

Reduction Rate of SiO₂ in Slag by Carbon-Saturated Iron

HAIPING SUN, KATSUMI MORI, and ROBERT D. PEHLKE

The reduction rate of SiO₂ from CaO-SiO₂-Al₂O₃ and CaO-SiO₂-Al₂O₃-TiO₂ slags by carbon-saturated iron melts was investigated over the temperature range 1350 °C to 1600 °C under an argon atmosphere. It was found that the reduction rate of silicon increased with increasing temperature and decreased with increasing ratio of CaO/SiO₂ in these slags. A kinetic analysis of the experimental results developed on the basis of the two film theory showed that the silicon transport rate from slag to metal phase was controlled by the rate of chemical reaction at the slag-metal interface. The rate constants obtained for the reaction were 10 g m⁻² s⁻¹ at 1550 °C. The apparent activation energy was 238.0 kJ mol⁻¹.

I. INTRODUCTION

REDUCTION of SiO₂ from slag by carbon dissolved in iron melts occurs in the lower levels of the slag layer in a cupola where the FeO content of the slag is relatively low. Prediction of the silicon content of tapped liquid iron during the cupola melting process could be affected by silicon pickup due to this reaction when an iron droplet falls through the slag layer. Accurate measurements of silica reduction rates are an important aspect in the computer simulation of the cupola process.

As it is also one of most important reactions in blast furnace operation, the reduction of silica from CaO-Al₂O₃-SiO₂ slags by carbon in liquid iron has been studied by many investigators.^[1-7] However, a considerable lack of agreement exists on the rate of the reaction. For example, the measured reaction rate, expressed as moles of SiO₂ m⁻² s⁻¹, at 1600 °C for carbon-saturated iron and an activity of silica in the slag of 0.30 are scattered from 9.17×10^{-4} ^[7] to 6.67×10^{-3} .^[4] Also, the rate-limiting step suggested by these investigations for silica reduction is not necessarily the same. However, it is generally agreed that the SiO₂ reduction reaction is a very slow reaction compared with the rates of other slag-metal reactions under similar conditions and that the reaction rate is strongly dependent on the temperature. The primary objective of this study was to determine the reaction rates at various conditions similar to those in a cupola and to determine the step or steps which control the rate of silica reduction.

II. EXPERIMENTAL PROCEDURES

An electric resistance furnace, as shown in Figure 1, was employed for heating and melting iron-carbon alloys in a graphite crucible. The reaction vessel was a vertical alumina tube of 60-mm ID and 1-m length. Both ends of the tube were closed with water-cooled brass caps, sealed with an O-ring, to prevent the oxidation of liquid iron by air. The temperature was measured with a

thermocouple placed just below the graphite crucible in the homogeneous temperature zone (15-cm long) and was controlled to within ± 0.5 °C.

About 200 g of iron-carbon alloy was first melted in a graphite crucible (30-mm ID) under an argon atmosphere. After the experimental temperature was attained, about 25 g of slag were placed on the surface of the liquid iron. The instant the slag was fully melted (which took about 1 minute) was taken as the starting point of the reaction. The drop in temperature due to the addition of slag was about 10 °C, but the melt recovered to the set experimental temperature within 2 to 3 minutes. The reaction time for most of the experiments was 6 hours. Some metal samples (1 to 3 g) were withdrawn after each hour using a quartz tube, and slag samples (0.2 to 1 g) were taken by sticking slag to a stainless steel rod every 2 hours. Initial metal and slag samples were taken before the slag addition. The progress of the reaction was followed by chemical analysis of these metal and slag samples.

Electrolytic iron (Fe >99.9 pct) and electrode graphite (ash <0.1 pct) were used to prepare the iron-carbon alloy. Slags were prepared by premelting mixtures of desired quantities of CaCO₃, SiO₂, Al₂O₃, and TiO₂ reagents.

The slag compositions and temperatures of the experiments are summarized in Table I.

III. EXPERIMENTAL RESULTS

The reduction rate of SiO₂ from CaO-SiO₂-Al₂O₃ or CaO-SiO₂-Al₂O₃-TiO₂ slags by carbon-saturated iron was investigated using slags with the basicity (CaO/SiO₂) varied from 0.82 to 1.42. The TiO₂ contents were varied from 0 to 4.75 pct. Temperatures were varied from 1350 °C to 1600 °C, and slag weights ranged from 25 to 75 g.

Figure 2 shows the change of silicon content in the metal and SiO₂ content in the slag with time during run 2. It was found that the silicon content of the liquid iron increased linearly and the SiO₂ content of the slag decreased linearly with reaction time at 1550 °C. The solid lines show the modeling prediction values. It was also found that the change of silicon content of the metal and that of the slag are stoichiometrically equal, which indicates that there was no SiO (g) formed as an intermediate product of the reaction which would leave the reaction system.

