Solubility of Oxygen in Iron–Silicon Melts in Equilibrium with Silica at 1873 K

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The solubility of oxygen in iron-silicon melts in equilibrium with silica was measured within the range from 0.1 up to 70 mass% Si at 1873 K. The experimental procedure involved alloys melting in silica crucibles under argon atmosphere. The sampling was made by melt sucking into quartz tubes, equipped with copper chillers. The oxygen content of analytical samples was determined with inert gas fusion analysis after careful sample preparation. The results obtained were treated by thermodynamic model, which allowed to calculated the activity and solubility of oxygen in Fe–Si melts up to 100 mass% Si.

The isotherm of oxygen solubility exhibits both intermediate minimum and maximum at 20 and 85 mass% Si, respectively. The corresponding values of oxygen saturated contents are as follows: 1.4 and 94 µg/g. The activity coefficient of oxygen shows alternating deviations from the additive behaviour. These are positive in the iron rich melts, containing up to 45 mass% Si. In the melts with higher silicon content the deviations from additivity are negative. The following values of interaction parameters were calculated: $\epsilon_{\text{FeO}}^{\text{Si}}=12.9\pm2.7$ and $\epsilon_{\text{SiO}}^{\text{Fe}}=-6.5\pm2.0$.

KEY WORDS: deoxidation; oxygen solubility; interaction parameter; Si; Fe; oxygen determination; gas fusion analysis.

1. Introduction

This paper addresses one major uncertainty regarding the concentration dependency of the solubility of oxygen in iron–silicon melts, viz. the position of its minimum. The minima have been experimentally found for a few deoxidizers of iron, such as chromium, aluminum and titanium. However, the existence and the position of the minimum for silicon are still unclear.

The deoxidation of iron with silicon has been repeatedly investigated and the relevant references are compiled and discussed in the steelmaking data sourcebook. At 1873 K the Si–O equilibrium in iron is believed to be reliably established up to 1–3 mass% Si. Within this range the oxygen solubility is steadily decreasing down to 30–50 µg/g. The further behaviour of oxygen solubility is, however, not reliably established. Goken and Chipman performed measurements up to 15 mass% Si and did not find the minimum. On the contrary, Tszen-Tszi et al. reported the minimum at 5–6 mass% Si.

The existence of intermediate minimum in the isotherm of oxygen solubility directly follows from the fact that pure liquid silicon saturated with silica dissolves more than 70 µg/g of oxygen at 1873 K. But the most interesting fact is that the solubility of oxygen in liquid silicon tends to increase with iron content. This suggests the occurrence of both minimum and maximum in the solubility curve. The aim of this study was to obtain the isotherm of oxygen solubility in Fe–Si melts over the wide concentration range at 1873 K with direct measurements and thermodynamic calculation.

2. Experimental

2.1. Alloys Melting and Sampling

Equilibrium experiments were carried out using the conventional technique of melting alloys in silica crucibles under inert atmosphere, followed by melt sampling into quartz tubes with copper chillers. The Fe–Si alloys were melted in a high frequency 10 kVA HF induction furnace under argon atmosphere. The reaction tube, crucibles (40 mm i.d. and 60 mm long) and thermocouple sheaths were made of pure quartz. The accuracy of the temperature control was about ±15 K.

Carbonyl iron, weighing 150–200 g, was heated up under Ar–10%H$_2$ atmosphere for 30–40 min. As soon as the melting was completed the atmosphere was changed to purified argon, followed by first sampling. This was made by sucking 15–20 g of melt into quartz tubes, 8 mm i.d., equipped with copper chillers. The initial oxygen content of the melt was about 800 µg/g, which was in much excess to solubility values. After sampling an appropriate amount of pure semiconductive silicon was added to the melt. The deoxidation reaction was, then, allowed to attain equilibrium.
idation kinetics of the nickel–iron liquid alloys with silicon was studied by Ishii and Ban-ya under experimental conditions similar to those of the present work. Their results evidence that the complete removal of oxide inclusions from the melt occurs within 15 min after silicon addition. Therefore, in the present work the holding time was accepted to be three-four times as long, i.e., 45–60 min. After attaining equilibrium two pin samples were taken out. For high-silicon alloys, containing more than 15 mass% Si, both silicon and iron were used as a charge.

