

Kinetics Model for the Growth of Silicon Carbide by the Reaction of Liquid Silicon with Carbon

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The kinetics and mechanism of reaction of glassy carbon with a pure silicon melt or a Si + Mo melt were investigated. The results showed that the growth of a continuous reaction-formed SiC layer followed a fourth-power rate law in the temperature range of 1430° to 1510°C. A model that could explain the fourth-power rate law was developed. In this model, an internal electric field was assumed to be set up over the reaction-formed SiC layer through a negative space charge, and then the diffusion of the carbon-ion vacancies across this layer, driven predominately by this electric field, was considered as the rate-limiting step for the SiC growth. Neither an increase in the processing temperature nor an addition of 10 wt% Mo into the silicon melt had a significant influence on the reaction kinetics. X-ray diffraction analysis revealed that the reaction products were β-SiC, and β-SiC + MoSi₂ for the Si-C and Si-C-Mo reactions, respectively.

I. Introduction

T_{HERE} has been a great deal of interest in reaction-bonded silicon carbide (RB-SiC) and fibrous SiC/Si composites as well as their liquid-phase reaction-processing technique.¹⁻⁶ This is largely because of the superior properties of these materials, and the remarkable advantages of this processing method. These materials display high thermal conductivity, thermal shock resistance, strength, and fracture toughness, and low friction coefficient and high wear resistance. Liquid-phase reaction-synthesis, one of the most promising processing methods, can produce fully dense and near-net-shape composites without the application of an external pressure and at relatively low temperatures and short times.⁶

The microstructure and mechanical properties of these materials are known to be dependent on the processing conditions, such as the infiltration temperature and time, as well as the pore size and its distribution in the preform. Therefore, a full understanding of the reaction kinetics and mechanisms is of great importance for optimization of the processing conditions to create composites with the desired microstructure and mechanical properties. However, there are only a few published data on the reaction kinetics, and the mechanisms are still far from being well understood. Fitzer and Gadow proposed a diffusion mechanism and derived a mathematical model to describe the rate of growth of SiC, which was based on the mass balance among the various mass transfer processes, such as mass transfer through the boundary layer in molten silicon, mass diffusion across the solid SiC layer, and reaction at the SiC/C interface. The effective diffusion coefficients at 1600° and 1800°C predicted from their model ($D_e = 4.2 \times 10^{-10}$ cm²/s at 1600°C, $D_e = 9.5 \times 10^{-10}$ cm²/s at 1800°C)⁷ were 1 and 2 orders of magnitude lower than the boundary diffusion coefficient of carbon ($D_{bc} \approx 8.86 \times 10^{-9}$ cm²/s at 1600°C, $D_{bc} \approx 2.90 \times 10^{-7}$ cm²/s at 1800°C obtained by extrapolating the data from the published literature⁸), respectively. The temperature range of their study was higher than the typical processing temperatures between 1420° to 1450°C. The other mechanism for SiC growth is solution–precipitation as proposed by Pampuch,⁹ Sawyer and Page,¹⁰ as well as Ness and Page,¹¹ in which they assumed that the carbon dissolved into molten silicon, and SiC precipitated from a supersaturated solution of carbon in silicon at elevated temperature.

In this paper, the particular emphasis is placed on an investigation of the reaction kinetics and mechanisms in the Si–C reaction over a lower temperature range of 1430° to 1510° C. Recently, a Si + Mo melt has been used to infiltrate a carbon preform to form SiC/MoSi₂ without any detectable residual silicon phase.^{12,13} This silicon-free material is expected to have superior high-temperature strength and creep resistance in comparison to materials containing a significant amount of the silicon phase. Therefore, the influence of Mo addition on the reaction kinetics and the microstructure of the reaction products are also studied.

