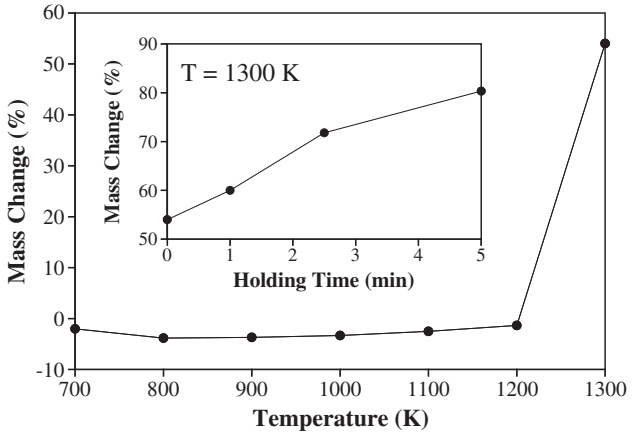


Fig. 1. Change in mass of the starting SiO_2 powder heated to the target temperatures of 700–1300 K under CH_4 flow. The inset figure shows the variation of the sample mass with isothermal holding time at 1300 K.

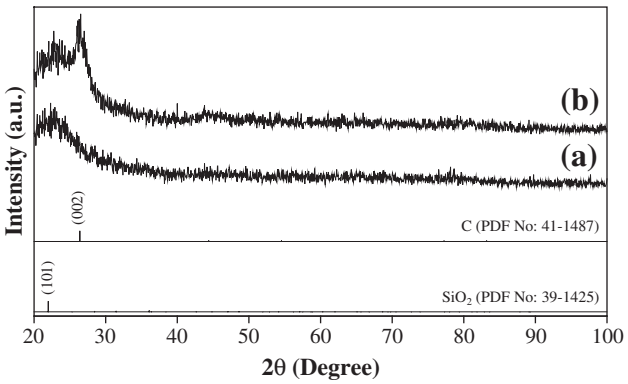


Fig. 2. XRD patterns of (a) SiO_2 powder and (b) the product obtained in CH_4 atmosphere at 1300 K (carbon content 42.6 wt.%).

process parameters that yield desired phases and to understand thermochemistry of material synthesis processes. Hence, thermodynamic calculations in the Si–O–C–Ar system were carried out using a modified version of Eriksson's computer program SOLGASMIX [15] as a function of input carbon mole fraction in the range 0–1 at atmospheric pressure and at 1600–1900 K for 10^{-3} mol SiO_2 and 0.5 mol Ar. In the system of interest, 21 species were considered to be as the constituents of the gas phase including SiO, SiO_2, CO, CO_2, Si, Si_2, O, O_2, SiC_2 and Si_2C. Condensed equilibrium phases were assumed to be C, SiO_2, Si, α-SiC and β-SiC. Input thermodynamic data in the form of Gibbs' free energy of the formation of the constituents considered in the present study were obtained from the thermochemical tables [16,17].

Fig. 4 depicts the diagrams constructed from the calculated results. A stability diagram for the condensed phases is displayed in Fig. 4a. As seen from the figure, condensed phase fields of SiO_2, SiO_2 + β-SiC, β-SiC and β-SiC + C are predicted. Single phase SiO_2 exists up to the input C mole fraction of 0.5 C at the temperature range studied. There is no condensed phase (only gas phase) field represented by a vertical line at ~0.5 at temperatures > 1630 K. A small SiO_2 + β-SiC phase field appears below 1630 K. Single β-SiC phase field is predicted at the C fractions between 0.5 and 0.75, while free C co-exists with β-SiC above 0.75.

