Mechanism of Oxidation of Si in Molten Cu by FeO in Slag*

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An experimental study has been made on the mechanism of mass-transfer between molten Cu–Si alloy and Li2O–SiO2–Al2O3–FeO slag at 1523 K. The explored reaction was the oxidation of silicon by FeO in slag taking place under the condition of rate-controlling by transport of silicon in the metal phase. The rate data were examined on the basis of the theory on simultaneous diffusion and chemical reaction in the liquid phase.

It is presumed that the zone of reaction between Si and O is located within the metal-side boundary layer. The location of the zone is supposedly controlled by mass-transfer fluxes of O from the slag-metal interface to the reaction zone and Si from the bulk metal to the zone. When the initial concentration of Si is high (≥0.08 mass%), the reaction zone is located in the vicinity of the slag-metal interface, until Si concentration is lowered considerably. In this case, the apparent mass-transfer coefficient of Si, $k_{app}$, is constant. When the initial concentration of Si is low (≤0.02 mass%), the reaction zone moves away from the interface during the reaction so that the distance through which Si is diffusing decreases, resulting in the increase in the mass transfer coefficient.

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I. Introduction

In a previous study, the authors investigated the rate-controlling mechanism of Si oxidation reaction between molten slag containing FeO and molten Cu–Si alloy for the purpose of establishing a suitable model system for kinetic studies on slag-metal reactions at high temperature(1). In the course of this previous study, a tendency for the apparent mass-transfer coefficient in the metal phase to increase with lowering of Si concentration in the metal was observed. In the present study, details of this phenomenon in the mass transfer of silicon is examined. Kinetic experiments are made on the Si oxidation reaction by FeO in slag with variation of concentrations of reactants, that are FeO in slag and silicon in metal. The result is explained by a reaction model which is based on the theory on simultaneous diffusion and chemical reaction in the liquid phase(13).

II. Experimental

The experimental apparatus was similar to that described previously(1). Experiments were made at 1523 K. The explored reaction between slag and metal is

$$\text{Si(in Cu)} + 2\text{FeO(in slag)} = \text{SiO}_2(\text{in slag}) + 2\text{Fe(in Cu)}.$$  (1)

The primary slag which was prepared from commercial reagents had a nominal composition of Li2O 28 mass%–SiO2 58 mass%–Al2O3 14 mass%. The charged slag consisted of the primary slag and FeO. The charged metal was Cu–Si alloy which was prepared from four-nine copper and five-nine silicon. Initial contents of FeO in the charged slag and Si in the charged metal were varied as 9–15 mass% and 0.004–0.15 mass%, respectively. The quantities of the slag and the metal were 33 x 10^{-3} kg and 200 x 10^{-3} kg, respectively.

A 5 kW silicon-carbide resistance furnace was used. A weighed Cu–Si alloy was melted in
an alumina crucible (40 mm in I.D., 48 mm in O.D. and 100 mm long) under a flow of purified Ar gas. After the furnace was brought to the experimental temperature of 1523 K, Ar-H₂ gas mixture (volume ratio: Ar/H₂ = 1/1) was passed through the furnace for 1.2–2.4 ks in order to deoxidize the molten Cu–Si alloy. The furnace was again flushed with Ar and a weighed Li₂O–SiO₂–Al₂O₃ primary slag was added and melted. After the slag-metal bath was stirred for 30 s with an alumina stirring rod, a small amount of sample of metal (∼5 × 10⁻³ kg) was withdrawn using a quartz tube. A predetermined amount of FeO was added to the slag to initiate the reaction. Then stirring with the alumina stirrer (stirring speed: 3.33 s⁻¹ = 200 rpm) was commenced immediately. At intervals 4–5 × 10⁻³ kg samples of metal phase were withdrawn for analysis of solutes in the metal phase. Samples of slag phase (∼0.5 × 10⁻³ kg) were withdrawn at appropriate times. The analyzed components in the metal and slag phases were as follows: Si, total oxygen and Fe in Cu, and total Fe in the slag. From the data of the kinetic experiments, the change in Si concentration with time was mainly examined.

