The Thermodynamic and Kinetic Consideration of Formation Mechanism of β-SiC Thin Film from Carbon Dense Film and SiO Gas

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A thin film including beta-silicon carbide (β-SiC) was synthesized by carbon silicification through a reaction between gaseous silicon monoxide (SiO) gas and carbon source derived from polyimide film (PIF). The sample obtained had film shape similar to that of the carbon source film. Two reacted regions were found on both surfaces of the carbon source film, as well as the un-reacted region in the middle of the sample with less than 3 h synthesis time. Formation mechanism of β-SiC film formed by the reaction between SiO gas and carbon source film at 1400°C was investigated based on relationship among SiC conversion ratio, reaction time and atmospheres. Formation processes were simulated thermodynamically and kinetically by the calculations solving differential equations concerning with a rate of chemical species. Results of the simulated curves for the SiC conversion ratio calculated from 6 chemical equations, 12 rate constants, 2 diffusion constants, 9 chemical species and 9 differential equations have a good agreement with the experimental results of the SiC conversion ratio as a function of reaction time.

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1. Introduction
Silicon carbide (SiC) has been used in industries as structural and functional materials because it has excellent properties such as high thermal and chemical stabilities, elastic modulus and hardness, electrical and thermal conductivities. However, because of its low toughness, it is difficult to produce SiC with micro fabrication and complicated shapes by machining process utilizing conventional method.

A useful synthesis method of SiC tailored in shapes is utilizing carbon silicification reaction between carbon source and silicon monoxide (SiO) gas. Kennedy and North synthesized a very fine β-SiC powder reflecting the morphology of its carbon precursor of acetylene carbon black. Similar results have also been reported by Ledoux, et al. on a high specific-surface-area SiC catalytic support formed from a high specific-surface-area carbon as skeletons. Until now, SiC powder, SiC fiber, and SiC block, were synthesized from carbon powder, activated carbon fiber and carbon block, respectively. Moreover, synthesized SiC layer on the carbon/carbon composites (C/C composites) was utilized as a pretreated adhesion to reduce the mismatch in thermal expansion coefficients between carbon substrate and surface coating of CVD-SiC.

Thus, there are some study about the synthesis of SiC through the reaction SiO gas and carbon source with relative high specific-surface-area and containing micropores, and formation mechanisms of the reaction was estimated thermodynamically and kinetically. In general, marked difficulties in kinetic behavior are diffusion mechanism in distributed pores.

We found that the dense carbon source derived from polyimide, whose shape can be controlled easily, transformed β-SiC through the silicification process. It is also clear that texture and structure of carbon source affect SiC conversion degree, and reaction rate of silicification was very low. To find a high-efficiency optimized synthesis conditions, it is necessary to clarify the formation mechanism of SiC in the silicification process. The aim of this study is to clarify the formation mechanism of SiC through the reaction between SiO gas and dense carbon source film in different atmospheres, and also to find a way to estimate the optimum synthesis condition of SiC.

2. Experimental
2.1 Synthesis process of SiC film
Commercial Kapton® type polyimide film (PIF: Torei-Dupont Co., Ltd.) with a thickness of 25 μm is used as a precursor of carbon source film. The carbon source film with dimension of 11.6×11.6 mm² and 21 μm in thickness, and mass of about 4.3 mg (0.48 mmol) was derived carbon film by heat-treating the PIF at 1000°C for 1 h (=3.6 ks) in N₂ gas. Gaseous SiO gas was generated from SiO fine powder (Kojundo Chemical Laboratory Co., Ltd) with particle size of 10 μm and 99.9% purity. SiO powder ranging from 0.5 to 2.5 g (11.3 to 55.8 mmol) was packed in the bottom of an alumina tubular reaction chamber and two sheets of PIF-derived carbon films were set on a SiC holder. The reaction chamber was set in an electric furnace, and the carbon source films reacted with SiO gas at 1400°C for 1 to 5 h in vacuo or in Ar atmosphere with a flowing rate of 1.0×10⁻² m³/h in the electric furnace, and then silicified films were obtained.