2.2. Sample Preparation and Chemical Analysis

Inert gas fusion technique was applied to determine the oxygen content of the Fe–Si alloys. It was the part of the analytical sample adjacent to copper chiller that was only analyzed. As the solidification rate of this part was the highest the corresponding analytical samples were assumed to be more representative.

In order to get accurate values of the bulk oxygen content it was essential to remove surface contaminations from analytical samples prior to analysis. This was made by two-step sample preparation procedure, which involved (i) abrading by a file or chemical etching and (ii) heating in the graphite crucible of analyzer under flowing helium. The analytical pin samples, containing less than 7 mass% Si, were cut with a SiC saw and abraded by a file. The samples, containing 50–70 mass% Si, were abraded by a file and broken into pieces. For hard and brittle alloys, containing 7–30 mass% Si, the chemical etching at room temperature was employed, which was composed from the following steps: 1) etching in 1HF (40%) + 1HNO₃ (65%) for 2 min, 2) etching in HF (40%) for 5 min, 3) drying by warm hair drier. Prior to analysis all samples were pre-treated in the graphite crucible under flowing helium for 120 s at 1300 K. This technique was reported to allow the removal of residual contaminants from the surface of analytical samples of both silicon and iron.

The oxygen analysis was made using TC-600 Leco Corp. (USA) commercial analyzer. The IR detectors were calibrated with the following reference materials: JSS GS-2b (14.6±3.4 μg/g), JSS GS-1c (46.0±3.8 μg/g), JSS GS-6a (136.0±9.0 μg/g). The use of iron-based reference materials for oxygen determination in silicon with gas fusion technique was validated elsewhere.

The classical gravimetric method was employed to determine the silicon content of the high-silicon alloys. In the low silicon range the silicon content was determined with glow-discharge spectrometer SA-2000 Leco Corp. (USA).

3. Results and Discussion

3.1. Oxygen Solubility in Fe–Si Liquid Alloys

The experimental values of oxygen solubility in Fe–Si melts, equilibrated with silica, are given in Table 1. Figure 1 compares the results of the present study with those which were reported in literature. In the low silicon range the reasonable agreement is confirmed. In logarithmic coordinates the experimental points follow the straight line with a slope −1/2, which is characteristic of SiO₂ stoichiometry. In contrast to previous works, the results of the present study evidence the strong negative deviations from the straight line just above 0.6–0.9 mass% Si. The solubility of oxygen rapidly decreases in the range from 1 up to 10 mass% Si, then, passes through a deep minimum at about 20 mass% Si and, finally, increases with silicon content.

At the minimum the saturated content of oxygen was measured to be less than 5 μg/g. This value is much lower than that reported by previous workers. In both cited works the analytical samples for oxygen analysis were taken from small ingots (10–40 g), which were quenched in hydrogen stream or cooled down slowly in the furnace. However, the procedure of the sample preparation was not particularly mentioned. We are inclined to attribute the above discrepancy to the fine pieces of silica contaminants, which could be entrapped into analytical samples. This problem was emphasized by Hirata and Hoshikawa, who studied the oxygen solubility in pure liquid silicon by melting it in the sealed silica ampoule. To take samples for oxygen analysis the quenched ingots were broken into pieces. However, due to fine silica contaminants the values of oxygen solubility were strongly overestimated and scattered. To get more accurate results it was necessary to remove silica contaminants by etching samples in a 50% HF solution for 24 h prior to analysis.

Hirata and Hoshikawa measured the oxygen solubility in pure liquid silicon within the temperature range from
1698 to 1820 K and represented their data in terms of the following formula:

\[ c_{O(\text{Si})} / \text{mass}\% = 456 \cdot \exp(-20\,000/T) \]  

(1)

Using different equilibration technique Narushima et al.\textsuperscript{4) measured the oxygen solubility within the same temperature range and reported the following equation:

\[ c_{O(\text{Si})} / \text{mass}\% = 2.15 \cdot \exp(-10\,638/T) \]  

(2)

At 1873 K the Eqs. (1) and (2) give the values of 0.0105 and 0.0073 mass\% O, respectively. To understand the source of such a disagreement we plotted in Fig. 2 the experimental points of both works\textsuperscript{4,9) together with functions (1) and (2). It is clear that within experimental error the raw points are in fair agreement. But the functions (1) and (2) greatly differ in the slope. The Eq. (1) yields too strong temperature dependence and overestimates the oxygen solubility at temperature above 1823 K. By simultaneous least-squared fit of the points of both works\textsuperscript{4,9) we derived the following formula:

\[ c_{O(\text{Si})} / \text{mass}\% = 7.44 \cdot \exp(-12\,812/T) \]  

(3)

It is seen from Fig. 2 that the functions (2) and (3) are actually similar. Therefore, the Eq. (2) reported by Narushima et al.\textsuperscript{4,9) was adopted in the present study to calculate the limiting value of oxygen solubility in Fe-Si melts at 100 mass\% Si. As can be seen from Fig. 1 this value is close to that we measured in Fe–68mass\%Si melt.

