

The Solubility of Alumina in Liquid Iron

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Solubility curves, pct O vs pct Al, representing the saturation of iron with Al_2O_3 , include both minimum and maximum points. In this article, it is shown that a two-parameter exponential form of $\log f_{\text{O}}$ as a function of pct Al represents the Al-O clustering in iron and the solubility of Al_2O_3 in iron better than using the first- and second-order interaction coefficients based on the epsilon formalism. The exponential form of the $(\log f_{\text{O}})$ -pct Al relationship is consistent with current clustering and central atom solvation models.

I. INTRODUCTION

THE saturation of iron with Al_2O_3 can be represented by pct O vs pct Al solubility curves. Solubility minima^[1-4] and maxima^[3,4] of oxygen as a function of aluminum content in iron have been established by several researchers, as well as in many other Fe-M-O systems.^[4,5,6] The slope of the log pct O vs log pct Al solubility curve prior to the minimum is approximately $-2/3$, as established by the equilibrium constant, K , of the dissolution of alumina:



$$K = [\text{Al}]^2[\text{O}]^3 \quad [2]$$

At the minimum, clustering of aluminum around the oxygen interstitials allows the solubility to increase. At the maximum, the oxygen interstitials have all been screened, so that the solubility product drops off again. The slope of log pct O vs log pct Al is approximately $-2/3$ after the maximum.

In this article, it is shown that a two-parameter exponential form of the activity coefficient of oxygen, $\log f_{\text{O}}$, as a function of pct Al represents the Al-O clustering in iron and the solubility of Al_2O_3 in iron better than using the first- and second-order interaction coefficients based on the epsilon formalism.

II. ACTIVITY COEFFICIENT FORMALISMS

Activity coefficients of oxygen, f_{O} , and aluminum, f_{Al} , are used to calculate the solubility of alumina in iron. The activity coefficient of oxygen, f_{O} , can be expressed in terms of the epsilon formalism interaction coefficients, e_{O}^{Al} and r_{O}^{Al} , in accord with Eq. [3].

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Al}} (\text{pct Al}) + r_{\text{O}}^{\text{Al}} (\text{pct Al})^2 + (\text{higher-order terms}) \quad [3]$$

Equation [3], using interaction coefficients compiled by Sigworth and Elliott,^[7] as well as the data of Fruehan,^[1] is presented in Figure 1. The higher-order terms have

been neglected, as is the usual case in the epsilon formalism, which results in a two-parameter quadratic. The two-parameter quadratic of Eq. [3] results in an inappropriate and unrealistic upward curvature for aluminum contents greater than 1.2 pct. It will be shown that this upward curvature predicts an oxygen solubility that decreases with increasing aluminum contents (pct Al > 1.2 pct) much faster than the observed slope of $-2/3$. The addition of higher-order interaction coefficients in the "truncated" equation would be expected to correct this upward curvature; however, they are not known. Therefore, an exponential function is proposed, namely,

$$\log f_{\text{O}} = (\log f_{\text{O}}^*) (1 - e^{-\kappa \text{ pct Al}}) \quad [4]$$

which uses the two parameters f_{O}^* and κ . Figure 1 compares the quadratic epsilon formalism and the exponential function. The exponential function better describes high aluminum content behavior than the two-parameter quadratic epsilon formalism. There is no physical reason for the increase in $\log f_{\text{O}}$ shown by the quadratic form of $\log f_{\text{O}}$.

In Eq. [4], $\log f_{\text{O}}$ decreases to a saturation value of $\log f_{\text{O}}^*$ as pct Al increases. As oxygen interstitials become screened by aluminum atoms, additional aluminum has less effect on the oxygen activity. This type of saturation behavior is consistent with the clustering and central atom solvation models of St. Pierre and Shumaker,^[8,9] Lupis *et al.*,^[10] and Wagner.^[11]

The initial slope of the $(\log f_{\text{O}})$ -pct Al curve as pct Al approaches zero is equal to e_{O}^{Al} . The initial slope can be found in terms of the f_{O}^* and κ parameters by taking the derivative of Eq. [4] with respect to pct Al:

$$\frac{d \log f_{\text{O}}}{d \text{ pct Al}} = \kappa (\log f_{\text{O}}^*) e^{-\kappa \text{ pct Al}} \quad [5]$$

In the limit, as pct Al approaches zero, the slope is $\kappa \log f_{\text{O}}^*$, which is equivalent to e_{O}^{Al} . Thus, Eq. [4] can be rewritten as

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Al}} \left(\frac{1 - e^{-\kappa \text{ pct Al}}}{\kappa} \right) \quad [6]$$

From Eq. [6], it is seen that the parameter κ essentially takes the place of all of the second- and higher-order terms of the epsilon formalism, thus expressing $\log f_{\text{O}}$ in a two-parameter equation.

