Silicon–Oxygen Equilibrium in δ-iron at the Solid–Liquid Equilibrium Temperature*

By Toshiharu FUJISAWA,** Makoto NOMURA*** and Hiroshi SAKAO**

Synopsis

Experiments were carried out using the zone melting technique on the silicon–oxygen equilibrium in δ-iron at the solid–liquid equilibrium temperature.

The deoxidation constant with silicon in liquid iron was \( \log K_{\text{Si}}(l) = -5.18 \) \([\%\text{Si}(l)] < 0.64\) at this temperature, which is in good agreement with the values given in the literature.

The silicon–oxygen equilibrium relationship in δ-iron at the solid–liquid equilibrium temperature is represented by the following equations:

\[
\log \frac{\alpha_{\text{Si}}(s) \alpha_{\text{O}}(s)^2}{\alpha_{\text{SiO}}(s)} = -7.19 \quad (\%\text{Si}(s) \leq 0.5) \\
\log f_{\text{Si}}(s) = 0.086 \%\text{Si}(s) \\
\log f_{\text{O}}(s) = -15.9 \%\text{O}(s) \\
\log f_{\text{O}}(s) = -9.05 \%\text{Si}(s) + 30 \%\text{Si}(s)^2 \quad (\%\text{Si}(s) \leq 0.1)
\]

I. Introduction

Deoxidizing elements and oxygen are less soluble in a solid iron than liquid iron, so that the precipitation of deoxidation products is an inevitable phenomenon during the solidification in the conventional steelmaking practices. It is, therefore, necessary to know the deoxidation equilibrium in δ-iron together with that in liquid iron to clarify quantitatively such a phenomenon. However, the deoxidation equilibrium in δ-iron has not yet been studied, while there have been many reports about the deoxidation of liquid iron.

In the present work, the solid–liquid equilibrium in Fe–Si–O alloy was measured using the floating zone melting technique, and the silicon–oxygen equilibrium relationship in δ-iron was determined.

II. Experiment

1. Preparation for Specimens

Electrolytic iron (Fe>99.95%) was melted in a magnesia crucible by high frequency inductive heating. The melt was deoxidized under a gas stream of Ar–H₂ (1:1) mixture to control the oxygen content. Suitable amounts of metallic silicon (Si>99.9%) were added into the melt. Then, the melt was sucked up into a silica tube of 8 mm I.D. and quenched in water. The rods were polished and cut into 7.7×250–300 mm.

2. Experimental Apparatus

The experimental apparatus used in the present work consists of a high frequency generator and a floating zone melting furnace. The schematic diagram of the furnace and the induction coil is shown in Fig. 1. The maximum output of the generator is 12 kW and the frequency about 390 kHz. The specimen (7.7 mm²) was inserted into an opaque silica tube of inner diameter 7.8–7.9 mm, then mounted in the furnace. When it is zone melted by traveling the induction coil upward, the molten zone contacts with the silica tube.

3. Experimental Procedure

1. Fe–Si–O System

After setting the specimen in the zone melting furnace, the furnace atmosphere was once evacuated below 1 Pa by a rotary pump, then the furnace was filled with the argon purified by a rare gas purifier. During the experiment, the argon was streamed in the furnace at a constant flow rate of about \(10^{-3} \text{ m}^3/\text{min}\), keeping the pressure about 10² Pa higher than the atmospheric pressure. The specimen was zone melted by traveling the induction coil upward at a constant rate (0.2–1 mm/min). After the zone melting for a suitable distance, the induction power supply was cut off. The specimen was quenched by increasing the argon flow rate.

2. Fe–Si System

Floating zone melting experiments were carried out also for low oxygen Fe–Si specimens (lower than 40 ppm) without the silica tube. The procedure was almost same as the case of the Fe–Si–O system except the following:

(1) The zone melting was done under the hydrogen atmosphere.

(2) The lower part of the specimen was rotated at 30 rpm to stabilize the molten zone.
3. Analyses

The lengthwise concentration profiles of silicon and oxygen in the specimen were determined by chemical analyses. The analytical methods and the accuracies are as follows:

1. Si: molybdenum-blue photometrical method (JIS-G1212)
   \[ \pm 0.004\% ; \%Si \geq 0.1 \]
   \[ \pm 0.002\% ; \%Si < 0.1 \]

2. O: argon fusion automatic coulometric method (±4 ppm).

Some of the specimens were sawed lengthwise and prepared for the metallographic examinations and EPMA analyses.