2.2 Evaluations
Amount of carbon silicification and amount of SiO vaporization were estimated by Eqs. 1 and 2:

\[ S_2 = \frac{(m_a - m_c)}{(M_{SiC}[40.10] - M_C[12.01])} \quad \text{Eq. 1} \]
\[ S_3 = \frac{(m_s - m_4)}{(M_{SiO}[44.09])} \quad \text{Eq. 2} \]

Where \( S_2 = \) amount of carbon silicification (mol), \( S_3 = \) amount of SiO vaporization (mol), \( m_a = \) mass of silicified film (g), \( m_c = \) mass of mass of carbon source film (g), \( m_s = \) mass of SiO powder before synthesis (g), \( m_4 = \) mass of SiO powder after synthesis (g). \( M_{SiC}, M_{SiO} \) show a molar mass of X constituent (g/mol).

Contribution ratio of vaporized SiO has been calculated by Eq. 3 using \( S_2 \) and \( S_3 \) obtained by Eq. 1 and 2:

\[ R_v = \frac{S_2}{S_3} \times 100 \quad \text{Eq. 3} \]

\( R_v = \) contribution ratio of vaporized SiO (mol%).

In the case of the SiC conversion ratio, ratio equation can be rearranged to give:

\[ a_m = \frac{(m_s/m_4 - 1)}{(M_{SiC}[40.10] - (M_C[12.01]) \times 2)} \quad \text{Eq. 4} \]
Where, $a_0 = \text{SiC conversion ratio (\%)}$.

In addition, another SiC conversion ratio ($a_2$) was calculated by using Eq. 5 from residual mass ($m_{res}$) of silicified films after being oxidized at 700°C in dry air atmosphere in thermogravimetry analyzer (TGA).

$$a_2 = \frac{(m_{res}/M_{SiC}[40.10]/2) \times 100}{((100 - m_{res})/M_{C}[12.01]) - (m_{res}/M_{SiC}[40.10]/2)} \quad \ldots \text{Eq. 5}$$

The samples obtained were investigated by X-ray diffraction analysis (XRD), energy dispersive X-ray spectroscopy (EDX) and X-ray photoemission spectroscopy (XPS). Texture and structure were observed by optical microscope and scanning electron microscopy (SEM).

2.3 Thermodynamic and kinetic calculations

**Equation 6** is the total reaction of silicification reaction between carbon source and SiO gas.

$$\text{SiO (g)} + 2\text{C} (s) = \text{SiC} (s) + \text{CO} (g) \quad \ldots \text{Eq. 6}$$

To correlate the existing experimental results, we propose the rates of SiC formation involving SiO and CO gases generated from 5 elementary reactions, according to the scheme shown in Fig. 1. SiO (g) I stands for SiO gas in the reaction chamber excluding that the boundary layers, SiO (g) II for SiO gas in the boundary layers and SiO (g) III for SiO gas out the reaction chamber. CO (g) I stands for CO gas in the boundary layers, CO (g) II for CO gas in the reaction chamber excluding that in the boundary layers and CO (g) III for CO gas out the reaction chamber, respectively. Rates of change for 9 chemical species can be expressed as the following 9 differential equations.

$$d[\text{SiO} (s)]/dt = -k_{ref}[\text{SiO} (s)] + k_{nt}[\text{SiO} (g) I] \quad \ldots \text{Eq. 7}$$

$$d[\text{SiO} (g) I]/dt = -k_{nt}[\text{SiO} (g) I][1 - \text{erf}(p/(4D_{nt})^{0.5})] + k_{ns}[\text{SiO} (g) II][1 - \text{erf}(p/(4D_{ns})^{0.5})] + k_{nt}[\text{SiO} (s)] - k_{nt}[\text{SiO} (g) I] - k_{ns}[\text{SiO} (g) III] \quad \ldots \text{Eq. 8}$$