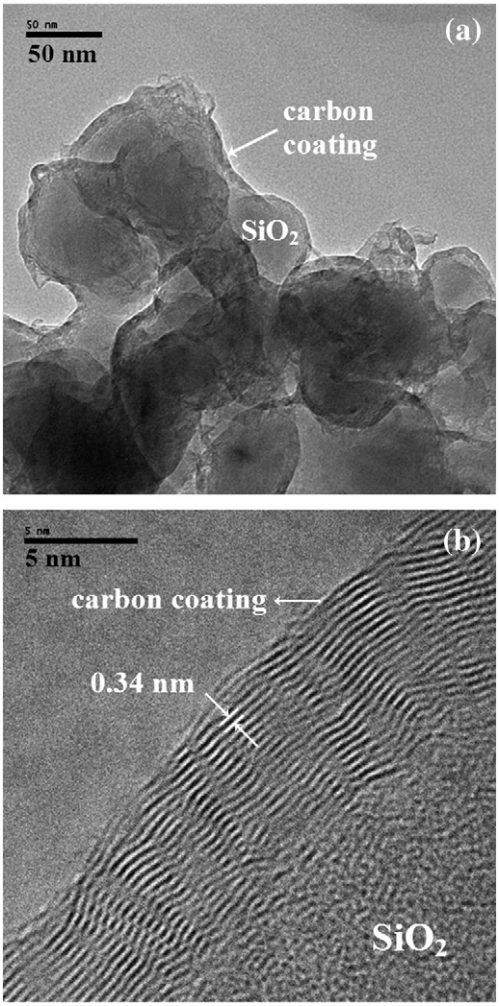


Fig. 3. HR-TEM images of the SiO_2 powder coated with pyrolytic carbon (C content 42.6 wt.%). The images are at (a) lower and (b) higher magnifications.

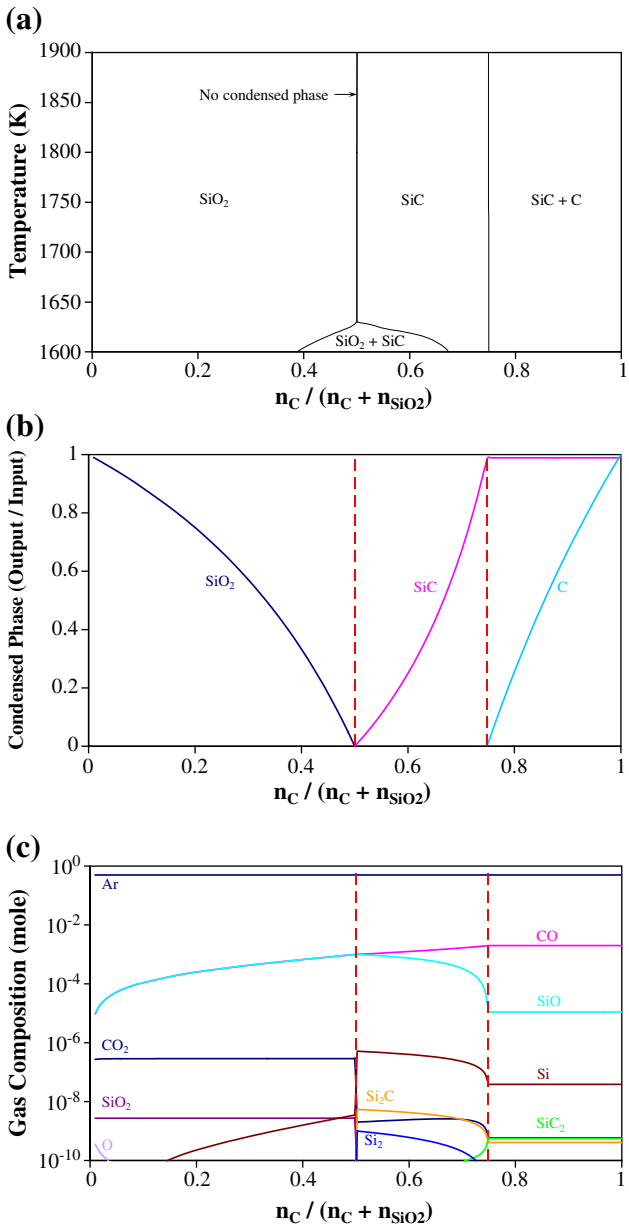


Fig. 4. (a) The equilibrium stability diagram showing condensed phase fields as a function of temperature and input carbon mole fraction. Variations of (b) equilibrium condensed phase yield and (c) gas composition with carbon mole fraction at 1800 K. SiC yield was calculated with respect to SiO_2. Dashed vertical lines in (b) and (c) represent the C mole fractions separating the phase fields.