II. Experimental Procedure

We studied the reaction kinetics of liquid silicon with solid carbon using a variety of carbon materials, such as polycrystalline graphite from Poco Graphite Inc., pyrolytic graphite from Union Carbide, and Sigradure G glassy carbon. The results of the reaction of liquid Si with polycrystalline graphite showed that liquid silicon physically penetrated into the pores of the graphite and reacted with the graphite. Once the surface pores of the graphite were closed upon the formation of SiC (reactionchoking), the penetration of liquid silicon stopped, but the reaction was carried on due to the diffusion of reactants through the reaction-formed SiC barrier layer to make this layer grow. Obviously, two conceptually independent processes of infiltration and reaction were involved in this reaction. In practice, however, these two processes were not separable at the temperature of this study, which made it impossible to study only the kinetics of the Si-C reaction. The pyrolytic graphite specimen after the reaction also showed that the penetration of liquid silicon took place together with the Si-C reaction. This penetration along the (0001) plane of graphite was due to the much weaker van der Waals bonds between these planes. As mentioned above, it was difficult to separate the kinetics of the penetration of liquid silicon from the Si-C reaction kinetics. Therefore, these graphitic materials are not suitable for studying reaction kinetics.

Sigradure G glassy carbon plate (EMC Industry, Flemington, NJ) with a density of 1.42 g/cm^3 was finally chosen as a carbon source for this kinetics study to react with either a pure Si melt or a Si + Mo melt, because the preliminary results showed no penetration occurred during the reaction process. This material

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is nonporous in macrorange, though it contains a number of very fine voids of 1 to 3 nm in diameter.¹⁴

The starting material for a Si + Mo melt was made by preparing a slurry of Si and Mo powders in methanol, wet ball milling, and evaporating to create a homogenous Si + Mo mixture. The homogeneity of this mixture was confirmed using SEM in the backscattering mode.

It can be seen from the Mo–Si phase diagram that there is a eutectic reaction of $MoSi_2$ and Si at a temperature of $1410^{\circ}C$ and at a composition of 90.4 wt% silicon. By using the Si + Mo melt of the eutectic composition to infiltrate the carbon preform, the advantages of relatively low processing temperature can still be retained. Thus, a 10 wt% Mo addition was selected to study its influence on the reaction kinetics.

The glassy carbon plate was buried in the silicon powder or the Si + Mo powder mixture, which was contained in a BNcoated graphite crucible. The crucible and reactants were kept in an alumina tube, heated to the temperature range of 1430° to 1510° C at a constant heating rate of 5° C/min, and held for a given time period under a vacuum of 10^{-1} torr. The reaction chamber was lined with a grafoil in the hot zone of the furnace which ensured a highly reducing atmosphere and prevented any possibility of oxidation of Si or SiC during reaction. After the reaction, the sample was cooled down at a rate of 15° C/min to room temperature, cut by a diamond saw, and polished with diamond compound paste to reveal the reaction product.

(c)

Extreme care was taken to avoid any damage to the reaction layer during cutting and polishing.

The variation in the thickness of the reaction-formed SiC layer with exposure time was used as a measure of the reaction kinetics. However, this thickness cannot be measured directly because of the nonuniform nature of the reaction-formed SiC layer as shown in Figs. 1 and 2. The average thickness was determined in our experiments by dividing the SiC area in the polished cross section by the length of a line parallel to the SiC/C interface. These area and length data were measured using an image analysis system. A similar procedure was used by other investigators to study reaction kinetics.¹⁵

The phase analysis of the reaction product was carried out by X-ray diffraction using CuK α radiation. The area radiated by X-ray was parallel to the SiC/C interface. Some of the silicon phase outside of the reaction product layer was removed by etching with 75% nitric acid and 25% hydrofluoric acid, which allowed the reaction product to be exposed to the X-ray radiation for phase analysis.

III. Results and Discussion

(1) Microstructural Features

Figure 1 shows the optical micrographs of the polished, unetched cross sections of the samples produced by the reaction of solid glassy carbon with liquid silicon at 1475°C for 20 and

(d)



(a) (b)
$$\frac{\beta - SiC}{C}$$
 Si $\beta - SiC$ G G G $Z5\mu m$

Fig. 1. Microstructure of reaction-formed SiC in the Si–C system (a) at 1475°C after 20 min, (b) at 1475°C after 180 min, (c) at 1510°C after 20 min, and (d) at 1510°C after 360 min.







