importance of carbon-monoxide-induced reaction in microwave heating synthesis of $\beta$-SiC from silicon powder in air

Saeki YAMAMURO$^1$,$^3$, Keigo SUZUKI$^1$ and Toshiro TANAKA$^1$

$^1$Department of Materials Science and Engineering, Faculty of Engineering, Ehime University, 3 Ban, Bunkyo-cho, Matsuyama 790–8577, Japan

Microwave heating is known to provide extremely rapid synthesis of silicon carbide (SiC) from mixtures of silicon and carbon powders. The formation mechanism has long been considered to be a solid-state reaction among the powders in the mixture. Here, we present a new reaction mechanism via a gas-phase route. We have confirmed successful synthesis of $\beta$-SiC powder by microwave-heating of a small amount of Si powder that was entered into a quartz tube and then embedded in graphite powder, although no direct contact between the Si and graphite powders was allowed. Scanning electron microscopy observations revealed that the $\beta$-SiC powder was formed by direct carbonization of the Si powder. Since the atmosphere during the reaction comprises a vast majority of carbon monoxide (CO) gas according to the Boudouard equilibrium, the carbonization appears to have taken place via the CO gas. The contribution of such a gas-phase reaction could account in part for the rapidity of the microwave-heating reactions reported so far, which can hardly be explained solely by solid-state reactions among the mixed powders.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words: Silicon carbide, Silicon, Microwave heating, Gas-phase reaction, Carbon monoxide, Air atmosphere

Microwave heating is known as a useful technique for synthesizing a variety of refractory ceramics such as carbides and nitrides.1–3 A good example of their syntheses is silicon carbide (SiC),4–9 an industrially important material owing to its superior mechanical strength and chemical stability, particularly at high temperatures.10 To obtain the SiC phase by microwave heating, silicon- and carbon-containing powders are generally used as the reactant substances; either silicon or silica powder is generally chosen as the silicon-containing substance, and either graphite or carbon black powder as the carbon-containing one. These powders are thoroughly mixed at the stoichiometric composition of a planned product (e.g., Si:C = 1:1 for SiC synthesis), and sometimes pressed into pellets to ensure firm contact (i.e., atomic diffusion) among the powders. These procedures are carried out in accordance with the idea that the microwave heating synthesis of SiC, particularly from silicon, is regarded as a solid-state reaction occurring via atomic diffusion,4,6 although some gas-phase reactions involving gaseous SiO also occur in carbothermal reduction of silica to yield SiC.5,7 In the case of synthesizing SiC from solid silicon, the reaction can be described as follows:

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

One of the major features of the microwave heating process is rapid synthesis. The reaction time is generally required to be in the range from 5 min to 10 or 20 min,4–7 with particular dependence on the reaction temperature. In a series of syntheses we conducted, it was confirmed that Si powder was fully carbonized to SiC within 3 min of microwave heating (2.5 GHz, 600 W).11 In one particular case, it was also reported that the reaction was nearly completed within 1 min for the synthesis of tungsten carbide.12 Such rapid reactions can hardly be explained solely by solid-state reaction. If the reactant powders are loosely packed, moreover, the carbonization reaction would be further delayed, because atomic diffusion among the powders would be considerably suppressed. Although there have been some reports of microwave-induced enhancement of atomic diffusion in certain substances,13 the actual mechanism of the rapid synthesis remains controversial.

This work is intended to verify a possible contribution of another reaction mechanism, in addition to the solid-state reaction, in the microwave synthesis of SiC from silicon. We have performed microwave-heating synthesis of SiC powder from silicon and graphite powders using a setup which completely eliminates direct contact between the two reactant powders. In this case, a solid-state reaction is virtually prevented and, thus enabling the contribution of a gas-phase reaction to be verified.

