Solubility of oxygen in iron-silicon melts

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Abstract. The oxygen solubility in Fe–Si melts in equilibrium with SiO$_2$ at 1873 K has been determined in a whole concentration range. 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 ppm. The following values of Wagner interaction parameters were calculated: $\varepsilon_{\text{SiO}}^{\text{Fe}} = 12.9 \pm 2.7$ and $\varepsilon_{\text{FeO}}^{\text{Si}} = -6.5 \pm 2.0$.

Earlier we have determined the oxygen solubility in Fe-Si melts in equilibrium with silica at 1873 K in the whole concentration range (Figure 1) [1]. The obtained positive value of Wagner interaction parameter $\varepsilon_{\text{SiO}}^{\text{Fe}} = 12.9 \pm 2.7$ has attracted the attention of investigators and caused a number of questions related to the experimental and calculation accuracy. Thus, the purposes of this work are to compare our experimental data with values available in the literature and to perform the thermodynamic analysis of existence possibility of the positive $\varepsilon_{\text{O}}^{\text{R}}$, where R is a deoxidizing element.

For the thermodynamic processing of the experimental data (Figure 1), we consider the following reaction of equilibrium of oxygen with solid SiO$_2$ in Fe–Si melts:

$$\text{SiO}_2 (s) \leftrightarrow [\text{Si}] + 2[\text{O}]. \quad (1)$$

Standard states were taken to be pure liquid silicon, gaseous oxygen at atmospheric pressure (0.1 MPa), and pure solid silicon dioxide. Due to the low solubility in the melt the effect of oxygen on its own activity coefficient can be neglected, i.e. $\gamma_{\text{O}} \approx \gamma_{\text{O}}^{\circ}$. We performed the formalistic description of the activity coefficient of oxygen in Fe–Si melts over the whole concentration range in terms of the ternary subregular formula [2]:

$$\ln \gamma_{\text{O}}^{\circ} = \gamma_{\text{O}}^{\circ} \left( \frac{x_{\text{Fe}}}{\gamma_{\text{O}}^{\circ} \gamma_{\text{O}}^{\circ}} + \varepsilon_{\text{O}}^{\text{Si}} \right) + x_{\text{Si}} \left[ \ln \gamma_{\text{Si}} \left( \frac{x_{\text{Fe}}}{\gamma_{\text{Si}} \gamma_{\text{Si}}} + \varepsilon_{\text{Si}}^{\text{Fe}} \right) + x_{\text{Si}} \left( \ln \gamma_{\text{Si}} \frac{\gamma_{\text{Si}}}{\gamma_{\text{Si}} \gamma_{\text{Si}}} + \varepsilon_{\text{Si}}^{\text{Si}} \right) \right]. \quad (2)$$

where $\varepsilon_{\text{O}}^{\text{Si}}$ and $\varepsilon_{\text{O}}^{\text{Fe}}$ are the Wagner interaction parameters.
Figure 1. Oxygen solubility in Fe-Si melts in equilibrium with SiO$_2$.

The interaction parameters $\varepsilon_{O(Fe)}^S$ and $\varepsilon_{O(Si)}^F$ were found by the least squares method from the experimental points given in Figure 2. Each point was given its own weight, inversely proportional to the relative standard deviation of the replicate measurements of oxygen content. Thus, the following values were obtained:

$$
\varepsilon_{O(Fe)}^S = 12.9 \pm 2.7 \quad \varepsilon_{O(Si)}^F = -6.5 \pm 2.0.
$$

Figure 2. Activity coefficient of oxygen in Fe-Si melts at 1873 K.
As is seen from this work data (Figure 2) the activity coefficient of oxygen in Fe–Si melts increases with silicon content. Moreover our data are in a good agreement with known value of activity coefficient of oxygen at infinite dilution in pure liquid iron [7]. The experimental points of work [3] are not corresponding to edge value [7]; and data [4] have a wide scattering in low silicon area.

One can deduce the following constant for reaction (1):

\[
K = a_{Si} \cdot a_{O}^2,
\]

\[
K'=[\%Si] \cdot [\%O]^2.
\] (3)

The dependence of \(\lg K'\) on the silicon content in Fe-Si melts at 1873 K obtained by different investigators (to 5 mass.%) is shown in Figure 3. For each data array, the equation of linear regression and correlation coefficient also are represented. The extrapolation of the equations to zero silicon content allowed us to find the following values of \(\lg K\) at 1873 K: –4.66; –4.48 and –4.81. As literature data [6] shown the \(\lg K'\) was determined in a range from –4.79 [8] to –4.18 [9]. At the same time, it should be noted the wide scattering of experimental data of [3, 4]. The estimated value \(\lg K = –4.81\) is in a good accordance with literature values within the experimental error.