In addition to the kinetic experiments, measurements were made of the activity of FeO in the Li₂O–SiO₂–Al₂O₃–FeO slag. Two methods were employed for the measurements; (i) equilibrating the slag with molten Cu under Ar atmosphere and (ii) an electrochemical method developed by Iwase et al.[5,6].

### III. Results and Discussion

#### 1. Variation in Si concentration in Cu with time

The rate of the slag-metal reaction represented by eq. (1) is controlled by Si transport in the metal phase. The change in Si concentration in the metal phase with time is given by eq. (2), as shown in the previous studies by the authors[1].

\[
-\ln \left( \frac{\text{mass}\%\text{Si}}{\text{mass}\%\text{Si}_0} \right) = k'_{\text{Si}} \frac{A}{V} t,
\]

where \( k'_{\text{Si}} \) is the apparent metal-side mass-transfer coefficient of Si, \( A \) is the interfacial area, \( V \) is the volume of the metal phase, \( t \) is reaction time, and \( [\text{mass}\%\text{Si}]_0 \) is the initial concentration of Si in the metal phase.

Typical results of experiments are shown in Fig. 1, where the logarithm of Si concentration is plotted against time. These results have been obtained from the experiments for different initial concentrations of FeO in the slag phase, that is, \((\text{mass}\%\text{FeO})_0 = 9–15\), and constant \([\text{mass}\%\text{Si}]_0 = 0.1\). In Fig. 1(a)–(c) the experimental data are represented by linear lines for certain reaction times. The slopes of the linear lines in the three runs are almost constant and independent of \((\text{mass}\%\text{FeO})_0\). From

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1. These procedures were necessary to obtain reproducible data.

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Fig. 1 Relation between log [mass%Si] and time.
the slopes, taking the interfacial area, \( A \), in eq. (2) to be the cross-sectional area of the crucible, one obtains the apparent mass-transfer coefficient, \( k_{Si} = (0.20 - 0.21) \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \). The \( k_{Si} \) value is in good agreement with that obtained previously\(^{(1)}\) from the data for \([\text{mass\% FeO}]_0 = 9 - 10.5\). In the low Si concentration range, the apparent mass-transfer coefficient, \( k_{Si} \), appears to increase with decreasing \([\text{mass\% Si}]_0\).

A series of experiments have been made, in which the initial concentration of Si ranges from 0.01 mass\% to 0.14 mass\%. The initial FeO concentration has been constant at 12.5 mass\%. The typical results are shown in Fig. 2. At \([\text{mass\% Si}]_0 > 0.04\), the linear relationships are obtained between log \([\text{mass\% Si}]\) and time in the time range from 0 to certain reaction times, while at \([\text{mass\% Si}]_0 < 0.02\), linear relationships are hardly observed between log \([\text{mass\% Si}]\) and time. However, for the sake of further discussion, linear lines are drawn tentatively between the data at zero time and those indicated with arrow in Fig. 2.

From the figure, it is indicated that the apparent mass-transfer coefficient, \( k_{Si} \), is almost constant at relatively higher initial Si concentration \([\text{mass\% Si}]_0 > 0.07\), i.e. \( k_{Si} = (0.20 - 0.24) \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \), while at lower \([\text{mass\% Si}]_0\), \( k_{Si} \) increases with decreasing \([\text{mass\% Si}]_0\). It is also shown in the figure that, as the slag-metal reaction proceeds, \( k_{Si} \) tends to increase with decrease of Si concentration. The dotted line in the figure is to be mentioned in III·3·(2).

Although \( k_{Si} \) depends on Si concentration at lowered \([\text{mass\% Si}]\) and/or in the cases of low \([\text{mass\% Si}]_0\), the data of kinetic experiments (as shown in Figs. 1 and 2) may be consistent with the assumption that the reaction rate is controlled by transport of Si in the metal phase. In most experiments, as typically shown in Fig. 1(a) and (c), silicon was oxidized to very low value of \([\text{mass\% Si}]\). Hence, \([\text{mass\% Si}]_i\), metal side silicon concentration at the slag-metal interface, can be neglected as compared with \([\text{mass\% Si}]\). However, it is difficult to explain the observed influence of Si concentration on \( k_{Si} \) on the assumption that the reaction proceeds exclusively at the slag-metal interface.

