A facile approach to microwave heating synthesis of silicon carbide from unmixed silicon powders

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Microwave heating is often used to fabricate silicon carbide (SiC) from mixtures of silicon and carbon powders. Mixing these reactant powders has been considered important because the carbonization of silicon has long been regarded as a solid-state reaction occurring via atomic diffusion among powders. Here, we present a facile alternative approach to microwave-heating synthesis of SiC from silicon powder which was simply embedded in graphite powder without mixing with the graphite powder. 10-min microwave heating in air turned the silicon powder into a consolidated chunk of almost fully carbonized β-SiC. This result suggests that carbon atoms experienced a millimeter-order mass transfer from graphite to silicon within 10 min. Atomic diffusion alone can hardly explain such a large transfer of carbon atoms within such a short period. The rapid reaction displayed by the long-distance mass transfer of carbon can be explained instead by gas-solid carbonization between carbon monoxide (CO) and solid silicon, since the atmosphere in which the reaction occurred comprised a vast majority of CO gas, according to the Boudouard equilibrium.

1. Introduction

Microwave heating, which can create high temperatures exceeding 1000°C within a very short time, is widely used to synthesize a variety of refractory ceramics such as carbides.1-3 Since the first report of this process in 1994,4 silicon carbide (SiC) has been a representative example of this synthesis,5-9 owing to its superior mechanical strength and chemical stability, particularly at high temperatures. To attain the SiC phase by microwave heating, mixtures of silicon- and carbon-containing powders are generally used as the reactant substances with the stoichiometric composition of the planned product.1,6,8 Silicon powder is mixed with graphite powder at an atomic ratio of Si:C = 1:1, for example, according to the following reaction:

$$\text{Si(s)} + \text{C(s)} \rightarrow \text{SiC(s)}$$  \hspace{1cm} (1)

These reactant powders are thoroughly mixed over hours of milling to ensure firm contact among the powders in the mixture. This mixing procedure has been considered important, because the microwave-heating synthesis of SiC, particularly from pure silicon, is generally regarded as a solid-state reaction occurring via atomic diffusion1,2,4,6 although some gas-gas and/or gas-solid reactions involving gaseous silicon monoxide (SiO) and/or carbon monoxide (CO) are also known to occur during carbothermal reduction of silica to yield SiC.5,7

We have recently reported a new carbonization mechanism induced by CO gas during microwave heating.10 In this reaction, silicon powder was carbonized by graphite powder which had no direct contact with the silicon powder, suggesting that carbon atoms were supplied via a gas-phase route. This result introduced the potential for improved microwave-heating synthesis using a simpler, more facile approach. Here we report microwave-heating synthesis of SiC from silicon and graphite powders employing a setup in which pure silicon powder was simply embedded in graphite powder while omitting the process of mixing the two powders. Although this synthesis method is simple, it has, to the best of our knowledge, never been reported so far probably due to the strong preconception that the carbonization of silicon during microwave heating is caused via solid-state reaction. The carbonization mechanism is also discussed from the viewpoints of atomic diffusion and a CO-induced reaction.

2. Experimental procedure

Silicon powder (99.9% purity, ca. 5 μm) was purchased from Kojundo Chemical Laboratory Co., Ltd., Japan, and graphite powder (ca. 75–106 μm) from Kanto Chemical Co., Inc., Japan. In a typical synthesis process, the graphite powder (1 g) was filled into an alumina crucible, and the
silicon powder (1 g) was then loosely spread on top of the graphite powder. The silicon powder was then covered by graphite powder (2 g) such as to sandwich it between upper and lower layers of graphite powders. An alumina lid was placed on the crucible containing the two reactant powders, which was then placed in a hollow in a block of heat-resistant brick. The crucible was surrounded by refractory ceramic fibers (Isowool; Isolite Insulating Products Co., Ltd.) to attain good heat protection and insulation. All of these setup steps are illustrated in Fig. 1. The crucible was irradiated by microwave (2.45 GHz, 600 W) in the multimode cavity mode for a predetermined period (1–15 min) in air using a commercially available microwave oven for household use.

