Kinetics of Silicon Oxidation from Liquid Iron Droplets*

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Synopsis

A levitation technique was applied to the kinetic studies on the desiliconization of liquid iron-silicon alloys from 0.15 to 10.60%Si at temperatures from 1550° to 1800°C, by using gas mixtures containing CO₂ or O₂ with He as a diluent. Gaseous SiO was found to be a reaction product at higher temperatures and at lower oxygen potentials, the reaction being controlled by gaseous diffusions of both CO₂ and SiO to or from the surface of a droplet. The rates were interpreted in terms of well established mass transfer correlations for a gas flowing past around a sphere. The formation of solid or liquid oxide at lower temperatures was explained by the diffusion of oxygen ion through the oxide layer.

I. Introduction

The rate of oxidation of silicon in liquid iron is very important in the processes of refining and teeming of steel. The same is true with carbon and many investigators¹⁾ have shown that the rate of decarburization is controlled by gaseous diffusion. The present investigation has been undertaken to study the mechanism of desiliconization, where two kinds of oxide, gaseous SiO and liquid or solid SiO₂ have the possibility to be formed, depending upon the oxidizing conditions. The presence of these phases leads to a more complex situation than that found with carbon where only a gaseous oxide is formed.

II. Experimental

In order to avoid crucible contamination which would affect seriously the composition of the oxidation

(A) Platinum catalyst	(G) Optical pyrometer
(B) Mg(ClO ₄) ₂	(H) Levitated droplet
(C) 45°-90° prism	(I) Levitation coil
(D) Optical flat	(J) 15 mm vycor reaction tube
(E) Copper mold	(K) Ground glass union
(F) Rubber stopper	(L) Manometer

Fig. 1. Schematic diagram of the apparatus

product, a levitation melting technique was used with a 15 kW generator having a frequency of 300 kc/sec.

The reaction tube made of Vycor tubing (O.D. 1.50 cm, I.D. 1.28 cm) shown in Fig. 1 consisted of two sections joined by a ground glass union. The upper section contained the gas inlet and an optical flat to view the upper surface of the droplet. The lower section contained the reaction zone, a copper mold and a gas outlet. The coil for levitation was mounted externally to the reaction tube and had seven turns made of 3 mm O.D. thin walled copper tubing, based on a design of Baker, Warner, and Jenkins.¹⁾ For better water cooling of the coil, its wall was thinned by passing nitric acid solution and compressed water was used as well.

The flow rates of He, CO₂, and H₂ were accurately controlled by means of needle valves to maintain the gas composition constant. Gases were purified by magnesium perchlorate, ascalite and magnesium chips heated at 600°C before leading to the reaction tube. Helium was used as a diluent and a coolant, because otherwise a temperature would rise beyond control.

Temperature were controlled to within $\pm 10^\circ\text{C}$ by adjusting the power input except when the surface of the droplet was completely covered with oxidation product. It was measured continuously with a two color optical pyrometer which had been previously calibrated against the melting point of iron.

Specimens of iron-silicon alloys weighing 0.7 to 1.4 ± 0.01 g were levitated under the atmosphere of hydrogen for deoxidation while He-CO₂ or -O₂ was going to waste. After the surface of the droplet was cleaned for 1 min, the reactive gas was introduced to the reaction tube by turning the changeover cock. After the lapse of various times up to 40 min, the droplets were solidified as rapidly as possible at a levitated state by increasing the flow rate of helium and the power supply to give more levitation force, in fear that the oxidation product should be entrapped in a metallic phase during the direct quenching into a mold. The specimens thus obtained were chemically analysed for silicon, after the metal was separated from oxide. The contents of iron and silicon in the oxidation products were also determined when the amount was sufficient.

III. Results and Discussion

1. Formation of Solid or Liquid Oxide

Specimens weighing 1.4 g and containing initially

* Received September 7, 1970.