4. Determination of the Solid-Liquid Equilibrium Distribution Coefficient in the Zone Melting Experiment

Figure 2 represents the schematic drawing of the redistribution of the solute during the zone melting when the molten zone is traveled at a constant rate \( f \), where \( l \) is the molten zone length, and \( X \) the traveling distance. The combination of the mixing by the inductive stirring in the liquid and the solute transfer promoted by the solid-liquid distribution sets up a diffusion boundary layer \( \delta \) in the molten zone adjacent to the solidification front.

According to the theories concerning to zone melting, there are three ways to determine the solid-liquid equilibrium distribution coefficient of solute, \( L = \frac{C_s}{C_L} \).

1. From the equilibrium relationship at the starting point

The equilibrium distribution coefficient can be determined from \( C_{00} \) by \( L = \frac{C_{00}}{C_{L0}} \) as \( C_{1B} = C_L = C_0 \) at the starting point. This method, however, has not been usually used. The reasons are (1) molten zone is unstable at the initial period of zone melting, and (2) it is difficult to determine precisely solute concentration at the zone with a remarkable change of composition. Furthermore, the equilibrium condition with \( \text{SiO}_2 \) cannot be established which must be satisfied in the present work, because it takes for a sufficient period and/or for a sufficient traveling distance. Thus, this method seems not to be suitable for the present purpose.

(2) From the concentration profile of solute in crystallized solid

The distribution of the solute in the crystallized solid after a passage of molten zone is described by Eq. (1):\(^{31}\)

\[ \ln \left( 1 - \frac{C_s}{C_0} \right) = \ln \left( 1 - L' \right) - \frac{L' \cdot X}{l} \quad \ldots \ldots \ldots (1) \]

where, \( L' = C_s/C_0 \): an effective distribution coefficient. The equilibrium distribution coefficient \( L \) can be obtained from the relation between the effective ones and traveling rates \( f \), according to Eq. (2) which will be shown soon later.

(3) From the distribution relationship of the final solidified region

When the molten zone is traveled so long that the amount of solute in solid entering the zone is the same as that freezing out, then a steady state is established. From the mass balance in the diffusion boundary layer in the molten zone, the following equation\(^2\) can be derived:

\[ \ln \left( \frac{1}{L'} - 1 \right) = \ln \left( \frac{1}{L} - 1 \right) - \frac{f \cdot \delta}{D} \quad \ldots \ldots \ldots (2) \]

where, \( D \): the diffusion coefficient of solute, and \( \delta \): the thickness of the boundary layer.

The effective distribution coefficient \( L' \) is determined from \( C_s \) and \( C_0 \) in the terminal zone of the specimen after the zone melting for a sufficient distance. The equilibrium distribution coefficient \( L \) can be calculated from the dependency of \( L' \) on \( f \) by using Eq. (2).

Ooka and co-workers\(^3\) have studied on the distribution of solute atoms in the floating zone melting iron. When the solute is relatively volatile such as manganese, the distribution curve cannot be represented by Eq. (1) in which only the segregation of solute has been considered. Thus, the solid-liquid distribution coefficient cannot be determined from the distribution curve. Also, as the dissolution or the precipitation of \( \text{SiO}_2 \) in the molten zone is expected to take place in the present experiments, it is impossible to determine the solid-liquid distribution coefficient from the distribution curve of solute in the solidified part. Therefore, the distribution coefficient was determined from the build-up of solute at the final zone.

III. Experimental Results

Figure 3 shows an example of the solute distribution in the Fe–Si–O specimen after the zone melting. At about 3~4 cm long zone melting, the concentrations of both silicon and oxygen reached constant values within the errors of chemical analyses. It means that the steady state has been attained. From the distribution coefficient of oxygen at the final zone, the zone melting distance necessary to attain the steady state can also be calculated by Eq. (1) to be about 7 cm in the case of Fig. 3. The discrepancy between the both can be explained as follows; the dissolution of \( \text{SiO}_2 \) may occur at the initial period to promote the attainment for the steady state, as the dissolution rate of \( \text{SiO}_2 \) into liquid iron is comparatively high.\(^4\)
In the case of the Fe–Si system, the steady state is attained at about 3 cm long zone melting. It agrees well with the result calculated by Eq. (1). The oxygen contents in the solidified parts of the Fe–Si specimens are 8–10 ppm, obviously much lower than those of the Fe–Si–O specimens with the same silicon content.

The compositions of the molten zone and the finally solidified part in the Fe–Si–O specimens are shown in Fig. 4. The respective runs at the same silicon content show a good agreement, independent of the solidification rate $f$.