The subsequent processing of experimental data allowed us to calculate \(e_{O(Fe)}^{Si}\):

\[
\frac{1}{2} \left( \frac{\lg K' - \lg f_{Si}'}{\lg f_{O}'} \right) = \frac{1}{2} \left( -a - e_{Si}^{O(Fe)} \right) [\%Si] = e_{O(Fe)}^{Si} [\%Si],
\] (4)

where \(a\) is a parameter of equation \(y = ax + b\) (see Figure 3).

In compliance with (7), the character of \(e_{O(Fe)}^{Si}\) depends on both the slope of function \(\lg K'\) and the interaction parameter \(e_{Si}^{O(Fe)}\), whose value ranges from 0.026 [10] to 0.327 [9] at 1873 K (from data [6]).

Thus, the sign of interaction parameter \(e_{O(Fe)}^{Si}\) as determined can be both positive and negative depending on the used thermodynamic data in mathematical treatment.
There are data of various works in sourcebook [6], in which the value of the interaction parameter $\varepsilon_{O(Fe)}^{Si}$ was determined from –32.1 to –7.2. The authors of [6] recommended the value –7.2. In 2004 – 2005, T. Miki and M. Hino calculated the following values of $\varepsilon_{Si(Fe)}^{O}$ at 1873 K: 1.42 [11] and –10.7 [12]. In this work, we obtained that the interaction parameter $\varepsilon_{O(Fe)}^{Si}$ is positive. However, it is known from the literature [13 – 15] that the parameter $\varepsilon_{O(Fe)}^{R}$ is negative for a deoxidizing element. But from data of [6, 16], the interaction parameters of a number of elements are: $\varepsilon_{Cu(Fe)}^{O} = –4.3$ [17], –3.5 [18], –17.2 [19]; $\varepsilon_{Au(Fe)}^{O} = –8.2$ [J. Ertal], –116.3 [20]; $\varepsilon_{Ag(Fe)}^{O} = –5.8$ [E.S. Tankins], –45.0 [20]. Therefore if the parameter of interaction between element and oxygen is negative, the element not necessarily is deoxidizer.

It was shown in [15] that the negative sign of parameter $\varepsilon_{O}^{R}$ was found by equation:

$$
\varepsilon_{O}^{R} = \left( -\frac{x}{y} \right) \left( \chi_{R}^{min} + \varepsilon_{R}^{O} \right).
$$

The authors of work [15] supposed to derivation of that formula, that the function $\ln \gamma_{O}$ was linear and its derivative was constant from the point of pure solvent $x_{R} = 0$ to $x_{R}^{min}$, i.e. the case was a priori excluded, when the behavior of function $\ln \gamma_{O}$ in the range from pure solvent to minimum in the isotherm of oxygen solubility was non monotonous. There is no physical objection such a behavior of $\ln \gamma_{O}$ in binary melts. To characterize such an event, one more term (i.e. second order parameter) should be kept in the equation.

Thus, the existent experimental data and thermodynamic analysis have proved that the character of the Wagner interaction parameter $\varepsilon_{O(Fe)}^{R}$ does not indicate whether the element R is deoxidizer or not. Copper and aurum are not deoxidizing elements for iron but they decrease the activity coefficient of oxygen in liquid melt [21]. Certainly, it doesn’t mean that the attractive forces between copper and oxygen atoms are stronger than between iron and oxygen ones. In this case, it is also necessary to consider the influence of element R and iron bonding energy. The authors [21] explained that occurrence that the Fe-Cu system showed a marked positive deviation from Raoult’s law, indicating that Fe-Cu bond energies are less than Cu-Cu or Fe-Cu ones. This effective repulsion between copper and iron atoms must be in same way accountable for the effect of copper in the decreasing activity coefficient of oxygen [21]. Similarly, the attractive forces between iron and silicon atoms may be a cause of the increasing activity coefficient of oxygen in Fe-Si melts containing up to 8 mass% Si.

It should be emphasized that the value of the interaction parameter $\varepsilon_{O(Fe)}^{Si}$ equal to –8.2 was obtained in this work from the experimental data [4] description using the ternary subregular solutions model. In the sourcebook [6], one can find it as –14. This difference was due to the use in this work of the equilibrium constant improved by the IVTANTHERMO data base [22]. However, the obtained negative value of $\varepsilon_{O(Fe)}^{Si}$ allows us to conclude that the thermodynamic model is suitable for the description.

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