It may be reasonable to assume that the Si oxidation by O takes place in a reaction zone located within a metal-side boundary film formed by oxygen penetration from the slag-metal interface into the metal phase.

2. Variation in oxygen concentration in Cu with time

(1) Thermodynamic examination

Dissolution of oxygen from the slag into the metal is examined thermodynamically on the basis of the following reactions.

\[
\text{FeO}(l) = \text{Fe(in Cu)} + \text{O(in Cu). (3)}
\]

\[
\text{SiO}_2(s) = \text{Si(in Cu)} + 2\text{O(in Cu). (4)}
\]

The equilibrium constant for the reaction (3) was derived from published data\(^{(4)(5)}\) as follows:

\[
K = \frac{N_{FeO} \gamma_{FeO}}{[\text{mass\% O}][\text{mass\% Fe}] f_{Fe} f_{O}} = 9.21 \times 10^2, \quad (5)
\]

where \( N_{FeO} \) is the mole fraction of FeO in the slag, \( \gamma_{FeO} \) is the activity coefficient of FeO, and \( f_{Fe} \) and \( f_{O} \) are the activity coefficients of Fe and O in Cu. The equilibrium product for the reaction (4), \([\text{mass\% Si}][\text{mass\% O}]^2\), is calculated directly from experimental data obtained from

Fig. 2 Relation between log \([\text{mass\% Si}]\) and time with various \([\text{mass\% Si}]_0\).
the study on Cu-Si-O/SiO\textsubscript{2}(s) equilibria made by Hendry and Bell\textsuperscript{(6)}. That is, 

\[ \text{mass}\%\text{Si} \times \text{mass}\%\text{O}^2 = 1.29 \times 10^{-2}. \]  

(6)

Equilibrium data obtained in the present study for the molten \text{Li}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{FeO} slag-Cu system are summarized in Table 1. The data denoted by No. 1, No. 2 and No. 3 in the table represent those at the end of runs for kinetic experiments. In the experiment for No. 3, Fe\textsubscript{2}O\textsubscript{3} was used instead of FeO. At the end of these runs, [mass\%Si] = tr. From this, the equilibrium for the reaction, FeO(in slag) = Fe(in Cu) + O(in Cu), is considered to be established. It is to be noted that FeO concentrations listed in the table have been calculated simply from “total” iron concentration.

The activities of FeO in the slag, \(a_{\text{FeO}}\), are calculated from the data in Table 1 and eq. (5). Here, the standard state of FeO is pure iron oxide melt in equilibrium with solid iron at 1523 K. The activity coefficients of Fe and O in Cu is estimated with first and second order interaction coefficients on weight percent scales\textsuperscript{(5)(7)}. The calculated \(a_{\text{FeO}}\) data are shown in Fig. 3. The \(a_{\text{FeO}}\) data obtained from e.m.f. measurements are also shown in the figure. The symbols \(\bullet\) and \(\circ\) in the figure designate the results taken from the data in Table 1 and the e.m.f. data, respectively. The activity coefficient of FeO, \(\gamma_{\text{FeO}}\), is estimated from the data shown in the figure. Here, a linear relationship between \(a_{\text{FeO}}\) and \(\gamma_{\text{FeO}}\) is assumed, because the data in Fig. 3 covers a narrow FeO

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**Table 1: Equilibrium data for the reaction FeO(in slag) = Fe(in Cu) + O(in Cu) at 1523 K.**

| No. | (mass\%FeO) | (mass\%Fe) | (mass\%O) | Time(s) | Remarks |
|-----|-------------|-------------|-----------|---------|---------|
| 1   | 8.09        | 0.281       | 0.0005    | \(5.4 \times 10^3\) | Data at the end of runs for kinetic study* |
| 2   | 11.0        | 0.0139      | 0.0108    | \(5.4 \times 10^3\) | |
| 3   | 11.7***     | 0.100       | 0.0021    | \(5.4 \times 10^3\) | |
| 4   | 11.9**      | 0.0810      | 0.0021    | \(7.2 \times 10^3\) | Equilibrium study |
| 5   | 12.1***     | 0.0967***   | 0.0023    | \(7.2 \times 10^3\) | |

* Initial concentrations
** Calculated from mass-balance.
*** Initial concentration of Fe\textsuperscript{2}O\textsubscript{3} = 0.052 mass\%.