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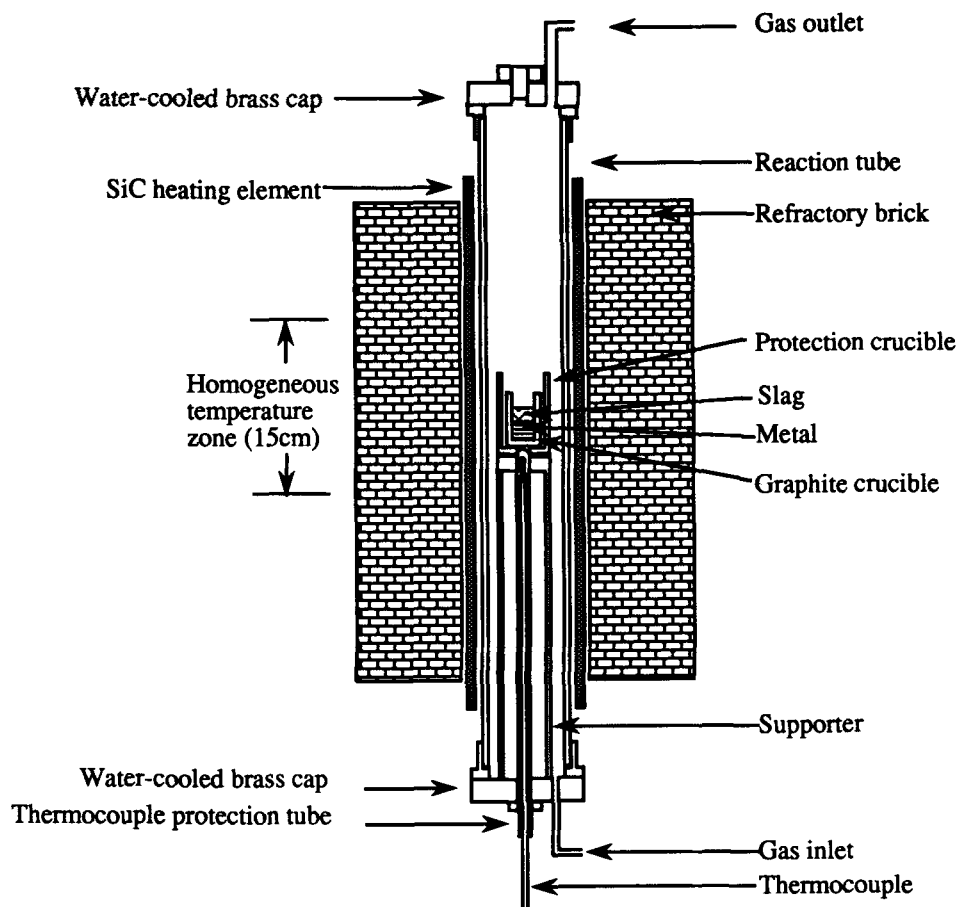


Fig. 1—Schematic diagram of the experimental apparatus.

Table I. Experimental Conditions

Run No.	Temperature (°C)	Basicity (CaO/SiO ₂)	CaO	SiO ₂	Al ₂ O ₃ (Pct)	TiO ₂	Slag	Metal (Weight, g)
1	1550	0.82	35.0	42.6	20.8	—	25.0	201.0
2	1550	1.03	41.1	39.8	21.7	—	25.0	202.0
3	1550	1.42	42.4	29.8	19.6	4.67	25.0	202.0
4	1350	0.83	33.6	40.6	20.3	4.60	25.0	200.0
5	1450	0.78	33.4	42.7	18.5	4.75	25.0	199.9
6	1550	0.83	33.6	40.6	20.3	4.60	25.0	201.0
7	1600	0.83	33.6	40.6	20.3	4.60	24.9	199.9
8	1550	1.01	36.5	36.0	18.3	4.68	24.7	200.7
9	1550	1.00	38.1	38.1	19.0	4.75	75.0	201.0

Several experiments were carried out with the slag basicity (CaO/SiO₂) varied from 0.82 to 1.42 at 1550 °C. As seen in Figure 3, the reduction rate of silicon decreased with increasing ratio of CaO/SiO₂ in the slag. It was found that the reduction rate of SiO₂ was proportional to the silica activity of the slag which is lower^[8] for higher basicity slags.

The effect of temperature on the reduction rate of silica was examined using the slag with CaO/SiO₂ = 0.8 and containing 20 pct Al₂O₃ and 4.60 pct TiO₂ in the temperature range of 1350 °C to 1600 °C. The results are shown in Figure 4. It is evident from this figure that the reduction rate of SiO₂ is strongly dependent on the temperature, which indicates that the chemical reaction

at the slag-metal interface is the rate-limiting step, or at least partly dominates the reaction rate of SiO₂ reduction.

The effect of TiO₂ in the slag on silica reduction was also studied using a slag with CaO/SiO₂ = 1.0 and containing 20 pct Al₂O₃ and 4.68 pct TiO₂ for comparison with the silicon reduction rate in the case without TiO₂ in the slag. As seen in Figure 5, the reduction rate of silicon is essentially independent of TiO₂ content in the slag when TiO₂ < 4.68 pct. The small difference in reaction rates between these two runs is considered to be the result of decreasing the SiO₂ content by addition of TiO₂ to the slag.

Kawai *et al.*^[9] have studied the reduction rate of silica using graphite crucibles of different diameters. They found

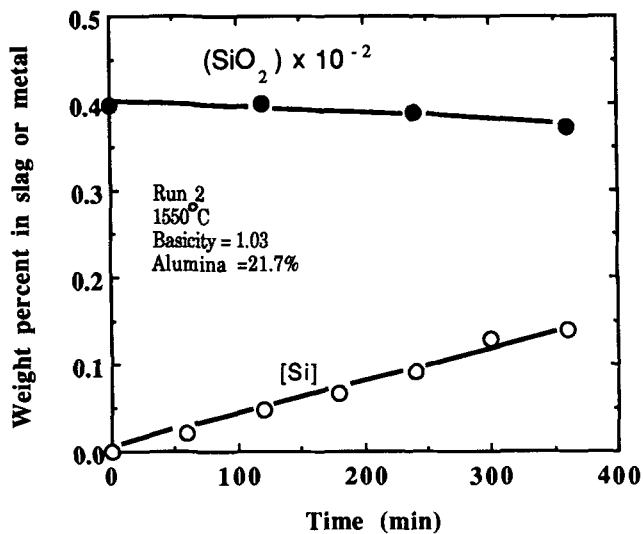


Fig. 2—Change of silica content in slag and silicon content in metal with time at 1550 °C.