 (\mathbf{U})

Fig. 2. Microstructure of reaction-formed SiC in the Si–C–Mo system (a) at 1430°C after 20 min, and (b) at 1430°C after 180 min.

180 min (Figs. 1(a) and (b)) and at 1510°C for 20 and 360 min (Figs. 1(c) and (d)). It can be seen that in all cases, a continuous but nonuniform SiC layer was formed from the Si-C reaction on the original surface of the glassy carbon. There was no penetration of liquid silicon into glassy carbon. The SiC layer became thicker and more uniform with increasing reaction time. Neither an increase in the reaction temperature within a range of 1430° to 1510°C nor an extension in the reaction time could change the microstructural morphology of the reactionformed and continuous SiC layer fundamentally. Although a continuous layer of reaction-formed β-SiC was observed in this study upon reaction of liquid silicon with glassy carbon, other researchers¹⁵ have observed discontinuous β-SiC upon reaction of P55 carbon fibers with liquid silicon in a short period of reaction time (less than 150 s). Therefore, the exact reaction product morphology may depend on the type of carbon precursor used. This, however, was not the case for the reaction of liquid silicon with glassy carbon in which a continuous β-SiC layer formed. In a reducing environment of this study, it was not possible to form an oxide of SiO₂. Therefore, the nonuniform reaction product should be a consequence of the Si-C reaction rather than the presence of an oxide at the interface. X-ray diffraction results verified that the continuous layer was composed of only β -SiC on all reacted samples. In addition, the reaction-formed β -SiC was not transformed to α -SiC in the temperature range of this study.

The microstructures evolved from the reaction of glassy carbon with the Si + 10 wt% Mo melt are shown in Fig. 2, where a continuous SiC layer was also formed by the reaction and grew with an increase in reaction time. A more careful microstructural examination shows that most of the Mo-rich phase, which was identified as MoSi2 by X-ray diffraction, precipitates discretely within the Si phase rather than at the SiC/C interface. This MoSi₂ phase most likely precipitates from the silicon melt during cooling, since the solubility of Mo in the silicon melt decreases at lower temperatures. The calculation of the free energy change for the formation of Mo₂C and SiC shows that the SiC is more stable relative to Mo₂C up to a temperature of about 1750 K.¹⁶ It is further indicated from this experiment that the formation of SiC is more favorable in comparison to the formation of molybdenum carbides in the temperature range of this study.

(2) Reaction Kinetics

The overall reaction rate for the Si-C reaction is plotted in Fig. 3 as the average thickness of the continuous SiC layer vs exposure time at 1430°, 1475°, and 1510°C. It can be seen that most of the SiC was formed in the early stage of the reaction, and the growth rate of this SiC layer decreased in the latter period of the reaction. During the reaction, the carbon got completely covered by the reaction-formed SiC layer and was spatially separated from the Si melt, so that one of the reactants (C or Si) had to diffuse through this SiC layer to keep the reaction going and SiC layer growing. We first tried to fit these kinetics data to a parabolic rate law by means of a least-squares regression. However, the correlation coefficient of this fit turned out so low (0.5 to 0.8) that the fit was unacceptable, which indicated that the diffusion of the reactants driven by chemical composition gradient would not be the mechanism of growth of the SiC layer. We also analyzed the data using a linear-parabolic law used to characterize oxidation of single-crystal Si,17,18 but again the correlation coefficient was low (0.6 to 0.8). Finally, we found that the variation in the average thickness of the reaction-formed SiC layer with reaction time in the temperature range of this study obeyed a fourth-power rate law with a correlation coefficient of above 0.9. These correlation coefficients for the different fit are summarized in Table I. The experimental data at 1510°C and their best-fit curves using parabolic, linear-parabolic, and fourth-power rate laws are shown in Fig. 4. Obviously, the fourth-power rate law describes these data better over the whole time range whereas the parabolic and linear-parabolic dependencies underestimate the thickness for shorter reaction times and overestimate for longer times. This is also true for the fit of the data at 1430° and 1475°C.



Fig. 3. Thickness of the SiC layer as a function of the reaction time for Si–C reaction at 1430° , 1475° , and 1510° C.