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**Fig. 3**: The activity of FeO in the slag.

**Fig. 4**: Relation among [mass\%Si], [mass\%Fe] and [mass\%O] in Cu in equilibrium with SiO\textsubscript{2}-FeO slag melts.
concentration range, i.e. $N_{FeO} < 0.11$, where $N_{FeO}$ is the mole fraction of FeO in the slag. The obtained values of $\gamma_{FeO}$ are $\gamma_{FeO} = 1.8(\bullet)$ and $\gamma_{FeO} = 2.8(\bigcirc)$. At present the reason for the small discrepancy between these two values of $\gamma_{FeO}$ is uncertain. Hence, the mean value is taken to be $\gamma_{FeO}$ in the following calculations. That is,

$$\gamma_{FeO} = 2.3. \tag{7}$$

Relationships among Fe, Si and O concentrations in molten Cu in equilibrium with SiO$_2$–FeO melts are examined on the basis of the thermodynamic data for the reactions (3) and (4) and the activity data for FeO–SiO$_2$ system$^{(6)}$. The results are illustrated in Fig. 4. Here, as an approximation, $a_x = [mass\% x]$ (x = Fe, Si or O) is assumed, $a_x$ being the activity of the solute x in molten Cu.

(2) Behavior of oxygen in the metal phase during the slag-metal reaction

Figures 5 and 6 illustrate typical examples of time changes in total oxygen concentration in the metal phase.

Figure 5 shows the result of a kinetic experiment with $[mass\% Si]_0 = 0.0910$ and $(mass\% FeO)_0 = 12.5$. In the figure, “total” oxygen concentration, $[O]_T$, and Si concentration are plotted against time. Here, in consideration of eq. (6), $[O]_T$ at zero time is assumed to be a value as low as $1 \times 10^{-4}$ mass%. After the initiation of the slag-metal reaction, a rapid increase in $[O]_T$ occurs simultaneously with the decrease in $[mass\% Si]$. As the reaction proceeds, $[O]_T$ increases with decreasing $[mass\% Si]$. When $[mass\% Si]$ is lowered to “trace”, $[O]_T$ is enhanced markedly to attain a maximum ($\approx 100 \times 10^{-4}$ mass%). Then, $[O]_T$ decreases with time from the maximum down to the equilibrium value for the Cu–Fe–O system. From Table 1, Fig. 3 and Fig. 4, the equilibrium O concentration in the molten Cu is considered to be limited within a range from about $1 \times 10^{-4}$ mass% at zero time to about $20 \times 10^{-4}$ mass% with changes in Si, Fe and FeO concentrations. Therefore, the markedly enhanced values of $[O]_T$ (Fig. 5) are regarded to be considerably higher than the equilibrium oxygen concentration. This suggests that oxide inclusions exist in the bulk metal. From Fig. 4, it is considered that the inclusions consist mainly of solid SiO$_2$.

Figure 6 shows variations in $[O]_T$ around the top of the peak shown in Fig. 5 with time in a
series of kinetic experiments with various \([\text{mass}\% \text{Si}]_0\) values ranging from 0.004 to 0.07 and constant \((\text{mass}\% \text{FeO})_0=12.5\). The figure indicates that the lowering of \([\text{mass}\% \text{Si}]_0\) causes a decrease in \([\text{O}]_T\). This suggests that the amount of the inclusions changes with total amount of the reaction product, \(\text{SiO}_2\).

To directly confirm the presence of \(\text{SiO}_2\) inclusions in the bulk metal, microscopic examination was made for solidified specimens of the metal phase. To prepare the samples, kinetic experiments were made with a small alumina crucible (20 mm in I.D.). The experimental conditions were as follows: \((\text{mass}\% \text{FeO})_0=12.5\), \([\text{mass}\% \text{Si}]_0=0.1\), slag depth = 17 mm and metal depth = 20 mm. The slag-metal bath was stirred with an \(\text{Al}_2\text{O}_3\) rod. After a predetermined reaction time (120–150 s), the crucible was quickly taken out from the furnace and quenched. Then observation of metal phase was made with a microscope. A large number of spherical \(\text{SiO}_2\) inclusions \((\sim 10 \mu\text{m in diameter})\) were observed to be included in the solidified specimens. A typical example of the microphotograph of the specimen is shown in Fig. 7. The figure represents a vertical section of the metal phase observed under polarized light. White spots shown in the figure correspond to solid \(\text{SiO}_2\) particles\(^\dagger\).

