Aluminum Deoxidation Equilibrium in Liquid Fe–36%Ni Alloy

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For thermodynamic prediction, the deoxidation equilibrium of aluminum in Fe–36%Ni alloy was investigated by employing a cold crucible under an Ar gas atmosphere at 1773 K. The interaction parameters between aluminum and oxygen by taking liquid Fe–36%Ni alloy as the basis (i.e., solvent) are evaluated as follows:

\[
\begin{align*}
\epsilon_{\text{Al}}^O &= -3.8, \\
\eta_{\text{Al}}^O &= -0.9, \\
\epsilon_{\text{O}}^\text{Fe} &= -6.4, \\
\eta_{\text{O}}^\text{Fe} &= 700, \\
\eta_{\text{Al}}^\text{Al} &= 3.1, \\
\eta_{\text{Al}}^\text{O} &= 833
\end{align*}
\]

within the composition range of [Al]<1 mass%.

The equilibrium constant for reaction \(2\text{Al}(\text{Fe}) + 3\text{O}_2(\text{gas}) = \text{Al}_2\text{O}_3(\text{s})\) was obtained in the temperature range of 1773 to 1973 K by using data from the present study and from previous works reported:

\[
\log K_{\text{Al}} = 0.58 - 24.460/T
\]

The deoxidation equilibrium of aluminum in Fe–36%Ni can thus be thermodynamically described in the range of [Al]<1 mass% using both the first and second order interaction parameters as well as the equilibrium constant determined in this study.

KEY WORDS: deoxidation equilibrium; equilibrium constant; interaction parameter; aluminum; nickel; deoxidation product, inclusion; cold crucible.

1. Introduction

Fe–36%Ni alloy, exhibiting anomalously low thermal expansion over a wide temperature range, is used as functional and electromagnetic materials.\(^1\) Since it is especially used as TV shadow mask, the demand has rapidly increased. \(\text{Al}_2\text{O}_3\) inclusions in this alloy, which are generated during deoxidation process, are very harmful for surface quality and therefore should be removed. However, enough data are not available for a reliable prediction of aluminum deoxidation equilibrium in this alloy.

In most investigations\(^2\)–10) on thermodynamic aspects of deoxidation equilibrium in Fe–Ni alloys, the effect of nickel on the activity coefficients of oxygen and deoxidizing elements in liquid iron have been evaluated by using their experimental results in Fe–Ni melts. For self-interaction parameters of aluminum and oxygen and the interaction parameter between aluminum and oxygen which were required in their evaluation, they employed the values reported by Sigworth \textit{et al.}\(^11,12\) or recommended by JSPS,\(^13\) both of which are based on liquid iron.

Sakao \textit{et al.}\(^2\) and Fisher \textit{et al.}\(^3\) carried out an experimental study on the reaction equilibrium between nickel and oxygen dissolved in liquid Fe–Ni and they reported similar values of interaction parameter between nickel and oxygen in iron, \(\epsilon_{\text{Ni}}^\text{O}\text{Ni}_{\text{Fe}}\) as can be seen in Table 1. Tankins\(^5\) and Cho \textit{et al.}\(^5\) also reported the values of \(\epsilon_{\text{Ni}}^\text{O}\text{Ni}_{\text{Fe}}\) but their values are different from those reported by the abovementioned authors to a substantial extent (see Table 1).

Katsuki \textit{et al.}\(^6\) and Ishii \textit{et al.}\(^8,9,10\) determined the interaction parameter between aluminum and nickel in liquid iron, \(\epsilon_{\text{Al}}^\text{Ni}_{\text{Fe}}\), by assessing aluminum deoxidation equilibrium in Fe–Ni melt, but the reported values are vastly different from each other as seen in Table 1. Cho \textit{et al.}\(^5\) derived the first and second order interaction parameters, i.e., \(\epsilon_{\text{Al}}^\text{Ni}_{\text{Fe}}\) and \(\eta_{\text{Al}}^\text{Ni}_{\text{Fe}}\) from thermodynamic analysis of aluminum deoxidation equilibrium for Fe–30, 50 and 70% Ni with CaO–Al\(_2\)O\(_3\) slags (see in Table 1).