In the present experiments, silicon powder (99.9% purity, c.a. 5 μm) was purchased from Kojundo Chemical
Laboratory Co., Ltd., Japan, and graphite powder (ca. 75–106 μm) from Kanto Chemical Co., Inc., Japan. The graphite powder was used as a good heat-generator and a supply source of carbon. In a typical synthesis process, the Si powder (0.5 g) was loosely filled into a short quartz tube (∼20 mm in length and 1 mm in wall thickness) with one end closed and the other open. The quartz tube was then placed in the center of an alumina crucible filled with the graphite powder (3 g). An alumina lid was placed on the crucible, 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 heat-insulation. All of these setups are illustrated in Fig. 1. A 2.45 GHz microwave was irradiated in the multimode cavity mode for a predetermined period (1–15 min) in air, using a commercially available microwave oven for household use. The power employed in the microwave heating was 600 W. After the heating was completed, the crucible including the quartz tube was air-cooled to room temperature.

After the reaction, the product formed was removed from the quartz tube and crushed into powder using an agate mortar. These powder specimens were examined by X-ray diffraction (XRD) measurement to determine their crystal structure. We used a Rigaku GeigerFlex X-ray diffractometer employing Cu Kα radiation. The Cu Kα2 peaks were subtracted from all the XRD profiles measured. We also used a field-emission scanning electron microscope (FE-SEM: Hitachi S-5500) operated at 5 kV to evaluate the morphology of the powders.

Figures 2(a) and 2(b) show typical photographs of a quartz tube after microwave heating and the powder obtained after removal from the quartz tube, respectively. The heating time for the two photographs was 15 min. As seen in Fig. 2(a), the quartz tube held its initial shape without cracking after the microwave heating, although black graphite powder was stuck firmly to the outer surface of the quartz tube. After heating for 1–3 min, the product powder (mostly Si) showed a slightly sintered nature and was easily crushed into powder. When the heating proceeded further, however, the sintering became markedly apparent; after 15-min heating, the Si powder was substantially consolidated, especially around the interface between the air and the Si powder in the quartz tube [see product A in Fig. 2(b)], although the lower portion of the Si powder in the tube still remained powdery (the product B). The XRD patterns of these powders are shown as a function of the microwave heating time (1–15 min) in Fig. 3. Each powder specimen, containing both consolidated and unconsolidated products, was mixed evenly with a mortar and used for the measurements. For 1-min heating, the profile exhibits a series of sharp peaks corresponding to the Si phase (depicted with closed squares in the figure) and some small peaks from silicon carbide with a cubic crystal structure (β-SiC) start to appear at the position of its main peak (2θ = 35.60°) for 3-min heating (a closed circle); to show it clearly, a portion of a magnified profile at around the main peak of β-SiC is also shown in the
Peaks from $\beta$-SiC are clearly detected for 5-min heating, and the peak intensity of $\beta$-SiC becomes stronger as the microwave heating time is increased further, accompanied by a gradual reduction in the peak intensity of Si. For 15-min heating, the intensity of the $\beta$-SiC main peak is nearly comparable to that of Si, indicating that a sizeable amount of the $\beta$-SiC phase is formed. Since there is no graphite in the quartz tube, carbon atoms for the carbonization were apparently supplied via a gas-phase route from the graphite placed outside of the quartz tube. The lattice constant of $\beta$-SiC was estimated as 0.436 nm, which is closely consistent with the referenced value (0.4359 nm). It should be noted that no peaks from SiO$_2$ are detected in any of the profiles, even after the specimens were heated in air at high temperatures.

In addition, peaks from silicon oxynitride (Si$_2$N$_2$O) and silicon nitrides ($\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$) are also detected for heating periods of 5 min or longer. To show this in detail, an enlarged XRD profile of the specimen for 15-min heating is shown in Fig. 4(a). The referenced peak data for Si$_2$N$_2$O, $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$ are also shown as bar charts in Fig. 4(b). It is confirmed that all of the weak peaks that are not assigned to either Si or $\beta$-SiC belong mainly to Si$_2$N$_2$O, together with a small amount of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$.

The FE-SEM images for the initially loaded Si powder and the $\beta$-SiC powder formed by 15-min microwave heating are shown in Figs. 5(a) and 5(b), respectively. Before microwave heating, the size of the Si particles was on the order of several micrometers, and their surfaces were relatively smooth [see Fig. 5(a)]. After microwave heating, however, a number of small, submicrometer-sized particles with irregular shapes can be observed sticking to the micrometer-sized particles and forming a bumpy surface [see Fig. 5(b)]. The dimensions of these micrometer-sized particles are similar to those of the Si particles (1–10 $\mu$m).

