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The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC

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Abstract

Uniform nano-sized beta-silicon carbide (β-SiC) powder was synthesized from the reaction of silicon (Si) and carbon black (C). Mixed Si and C-black powder were pressed into pellets and the influence of four parameters, temperature (1250, 1300 and 1350 °C), heating rate (20 and 50 °C/min), soaking time (1 and 3 h) and atmosphere (vacuum and argon), were tested. It was found that higher temperatures, higher heating rates and longer soaking times in a vacuum system lead to lower free Si content in the SiC powder created. Temperature was the parameter with the greatest influence on the Si content of the SiC powder. This study also found that the Si–C reaction occurs through gas–solid (SiO–C) and solid–solid (Si–C) reactions that occur simultaneously.

Keywords: SiC powder; Synthesis; Si–C reaction; Free Si; Reaction parameters

1. Introduction

Silicon carbide (SiC) is a material used in advanced ceramic applications due to its strength, hardness, corrosion resistance, low thermal expansion coefficient and high thermal conductivity. Due to its covalent bonding, SiC is difficult to sinter without sintering aids or pressure [1,2]. SiC powder can be produced through many methods, but most of the SiC powder produced today is manufactured using the Acheson process [3]. This process is a several hour long carbothermic reaction of SiO_2 with carbon powder at temperatures around 2200–2400 °C. Due to the high reaction temperatures and long reaction times of the process, the powders produced have a large particle size and consist of mostly alpha-phase SiC. However, using a fine high purity starting powder, well-sintered SiC bodies can be produced with less additives and pressure. Currently, fine SiC powder can be synthesized through pyrolysis of organosilicon polymers [4,5] and gas-phase reaction methods [6,7]. The pyrolysis method involves the decomposition of polymers, such as trichloromethylsilane or polycarbosilane, at 1000–1500 °C. For gas-phase synthesis, silane or chlorosilane is reacted with hydrocarbons to produce SiC. Although these methods produce fine high purity particles, they have a low yield of SiC and generate hazardous gas products, such as HCl or CH_4.

Because inexpensive silica and carbon are used as starting materials, carbothermal reduction is cheaper and more efficient than gas synthesis, making it the best choice for SiC production. Much research has been done to develop methods of reducing the temperature of the carbothermal reduction process. For example, high-energy reaction milling can synthesize nano-sized SiC powder without heating [8–10]. Microwave heating is another technique that produces fine and uniform SiC powder at lower temperatures and shorter times than the conventional process [11,12]. However, thermodynamic data [9,13] shows that at room temperature the reaction of silicon (Si) and carbon (C) to form SiC has a negative free energy of formation, whereas the silica (SiO_2) and carbon (C) reaction has a large positive free energy of formation [14,15]. This means that theoretically SiC can be formed at lower temperatures by using the Si–C reaction than the SiO_2–C reaction.

In this research, beta-silicon carbide (β-SiC) was synthesized from the reaction of Si and C, and the influence of temperature, soaking time, heating rate and atmosphere on the reaction were studied. After the powders were created, the amount of free Si and C was measured, and this data was used to determine the underlying mechanisms of the reaction. The morphology and surface area of SiC powder were also examined.

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Table 1
Chemical composition and physical properties of Si and C powder

Powder	Element (wt%)								Total oxygen (wt%)	Surface area (m^2/g)	Average size (μm)	Average density (g/cm^3)
	Si	Fe	Ca	Al	Ti	Sn	C	S				
Silicon	97.35	0.44	0.42	1.2	0.11	0.49	–	–	2.54	1.62	11.68	2.42
Carbon black	0.13	–	–	–	–	–	98.53	1.34	7.57	80	–	2.05

Table 2
Free Si, C and O contents, weight loss and specific surface area of synthesized β-SiC powders