Next, these results were analysed by using Eq. (2) given by Burton et al. $^2$ Figure 5 shows the relation between $\ln \left(1/L_{11} - 1\right)$ and $f$. At the higher silicon content, $\ln \left(1/L_{11} - 1\right)$ is a fixed value, independent of $f$. At the lower silicon content, however, there is no obvious relationship, otherwise a decreasing tendency with increasing $f$. If the analytical errors marked by $\Delta$ and the relationship recognized in the case of higher silicon content are taken in consideration, then it should be rather appropriate to consider that $L_{11}$ is also a fixed value even at the low silicon content.

In the Fe–Si specimen, there are definite dependencies of $\ln \left(1/L_{11} - 1\right)$ on the traveling rate of molten zone. The relations are well represented by straight lines with a negative gradient. From this gradient, the value of $\delta/D$ was calculated to be about 0.1 min/mm. As the diffusion coefficient of silicon in liquid iron is $D_{Si}=2\times 10^{-5}$ cm$^2$/sec, $\delta$ can be estimated to be about $2\times 10^{-3}$ cm in this case. According to Pfann, $^1$ $\delta$ is about $10^{-3}$ cm for a vigorous stirring and $10^{-1}$ cm for a mild one. Therefore, it would be expected for the molten zone to be stirred vigorously.

In the Fe–Si system, the $L_{11}$ obtained from the intersection of the line and vertical axis agrees well with the result of the previous work $^6$ within the experimental errors. The dependency on the silicon content recognized also coincides well with the previous work. $L_{11}$ in the Fe–Si–O system is different from that in the Fe–Si system, due to the effect of the interaction between silicon and oxygen, as will be described later.

Figure 6 shows the relation between $\ln \left(1/L_{00} - 1\right)$ and $f$ in the Fe–Si–O system. $L_{00}$ is also fixed to be a constant value as well as $L_{11}$ within the experimental errors. The composition dependency of $L_{00}$ is also due to the interaction between silicon and oxygen.
IV. Discussion

1. Discussion of Experimental Conditions

1. Applicability of the Solidification Model Given by Burton et al.2)

Since Eq. (2), which was used in the present work, has been derived from the equation of mass balance concerning to the diffusion boundary layer in liquid phase, the following conditions must be satisfied:

(1) The solid and liquid phases are in equilibrium at the solidification front, and the solute contents can be related by the solid–liquid equilibrium distribution coefficient $L$.

(2) The solidification front is flat, i.e. the so-called planar solidification condition is satisfied.

(3) The inlet and outlet rates of solutes in the molten zone are balanced and a steady state is accomplished. Equation (2) can be available also for the condition in which the diffusion cannot be ignored in the solid phase, but not Eq. (1).

The condition (1) is the fundamental assumption which is made in the most theoretical treatments of solidification. This assumption has led to the values of $L_s$ from the present measurements of the Fe–Si system, which are in good agreement with the results of the previous work6 on the solid–liquid equilibrium. Consequently, all necessary conditions for Eq. (2) are satisfied in the present investigation, and the equilibrium distribution coefficient $L$ can be obtained from the correlation between $L'$ and $f$. As mentioned above, it is the case in the Fe–Si system (Fig. 5). In the Fe–Si–O system, however, no dependency of $L'$ on $f$ was recognized as shown in Figs. 5 and 6. It means apparently $\delta \rightarrow 0$, according to Eq. (2). Even if the melting condition of the ternary system is somewhat different from that of the Fe–Si system, $\delta = 0$ is far beyond reason.

Consequently, Eq. (2) is not strictly applicable for the Fe–Si–O system. One of the reasons may be the occurrence of reactions between the solutes in the diffusion boundary layer, which has not been considered for the derivation of Eq. (2), i.e., in the case of the Fe–Si–O system, it should be taken into account that the deoxidation reaction with silicon takes place in the boundary layer. It is sufficiently possible to occur, because (1) the solutes are rejected from the crystallized solid and enriched in the liquid phase, (2) the interface is favorable for the nucleation of SiO$_2$, and (3) the bulk composition of the molten zone is in good agreement with the equilibrium composition with SiO$_2$, as will be mentioned later (Fig. 7).

Therefore, under the steady state condition, the enrichment of solutes is balanced with the consumption by the deoxidation reaction, and the composition of the molten zone at the solidification front becomes approximately the same as that in the bulk.

It is consequently concluded that the solidification model given by Burton et al.30) is not strictly applicable for the Fe–Si–O system, but that the equilibrium distribution coefficient can be obtained by $L = L'$ within the limit of experimental accuracy, when three conditions mentioned above are satisfied.

