The synthesis of ultrafine SiC powder by the microwave heating technique

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Ultrafine powders of silicon carbide synthesized by microwave and conventional heating are described. Silicon carbide powders with diameters in the nanometer range were formed by reducing SiO_2 with various forms of carbon in a nitrogen atmosphere. Ultrafine SiO_2 powder, phenolformaldehyde resin and ultrafine carbon black were used as starting materials. The properties of the powders were determined by means of X-ray diffraction, TEM, etc. The results showed that the technique and conditions for preparing samples, as well as the temperature and type of heating, had obvious effects on the powders characteristics.

1. Introduction

In the field of modern ceramics, much attention has been paid to ultrafine powders. Physical and chemical property dependence on particle size, which might be different from that of bulk materials, has been a most interesting subject. Ultrafine ceramic powders are useful to obtain materials for the new applications that technological advancement demands. Silicon carbide has attractive high-temperature properties. This material retains its strength at elevated temperatures without a significant deterioration in its structural integrity. Strong covalent bonding between the constituent elements in this material gives rise to a combination of properties, such as low thermal expansion coefficient, high Young's modulus and hardness that are important for designing high-performance materials. Consequently the materials made from SiC have opened new areas in the field of materials design such as those seen in metal- and ceramic-matrix composites [1, 2].

In recent years, microwave energy has been introduced as a possible avenue to achieve superior processing of ceramics [3]. By direct coupling, microwaves can volumetrically heat materials with favourable dielectric properties. This is very different from conventional heating processes, which rely on external radiant energy to heat materials. Microwave heating also appears to enhance diffusion of certain chemical species in ceramics and accelerates certain processes. Many experimental studies have reported that the microwave energy offers many advantages in processing of ceramic materials. For example, it was determined that the reaction times for synthesis of some ceramic materials can be reduced by as much as three orders of magnitude using the microwave heating technique.

In the present work, ultrafine SiC powders have been synthesized by reducing ultrafine silicon with various forms of carbon. The effect of temperature and the role of carbon types on the production of SiC powders have been discussed.

2. Experimental procedure

The ultrafine powder of precipitated silica (99.98 wt %) was used as the starting material. Char pyrolysed from phenolformaldehyde resin, phenolformaldehyde resin and ultrafine carbon black was used as reducing agent. In terms of the molar ratio (C/SiO_2) in the raw batch, a slightly higher C/SiO_2 ratio than the stoichiometric ratio (3:1) is always desired to prevent the reaction

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

which can deplete the SiC product, reduce the yield, and cause oxygen contamination in the final product. Excess carbon ($C:SiO_2$ molar ratio higher than 3) has an added advantage. It might act as a barrier between the fine SiC powder products to prevent neck growth or adhesion of SiC particles, which could cause the undesirable agglomeration of fine SiC powders [4]. Mixtures made from silica and char and from silica and carbon black were thoroughly mixed and pelletized into cylindrical discs. The mixtures made from phenolformaldehyde resin and silica was prepared as follows: phenolformaldehyde resin was dissolved into an alcohol solution, then mixed with silica in a ball mill for 20 h. After drying, the mixture was heated in an electric furnace with a highly pure nitrogen atmosphere. The heating rate was 3 °C min^{-1}, and the final temperature was about 950 °C.

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Microwave heating was carried out in multimode cavities into which 2.45 GHz microwave radiation was introduced through a waveguide. Each sample was placed in a BN crucible enclosed by alumina fibre insulation. Prior to a run in the microwave furnace, the cavity was pumped down to 800 mtorr (1 torr = 133.322 Pa) and then backfilled with pure nitrogen. Samples were heated to various temperatures at a heating rate of 40 °C min^{-1} and held at the peak temperature for 20 min. The temperature was determined by a high precision optical pyrometer.

Conventional heating was processed in an $MoSi_2$ resistance furnace at 1500 °C in an atmosphere of nitrogen, with the temperature measured and controlled by a thermocouple inserted into the furnace cavity at a point near the sample. The experimental time was 2, 3 and 4 h, respectively.

The as-processed products were in powder form and had a green colour. The residual carbon was removed by oxidation in air at 550 °C for 16 h, and the silica was dissolved by treating the samples with 20% HF and washing them with alcohol.

