

Formation of Silica-Coated Carbon Powder and Conversion to Spherical β -Silicon Carbide by Carbothermal Reduction

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Spherical β -SiC powders that are a few micrometers in size have been prepared by heating a mixture of phenolic resin powder and fine-grained fumed silica at 1600°C in argon. The overall process is composed of two consecutive steps: (i) the formation of silica-coated spherical carbon powder and (ii) carbothermal reduction. The irregularly shaped resin powder transforms to a spherical-shaped morphology in the first step, and the resulting silica-coated spherical carbon powder is converted to β -SiC in the second step. The key factor in the first step is the utilization of fumed silica that has hydrophobic surface functional groups. Hydrophobic interactions at the point of intimate contact between the resin powder and the silica likely reduce the surface energy of the resin powder, thereby discouraging interparticle coalescence. The resulting β -SiC powder exhibits a radially developed columnar microstructure. Hollow β -SiC spheres also can be prepared by controlling the reaction conditions in the carbothermal reduction step.

I. Introduction

RECENTLY, several researchers have synthesized spherical SiC powder by heating a gel that was derived via the hydrolysis of organo-alkoxysilanes or mixtures of organo-alkoxysilanes and tetralkoxysilanes.^{1–4} Many of these sol-gel-derived SiC powders are monodisperse, and their size can be controlled by properly selecting the reaction conditions. Ultrasonic spray pyrolysis also has been used to synthesize spherical SiC powders.⁵

Here, we report another method for the preparation of spherical β -SiC powders. This method seems to be less expensive than conventional methods, because commercially available polymeric resin powders are used as the carbon source. Moreover, the process is simpler, because one-step preparation is possible: the mixture of resin powder and fine-grained fumed silica (SiO₂) can be heated at >1600°C in argon. The mechanism for irregular-to-spherical shape conversion and the microstructure of β -SiC powder is communicated.

II. Experimental Procedure

Novolac-type phenolic resin powder (with a glass-transition temperature (T_g) of 83°C) and fumed silica (CAB-O-SIL[®] TS-530, Cabot Corp., Tuscola, IL) were used as the respective carbon and

silicon sources. The fumed silica is known to have three-dimensional, chainlike agglomerates ~0.2–0.3 μ m in size; the fumed silica shows an extremely hydrophobic character, because the surface hydroxyl (—OH) group of silica is replaced by a trimethylsilyl (—OSi(CH₃)₃) group.

To prepare the spherical β -SiC powder, the phenolic resin and fumed silica (in a 1:1 weight ratio) were mechanically mixed and placed in an alumina boat-type crucible. The resulting silica-coated resin powder was carbonized at 1000°C for 1 h, to produce the silica-coated spherical carbon powder, and further converted to β -SiC via carbothermal reduction at 1600°C for 3 h. Heat treatment was conducted in a horizontal alumina tube furnace under an argon flow (flow rate of 0.1 L/min). The preparation can be made either in one step or two consecutive steps. The final spherical β -SiC powder was collected after the excess silica component was removed through treatment with 48% aqueous hydrofluoric acid (HF).

The reaction products were characterized using X-ray diffraction (XRD) (Model D/MAX-3C, Rigaku, Tokyo, Japan) coupled with CuK α radiation; scanning electron microscopy (SEM) (Model JSM-840A, JEOL, Tokyo, Japan) and particle-size analysis (PSA) (Model MASTERSIZER/E, Malvern Instruments, Malvern, U.K.) also were used for characterization. The volatile matter, including free carbon, was determined by tracing the thermogravimetric analysis (TGA) (Model TGA7, Perkin-Elmer, Norwalk, CT) profile from room temperature to 900°C in air.

III. Results and Discussion

(1) Preparation of Spherical β -Silicon Carbide Powder

Figure 1(a) shows an SEM micrograph of the phenolic resin powder that was used as the carbon source. The precursor resin powder had an irregular shape, with an average particle size of 23 μ m. When the resin powder was mixed with the CAB-O-SIL[®] TS-530 fine-grained fumed silica and heated up to 1000°C in an argon atmosphere, the resin powder transformed to spherical carbon, with the silica component existing as a coating on the particles. Continued heating up to 1600°C for 3 h under an argon atmosphere and then removal of any excess silica component using an HF treatment produced a spherical-shaped material that had an average particle size of 18 μ m (see Fig. 1(b)). The final product was identified as β -SiC, using XRD. Figure 2 shows that the product gives diffraction lines that belong to β -SiC, without any discernable impurity phases.