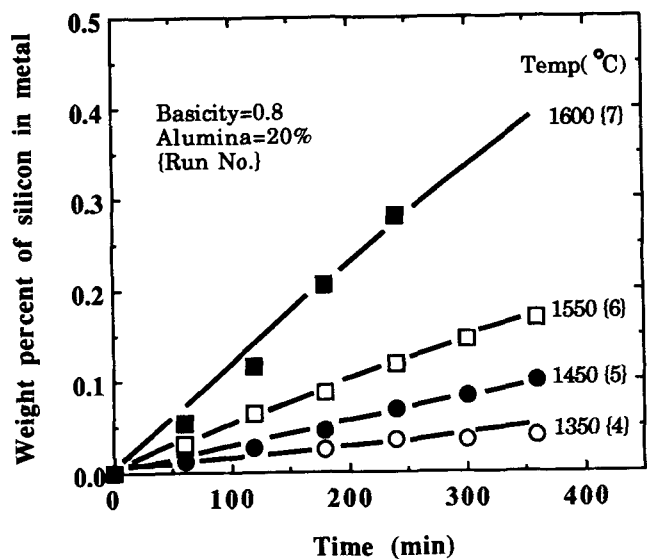


Fig. 4—Change of silicon content in metal with time for temperatures from 1350 °C to 1600 °C.

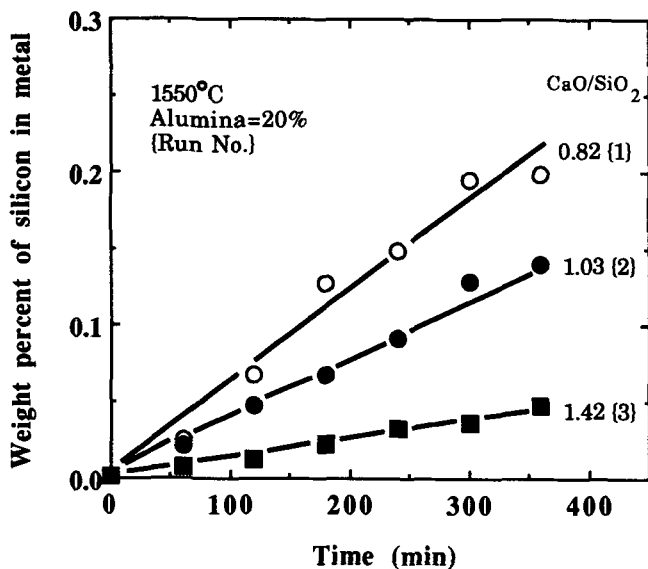


Fig. 3—Change of silicon content in the metal with time for various slag basicities at 1550 °C.

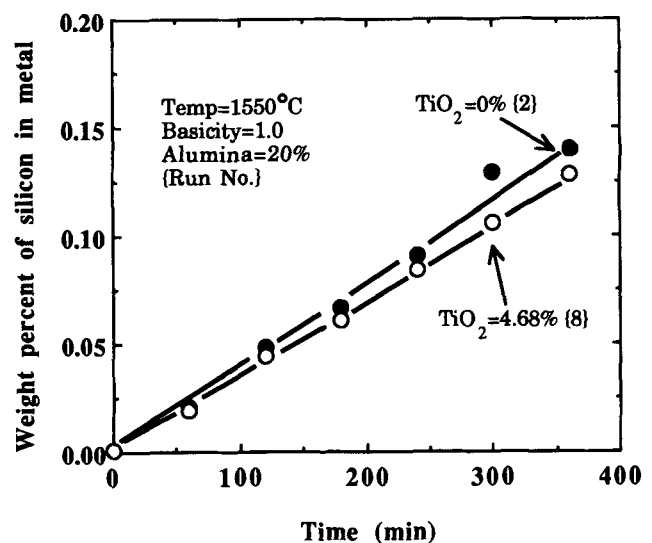


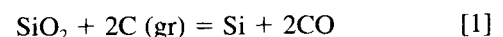
Fig. 5—Effect of TiO₂ in slag on the reduction rate of silicon at 1550 °C.

that the ratio of the slag/graphite to slag/metal interfacial area influences the reaction rate; *i.e.*, as the ratio increases, the rate of reduction increases. They explained that an increase in the slag-graphite area increases the silicon reduction rate, because an increase in an anode reaction rate ($C(\text{gr}) + O^{2-} = CO + 2e^-$) at the slag-graphite interface enhances the cathode reaction ($Si^{4+} + 4e^- = [Si]$) at the slag-metal interface. Pomfret and Grievson^[10] carried out experiments to test the influence of slag/graphite interfacial area, and they found that the reaction rate was independent of this parameter. To confirm this, the effect of slag-graphite area on silica reduction rate was studied using 25 and 75 g of slag in the present study. The slag-graphite area was calculated to be 12.9 and 38.8 cm², respectively, using 2.57 g/cm³[11] for the slag density at 1550 °C. As seen in Figure 6, the reduction rate of silicon is independent

of the slag-graphite interface area and the contribution of an anode reaction to the silicon reduction rate is considered small and negligible for the present experimental condition. Thus, reaction is considered only to take place at the slag-metal interface in the present study.

