

## Simple method to synthesize nanocrystalline beta-SiC

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Silicon carbide (SiC) is an attractive material for advanced ceramics applications due to its outstanding strength under oxidizing and high-temperature conditions, low thermal expansion coefficient and excellent corrosive resistance. It has been recognized that the final properties of SiC ceramic depend largely on the characteristics of the starting powder from which the ceramics are sintered. The preparation of high-performance SiC ceramics requires ultrafine particles and chemically pure starting powders. Various methods, such as sol-gel processes [1], pyrolysis of silane compounds [2, 3], laser- or plasma-driven chemical vapor deposition [4–6], have been proposed for the synthesis of ultrafine SiC powder. These methods can manufacture high purity ultrafine SiC powder at 1500 °C or even lower temperature. In terms of economy and efficiency, however, the carbothermal reduction of SiO<sub>2</sub> is the best choice. It involves inexpensive SiO<sub>2</sub> and carbon (or carbon precursors) as the starting materials.

Because the carbothermal reduction of SiO<sub>2</sub> is a heterogeneous solid-state reaction, the mixing condition of the two raw materials greatly influences the properties of the powder that is produced. In order to produce high-quality SiC powder, a fine starting reactant is required. Several authors have used silica sol as silicon resource for the production of SiC [7–10]. Fine and high-purity β-SiC was produced in these processes.

In this study, we used water glass (sodium silicate) solution as silicon sources to synthesize SiC. There are three advantages in using sodium silicate solution. First, sodium silicate solution can mix fully with soluble carbon precursor, such as sugar. After decomposition of sugar, the intimate mixing of the reactants can be formed. It provides high surface contact between SiO<sub>2</sub> and carbon. 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 sodium silicate is much cheaper than silica sol. 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.

Technical-grade sodium silicate solution (Beijing Chemical Company) was used as raw silicon sources. The composition of the material was analyzed by chemical method and X-Ray Fluorescence Spectrom-

eter (XRF-1700, Shimadzu, Japan). There are 8.9 wt% Na<sub>2</sub>O and 28.9 wt% SiO<sub>2</sub> in the solution and the impurities of the solid content is less than 0.52 wt%. Sugar (saccharose) was used as carbon sources. Sodium silicate solution and saccharose were dissolved in distilled water to form a solution, in which original carbon:silicon ratio is 5. After spray drying this solution, a powder was obtained. The carbothermal reduction of the powder was performed in a high temperature graphite resistance furnace. The powder was heated at 600 °C for 2 hr to carbonize the saccharose and then heated up to 1300–1600 °C for 2 hr in flowing argon (1 L/min) to synthesize SiC. Residual carbon after reaction was eliminated through heating the produced powders at 700 °C for 5 hr in air. The influence of reaction temperature on crystallographic composition of carbothermal reduction products was investigated by X-ray diffraction (D/max 2200 PC, Rigaku, Japan). X-Ray Fluorescence Spectrometer and SEM (S-4300, Hitachi, Japan) coupled with EDS were used to analyze the composition of the product. TEM (JEM200CX, JEOL, Japan) was adopted to observe the morphology and measure the size of SiC powders.

SEM micrograph of the spray dried precursors shows that the powders were monodispersed spherical powders with particle size of 5–20 μm. X-ray diffraction pattern of the precursors revealed no peaks, which indicated the precursors were in the amorphous.

The X-ray patterns in Fig. 1 show the formation of the reaction products as a function of reaction temperature. Although the sublimation temperature of Na<sub>2</sub>O is 1275 °C [11], the oxide still can be detected after the precursors was heated at 1300 °C for 2 h. The formation of crystalline Na<sub>2</sub>O·2SiO<sub>2</sub> and SiO<sub>2</sub> indicated that amorphous glass phase of sodium silicate had taken place thermal phase transformation. It also can be seen that carbothermal reduction did not take place at 1300 °C. This means no reaction of SiO<sub>2</sub> occurred at this temperature. Distinct changes were presented in the pattern of the product pyrolyzed at 1400 °C. The peaks of Na<sub>2</sub>O·2SiO<sub>2</sub> were disappeared, indicating the escape of sodium oxide completed. The carbothermal reduction of SiO<sub>2</sub> took place at this temperature. The small peak at  $2\theta = 35.6^\circ$  showed the formation of β-SiC at 1400 °C, though the peak of crystalline β-SiC was not very evident. Further increasing temperature to 1450 °C, sharp peak of SiO<sub>2</sub> phase was transformed into amorphous. This is possibly induced by the

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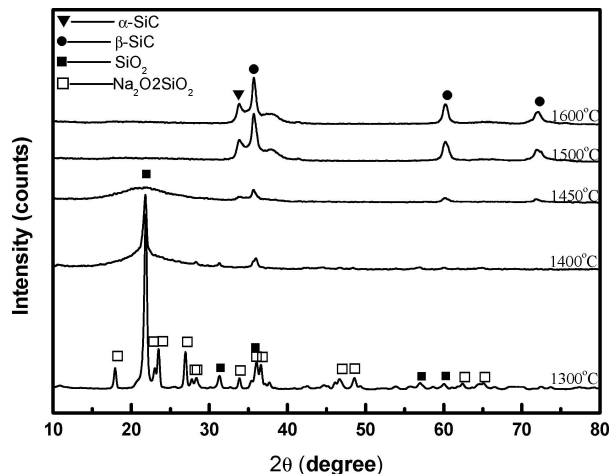


Figure 1 X-ray diffraction patterns of the reaction products at various temperatures for 2 hr in flowing argon.

particle size of  $\text{SiO}_2$  remained in the product decreased to nano-scale. When the reaction temperature was up to  $1500^\circ\text{C}$ ,  $\text{SiO}_2$  phase completely disappeared and single phase  $\beta\text{-SiC}$  formed. The conversion of  $\text{SiO}_2$  was completed.