2. SiO$_2$ in Crystallized Solid

If SiO$_2$ is formed at the solidification front by the deoxidation reaction with silicon, it must be taken into consideration that SiO$_2$ is possible to be entrapped into the crystallized part during the solidification. The more the advancing rate of the interface, i.e. the traveling rate of the molten zone $f$, exceeds the leaving rate of SiO$_2$ from the interface, the more the amount of SiO$_2$ entrapped is remarkable. In the analytical methods used, this SiO$_2$ entrapment has no effect on the result of silicon analyses, but does much on that of oxygen analyses so that its content should increase with increasing $f$. However, it is evident from Fig. 4 that in the series of the same silicon content the oxygen contents of the crystallized solids in respective specimens coincide well with each other independent of $f$. Therefore, the entrapment of SiO$_2$ precipitated in the molten zone seems to be negligibly small.

A microscopic examination showed few globular nonmetallic inclusions with diameter less than 2 $\mu$m in the crystallized solid of the Fe–Si–O specimen. These are probably of silica or silicate. The volumetric fraction of inclusions was estimated from the mean diameter and the number of inclusions, then the amount of oxygen in the inclusions was calculated, assuming that those inclusions were of SiO$_2$. This calculation has confirmed that the effect of the inclusions on the analytical value of the oxygen content is within the experimental error, i.e. even if all of these inclusions had been trapped in the crystallized part during the solidification, they did not affect on the experimental results.

After the solidification, the crystallized part was kept at relatively high temperature for a while. Therefore, the reaction to form SiO$_2$ is possible to occur due to the decrease of the solubility product of silicon and oxygen in the solid phase with the descending temperature. This case, on the contrary to the above mentioned case, affects on the analytical value of silicon content in the crystallized part. But no effect is anticipated when the silicon content is much higher than oxygen content. Only when the silicon content is very low, the effect is possible to arise. It will be described later on this respect.

2. Silicon–Oxygen Equilibrium in Molten Zone

The deoxidation reaction of liquid iron with silicon and the equilibrium constant are represented by Eqs. (3) and (4), respectively, as follows:

$$\text{SiO}_2(\text{solid}) = \text{Si} + \text{O}_2 \quad \text{(3)}$$

$$K_{\text{eq}}(l) = \frac{a_{\text{Si}}(l) \cdot a_{\text{O}_2}(l)^2}{a_{\text{SiO}_2}} \quad \text{(4)}$$

Research Article
where $a_{\text{Si}}(l)$ and $a_{\text{O}}(l)$ are the activities of silicon and oxygen in liquid iron, respectively, when the reference state of the activity is chosen at infinite dilution and the concentrations of solutes are represented by weight percent. $a_{\text{SiO}}$ is the activity of SiO$_2$ relative to the pure solid. As the molten zone has a contact with the silica tube, $a_{\text{SiO}}$ can be regarded as unity in the present work. Consequently, Eq. (4) becomes Eq. (5), and the solubility product is represented by Eq. (6),

$$K_{\text{Si}(l)} = a_{\text{Si}}(l) \cdot a_{\text{O}}(l)^2 \quad \ldots \ldots \ldots (5)$$

$$K'_{\text{Si}(l)} = \{\%\text{Si}(l)\} \cdot \{\%\text{O}(l)\}^2 \quad \ldots \ldots \ldots (6)$$

Assuming that $K_{\text{Si}(l)}$ is approximately constant in the range of the present measurements, $\log K_{\text{Si}(l)} = -5.14$ can be calculated from the results shown in Fig. 4.

As the equilibrium constant $K_{\text{Si}(l)}$ depends only on temperature, $K_{\text{Si}(l)}$ holds a fixed value independent of the metal composition at a certain temperature. In the present experiments, it is quite difficult to measure the temperature of the molten zone. So, instead of its measurements, it is necessary to estimate it by a suitable way. Under the condition of the present experiments, the temperature at the solidification front is considered to be equal to the solid-liquid equilibrium temperature of alloy. Though the bulk temperature of molten zone will be somewhat higher than the interfacial temperature, the difference may be not so much. Therefore, the molten zone temperature was approximated with the solid-liquid equilibrium temperature of the metal alloy.