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1.22, 1.32, or 1.64%Si were held at 1 550°C in He-CO₂ or O₂, flowing at 500 ml/min for various times. The temperature rose by about 100°C due to the initial exothermic reaction and then it was controlled to a desired value. The droplets gradually were covered with oxide, starting from a film like interference fringe to a thick oxide layer (Photo. 1). As the amount of oxide increased, it tended to collect on the underside of the droplet and finally caused it to fall, the balance between its weight and the levitation force being lost. The chemical analysis showed that the oxide formed by He-CO₂ was iron silicate containing 50 to 55 wt% FeO (nearly saturated with silica), independently of time.

A series of desiliconization curves was obtained, as shown in Fig. 2. Each point represents at least three separate experiments. Roughly speaking, the plots seem to be parabolic with time. The rate increases with increasing oxygen potential of the reactive gas in order of CO₂-CO, CO₂, and O₂. Samples containing 50 mg CaO powder were also oxidized under the same conditions as before and the greater desiliconization rate by a factor of 3.4 was obtained (Fig. 3).

The parabolic behaviors of desiliconization support the view that the diffusion of a particular species in the formed oxide layer controls the rate of the reaction. Supposing that the oxide shell is thin enough to be treated as a plain plate, for the sake of simplicity, the

Photo. 1. Photographs of the upside of the droplet ($\times 70$) ($P_{\text{CO}_2}=0.05$ atm, 550 ml/min, 1 550°C)

following rate equation is obtained.

$$N_{\text{Si}} = aN_c = \frac{aD_c A(C_1 - C_2)}{l} \dots\dots\dots(1)$$

Mass balance between the metallic and oxide phases gives,

$$\frac{Al(C_1 + C_2)}{2} = \frac{(S_o - S)V}{a} \dots\dots\dots(2)$$

where Fe³⁺, Fe²⁺, Si⁴⁺, or O²⁻, being considered as a diffusing species, give 0.75, 0.5, 1.0, and 0.5 as the value of a , respectively. Combining Eqs. (1) and (2), it yields,

$$N_{\text{Si}} = \frac{D_c(C_1^2 - C_2^2)}{2(S_o - S)} \cdot \left(\frac{A}{Va}\right)^2 \dots\dots\dots(3)$$

Fig. 2. Oxidation of iron-1.2, 1.3, or 1.6% silicon droplets by various oxidizing gases at 1 550°C

Fig. 3. Analysis of the data in Fig. 2 according to Eq. (4)

Converting the unit of silicon content from moles/cm³ to wt% and integrating Eq. (3), the change in silicon content is expressed by Eq. (4).

$$\Delta \text{Si}(\%) = \frac{16800a}{d\rho M} \sqrt{D_c(C_1^2 - C_2^2)t} \dots \dots \dots (4)$$

The linear relationships hold between $\Delta \text{Si}(\%)$ and $\sqrt{t}$ in Fig. 3 except the plots towards the end of some heats, as expected by Eq. (4). The difference among the slopes of the straight lines shown in Fig. 3 should be due to that in the oxide composition, because the slope of the straight line is related to $a\sqrt{D_c(C_1^2 - C_2^2)}$. The value of C_1 was estimated for $P_{\text{CO}_2}=0.3$ for example, by using the following numerical values and assuming oxygen ion as a diffusing species. ($a=0.5$, $D=10^{-6}$ cm²/sec, $d=0.72$ cm, ρ at 1550°C=7.1 g/cm³ and slope in Fig. 3=0.095%/√min) If $C_1 \gg C_2$, 7.5×10^{-3} moles/cm³ was obtained for C_1 . When $D=10^{-5}$ cm²/sec is taken, C_1 would be 2.4×10^{-3} moles/cm³.

Gaskell²⁾ estimated from the density measurements of FeO-SiO₂ system that the concentrations of free oxygen ion are 1.3×10^{-3} , 4.8×10^{-3} , and 6.4×10^{-2} moles/cm³ for 39, 71, and 10 wt% FeO, respectively. Considering the average composition of the oxide, the obtained value of $C_1=2$ to 7×10^{-3} moles/cm³ seems to be in good agreement with Gaskell's estimation. Any of Fe²⁺, Fe³⁺, and Si⁴⁺ was found to be impossible to be a diffusing species by the similar discussions.