### 3.2. Thermodynamic Model

The thermodynamic treatment of experimental results is based on the following reaction:

\[ \text{SiO}_2(s) \rightleftharpoons [\text{Si}] + 2[O] \]  

(4)

where the symbols in square brackets represent the components of the melt. At the equilibrium the following relation holds between the chemical potentials of components:

\[ \mu^{(i)}_{\text{SiO}_2} = \mu^{(\text{melt})}_{\text{Si}} + 2 \mu^{(\text{melt})}_{O} \]  

(5)

It is convenient to accept the pure liquid silicon and diatomic gaseous oxygen at 101325 Pa as a reference states for silicon and oxygen in the melt, respectively. The pure solid silica is accepted as a reference state for silica. Besides, its activity is equal to unity for the present conditions. Then, the expressions for chemical potentials of components can be written like this:

\[ \mu^{(i)}_{O} = \frac{1}{2} \mu^{(\text{g})(O)}_{2} + RT \ln(x_{O} \cdot \gamma_{O}) , \]
\[ \mu^{(i)}_{\text{Si}} = \mu^{(\text{l})(O)}_{\text{Si}} + RT \ln(x_{\text{Si}} \cdot \gamma_{\text{Si}}) , \]
\[ \mu^{(i)}_{\text{SiO}_2} = \mu^{(\text{g})(O)}_{\text{SiO}_2} (a_{\text{SiO}_2} = 1) \]

where \( x_{O}, x_{\text{Si}} \) and \( \gamma_{O}, \gamma_{\text{Si}} \) – mole fractions and activity coefficients of silicon and oxygen in the melt, respectively; \( \mu^{(\text{g})(O)}_{2}, \mu^{(\text{l})(O)}_{\text{Si}}, \mu^{(\text{g})(O)}_{\text{SiO}_2} \) – the chemical potentials of pure components in their reference states. From Eqs. (5), (6) one can deduce the law of mass action:

\[ (x_{\text{Si}} \cdot \gamma_{\text{Si}}) \cdot (x_{O} \cdot \gamma_{O})^2 = K(T) \]  

(7)

The temperature dependence of equilibrium constant \( K(T) \) was calculated using the IVTANTHERMO data base for thermo-chemical properties of pure substances:\textsuperscript{10)}

\[ \ln K = \frac{\mu^{(l)}_{\text{SiO}_2} - \mu^{(l)}_{\text{Si}} - \mu^{(l)}_{O}}{RT} = -113\,805 \frac{T}{29.8} \]  

(8)

Due to the low solubility in the melt the effect of oxygen on its own activity coefficient can be neglected, i.e. \( \gamma_{O} \equiv \gamma^{O}_0 \). For the same reason the activity coefficient of silicon can be directly calculated from the Fe–Si binary system. The thermodynamic properties of the binary Fe–Si melts have been measured and critically discussed by Zaitsev et al.\textsuperscript{11) They performed a consistent description of components activities over the whole concentration range in terms of the model of ideal-associated solution. The following values were reported for the formation constants of clusters Fe\textsubscript{2}Si, Fe\textsubscript{2}Si, FeSi and Fe\textsubscript{2}Si\textsubscript{2}:

\[ k_{\text{Fe},\text{Si}} = \exp(17\,281/T-3.444), \]
\[ k_{\text{Fe}2\text{Si}} = \exp(13\,334/T-1.958), \]
\[ k_{\text{FeSi}} = \exp(12\,006/T-2.851), \]
\[ k_{\text{Fe}2\text{Si}2} = \exp(12\,190/T-3.533) \]  

(9)