It has been confirmed in our previous work that the solid-liquid equilibrium temperature of Fe-Mn-Si alloy can be approximately estimated by the gradients of liquidus lines in both Fe-Mn and Fe-Si binary phase diagrams. If the similar relationship is held for the Fe-Si-O system, the temperature is represented by Eq. (7) as a function of the concentrations of silicon and oxygen in the liquid phase:

$$T(K) = 1811 - 11.4[\%\text{Si}(l)] - 62.5[\%\text{O}(l)] \quad \ldots \ldots \ldots (7)$$

Here for the lowering degree of the solidification temperature of the melt by the addition of silicon, the result of the present work is used, and for that by oxygen, the result of Kusano et al. When the experimental results were substituted into Eq. (7), the solid-liquid equilibrium temperature was calculated to be $1531^\circ - 1537^\circ C$ (the mean temperature $1535^\circ C$). Therefore, the present experiments can be regarded as the isothermal ones.

Equilibrium constant $K_{\text{Si}(l)}$ is, using the interaction coefficients,

$$\log K_{\text{Si}(l)} = \log \{\%\text{Si}(l)\} \cdot \{\%\text{O}(l)\}^2 + \log f'_{\text{Si}}(l) + \log f'^{\prime\prime}_{\text{Si}}(l) \quad \ldots \ldots \ldots (8)$$

As silicon and oxygen contents are relatively low in the present experiments, each interaction coefficient $f'_i$ can be written by

$$\log f'_i = \epsilon_i \cdot [\%j] \quad \ldots \ldots \ldots \ldots \ldots (9)$$

and Eq. (8) becomes

$$\log K_{\text{Si}(l)} = \log \{\%\text{Si}(l)\} \cdot \{\%\text{O}(l)\}^2 + \{\epsilon_{\text{Si}}(l) + 2\epsilon_{\text{O}}(l)\} \cdot [\%\text{Si}(l)]$$

$$+ \{\epsilon_{\text{Si}}(l) + 2\epsilon_{\text{O}}(l)\} \cdot [\%\text{O}(l)] \quad \ldots \ldots \ldots (10)$$

There have been many reports about the value of $\epsilon_{\text{Si}}(l)$. In the present work, the value derived by Sakao et al., $\epsilon_{\text{Si}}(l) = 0.0744$, is used for the reason mentioned in the previous work.

Matoba et al. and Chipman and Pillay have investigated the equilibrium between H$_2$ - H$_2$O mixture and liquid iron alloy, and obtained $-0.137$ and $-0.16$ for $\epsilon_{\text{Si}}(l)$, respectively. Syui Tsz-Tszi et al. have measured the deoxidation equilibrium with silicon in solid iron and obtained $-0.125$. Schenck et al. have measured the equilibrium between CO- CO$_2$ mixture and liquid iron alloy, and obtained $-0.131$. Sigworth and Elliott have recommended the Schenck and co-workers’ value. Janke and Fischer have also recommended the value of $-0.13$. Accordingly, $\epsilon_{\text{Si}}(l) = -0.131$ reported by Schenck et al. is used in the present work.

The value of $\epsilon_{\text{Si}}(l)$ was calculated from that of $\epsilon_{\text{Si}}(l)$ to $\epsilon_{\text{O}}(l)$ by using Eq. (11):

$$\epsilon_{\text{Si}} = (M_{\text{Si}}/M_0) \cdot \epsilon_{\text{Si}} + (1/230) \cdot [1 - (M_{\text{Si}}/M_0)] \quad \ldots \ldots \ldots (11)$$

where, $M_{\text{Si}}$ and $M_0$; atomic weights of silicon and oxygen, respectively.

The data for $\epsilon_{\text{Si}}(l)$ derived by Sakao and Sano was extrapolated to the mean temperature of the present experiments, and $\epsilon_{\text{Si}}(l) = -0.21$ was used. Even if the term of $\epsilon_{\text{Si}}(l)$ in Eq. (10) is neglected, it gives almost no effect on the result, because the oxygen content is relatively low in the present experiments.

Using each value of the interaction parameter selected above, $\log K_{\text{Si}(l)}$ can be calculated from the experimental results.

$$\log K_{\text{Si}(l)} = -5.18[\%\text{Si}(l)] < 0.64 \quad \ldots \ldots \ldots (12)$$

The relationship between silicon and oxygen contents for the liquidus composition calculated from Eq. (12) is drawn by the solid line in Fig. 4.

The values of $\log K_{\text{Si}(l)}$ and $K'_{\text{Si}(l)}$ determined in the present work are compared with those in the literature and shown in Fig. 7. The present results are in good agreement with the extrapolated values of many other investigators. Consequently, the composition of the molten zone seems to be the value in equilibrium with SiO$_2$. It is obvious from this figure that some errors arisen in the estimation of the experimental temperature do not alter the above conclusion.

