Kinetics of Dissolution of SiO Gas in Liquid Fe–C Alloys

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The dissolution rate of SiO gas in liquid iron (Fe-2 wt% C and Fe-4 wt% C alloys) was investigated at 1 843, 1 868, and 1 893 K. SiO gas was generated from a silica-graphite particle mixture, and then, it was introduced onto the surface of liquid iron through an alumina lance with CO carrier gas. The effect of gas-phase mass transfer on the dissolution rate of SiO gas was minimized by adjusting the CO gas flow rate. The rate of silicon transfer remained almost constant regardless of the initial carbon content in liquid iron, whereas it increased with increasing temperature. From the experimental results, it was concluded that the adsorption of SiO gas onto the surface of liquid iron was the rate-determining step.

KEY WORDS: hot metal; ironmaking process; rate-determining step; SiO gas; Si transfer.

1. Introduction

Silicon is one of the most important constituents in the hot metal. In the steel-making process silicon in hot metal increases the converter temperature by the exothermic reaction with oxygen. Therefore, the amount of scrap used in BOF process depends on Si content in hot metal. However, excessive silicon content may decrease the dephosphorization rate due to its stronger affinity to oxygen rather than phosphorus.1,2) In addition, the high level of silicon of the hot metal may increase the running cost due to increased slag volume and lime consumption, as well as the accelerated chemical attack of the refractory lining in the converter.3–5) Therefore, control of the silicon content in the hot metal is essential to optimize the steelmaking process.

In iron-making process, silicon is charged into blast furnace in the form of ash of coke and gangue of sinter, and it is transferred in various ways through metal-slag, gas-liquid and gas-solid reactions. Silicon in the hot metal is originated from the SiO2 in the slag or in the coke’s ash.6–9) Many researchers reported that silicon transfer to the hot metal is occurred via SiO gas.5–10) SiO gas can also react with solid carbon in coke, which forms SiC on the coke surface and the corresponding reduces contact angle between slag and coke.11) Change in the contact angle between slag and coke may affect the slag hold-up in the lower part of blast furnace.12) It is therefore expected to affect the dissolution of solid ash layer, which suppress the carburization of solid iron, at the coke surface.13) The dissolution of silicon in the hot metal via SiO gas may happen by Eq. (1).

\[
\text{SiO}_2(g) + [C] = [Si] + CO(g) \quad \text{................................(1)}
\]

where \([C]\) and \([Si]\) are carbon and silicon in liquid iron.

Here, possible elementary reaction steps are
(a) gas phase mass transfer of SiO gas to the metal surface
(b) adsorption of SiO on the metal surface
(c) chemical reaction between adsorbed SiO and \([C]\)
(d) desorption of CO from the metal surface
(e) gas phase mass transfer of CO gas away from the metal surface

Tsuchiya et al.9) and Ozturk and Fruehan18) investigated the dissolution rate of SiO in carbon-saturated liquid iron. These results are summarized in Fig. 1. Tsuchiya et al. found that the reaction rate gradually increased with increasing temperature for carbon-saturated iron, while it did not change so much with increasing temperature for 2.78 wt% C alloy and pure iron. They concluded that the chemical reac-

\[
\begin{align*}
\text{Temperature (K)} & \quad 1600 & \quad 1700 & \quad 1800 & \quad 1900 & \quad 2000 \\
\text{Rate constant } (\text{mol/cm}^2\cdot\text{s atm}) & \quad 0 & \quad 1 & \quad 2 & \quad 3 & \quad 4 \\
\text{Data} & \quad □ \quad \text{Tsuchiya et al.9)} \quad C_{\text{ini}}=0 \text{ wt%} & \quad ○ \quad \text{Tsuchiya et al.9)} \quad (C_{\text{ini}}=2.78 \text{ wt%}) & \quad △ \quad \text{Tsuchiya et al.9)} \quad (C_{\text{sat}}) & \quad ▽ \quad \text{Ozturk and Fruehan18)} \quad (C_{\text{sat}})
\end{align*}
\]