Heating temperature-rate-time	Atmosphere	Free Si (wt%)	Free C (wt%)	Total oxygen (wt%)	Weight loss (%)	Specific surface area (m^2/g)
1250-50-1	Vacuum	6.464	0.085	–	2.48	–
1250-50-1	Ar	12.935	0.078	–	0.057	–
1300-50-1	Vacuum	1.235	0.108	0.019	2.710	22.36
1300-50-1	Ar	5.190	0.086	0.008	0.998	29.32
1350-50-1	Vacuum	0.106	0.141	0.014	Broken pellet	19.75
1350-50-1	Ar	0.347	0.075	0.001	Broken pellet	25.06

2. Experimental procedure

Si powder of 97% purity (Riedel-DeHaën) was mixed with carbon black in a polyethylene bottle using alumina balls and ethyl alcohol as medium. The chemical composition and physical properties of the Si and carbon powders are shown in Table 1. A mixed powder of 1:1 Si and C mole ratio was prepared. After mixing, the slurry was dried in an oven and formed into pellets. The pellets were pressed at 43 MPa pressure to a 12 mm diameter and 3.6 mm thickness. Pellet samples were placed in covered carbon crucibles and fired in a controlled atmosphere furnace at temperature of 1250, 1300 and 1350 °C, with soaking times of 1 and 3 h. Two different heating rates, 20 and 50 °C/min, were used, and the reaction was carried out in both a vacuum and an argon atmosphere. The controlled pressures in vacuum and argon atmosphere were 4 Pa and 1.01×10^5 Pa, respectively. After the reaction, the pellets were measured for weight loss and ground to pass through 325 mesh sieve for characterization.

The crystalline phases of the synthesized powder were identified using a X-ray diffractometer (XRD: Model XRD-6000, Shimadzu). The free Si was measured by using the standard method JIS R1616, and C content was measured with a multiphase carbon and moisture determinator (Model RC-412). The oxygen content was measured by using a nitrogen/oxygen determinator (Model TC-436). The shape and size of the powder were determined with field emission scanning electron microscopy (FE-SEM: Model JSM-6304F, JEOL). Specific surface area of the powder was measured by using nitrogen adsorption based on the Braunauer–Emmett–Teller (BET) theory (Model Autosorb-1, Quantachome).

3. Results

3.1. SiC powder synthesized in vacuum and Ar atmosphere

Pellets of mixed Si and C-black powders were fired at 1300 and 1350 °C with soaking times of 1 h and a heating rate of 50 °C/min. The weight loss, free Si, C and O contents of SiC powders synthesized in vacuum and argon atmosphere under these conditions are compared in Table 2. At 1300 °C, samples reacted in the vacuum atmosphere had a higher weight loss than those reacted in the Ar atmosphere. At 1350 °C, the samples broke in both atmospheres due to the formation of high amounts of SiO and CO gas. The free Si content in the SiC powders produced in a vacuum was lower than that for those produced in Ar, but there was not a great difference in the free C content. The oxygen content for both atmospheres was below 0.02 wt%. The XRD peaks in Fig. 1 show Si peaks along with the β-SiC

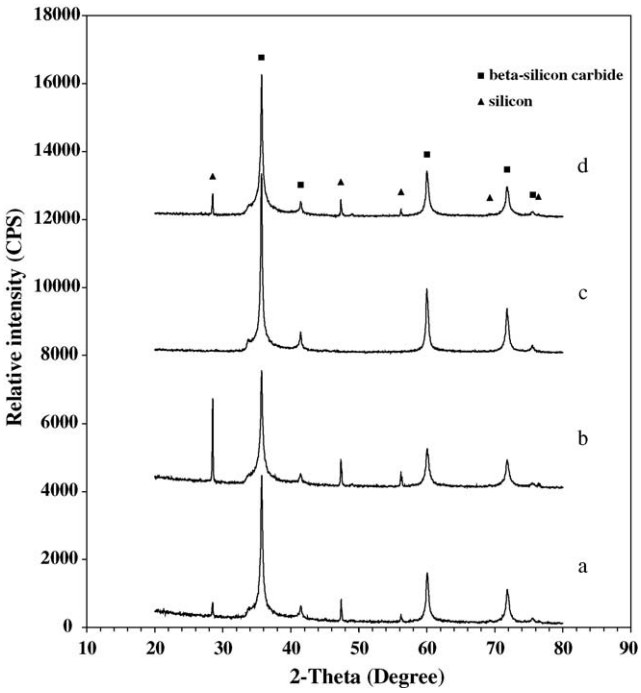

Fig. 1. XRD results of SiC powder synthesized with heating rate 50 °C/min for 1 h at: (a) 1300 °C in vacuum (b) 1300 °C in Ar (c) 1350 °C in vacuum and (d) 1350 °C in Ar.