A TGA profile of the silica-removed β -SiC powder was obtained. The amount of volatile matter was <1 wt%, much of which originates from the free carbon.

(2) Irregular-to-Spherical Conversion Mechanism

The irregularly shaped resin powder transforms to a spherical shape during the carbonization step. The key factor in this step is the use of fumed silica that has a hydrophobic surface functional group. This observation was ascertained using several control experiments. First, a simple carbonization of phenolic resin without silica addition produced a lump-shaped carbon mass, which

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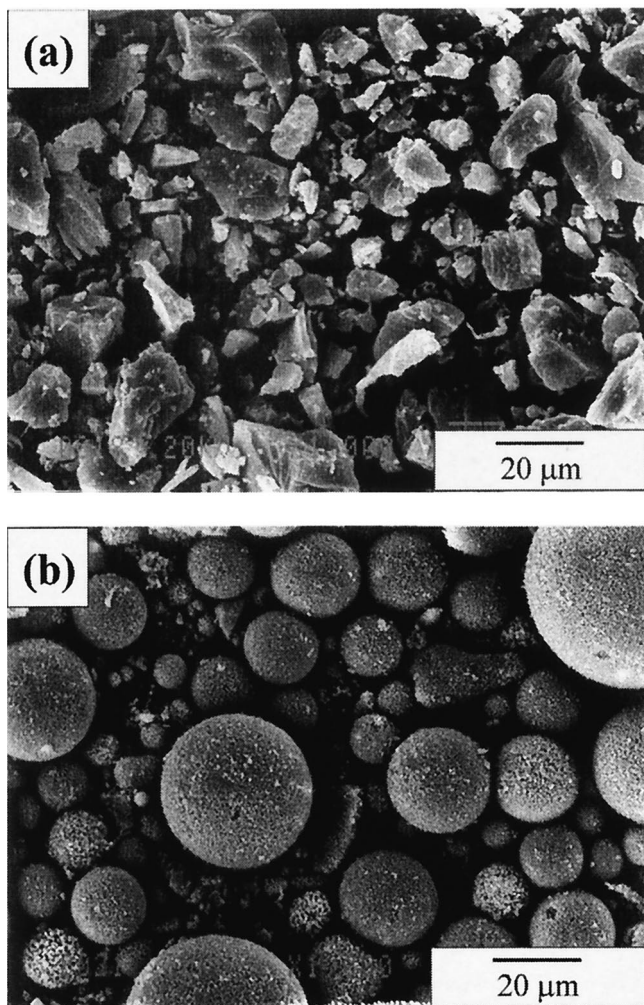


Fig. 1. SEM micrographs of (a) phenolic resin powder that was used as the carbon source and (b) the β -SiC powder.

was the result of interparticle cohesion. Secondly, when another fumed silica (CAB-O-SIL[®] M-5, Cabot Corp.) was used instead of CAB-O-SIL[®] TS-530 silica, the resulting carbon appeared as a lump, which was indicative of a massive coalescence between the resin particles. The difference between the M-5 and TS-530 fumed silicas is the surface functional group. The surface of the M-5 fumed silica is covered by the hydrophilic hydroxyl group, whereas it is replaced by the hydrophobic trimethylsilyl ($-\text{OSi}(\text{CH}_3)_3$) group on the surface of the TS-530 fumed silica. Thirdly, when another hydrophobic silica (CAB-O-SIL[®] TS-720, Cabot Corp.) was used in the carbonization step, the resulting carbon was an agglomerate-free spherical shape.

Another control experiment was conducted to examine the temperature range at which the irregularly shaped resin powder transforms to a spherical shape. When the phenolic resin/TS-530 silica mixture was heated at 80°C (below the resin T_g value), the initial irregular morphology was sustained. When heated at temperatures greater than T_g , however, the resin powder transformed to a spherical shape. Thus, the onset temperature for the irregular-to-spherical transformation apparently is close to the T_g value of the resin.

