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# Effect of process parameters on the production of nanocrystalline silicon carbide from water glass

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**Abstract**

Nanocrystalline silicon carbide was synthesized from the precursor prepared by spray drying slurry of water glass and carbon black. The effect of process parameters, such as reaction temperature, reaction time and carbon content, on phase evolution, crystallite size and specific surface of the resulting samples were characterized by XRD, SEM and BET. The results show the powder produced in this process has a very fine crystallite size and high specific area and the reaction can be completed at 1550 °C for 2 h when the C/Si ratio is 5 or larger. In addition, the powder is of high purity, because sodium oxide in the precursor can be eliminated by the escape of sodium at high temperature. It is a simple and cost-efficient method to synthesize nanocrystalline silicon carbide using cheap and abundant water glass as silicon source.


*Keywords:* D. SiC; Water glass; Carbothermal reduction

## 1. Introduction

It has been recognized that the final properties of SiC ceramics depend largely on the characteristic of the starting powders. In general, the preparation of high-performance SiC ceramics requires ultrafine SiC powders. In order to optimize the production of the ultrafine particles, a number of alternative methods, such as sol–gel process [1], thermal decomposition of silane compound [2,3] and chemical vapor deposition [4–6], have been developed because of the limitation of conventional Acheson process. However, the powders prepared by these methods are relatively expensive, due to low production rate of the methods and their demand for expensive equipments and raw materials. Industrially, the carbothermal reduction of silica to produce SiC powders is more interesting, since inexpensive silica and carbon (or carbon precursors) are chosen as the starting materials.

Although the overall reaction of the carbothermal reduction of silica could be expressed by:

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

the reaction is rather complex and proceeds in a number of steps. The commonly accepted mechanism is that SiC is synthesized through intermediate silicon monoxide (SiO) gas. Hence, the extent of this reaction is strongly influenced by the contact area between the reactants and the distribution of the carbon within the silica. In order to obtain the mixtures of silica and carbon with intimate contact, several authors have used silica sol [7–9] or silica gel [10] as silicon resources to synthesize SiC. Fine and high-purity β-SiC was produced in these processes.

In this study, we reported the synthesis of nanocrystalline β-SiC powders by carbothermal reduction of the precursors prepared by spray drying a slurry of water glass (sodium silicate) and carbon black. There are three advantages in using water glass as silicon resources. First, water glass can fully mix with carbon black and the intimate mixing of the reactants can be formed after spray drying the slurry. Therefore, SiC would be produced at a comparatively low temperature. Second, using it as silicon sources can remarkably reduce the cost of the produced SiC, since the price of water glass is much cheaper than silica sol or silica gel. Third, the composition of SiC produced by this process is easily adjustable by adding other components which are soluble in water. These components can be used as sintering additives or to obtain ceramic composites with homogeneous distribution of the components.

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## 2. Experimental

Technical-grade water glass solution (Beijing Chemical Company) was used as raw silicon sources. The composition of the solution was analyzed by chemical method and X-ray Fluorescence Spectrometer (XRF-1700, Shimadzu, Japan): 37.8 wt% solid content (8.9 wt% $Na_2O$ and 28.9 wt% $SiO_2$), less than 0.2 wt% impurities. Carbon black of 0.1 μm (Chuannan Mine Field Carbon Factory of Sichuan Petroleum Administration) was used as carbon sources.

Firstly, a given amount of carbon black was added to the water glass solution. Tween-80 (CP, Guangzhou Chemical Company) used as dispersant was also added into the solution. The slurry was mixed under high agitation for about 4 h. Then, the resulting mixture was spray dried in a spray dryer unit at a rate of 1.5 kg/h with inlet and outlet temperatures keeping at 220 and 110 °C. Carbothermal reduction of spray dried precursors was performed in a high temperature graphite resistance furnace, using a graphite crucible, heated at 10 °C/min in flowing argon (1 L/min) up to 1200–1700 °C and held for 0.5–8 h. Finally, the produced powders were heated at 700 °C in air to eliminate the unreacted free carbon black.

The precursor and synthesized powders were characterized using X-ray diffraction (D/max 2200 PC, Rigaku, Japan, Cu Kα radiation using for X-ray diffraction) for structural evolution, while the crystallite sizes of the powders were estimated from the (2 2 0) peaks of XRD patterns using the Scherrer formula. Free carbon content of the synthesized powder was determined by firing the powder to constant weight in air at 700 °C. The powders were observed under a scanning electron microscope (S-4300, Hitachi, Japan). BET (NOVA4000, Quantachrome, America) was also used for characterization.