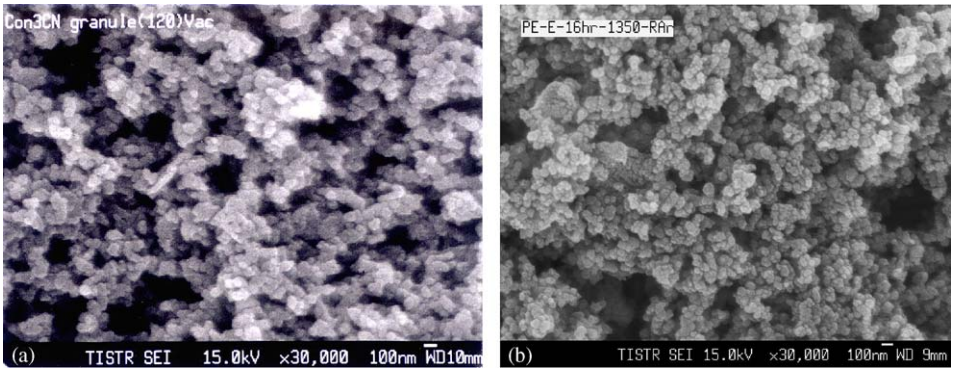

Fig. 2. FE-SEM micrographs of SiC powder synthesized at 1350 °C, heating rate 50 °C/min for 1 h in: (a) vacuum and (b) Ar.

peaks. Higher intensity Si peaks were observed for samples synthesized in Ar, which correlates with the data in Table 2.

Fig. 2 shows that the powders created in both atmospheres have an equiaxed morphology and uniform size. However, the specific surface area in Table 2 shows that powders synthesized in Ar has a little higher specific surface area than those produced in vacuum under the same conditions.

3.2. SiC powder synthesized at various reaction temperatures, heating rates and soaking times

The XRD results of powder synthesized at different temperatures, heating rates and soaking times are shown in Figs. 3 and 4. Peaks of β-SiC and Si were observed for powders produced at 1250 and 1300 °C, but only β-SiC peaks was observed for powders created at 1350 °C. For powders produced at the same heating rate, soaking time and reaction atmosphere, it was found that a higher reaction temperature resulted in a smaller amount of free Si. While it has already been established in part 1 that the Si–C reaction in vacuum results in smaller amounts of free Si, Fig. 5 shows that as temperature increases the difference of free Si content in both atmospheres decreases until the temperature reaches a point of equal content. The effect of heating rate on the powders is shown in Figs. 4 and 6. The higher heating rate of 50 °C/min resulted in a more complete reaction (smaller amount of free Si) than the slower heating rate of 20 °C/min. At the lowest reaction temperature (1250 °C), the two heating rates created powders with significant differences in the amount of free Si,

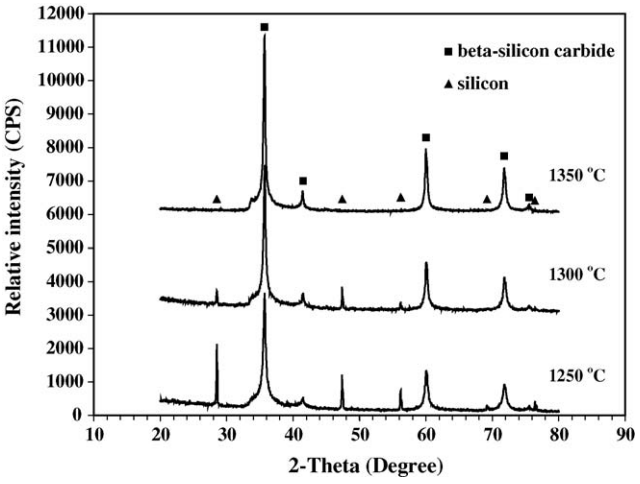

Fig. 3. XRD results of synthesized powder produced at 1250–1350 °C for 1 h, heating rate 50 °C/min in vacuum.