According to the model of ideal-associated solution:\textsuperscript{12)} the activities of silicon \( a_{\text{Si}} = x_{\text{Si}} \cdot \gamma_{\text{Si}} \) and iron \( a_{\text{Fe}} = x_{\text{Fe}} \cdot \gamma_{\text{Fe}} \) are equal to the mole fractions of non-associated atoms \( y_{\text{Si}} \) and \( y_{\text{Fe}} \), respectively. For a given temperature \( T \) and silicon content \( x_{\text{Si}} \) the values of \( y_{\text{Si}} \) and \( y_{\text{Fe}} \) can be calculated by solving numerically the set of two transcendental equations:

\[ y_{\text{Fe}} + \sum_{j} k_{j}(T) \cdot (q_{\text{Fe}}^{j} - (q_{\text{Fe}}^{j} + q_{\text{Si}}^{j} - 1) \cdot (1 - y_{\text{Si}})) \cdot y_{\text{Fe}}^{q_{\text{Fe}}^{j}} \cdot y_{\text{Si}}^{q_{\text{Si}}^{j}} = 1 - y_{\text{Si}} , \]
\[ y_{\text{Si}} + \sum_{j} k_{j}(T) \cdot (q_{\text{Si}}^{j} - (q_{\text{Fe}}^{j} + q_{\text{Si}}^{j} - 1) \cdot x_{\text{Si}}) \cdot y_{\text{Fe}}^{q_{\text{Fe}}^{j}} \cdot y_{\text{Si}}^{q_{\text{Si}}^{j}} = x_{\text{Si}} \]  

(10)

where \( q_{\text{Fe}}^{j} \) and \( q_{\text{Si}}^{j} \) are the numbers of iron and silicon atoms of \( j \)-th cluster, respectively (for instance, \( q_{\text{Fe}} = 3 \) and \( q_{\text{Si}} = 1 \) for Fe\textsubscript{2}Si\textsubscript{2} cluster). The summation is made over all binary clusters.
With available model for silicon activity, Eqs. (9) and (10), the equation Eq. (7) can be applied to recalculate the activity coefficient of oxygen in the melt from the values of its solubility, summarized in Table 1. The results of such a treatment are shown in Fig. 3. The dash line in Fig. 3 refers to an additive approximation:

$$\ln \gamma_{O(Fe-Si)}^o = x_{Fe} \ln \gamma_{O(Fe)}^o + x_{Si} \ln \gamma_{O(Si)}^o$$  \hspace{1cm} (11)

The value of the activity coefficient of oxygen at infinite dilution in pure liquid iron $\ln \gamma_{O(Fe)}^o$ is known from literature:

$$\ln \gamma_{O(Fe)}^o = -16500/T + 4.29$$  \hspace{1cm} (12)

The expression for $\ln \gamma_{O(Si)}^o$ was recalculated using the solubility of oxygen in pure liquid silicon Eq. (2) and the equilibrium constant Eq. (8) of the reaction (4):

$$\ln \gamma_{O(Si)}^o = -46265/T + 15.18$$  \hspace{1cm} (13)

At 1873 K the limiting values of oxygen activity coefficient are as follows: $\ln \gamma_{O(Fe)}^o = -4.5$ and $\ln \gamma_{O(Si)}^o = -9.5$. It is seen from Fig. 3 that our experimental points correspond well to both limiting values. Besides, the activity coefficient of oxygen shows alternating deviations from the additive behaviour Eq. (11). These are positive in the iron rich melts, containing up to 60 at% Si. In the melts with higher silicon content the deviations from additivity are negative. Such a behaviour might result from the complex atomic interactions in Fe–Si binary liquid alloys, which involve both metallic and covalent type of bonding. In Fe-rich melts the covalent bonding between unlike atoms is considered to form clusters Fe$_x$Si$_y$ while in Si-rich melts the Si–Si covalency is also assumed to persist from solid Si. As a result both Si–O and Fe–O bonding energies may become complex function of the melt composition.