## 3. Results and discussion

### 3.1. The spray dried precursor

Fig. 1 shows a SEM micrograph of the precursor powders. As it can be seen, the precursors were spherical powders with particle size of 5–20 μm. It would provide intimate contact between the reactants since carbon was coated by water glass.

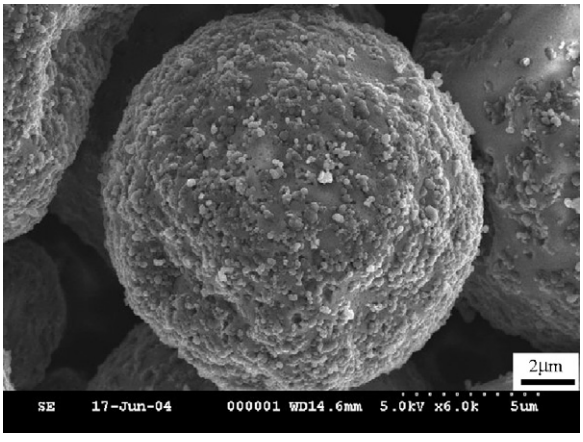


Fig. 1. SEM micrograph of the spray dried precursors.

Thus, the precursor would result in a high reaction rate and yield.

### 3.2. The effect of process parameters on the production of SiC

#### 3.2.1. Effect of reaction temperature

Reaction temperature is an important factor which influences carbothermal reduction kinetics and formed phase of silicon carbide. In general, an increase in temperature accelerates carbothermal reduction rate, and extremely high temperature leads to the transformation of SiC polymorphs.

Fig. 2 shows the XRD patterns of the precursor and powder produced from water glass and carbon black with silica-to-carbon ratio of 1:5 at various temperatures for 5 h in flowing argon. It can be seen that, there are no peaks in X-ray diffraction pattern of the precursor, indicating it is in the amorphous state. After heating at 1200 °C, thermal phase transformation took place in amorphous water glass, resulting in the formation of sodium disilicate ($Na_2Si_2O_5$) and cristobalite ($SiO_2$). As the temperature was increased to 1300 °C, the amorphous sodium disilicate phase was remarked by decreased because of the escape of sodium. It could be attributed to the sublimation of sodium oxide (approximately 1275 °C [11]) and the evaporation of sodium metal formed from the reduction of sodium oxide at high temperature. The escape of sodium was conformed by analysis of the deposits on the inner wall of the furnace. XRD revealed that the composition of the deposit is sodium carbonate.

Further increase in reaction temperature resulted in the complete escape of sodium. XRF revealed that sodium contents of the powder synthesized at 1400 °C for 5 h was 136 ppm. Because of the intimate contact available for carbon and silica in the precursor, SiC was formed at 1400 °C. Although the peak of crystalline β-SiC was not very evident, the peak shoulders of $SiO_2$ at $d = 0.248$ nm implied the formation of β-SiC. At above 1500 °C, sharp and well defined peaks of β-SiC and no peaks of

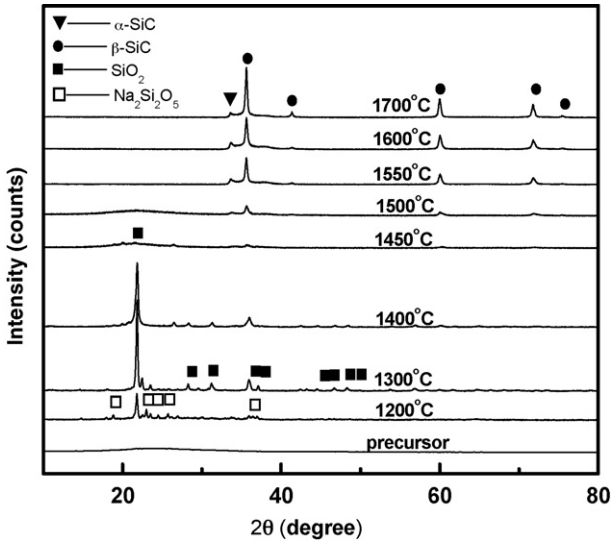


Fig. 2. XRD patterns of the precursor and products synthesized at various temperatures for 5 h in flowing argon.