As for the effect of lime, both the higher diffusivity and concentration of oxygen ion in a basic oxide presumably account for the higher reaction rate. The rapid desiliconization by oxygen is also explained by the formation of oxide richer in FeO (more than 60 wt% for the first 15 min). Gases containing CO produced solid silica with little amount of FeO. The reaction proceeded more slowly owing to the less diffusivity and concentration of O⁼ in the oxide.

2. Gaseous Oxide Formation

When the temperature was raised to 1700°C for instance, keeping other conditions unchanged, the considerable fuming was observed closely to the droplet surface, being accompanied by greyish brown deposit on the wall of the reaction tube, while the surface was free of any condensed oxide phases. The deposit was found to be solid SiO with a small amount of FeO from the weight change at complete combustion in the air.

The silicon contents of the droplets changed linearly with time until the surface was covered with liquid iron silicate, as shown in Fig. 4. This behavior is similar to that of decarburization, where mass transport of oxidizing gas is rate determining. The rate of desiliconization was far greater than those at lower temperatures, that calls attention to the diffusion of gases, namely CO₂ as a reactant and SiO as a product.

Effects of Partial Pressure of CO₂ and Initial Silicon Concentration

The reaction rates for the first 1 min were determined by both the chemical analysis of silicon content and the change in the weight of specimen. They are

plotted as functions of P_{CO_2} in He (Fig. 5 (a)) and the initial silicon concentration (Fig. 5 (b)). The rate increases with increasing P_{CO_2} until the surface is covered completely with iron silicate and the desiliconization virtually ceases. The approximate critical P_{CO_2} was found to be 0.16 atm for 1.32%Si specimens and 0.10 atm for 5.85%Si at 1700°C, 500 ml/min. With the more initial silicon concentration, the greater rate was obtained until reaching a limit. These findings differ from those of decarburization, where the rate is independent of the initial carbon concentration. This seems to be inconsistent with the linear behavior of the reaction theoretically, but the influence of the previous deposit on gaseous diffusion might be responsible, as the reaction proceeded.

The value of $P_{\text{CO}_2}/\dot{n}$ was plotted against P_{CO_2} in Fig. 6 for all experiments. It shows that the linear relationship holds below the critical P_{CO_2} and the slopes of straight lines depend on the flow rate, the initial silicon concentration, and the weight of specimen.

In order to explain these observations, the following reaction mechanism was considered phenomenological-

Fig. 4. Effect of the initial composition of iron-silicon droplets on the oxidation rate of silicon at 1700°C

Fig. 5. Effect of P_{CO_2} and initial silicon content on desiliconization rates (1700°C, 500 ml/min)

Fig. 6. Analysis of desiliconization rates according to Eq. (6)

ly.

Firstly, the reaction between CO_2 and Si in metal to form SiO_2 as an intermediate compound would occur on the surface of droplet and then SiO_2 would be reduced by Si to form SiO gas. The detailed mechanism is not considered here. Assuming the rapid diffusion of Si , the establishment of chemical equilibria and the steady state of each reaction, the reciprocal of $\dot{n}$ is expressed approximately by Eq. (5), where the resistance terms of mass transport of gases in two steps are added.

$$\frac{1}{\dot{n}} = \frac{1}{k_{\text{CO}_2} P_{\text{CO}_2}} + \frac{1}{k_{\text{SiO}} K_2 \sqrt{a_{\text{Si}}}} \quad \dots\dots\dots (5)$$

where K_2 denotes the equilibrium constant of reaction (II), $P_{\text{SiO}}/\sqrt{a_{\text{Si}}}$. Multiplying both sides of Eq. (5) by P_{CO_2} , Eq. (6) is obtained.

$$\frac{P_{\text{CO}_2}}{\dot{n}} = \frac{1}{k_{\text{CO}_2}} + \frac{1}{k_{\text{SiO}} K_2 \sqrt{a_{\text{Si}}}} \cdot P_{\text{CO}_2} \quad \dots\dots\dots (6)$$