Fig. 4b and c displays variations of condensed phase and gas compositions with input C mole fraction at 1800 K, respectively. As seen from the Fig. 4b, in the single SiO_2 region, the condensed SiO_2 content decreases as the C mole fraction is raised. It becomes zero at ~0.5. In the single β-SiC phase field, SiC yield increases with input mole fraction of C and it is found to be almost unity at 0.75. Fig. 4c reveals that the main components in the gas phase are predicted to be SiO and CO, while CO_2, SiO_2, Si, Si_2, O, SiC_2 and Si_2C species are the minor ones for all the C mole fractions. Via equilibrium concentrations of the products and the reactants, it is possible to suggest reaction pathways to the formations of gaseous species and solid SiC. This will be discussed later in this section.

Using the thermodynamic prediction as a guide to synthesize the desired phase SiC with high yield, the initial C mole fraction in the SiO_2–C reactant mixture is determined to be 0.75 corresponding to 37.5 wt.%C, which is also the amount of C required for the formation of SiC in accordance with the overall reaction:

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

For the carbothermal conversion studies, the coated powders with slightly overstoichiometric carbon contents (40 and 42.6 wt.%) were selected to ensure that SiC formation is complete.

Fig. 5 shows change in mass of the C coated oxide powders as a function of isothermal holding time at1700, 1750 and 1800 K. Full symbols in the figure represent the data obtained from the coated powder containing 42.6% C. It is clearly seen from the figure that mass loss increases with temperature and time, indicating that the extent of carbothermal reduction increases as expected. The mass losses of 21.2% at 1700 K, 38.7% at 1750 K and 50.65% at 1800 K for zero isothermal holding time illustrates that the reduction takes place significantly during heating to the target temperatures. It is also seen that final mass change values of ~60% at all the temperatures studied slightly exceeds the theoretical loss (58.3%) for full SiC conversion calculated in accordance with reaction (3). This behavior is ascribed to the oxide loss during the carbothermal conversion. Open symbols in Fig. 5 represent the data points for the coated powder with lower carbon content (40%) at 1700, 1750 and 1800 K for the isothermal periods of 180 min, 45 min and 30 min, respectively. In this case, mass losses are found to be ~62%, which is slightly higher than those obtained from the powder having 42.6% C. This result is attributable to less free carbon remained in the products when the lower carbon content powder used, as XRD analysis suggests.

Fig. 6 displays the XRD patterns of the powders at various stages of the carbothermal reduction. The unmarked patterns in the figure belong

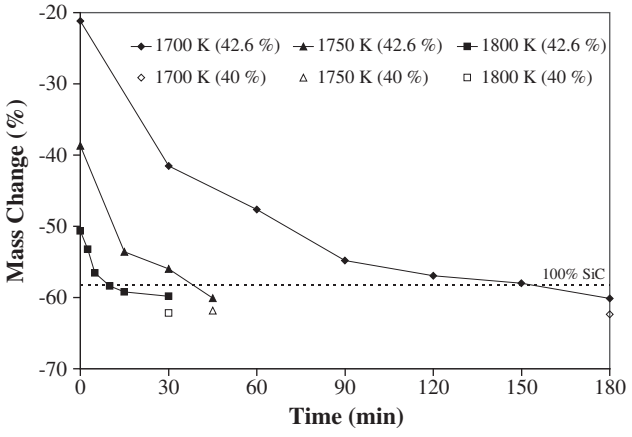


Fig. 5. Influence of reaction temperature and isothermal holding time on the mass change in the carbon coated oxide powders. Closed and open symbols represent the data points obtained from the starting powders having 42.6% C and 40% C, respectively.