Table 1
Mean crystallite sizes of SiC calculated using the Scherrer formula from (2 2 0) diffraction peak of β-SiC as a function of reaction temperature and time

| Heat treatment temperature (°C) | Heat treatment time (h) | Mean crystallite size (nm) |
|---|---|---|
| 1450 | 5 | 26.7 |
| 1500 | 5 | 28.8 |
| 1550 | 0.5 | 26.7 |
| 1550 | 1 | 31.1 |
| 1550 | 2 | 41.0 |
| 1550 | 5 | 60.0 |
| 1550 | 8 | 71.4 |
| 1600 | 5 | 71.4 |
| 1700 | 5 | 112.8 |

silica were detected, indicating complete conversion of silica. XRF revealed that the powder synthesized at 1550 °C for 5 h has characteristics of high quality with oxygen contents of 1.68%, sodium contents of 61 ppm.

Fig. 2 also showed that there was a small additional peak near $2\theta = 33.5^\circ$ in the patterns of the powders produced above 1400 °C. According to the computer simulation results calculated by Pujar and Cawley [12], the additional peak results from stacking faults. Another viewpoint attributes this additional peak to the existence of the 2H polytype [13]. The presence of the 2H polytype should induce a much stronger reflection peak near $2\theta = 38.3^\circ$. However, no such peak is observed in the XRD patterns. Therefore, this peak should result from the stacking faults.

Although an increase of reaction temperature can accelerate the completeness of reaction (1), it leads to the growth of crystallize sizes of SiC and causes a higher driving force for sintering. Table 1 lists the crystallite size of the product calculated using the Scherrer formula from (2 2 0) diffraction peak of β-SiC. For most of the powders produced above 1400 °C, mean crystallite sizes of the product are in the range of a few ten nanometers (<100 nm). For example, the mean crystallite size of samples produced at 1550 °C is 60 nm. The result also indicated that crystallite size increased significantly with the increase of the applied reaction temperatures. In addition, a drastic sintering begins to occur at higher temperature. This can be proved by the SEM micrograph of powder samples produced at 1550 and 1700 °C (see Fig. 3).

Temperature also influences the surface area of the product (see Fig. 4). It can be seen that surface area of the products increased with increasing temperature. The reason could result from water glass. According to the phase diagram of $Na_2O$–$SiO_2$ [14], it would result in the formation of liquid phase during heating steps at the high temperatures (above approximately 800 °C). The liquid would decrease the content of pore in the samples, resulting in the decrease of the surface area of the product. The increase of reaction temperature accelerated the escape of sodium, decreasing the effect of liquid phase. Therefore, the highest surface area powders were obtained at higher temperatures, i.e., between 1550 and 1600 °C. But, the higher the temperature, the higher the efficiency of fine particles forming agglomerates by sintering of the primary crystalline particles. Thus, a drastic drop of the specific surface area was observed at temperature higher than 1600 °C.

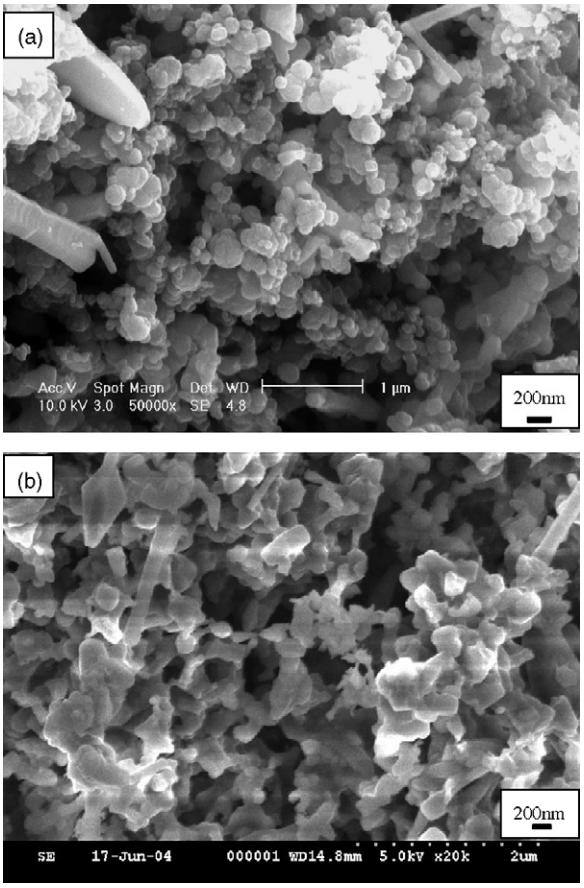


Fig. 3. SEM micrograph of samples produced at different reaction temperatures for 5 h in flowing argon: (a) 1550 °C and (b) 1700 °C.

