

Mechanism for the formation of SiC by carbothermal reduction reaction using a microwave heating technique

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A pure phase of SiC was formed by microwave heating (2.45 GHz) a powder mixture consisting of SiO₂:carbon black in a 1:3 molar ratio at 1300°C for 0.5 h in a nitrogen atmosphere. In contrast, when the same powder mixture was heated at 1700°C for 0.5 h in a nitrogen atmosphere using a conventional electric furnace, low crystallinity SiC was formed with carbon black remaining as an impurity. The mechanism for the formation of SiC from a powder mixture of SiO₂ and carbon using microwave heating is discussed on the basis of chemical thermodynamics, and compared to that for conventional heating with a carbothermal reduction reaction. As a result, the advantage of carbothermal reduction reaction by microwave heating was confirmed.

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1. Introduction

Conventional ceramic powder compacts are typically sintered using thermal energy such as convective heat transfer and radiant heat from an electric element or the combustion of organic fuel. The powder compacts are then heated from the surface to the bulk interior by thermal conduction, which requires the consumption of significant processing time and energy to achieve sintering. However, there are some ceramic materials that can absorb electromagnetic waves and generate heat energy due to electric conduction, electric dipole vibration, and magnetic dipole vibration. Of particular interest are electromagnetic waves in the frequency range from 0.3 to 300 GHz, the generation of which only requires a common and inexpensive magnetron generator. In principle, the exothermic phenomenon (heat energy; P : W/m³) occurs from the interior of the starting material, which absorbs a microwave according to the following equation:¹⁾

$$P = 1/2\sigma|E|^2 + \pi f\epsilon_0\epsilon_r''|E|^2 + \pi f\mu_0\mu_r''|H|^2 \quad (1)$$

where σ is the electric conductivity (S/m), E is the electric field (V/m), f is the frequency (s⁻¹), ϵ_0 is the vacuum dielectric constant (F/m), ϵ_r'' is the dielectric loss, μ_0 is the vacuum magnetic permeability (H/m), μ_r'' is the magnetic loss, and H is the magnetic field (A/m). However, not all ceramic materials are heated when irradiated with microwaves. Therefore, microwave heating techniques are seldom used in the direct sintering of ceramic materials. An example of application to heat technology is the use of SiC furniture heated with microwaves, where ceramic products placed on the SiC furniture are indirectly sintered by the heat energy from the SiC furniture.²⁾

In this study, the fabrication of SiC by microwave heating of a powder mixture consisting of silica and carbon was conducted. To date, some carbides, composites, and nitrides have been

synthesized using microwave techniques.^{3)–6)} In the case of SiC, SiO₂ and carbon were used as starting materials.⁷⁾ However, the mechanism for the formation of SiC by microwave heating on the basis of chemical thermodynamic considerations has not been studied yet. In order to clarify the formation mechanism, detection of the intrinsic temperature during processing is necessary. Therefore, a thermocouple was directly embedded into the starting powder to analyze the sample temperature. In addition, in situ optical observation of the sample was performed during heating. Finally, the role of microwave heating on the carbothermal reduction reaction of a powder mixture consisting of SiO₂ and carbon is clarified and compared to that for conventional heating using an electric furnace.

2. Experimental procedure

Silica (0.2–10 μm, quartz) and carbon black (24 nm, amorphous) were used as starting materials. A powder mixture of silica:carbon black with a 1:3 molar ratio was placed into a sample holder made of porous alumina insulation fixed in the microwave heating apparatus schematically presented in Fig. 1. The maximum power of the magnetron in this microwave heating apparatus was 6 KW (2.45 GHz). The increase in temperature was basically monitored using a pyrometer at the surface of the sample holder. The sample holder was filled with nitrogen gas at a flow rate of 6 L/min. The heating temperatures and duration time used were 1000–1400°C and 0.5 h, respectively, with a heating rate of approximately 20°C/min. After heating, the electric power of the magnetron was immediately turned off and the sample cooled spontaneously. A type-B thermocouple was also set directly into the powder mixture and the true temperature of the sample was recorded during microwave heating processing. Here the thermocouple was covered with a stainless steel (SUS) with 3.2 mm diameter and the sheath was fixed on the metal chamber inside the microwave heating apparatus. This means that there is a perfect connecting electrically between the sheath and the chamber. Under this condition, the electric potential