The presence of \(\text{SiO}_2(\text{s})\) inclusions suggests the formation of the reaction zone of Si oxidation within the metal phase. A portion of the reaction products may be entrained by fluid flow caused by stirring, resulting in the existence of \(\text{SiO}_2\) inclusions in the bulk metal phase. The formation of the reaction zone may be due to mass-transfer of oxygen from the slag-metal interface within the metal-side boundary film.

3. Examination of the reaction zone

(1) Reaction model

The reaction taking place in the reaction zone in the metal-side boundary film is represented by eq. (8).

\[
\text{Si} + 2\text{O} = \text{SiO}_2. \tag{8}
\]

At the slag-metal interface an equilibrium represented by eq. (9) is assumed.

\[
\text{FeO} = \text{Fe} + \text{O}
\]

and

\[
m = C_i C_{\text{FeO}}^{1/2} C_{\text{Fe}}^{1/2}, \tag{9}
\]

where \(i\) represents the interface, \(C_x\) is the mole number of component \(x\) per unit volume \((x=\text{Fe}, \text{O}, \text{FeO})\) and \(m\) is an index of equilibrium. It is assumed that the reaction zone is a reaction plane located at a distance of \(X_R\) from the interface. Here, \(X_R \leq \delta\), where \(\delta\) is the thickness of the metal-side boundary film. Equation (10) is assumed, because the equilibrium constant of the reaction represented by eq. (8), i.e. \(K = [\text{mass}\% \text{Si}] [\text{mass}\% \text{O}]^2\) (eq. (6)), is so small that reaction product is largely favored at equilibrium.

\[
C^*_0 \ll C_0 \text{ and } C^*_\text{Si} \ll C_{\text{Si}}, \tag{10}
\]

where the suffix \(\ast\) represents the reaction plane. The mass flux of \(\text{O}\) between the slag-metal interface and the reaction plane, \(\dot{N}_O\), and that of \(\text{Si}\) between the bulk metal and the reaction plane, \(\dot{N}_{\text{Si}}\), are represented as follow:

\[
\dot{N}_O = \frac{D_0}{X_R} C_0 \tag{11}
\]

and

\[
\dot{N}_{\text{Si}} = \frac{D_{\text{Si}}}{\delta - X_R} C_{\text{Si}}. \tag{12}
\]

\(^\dagger\) When the crucible is quenched, convective flow occurs in the metal phase. So, the distribution of the inclusions in the solidified metal phase illustrated in Fig. 7 may be different from that in the molten state.
The mass flux of Fe between the slag-metal interface and the bulk metal, \( N_{Fe} \), is assumed as follows.

\[
N_{Fe} = \frac{D_{Fe}}{\delta} (C_{Fe}^{0} - C_{Fe}). \quad (13)
\]

The \( D_{x} \) (\( x = O, \ Si \) and \( Fe \)) is the diffusion coefficient of the component \( x \). Steady state is assumed in the diffusion processes of Si, O and Fe.

\[
\frac{1}{2} N_{O} = N_{Si} \quad \text{(14)}
\]

and

\[
N_{O} = N_{Fe}. \quad \text{(15)}
\]

From the above equations, one obtains the equation for the reaction rate, \( N_{Si} \), and the apparent mass transfer coefficient of Si, \( k_{si} \).

\[
N_{Si} = k_{si} C_{Si}. \quad \text{(16)}
\]

\[
k_{si} = k_{si}^{0} f_{e}. \quad \text{(17)}
\]

\[
k_{si}^{0} = \frac{D_{Si}}{\delta}. \quad \text{(18)}
\]

\[
f_{e} = 1 + \frac{D_{0} C_{O}^{0}}{2D_{Si} C_{Si}}. \quad \text{(19)}
\]