Fig. 1. Variation of overall rate constant at different initial carbon content with temperature \([□ \quad \text{Tsuchiya et al.9)} \quad C_{\text{ini}}=0 \text{ wt%}) \quad ○ \quad \text{Tsuchiya et al.9)} \quad (C_{\text{ini}}=2.78 \text{ wt%}) \quad △ \quad \text{Tsuchiya et al.9)} \quad (C_{\text{sat}}) \quad ▽ \quad \text{Ozturk and Fruehan18)} \quad (C_{\text{sat}})].
tion between adsorbed SiO gas and carbon on the surface of liquid Fe–C alloy was one of the rate-limiting steps. On the other hand, Ozturk and Fruehan investigated much lower reaction rates than Tsuchiya et al. for carbon-saturated iron, and furthermore the reaction rate did not change with increasing temperature. They concluded that the gas phase mass transfer of SiO to the metal surface is the rate-limiting step. Disagreements between the reported data encouraged us to re-examine the dissolution rate of SiO in liquid Fe–C alloy. In this study, the dissolution rate of SiO was investigated with an improved experimental setup, which enabled us to evaluate the individual elementary reaction steps. The principal variables are initial carbon content and temperature. Based on the experimental data, the reaction mechanism is discussed.

2. Experimental

2.1. Experimental Apparatus

Figure 2 shows a schematic illustration of the experimental apparatus. A vertical-type electric resistance furnace equipped with a mullite reaction tube (inner diameter (ID): 90 mm, length: 900 mm) was used. In the center of the reaction tube, a specially designed graphite assembly was placed to investigate the SiO dissolution rate in liquid Fe–C alloy. This graphite assembly is composed of two parts: the upper part (a graphite crucible) contains a silica-graphite powder mixture (12 g of fused silica particles (99.5% purity, Boram Chemetal, 0.2–0.4 mm diameter) and 4.8 g of graphite particles (99.98% purity, SGL Carbon, 0.2–0.5 mm diameter)). The silica-graphite particle mixture was placed between 40 g of graphite granules of 1–2 mm in diameter. A graphite cover was tightly sealed the crucible with alumina cement and CO gas was supplied through an alumina lance (4 mm ID) that was inserted through the graphite cover. CO gas (99.995% purity) was purified by being passed through silica gel, magnesium perchlorate, and ascarite in series. At the bottom of this crucible, six holes (0.5 mm diameter for each) were drilled, which allowed the stream of the CO–SiO gas mixture to flow down to an empty buffer room. A alumina lance (4 mm ID) was fitted at the bottom of this room, allowing gas-flow downward onto the metal surface. The lower part of the graphite assembly provided enough space for the placement of an alumina crucible (99.5% purity, 25 mm ID, 30 mm height) holding 30 g of Fe–C alloy. The distance between the end of the alumina lance and the surface of the Fe–C alloy was set as 3 mm. Ar gas (99.9999% purity, further purified by being passed through silica gel and magnesium perchlorate in series) atmosphere was maintained in the reaction tube to prevent oxidation of the graphite assembly.

2.2. Experimental Procedure

Once the graphite assembly was placed in the mullite reaction tube, it was heated at a heating rate of +10 K/min in Ar atmosphere. During the experiments, the temperature of the furnace was monitored using a B-type thermocouple (Pt-6%Rh/Pt-30%Rh) and controlled using a proportional-integral-derivative (PID) controller. The thermocouple was placed outside of the reaction tube, and the temperature of the sample was calibrated in advance by measuring the temperature at the sample position with another B-type thermocouple. Once a target temperature was reached, CO gas was introduced into the graphite crucible from the top through the alumina lance. The CO–SiO gas mixture was then introduced onto the liquid Fe–C alloy surface. After the sample was held for a pre-determined time, the CO gas flow was stopped and the furnace was cooled down to room temperature by shutting its power off. After the experiments, the silicon content of the Fe–C alloys was analyzed using an inductively coupled plasma spectrometer (Shimadzu, ICP E-9000). The carbon content was analyzed using a carbon/sulfur analyzer (LECO-C/S, CS230). In the present study, the experimental temperatures were set as 1 843, 1 868, and 1 893 K, and the initial carbon contents of the Fe–C alloys were set as 2 and 4 wt%.