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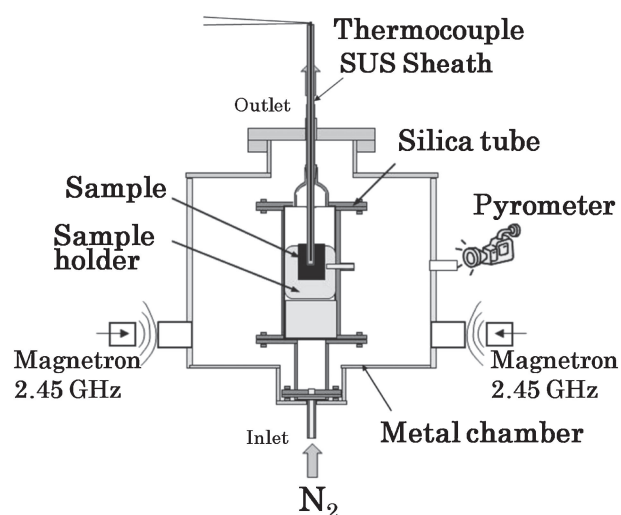


Fig. 1. Schematic diagram of the microwave heating apparatus used.

between the sheath and the chamber has no difference. Hence all metal surfaces including the sheath reflect the microwave perfectly.⁸⁾ Hence, the thermocouple can measure the intrinsic temperature of the sample. After heating, the crystal phases of the resultant samples were identified using X-ray diffraction (XRD; XD-D1, Shimadzu).

The same starting powder mixture was also heated at 1700°C for 0.5 h in an electric tube furnace in a nitrogen gas atmosphere at a flow rate of 6 L/min for comparison with the samples produced using the microwave heating apparatus.

3. Results and discussion

3.1 Formation of SiC

Figure 2 shows XRD diffraction patterns of the samples after heating the starting powder mixture at various temperatures, as recorded by the pyrometer, for 0.5 h using the microwave heating apparatus. The results indicate that SiC started to form in the sample at 1000°C, although SiO₂ was also detected in the sample at this temperature. SiO₂ was retained in the sample up to 1200°C. After heating at 1300°C, a pure phase of SiC was obtained, as evidenced by the lack of other diffraction peaks.

Figure 3 shows SEM photographs of the starting powders of SiO₂ and carbon black, and samples after heating at 1200 and 1300°C for 0.5 h. SiO₂ particles with diameters of approximately 10 μm were sometimes observed in the sample heated at 1200°C. However, these SiO₂ particles became as small as 1–2 μm after heating at 1300°C. As a result, the SiO₂ particles reacted and became SiC particles with 1–2 μm in diameter.

According to thermodynamic considerations, the SiC formation reaction can be described as follows:



According to reaction (2) and the free energy ΔG of generation data available in the JANAF thermochemical data tables,⁹⁾ it is clear that reaction (2) occurs at over 1527°C (1800 K) due to the condition of $\Delta G < 0$. However, SiC was already detected in the sample at 1000°C in this experiment, as shown in Fig. 2. Therefore, there is a possibility that the temperature inside the sample was higher than that displayed by the pyrometer for the sample holder surface. Therefore, a thermocouple was directly embedded in the starting sample and the sample temperature was recorded during processing.