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III. THE SOLUBILITY OF ALUMINA IN IRON

The solubility of alumina in iron can be expressed as

$$\log \left(\frac{\text{pct O}}{K^{1/3}} \right) = -\log (f_{\text{O}}) - \frac{2}{3} \log (\text{pct Al}) - \frac{2}{3} \log (f_{\text{Al}}) \quad [7]$$

The solubility limits of aluminum and oxygen in iron using both the epsilon formalism (Eq. [3]) and the exponential form (Eq. [4]) for the $\log f_{\text{O}}$ term in Eq. [7] are shown in Figure 2. Also presented in Figure 2 are the data of Fruehan^[1] and d'Entremont *et al.*^[3] In the latter case, data for 1600 °C were estimated from the direct data at 1740 °C. There is a wide disparity in the literature for the value of the equilibrium constant,

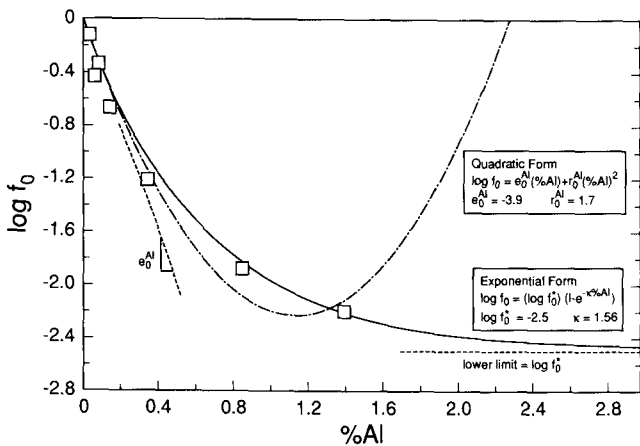


Fig. 1—Activity coefficient of oxygen as a function of aluminum content in alumina-saturated Fe-Al alloys at 1600 °C. Data from Fruehan.^[1]

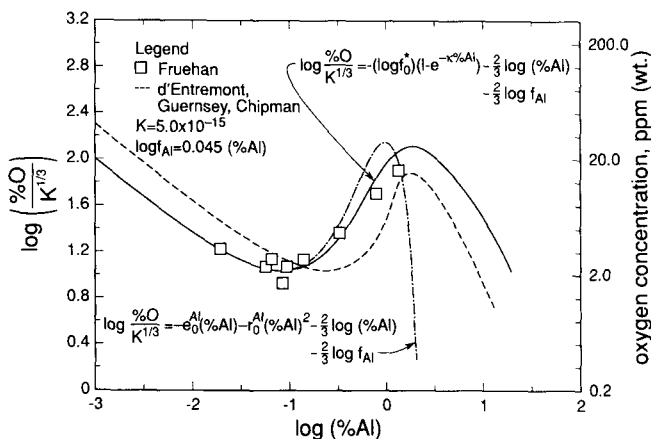


Fig. 2—Solubility relationships for Al_2O_3 in iron at 1600 °C. Comparisons of predictions with data.

K , due to inherent experimental difficulties.^[12] The equilibrium constant was assigned a value of 5×10^{-15} , which is representative of the values in the literature.^[1,5,6] The solubility after the maximum using the exponential function does not drop off nearly so sharply as with the use of the quadratic interaction coefficient expression. The new calculated curve more closely fits the experimental data of d'Entremont *et al.*^[3] at high aluminum contents. Also, the slope approaches $-2/3$, which again is consistent with the d'Entremont *et al.*^[3] results. It does not equal $-2/3$, because the $\log f_{\text{Al}}$ term has significance at these higher values of pct Al.

IV. CONCLUSIONS

The use of a two-parameter exponential function for expressing $\log f_{\text{O}}$ as a function of pct Al instead of the usual first- and second-order interaction coefficient formalism allows the solubility of alumina in iron to be described in a more realistic manner. The exponential form of $\log f_{\text{O}}$ is consistent with current clustering and central atom solution models. The exponential form does not predict a sharp increase in $\log f_{\text{O}}$ above 1.2 pct Al, as does the quadratic first- and second-order epsilon formalism. The exponential form of $\log f_{\text{O}}$ more closely fits experimental solubility data at high aluminum contents. Also, the slope after the solubility maximum approaches $-2/3$, which again is consistent with experimental data.

The two parameters f_{O}^* and κ have physical significance. The $\log f_{\text{O}}^*$ term is the saturation value of $\log f_{\text{O}}$, and $\kappa \log f_{\text{O}}^*$ is the initial slope at pct Al equal to zero, which is equivalent to e_0^{Al} . The parameter κ essentially takes the place of the second- and higher-order terms of the epsilon formalism.

The solubilities in other Fe-M-O systems exhibiting similar solubility minima and maxima, such as Fe-Ti-O and Fe-V-O, are compatible with this type of treatment.

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