After the heating was completed, the crucible was air-cooled to room temperature. The product formed was removed from the crucible and crushed into powder using an agate mortar. These resulting powder specimens were examined by X-ray diffraction (XRD) measurement using a Rigaku GeigerFlex X-ray diffractometer employing Cu Kα radiation. The Cu Kα₁ peaks were subtracted from all the measured XRD profiles. A field-emission scanning electron microscope (FE-SEM: Hitachi S-5500) operated at 5 kV was also used to evaluate the morphology of the powders.

3. Results and discussion

Figure 2 shows top- and side-viewed photographs of a typical product specimen after microwave heating for 10 min. The specimen was removed from the exact position where the silicon powder was initially embedded. As seen in the figure, the product powder was consolidated into a solid chunk (~20 mm in diameter and ~8 mm in thickness). The side view of the chunk showed a greenish color like olive green at around its core, which is often observed in SiC with a cubic crystal structure (β-SiC). Since the dimensions of the consolidated chunk were similar to those of the overall loaded silicon powder, direct carbonization of the silicon powder seems to have taken place.

Figure 3 shows XRD patterns of the product powders as a function of the microwave heating period (1–15 min). A peak appearing at 2θ = 26.60° in each profile comes from graphite (depicted as a closed upturned square) which became attached to the surface of the consolidated chunks.

The profile for 1-min heating exhibits a series of sharp peaks corresponding to the reflections from the silicon phase (closed squares). After 3-min heating, the peak intensity of silicon showed a sharp reduction, accompanied by the appearance of extra peaks (closed circles) corresponding to β-SiC. As the heating time was increased further, the peak intensity of β-SiC increased gradually together with a gradual reduction in the peak intensity of silicon. Surprisingly, peaks from silicon were almost completely diminished after 10-min heating, suggesting that carbonization was nearly completed. All these results, shown in Figs. 2 and 3, indicate that a mass transfer of carbon occurred from the graphite to silicon powder during the reaction. The carbon atom transfer distance can reach at least 4 mm, which was estimated as half the thickness of the consolidated product, within 10 min.
In addition, a weak peak related to α-SiC is also detected at around 2θ = 33.50° (closed star) for heating periods of 3 min or longer. To show this in detail, an enlarged XRD profile of the specimen for 10-min heating is shown in Fig. 4(a). The referenced peak data for three representative α-SiC phases (2H-, 4H- and 6H-SiC) are also shown as bar charts in Fig. 4(b). Although the position of this peak seems to most closely match the (100) reflection from 2H-SiC at a glance, there exist some discrepancies; the most intense main peak from 2H-SiC is nearly missing at 2θ = 38.15° despite the absence of crystallographic orientation in the randomly oriented polycrystalline powder. Furthermore, there is another feature that the (111) peak from β-SiC is accompanied by high background intensity especially at its lower angle side. It has been pointed out that all these features cannot be reproduced by a simple mixture of β-SiC and other polytypes including 2H-SiC, but can be understood in terms of the presence of stacking faults created in β-SiC. Our result seems to better match the interpretation based on the stacking faults.

Low-magnification FE-SEM images of the initially loaded silicon powder and the β-SiC powder formed by 10-min heating are shown in Figs. 5(a) and 5(b), respectively. Magnified images of the same β-SiC powder is also shown in Fig. 5(c). Before microwave heating, the size of the silicon particles was on the order of several micrometers, and their surfaces were relatively smooth. After microwave heating, however, a number of small agglomerated particles (0.1–1 μm) with irregular shapes sticking to the micrometer-sized particles form a bumpy, porous surface. The dimensions of these micrometer-sized particles were similar to those of the Si particles (1–10 μm).