It is expected that $P_{\text{CO}_2}/\dot{n}$ changes with P_{CO_2} in a linear manner, the intercept with the axis and the slope giving the values of $1/k_{\text{CO}_2}$ and $1/k_{\text{SiO}} K_2 \sqrt{a_{\text{Si}}}$, respectively. Similarly, Eq. (7) is obtained from Eq. (5), yielding the linear relationship between $\sqrt{a_{\text{Si}}}/\dot{n}$ and $\sqrt{a_{\text{Si}}}$.

$$\frac{a_{\text{Si}}}{\dot{n}} = \frac{1}{k_{\text{SiO}} K_2} + \frac{1}{k_{\text{CO}_2} P_{\text{CO}_2}} \cdot \sqrt{a_{\text{Si}}} \quad \dots\dots\dots (7)$$

This also gives $1/k_{\text{SiO}} K_2$ and $1/K_{\text{CO}_2} P_{\text{CO}_2}$ by the intercept and slope. The numerical values of k_{CO_2} and k_{SiO} obtained from the above two relations (Eqs. (6) and (7)) should agree, as far as the assumptions for the reaction mechanism are reasonable.

For k_{CO_2} and k_{SiO} , 3.49×10^{-4} and 1.61×10^{-3} moles/cm² sec atm were respectively obtained from Fig. 6, for 1.4 g specimens with 1.32% initial silicon at flow rates from 500 to 1 000 ml/min, because the flow rate dependence was not significantly observed in this range. The flow rate of 250 ml/min gave less values for both k_{CO_2} and k_{SiO} , namely 2.86×10^{-4} and 1.43×10^{-3} moles/cm² sec atm. The figure also gives $3.71 \times$

Fig. 7. Analysis of desiliconization rates according to Eq. (7)

10^{-4} and 1.36×10^{-3} moles/cm² sec atm to k_{CO_2} and k_{SiO} for 0.7 g specimens with 5.85% silicon at 500 ml/min. Here, K_2 of 0.250 was used according to JANAF thermochemical tables.³⁾ Densities of iron-silicon alloys were referred to Dzhemilev, Popel', and Tsarevskiy,⁴⁾ and the values reported by Chipman and Baschwitz¹²⁾ were used as the activities of silicon, assuming a regular behavior.

Figure 7 shows the effect of initial silicon activity according to Eq. (7), where a straight line is drawn on the basis of k_{CO_2} and k_{SiO} obtained from Fig. 6. The validity of Eq. (5) is confirmed by the fact that the plots are not very far from the line.

The measured values of k_{CO_2} are now discussed in the light of the estimation by the empirical mass transfer correlation for a gas flowing past around a sphere, which was applied to the decarburization rates by Distin, Hallet, and Richardson.⁵⁾

$$Sh = 2 + 0.5(Gr' \cdot Sc)^{0.25} + n(Re \cdot Sc^{0.5})^{0.62} \quad \dots\dots\dots (8)$$

where,

$$Gr' = Gr_M + \left(\frac{Sc}{Pr} \right)^{0.5} \cdot Gr_H$$

The first term of Eq. (8) expresses the effect of radial diffusion, the second of natural convection, and the third of forced convection. The average of room, T_b and droplet surface temperatures, T_o was used for a film temperature T_f . The values of diffusivity D , viscosity μ , and thermal conductivity k' for the mixed gas were estimated according to Bird, Stewart, and Lightfoot.⁶⁾ The numerical values of the physical properties used are listed below for desiliconization by P_{CO_2} of 0.0264 atm. $T_f = 1\,133^\circ\text{K}$, $D = 5.53$ cm²/sec, $\mu = 4.27 \times 10^{-4}$ poise, $k' = 7.35 \times 10^{-4}$ cal/cm sec $^\circ\text{K}$, $C_p = 1.03$ cal/g $^\circ\text{K}$, $\rho = 5.44 \times 10^{-5}$ g/cm³, $\rho_M = 6.83$ g/cm³ (1.32%Si), 6.51 g/cm³ (5.85%Si), $d = 0.731$ cm (1.32%Si, 1.4 g), 0.590 cm (5.85%, 0.7 g), $d_T = 1.28$ cm.