It can be also concluded from these results that all of the experimental results in the Fe-Si-O system represent the equilibrium compositions of liquidus and solidus under the presence of solid SiO$_2$. Therefore, the experimental results were used for the following analyses without any correction.
3. Determination of $L_0$ and $f_{oi}(s)$

The distribution equilibrium of oxygen between liquid and solid (δ-iron) in the Fe-Si-O system can be represented by

$$L_0 = \frac{ao(s)}{ao(l)} \quad \text{(13)}$$

where $L_0$ is the equilibrium constant, and $ao(s)$ and $ao(l)$ the activities of oxygen in δ-iron and in liquid iron, respectively, when the reference state of the activity is chosen at infinite dilution and the concentration of oxygen is represented by weight percent. Equation (13) can be rearranged by using the interaction coefficients as follows:

$$\log L_0 = \log L_0 + \log f_{oi}(s) + \log f_{oi}(l) - \{ \log f_{a}(l) + \log f_{oi}(l) \} \quad \text{(14)}$$

where, $L_0 = [\%O(s)]/[\%O(l)]$: the solid-liquid equilibrium distribution coefficient of oxygen. As mentioned above, the interaction coefficient in liquid iron $f_z(l)$ can be expressed by $\phi(l)$, and Eq. (14) becomes

$$\log L_0 = \log L_0 + \log f_{oi}(s) + \log f_{oi}(l) - [\phi(l) \cdot [\%O(l)] + \phi(l) \cdot [\%Si(l)]] \quad \text{(15)}$$

According to the Kusano and co-workers' report on the solubility of oxygen in δ-iron,7~ $L_0$ in the Fe-O system is constant and independent of the concentration of oxygen and consequently independent of the temperature. Therefore, the following relationship is obtained:

$$\log L_0 - \log L_0 = \log f_{oi}(s) - \phi(l) \cdot [\%O(l)] \quad \text{(15-1)}$$

If $\log f_{oi}(s)$ can be also expressed by $\phi(l)$, then

$$\phi(l) = \phi(l)/L_0 \quad \text{(16)}$$

is obtained. By substituting $\phi(l) = -0.21^{13}$ and $L_0 = 0.076^{27}$ into Eq. (16), the effect of the terms $[\log f_{oi}(s) - \phi(l) \cdot [\%O(l)]]$ in Eq. (15) is confirmed to be much smaller than the experimental error under the present experimental condition. Thus, Eq. (15) can be simplified in

$$\log L_0 = \log L_0 + \log f_{oi}(s) - \phi(l) \cdot [\%Si(l)] \quad \text{(17)}$$

Then, the present experimental results were analyzed by using Eq. (17) and $\phi(l) = -0.131$ given by Schenck et al.12~ The result is shown in Fig. 8. The maximum experimental errors which were estimated from the accuracies of chemical analyses of each element concerned are figured by $\Phi$ only for the representative experimental points to avoid the complication of the figure. The experimental results of Nishikawa et al.21~ in the Fe-O-Si system were also analyzed by using Eq. (17), and shown in the same figure for the comparison. The value of $[\log L_0 - \log f_{oi}(s)]$ increases at a remarkable rate with increasing [%Si(s)] up to 0.1%. Beyond this silicicon content, a slightly increasing then decreasing tendency can be recognized. However, taking into account of the experimental accuracy, no fluctuating tendency seems to be rational. Because of non-linear relation between $[\log L_0 - \log f_{oi}(s)]$ and [%Si(s)], a parabolic function is assumed in [%Si(s)] $\leq$ 0.1,

$$\log L_0 = -0.925 \quad (L_0 = 0.119) \quad \text{(18)}$$

$$\log f_{oi}(s) = -9.05[\%Si(s)] + 30[\%Si(s)]^2$$

($[\%Si(s)] \leq 0.1$). \quad \text{(19)}

Also, from the experimental points of Nishikawa et al.,21~ log $L_0 = -1.12$ ($L_0 = 0.076$) and log $f_{oi}(s) = -7.4[\%Si(s)]$ have been obtained. The value of log $f_{oi}(s)$ is almost the same magnitude as the present result, i.e. the gradient of the straight line which ties the present experimental points of [%Si(s)] = 0.012% and [%Si(s)] = 0.06% is 7.6. As mentioned above, the value of $L_0$ obtained in the present work is equal to the value of $L_0$ in the Fe-O binary system. Then, the data of $L_0$ in the Fe-O system given in the literature are tabulated in Table 1 for comparison. The value of $L_0$ obtained in the present work is larger than that of Nishikawa et al.,21~ but smaller than that of Nilles,25~ which was calculated to be 0.184 from the solubility of oxygen in δ-iron measured by Tankins...
and Gokcen\(^{28}\) and the solubility of oxygen in liquid iron measured by Taylor and Chipman.\(^{29}\)