Here, \( k_{si}^{0} \) corresponds to the mass transfer coefficient value of Si in the case where the reaction proceeds at the slag-metal interface. The term denoted by \( f_{e} \) corresponds to the "enhancement factor" defined by Pluschkell et al.\(^{(9)}\), and is a measure of decrease in diffusion distance of Si due to the formation of the reaction plane within the boundary film. From eq. (9) and eqs. (11)-(15), one obtains

\[
C_{Fe}^{0} = \frac{1}{2} \left( C_{Fe} + \frac{2D_{Si}}{D_{Fe}} C_{Si} \right) + \frac{1}{2} \left( C_{Fe} + \frac{2D_{Si}}{D_{Fe}} C_{Si} \right)^{2} + \frac{4D_{0}}{D_{Fe}} mC_{Fe}^{0} \right)^{1/2}. \quad (20)
\]

Since the reaction is of rate-controlling in the metal phase, eq. (21) is assumed for FeO concentration at the slag-metal interface.

\[
C_{FeO}^{0} = C_{FeO}. \quad (21)
\]

Concentration profiles in the metal phase is illustrated in Fig. 8. Here, the mass-balance for reaction \( 2FeO + Si = SiO_{2} + 2Fe \), that is,

\[
C_{Fe} = 2(C_{Si}^{0} - C_{Si}) = (V_{s}/V_{m})(C_{FeO}^{0} - C_{FeO}) \quad (22)
\]

holds. The suffix 0 represents the initial concentration, and \( V_{s} \) and \( V_{m} \) are volumes of slag and metal, respectively.

If \( C_{FeO}^{0}, C_{Si}^{0} \) and \( C_{Si} \) are given, one can evaluate \( C_{O}^{0} \), using eqs. (9), (20), (21) and (22). The variation in \( f_{e} \) with \( C_{Si} \) may be estimated using eq. (19). Thus, when \( k_{si}^{0} \) is given, one can estimate the change in \( C_{Si} \) as a function of time by numerically integrating eq. (16).

The diffusion coefficients of O in Cu, \( D_{O} = 1.12 \times 10^{-8} \text{ m}^{2} \cdot \text{s}^{-1} \)\(^{(10)}\), and Fe in Cu, \( D_{Fe} = 5.9 \times 10^{-9} \text{ m}^{2} \cdot \text{s}^{-1} \)\(^{(11)}\), are employed. The diffusion coefficient of Si in Cu, \( D_{Si} \), has been estimated to be \( D_{Si} = 6.4 \times 10^{-9} \text{ m}^{2} \cdot \text{s}^{-1} \) on the basis of a hard-sphere model\(^{(12)}\) calculation. The equilibrium constant of eq. (5) for the reaction \( FeO(l) = Fe + O \) is applied to the interfacial equilibrium represented by eq. (9). Here, the \( \gamma_{FeO} \) value of eq. (7) is used and \( f_{Fe} \) and \( f_{O} \) are put equal to unity.
2) Computations from the model and comparison of calculations with experimental results

From the experimental results of Fig. 1(a)–(c) and of the previous report(1), at \([\text{mass\%Si}]_0 \geq 0.07\) and \((\text{mass\%FeO})_0 = 9-15\), a mean value of \(k_{\text{Si}}^0, k_{\text{Si}}^0 = 0.20 \times 10^{-3} \text{m \cdot s}^{-1}\), has been obtained. From this, assuming \(k_{\text{Si}}^0 = 0.20 \times 10^{-3} \text{m \cdot s}^{-1}\), one can evaluate "observed" values of \(f_e = \frac{k_{\text{Si}}}{k_{\text{Si}}^0}\) by the use of the value of \(k_{\text{Si}}^0\) obtained from the linear part of the log \([\text{mass\%Si}]\)-t relation illustrated in Fig. 2. Here, it is to be noted that the "observed" \(f_e\) values for the results at \([\text{mass\%Si}]_0 < 0.02\) should be regarded as approximate values, because exactly the log \([\text{mass\%Si}]\)-t relations are not linear.