3. Results and discussion

The shape and size of the powder were observed using transmission electron microcopy (TEM). X-ray diffraction (XRD) analysis was conducted to identify the crystalline phase of the powder. Fig. 1 shows that the XRD pattern of the particles was that of β-SiC with a small content of α-SiC. No Si_3N_4 nor Si_2N_2O was found in any of the samples, because the excess carbon prevented their formation [5]. From the results of chemical analysis, the SiC content of the powder was determined to be 98.6 wt %.

The overall reaction of formation for SiC powder through carbothermal reduction of silica can be represented as

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

Reaction 2 is believed to proceed via a two-step process, first with the formation of SiO gas

$$SiO_2 + C = SiO + CO \quad (3)$$

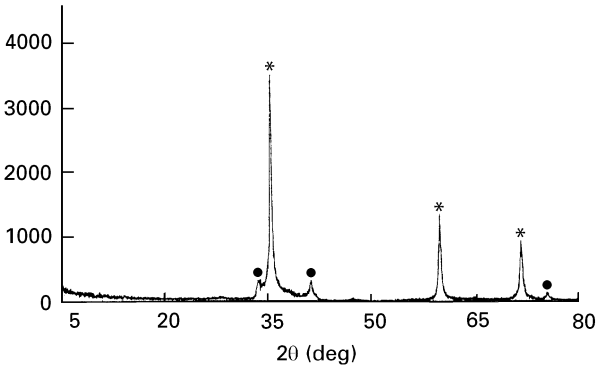


Figure 1 XRD patterns of SiC powders formed from resin and silica by microwave heating for 20 min: (●) α-SiC, (∗) β-SiC.

and/or

$$SiO_2 = SiO + 1/2O_2 \quad (4)$$

In the presence of carbon, the chemical potential of O_2 gas produced is reduced by forming a thermodynamically stable gas CO

$$2C + O_2 = 2CO \quad (5)$$

These subsequently react with carbon and CO, as follows

$$SiO + 2C = SiC + CO \quad (6)$$

and

$$SiO + 3CO = SiC + 2CO_2 \quad (7)$$

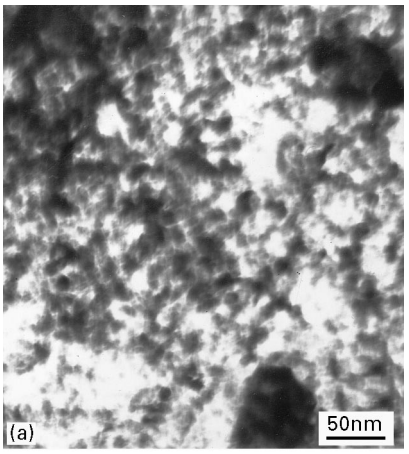
any CO_2 formed is expected to be consumed immediately by the surrounding carbon particles to yield CO gas

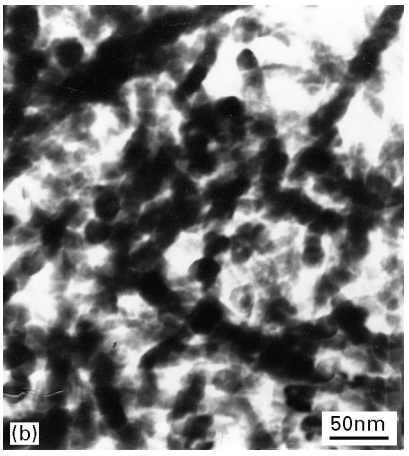
$$CO_2 + C = 2CO \quad (8)$$

Klinger *et al.* [6] have studied reactions between silica and graphite from 1445–1765 °C. They observed that all particles of the SiC reaction product were approximately the size of the graphite particles and no distinction between SiC and graphite could be made, and that the measured weight-loss data could be explained only by assuming the dissociation of silica into oxygen and gaseous SiO, which subsequently reacted with graphite to form SiC. Lee and Cutler [7] investigated reactions of rice hulls and concluded that the rate-controlling step for the formation of SiC was the formation of gaseous SiO. Therefore, the formation of gaseous SiO was an important intermediate step in the overall carbothermic reduction. The total nitrogen flow rate used in the conventional process was 2.0×10^{-5} m^3 s^{-1} at ambient pressure. Such a flow rate of nitrogen could avoid a loss of gaseous SiO and effectively remove the CO product.

As determined by the X-ray small-angle scattering method, the particle sizes of this powder were between 3 and 80 nm diameter, with the smaller ones of rounded shape, forming short chains, and the larger ones in a more crystal-like shape, as can be seen in Fig. 2.