4. Deoxidation Equilibrium with Silicon in \(\delta\)-iron

When the reaction between a deoxidation element \(R\) and oxygen dissolved in iron forms an oxide \(R_mO_n\), the following equilibrium relationships are available for the liquid and solid iron, respectively,

\[
R_mO_n \rightleftharpoons mR + nO \tag{20}
\]

\[
K_{R(l)} = \frac{a_R(l)^m}{a_{RmO_n}} \tag{21}
\]

\[
K_{R(S)} = \frac{a_R(S)^m}{a_{RmO_n}} \tag{22}
\]

In these equations, \(K_{R(l)}\) and \(K_{R(S)}\) are the equilibrium constants in liquid and solid iron, respectively, and \(a_i(l)\) and \(a_i(S)\) are the activities of component \(i\) in liquid and solid iron, respectively, where the reference state of activity is chosen at infinite dilution and concentration of solute is represented by weight percent.

\(a_{RmO_n}\) is the activity of \(R_mO_n\) relative to pure substance. At the solid-liquid equilibrium temperature, Eqs. (23) and (13) are available for the distributions of \(R\) and \(O\) between solid and liquid iron, respectively,

\[
L_R = a_R(S)/a_R(l) \tag{23}
\]

\[
L_O = a_O(S)/a_O(l) \tag{13}
\]

Now substituting Eqs. (21), (23) and (13) into Eq. (22), one obtains

\[
K_{R(S)} = K_{R(l)} \cdot (L_R)^m \cdot (L_O)^n \tag{24}
\]

This is a general equation by which the deoxidation equilibrium constant with \(R\) in solid iron, \(K_{R(S)}\), can be calculated from that in liquid iron \(K_{R(l)}\).

When \(R\) is silicon, \(R_mO_n\) is \(SiO_2\) and therefore Eq. (24) becomes

\[
K_{Si(S)} = K_{Si(l)} \cdot (L_{Si})^m \cdot (L_O)^n \tag{25}
\]

\(L_{Si}\) has been obtained in our previous work,\(^{4}\) and \(K_{Si(l)}\) and \(L_{Si}\) have been shown by Eqs. (12) and (18), respectively. Therefore, \(K_{Si(S)}\) in \(\delta\)-iron at the solid-liquid equilibrium temperature is

\[
\log K_{Si(S)} = \log \left[ \frac{a_{Si}(S) \cdot a_O(S)}{a_{SiO_2}} \right] = -7.19
text{(\text{[\%Si(S)]} \leq 0.5) \tag{27}}
\]

In the same manner as Eq. (8), Eq. (27) can be rewritten as Eq. (28) by using the interaction coefficients,

\[
\log K_{Si(S)} = \log \left[ \frac{[\%Si(S)] \cdot [\%O(S)]^2}{\rho_{Si(S)}} \right] + \log f_{Si(S)}^O + \log f_{O(S)}^O + 2 \log f_{SiO_2(S)}^O - \log a_{SiO_2} \tag{28}
\]

According to our previous work,\(^*\) \(f_{Si(S)}^O\) is represented by

\[
\log f_{Si(S)}^O = 0.086[\%Si(S)] \tag{29}
\]

The value of \(f_{O(S)}^O\) has been already obtained from Fig. 8, and represented by Eq. (19) in the concentration range \([\%Si(S)] \leq 0.1\). The value of \(\rho_{Si(S)}\) is calculated from the coefficient of the first order term in Eq. (19), \(\rho_{Si(S)} = -9.05\), by using Eq. (11), and \(f_{SiO_2(S)}^O\) is approximated as follows:

\[
\log f_{SiO_2(S)}^O = -15.9[\%O(S)] \tag{30}
\]

As is mentioned above, it can be considered

\[
\log f_{Si(S)}^O = 0 \text{ (} f_{Si(S)}^O = 1 \text{)} \tag{31}
\]

The equilibrium relationship between silicon and oxygen in \(\delta\)-iron can be calculated from Eq. (28) by using each value of the activity coefficient mentioned above. It is shown by a solid line drawn for the solidus composition in Fig. 4.