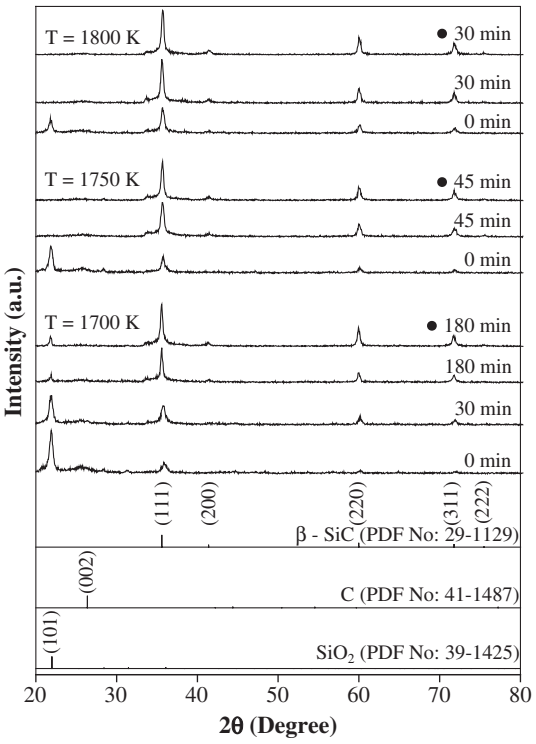


Fig. 6. XRD patterns of the samples after carbothermal conversion at 1700–1800 K for various isothermal holding times. The unmarked and (●) marked patterns are from the products using the starting powders with 42.6 wt.%C and 40 wt.%C, respectively.

to the products synthesized from the powder with 42.6% C. The ones marked with (●) were obtained from the powder containing 40% C. Standard line patterns of the matched materials (C, SiO_2 and β-SiC) [13] are also shown in the figure. It is clearly seen from the patterns that intensities of β-SiC peaks increase with reaction time and temperature, while those of C and SiO_2 decrease. This result indicates that the extent of carbothermal conversion increases as the time and temperature are raised, in agreement with the mass loss data. The absence of the SiO_2 peak at $2\theta_{101} \approx 22°$ in the XRD patterns at 1750 K for 45 min and at 1800 K for 30 min for both C contents indicates that silica is consumed completely by carbothermal reactions. The patterns of the products obtained from the starting powder of higher carbon content (42.6%) at these conditions, however, exhibit a trace of free carbon peak (not clearly seen in the displayed patterns) at $2\theta_{002} \approx 26.3°$, while the coated powder with less carbon content (40%) yields almost pure β-SiC. Interplanar spacings of the (111), (200), (220) and (311) planes from this phase present in the product were calculated to be 0.251, 0.217, 0.154 and 0.131 nm, respectively. It was found that they were in good agreement with the values of 0.2512, 0.2182, 0.1542 and 0.1315 nm published for β-SiC.

The products obtained at the final holding times (180 min at 1700 K, 45 min at 1750 K, 30 min at 1800 K) from the coated powders exhibit morphologies which consist of a mixture of whiskers and particles as shown in the images of Fig. 7. Whiskers mostly have smooth surfaces and whisker content was observed to be comparable with that of SiC particles. Table 1 shows the effect of C content of the starting powder on mean whisker diameter, mean particle and crystallite sizes of the final products. The mean size values for particles synthesized from the coated powders containing 40% and 42.6% C were found to be in the ranges of 81.6–102.4 nm and 86.3–112.6 nm, respectively. The crystallite sizes were calculated to be 45.2–56.8 nm for those of 40% C and 39–79.7 nm for those of 42.6% C. Mean whisker diameters for the starting powder having 40% C were 97.3 nm at 1800 K, 104.4 nm at 1750 K and 115.3 nm at 1700 K, while the corresponding values for the higher C content were