Fig. 2 shows the TEM morphology of SiC powders synthesized from phenolformaldehyde resin and silica by microwave heating at 1180, 1240 and 1350 °C. It can be seen that the particle size of the powders increased with increase in temperature, for the particle growth rate increased quickly with increase in temperature. Therefore, temperature plays an important role in the size of the SiC particles. TEM observation of the powders, produced from resin and silica by conventional heating at 1500 °C for 2, 3 and 4 h, respectively, showed that the particle size of the powders increased only slightly with increasing experimental time, but the content of α-SiC increased with increase in experimental time (Fig. 3). The mechanism of β–α phase transformation in SiC under ceramic fabrication conditions has been observed and studied by several workers, and it has been concluded that the reaction sintered (RS) and chemically vapour-deposited (CVD) SiC predominantly consists of the β-form,





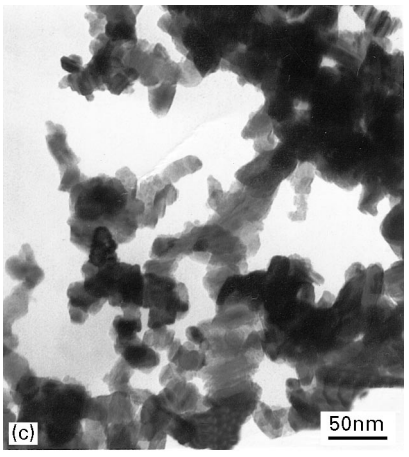
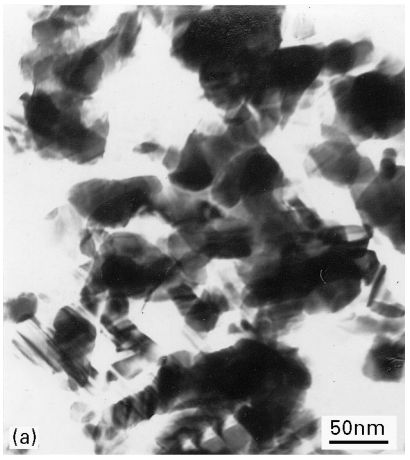
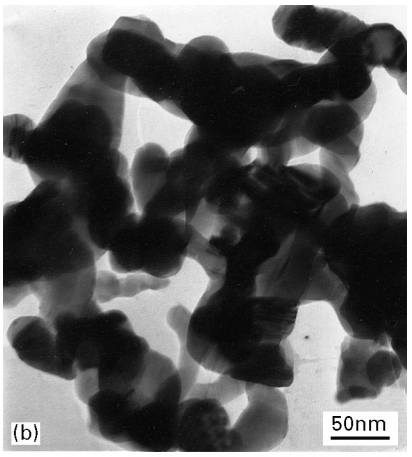


Figure 2 TEM morphology of SiC powders synthesized from the resin and silica by microwave heating for 20 min at: (a) 1180 °C, (b) 1240 °C, (c) 1350 °C.





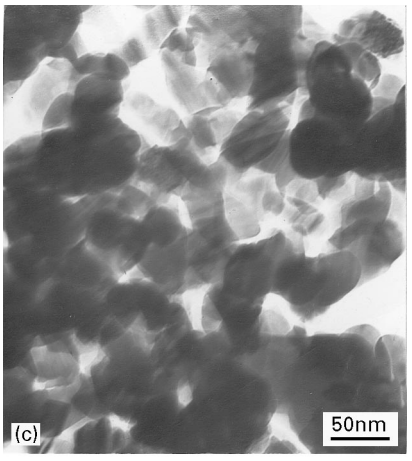


Figure 3 TEM morphology of SiC powders synthesized from resin and silica by conventional heating at 1500 °C for (a) 2 h, (b) 3 h, (c) 4 h.

but a small volume fraction of the α-form is always present under these processing conditions. It should be noted that the β–α transformation is a kinetically controlled process, and often several days are needed to achieve complete conversion [2, 8].

The particle sizes of SiC powders synthesized from silica and carbon black and from silica and char were larger than those from silica and phenolformaldehyde resin as can be seen by the comparison of Fig. 4 with Fig. 2. Fig. 5 illustrated that the particle of SiO_2 in the SiO_2/C composites pyrolysed from SiO_2/resin was tightly enclosed by a layer of char. Because of the tight contact between carbon and SiO_2, and the smaller sizes of carbon and SiO_2, the rate for forming SiC was higher, and the particle size of SiC powders was smaller. Blumenthal *et al.* [9] observed an increase in the reaction rate with increasing interfacial area between reactants as the particle size of silica was decreased. This suggested that the particle sizes of carbon and silica were important in determining the rate of carbothermic reduction and particle sizes of SiC reaction product.