3. Results

3.1. Effect of Gas Flow Rate

Figure 3 shows typical X-ray diffraction (XRD) analysis results of the silica-graphite mixture after experiments. The main peaks represent SiO$_2$ and graphite, and no SiC peak was observed. Therefore, it is considered that the weight

![Fig. 2. Schematic of experimental apparatus.](image)

![Fig. 3. XRD pattern of SiO$_2$–C mixture after experiment.](image)
loss of the silica-graphite mixture in this study was due to the SiO gas generation. The CO gas flow rate was varied from 100–1 000 ml/min STP. Figure 4 shows the weight loss of the silica-graphite mixture as a function of the reaction time. Since the weight of the silica-graphite mixture decreased linearly for 60 min, it was considered that the SiO gas generation rate was kept constant. The partial pressure of SiO gas was then calculated from the weight change of the silica-graphite mixture and the CO gas flow rate. Table 1 summarizes the calculated partial pressures of SiO gas in each experimental condition.

If the gas phase mass transfer of SiO to the metal surface is the rate-limiting step, the reaction rate can be expressed by Eq. (2):

\[ \nu = \frac{dN_S}{dt} = \frac{k_e}{RT}A(P_{SiO} - P_{SiO}^e) \]  

where \( \nu \) is the reaction rate (mol/s), \( N_S \) is the number of moles of silicon in iron, \( k_e \) is the gas phase mass transfer coefficient, \( R \) is the gas constant, and \( A \) is the reaction area. \( P_{SiO}^e \) is the equilibrium SiO pressure on the metal surface. \(^1\) The equilibrium constant of the reaction (1) is expressed by Eq. (3).

\[ K_i = \frac{a_S P_{CO}^e}{a_C P_{SiO}^e} \]

where \( a_S \) and \( a_C \) are the activities of silicon and carbon in the 1 wt% standard state, respectively. Here, the Gibbs free energy of the reaction (1) is given by Eq. (4). \(^1^9\)

\[ \Delta G^\circ = -113 926 - 8.25T(J / mol) \]  

In the present experimental condition, equilibrium partial pressure of SiO gas, \( P_{SiO}^e \), was in the range of 1.05–3.37 \times 10^{-2} \text{ atm at } 1 893 \text{ K}. Here, \( a_S/a_C \) value was calculated from the experimental results, and obtained in the range of 3.93–12.7 \times 10^{-2}. Details will be discussed in the section 4.2.3. \( P_{SiO}^e \) was negligibly small. Figure 5 shows a plot of the rate constant as a function of the gas flow rate with the sample containing 4 wt%C at 1 893 K. The rate constant increases with an increase in the gas flow rate up to 500 ml/min STP, and becomes almost constant as the gas flow rate increases further. In the present experimental geometry, the gas phase mass transfer coefficient can be calculated using the non-dimensional equation proposed by Saito et al. \(^2^0\)

\[ Sh = \frac{m(r_e/d)^{-1}}{Re^{0.87} Sc^{0.16}} \text{ (m = 0.56 ± 0.06)} \]

where \( Sh \) is Sherwood number \( (= k_d D_{SiO-CO}) \), \( Re \) is Reynolds number \( (= d U p_C/\mu_C) \), \( Sc \) is Schmidt number \( (= \mu_C/\rho_C D_{SiO-CO}) \), \( d \) is the diameter of the alumina lance (m), \( r_e \) is the radius of alumina crucible (m), \( D_{SiO-CO} \) is diffusion coefficient of the SiO–CO gas mixture \( (m^2/s) \), \( U \) is the gas velocity near the outlet of the alumina lance at the experimental temperature \( (m/s) \), \( p_C \) is the density of the SiO–CO gas mixture \( (kg/m^3) \), and \( \mu_C \) is the viscosity of the SiO–CO gas mixture \( (Pa/s) \). Calculation of diffusion coefficient and density of the SiO–CO gas mixture is provided in Appendix.

### Table 1

| CO gas flow rate (ml/min) | \( P_{SiO} \) (atm) |
|--------------------------|------------------|
| 100                      | 0.00372          |
| 400                      | 0.00279          |
| 500                      | 0.00304          |
| 700                      | 0.00357          |
| 1 000                    | 0.00507          |

Figure 4. Variation of weight loss of silica-carbon particle mixture with time for different CO gas flow rates at 1 893 K.