The fourth-power rate law can be expressed as

$$\delta = kt^{1/4} \tag{1}$$

where δ is the average thickness of the continuous SiC layer, t is the reaction time, and k is a constant as listed in Table II. In the temperature range of 1430° to 1510° C, k is almost always equal to 3 for the Si-C system, which indicates that the processing temperature of this study has little influence on the reaction kinetics. This might be due to the exothermic reaction between solid carbon and molten silicon in which a large amount of the heat of reaction will be given off so that the local temperature near the reaction front will be increased. The calculated temperature increment can reach 630 K for a sample consisting of 28.3 vol% carbon fiber and 71.7 vol% silicon under adiabatic conditions.9 Thus, although the practical temperature increment due to the reaction heat may be lower than the 630 K in our study, the 80 K difference in temperature for the kinetics study may not be large enough to compensate for the effect of the exothermic reaction.

The growth rate of the SiC layer, produced by the reaction of glassy carbon with Si + Mo melt at different temperatures, is shown in Fig. 5. The least-squares regression analysis of the experimental data indicates that the variation in the average thickness of the SiC layer with time also obeys a fourth-power rate law with a value of about 3 for the constant k (Table II), and is hardly affected by changes in the processing temperature. In addition, there is a small increase in the growth rate of the SiC layer by adding 10 wt% Mo to the silicon melt, as shown in Fig. 6.

 Table I.
 Correlation Coefficients for the Fit to a Parabolic, Linear-Parabolic, and Fourth-Power Rate Law

Rate law	Correlation coefficient		
	1430°C	1475°C	1510°C
Parabolic Linear-parabolic Fourth-power	0.61 0.71 0.89	0.51 0.68 0.90	0.80 0.85 0.97



Fig. 4. Comparison of the experimental data of the Si–C reaction at 1510°C with the predictions of parabolic, linear-parabolic, and fourth-power rate laws at the same temperature.

Table II. k Values for Si–C and Si–Mo–C Reactions at 1430°, 1475°, and 1510°C

	$k (\mu m/min^{1/4})$		
Reaction	$T = 1430^{\circ}{\rm C}$	$T = 1475^{\circ}\mathrm{C}$	$T = 1510^{\circ}\mathrm{C}$
Si–C	2.99	3.13	3.05
Si-Mo-C	3.31	3.15	3.19



Fig. 5. Thickness of the SiC layer as a function of the reaction time for Si–C–Mo reaction at 1430°, 1475°, and 1510°C.

(3) A Model for Reaction Kinetics and Mechanism

The reaction of carbon with silicon to form SiC can take place almost immediately after the solid carbon sample is immersed into molten silicon at a temperature slightly above the melting point of silicon.¹³ A continuous solid SiC layer is formed on the original surface of carbon, thereby preventing the molten silicon from directly contacting carbon, so that either silicon or carbon has to diffuse through the SiC layer to sustain the reaction. Since the reaction of carbon with the silicon melt proceeds extremely fast compared to the diffusion in solid, the diffusion of the silicon and/or the carbon is considered to be the rate-limiting step for the whole process.

In the temperature range of 1430° to 1510°C of this study, a considerable concentration of lattice and/or electronic defects could exist in the reaction-formed SiC. Because of the lower electron affinity of the chemisorbed silicon, the silicon would give an electron to the SiC layer with a simultaneous formation of the silicon ion at the Si/SiC interface,

$$\mathrm{Si} \leftrightarrow \mathrm{Si}^+ + \mathrm{e}^\prime$$
 (2*a*)

whereas at the SiC/C interface, carbon would be ionized by obtaining an electron, that is,

$$C + e' \leftrightarrow C^{-} \tag{2b}$$

The ionization to higher degree requires higher energy, so only the ionization to first degree will happen in this case. Since the



Fig. 6. Thickness of the SiC layer as a function of the reaction time for Si–C and Si–C–Mo reactions at 1430°C.

self-diffusion of either silicon or carbon in the β -SiC occurs via a vacancy mechanism,¹⁹ we can rationally assume that the major lattice defects in the β -SiC layer are of Schottky type, that is, the carbon-ion vacancy with the positive charge (z = 1) and silicon-ion vacancy with the negative charge. Because of the much faster self-diffusion of carbon in β -SiC in comparison to silicon,¹⁹ another reasonable assumption is that the growth rate of the SiC layer is controlled by the diffusion of carbon-ion vacancy with electrons so that the electric charge neutrality of the materials can be maintained.