### 3.2.2. *Effect of reaction time*

The reaction time at the synthesis temperature also had effect on the synthesis of SiC. Fig. 5 shows the XRD patterns of the powders produced at 1550 °C for various times in

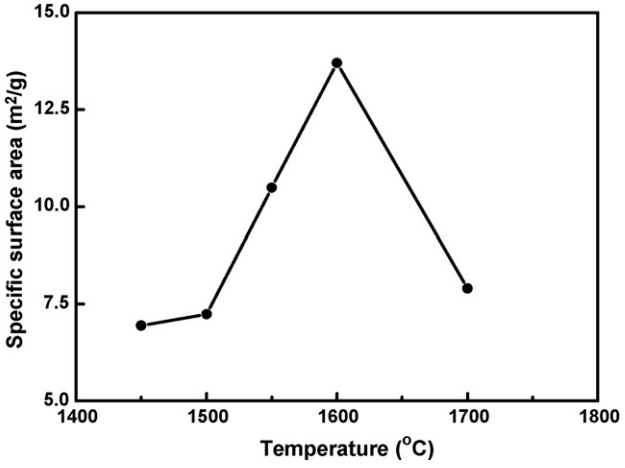


Fig. 4. BET surface area of the reaction products at various temperatures for 5 h in flowing argon.

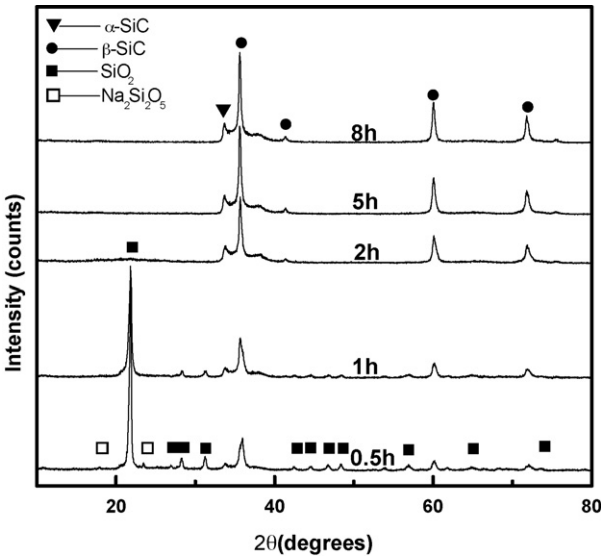


Fig. 5. X-ray diffraction patterns of the reaction products at 1550 °C for various times in flowing argon.

flowing argon. It can be seen that the increase of the holding time leads to the increase of the SiC yield. When time goes up to 2 h at 1550 °C, the formation of SiC powders with trace of $SiO_2$ was observed. Further increase in reaction time, no visible change in the SiC content yielded. But, the SiC peak is sharper, indicating that the size of crystallite grow up. The effect of variation of the reaction time on the crystallite size is shown in Table 1.

The result of BET surface area of the precursors pyrolyzed at 1550 °C for various dwell time (Fig. 6) showed that the BET surface area of the samples increased with the reaction time. This would be attributed to the decrease of $Na_2O$ content in the produced samples. However, when the reaction time was longer than 1 h, a new effect acts. The formed SiC crystallites grew up, so that the BET surface began to decrease. Thus, if SiC formation is complete, heat treatment should be stopped to avoid a decrease of the specific surface area.

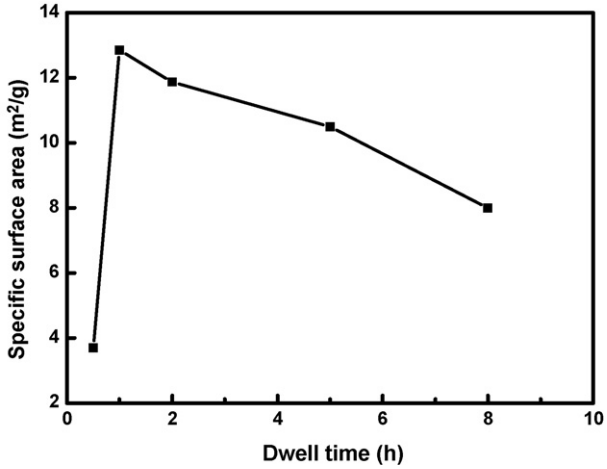


Fig. 6. BET surface area of the reaction products at 1550 °C for various times in flowing argon.