Summarizing the above-mentioned results, an irregular-to-spherical conversion mechanism has been proposed. The resin powder becomes softer when the heating temperature approaches the T_g value of the resin powder. Under these circumstances, when the resin particles are in intimate contact with silica powder, some mixing or wetting occurs on the surface of the resin particles, because the $-\text{OSi}(\text{CH}_3)_3$ group on the silica surface has a high affinity for the hydrophobic resin constituents. The net result will be a reduction in the surface energy of the resin particles, to

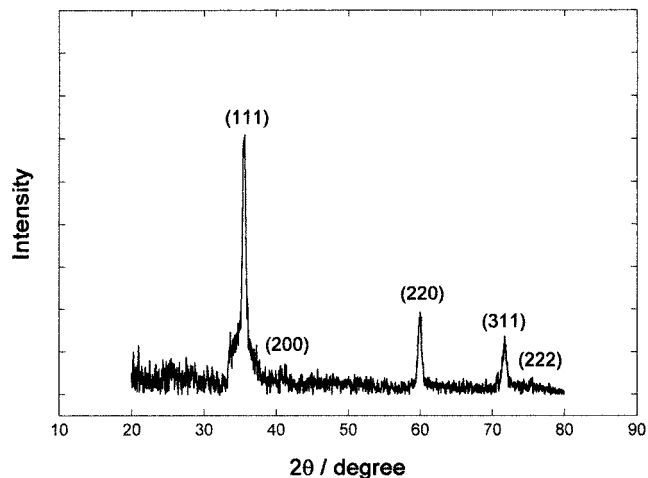


Fig. 2. XRD pattern of the β -SiC powder.

discourage interparticle coalescence. Individually isolated resin particles then transform to spheres, to further minimize the surface energy. The resin powders that are once-converted to a spherical shape at the onset temperature then are carbonized and become silica-coated spherical carbons and then β -SiC on further continued heating up to 1600°C. In the absence of silica, however, the resin powders have a relatively higher surface energy, because of the lack of hydrophobic interactions, such that the particles coalesce and form a lump. The same situation prevails even with the addition of M-5 fused silica, because the hydrophilic hydroxyl groups do not interact with the hydrophobic resin surface.

(3) Microstructure of β -Silicon Carbide

Figure 3(a) shows the surface morphology of a silica-removed β -SiC sphere. The surface is coarsened as a result of cohesion between the submicrometer-sized primary particles. Figure 3(b) shows the cross-sectional view of a β -SiC sphere, where a radially developed columnar microstructure can be recognized. SiC is known to form via the reaction between solid-state carbon and gaseous SiO in the carbothermal reduction at 1600°C.⁶ Thus, in this preparation, the reaction seems to start from the surface region, where carbon and silica are in contact with each other. As the reaction proceeds, the reaction boundary moves toward the center of the sphere while the SiC layer becomes thicker. Along this reaction, the radial columnar microstructure develops inside the spheres.

Figure 3(c) presents a cross-sectional view of a β -SiC sphere that was carbothermally prepared at 1600°C for 1 h in an argon atmosphere; a skin-core structure can be recognized. The reaction time is shorter than that observed in Fig. 3(b); therefore, the carbothermal reduction is incomplete. As a result, the β -SiC wall of a radial columnar microstructure develops at the outside skin region, whereas unreacted carbon remains at the core region. This observation further confirms the inward movement of the reaction boundary for β -SiC formation. Figure 3(d) shows a cross-sectional view of a hollow β -SiC sphere that was obtained after oxidizing the core carbon at 800°C in air. It is very likely from this observation that hollow β -SiC spheres of different wall thickness can be prepared by controlling the extent of carbothermal reduction. The reaction temperature and time, and the Si/C ratio in the precursor mixture, may be the controllable variables.

IV. Conclusion

Spherical β -SiC powders have been prepared from a mixture of phenolic resin and fumed silica powder via carbothermal reduction at 1600°C in an argon atmosphere. Among the fumed silica used, only those forms that have a hydrophobic surface functional group are