For n in Eq. (8), 0.60 and 0.50 were respectively used for 0.7 g and 1.4 g specimens.

According to Eq. (8), the values of Sh and k_{CO_2} are estimated for given conditions. The estimated values of k_{CO_2} are shown in Fig. 8 for 1.4 and 0.7 g specimens separately as a function of (flow rate)^{0.62}. Since the droplet is not so small as compared with the diameter of the reaction tube, the wall effects should not be

Fig. 8. Estimated and measured mass transfer coefficients

ignored. Citing the correction factors for friction force from a book of Happel and Brenner,⁷⁾ related to the ratio of diameters of a rigid sphere and a cylinder, linear velocity U , Re and then k_{CO_2} were corrected, as shown in Fig. 8. The measured k_{CO_2} lies between the estimate with wall correction and that without it. Taking into account that the correction should be made for a circulating liquid sphere, the measured and estimated values are considered to be in good agreement for both 0.7 and 1.4 g specimens. At 250 ml/min, the measured rate is smaller than the estimate. As the flow rate is decreased, it is stoichiometrically impossible for the measured reaction rate to reach the estimate, because the supply of CO_2 is not sufficient, the efficiency of CO_2 reaching 100%.

Condensation of SiO

It has been found by some investigators⁸⁾ that solid SiO is stable in a thermodynamic sense. Considering that the deposit was mainly solid SiO in this study, the condensation of SiO gas in the hydrodynamic boundary layer seems to be responsible for that the measured k_{SiO} is greater than k_{CO_2} . The following is the estimation of the degree of supersaturation which was necessary for the condensation of SiO, based on the concept of Turkdogan.⁹⁾

Figure 9 is a schematic profile of temperature and P_{SiO} in the laminar boundary layer. The values of Pe and P_{SiO} at equilibrium, are determined thermodynamically when a temperature profile is known. If the supersaturation is required for the nucleation, the virtual vapor pressure Pn should be s times greater than Pe . The tangent to the curve Pn from the point P_0 , which represents P_{SiO} at the surface of droplet, should yield the flux of transport of SiO by convection-condensation process. Assuming that δ_T , the boundary layer thickness for temperature is approximated by δ_{CO_2} , that for diffusion of CO_2 , which was obtained experi-

Fig. 9. Vapor concentration and temperature profiles in the boundary layer

mentally, the temperature profile is expressed by Eq. (9).

$$T = T_0 - \frac{T_0 - T_b}{\delta_{CO_2}} \chi \quad \text{.....(9)}$$

The boundary layer thicknesses δ_{CO_2} and δ_{SiO} are expressed by the definition.

$$\delta_{CO_2} = \frac{D_{CO_2}}{RT_f k_{CO_2}}, \quad \delta_{SiO} = \frac{D_{SiO}}{RT_l k_{SiO}} \quad \text{.....(10)}$$

where

$$T_l = \frac{(T_0 + T_c)}{2}$$

From Eq. (10), Eq. (11) is derived by using that the gas diffusivity is proportional to $T^{1.5}$.

$$\begin{aligned} \frac{\delta_{SiO}}{\delta_{CO_2}} &= \frac{(D_{SiO})T_l}{(D_{CO_2})T_f} \cdot \frac{k_{CO_2}}{k_{SiO}} \cdot \frac{T_f}{T_l} \\ &= \left(\frac{D_{SiO}}{D_{CO_2}} \right)_{T_f} \cdot \frac{k_{CO_2}}{k_{SiO}} \cdot \left(\frac{2T_f}{T_c + T_0} \right)^{0.5} \quad \text{.....(11)} \end{aligned}$$

The tangent from P_0 to the curve Pn is

$$\frac{P_0}{\delta_{SiO}} = \frac{dPn}{d\chi} = s \frac{dPe}{d\chi} \bigg/ \frac{dT}{d\chi} = s \frac{dPe}{d\chi} \cdot \frac{\delta_{CO_2}}{T_0 - T_b} \quad \text{... (12)}$$

by using $Pn = s \cdot Pe$ and Eq. (9).