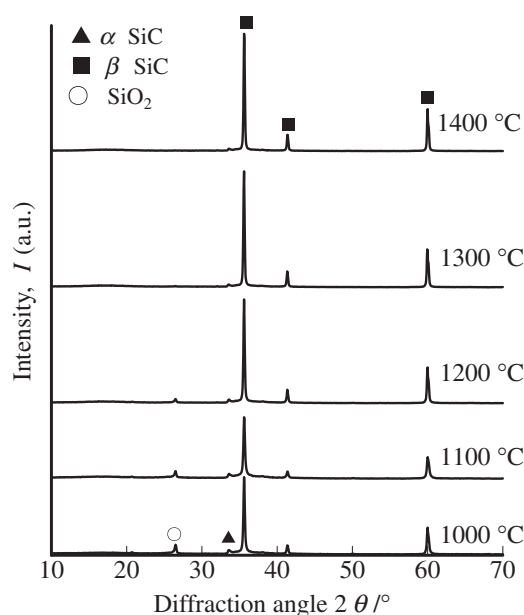


Fig. 2. XRD diffraction patterns of the samples after heating the starting powder mixture at various temperatures (recorded by the pyrometer at the sample holder surface) for 0.5 h using the microwave heating apparatus.

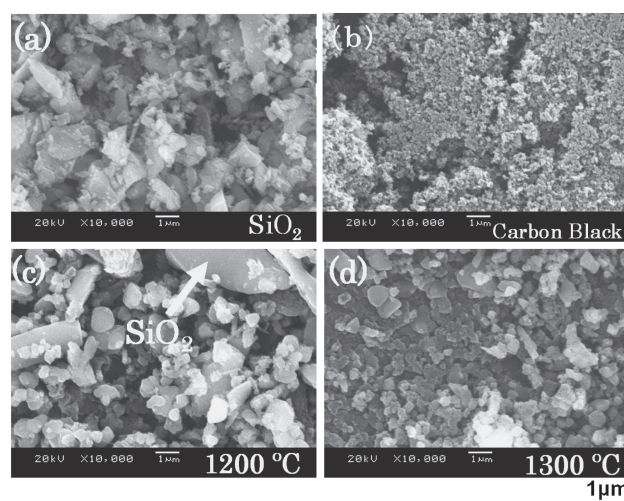


Fig. 3. SEM photographs of the starting powders of (a) SiO₂ and (b) carbon black and resultant samples after heating at (c) 1200 and (d) 1300°C for 0.5 h.

Figure 4 shows the temperature profiles for the thermocouple and pyrometer during microwave generation, and the temperature difference. According to this figure, the temperature of the thermocouple smoothly increased during microwave generation without spike behavior due to discharge and local heating. In addition, the temperature of the thermocouple immediately started to decrease after stopping the microwave generation. Hence, it was noticed that the thermocouple could measure the intrinsic temperature of the sample during microwave heating. By the way, when the temperature of the pyrometer indicated 1000°C, the temperature of the thermocouple was approximately 1400°C; therefore, the true temperature was at least 400°C higher than the temperature display of the pyrometer at the surface of the sample. In order to consider the formation reaction of SiC, a

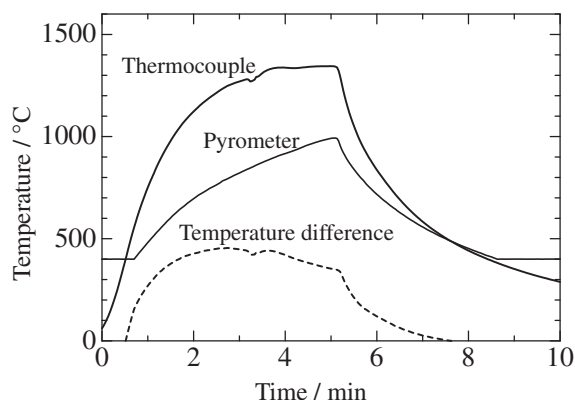


Fig. 4. Temperature profiles of thermocouple and pyrometer during microwave heating.