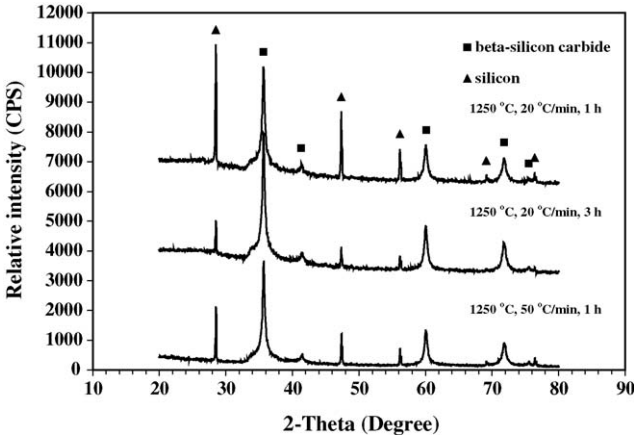

Fig. 4. XRD results of synthesized powder produced at 1250 °C for 1 and 3 h, heating rate 20–50 °C/min in vacuum.

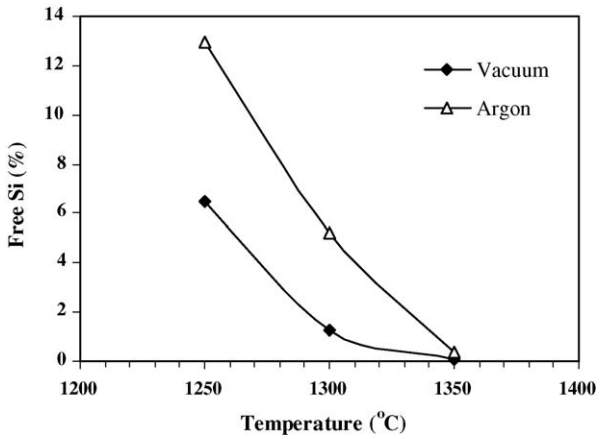

Fig. 5. Free Si content in β-SiC powders synthesized at 1250–1350 °C for 1 h, heating rate 50 °C/min in vacuum and Ar atmosphere.

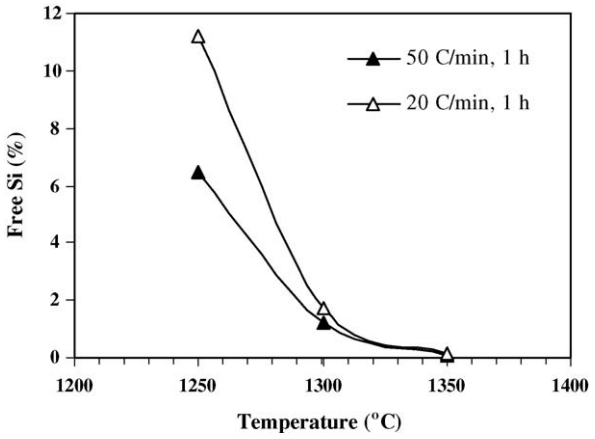

Fig. 6. Free Si content in β-SiC powders synthesized at 1250–1350 °C for 1 h, heating rate 50 and 20 °C/min in vacuum.