The formalistic description of the activity coefficient of oxygen in Fe–Si melts over the whole concentration range we performed in terms of the ternary subregular formula:

$$\ln \gamma_{O(Fe-Si)}^o = x_{Fe} \ln \gamma_{O(Fe)}^o + x_{Si} \ln \gamma_{O(Si)}^o + x_{Si} x_{Fe} \left( \ln \gamma_{O(Fe)}^o \gamma_{O(Si)}^o + \epsilon_{O(Fe)}^S + \epsilon_{O(Si)}^F \right)$$  \hspace{1cm} (14)

\begin{align*}
\ln \gamma_{O(Fe)}^o & = x_{Fe} \ln \gamma_{O(Fe)}^o + x_{Si} \ln \gamma_{O(Si)}^o + \epsilon_{O(Fe)}^S \\
\ln \gamma_{O(Si)}^o & = x_{Si} \ln \gamma_{O(Si)}^o + x_{Fe} \ln \gamma_{O(Fe)}^o + \epsilon_{O(Si)}^F 
\end{align*}

Here, $\epsilon_{O(Fe)}^S$ and $\epsilon_{O(Si)}^F$ represent interaction parameters. To find their values Eq. (14) was fitted to experimental points, shown in Fig. 3. Each point was given its own weight, inversely proportional to the relative standard deviation of the replicate measurements of oxygen content (see Table 1). The following optimal values were obtained:

$$\epsilon_{O(Fe)}^S = 12.9 \pm 2.7 \quad \epsilon_{O(Si)}^F = -6.5 \pm 2.0$$  \hspace{1cm} (15)

Using Eq. (7) and taking into account the expressions, Eqs. (8)–(10) and (12)–(15), we calculated the isotherm for 1723 K was made by applying the known temperature dependencies of $\ln K$, $\ln \gamma_{O(Fe)}^o$, $\ln \gamma_{O(Si)}^o$ and $\epsilon_{O(Fe)}^S$, while the interaction parameters $\epsilon_{O(Fe)}^S$ and $\epsilon_{O(Si)}^F$ were assumed to be temperature-independent. The calculation results for 1723 K are in good agreement with the curve, which was estimated by Yanaba et al. from the solubility of oxygen in pure liquid silicon and the effect of iron on the solubility of oxygen in Si–Fe melts. Thus, two independent estimates confirm the increase in the solubility of oxygen in liquid silicon with iron content. The complete set of thermodynamic parameters for the Fe–Si–O melts in equilibrium with silica at 1873 K is given in Table 2.

4. Conclusions

The solubility of oxygen in iron–silicon melts in equilibrium with silica was established within the range from 0.1 up to 100 mass% Si at 1873 K by direct measurements and
thermodynamic calculation. The isotherm of oxygen solubility exhibits both intermediate minimum and maximum at 20 and 85 mass% Si, respectively. The corresponding values of oxygen saturated contents are as follows: 1.4 and 94 μg/g. The activity coefficient of oxygen shows alternating deviations from the additive behaviour. These are positive in the iron rich melts, containing up to 45 mass% Si. In the melts with higher silicon content the deviations from additivity are negative. The following values of interaction parameters were calculated: $\varepsilon_{\text{SiO}(\text{Fe})}/H_{11005} = 12.9 \pm 2.7$ and $\varepsilon_{\text{FeO(Si)}}/H_{11006} = -6.5 \pm 2.0$.

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| Silicon content mass. % | Oxygen solubility $x_\text{O}$ μg/g | $\ln y_\text{O}^{\text{Si}}$ | $\ln y_\text{O}^{\text{Fe}}$ |
|------------------------|------------------------|-----------------|-----------------|
| 0.1                   | 0.002                  | -6.27           | -4.49           |
| 0.2                   | 0.004                  | -6.26           | -4.47           |
| 0.5                   | 0.010                  | -6.23           | -4.40           |
| 1.0                   | 0.020                  | -6.18           | -4.28           |
| 2.0                   | 0.039                  | -6.06           | -4.09           |
| 5.0                   | 0.095                  | -5.88           | -3.70           |
| 10.0                  | 0.18                   | -4.78           | -3.56           |
| 15.0                  | 0.26                   | -3.49           | -3.84           |
| 20.0                  | 0.33                   | -2.28           | -4.37           |
| 30.0                  | 0.46                   | -1.09           | -5.72           |
| 40.0                  | 0.57                   | -0.57           | -7.08           |
| 50.0                  | 0.67                   | -0.29           | -8.21           |
| 60.0                  | 0.75                   | -0.14           | -9.93           |
| 70.0                  | 0.82                   | -0.06           | -9.54           |
| 80.0                  | 0.89                   | -0.02           | -9.77           |
| 90.0                  | 0.95                   | -0.004          | -9.75           |
| 100.0                 | 1.0                    | 0.0             | -9.52           |