Fig. 1 also showed that there was a small additional peak near  $2\theta = 33.5^\circ$  in the patterns of the powders produced above  $1400^\circ\text{C}$ . According to the computer simulation results calculated by Pujar *et al.* [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 would result from stacking faults.

The grain size of the product was estimated with the Scherrer formula:

$$D_{hkl} = k\lambda / (B_{1/2} \cos \theta) \quad (1)$$

where  $D_{hkl}$  is the grain size in the direction perpendicular to the crystal face (hkl),  $k$  is Scherrer constant,  $\lambda$  is the wavelength of X-ray,  $B_{1/2}$  is the broadness at half high of the diffraction peak, and  $\theta$  is the Bragg angle of crystal face (hkl). After deducting the apparatus broadening, the grain size of SiC was calculated from (220) diffraction peak. For all of the powders produced above  $1400^\circ\text{C}$ , the grain sizes are in the range of 14–24 nm. TEM also used to determined grain size of the products. Fig. 2 is the TEM micrograph of SiC produced at  $1500^\circ\text{C}$  for 2 hr. It shows that the powder is very fine equiaxial crystallites with the diameters of about 14 nm. This result corresponds to the XRD analysis. It also can be seen that there are two types of particle agglomerates. As shown in Fig. 2, one is a loose agglomerate, another is a tight agglomerate and the morphology seems to be spherical.

Fig. 3 shows the results from the EDS. In the EDS spectra of powders, there exist three peaks due to C, O and Si, respectively. The peak of Na cannot be detected, which revealed that there is no Na in the surface of powders. Element oxygen is donated by the oxide

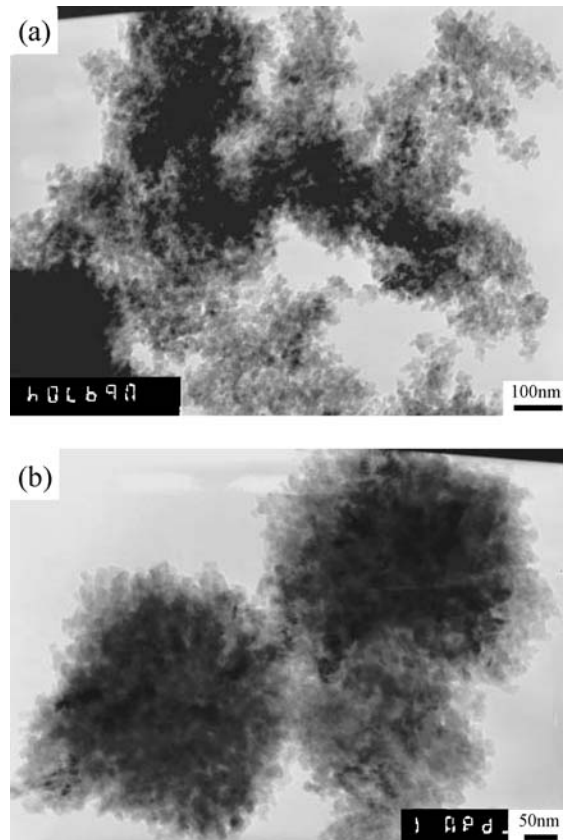


Figure 2 TEM micrograph of SiC synthesized at  $1500^\circ\text{C}$  for 2 hr in flowing argon.

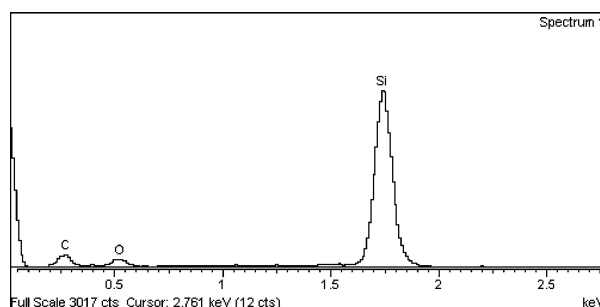


Figure 3 EDS analysis taken from a single particle of the product synthesized at  $1500^\circ\text{C}$  for 2 hr in flowing argon.

surface of powders. X-Ray Fluorescence Spectrometer was also used to analyze the composition of the product pyrolyzed at  $1500^\circ\text{C}$  for 2 hr. The result showed that the content of O and Na were 2.66 wt.% and 91 ppm, respectively. The content of Na is so low that it would not influence the properties of SiC produced by this process.

Nanocrystalline  $\beta\text{-SiC}$  powders with the diameter about 14 nm have been synthesized by carbothermal reduction from sodium silicate and saccharose. The cost of the ultrafine SiC produced by this process would be very low, because the low-cost sodium silicate is used as silicon sources.

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