IV. DISCUSSION

The overall reaction of SiO₂ reduction by carbon in liquid iron at the slag-metal interface can be expressed by



With a standard state of solid pure SiO₂ for SiO₂ in the slag, graphite for carbon in the metal, 1 wt pct silicon referred to infinite dilution for silicon in the metal,

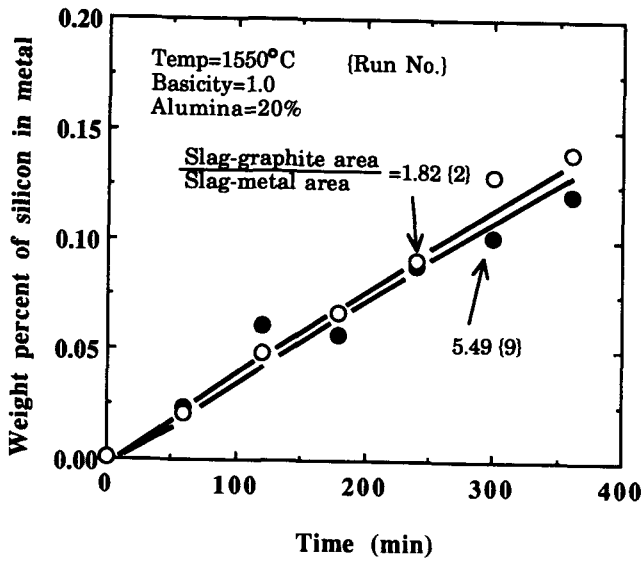


Fig. 6—Effect of slag/graphite to slag/metal area ratios on the reduction rate of silica at 1550 °C.

and pure CO gas at 1 atm for CO gas, the free energy change for the reaction is

$$\Delta G^\circ = 566.5 - 0.3746T \text{ (kJ)}^{(12,13)} \quad [2]$$

$$\ln K_{\text{Si}} = \ln \frac{a_{\text{SiO}_2} P_{\text{CO}}^2}{a_{\text{Si}} a_{\text{C}}^2} = -\frac{68,138}{T} + 45.06 \quad [3]$$

The mechanism of this reaction is assumed to be through diffusion of silica in the bulk slag to the slag-metal interface where chemical Reaction [1] follows and then, in turn, is followed by diffusion of silicon from the interface into the bulk metal phase. The transport of carbon in the metal phase is considered not to be rate limiting, because the carbon content of the liquid iron is substantially larger than that of the silicon content and also because the diffusion coefficient of carbon is greater than that of silicon.

Using these assumptions, the process of silicon reduction can be described by the following relationships.

The rate of silicon transport in the slag phase is

$$\frac{d[\text{Si}]}{dt} = \frac{A}{W_m} k_s \rho_s \{(\text{Si}) - (\text{Si})^*\} \quad [4]$$

The rate of the chemical reaction at the slag-metal interface by the mass action law is

$$\frac{d[\text{Si}]}{dt} = \frac{A}{W_m} k_{\text{Si}} \left\{ a_{\text{C}}^2 a_{\text{SiO}_2}^* - \frac{a_{\text{Si}}^* P_{\text{CO}}^2}{K_{\text{Si}}} \right\} \quad [5]$$

where

$$a_{\text{SiO}_2} = \gamma_{\text{SiO}_2} N_{\text{SiO}_2} = (\text{Si}) \frac{\gamma_{\text{SiO}_2}}{M_{\text{Si}} \sum \frac{(\text{MO}_n)}{M_{\text{MO}_n}}} \quad [6]$$

$$a_{\text{Si}} = f_{\text{Si}}[\text{Si}] \quad [7]$$

$$\log f_{\text{Si}} = e_{\text{Si}}^{\text{C}} [\text{C}] + e_{\text{Si}}^{\text{Si}} [\text{Si}] \quad [8]$$

$$e_{\text{Si}}^{\text{C}} = \frac{380}{T} - 0.023^{(14)} \quad [9]$$

$$e_{\text{Si}}^{\text{Si}} = \frac{34.5}{T} + 0.089^{(12)} \quad [10]$$

The rate of silicon transport in the metal phase is

$$\frac{d[\text{Si}]}{dt} = \frac{A}{W_m} k_m \rho_m \{[\text{Si}]^* - [\text{Si}]\} \quad [11]$$

Combining Eqs. [4], [5], and [11], the change of silicon content in the metal can be written as

$$\frac{d[\text{Si}]}{dt} = \frac{A}{W_m} \frac{(\text{Si}) - \frac{[\text{Si}]}{K'_{\text{Si}} a_{\text{C}}^2}}{\frac{1}{k_s \rho_s} + \frac{P_{\text{CO}}^2}{k_m \rho_m K'_{\text{Si}} a_{\text{C}}^2} + \frac{M_{\text{Si}} \sum \frac{(\text{MO}_n)}{M_{\text{MO}_n}}}{k_{\text{Si}} a_{\text{C}}^2 \gamma_{\text{SiO}_2}}} \quad [12]$$

where

$$K'_{\text{Si}} = \left. \frac{[\text{Si}] P_{\text{CO}}^2}{(\text{Si}) a_{\text{C}}^2} \right|_{\text{eq}} = K_{\text{Si}} \frac{\gamma_{\text{SiO}_2}}{f_{\text{Si}} M_{\text{Si}} \sum \frac{(\text{MO}_n)}{M_{\text{MO}_n}}} \quad [13]$$

The change of silicon content in the slag can be obtained using the following mass balance equation for silicon in the system

$$\frac{d[\text{Si}]}{dt} W_m + \frac{d(\text{Si})}{dt} W_s = 0 \quad [14]$$

The values of γ_{SiO_2} in CaO-SiO₂-Al₂O₃ slags at 1550 °C and 1600 °C obtained by Rein and Chipman⁽⁸⁾ were used in the present study. Values of γ_{SiO_2} at 1350 °C and 1450 °C were estimated by extrapolating their values at 1550 °C and 1600 °C. The value of K'_{Si} was then calculated using Eq. [13]. The interfacial area, A , was simply taken as the cross-sectional area of the crucible. Since the experiments utilized graphite crucibles, the activity of carbon in liquid iron is unity with reference to graphite. The pressure of CO gas generated at the slag-metal interface was considered to be one atmosphere.