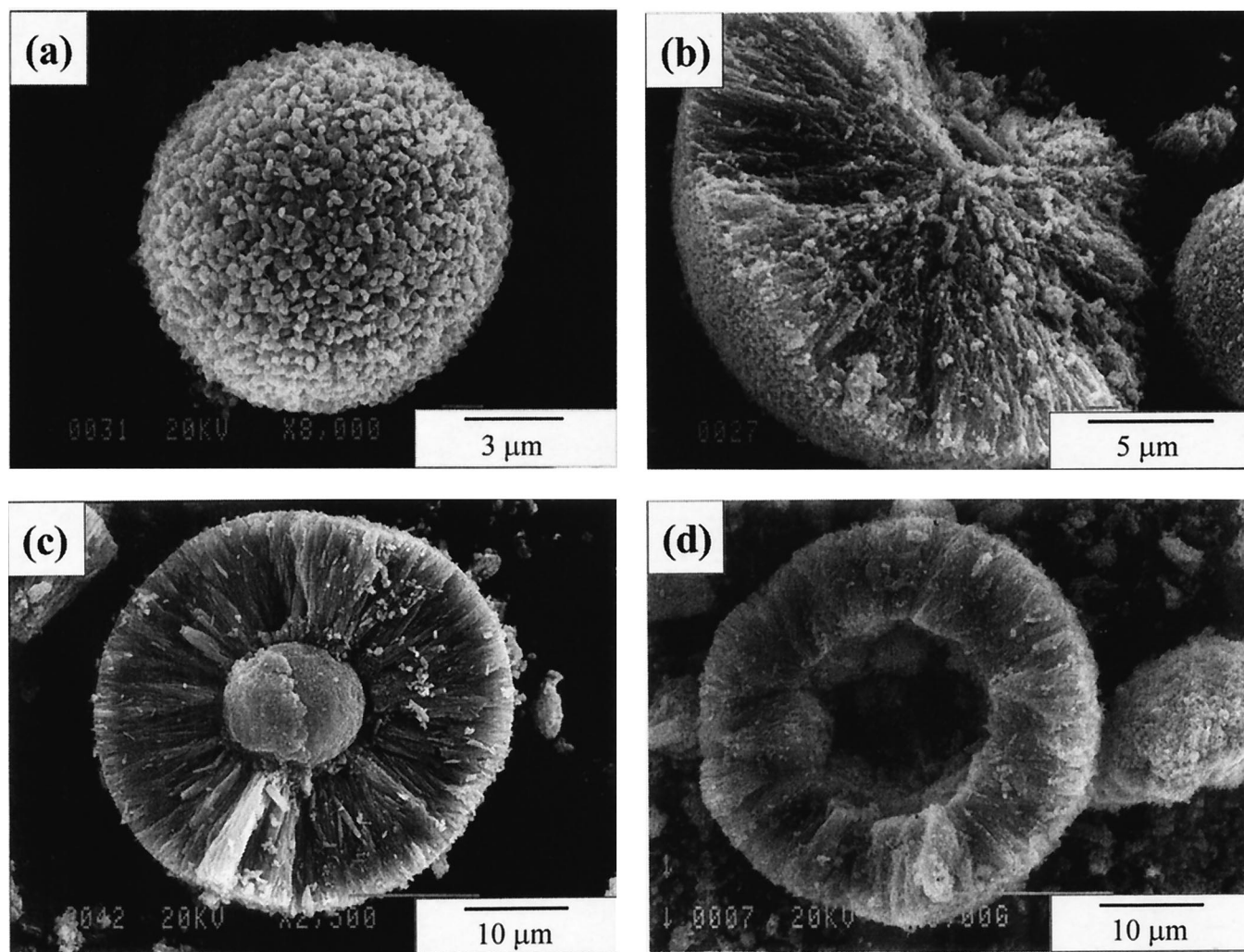


Fig. 3. SEM micrographs of a β -SiC sphere that was carbothermally reacted at 1600°C for 3 h ((a) outside view and (b) cross-sectional view). Cross-sectional views of a hollow β -SiC sphere that was carbothermally reacted at 1600°C for 1 h also are shown ((c) as-prepared and (d) after oxidizing the core carbon at 800°C in air).

effective in converting the irregularly shaped resin powder to spherical β -SiC. The irregular-to-spherical conversion occurs around the glass-transition temperature of the resin. The underlying role of hydrophobic silica is to reduce the surface energy of the resin particles, which eventually inhibits the interparticle coalescence. The resulting SiC powder is composed of submicrometer-sized primary particles, and the crystallites grow from the outer surface toward the core region, which leads to the formation of a radially developed columnar microstructure. The free-carbon content is <1 wt%. Hollow β -SiC spheres could be prepared by shortening the reaction time in the carbothermal reduction step. Finally, considering the fact that the particle size and particle-size distribution of β -SiC powder is primarily determined by the particle size of resin powder itself, it is likely that β -SiC powders of different size can be prepared by controlling the size of the resin powder.

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