$$d[\text{CO} (g) I]/dt = k_{nt}[\text{SiO} (g) I][1 - \text{erf}(p/(4D_{nt})^{0.5})] - k_{ns}[\text{CO} (g) I][1 - \text{erf}(p/(4D_{ns})^{0.5})] - k_{nt}[\text{SiO} (g) II][C(s)]^{2} + k_{ns}[\text{CO} (s)] [\text{CO} (g) I] \quad \ldots \text{Eq. 9}$$

$$d[C(s)]/dt = 2[-k_{ns}[\text{CO} (g) II][C(s)]^{2} + k_{nt}[\text{SiO} (g) II][C(g) I]] \quad \ldots \text{Eq. 10}$$

$$d[\text{SiC} (s)]/dt = k_{nt}[\text{SiO} (g) II][C(s)]^{2} - k_{ns}[\text{SiC} (s)][\text{CO} (g) I] \quad \ldots \text{Eq. 11}$$

$$d[\text{SiO} (g) II]/dt = 0 \quad \ldots \text{Eq. 12}$$

$$d[\text{SiO} (g) III]/dt = 0 \quad \ldots \text{Eq. 13}$$

$$d[\text{CO} (g) II]/dt = 0 \quad \ldots \text{Eq. 14}$$

$$d[\text{CO} (g) III]/dt = 0 \quad \ldots \text{Eq. 15}$$

In Fig. 1, $t =$ reaction time (100 s which represents a calculation step time), the part of Eq. 16 is ratio of gas species diffusing through reacted regions. Thickness of reacted region was assumed by Eq. 17.

$$\frac{1 - \text{erf}(p/(4D_{nt})^{0.5})}{\text{erf}(p/(4D_{ns})^{0.5})} \quad \ldots \text{Eq. 16}$$

$$p = A_{\rho_{SiC}}[\text{SiC} (s)]/M_{SiC} \quad \ldots \text{Eq. 17}$$

where, $A_{\rho} =$ geometric surface area ($\text{cm}^{2}$), $\rho_{SiC} =$ density of SiC ($\text{g/cm}^{3}$), $\text{[SiC] (s)}$ and $M_{SiC}$ are amount of SiC formed and molar mass, respectively. The number “2” in Eq. 17 indicated the sheets of carbon source films in the reaction chamber. To a diffusion approximation, the carbon source film is assumed as an infinite flat sheet.

Nine differential equations were solved numerically and successively by using Runge-Kutta- Fehlberg method; and we could obtain amount of 9 species as a function of reaction time, and then a SiC conversion ratio curve ($a_c$) calculated as a function of reaction time was given by Eq. 18.

$$a_c = \frac{(m_{res}(t))/m_{res}-1}{M_{SiC}[40.10]/[M_{C}[12.01]\times2]-1} \quad \ldots \text{Eq. 18}$$

In addition, the calculation was carried out for 180 steps with each step of 100 s. As concerning to the rate constants, $k_{nt}$ in equations F1 and F3 shown in Fig. 1, the transition state theory of kinetics can be applied to them as following.
The rate constants of forward and backward, \( k_{\text{f}} \) and \( k_{\text{b}} \), in equations F2 and F4 are assumed as 1. In equations F5 and F6, these reactions are kinetically irreversible because gas stream was released outside the chamber through a small pore with diameter of 1 mm, thus \( k_{\text{b}} \) in equations F5 and F6 are assumed as 0. Values of \( k_{\text{f}} \) and \( k_{\text{b}} \) were calculated from the experimental value of vaporization of SiO powder, and value of \( k_{\text{b}} \) is assumed to equal to \( k_{\text{f}} \). The other values of \( k_{\text{f}} \) and \( D_0 \) were found out by using try-and-error method of searching solutions on differential equations giving the Sic conversion ratio \( \alpha \) calculated as a function of reaction time, which was in good agreement with the experimental results of the Sic conversion ratios \( \alpha_0 \), \( \alpha_\infty \) and SiO vaporization \( \dot{S}_e \) with reaction time.