β-SiC has the zinc blende crystal structure and its lattice parameter is equal to 4.387 Å at 1783 K as obtained by means of linear extrapolation.²⁰ From this information, the total number of carbon ions in β-SiC, $N = 4.73 \times 10^{22}$ cm⁻³, is calculated. Since the lattice defects are of Schottky type, the concentration of the carbon-ion vacancy, n_{ve} , can be described by the following equation:²¹

$$n_{\rm vc} = N \exp(-E_{\rm vc}/kT) \tag{3}$$

where $E_{\rm vc}$ is the energy expended in creating a vacancy and is approximately equal to 6 eV.⁸ So we get $n_{\rm vc}^{1783} = 5.38 \times 10^5$ cm⁻³ at T = 1783 K. In addition, the concentration of the intrinsic electrons in the conduction band of β -SiC at 1783 K, $n_e^{1783} = 1.70 \times 10^{18}$ cm⁻³, can also be obtained by linear extrapolation.²² It is obvious that the concentration of electrons in the β -SiC layer is much larger than the carbon-ion vacancy concentration, i.e., $n_e >> zn_{\rm vc}$, which should cause a negative space charge. In the first approximation, we can assume that

$$n_{\rm e} = a z n_{\rm vc} \tag{4}$$

where *a* is a constant and obviously much greater than unity.

Since Si was in a sufficient amount for the reaction, the electron concentration at the phase boundary of Si/SiC is kept constant by the inexhaustible electron supply of the Si phase. According to Eq. (4), the concentration of carbon-ion vacancies at the Si/SiC interface (x = 0), n_{vc}^{0} , should also be constant, i.e.,

$$n_{\rm Vc} = n_{\rm Vc}^0 \qquad (\text{at } x = 0)$$
 (5a)

In addition, the concentrations of the carbon-ion vacancies and electrons should decrease continuously from the Si/SiC interface to the SiC/C interface $(x = \delta)$, since the corresponding chemical equilibrium is assumed at both interfaces. The concentration profile and the flux direction of these defects are shown in Fig. 7. It is similar to the oxidation model by Engell et al.,²³ in which a positive space charge was present instead of a negative space charge in the Si-C reaction. In this oxidation model, the concentration of lattice defects at any instant of oxide growth was found to decrease exponentially in comparison to the concentration of lattice defects at the surface of metal (x = 0).²³ It is reasonable to assume that the carbon-ion vacancies in our case distribute across the space charge layer of SiC in the same manner as in the case of the oxidation described above. Thus, the concentration of carbon-ion vacancies decreases from the Si/SiC interface to the SiC/C interface exponentially. As a consequence, the concentration at the Si/SiC interface is much higher than that at the SiC/C interface, $n_{\rm Vc}^{\delta}$, i.e.,

$$n_{\rm Vc}^0 >> n_{\rm Vc}^\delta \tag{5b}$$

Furthermore, the electric potential should also be independent of the thickness of the SiC layer because a chemical equilibrium is established at both interfaces, which leads to the boundary conditions given below:

$$V^0 = 0$$
 (at $x = 0$) (6*a*)

$$V^{\delta} = 0 \qquad (\text{at } x = \delta) \tag{6b}$$

where V_0 is a constant electric potential at the SiC/C interface with respect to the SiC/Si interface.

The flux of carbon-ion vacancies, j_{vc} , can be written as



Fig. 7. Concentration profiles and diffusion flux of carbon-ion vacancies and electrons.

$$j_{\rm vc} = -D\frac{{\rm d}n_{\rm vc}}{{\rm d}x} - zen_{\rm vc}B\frac{{\rm d}V}{{\rm d}x}$$
(7)

where D and B are the diffusion coefficient and mobility of the carbon-ion vacancies, respectively, x donates the coordinate perpendicular to the original of a carbon sample, and V is the electrical potential across the SiC layer. The flux of electrons can also be described by a similar equation. Both relations have to be combined with the Poisson equation

$$\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} = -\frac{1}{\varepsilon \varepsilon_0} (n_\mathrm{e} - z n_\mathrm{vc}) e \tag{8}$$

where *e* is the elementary charge, ε_0 the permittivity of free space, and ε the dielectric constant of β -SiC.