Whiskers with diameters of 300 nm or less were also observed as shown in Fig. 5(c). Since only β-SiC could be detected by XRD measurement in the present experiment, the whiskers must have consisted of β-SiC, much like those reported in other works in which formations of similar whiskers consisting of β-SiC have been often reported in microwave-heating syntheses. It is generally accepted that β-SiC whiskers are formed by a gas-gas reaction involving SiO and CO gases to smoothly supply the reactant species to the tip of each growing whisker. The reaction is given by the following formula:

\[
\text{SiO(g)} + 3\text{CO(g)} \rightarrow \text{SiC(s)} + 2\text{CO}_2\text{(g)}
\]

In the present synthesis, the SiO gas may come from a native oxide covering the surface of each silicon particle. The presence of a number of small agglomerated particles, which formed a porous morphology on the surfaces of β-SiC particles, also implies an additional route to yielding SiO gas via oxidizing reaction of silicon induced by CO₂ gas, as reported by Tsuda et al. 15)
In order to discuss the carbonization mechanism based on atomic diffusion, it is important to know the temperature and diffusion length during the reaction. Microwave heating generally creates high temperatures of 1000–1400°C, depending on such heating conditions as the input power and heating setup. Our preliminary experiments also confirmed that silicon powder that was vacuum-sealed in a quartz tube and then embedded in graphite powder was melted after 15-min microwave heating, suggesting that the temperature reached and/or exceeded the melting point of silicon (1414°C). When 1300–1400°C is chosen as a typical reaction temperature, the diffusion coefficient, \( D_x \), of carbon atoms in a silicon crystal can be estimated to be on the order of \( 10^{-8} \text{mm}^2/\text{s} \). The diffusion length, \( x \), can then be estimated by the following formula as a function of time, \( t \):

\[
x = \sqrt{D_x \cdot t}
\]

When \( t = 600 \text{s} \), we obtained \( x \approx 2 \mu\text{m} \). This value is significantly insufficient to account for the scale of the actual length (\(~4 \text{mm}\)) through which carbon atoms were transferred during the reaction. If the reactant powders were loosely packed, moreover, atomic diffusion among the powders would be further suppressed. Thus, the long-distance mass transfer of carbon atoms observed in the present synthesis is not explainable solely by the solid-state reaction mechanism.

In our previous work, we reported carbonization of silicon induced by CO gas; silicon powder was carbonized into \( \beta\)-SiC, although atomic diffusion between silicon and graphite powders was completely eliminated by the thin wall (1-mm thick) of a quartz tube. \(^{10}\) A CO-gas-induced reaction of this type was originally proposed for the formation of \( \beta\)-SiC by electrical furnace heating, in which a silicon wafer was carbonized in an inert atmosphere containing a small amount of a CO/CO\(_2\) gas mixture. \(^{15}\)

The overall reaction for carbonization can be given as follows:

\[
\text{Si(s)} + 2\text{CO(g)} \rightarrow \text{SiC(s)} + \text{CO}_2(g)
\]

In the present synthesis, the crucible was filled with a vast majority of CO gas (more than 99%) during the reaction due to the Boudouard equilibrium. \(^{17}\) Since silicon powder was directly embedded in graphite powder in this experiment, CO gas was more likely to be supplied smoothly. This could result in a rapid reaction yielding no byproducts such as silicon oxynitride (e.g., Si\(_2\)N\(_2\)O) and/or silicon nitrides (e.g., \( \alpha\)-Si\(_3\)N\(_4\) and \( \beta\)-Si\(_3\)N\(_4\)) in contrast to the previous work, where silicon powder was entered into a quartz tube and then embedded in graphite powder.

4. Conclusions

We have demonstrated nearly full carbonization of un mixed silicon powder embedded in graphite powder within 10 min of microwave heating in air. After the reaction, the Si powder was consolidated into a solid chunk of \( \beta\)-SiC in the position where the silicon powder was initially placed. The XRD and FE-SEM experiments confirmed that the silicon powder was directly carbonized into \( \beta\)-SiC powder. These results suggest that carbon atoms experienced a millimeter-order mass transfer from graphite to silicon. Since the atmosphere during the reaction comprises a vast majority of CO gas, gas-solid carbonization between CO gas and solid silicon most likely accounts for the results.

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