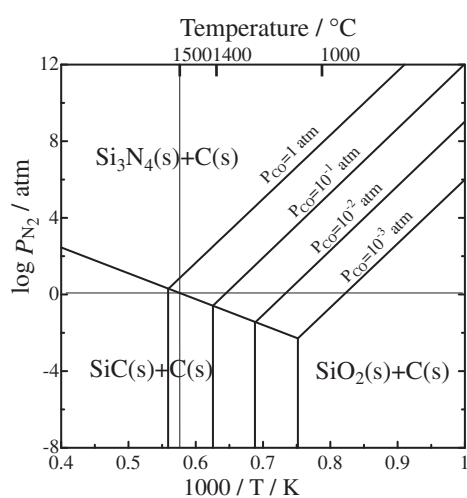
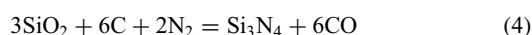
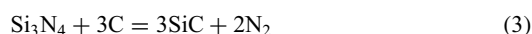


Fig. 5. Relationship between the stable condensed phases, $\log P_{N_2}$, $\log P_{CO}$, and temperature in the Si-C-N-O system.

more detailed discussion based on chemical thermodynamic considerations is required.

3.2 Chemical thermodynamic consideration

Figure 1 shows that the silica reaction tube was not completely sealed, because the outlet was open to the air. However, N_2 gas was flowed at the rate of 6 L/min from the inlet to the outlet of the apparatus during processing. Therefore, at a reaction temperature over 1000°C , the atmosphere was considered to be composed of N_2 and CO , which was formed by the reaction between O_2 in the N_2 gas cylinder and carbon black. **Figure 5** shows the relationship between the stable condensed phases, $\log P_{N_2}$, $\log P_{CO}$ and the temperature for the Si-C-N-O system.¹⁰⁾ This figure can be drawn using Eq. (2) and the following two reactions on the basis of JANAF thermodynamic data;



Firstly, from reaction (2), the change in the partial pressure of $CO(g)$ ($\log P_{CO}$) can be calculated under coexistence with SiC and SiO_2 according to the temperature. Subsequently, the change in the partial pressure of $N_2(g)$ ($\log P_{N_2}$) can be calculated under coexistence with α - Si_3N_4 and β - SiC according to the temperature. Finally, the partial pressure of $N_2(g)$ ($\log P_{N_2}$) can be



Fig. 6. Optical photograph of the sample heated at 1000°C (pyrometer) inside the microwave heating apparatus.

calculated under coexistence with α - Si_3N_4 and SiO_2 and the fixed condition of ($\log P_{CO}$) calculated from reaction (2).

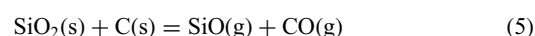
Figure 5 indicates that at the heating temperature (ca. 1400°C) recorded by the pyrometer, the α - Si_3N_4 phase is stable. From thermodynamic considerations, SiC cannot be formed. When the temperature of the pyrometer indicated 1000°C , the thermocouple embedded in the sample was approximately 1400°C (Fig. 4); however, 1400°C is slightly lower than the formation temperature of SiC according to Eq. (2). Therefore, in situ observation of the sample at 1000°C (pyrometer) was performed.

Figure 6 shows an optical photograph of the sample at 1000°C (pyrometer) inside the microwave heating apparatus. Hot spots were observed in some parts of the sample. The thermocouple embedded into the sample indicated the averaged temperature inside the sample, with the hot spots beyond 1500°C , at which temperatures SiC can form according to Eq. (2). As a result, unreacted SiO_2 was retained at lower temperature areas in the sample, as detected by XRD analysis (Fig. 2). At over 1300°C (pyrometer), the actual temperature of the thermocouple inside the sample was over 1500°C , so that reaction (2) occurred completely and a pure phase of SiC was obtained.

3.3 Mechanism for the formation of SiC by microwave heating

In Eq. (1), the first term is defined as Joule loss, and the second and third terms represent dielectric loss and magnetic hysteresis loss, respectively. In the case of a starting sample consisting of SiO_2 and carbon black, the Joule loss term becomes important. On the contrary, dielectric loss and magnetic hysteresis loss can be neglected. Therefore, carbon and SiC are heated due to Joule loss energy transfer when irradiated with microwaves.