Comparison is made between the "observed" \(f_e\) and theoretical value calculated with eq. (19). As is seen in eq. (19), theoretically, \(f_e\) varies with \(C_{\text{Si}}\). However, in the present study, one can relate the "observed" \(f_e\) to \(C_{\text{Si}}\) at zero time, \(C_{\text{Si}}^0\), since the "observed" \(f_e\) has been obtained from the linear line including the data at zero time, i.e. \(C_{\text{Si}}^0\). Hence, theoretical calculation is made for \(C_{\text{Si}} = C_{\text{Si}}^0\) to obtain the \(f_e\) value at zero time, \(f_e^0\). Here, \((\text{mass\%FeO})_0 = 12.5\).

The "observed" \(f_e\) and the theoretical \(f_e^0\) are shown in Fig. 9 as functions of \([\text{mass\%Si}]_0\).

![Fig. 9 Relation between \(f_e^0\) and the initial concentration of Si.](image)

The agreement between observation and calculation is reasonable. It is seen from the figure that in a higher region of \([\text{mass\%Si}]_0\) (i.e. \([\text{mass\%Si}]_0 \geq 0.08\)) \(f_e^0\) is almost independent of \([\text{mass\%Si}]_0\) and \(f_e^0 \approx 1\). In a lower region of \([\text{mass\%Si}]_0\), \(f_e^0\) increases rapidly with decreasing \([\text{mass\%Si}]_0\).

According to the present reaction model, the value of \(f_e\) varies with change in Si concentration with the progress of the reaction. The variation in \(f_e\) with Si concentration has been calculated and illustrated in Fig. 10. Here, the initial concentrations are taken to be \((\text{mass\%FeO})_0 = 12.5\) and \([\text{mass\%Si}]_0 = 0.15-0.01\). Arrows in the figure show the initial Si concentration. In the calculation, the mass of metal is kept constant at \(200 \times 10^{-3} \text{kg}\). The mass of slag is varied from the initial mass of \(33 \times 10^{-3} \text{kg}\) accordingly with the decrease in FeO and the increase in SiO2 resulting from the reaction expressed by eq. (1). The dotted line in the figure indicates the relation between \(f_e^0\) and \([\text{mass\%Si}]_0\) shown in Fig. 9. In Fig. 10, a general tendency for \(f_e\) to increase with decrease in Si concentration is illustrated evidently. It is also illustrated that, at any \([\text{mass\%Si}]_0\), \(f_e\) value increases with lowering initial Si concentration. In the case of higher \([\text{mass\%Si}]_0\) (i.e. \([\text{mass\%Si}]_0 = 0.15, 0.1\)), \(f_e\) is almost constant at unity in a wide range of Si concentration. At considerably lowered Si concentrations a rapid increase in \(f_e\) occurs. In the case of lower \([\text{mass\%Si}]_0\) \(([\text{mass\%Si}]_0 = 0.02, 0.01)\), \(f_e\) depends on Si concentration so greatly.

![Fig. 10 Variation of \(f_e\) as a function of \([\text{mass\%Si}]\).](image)
that, even in a narrow Si concentration range near the initial concentration, \( f_e \) does not appear to be constant nor approximately equal to unity.

The relationships between \( f_e \) and Si concentration for various [mass\%Si\( _0 \)] values shown in Figs. 9 and 10 may give an adequate explanation of the variation in \( k_{\text{Si}} \) illustrated in Fig. 1(a)-(c) and Fig. 2.

In the case of higher [mass\%Si\( _0 \)] values, as is mentioned above, the relation \( f_e \approx 1 \) holds until silicon oxidation reaction proceeds to considerably lower [mass\%Si\( _0 \)]. In this case, the distance, \( X_R \), between the slag-metal interface and the reaction plane is small enough as compared with the thickness, \( \delta \), of the boundary film. Therefore, the reaction zone may be considered to coincide practically with the slag-metal interface, and this location of the reaction zone is maintained stationary during the slag-metal reaction.

The rapid increase in \( f_e \) at lowered [mass\%Si\( _0 \)] and/or lowered [mass\%Si] indicates that the reaction zone moves away from the interface during the progress of reaction so that the distance through which Si is diffusing decreases.