Distance beyond which condensation occurs, χ_c is defined by Eq. (13)

$$\chi_c = \delta_{SiO} \left(1 - \frac{Pn}{P_0} \right) \quad \text{.....(13)}$$

Pe is expressed by Eq. (14), according to Kubachewski, Evans, and Alcock.⁸⁾

$$\log Pe = - \frac{17750}{T} - 2.77 \log T + 16.77 \quad \text{.....(14)}$$

Solving Eqs. (9), (11), (12), (13), and (14), the values of T_c , Pn , δ_c , and s for the oxidation by P_{CO_2} of 0.0264 atm were estimated by using the measured k_{CO_2} and k_{SiO} , $D_{SiO}/D_{CO_2} = 1.07$, $T_b = 293^\circ K$, and $T_0 = 1973^\circ K$. P_0 was calculated by the measured rate $\dot{n}$ and Eq. (15).

$$\dot{n} = k_{SiO} P_0 \quad \text{.....(15)}$$

Table 1. Summary of calculations for condensations of SiO ($P_{\text{CO}_2}=0.0264$, 500 ml/min, 1700°C)

Weight (g)	Si (%)	k (moles/cm ² sec) $\times 10^4$		T_c (°K)	δ (cm) $\times 10^2$		χ_c (cm) $\times 10^2$	P_o (atm) $\times 10^4$	P_e (atm) $\times 10^4$	P_n (atm) $\times 10^4$	s
		CO ₂	SiO		CO ₂	SiO					
0.7	5.85	3.71	17.5	1575	16.0	4.55	3.77	31.9	4.42	5.35	1.21
1.4	1.32	3.49	16.1	1564	17.0	4.94	4.14	15.4	3.76	2.50	0.664

The calculations are summarized in Table 1 for 0.7 g and 1.4 g specimens. The table shows that SiO condenses at the distance beyond 0.038 cm from the surface, for 0.7 g droplet, where the temperature is 1300°C and the partial pressure of SiO is 5.4×10^{-4} atm. The value of s less than 1.00 in Table 1 is due probably to the rough approximations (See Appendix). It follows from this table that the homogeneous nucleation of solid SiO does not require great supersaturation. Thus, it is likely that the diffusion of SiO gas is enhanced by the nucleation-condensation process.

Effect of Weight of Specimens

Whichever of transports of CO₂ and SiO may be more important in the reaction (see Eq. (5)), the ratio of total desiliconization rates between two specimens with different weights should be equal to that of mass transfer coefficients of gas, only if those of CO₂ and SiO have the same dependence on the weight of specimen. Table 2 shows the agreement of experimental results with theoretical estimations for specimens with various initial silicon concentrations.

Effect of Temperature

The reaction rates are plotted against the reciprocal of absolute temperature for 1.32% and 5.85% iron-silicon alloys (Fig. 10). At 1800°C or higher, the vaporization of iron retarded seriously the silicon reaction by consuming CO₂ to form FeO. At lower temperatures than 1650°C, solid silica was formed and the rates were too small to be plotted in the figure. The apparent activation energy for 1.32%Si at higher temperatures than 1700°C is 8.2 kcal/mole, whereas it is 93.9 kcal/mole between 1650° and 1700°C. Suppose that 8.2 kcal/mole corresponds to the temperature dependence of k_{CO_2} and 93.9 kcal/mole does to that of K_2k_{SiO} , the apparent activation energy of k_{SiO} is calculated to be 20.6 kcal/mole, taking account of +73.6 kcal/mole, a half of the enthalpy change of reaction (II). Although the transport of gas is not an activation process, the activation energy was calculated to be 6.2 kcal/mole apparently in the temperature range concerned. However, this treatment of activation energies is not accurate enough to discuss the difference between the experimental estimations, and the theory for gas diffusion, owing to the lack of available data.

Consequently, it is presumed that the transport of CO₂ in reaction (I) controls the process more predominantly than that of SiO in reaction (II) at higher temperatures and *vice versa* at lower temperatures.