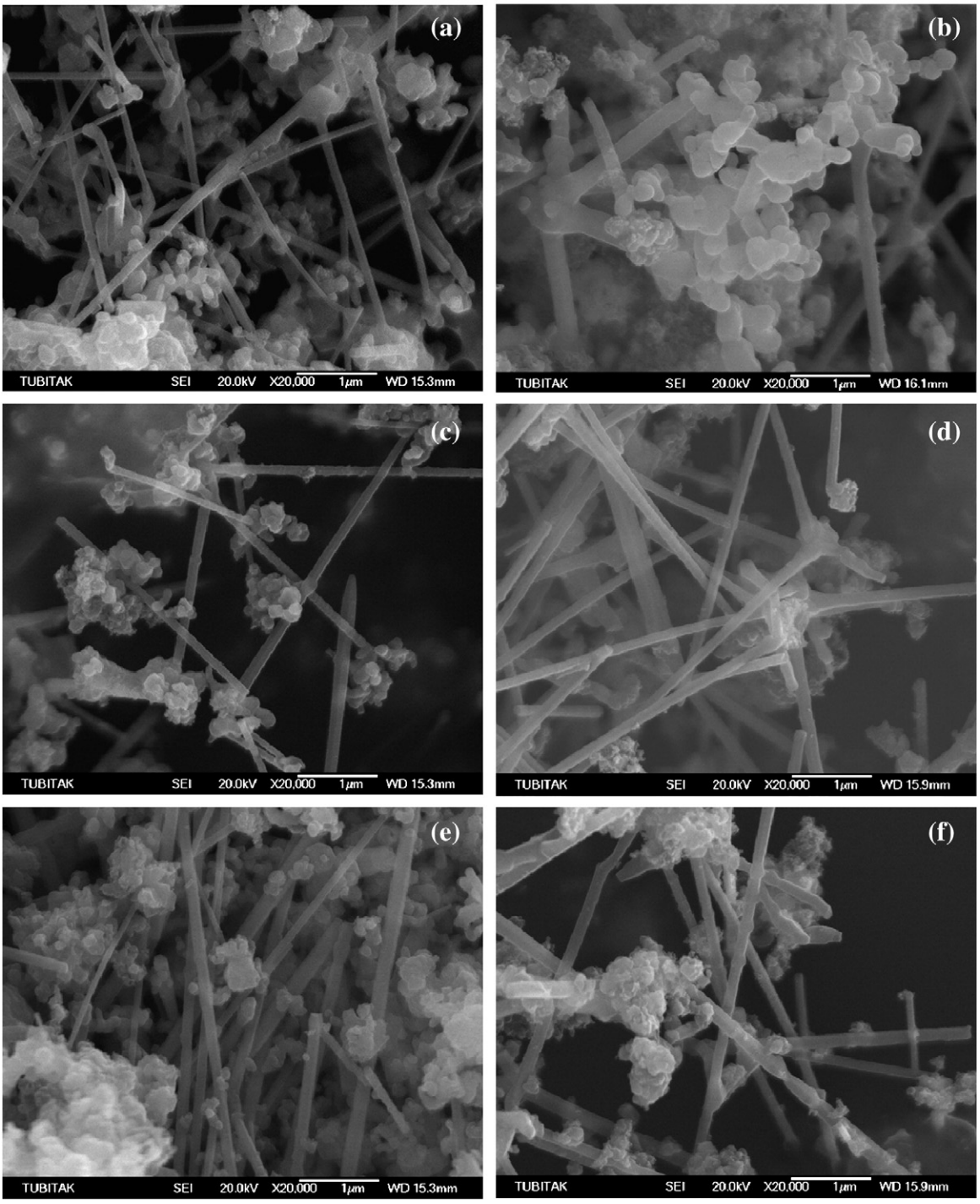


Fig. 7. FEG-SEM images of the samples after carbothermal reactions at (a, b) 1800 K, (c, d) 1750 K and (e, f) 1700 K for 30 min, 45 min and 180 min, respectively. The images on the left and right represent the morphologies of the products obtained from the C coated powders with 40% C and 42.6% C, respectively.

141, 138.8 and 153.4 nm. These findings indicate that mean sizes of particles, whiskers and crystallites generally increase with the C content of the starting powder for a given synthesis condition. This effect is more pronounced for whiskers, possibly owing to enhanced generation of the reactant gaseous species (such as CO or SiO), which play an important role in SiC formation.

It is plausible that carbothermal reactions start initially at the interface between carbon coating and SiO_2, where there is intimate contact between the solid reactants. The initial reaction will produce SiO and CO gases as predicted by the thermodynamical analysis. Fig. 4b and c indicates that the amounts of these species found to be equal at C mole fractions <0.5 implying that the SiO and CO products are formed via the following reaction:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (4)$$

Further reactions leading to SiC can also be suggested using the results of equilibrium calculations. SiC yield is predicted to increase as C mole fraction becomes higher than 0.5 (Fig. 4b). The variation of gas composition with increased C mole fraction in the single phase SiC region reveals that the amount of major specie CO increases while SiO decreases (Fig. 4c). This suggests that gaseous SiO reacts with free C,

Table 1
The effect of C content of the starting powder on mean whisker diameter, mean particle and crystallite sizes of the final products.