Table 3
Free Si and C contents and weight loss of synthesized β-SiC powders

Heating temperature-rate-time	Atmosphere	Free Si (wt%)	Free C (wt%)	Weight loss (%)
1250-20-1	Vacuum	11.180	0.070	1.66
1250-20-3	Vacuum	3.835	0.073	2.54
1300-20-1	Vacuum	1.719	0.077	2.54
1300-20-3	Vacuum	1.100	0.104	3.62

but at the highest reaction temperature (1350 °C) the free Si content of powders produced by the different heating rates was almost equivalent. The influence of the soaking time is shown in Table 3. Increasing the soaking time increased the weight loss but decreased the free Si content. From these experimental results, temperature seems to be the most significant factor in the reaction. At lower temperatures the heating rate, soaking time and atmosphere showed more influence on the Si content after the reaction than at high temperatures. Fig. 7 shows that all the powders created had the same morphology despite any difference in the reaction parameters. All the powders created had an equiaxed morphology and a fine particle size of 10–100 nm.

4. Discussion

Normally, SiC powder is produced by the reaction of SiO_2 and C. It is well known that the reaction mechanism in the carbothermal reduction of SiO_2 process proceeds through the intermediate gaseous silicon monoxide (SiO) according to the following reactions [14–16]:

$$SiO_2 + C = SiO_{(g)} + CO_{(g)} \quad (1)$$

$$SiO_{(g)} + 2C = SiC + CO_{(g)} \quad (2)$$

$$SiO_2 + 3C = SiC + 2CO_{(g)} \quad (3)$$

The Gibbs free energy change of SiO_2–C system (reaction (3)) at temperature range from 1200 to 1400 °C is positive ($\Delta G \approx 104$ to 37 kJ) [13,17]. In contrast, the Gibbs free energy change of Si–C system (reaction (4)) at the same temperature range is negative ($\Delta G \approx -61$ kJ). Therefore, SiC formation from the reaction of Si and C can occur at a lower temperature

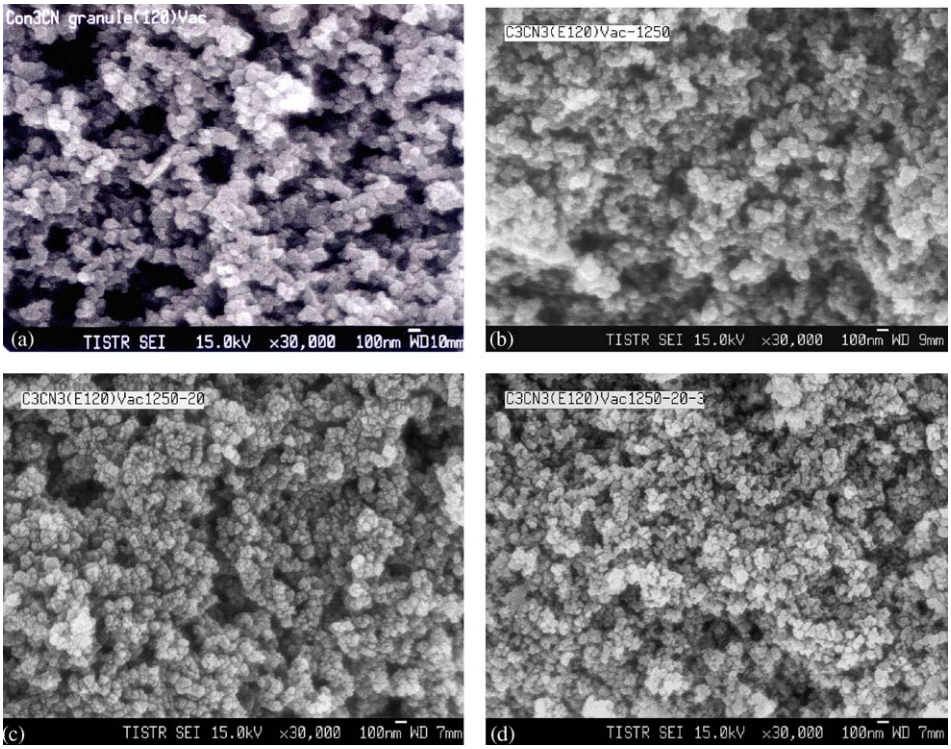

Fig. 7. FE-SEM micrographs of β-SiC powder synthesized in vacuum at: (a) 1350 °C, 50 °C/min, 1 h, (b) 1250 °C, 50 °C/min, 1 h, (c) 1250 °C, 20 °C/min, 1 h and (d) 1250 °C, 20 °C/min, 3 h.