3. Results and discussions
3.1 Formation of siliconized film
From the results of XRD and XPS, the formation of β-SiC in the siliconized film was verified, whereas no Si or SiO was detected.

Table 1 shows the amount of siliconization \( \dot{S}_e \), the amount of SiO vaporization \( \dot{S}_e \) and the contribution ratio of vaporized SiO \( R_e \) to the siliconization in vacuo or in Ar atmosphere. It is found that the values of \( \dot{S}_e \) and \( \dot{S}_e \) in vacuo is larger than those in Ar atmosphere, but the value of \( R_e \), i.e. the ratio of SiO changed to SiC during reaction is very low. In vacuo, SiO powder is completely vaporized at 30 mins and some SiO was found at the low temperature zone in the downstream of the electric furnace. These results suggest that the residence time of SiO vapor passing through the carbon source film is very short, thus the contribution ratio of vaporized SiO would be relatively low.

The morphology of cross-section of the siliconized films is shown in Fig. 2. The siliconization reaction proceeds from the surface to the center of the carbon source film. It is found the siliconized film that was prepared at 1400°C for 1 hour in vacuo consisted of two layers that had been completely changed to a reacted region. However, in the film that is prepared in Ar, it is found that two reacted regions with thickness of 5 μm formed on the both sides of the film, and the carbon in the inner remains unreacted. By careful observation of the pore in the film, it is found that the elliptic front edge of the reaction around the pore proceeds to the inner of the film. It means that the silicon source that diffused through the SiC layer preferentially diffuse through the pore, suggesting that the Si species that diffuse both through SiC layers and in pores may be SiO vapor. However, it is still unclear how SiO diffuses in the siliconized film.

Figure 3 shows the dependence of SiC conversion ratio \( \alpha_0 \) and \( \alpha_\infty \) on the reaction time. SiC conversion ratio in Ar increased linearly with reaction time to 100% in 3 hours (for \( \alpha_0 \)) or 4 hours (for \( \alpha_\infty \)). SEM observation of the cross-section and TGA analysis show there is no carbon residue in the film prepared in 4 and 5 hours. However, SiC conversion ratio \( \alpha_\infty \) in vacuo is about 13% in 0.5 and 1 hour, indicating the reaction stopped at 0.5 hour. The reacted region formed in vacuo consists of SiC and carbon homogeneously, thus, very small pores in the reacted region oxidized at 700°C were observed. It is concluded that the atmosphere during reaction has a significant effect on SiC conversion ratio.

3.2 Kinetic and thermodynamical calculation of SiC formation
The rate constants \( k_{\text{f}} \) and diffusion constants \( D_0 \) of all step reactions are calculated from the amount of SiO vaporization \( \dot{S}_e \) and SiC conversion ratios \( \alpha_0 \) and \( \alpha_\infty \). Fig. 4 shows the relation of \( \dot{S}_e \) with reaction time, and the simulated curves. In the case that SiO is heated without carbon source film in Ar atmosphere, the value of \( \dot{S}_e \) increased parabolically with reaction time. A simulated curve (\( [A] \) in Fig. 4) concerning with
S, can be fitted by using $k_{1f} > 1.0 \times 10^{-4}$ and $k_{2f} = 3.4 \times 10^{-3}$. Starting from the two constants, we can calculate the other constants with the results in the case with carbon source film. Fig. 5 shows the relation of the experimental results of SIC conversion ratio $a_{in}$ and $a_{1g}$ with time, and the calculated one, $a_{1}$, shown in Fig. 5 with solid lines. The fitted $a_{1}$ curves are calculated from estimated values of $k_{ad}$ and $D_{r}$ given in Table 2.