Figure 5. Variation of overall reaction rate constant \( (k_f') \) as a function of CO gas flow rate at 1 893 K.
4. Discussion

4.1. Liquid Phase Mass Transfer in Fe–C Alloy

When the liquid phase mass transfer of Si in liquid Fe–C alloy is a rate-limiting step, liquid phase mass transfer coefficient can be calculated by Eq. (6)

\[ \ln \left( \frac{C_e}{C_t} \right) = -k_{Si(l)} \frac{A}{V} t \] ........................ (6)

Where \( C_e \), \( C_t \), \( C_o \), \( k_{Si(l)} \), \( A \), and \( V \) represent equilibrium Si content in liquid Fe–C alloy (wt%), Si content at time \( t \) (wt%), initial Si content (wt%), liquid phase mass transfer coefficient (m/s), reaction area (m\(^2\)), and volume of liquid Fe–C alloy (m\(^3\)), respectively. In order to obtain \( k_{Si(l)} \), equilibrium Si content should be known. It can be calculated by using Eq. (7).

\[ \Delta G^o = -RT \ln \frac{a_c P_{CO}}{a_S P_{SiO}} \] ........................ (7)

By substituting \( \Delta G^o \), which can be calculated using Eq. (3), \( P_{SiO} \) and \( P_{CO} \) into Eq. (7), the ratio of activity of carbon to that of silicon (\( a_c/a_S \)) can be obtained. Accordingly, the equilibrium Si content at the carbon content of 2 wt% and 4 wt% can be calculated. Calculation of activity of Si and carbon will be discussed in section 4.2.2. The equilibrium Si content is estimated to be about 15 and 24 wt% for Fe-2 wt% C and Fe-4 wt% C alloys, respectively. The calculated liquid phase mass transfer coefficients \( (k_{Si(l)}) \) from Eq. (7) are summarized in Table 2.

On the other hand, theoretical liquid phase mass transfer coefficient of Si in liquid iron can be also calculated by Eq. (8)

\[ k_{Si(l)} = \frac{D}{\delta} \] ........................ (8)

Where \( D \) is the silicon diffusivity coefficient in the liquid Fe–C alloy (m\(^2\)/s), and \( \delta \) is the thickness of the boundary layer (m). By substituting the Si diffusivity coefficient (\( 1.0 \times 10^{-8} \) m\(^2\)/s at 1 823 K),\(^{21}\) in Fe–C sat. and liquid the Fe–C alloy height (\( 9.0 \times 10^{-3} \) m) into the Eq. (8), the theoretical liquid phase mass transfer coefficient of silicon can be estimated to be \( 1.1 \times 10^{-6} \) m/s. This value would be the slowest mass transfer coefficient. However, since experimentally obtained liquid phase mass transfer coefficient is much smaller, liquid phase mass transfer of silicon is not a rate-limiting step.

4.2. Rate-Limiting Step

As the gas phase mass transfer or the liquid phase mass transfer is not a rate-limiting step, elementary reaction steps can be expressed by Eqs. (9)–(13).

\[ \text{SiO(g) vac} \rightarrow \text{SiO(ad)} \] ........................ (9)
\[ \text{C(g) vac} \rightarrow \text{C(ad)} \] ........................ (10)
\[ \text{SiO(ad) + C(ad)} \rightarrow \text{Si(ad) + CO(ad)} \] ........................ (11)
\[ \text{Si(ad)} \rightarrow [\text{Si}] \rightarrow \text{vac} \] ........................ (12)
\[ \text{CO(g) vac} \rightarrow \text{CO(ad)} \] ........................ (13)

where \( \text{SiO(ad)} \), \( \text{CO(ad)} \), \( \text{Si(ad)} \), \( \text{C(ad)} \), and vac. denote the SiO adsorbed, the CO adsorbed, the Si adsorbed, the C adsorbed and the vacant sites on the liquid iron surface, respectively. The equilibrium constant for each reaction are expressed by Eqs. (14)–(18), respectively.