Substituting Eq. (4) into Eq. (8) and knowing that the value of a is much greater than unity, the Poisson equation can be rewritten as

$$\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} = -\frac{azen_{\mathrm{Vc}}}{\varepsilon\varepsilon_0} \tag{9}$$

As discussed above, the growth rate of the SiC layer is determined by the diffusion of carbon-ion vacancies across the SiC layer. Therefore, we get Eq. (10) for the relationship between the growth rate of the SiC layer and the flux of the carbon-ion vacancies as follows:

$$j_{\rm vc} = n_{\rm vc}^{\delta} \frac{\mathrm{d}\delta}{\mathrm{d}t} \tag{10}$$

We assume that the diffusion of carbon-ion vacancies from the Si/SiC interface to the SiC/C interface is driven predominately by the electric field, i.e.,

$$j_{\rm vc} = -zen_{\rm vc}B\frac{{\rm d}V}{{\rm d}x} \tag{11}$$

and the growth of SiC layer under steady state is

$$\frac{dj_{v_c}}{dx} = 0 \tag{12}$$

Differentiating Eq. (11) and substituting into Eq. (12), we obtain

$$\frac{\mathrm{d}n_{\mathrm{vc}}}{\mathrm{d}x}\frac{\mathrm{d}V}{\mathrm{d}x} + n_{\mathrm{vc}}\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} = 0 \tag{13}$$

Substituting Eqs. (9) and (11) into Eq. (13) yields

$$\frac{\mathrm{d}n_{\mathrm{vc}}}{\mathrm{d}x} = -\frac{\alpha}{2}n_{\mathrm{vc}}^3 \tag{14}$$

where

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$$\alpha = \frac{2a(ze)^2B}{j_{\rm Vc}\epsilon\epsilon_0}$$

Integration of Eq. (14) with the limiting condition (5a) yields

$$n_{\rm Vc} = \frac{1}{\left(\alpha x + (1/n_{\rm Vc}^0)^2\right)^{1/2}}$$
(15)

Substituting Eq. (15) into Eq. (11), we get

$$\frac{\mathrm{d}V}{\mathrm{d}x} = -\frac{j_{\mathrm{vc}}}{zeB} (\alpha x + (1/n_{\mathrm{vc}}^0)^2)^{1/2} \tag{16}$$

Integrating Eq. (16) with the boundary condition (6a), we obtain

$$\beta V = (\alpha x + (1/n_{\rm Vc}^0)^2)^{3/2} - (1/n_{\rm Vc}^0)^3$$
(17)

where

$$\beta = -\frac{3ze}{2j_{\rm Vc}}\alpha B = -\frac{3a(ze)^3B^2}{j_{\rm Vc}^2\epsilon\epsilon_0}$$

Substituting another boundary condition (6b) into Eq. (17), we get

$$\beta V_0 = (\alpha \delta + (1/n_{\rm Vc}^0)^2)^{3/2} - (1/n_{\rm Vc}^0)^3$$
(18)

This equation gives the relationship between the carbon-ion vacancy flux j_{vc} and other parameters such as the concentration n_{vc}^{0} , the mobility *B*, and the potential V_{0} .