Estimation of Critical Conditions to Form Condensed Phases

Silicon content at oxide formation towards the end

Table 2. Rates of desiliconization ($\dot{n}$ (mole/cm² sec) $\times 10^6$) related to specimen weights ($P_{\text{CO}_2}=0.0264$, 500 ml/min, 1700°C)

		Initial silicon concentration (%)			
		1.32	2.45	3.60	5.85
Weight (g)	0.7	2.68		4.72	5.54
	1.0		3.98		
	1.4	2.44	3.78	4.28	4.76
Ratio	Experimental	1.10	1.05	1.10	1.16
	Theoretical	1.10	1.04	1.10	1.10

Fig. 10. Relationship between desiliconization rates and temperature (1.4 g, 500 ml/min)

of the process is determined by the relative rate of the diffusion of silicon from the bulk of a droplet to the surface, compared with that of gas diffusion. The diffusion in a droplet is expressed by Eq. (16).

$$-\frac{d\text{Si}(\%)}{dt} = \frac{AD_{\text{Si}}\text{Si}(\%)}{V\delta_M} \dots\dots\dots(16)$$

where the concentration at the surface was reasonably assumed to be zero at oxide formation. Choosing the results of 5.85%Si specimens in Fig. 4 for example, the value of D_{Si}/δ_M was obtained to be 3.3×10^{-3} cm/sec, where $-d\text{Si}/dt=0.40$ wt%/min, $\text{Si}=0.18\%$, $A/V=10.2$ l/cm at oxide formation. δ_M is 1.5×10^{-2} cm, using $D_{\text{Si}}=4.9 \times 10^{-5}$ cm²/sec at 1700°C by Calderon, Sano, and Matsushita.¹⁰⁾

Turkdogan, Grieveson, and Darken¹¹⁾ evaluated the critical P_{CO_2} for a vaporization-oxidation process of metals, by equalizing the free vaporization rate of a

metal in vacuo to the diffusion rate of CO_2 under given hydrodynamic conditions. If this is the case in maintaining the surface of a droplet bare to form SiO gas, the critical P_{CO_2} is estimated to be 0.16 atm. The agreement with the experiments (Fig. 5) is satisfactory.

IV. Conclusions

The removal of silicon from liquid iron-silicon alloys using CO_2 is predominantly controlled by gaseous diffusion when the conditions for the formation of SiO gas are satisfied. On the other hand, at lower temperatures and for higher P_{CO_2} , the reaction product was found to be solid silica or liquid iron silicate, where the reaction proceeds far more slowly and the diffusion of oxygen ion in the oxide layer is rate controlling.

These observations are of great practical significance in relation to the mechanism of desiliconization in a basic oxygen furnace, where silicon initiates to be removed even before the complete slag formation. Very high temperature near the fire point seems to be favorable for gaseous oxide formation by CO_2 as a combustion product of CO .

Acknowledgements

Thanks are due to Dr. R. G. Ward, formerly, Professor, McMaster University, Hamilton, Ontario, Canada, and presently, Director of Research, Broken Hill Proprietary, Melbourne, Australia for helpful suggestions when one of the authors started this study at McMaster. The authors are also indebted to Miss Mizuko Iwata for her technical assistance.

A part of this work was presented at the International Conference of the Science and Technology on Iron and Steel held in September, 1970 in Tokyo.