Synthesis conditions (temperature–time)	Carbon content of the coated powder (wt.%)	Mean whisker diameter (nm)	Mean particle size (nm)	Crystallite size (nm)
1800 K–30 min	40.0	97.3 ± 44.0	102.4 ± 35.7	45.2
	42.6	141.0 ± 46.4	86.3 ± 49.7	47.7
1750 K–45 min	40.0	104.4 ± 47.3	86.6 ± 36.3	54.9
	42.6	138.8 ± 27.8	97.6 ± 49.4	39.0
1700 K–180 min	40.0	115.3 ± 42.1	81.6 ± 31.8	56.8
	42.6	153.4 ± 42.7	112.6 ± 59.7	79.7

leading to the formation of SiC and more CO in accordance with the following reaction:

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \quad (5)$$

It is believed [5,18] that particulate SiC forms by gas–solid reactions such as reaction (5). SiC particle formation may also occur by reaction (6)

$$SiO_{2(s)} + 4CO_{(g)} \rightarrow SiC_{(s)} + 3CO_{2(g)} \quad (6)$$

CO_2 product will be immediately consumed by free C via reaction (7)

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \quad (7)$$

Reaction (7) is consistent with the thermodynamic results as the CO_2 concentration in the gas phase is always much lower than that of CO, especially in the phase fields containing SiC phase (Fig. 4c).

Formation of SiC whiskers may be explained as follows. The two widely accepted whisker growth mechanisms are vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms. Here, V, L and S stand for vapor, liquid catalyst and solid crystalline seed, respectively. SiC whiskers are usually grown in the presence of catalysts such as Ni, Fe through VLS mechanism. In this mechanism, gaseous species (such as SiO and CO) attach to a liquid catalyst located at the tip of the whisker, the constituents incorporate into the liquid and solid SiC then precipitates from supersaturated liquid at the liquid–solid interface [19]. Whiskers produced by VLS process characteristically have a spherical cap or bead. In the present study, it is more likely that SiC whiskers are formed by VS mechanism rather than VLS mechanism as no catalyst was introduced and no sign of liquid (e.g. bead formed at the tip of whisker) was observed from the SEM images (Fig. 7). The formation of SiC whisker cannot be explained by the solid–solid (SiO_2–C) reaction of (3) and by the gas–solid (SiO–C or CO–SiO_2) reactions of (5) and (6) because as soon as SiC is formed on solid SiO_2 or C, the supply of the relevant species to the tip or to the interface through SiC layer (solid-state diffusion) is difficult. In contrast, the mass transport of the gaseous species (SiO and CO) to the whisker tip via diffusion in the gas phase is sufficiently fast, resulting in one-dimensional growth with high aspect ratio. Therefore, SiC whisker growth via VS mechanism is more likely to occur by gas-gas reactions between the gaseous reactants (vapor) over the SiC nuclei (solid) initially formed by the reactions (5) and (6). It may take place primarily through the direct reaction between gaseous SiO and CO species [3,18] which results in SiC deposits on the whisker tip in accordance with reaction (8).

$$SiO_{(g)} + 3CO_{(g)} \rightarrow SiC_{(s)} + 2CO_{2(g)} \quad (8)$$

The gaseous product CO_2 is then reduced to CO via reaction (7). The continuous generation of gaseous CO and SiO species and chemical vapor deposition of SiC from these species during the process lead to further whisker growth. It should be noted that the sums of the reactions (4) and (5) or (6) and (7) or (4), (7) and (8), which are supposed to be intermediate reactions, yield the overall reaction (3).