Figure 7 shows the mechanism for the formation of SiC by the carbothermal reduction reaction from SiO_2 and carbon black using microwave heating. Firstly, when microwaves are irradiated, carbon black is heated due to the Joule loss effect. During this time, hot spots at which exothermic reactions occur begin to appear in some areas of the sample. The temperature around the hot spots increases to over 1500°C , which results in the generation of $SiO(g)$ from SiO_2 according to the following reaction:



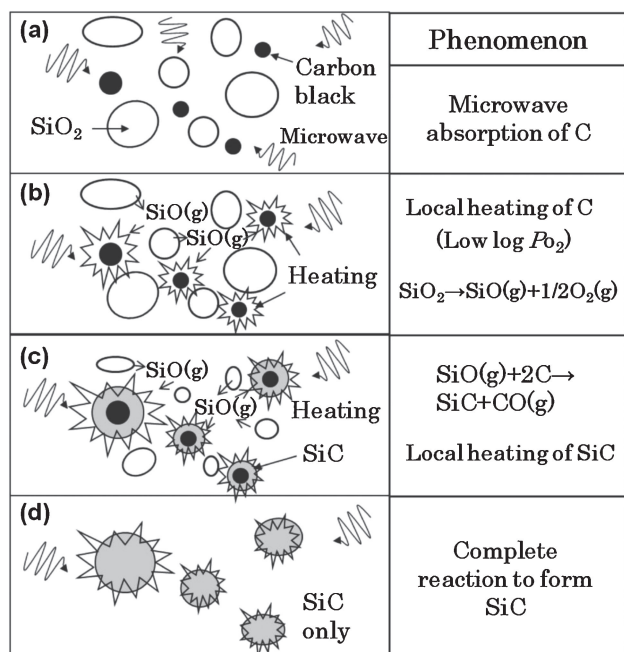


Fig. 7. Schematic diagram showing the mechanism for the formation of SiC by carbothermal reduction reaction from SiO_2 and carbon black using microwave heating.

On the other hand, the partial pressure of $CO(g)$ in the presence of carbon black in the system was determined by the following reaction:



The partial pressure of $O_2(g)$ is not clear in the $N_2(g)$ atmosphere with a gas flow rate of 6 L/min. If the partial pressure of $O_2(g)$ (P_{O_2}) is estimated to be 10^{-5} (atm) in $N_2(g)$, the equilibrium P_{CO} can be calculated as 2.0×10^5 (atm) at $1527^\circ C$ (1800 K) on the basis of reaction (6) and the JANAF thermochemical data as follows;

$$\text{equilibrium constant: } k_p = (P_{CO})^2 / P_{O_2} \quad (7)$$

$$\log k_p = 2 \log P_{CO} - \log P_{O_2} = 15.622 \quad (8)$$

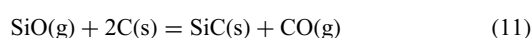
That is, the P_{CO} is extremely high, so that $CO(g)$ is exhausted and the P_{CO} decreases to the atmospheric pressure, namely 1 atm. Therefore, according to reaction (5) and $P_{CO} = 1$ ($\log P_{CO} = 0$) (atm), the partial pressure of $SiO(g)$: P_{SiO} could be calculated as 7.1×10^{-3} (atm) on the basis of reaction (5) and the JANAF thermochemical data as follows:

$$\text{equilibrium constant: } k_p = (P_{SiO}) / (P_{CO}) \quad (9)$$

$$\log k_p = \log P_{SiO} - \log P_{CO} = -2.149 \quad (10)$$

This partial pressure value was thought to be high, which results in the formation of $SiO(g)$ in the sample by reaction (5).