Nomenclature

A : surface area (cm^2)
 a : molar equivalent of silicon to diffusing species (—)
 a_{Si} : activity of silicon in iron-silicon alloy (—)
 C_1 : concentration of diffusing species at oxide-gas interface (moles/cm^3)
 C_2 : concentration of diffusing species at oxide-metal interface (moles/cm^3)
 C_p : heat capacity of gas ($\text{cal/g}^\circ\text{K}$)
 D : diffusion constant (cm^2/sec)
 d : diameter of droplet (cm)
 d_T : inner diameter of reaction tube (cm)
 g : acceleration of gravity (cm/sec^2)
 h : heat transfer coefficient ($\text{cal/sec cm}^2 ^\circ\text{K}$)
 k : mass transfer coefficient ($\text{moles/cm}^2 \text{ sec atm}$)
 k' : thermal conductivity of gas ($\text{cal/sec cm} ^\circ\text{K}$)
 P : partial pressure (atm)
 P_e : vapor pressure (atm)
 P_n : vapor pressure required for nucleation (atm)
 S : concentration of silicon (moles/cm^3)
 S_o : initial concentration of silicon (moles/cm^3)
 s : degree of supersaturation (—)
 T : absolute temperature ($^\circ\text{K}$)
 T_c : temperature at condensation of SiO ($^\circ\text{K}$)
 U : linear velocity of gas in tube (cm/sec)
 V : volume of droplet (cm^3)

χ : distance from the surface of droplet (cm)
 χ_c : distance from the surface of droplet beyond which condensation occurs (cm)
 δ : boundary layer thickness (cm)
 μ : gas viscosity (g/cm sec)
 ρ : density (g/cm^3)
 Gr_H : Grashof number for heat transfer ($gd^3\rho_f^2(T_o - T_b)/\mu_f^2 \cdot T_f$)
 Gr_M : Grashof number for mass transfer ($gd^3\rho_f(\rho_o - \rho_b)\mu_f^2$)
 Nu : Nusselt number (hd/k')
 Pr : Prandtl number ($(\mu C_p/k')_f$)
 Re : sphere Reynolds number ($\rho_f U d/\mu_f$)
 Sc : Schmidt number ($(\mu/\rho D)_f$)
 Sh : Sherwood number (kd/D)

Subscripts

b : property in bulk gas
 c : property of diffusing species
 f : property at film temperature T_f
 M : property in metal phase
 o : property at surface of droplet

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Appendix

In the foregoing paper, the boundary layer for heat transfer δ_T was assumed to be equal to that for mass transfer of CO_2 , δ_{CO_2} . However, δ_T is theoretically different from δ_{CO_2} , so that the values of δ_T are estimated in Appendix by using the following dimensionless equation analogous to Eq. (8), and then the influence of the correction of δ_T on the numerical values in Table I was inspected.

$$Nu = 2 + 0.5(Gr'' \cdot Pr)^{0.25} + n(Re \cdot Pr^{0.5})^{0.62}$$

where
$$Gr'' = Gr_H + \left(\frac{Pr}{Sc}\right)^{0.5} \cdot Gr_M$$

At the same time, the activity of silicon in liquid iron recently measured by R. J. Fruehen (*Met. Trans.*,

Table A. Summary of recalculations for the condensation of SiO ($P_{\text{CO}_2}=0.0264$, 500 ml/min, 1 700°C)

Weight (g)	Si (%)	k (moles/cm ² sec) $\times 10^4$		T_c (°K)	δ (cm) $\times 10^2$		z_c (cm) $\times 10^2$	P_o (atm) $\times 10^3$	P_e (atm) $\times 10^5$	P_n (atm) $\times 10^4$	s	$\delta_T/\delta_{\text{CO}_2}$
		CO ₂	SiO		CO ₂	SiO						
0.7	5.85	3.71	10.5	1 361	16.0	6.39	5.85	4.62	1.12	3.94	25.34	1.003
1.4	1.32	3.49	9.61	1 253	17.0	7.89	7.41	2.57	0.105	1.60	151.6	1.017

1, (1970), 865) was used for the recalculation instead of reference (12). The activity coefficient of silicon at 1 700°C was estimated from his data at 1 600°C, assuming the regular solution. This gave the greater activities of silicon by a factor of 2.8 and 2.1 than the previous values at 1.32%Si and 5.85%, respectively.

The results of the recalculation are tabulated in Table A.

The values of $\delta_T/\delta_{\text{CO}_2}$ are almost equal to unity for both cases, so that the significant change in the numerical values should be mainly due to the choice of the activity data. However, the fact that the estimated degrees of supersaturation greatly exceed or nearly equal unity should be a good evidence for the possibility that the formation of SiO may be enhanced by the condensation within the boundary layer.