\[ K_{SiO} = \frac{P_{SiO}}{P_{SiO} \cdot (1 - \Sigma \theta)} \] ........................ (14)
\[ K_{CO} = \frac{\theta_c}{\theta_c \cdot (1 - \Sigma \theta)} \] ........................ (15)
\[ K_{11} = \frac{\theta_{SiO} \theta_{CO}}{\theta_{SiO} \theta_{C}} \] ........................ (16)

Table 2. Calculated liquid phase mass transfer coefficient for Fe-2 wt% C and Fe-4 wt% C alloys.

| Temperature | \( k_{Si(l)} \) Fe-2 wt% C | \( k_{Si(l)} \) Fe-4 wt% C |
|-------------|-----------------------------|-----------------------------|
| 1 843       | \( 7.79 \times 10^{-8} \) m/s | \( 3.74 \times 10^{-8} \) m/s |
| 1 868       | \( 9.97 \times 10^{-8} \) m/s | \( 6.21 \times 10^{-8} \) m/s |
| 1 893       | \( 1.26 \times 10^{-7} \) m/s | \( 8.85 \times 10^{-8} \) m/s |
where \( \theta \) is the fractional coverage by species \( i \) on the surface of liquid iron. Possible rate-limiting steps are examined in the following sections.

4.2.1. Adsorption of SiO on the Liquid Iron Surface

If we assume that the adsorption of SiO on the surface of liquid iron is the rate-limiting step, the reaction rate can be expressed by Eq. (19):

\[
\nu = \frac{dN_{SiO}}{dt} = k_f A P_{SiO} (1-\Sigma \theta) \quad \text{..... (19)}
\]

The fraction of vacant site can be expressed by Eq. (20) and the fractional coverage of SiO can be expressed by Eq. (21).

\[
1 - \Sigma \theta = \frac{1}{1 + a_c K_{10} + \frac{a_{Si}}{K_{12}} + \frac{P_{CO}}{K_{13}} + \frac{a_{Si} P_{CO}}{a_c K_{10} K_{12} K_{13}}} \quad \text{..... (20)}
\]

\[
\theta_{SiO} = \frac{a_{Si} P_{CO} (1-\Sigma \theta)}{a_c K_{10} K_{12} K_{13}} \quad \text{..... (21)}
\]

By substituting Eqs. (20) and (21) into Eq. (19), we can obtain Eq. (22)

\[
\nu = k_f A P_{SiO} \left( \frac{1}{1 + a_c K_{10} + \frac{a_{Si}}{K_{12}} + \frac{P_{CO}}{K_{13}} + \frac{a_{Si} P_{CO}}{a_c K_{10} K_{12} K_{13}}} \right) - k_a A \left( \frac{a_{Si} P_{CO} (1-\Sigma \theta)}{a_c K_{10} K_{12} K_{13}} \right) \quad \text{..... (22)}
\]

the backward reaction rate in Eq. (22) can be determined by the partial pressure of CO gas and the ratio of activity of silicon to that of carbon \( (a_{Si}/a_c) \). According to Tsuchiya et al., when the partial pressure of CO gas changed from 0.5 to 1 atm, SiO gas dissolution rate was slightly changed from \( 3.2 \times 10^{-2} \) to \( 3.40 \times 10^{-2} \) \%/min) at 1 843 K.\(^9\) The activity ratio between silicon and carbon was found to be almost constant through the reaction time, and details are given in the section 4.2.3. Based on these results, it is considered that the effect of backward reaction is ignorable. Therefore, Eq. (22) can be simplified to Eq. (23)

\[
\nu = k'_f A P_{SiO} \quad \text{..... (23)}
\]

\[
k'_f = k_f \left( \frac{1}{1 + a_c K_{10} + \frac{a_{Si}}{K_{12}} + \frac{P_{CO}}{K_{13}} + \frac{a_{Si} P_{CO}}{a_c K_{10} K_{12} K_{13}}} \right) \quad \text{..... (23)}
\]

At a fixed temperature, \( k'_f \) (apparent rate constant), \( A \), and \( P_{SiO} \) are constants. Therefore, the reaction rate \( \nu \) would be kept constant during the experiments. Figure 7 shows that the reaction rate remains constant over time. Therefore, the adsorption of SiO on the liquid iron surface is considered as one of the rate-limiting steps.