Subsequently, the generated $SiO(g)$ moves to carbon black particles at high temperatures over $1500^\circ C$ where SiC is then formed as follows:



That is, carbon black particles act as nuclei for the formation of SiC. In addition, the SiC formed could continue to be heated due to the Joule loss effect of microwave absorption, and further $SiO(g)$ infiltrates into the SiC layer to the carbon remaining at the center, as shown in Fig. 7(c). Thus, the formation reaction of SiC could be accelerated to form SiC particles. SiC particles could

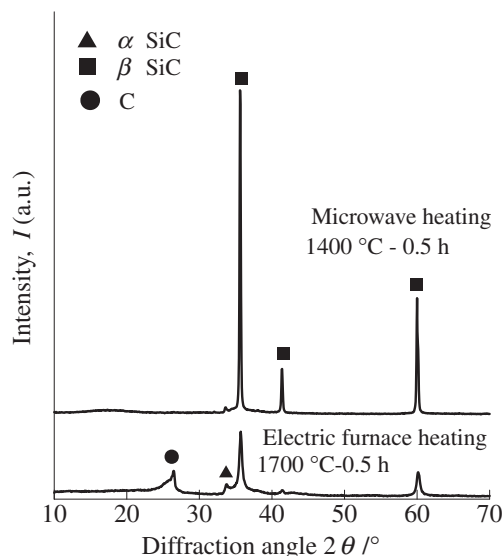


Fig. 8. XRD patterns of the samples prepared by microwave heating and conventional heating in an electric tube furnace at $1400^\circ C$ for 0.5 h and $1700^\circ C$ for 0.5 h, respectively.

then combine with each other to form larger particles with diameters of 2–3 μm .

3.4 Advantage of SiC formation by microwave heating

In an attempt to clarify the advantage of microwave heating, the same starting powder mixture of SiO_2 and carbon black was heated using an electric tube furnace at $1700^\circ C$ for 0.5 h in a nitrogen gas atmosphere at a flow rate of 6 L/min. **Figure 8** shows an XRD pattern of the sample compared with that for a sample prepared by microwave heating at $1400^\circ C$ for 0.5 h. The crystallinity of SiC prepared by conventional electric furnace heating was lower than that for samples prepared by microwave heating, as evidenced by the low XRD intensities for SiC in the sample. In addition, a small amount of carbon black remained in the sample after heating, which confirmed that single phase crystalline SiC was not completely formed in the case of electric tube furnace heating.

When microwave heating was conducted, the starting powder mixture was heated from the interior. Therefore, the temperature outside the sample was lower than that inside the sample. $SiO(g)$ is firstly generated according to Eq. (5), but is not exhausted from the sample, because the partial pressure of the $SiO(g)$: P_{SiO} decreases outside sample. Therefore, when microwave heating was used, the reaction field was limited to the interior of the sample. All reactions are completed inside the sample, which increases the effectiveness of the reaction, so that the crystallinity of the resultant SiC has a tendency to increase. On the contrary, when the starting powders were heated in the reaction tube using an electric element, both the sample and tube furnace were heated, so that most of the generated $SiO(g)$ is exhausted away from the sample in the reaction tube, which results in a low yield of SiC with low crystallinity. Thus, microwave heating is considered to be a more effective method for the fabrication of SiC prepared by the carbothermal reduction reaction.

4. Summary

SiC powder was fabricated by carbothermal reduction method using a microwave (2.45 GHz) heating technique. When a

powder mixture consisting of SiO₂:carbon black at a molar ratio of 1:3 was heated at 1300°C for 0.5 h, single phase SiC was formed. Some hot spots were generated inside the sample during processing, which accelerated the formation of SiO(g) and the subsequent reaction with carbon to form SiC. A thermocouple placed into the starting sample confirmed that the intrinsic temperature was at least 400°C higher than that indicated by the pyrometer on the sample holder surface. As a result, application of microwave heating to the carbothermal reduction reaction between SiO₂ and C accelerated the formation of SiC and increased its crystallinity.

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