Substituting $x = \delta$ into Eq. (15), Eq. (15) can be rewritten as follows:

$$(\alpha\delta)^{-1/2} = \frac{n_{\rm Vc}^0}{\sqrt{(n_{\rm Vc}^0)^2 - (n_{\rm Vc}^\delta)^2}} n_{\rm Vc}^\delta$$
(19)

Since $n_{\rm Vc}^0 >> n_{\rm Vc}^\delta$, Eq. (19) can be simplified to

 $(\alpha\delta)^{-1/2} \approx n_{\rm Vc}^{\delta}$

and then we have

$$n_{\rm Vc}^0 >> (\alpha \delta)^{-1/2} \tag{20}$$

Equation (20) is equivalent to the relation

 $\alpha \delta >> (1/n_{\rm Vc}^0)^2$

Therefore, Eq. (18) is modified to

$$\beta V_0 = (\alpha \delta)^{3/2} \tag{21}$$

Substitution of α and β into Eq. (21) yields

$$j_{v_c} = \frac{9\varepsilon\varepsilon_0 BV_0^2}{8a} \cdot \frac{1}{\delta^3}$$
(22)

Finally, by substitution of the relationship between the flux j_{ve} and the growth rate $d\delta/dt$ given by Eq. (10), the fourth-power rate law in the form of differential equation is obtained as follows:

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = \frac{k_0}{4} \frac{1}{\delta^3} \tag{23}$$

where

$$k_0 = \frac{9}{2} \frac{V_0^2}{a n_{\rm vc}(\delta)} B \varepsilon \varepsilon_0 \tag{24}$$

which is in a good agreement with the results of regression analysis of the experimental data.

In order to make direct comparison of this model with experimental data, we integrate Eq. (23) with $\delta = 0$ when t = 0and get

$$\delta^4 = k_0 t \tag{25}$$

$$\delta = k_0^{-1/4} t^{1/4} \tag{26}$$

With the aid of the Nernst-Einstein equation, $D = Bk_BT (k_B \text{ is Boltzmann's constant)}$ and Eq. (4), we can obtain an equation for calculating the variation of thickness of SiC with reaction time as follows:

. . .

$$\delta = \left(\frac{9}{2} \frac{\varepsilon \varepsilon_0 z V_0^2 D}{k_{\rm B} T} \frac{D}{n_{\rm e}^{\delta}}\right)^{1/4} t^{1/4}$$
(27)

where n_e^{δ} is the electron concentration at the SiC/C interface. At $T = 1510^{\circ}$ C, V_0 is equal to -2.02 V (see Appendix), and boundary diffusion coefficient of carbon can be calculated by extrapolating data from the published literature,⁸ i.e., $D_{\rm bc} \approx$ 1.43×10^{-9} cm²/s. Since the electron concentration at the SiC/ C interface is unknown, we use the equilibrium concentration of electrons in the SiC layer, i.e., $n_{\rm e}^{1783} = 1.70 \times 10^{18} \,{\rm cm}^{-3}$, instead of n_e^{δ} to calculate the thickness of SiC at different reaction times. This calculated thickness of SiC layer, as a function of reaction time, is plotted in Fig. 8 together with the corresponding experimental data and best fit to the fourthpower rate law. The calculated curve using Eq. (27) is much below the experimental values. However, if we multiply this calculated curve by 4 and replot the curve, it becomes amazingly close to the experimental curve at 1510°C. This discrepancy by a factor of 4 can be attributed to the use of the equilibrium concentration in calculating the theoretical curve, which will underestimate the thickness values because the equilibrium concentration should be higher than the concentration at the SiC/C interface.

IV. Conclusions

(1) The morphology of the reaction-formed β -SiC may depend upon the nature of carbon precursor used in the kinetics study. A continuous reaction-formed β -SiC is observed in this study when a glassy carbon is reacted with liquid silicon. In contrast, graphite precursors displayed the physical penetration and are not suitable for the reaction kinetics study.

(2) The products of the reaction of a pure Si melt with glassy carbon are composed of a continuous β -SiC layer and β -SiC precipitates dispersed in the silicon phase. For the reaction of a Si + Mo melt with glassy carbon, in addition to the β -SiC layer and β -SiC precipitates present in the microstructure, a MoSi₂ phase exists either adjacent to the SiC/Si interface or dispersed in the silicon phase.

(3) The growth rate of the continuous SiC layer obeys a fourth-power rate law for the reaction of glassy carbon with either a pure Si melt or a Mo-alloyed Si melt. A model which can explain the experimentally observed rate law is proposed, in which a negative space charge is assumed to exist in the



Fig. 8. Comparison of the theoretical curve with experimental data of Si–C reaction at 1510°C.