Now, we investigate the case that SIO powder is heated with carbon source film in Ar. According to the above-calculated results from the amount of SIO vaporization, $k_{1f}$, SIO supplying rate should be larger than $1.0 \times 10^{-4}$. Otherwise, the slope of $a_{1}$ curve would be so small that SIC conversion ratio could not reach 100%. ($k_{1f} = 1.0 \times 10^{-5}$, curve [1] in Fig. 5). For larger $k_{1f}$ value, the fitted $a_{1}$ curve does not change. It can be known that the silicification reaction in the present experiments is not “SIO vapor supply-controlled reaction”. It was further demonstrated by the fact that $k_{1f} = 1.0 \times 10^{-2}$ is necessary to fit the simulated curve [C] in Fig. 4 to the experimental results in vacuo. Since $k_{1f}$ is a constant independent on atmosphere, so we can set $k_{1f} > 1.0 \times 10^{-2}$. In addition, to fit the results of SIC conversion ratio and the amount of SIO vaporization, $k_{1f} = 3.0$ is required.

If $k_{1f}$, the rate constant of the interfacial reaction, is smaller than the optimum value $2.5 \times 10^{-3}$, the slope of $a_{1}$ curve would be small ($k_{1f} = 2.0 \times 10^{-3}$, curve [2] in Fig. 5). If $k_{1f}$ is larger, the slope of $a_{1}$ curve is also larger ($k_{1f} = 3.0 \times 10^{-3}$, curve [3] in Fig. 5). This reaction is regarded as “rate-controlled reaction in interface”.

Finally, consider the diffusion constants. The curve [4] calculated from the value of $D_{2r} = D_{3r} = 1.0 \times 10^{-7}$ and the curve [5] calculated from the value of $D_{2r} = D_{3r} = 5.0 \times 10^{-8}$ are not optimized. It is known that if the diffusion constant of SIO in the reacted regions is larger than the optimum value of $2.5 \times 10^{-3}$, $a_{1}$ curve increased linearly. If the value of $D_{2r}$ is smaller than the optimum value, $a_{1}$ would rapidly reach the saturation value, and the reaction rate is quite low. The diffusion constant of CO, $D_{1}$ is set to be $1 \times 10^{-10}$, and no change of $a_{1}$ SIC conversion ratio is detected. This is because the Gibbs’ free energy of reaction F3, $\Delta G^\circ = -79.32$ (kJ/mol), relatively large value to negative, the reaction still proceed to form SIC regardless of the increase of CO gas near the reaction interface. Even if $D_{2} = D_{3}$ is not true considering the molecular weight and size of SIO and CO, the calculation results of the diffusion constants imply that in the present condition, the silicification reaction is not “diffusion-controlled reaction in
the reacted region” at the initial stage of the reaction, but gradually changed to “diffusion-controlling reaction in the reacted region” for the diffusion constants shows effect on the reaction.

By considering the 6 chemical equations and 9 chemical species, we solved the differential equations that describe the changing rate of the concentration of the 9 species, and calculated the rate constants $k_{st}$ and diffusion constants $D_i$, as given in Table 2. It should be emphasized that the difference of atmosphere can be described by $k_{st}$ and $k_{st}$, the emission rates of SiO(g) and CO(g) to outside the reaction, and the increase of the amount of SiO vaporization with or without carbon source comparing curve [A] and [B] in Fig. 4 can be calculated clearly. From these results, the model proposed in this paper not only explained the reaction mechanism of silicification from dense carbon source film, but also be expected to give guidance for the preparation conditions of SiC film.

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<th>in Ar atmosphere</th>
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4. Conclusion

Formation processes of SiC from SiO gas and carbon source films were simulated thermodynamically and kinetically by the calculations solving differential equations concerning with a rate of chemical species.

Results of the simulated curves for the SiC conversion ratio calculated from 6 chemical equations, 12 rate constants, 2 diffusion constants, 9 chemical species and 9 differential equations have a good agreement with the experimental results of the SiC conversion ratio as a function of reaction time.

The calculation results of solving each constants imply that the formation processes of SiC is “rate-controlled reaction in interface” at the initial stage of the reaction, and then gradually changed to “diffusion-controlling reaction in the reacted region”.

From these results, the model proposed in this paper not only explained the reaction mechanism of silicification from dense carbon source film, but also be expected to give guidance for the preparation conditions of SiC film.

References