By virtue of positive values of \(\epsilon_{\text{Al}}^\text{Ni}_{\text{Fe}}\) and negative ones of \(\epsilon_{\text{Ni}}^\text{O}\text{Ni}_{\text{Fe}}\) as seen in Table 1, nickel tends to increase the activity of oxygen but decrease the activity of aluminum in Fe melt. Since \(\epsilon_{\text{Al}}^\text{Ni}_{\text{Fe}}\) is much larger than \(\epsilon_{\text{Ni}}^\text{O}\text{Ni}_{\text{Fe}}\) in absolute value, nickel exerts much greater influence on aluminum than on oxygen, and hence the extent of decrease in aluminum activity is much larger than the extent of increase in oxygen activity by existence of nickel in the melt. In other words, for a given aluminum content, the aluminum activity is lower in Fe–Ni alloy than in Fe melt without nickel, and hence the equilibrium oxygen content is higher in Fe–Ni alloy.

Knowing that the concept of Wagner’s interaction parameters\(^14\) is based on dilute solutions, it is somewhat difficult to apply the same concept to high alloy systems such as invar which contains 36 mass% nickel, even though higher order interaction parameters are introduced. In order to overcome this difficulty, Fujiwara \textit{et al.}\(^15\) evaluated the in-
teraction parameter between aluminum and oxygen based on liquid Fe–36mass%Ni, i.e., $e_{O/Al(Fe–36%Ni)}$ by investigating deoxidation equilibrium for aluminum in Fe–36%Ni under H₂/H₂O gas mixture at 1 973 K and the result is given in Table 1. However, their work was confined to a narrow range in low aluminum concentrations.

The objective of the present study is to obtain the thermodynamic data of aluminum deoxidation equilibrium over a wide range of aluminum content covering up to 1 mass% Al in Fe–36%Ni alloy at 1 773 K. Liquid Fe–36%Ni is chosen as a base melt to avoid a separate consideration of nickel on other elements. The equilibrium constant as well as the first order and second order interaction parameters have been determined at 1 773 K.

2. Experimental

2.1. Procedure

Electromagnetic levitation-melting technique using a cold crucible was employed to study aluminum deoxidation equilibrium in liquid Fe–36%Ni. The cold crucible is a copper crucible constructed in segments, each of which is water-cooled (flow rate: 20 l/min). A high frequency current (20 kW and 170 kHz) was applied to the coil surrounding the crucible. This non-contact levitation melting enables to avoid any contamination or side effect which could otherwise result from a container like alumina crucible. Furthermore, inclusion particles, which are deoxidation products, are completely exposed on the surface of the molten metal and accumulated at the bottom of the metal in the form of a thin film by gravity. Therefore, metal and oxide are perfectly separated from each other and hence all oxygen and aluminum existing in the metal can be regarded as solute, not in the form of oxide.

The experimental apparatus is shown in Fig. 1. Gas purification trains and gas flow meters are also constructed. The melt temperature was measured using a two-color optical pyrometer calibrated preliminarily against a thermocouple (Pt–30%Rh/Pt–6%Rh).

Nickel and iron of electrolytic grade and high purity aluminum (99.99 mass%) were used in preparing alloys. Master alloys of Fe–36%massNi and Fe–36%massNi–1%massAl were made in an alumina crucible using an induction furnace. For each run of experiment, 35–40 g of Fe–36%Ni alloy and an appropriate amount of Fe–36%Ni–1%Al alloy were placed in the cold crucible and then purged under a purified Ar–1vol%H₂ gas mixture for 15 min. After the sample has been heated to the desired temperature, the atmosphere was changed to argon gas, which was purified by passing through an Mg chip column at 723 K. It was confirmed that the system reached equilibrium approximately in 10 min at 1 773 K as shown in Fig. 2. In order to ensure complete equilibration, samples were kept levitated for 15 min and then quenched by turning off the power. The melt fell on the water-cooled cold crucible and rapidly quenched in a purified He gas stream. The quenched sample was cut into cubic-shaped pieces for oxygen and aluminum analyses.