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growing SiC layer. The diffusion of the carbon-ion vacancy through this layer under an electric field is proposed as the ratelimiting step for the growth of the SiC layer.

There are no appreciable effects, on either the reaction (4)kinetics or the morphology of the reaction products, of an increase in the temperature from 1430° to 1510°C or of the addition of 10 wt% Mo into the pure Si melt.

APPENDIX

Electrical Potential Difference across the Reaction-Formed SiC Layer

As described in this model, during the immersion of a glassy carbon sample in a silicon melt at high temperatures, the silicon next to the Si/SiC interface would be ionized by losing an electron, owing to its relatively low electronegativity in comparison to carbon.

$$Si \leftrightarrow Si^+ + e'$$
 (A-1)

Meanwhile, carbon would get the electron forming a negatively charged carbon ion at the C/SiC interface.

$$C + e' \leftrightarrow C^-$$
 (A-2)

In general, the whole reaction can be written as follows by an addition of Eq. (A-1) and Eq. (A-2):

$$Si + C \leftrightarrow Si^+ + C^- (=SiC)$$
 (A-3)

The carbon ion will diffuse across the SiC layer through a vacancy-diffusion mechanism, contacting the silicon melt and reacting with silicon melt to form SiC.

The Gibbs free energy change for reaction (A-3), $\Delta G_{\rm T}$, is calculated as

$$\Delta G_{\rm T} = \Delta G_{\rm T}^{\circ} + RT \ln \frac{a_{\rm Si} a_{\rm C}}{a_{\rm Si} a_{\rm C}} \tag{A-4}$$

where $\Delta G_{\rm T}^{\circ}$ is the standard Gibbs free energy change for reaction (A-3) at temperature T, and a_{Si^+} , a_{Si} , a_{C^-} , and a_C are the activities of silicon ions, silicon, carbon ions, and carbon, respectively. The $\Delta G_{\rm T}^{\circ}$ is given by

$$\Delta G_{\rm T}^{\circ} = \Delta G_{\rm SiC}^{\circ} - \Delta G_{\rm Si}^{\circ} - \Delta G_{\rm C}^{\circ} \tag{A-5}$$

where $\Delta G_{\rm sic}^{\circ}$, $\Delta G_{\rm si}^{\circ}$, and $\Delta G_{\rm c}^{\circ}$ are the standard Gibbs free energy changes for SiC, Si, and C at temperature T, respectively, and their values can be obtained from the literature.²⁴ At T = 1783K, $\Delta G_{1783}^{\circ} = 56455$ J/mol.

Since the solubility of carbon in silicon melt is very small, we can consider the silicon melt next to SiC layer as a dilute solution. Therefore,

$$a_{\mathrm{C}^-} = X_{\mathrm{C}^-} \tag{A-6a}$$

$$a_{\rm Si^+} = X_{\rm Si^+} = 1 - X_{\rm C^-} \approx 1 \tag{A-6b}$$

where X_{Si^+} and X_{C^-} are the molar fraction of silicon and carbon in silicon melt near the SiC layer. Since the activity of elemental substance is equal to unity,

$$\begin{aligned} a_{\rm si} &= 1\\ a_{\rm c} &= 1 \end{aligned} \tag{A-6c}$$

The electromotive force, V, produced by reaction (A-3) is related to the Gibbs free energy change for this reaction by

$$\Delta G_{\rm T} = z \mathcal{F} V \tag{A-7}$$

where \mathcal{F} is Faraday's constant (=96487 C/mol), and z is the number of moles of electrons transported during the electrochemical reaction, in this case, z = 1.

Substituting Eqs. (A-7) and (A-6) into Eq. (A-4), we get

$$V = -\frac{1}{2\mathscr{F}} [\Delta G_{\rm T}^0 + RT \ln (X_{\rm Si} + X_{\rm C}^-)]$$
 (A-8)

Under the assumption that X_{C^-} is equal to the solubility of carbon in silicon that is equal to 10^{-4} g/cm³, $^{9}V = 2.02$ V.

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