The values of $k_m \rho_m = 0.130 \text{ g cm}^{-2} \text{ s}^{-1}$ obtained by Mori *et al.*⁽¹⁵⁾ and $k_s \rho_s = 0.001 \text{ g cm}^{-2} \text{ s}^{-1}$ by Shinozaki *et al.*⁽¹⁶⁾ were used for the mass transport coefficients of silicon in the metal and the slag phases. Since the chemical reaction at the interface is the rate-limiting step in the reduction of silica in slag by carbon in liquid iron, it is reasonable to neglect the effect of temperature and metal or slag compositions on the values of $k_m \rho_m$ and $k_s \rho_s$.

The chemical reaction rate constants for silicon reduction by carbon in liquid iron, k_{Si} , were determined by comparing the experimental results with the predictions from the rate Eq. [12], and they are shown in Table II. The solid lines in Figures 2 through 6 show the calculated silicon content in the metal and slag as a function of time using these values of k_{Si} . As seen in

Table II. Measured Reaction Rate, Rate Constant, Relative Resistances to Each Silicon Transport Step, and SiO₂ Activities Calculated for Each Run

Run No.	Temperature (°C)	Basicity (CaO/SiO ₂)	Rate*	k_{Si}^{**} (gm ⁻² s ⁻¹)	k_{Si}^{***}	R_s	R_m (Pct)	R_c	a_{SiO_2}	$\gamma_{SiO_2}^{[8]}$
1	1550	0.82	1.05×10^{-3}	10.13	9.75	1.48	3.2×10^{-3}	98.5	0.295	0.639
2	1550	1.03	6.56×10^{-4}	10.98	10.67	0.99	3.4×10^{-3}	99.0	0.170	0.418
3	1550	1.42	2.06×10^{-4}	10.24	10.94	0.42	3.2×10^{-3}	99.6	0.057	0.165
4	1350	0.83	2.36×10^{-4}	1.76	1.76	0.35	6.1×10^{-3}	99.6	0.377	0.823
5	1450	0.78	4.47×10^{-4}	3.66	3.78	0.63	1.1×10^{-3}	99.4	0.343	0.718
6	1550	0.83	8.33×10^{-4}	8.11	8.02	1.23	2.5×10^{-3}	98.8	0.293	0.639
7	1600	0.83	2.00×10^{-3}	21.62	19.14	3.07	2.4×10^{-3}	96.9	0.271	0.604
8	1550	1.01	5.92×10^{-4}	9.62	9.61	0.99	3.0×10^{-3}	99.0	0.175	0.418
9	1550	1.00	6.06×10^{-4}	9.80	9.56	0.96	3.0×10^{-3}	99.0	0.177	0.418

*mole SiO₂ m⁻² s⁻¹

** k_{Si} from Eq. [12]

*** k_{Si} from Eq. [17]

Table II, approximately the same values of k_{Si} were obtained for the runs at 1550 °C.

According to the overall rate Eq. [12], the total resistance to the reaction is

$$R = \frac{1}{k_s \rho_s} + \frac{P_{CO}^2}{k_m \rho_m K'_{Si} a_C^2} + \frac{M_{Si} \sum (MO_n)}{k_{Si} a_C^2 \gamma_{SiO_2}} \quad [15]$$

The relative resistances of silicon transport in the slag (R_s , pct) and silicon transport in the metal (R_m , pct) and the chemical reaction at the slag-metal interface (R_c , pct) are

$$R_s = \frac{100}{k_s \rho_s R}, \quad R_m = \frac{100 P_{CO}^2}{k_m \rho_m K'_{Si} a_C^2 R}$$

$$\text{and } R_c = \frac{100 M_{Si} \sum (MO_n)}{k_{Si} a_C^2 \gamma_{SiO_2} R} \quad [16]$$

respectively. The values for each experiment are shown in Table II. Comparing the values of the relative resistances to silicon transport in the slag ($R_s = 0.3$ to 3 pct) or in the metal ($R_m = 1.0$ to 6.0×10^{-3} pct), the relative resistance to chemical reaction at the slag-metal interface ($R_c > 96$ pct) is much larger. Thus, it is considered that the reduction rate of silicon is limited by the rate of the chemical reaction at the interface. This conclusion was also reached in the investigations by Turkdogan *et al.*,^[1] Ashizuka *et al.*,^[5] and Kawai *et al.*^[9] However, other investigations have suggested a different controlling mechanism for SiO₂ reduction. For example, Rawling and Elliott^[18] concluded that oxygen transport in the metal phase was the rate-controlling step in the temperature range of the present study (<1600 °C), but that above 1650 °C, mixed control between oxygen transport and chemical reaction at the metal-slag interface prevails.

Assuming the reduction rate of silicon is limited by the rate of the chemical reaction at the interface and ignoring the transport process of silicon in the slag and the metal and the effect of reversal of Reaction [1] because

the silicon concentration is far below its equilibrium content with respect to the slag ($[Si]_{eq} = 16.0$ to 19.0 pct^[17] for runs at 1550 °C), the rate of silica reduction by carbon-saturated iron can be written as

$$\frac{d[Si]}{dt} = \frac{A}{W_m} k_{Si} a_{SiO_2} \quad [17]$$

The values of k_{Si} obtained from experimental results according to this rate equation are also listed in Table II. The small differences between k_{Si} derived from Eqs. [12] and [17] are caused by neglecting the transport processes for silicon in the slag and the metal and the effect of reversal of the reaction included in Eq. [17]. The value of k_{Si} is approximately 10 g m⁻² s⁻¹ at 1550 °C.

Figure 7 shows the relationship between measured silica reduction rates and silica activity in the slag. A linear relationship is found between them, as predicted from theoretical considerations. The rates measured by Ashizuka *et al.*,^[5] Kawai *et al.*,^[9] and Rawling and Elliott^[18] at 1550 °C are also shown in the figure for comparison with the results of the present study. The slope of the line obtained in the present study is higher than the other three.