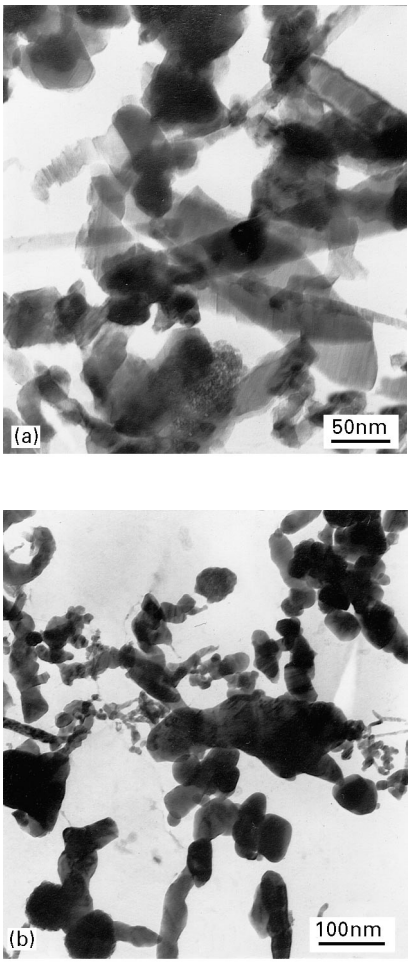


Figure 4 TEM morphology of SiC powders synthesized by microwave heating at 1180 °C for 20 min, (a) from char, (b) from carbon black.

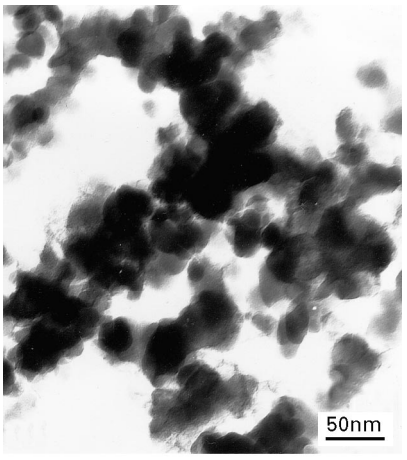


Figure 5 TEM morphology of SiO_2/C composite prepared from SiO_2/resin composite.

The temperature of a physical process is a critical parameter which is directly related to many kinetic and thermodynamical effects. Generally, the measurement of temperature by contact is a result of a volumetric average of the temperature near the measuring probe. Most probes do disturb the thermal field during measurement. Optical pyrometry requires access to the surface of the sample which results in heat loss from the surface being measured. Under normal equilibrium conditions, thermocouples can be adequate measuring devices and are used in many applications. In a microwave environment, the electromagnetic field present can change the behaviour of a metallic thermocouple especially at the tip. In the microwave process, the internal temperature of the sample, especially at the interface between carbon and silica, is higher than the surface temperature. Therefore, a new method and devices are needed for exact measurement of the temperature in a microwave furnace.

In comparison with conventional heating, microwave heating shows much more advantages. The two heating methods have a different heating mechanism. Conventional heating mostly acts by heat radiation or heat conduction. Its energy just acts upon the surface of the sample. The bulk temperature elevation must be obtained through the heat diffusion. Therefore, the heating rate is lower and the heating time is longer in conventional heating, from which the size of SiC powders is large, as can be seen from Fig. 3. However, the bulk can be heated as a whole at a high heating rate by microwave heating. So, microwave heating can evidently decrease the synthesis temperature and largely reduce the reaction time. A much lower formation temperature and high formation rate not only save energy and time, but also prevent the growth of the crystal grain and transformation of the crystal type at high temperature during the long formation period. So ceramic powder with ultrafine grains, uniform size and single crystal type, could be obtained by microwave heating.

4. Conclusion

Silicon carbide ultrafine powders can be produced by reducing ultrafine silica powder with various forms of carbon in a microwave or conventional furnace. The main product is β-silicon carbide. SiC powder formed from phenolformaldehyde resin is much finer than that from other carbon forms. SiC powders can be synthesized at a lower temperature in a shorter time by microwave heating.

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