From the above discussion, it is concluded that the constant \( k_{\text{Si}} \approx 0.20 \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \) obtained from the experiments at [mass\%Si\( _0 \) \( \approx 0.1 \) and (mass\%FeO)\( _0 \) \( \approx 9 \)] has been a characteristic value of the apparent mass-transfer coefficient obtained under the condition where the reaction zone is located in the vicinity of the slag-metal interface. Therefore, \( k_{\text{Si}} = 0.20 \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \) should be regarded exactly as an approximate value for the mass transfer coefficient.

Change in Si concentration with time has been estimated with integrating eq. (16) numerically. The results of calculation are shown in Fig. 11 together with the experimental data. In the calculation, \( k_{\text{Si}} = 0.20 \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \) is employed. As shown from the figure, the calculated log [mass\%Si]-t relations are in reasonable agreement with the experimental results.

As illustrated by dotted lines in Fig. 2, a few data showed irregular change in Si concentration with time. Poorly reproducible results were obtained from the experiments, where the deoxidization of the metal under Ar-H\( _2 \) atmosphere was not appropriately made. The mechanism of the phenomena leading to the irregular results is not clarified at present. It might be possible that small particles of SiO\( _2(s) \) inclusions affect the slag-metal reaction. Further studies on the behavior of the solid SiO\( _2 \) in the metal phase are now being carried out.

(3) Summarizing remarks

As described above, it has been found that a reaction zone is formed within the metal-side boundary film, in the present reaction system. On the basis of the reaction model where movement of the reaction zone is taken into account, the change in the apparent mass-transfer coefficient with Si concentration in the metal phase has been explained reasonably. It may be considered that FeO content in the slag phase affects the formation and movement of the reaction zone. In fact, when experiments were done at lower (mass\%FeO\( _0 \) values \( \approx 5-9 \)) in the previous study\(^{1(3)} \), the increase in \( k_{\text{Si}} \) was not observed with decreasing Si concentration in the metal phase. In this case of low FeO contents, the driving force of penetration of oxygen into the metal phase may be lower considerably than in the case of higher FeO contents. Thus the reaction zone may stationary
be located at the slag-metal interface or in the vicinity of the interface.

The slag-metal reaction of the present study is an oxidation reaction of Si which is a strong deoxidizer dissolved in molten Cu. Therefore, the results of the present study may be generally related to kinetic mechanisms of reactions between molten slag and molten metal containing solute elements which interact strongly with oxygen. Pluschkell et al.\(^{(9)}\) investigated kinetics of oxidation of aluminum in steel melts by iron and manganese oxides in slag during Ar-injection stirring. The rate data were analyzed in terms of "enhancement factor" derived on the assumption that a reaction zone was formed within metal-side boundary film. Though the paper of Pluschkell et al. lacks detailed examinations on the reaction zone, the paper should be regarded as a notable report that proposed a highly interesting problems on slag-metal reactions.

### IV. Conclusion

A kinetic study has been made on the mechanism of Si oxidation reaction between a molten Li\(_2\)O-SiO\(_2\)-Al\(_2\)O\(_3\)-FeO slag and Cu-Si alloy. Based on the results of kinetic experiments which were made under the condition of rate-controlling by Si transport in the metal phase, the mechanism of the reaction, especially that of the reaction zone, has been examined. The results are summarized as follows:

1. It has been found that the Si oxidation reaction of the present slag-metal system takes place in a reaction zone within the metal-side boundary film.

2. The reaction zone is formed by diffusive transport of dissolved oxygen penetrating from the slag-metal interface into the metal phase.

3. When the initial concentration of Si is high, the reaction zone is located in the vicinity of the slag-metal interface, resulting in constant \(k_{Si}^{'}\), until Si concentration is lowered considerably in the course of the reaction. When the initial concentration of Si is low, the reaction zone is located always apart from the interface, resulting in large \(k_{Si}^{'}\).

4. As Si concentration decreases with progress of the reaction, the reaction zone moves within the metal-side boundary film, resulting in increase in \(k_{Si}^{'}\).

5. It is concluded that, in a slag-metal reaction system at high temperature, the reaction zone is not always located at the slag-metal interface.

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