Figure 8 shows the influence of temperature on k_{Si} , which follows the Arrhenius equation. The apparent activation energy calculated from the slope is 238.0 kJ mol⁻¹. This large apparent activation energy also supports the assumption that the rate-limiting step is chemical reaction at the interface.

V. ESTIMATION OF SILICON PICKUP IN THE CUPOLA FURNACE

The rate of silicon reduction in the lower portion of the slag layer in a cupola where FeO is low has been calculated using the assumption of an Fe-C-Si alloy in the shape of a sphere immersed in a CaO-SiO₂-Al₂O₃ slag and a ratio of slag weight to metal weight of 10:1. The temperatures, slag, metal compositions, and iron droplet weight used in the calculations are presented in Table III.

The reaction rates were calculated using overall rate

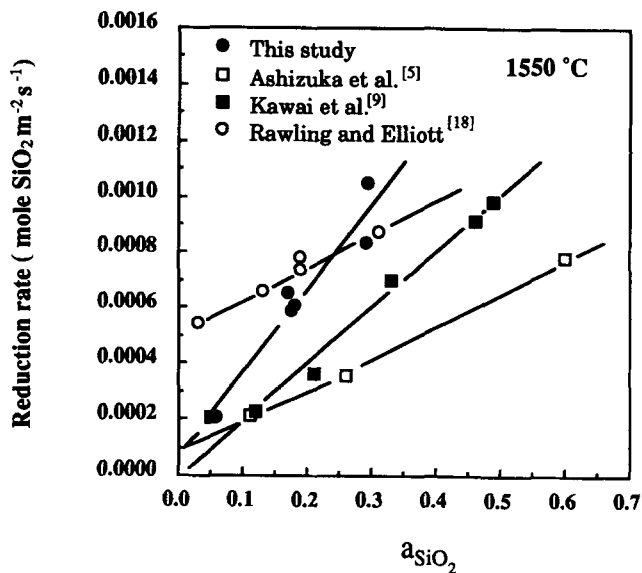


Fig. 7—Variations in the reduction rate of silica by carbon-saturated iron as a function of the activity of silica in slag at 1550 °C.

Eq. [12], and the pressure of CO gas generated at the slag-metal interface was assumed to be 1 atm. The carbon content of the metal was calculated using a stoichiometric relationship between silicon and carbon content according to the following equation:

$$\frac{d[C]}{M_C dt} = -\frac{2d[Si]}{M_{Si} dt} \quad [18]$$

The carbon activity in liquid iron relative to graphite was calculated by

$$a_C = \gamma_C N_C \quad [19]$$

$$\ln \gamma_C = \ln \gamma_C^0 + \varepsilon_C^C N_C + \varepsilon_C^{Si} N_{Si} \quad [20]$$

$$\ln \gamma_C^0 = \frac{100M_C}{M_{Fe}RT} \Delta G_{[pct C]}^0 \quad [21]$$

$$\Delta G_{[pct C]}^0 = 136.7 - 0.3674T \quad \text{kJ mol}^{-1} [14] \quad [22]$$

where ε_C^C and ε_C^{Si} were calculated from $e_C^C = 0.195^{[19]}$ and $e_C^{Si} = 162/T - 0.08$.^[12] The results of these calculations are presented in Table III and Figures 9 through 13.

Figure 9 shows the effect of carbon content in the alloy on the reaction rate at 1550 °C. An increase in carbon content in the metal increases the silicon pickup rate and the carbon loss rate. Figure 10 shows the effect of slag basicity on the reaction rate at 1550 °C. An increase in slag basicity decreases the silicon pickup rate and the carbon loss rate. Figure 11 shows the effect of temperature on the reaction rate. The silicon pickup rate and the carbon loss rate increase at higher temperatures. Figure 12 shows the effect of silicon content of the alloy on the reaction rate at 1550 °C. An increase of silicon content in the metal increases the silicon pickup rate and the carbon loss rate, because the carbon activity increases with increasing silicon content. Figure 13 shows the effect of droplet weight on the reaction rate at 1550 °C. A decrease in the droplet size increases the silicon pickup rate and the carbon loss rate, because the ratio of surface area to metal weight is larger for a smaller droplet.

However, as seen in Table III and Figures 9 through 13, the values of rate of silicon or carbon content changes are small, which means that this reaction is not of great importance in cupola operations.

VI. CONCLUSIONS

The reduction rate of SiO₂ from CaO-SiO₂-Al₂O₃ or CaO-SiO₂-Al₂O₃-TiO₂ slags by carbon-saturated iron was investigated using slags with the basicity (CaO/SiO₂) varied from 0.82 to 1.42. The TiO₂ content of the slags was varied at 0 and 4.75 pct. The temperature was varied from 1350 °C to 1600 °C. The low reaction rate and relatively high activation energy of the SiO₂ reduction suggest that the chemical reaction at the slag-metal interface is the slowest step in the overall reaction. A kinetic model for reduction of SiO₂ in slags by Fe-C alloys was developed based on the experimental results. The