4. Conclusions

SiO_2 particles gained mass rapidly during heating under CH_4 atmosphere owing to enhanced CH_4 pyrolysis at 1300 K. Pyrolytic C shell/SiO_2 core nanocomposite particles with high C loadings (40–50wt.%) were synthesized in a short time (<5 min) by chemical vapor deposition of C from CH_4 on particulate SiO_2. HR-TEM images of the product containing 42.6wt.% C revealed that pyrolytic carbon layer 5–8 nm thick was grown on SiO_2 particles. Carbothermal reactions in the coated powders with slightly overstoichiometric carbon contents of 40 and 42.6 wt.% yielded a mixture of SiC particles and whiskers under Ar flow at 1700–1800 K. XRD and mass measurements indicated that the extent of carbothermal conversion increased with temperature and time. It was observed that almost pure nanocrystalline SiC particles/whiskers of ~100 nm were produced from the C coated powder containing 40 wt.% C at 1750 K for 45 min and at 1800 K for 30 min. SiC whisker diameter was found to be larger when the starting powder with higher C content was used. Whiskers were proposed to grow by a vapor–solid mechanism. This study demonstrated that either C shell–SiO_2 core nanocomposite particles or SiC powders could be synthesized in the same reactor. Equilibrium thermodynamic analysis by the method of minimization of Gibbs' free energy in the Si–O–C–Ar system predicted the thermochemical reactions leading to SiC.

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References

[1] Weimer AW. Carbide, nitride and boride materials synthesis and processing. London: Chapman&Hall; 1997.
[2] Koch CC. Nanostructured materials processing, properties and applications. New York: William Andrew Publishing; 2007.
[3] Saito M, Nagashima S, Kato A. Crystal growth of SiC whisker from the $SiO_{(g)}$–CO system. J Mater Sci Lett 1992;11:373–6.
[4] Kennedy P, North B. The production of fine silicon carbide powder by the reaction of gaseous silicon monoxide with particulate carbon. Proc Br Ceram Soc 1983;33:1–15.
[5] Koc R, Cattamanchi SV. Synthesis of beta silicon carbide powders using carbon coated fumed silica. J Mater Sci 1998;33:2537–49.
[6] Tong L, Reddy RG. Thermal plasma synthesis of SiC nano-powders / nano-fibers. Mater Res Bull 2006;41:2303–10.
[7] Wu R, Yang G, Pan Y, Chen J, Zhai R, Wu L, et al. Prism-shaped SiC nanowhiskers. J Alloys Compd 2008;453:241–6.
[8] Jin HB, Li JT, Cao MS, Agathopoulos S. Influence of mechanical activation on combustion synthesis of fine silicon carbide (SiC) powder. Powder Technol 2009;196:229–32.
[9] Ghosh B, Pradhan SK. Microstructural characterization of nanocrystalline SiC synthesized by high-energy ball-milling. J Alloys Compd 2009;486:480–5.
[10] Raygan S, Kondori B, Yangijeh HM. Effect of mechanical activation on the production of SiC from silica sand. Int J Refract Met H 2011;29:10–3.
[11] Katsunori K, Seiichiro H, Masayoshi S, Yoshiro O. Lubricities of SiO_2 particles coated with carbon. J Ceram Soc Jpn 2004;112:210–3.
[12] Vital A, Richter J, Figi R, Nagel O, Aneziris CG, Bernardi J, et al. One-step flame synthesis of ultrafine SiO_2–C nanocomposite particles with high carbon loading and their carbothermal conversion. Ind Eng Chem Res 2007;46:4273–81.
[13] Joint Committee on Powder Diffraction Standards (JCPDS). Swartmore PA: International Center for Diffraction Data; 2008.
[14] Eriksson G. Thermodynamic studies of high temperature equilibrium. Chem Scr 1975;8:100–3.
[15] Besmannn TM. SOLGASMIX-PV, a computer program to calculate equilibrium relationships in complex chemical systems. Report No: ORNL/TM-5775. Oak Ridge National Laboratory; 1977.

[16] Chase MW, Davies CA, Downey JR, Frurip DJ, McDonald RA, Syverud AN. JANAF thermochemical tables. 3rd ed.J Phys Chem Ref Data 1985;14(Suppl l).
[17] Barin I. Thermochemical data of pure substances. WeinHeim: VCH Verlagsgesellschaft; 1993.
[18] Luo X, Ma W, Zhou Y, Liu D, Yang B, Dai Y. Synthesis and photoluminescence property of silicon carbide nanowires via carbothermic reduction of silica. Nanoscale Res Lett 2010;5:252–6.
[19] Lee JS, Byeun YK, Lee SH, Choi SC. In situ growth of SiC nanowires by carbothermal reduction using a mixture of low-purity SiO_2 and carbon. J Alloys Compd 2008;456:257–63.



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