Since a slight change in volume (~3%) occurred during the carbonization from solid Si to $\beta$-SiC, direct carbonization of the Si particles seems to have taken place.

As shown in Fig. 5(b), a number of whiskers with diameters of 20–60 nm are also observed. An enlarged image of the whiskers is shown in Fig. 4(c). Selected area electron diffraction measurement of these whiskers confirmed that they consist primarily of $\beta$-SiC with a core–shell morphology resembling that reported by Tsuda et al. It is generally considered that SiC whiskers are formed by a gas-phase reaction involving SiO and CO gases, which is given by the following formula:

$$2\text{Si} + \text{CO} \rightarrow \text{SiC} + \text{CO}_2$$
In the present synthesis, the SiO gas may originate from a native oxide covering the surface of each Si particle and/or Si particles that were partially oxidized during the microwave heating. Since pure Si was the major phase of the reactant in the present synthesis, reaction (2), which proceeds via SiO gas, may be a minor route to yielding β-SiC. Additionally, a characteristic feature of reaction (2) is that β-SiC is usually formed at a different site from the Si source. In the present synthesis, however, each Si particle seems to have been carbonized directly into a β-SiC particle. This result also contradicts reaction (2).

To clarify the carbonization mechanism involved in a gas-phase reaction, it is important to know the temperature and the atmosphere during the reaction. In microwave heating, the temperature generally reaches 1000–1400°C for a couple of minutes,7 depending on such heating conditions as input power and heating setups. In our preliminary experiment, it was also confirmed that the Si powder that was tightly vacuum-sealed in a quartz tube and then embedded in graphite powder was melted and consolidated into a small piece after 15 min heating. This suggests that the temperature during the microwave heating reached and/or went beyond the melting point of silicon (1414°C). At such high temperatures, oxygen in the air reacts immediately with solid carbon, forming a mixture of CO/CO2 gases as described by the so-called “Boudouard equilibrium”:17

\[
\text{CO}_2(g) + \text{C}(s) = 2\text{CO}(g) \quad (3)
\]

The alumina lid on the crucible creates a relatively closed system, which largely suppresses the entry of O2 gas from outside the crucible. Thermodynamical calculation of the partial pressures of CO and CO2 gases on the basis of Eq. (3) yielded the result that CO gas accounts for a large percentage (more than 99%) as compared with CO2 at above 1000°C. Under these conditions, the possible overall reaction for the carbonization may be written as follows:

\[
\text{Si}(s) + 2\text{CO}(g) \rightarrow \text{SiC}(s) + \text{CO}_2(g), \quad (4)
\]

where CO gas acts as the source of supply of carbon atoms to silicon. The resulting CO2 gas will then react immediately with the graphite powder to form CO gas. A reaction of this type was also proposed for the formation of β-SiC by electrical furnace heating, in which a silicon wafer was carbonized in an inert atmosphere containing a small amount of a CO/CO2 gas mixture.14 It is reasonable to think that this reaction mechanism makes a sizeable contribution to the microwave-heating synthesis as well. Carbonization by such a gas-phase reaction could account in part for the rapid synthesis in microwave-heating syntheses of SiC and other materials.

In conclusion, we have demonstrated that β-SiC powder can be formed by microwave heating of Si powder which has no direct contact with graphite powder. The FE-SEM observations suggested that the Si powder is directly carbonized into β-SiC powder. These results suggest that carbon atoms are transported from graphite to silicon via a gas-phase. According to the Boudouard equilibrium, the atmosphere during the reaction comprises a vast majority of CO gas, and hence, the CO gas should be involved in the carbonization.

Acknowledgments This work was supported in part by the Advanced Institute of Materials Science. The authors are indebted to our department’s Research and Education Center of Materials Engineering for the FE-SEM observations. We would also like to thank K. Tsurusaki for his assistance with the experiments.

References