Table III. Model Calculation Conditions and Calculated Reaction Rates

Cal No.	Iron Droplet Type	(g)	Slag*	Temperature (°C)	k_{Si} (g m ⁻² s ⁻¹)	$\Delta[\text{Pct C}]/\Delta t$ (s ⁻¹)	$\Delta[\text{Pct Si}]/\Delta t$ (s ⁻¹)
Cal-1	2C-Fe	1	A	1550	10.13	-0.48×10^{-5}	0.57×10^{-5}
Cal-2	3C-Fe	1	A	1550	10.13	-2.32×10^{-5}	2.70×10^{-5}
Cal-3	4C-Fe	1	A	1550	10.13	-8.27×10^{-5}	9.67×10^{-5}
Cal-4	C(sat)-Fe	1	A	1550	10.13	0	4.10×10^{-4}
Cal-5	4C-Fe	1	B	1550	10.13	-4.90×10^{-5}	5.73×10^{-5}
Cal-6	4C-Fe	1	C	1550	10.13	-1.78×10^{-5}	2.10×10^{-5}
Cal-7	4C-Fe	1	A	1350	1.76	-2.32×10^{-5}	2.72×10^{-5}
Cal-8	4C-Fe	1	A	1450	3.78	-3.82×10^{-5}	4.47×10^{-5}
Cal-9	4C-Fe	1	A	1600	21.62	-1.67×10^{-4}	1.95×10^{-4}
Cal-10	4C-1Si-Fe	1	A	1550	10.13	-1.07×10^{-4}	1.24×10^{-4}
Cal-11	4C-2Si-Fe	1	A	1550	10.13	-1.37×10^{-4}	1.61×10^{-4}
Cal-12	4C-3Si-Fe	1	A	1550	10.13	-1.77×10^{-4}	2.07×10^{-4}
Cal-13	4C-Fe	0.5	A	1550	10.13	-1.04×10^{-4}	1.22×10^{-4}
Cal-14	4C-Fe	2	A	1550	10.13	-6.55×10^{-5}	7.68×10^{-5}

*Slag A: 35CaO-45SiO₂-20Al₂O₃, CaO/SiO₂ = 0.78
 Slag B: 40CaO-40SiO₂-20Al₂O₃, CaO/SiO₂ = 1.00
 Slag C: 45CaO-35SiO₂-20Al₂O₃, CaO/SiO₂ = 1.29

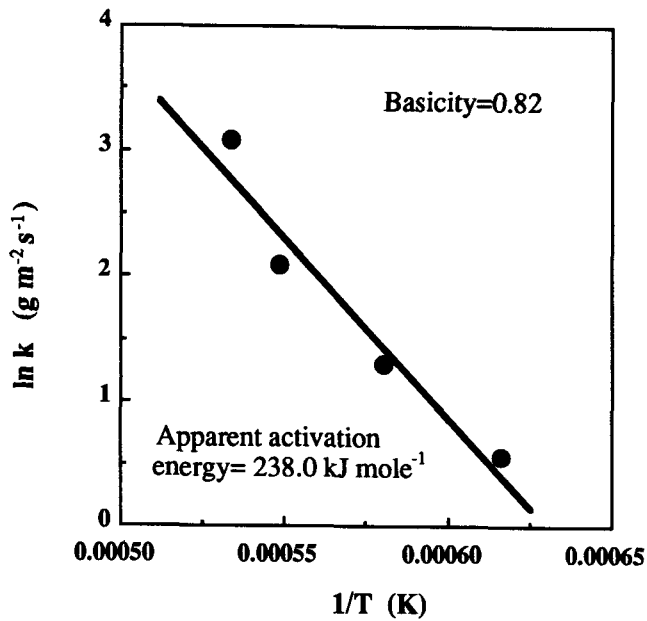


Fig. 8—Arrhenius plot for the rate constant k_{Si} of silica reduction in slags by carbon-saturated iron.

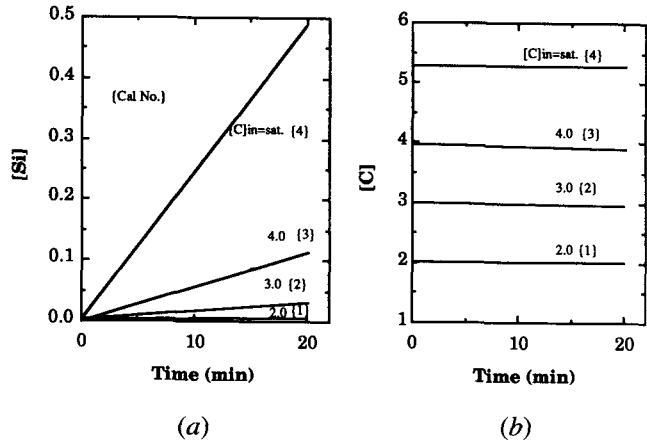


Fig. 9—Effect of carbon content of the alloy on the reaction rate at 1550 °C: (a) change of silicon content of metal with time and (b) change of carbon content of metal with time.

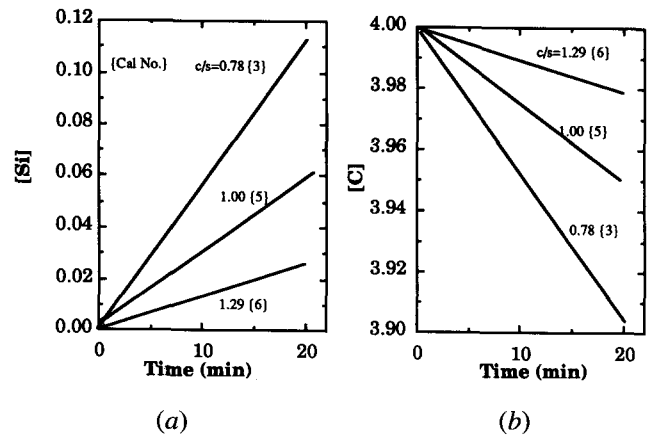


Fig. 10—Effect of slag basicity on the reaction rate at 1550 °C: (a) change of silicon content of metal with time and (b) change of carbon content of metal with time.