4.2.2. Dissolution of SiO in Liquid Iron

If the dissociation of SiO on the liquid iron surface is the rate-limiting step, the reaction rate can be described by Eq. (24).

\[
\nu = \frac{dN_{SiO}}{dt} = k_f A \theta_{SiO} \theta_C - k_a A \theta_{SiO} \quad \text{..... (24)}
\]

By substituting Eqs. (14), (15), (17) and (18) into Eq. (24), we can obtain

\[
\nu = \frac{dN_{SiO}}{dt} = k_f A K_{10} (1-\Sigma \theta)^2 P_{SiO} a_c - k_a A a_{Si} P_{CO} (1-\Sigma \theta)^2 \quad \text{..... (25)}
\]

For the same reasons as described in the section 4.2.1, we may ignore the backward reaction, and Eq. (25) can be simplified to Eq. (26).

\[
\nu = k_f A K_{10} (1-\Sigma \theta)^2 P_{SiO} a_c \quad \text{..... (26)}
\]

Since \( k_f, A, K_{10}, 1-\Sigma \theta \) and \( P_{SiO} \) are constants during the experiments, it is considered that the reaction rate would simply be proportional to the activity of carbon in liquid iron. Here, the activity of carbon is calculated according to Eqs. (27) and (28):

\[
a_c = f_c [%C] \quad \text{..... (27)}
\]

\[
\log f_c = e_i [%C] + e_j [%Si] \quad \text{..... (28)}
\]

where \( f_i \) is the activity coefficient of species \( i \) and \( e_i \) is the interaction parameter between \( i \) and \( j \) in liquid iron. The interaction parameters were obtained from Refs. (22) and (23).

Figure 8 shows the variation of the reaction rate with the activity of carbon. It is shown that reaction rate does not proportional to the activity of carbon. Consequently, the dissociation of SiO on the liquid iron surface would not be a rate-limiting step.
4.2.3. Desorption of CO

If the desorption of CO gas from the liquid iron surface is the rate-limiting step, the reaction rate can be described by Eq. (29).

$$ \frac{dN}{dt} = k_f A \theta_{CO} - k_a A (1 - \Sigma \theta) P_{SiO} \quad \text{(29)} $$

The backward reaction can also be ignored as described in the section 4.2.1. Here, $\theta_{CO}$ can be expressed by Eq. (30).

$$ \theta_{CO} = K_9 K_{10} K_{11} K_{12} \frac{a_C}{a_S} (1 - \Sigma \theta) P_{SiO} \quad \text{(30)} $$

By substituting Eq. (30) into Eq. (29), Eq. (31) is obtained.

$$ v = k_f A K_9 K_{10} K_{11} K_{12} \frac{a_C}{a_S} (1 - \Sigma \theta) P_{SiO} \quad \text{(31)} $$

Since $k_f$, $A$, $K_9$, $K_{10}$, $K_{11}$, $K_{12}$ and $P_{SiO}$ are constants, the reaction rate would be proportional to the ratio of activity of carbon to that of silicon ($a_C/a_S$). Figure 9 shows the variation of the reaction rate with respect to the $a_C/a_S$ ratio. It is shown that reaction rate does not proportional to the $a_C/a_S$ ratio. Accordingly, the desorption of CO from the liquid iron surface would not be a rate-limiting step. Through discussion above, it is concluded that the adsorption of SiO gas onto the liquid iron is the rate-limiting step.