The equilibrium relationship between solid and liquid phases can be also calculated from \(L_{Si}\) and \(L_O\). The tie lines obtained in this way are shown by broken lines in Fig. 4. The value of \(L_{Si}\) in Fe–Si–O alloy equilibrated with SiO\(_2\) is calculated to be about 0.8, and agrees well with the present experimental results, while \(L_{Si}\) in Fe–Si binary alloy is 0.70–0.72 in the range of \([\%Si(S)] = 0–0.5\), according to the previous work.\(^(4)\) Namely, the discrepancy in the values of \(L_{Si}\) between the Fe–Si and the Fe–Si–O systems shown in Fig. 5 is due to the strong interaction between silicon and oxygen dissolved in the solid iron.

However, the measured value of \([\%Si(S)] = 0.002\) alone differs considerably from calculated one. The formation of SiO\(_2\) may occur in the solid phase, and affects on the analytical value of silicon content resulting in the lower value than the true one. Based on this assumption, the amount of reacted silicon was estimated to be about 200 ppm from the difference between the measured silicon content and the calculated one. It is nearly the same magnitude as the error of chemical analysis. So, we cannot conclude that the discrepancy is solely due to the reaction, but such reaction does not affect on any other measured values of higher silicon content.

### Table 1. Comparison of solid-liquid equilibrium distribution coefficient of oxygen in Fe–O alloy.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>(L_O)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tiller (^{23}) (1959)</td>
<td>0.1</td>
<td>Taken from phase diagram</td>
</tr>
<tr>
<td>Fischer et al. (^{23}) (1960)</td>
<td>0.02</td>
<td>Zone melting</td>
</tr>
<tr>
<td>Chipman &amp; Elliott (^{24}) (1963)</td>
<td>0.02</td>
<td>Taken from phase diagram</td>
</tr>
<tr>
<td>Nilles (^{25}) (1964)</td>
<td>0.184</td>
<td>Estimation</td>
</tr>
<tr>
<td>Hepworth et al. (^{26}) (1966)</td>
<td>0.059</td>
<td>Fe–H(_2)/H(_2)O equilibrium &amp; estimation</td>
</tr>
<tr>
<td>Kusano (^{27}) et al. (1968)</td>
<td>0.076</td>
<td>Solid–liquid equilibrium</td>
</tr>
<tr>
<td>Ooka et al. (^{28}) (1968)</td>
<td>0.091(^{11})(^*)</td>
<td>Zone melting</td>
</tr>
<tr>
<td>Fischer &amp; Frye (^{27}) (1970)</td>
<td>0.10(^{1})(^*)</td>
<td>Zone melting</td>
</tr>
<tr>
<td>This work</td>
<td>0.119</td>
<td>Zone melting of Fe–Si–O alloy</td>
</tr>
</tbody>
</table>

\(*\) Estimation in this work.
V. Summary

Zone melting experiments have been done to investigate the solid-liquid equilibrium relationship in Fe-Si-O alloy. Under the present experimental conditions, the solidification model given by Burton et al. is fully applicable to the Fe-Si binary system. On the other hand, the equation of Burton et al. is not strictly applicable to the Fe-Si-O ternary system because of the occurrence of the deoxidation reaction with silicon. However, it was confirmed that the equilibrium distribution coefficient could be obtained by \( L=L' \) in the limit of the experimental error.

Using the equilibrium distribution coefficients obtained in this way, the equilibrium relationship between silicon and oxygen in \( \delta \)-iron was determined.

The deoxidation equilibrium constant with silicon in liquid iron is \( \log K_{SiO}(l) = -5.18 \) (\( \%\text{Si}(l) < 0.64 \)) at the solid-liquid equilibrium temperature, 1531\(^\circ\)C to 1537\(^\circ\)C, which is in good agreement with the values given in the literature.

The silicon-oxygen equilibrium relationship in \( \delta \)-iron at the solid-liquid equilibrium temperature is represented by the following equations.

\[
\log \left[ \frac{a_{\text{Si}}(s) \cdot a_{\text{O}}(s)^2}{a_{\text{SiO}}(s)} \right] = -7.19 \quad (\%\text{Si}(s) \leq 0.5)
\]

\[
\log f_{\text{SiO}}(s) = 0.086(\%\text{Si}(s))
\]

\[
\log f_{\text{Si}}(s) = -15.9(\%\text{O}(s))
\]

\[
\log f_{\text{O}}(s) = -9.05(\%\text{Si}(s)) + 30(\%\text{Si}(s))^2
\]

(\( \%\text{Si}(s) \leq 0.1 \))

\[
\log f_{\text{O}}(s) \approx 0.
\]

REFERENCES


9) S. Matoba, K. Gunji and T. Kuwana: Tetsu-to-Hagane, 45 (1959), 1328.