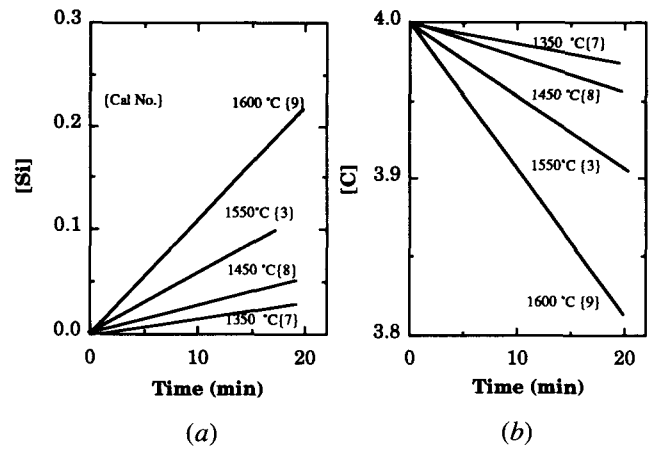


Fig. 11—Effect of temperature on the reaction rate of silica in slag A: (a) change of silicon content of metal with time and (b) change of carbon content of metal with time.

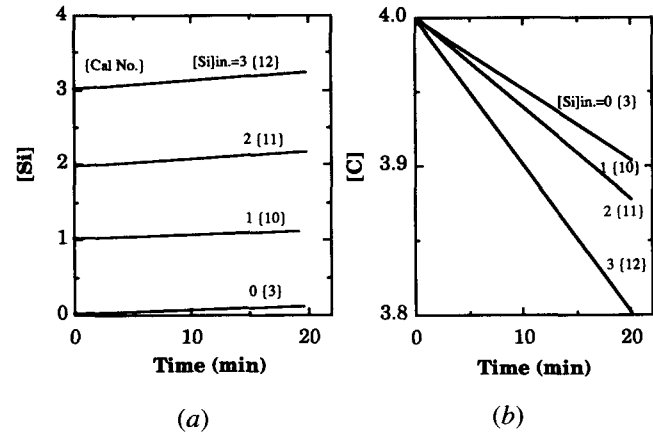


Fig. 12—Effect of silicon content of the alloy on the reaction rate at 1550 °C: (a) change of silicon content of metal with time and (b) change of carbon content of metal with time.

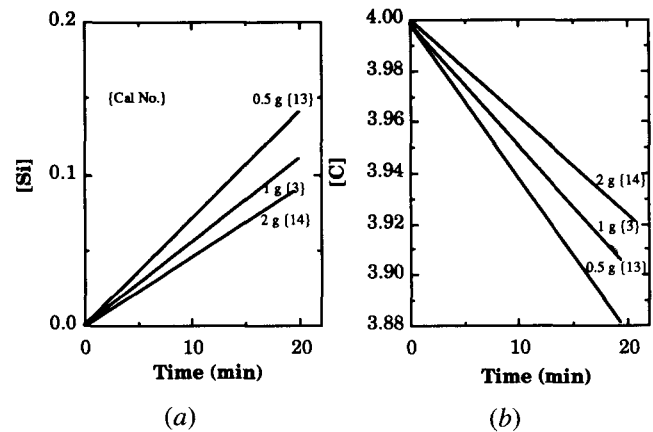


Fig. 13—Effect of droplet weight on the reaction rate at 1550 °C: (a) change of silicon content of metal with time and (b) change of carbon content of metal with time.

reduction rate was proportional to the silica activity in the slag, and the rate constant was approximately $10 \text{ g m}^{-2} \text{ s}^{-1}$ at $1550 \text{ }^\circ\text{C}$. The silicon transport rate from the slag to the metal is controlled by the rate of the chemical reaction at the slag-metal interface. The apparent activation energy for the reduction reaction is $238.0 \text{ kJ mol}^{-1}$. The silicon pickup and the carbon loss by the silica reduction reaction in a cupola are relatively small considering the short time of droplet contact with slag and the low reaction rate.

NOMENCLATURE

A	reaction area, m^2
a_{Si}	activity of silicon in metal
e_{Si}^{C}	interaction parameter between carbon and silicon in metal
$e_{\text{Si}}^{\text{Si}}$	self-interaction parameter of silicon in metal
f_{Si}	activity coefficient of silicon in metal
ΔG°	free energy of the reaction at standard state, J mol^{-1}
$\Delta G_{\text{(pct C)}}^0$	free energy change of carbon dissolution in iron, J mol^{-1}
K_{Si}	equilibrium constant of Reaction [1]
K'_{Si}	apparent equilibrium constant of Reaction [1]
k_m	mass transfer coefficient in metal, m s^{-1}
k_s	mass transfer coefficient in slag, m s^{-1}
k_{Si}	rate constant of Reaction [1], $\text{g m}^{-2} \text{ s}^{-1}$
(MO_n)	weight percent of oxide (CaO , SiO_2 , Al_2O_3 , and TiO_2) in slag
M_{MO_n}	molecular weight of oxide (CaO , SiO_2 , Al_2O_3 , and TiO_2), g mol^{-1}
M_{Si}	molecular weight of silicon, g mol^{-1}
N_{C}	mole fraction of carbon in metal
P_{CO}	pressure of CO , atm
$[\text{Si}]$	content of silicon in metal, wt pct
(Si)	content of silicon in slag, wt pct
T	temperature, K
t	reaction time, s
W_m	metal weight, g
W_s	slag weight, g
γ_{SiO_2}	activity coefficient of SiO_2 in slag
γ_{C}	activity coefficient of carbon in metal by Raoult's law
γ_{C}^0	activity coefficient of carbon at infinite dilution by Raoult's law

$\varepsilon_{\text{C}}^{\text{C}}$	self-interaction coefficient of carbon in metal
$\varepsilon_{\text{C}}^{\text{Si}}$	interaction coefficient between silicon and carbon in metal
ρ_m	metal density, kg m^{-3}
ρ_s	slag density, kg m^{-3}

Superscript and Subscript

eq	indicates equilibrium
*	indicates quantity at surface

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