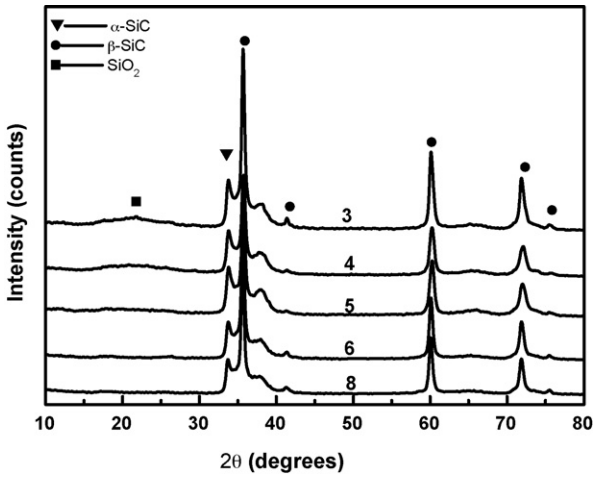


Fig. 7. X-ray diffraction patterns of the reaction products with different C/Si mole ratio at 1550 °C for 2 h in flowing argon.

### 3.2.3. Effect of carbon content

Although the overall reaction of the carbothermal reduction of silica could be expressed by reaction (1), it proceeded via a nucleation and growth process. According to the model of core shrinking [15], SiO is firstly formed at contact points of C and $SiO_2$.

$$C(S) + SiO_2(S) = SiO(g) + CO(g) \quad (2)$$

Once CO is formed, it may react with $SiO_2$ to synthesize SiO(g).

$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g) \quad (3)$$

Then, $CO_2$ reacts with carbon to synthesize CO,

$$2C(s) + CO_2(g) = 2CO(g) \quad (4)$$

which, in turn, reacts with silica according to reaction (3) to continue the cycle. The SiO reacts to form new SiC nuclei in the following manner:

$$2C(s) + SiO(g) = SiC(s) + CO(g) \quad (5)$$

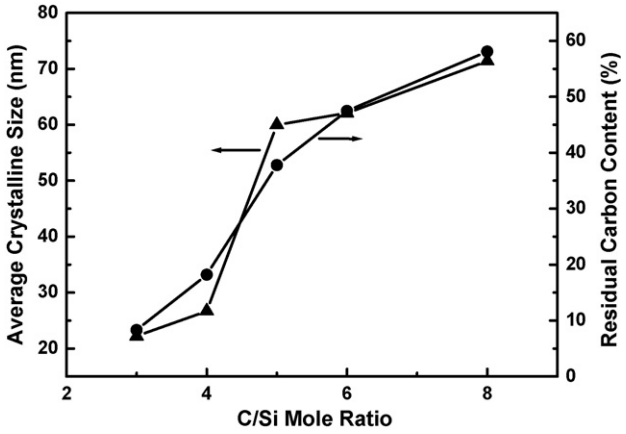


Fig. 8. The mean crystallite size and residual carbon content in the produced powders at 1550 °C for 2 h as a function of C/Si mole ratio.

Since the reaction resolves the formation of SiO, the contact area between reactants has a substantial influence on the carbothermal reduction. It is a good way to increase the contact area by increasing the content of carbon black in the precursor. Excess carbon also could act as dispersant and a barrier to prevent neck growth or adhesion of SiC particles and the loss of SiO. From Fig. 7, with increase in the carbon content in the precursor, a significant increase in the silicon carbide formation in resulting powder was observed. When a ratio of carbon and silica is 5, the complete of carbothermal reduction could be observed at 1550 °C for 2 h. Further increase in the carbon content in the precursor did not lead to substantial change in the intensity of SiC peak, while the amount of free carbon included in the samples was increased (see Fig. 8). These results are in agreement with the above statement. However, Fig. 8 also shows that the crystallite size increases with the increase of carbon content. This would be attributed to the formation of liquid phase at high temperature. It would prevent the growth of SiC nuclei. The increase of carbon content leads to the decrease of water glass in the precursor. Thus, the effect of liquid phase is reduced.

## 4. Conclusions

1. Technical-grade water glass can be used as silicon source to synthesize nanocrystalline silicon carbide powder.
2. An increase in reaction temperature can accelerate the reaction rate. Extremely high temperature is not useful because it can leads to a rapid growth of crystallite and to a higher driving force for sintering.
3. The SiC yield and crystallite size increased with prolonged reaction time.
4. The enhancement of carbon content in the precursor lead the increase of the reaction rate and crystallize size of the products.

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