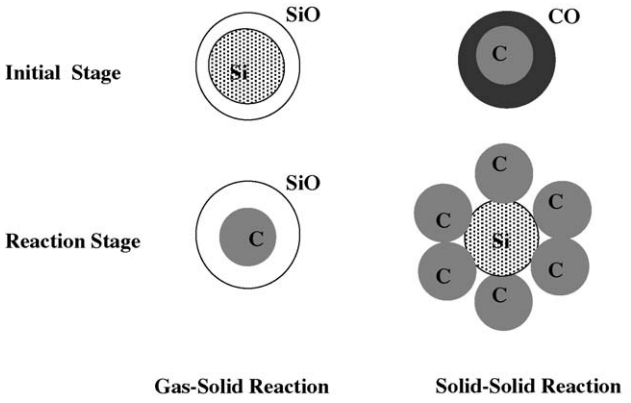

Fig. 8. Si–C reaction mechanism of SiC forming.

than that of the SiO_2 and C system. Lower free Si content and higher weight loss was measured for SiC powders synthesized in vacuum, therefore the results of this experiment show that Si and C react better in vacuum than in an Ar atmosphere. The breaking of the pellets at 1350 °C was due to the large amount of gas products in the reaction. According to this experimental result, SiC was not created directly from Si–C reaction, instead gaseous phases of SiO and CO were generated as intermediate products in the reaction. Si and C initially reacted with the limited amount of oxygen on the surface of the Si and C particles to form SiO and CO (reactions (5) and (6)). Consequently, SiO reacted with C in a gas–solid reaction and Si reacted with C in a solid–solid reaction simultaneously (reaction (7)). The Si and C reactions are:

$$Si + C = SiC \quad (4)$$

$$Si + \tfrac{1}{2}O_{2(g)} = SiO_{(g)} \quad (5)$$

$$C + \tfrac{1}{2}O_{2(g)} = CO_{(g)} \quad (6)$$

$$Si + 3C + SiO_{(g)} = 2SiC + CO_{(g)} \quad (7)$$

In the temperature range of 1200–1400 °C, the Gibbs free energy change of reaction (7) is −140 kJ, which is lower than that of reaction (4) ($\Delta G \approx -61$ kJ). Therefore, reaction (7) can perform better than reaction (4) at the same temperature range. In a vacuum the SiO and CO gases generated at the surface of the Si and C particles are removed rapidly. This will result in a more complete reaction due to high contact area of SiO to C and Si to C (Fig. 8). In contrast, reaction in an Ar atmosphere will result in less contact area due to slower removal of SiO and CO gases from particle surface which will decrease the rate of the SiC forming reaction resulting in higher Si content and less weight loss. It was found that higher reaction temperatures, greater heating rates, longer soaking times in a vacuum provided the best conditions for the Si–C reaction.

5. Conclusions

(1) The reaction of Si and C-black powder can produce uniform nano-sized β-SiC powder in both a vacuum and an Ar atmosphere.
(2) β-SiC powder synthesized in a vacuum had lower free Si content than that synthesized in an Ar atmosphere.
(3) Using higher reaction temperatures, heating rates or longer soaking times in a vacuum system can produce lower free Si content of β-SiC powder.
(4) Free C content in synthesized β-SiC powder was not significantly affected by differences in temperature, heating rate, soaking time and atmosphere.
(5) At lower temperatures, the influence of heating rate, soaking time and atmosphere on the Si–C reaction is greater than at high temperatures.
(6) Si–C reaction with some amount of oxygen in the system produced SiC through simultaneous gas–solid (SiO–C) and solid–solid (Si–C) reactions.

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