4.3. Temperature Dependence

Figure 10 shows the variation of the natural logarithm of the apparent rate constant with reciprocal of absolute temperature. The temperature dependences of the rate constant for Fe-2 wt%C and Fe-4 wt%C alloys are expressed by Eqs. (32) and (33), respectively.

$$ \ln k'(mol/cm^2/s/atm) = -0.3 - \frac{16350}{T} \quad \text{(2 wt% C)} \ldots \text{(32)} $$

$$ \ln k'(mol/cm^2/s/atm) = 9.3 - \frac{4110}{T} \quad \text{(4 wt% C)} \ldots \text{(33)} $$

From Eqs. (32) and (33), the apparent activation energy for the dissolution of SiO gas in liquid iron is estimated to be 135.9 and 286.1 kJ/mol for Fe-2 wt%C and Fe-4 wt%C alloys, respectively. The above equations are applicable until the carbon content in liquid Fe–C alloy is varied by 0.4 wt%. For comparison, the reported data by Tsuchiya et al. are plotted in Fig. 10 together. The absolute values of Tsuchiya et al. are much higher than the present results. The apparent activation energy for carbon-saturated iron was 237.1 kJ/mol, which is close to the present results with Fe-4 wt%C alloys. However, there is no temperature dependence when the initial carbon content was 2.78 wt% in the experiments of Tsuchiya et al. As investigated in the present work, the apparent activation energy might decrease with decreasing the initial carbon content. The change of the apparent activation energy might be related to the temperature dependence of $K_{10}$, $K_{11}$, $K_{12}$, and $K_{13}$. 
5. Conclusions

The silicon content control in the hot metal is a state-of-the-art process. For better understanding of the elementary reaction rates, the dissolution rate of SiO gas in liquid iron was investigated at 1 843, 1 868, and 1 893 K. The SiO gas was generated from the reaction between silica and graphite particles. The partial pressure of SiO gas was estimated from the weight change of the silica-graphite mixture and the CO carrier gas flow rate. The dissolution rate of SiO gas in liquid Fe–C alloys increased with increasing temperature. The apparent activation energy for Fe-2 wt%C and Fe-4 wt%C alloys was 135.9 and 286.1 kJ/mol, respectively. From a systematic consideration of the reaction mechanism, it was concluded that the adsorption of SiO gas onto the liquid iron surface was the rate-limiting step.

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Appendix

The inter-diffusivity of gas mixture can be estimated theoretically by Eq. (A-1),

\[ D_{AB} = 1.858 \times 10^{-7} T^{1/2} \left[ \frac{(M_A + M_B)}{M_A M_B} \right]^{1/2} \rho \frac{\sigma_{AB}^2}{\Omega_b} \]  \hspace{1cm} (A-1)

where \( \sigma_{AB} \) is the characteristic length (Å), \( M_i \) is a molecular weight of \( i \)-th component (g/mol), \( \rho \) is pressure (atm), \( \Omega_b \) is a collision integral for diffusivity \( = \kappa T / \epsilon \), \( \kappa \) is the Boltzmann constant, \( \epsilon \) is the maximum attractive energy between two molecules, and \( T \) is the absolute temperature. Since force constant \( (\kappa \epsilon / \sigma) \) for SiO gas does not exist, that the value for CO \(_2\) gas, whose molecular weight is similar to SiO gas, was used.\(^{10}\) Consequently, according to the Eq. (A-1), inter-diffusivity constant for SiO–CO gas was calculated as \( 3.58 \times 10^{-4} \) m\(^2\)/s at 1 893 K. The viscosity of a gas mixture can be calculated by using equation proposed by Wilke.\(^{21}\) The viscosity of a single component gas can be calculated by Eq. (A-2).

\[ \mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_b} \]  \hspace{1cm} (A-2)

where \( \Omega_b \) is a collision integral for viscosity \( = \kappa T / \epsilon \). The viscosity of CO and SiO were calculated to be \( 6.23 \times 10^{-4} \) and \( 5.85 \times 10^{-4} \) g/cm·sec at 1 893 K, respectively. Here, the viscosity of SiO gas was calculated by using the CO\(_2\) information. Then, the viscosity of gas mixture of SiO and CO was calculated by Eq. (A-3).\(^{22}\)

\[ \mu_{mix} = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{1}{\sum_{i=1}^{n} \Phi_i}} \]  \hspace{1cm} (A-3)

Here, \( \Phi_i \) is

\[ \Phi_i = \left[ \frac{1}{\sqrt{1 + M_i / M_j}} \right] \left[ 1 + \frac{1}{\mu_i / \mu_j} \left( \frac{M_i}{M_j} \right) \right] \]  \hspace{1cm} (A-4)

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