2.2. Chemical Analysis

The total oxygen content in a sample was determined by combustion infrared absorption spectroscopy. For aluminum analysis the sample was dissolved by aqua regia (a mixed solution of HCl : HNO₃ = 3 : 1) and the total alu-
In order to investigate the equilibrium between aluminum and oxygen in liquid Fe–36%Ni, it is essential to determine the interaction parameters between aluminum and oxygen for the deoxidation reaction in liquid Fe–36%Ni represented by Eq. (1). Equation (2) is the equilibrium constant expression of the reaction of Eq. (1).

\[
\text{Al}_2\text{O}_3(s) = 2\text{Al} + 3\text{O} \quad \text{(1)}
\]

where \(a_{\text{Al}}, a_{\text{O}}, \text{and } a_{\text{Al}_2\text{O}_3}\) are activities of aluminum, oxygen and alumina, respectively. In the present analysis, the activities of Al and O in liquid Fe–36%Ni alloy are defined relative to 1 mass% Henrian standard state based on liquid Fe–36%Ni (not on pure liquid Fe), and for the activity of alumina pure solid \(\text{Al}_2\text{O}_3\) is taken as the standard state.

Assuming that the deoxidation product is pure alumina,

\[
K_{\text{AO}} = \frac{a_{\text{Al}_2\text{O}_3}^2}{a_{\text{Al}}^2 a_{\text{O}}^3} \quad \text{(2)}
\]

where \(f_{\text{Al}}\) and \(f_{\text{O}}\) denote activity coefficients of aluminum and oxygen in liquid Fe–36%Ni, respectively, and \([\%\text{Al}]\) and \([\%\text{O}]\) are the concentration of Al and O in mass%, respectively, in the alloy.

By defining the deoxidation product of aluminum by Eq. (4)

\[
K'_{\text{AO}} = [\%\text{Al}]^2 [\%\text{O}]^3 \quad \text{(4)}
\]

Combination of Eq. (3) and Eq. (4) yields Eq. (5):

\[
\log K'_{\text{AO}} = \log K_{\text{AO}} - 2 \log f_{\text{Al}} - 3 \log f_{\text{O}} \quad \text{(5)}
\]

Since it is necessary to take higher order terms of interaction parameters into account at higher concentrations of aluminum, activity coefficients are expanded to the second order terms as follows:

\[
\begin{align*}
\log f_{\text{Al}} &= e_{\text{Al}}[\%\text{O}] + r_{\text{Al}}[\%\text{Al}]^2 + e_{\text{Al}}[\%\text{Al}] + r_{\text{Al}}[\%\text{Al}]^2 + r_{\text{Al}}[\%\text{O}]^2 + r_{\text{Al}}[\%\text{Al}] [\%\text{O}] \quad \text{(6)} \\
\log f_{\text{O}} &= e_{\text{O}}[\%\text{O}] + e_{\text{O}}[\%\text{Al}] + r_{\text{O}}[\%\text{Al}]^2 + r_{\text{O}}[\%\text{Al}] [\%\text{O}] + r_{\text{O}}[\%\text{O}]^2 \quad \text{(7)}
\end{align*}
\]

where \(e_i\) and \(r_i\) represent the first and second order interaction parameter between \(i\) and \(j\) (the effect of \(j\) on \(i\) ), respectively. The above expressions for the activity coefficients also contain the cross-product second order parameters \((r_{ij})\) as well as the squared second order parameters \((r_{ii})\).

Relationships among various interaction parameters may be formulated as follows:

\[
\begin{align*}
e_{\text{Al}} &= (M_j/M_i) e_{\text{Al}} + (1/230)(M_i - M_j)/M_i \quad \text{(8)} \\
r_{\text{Al}} &= 2(M_j/M_i) r_{\text{Al}} + (1/10^3) e_{\text{Al}} - (M_i - M_j)/(2.3 \times 10^4 M_i) \quad \text{(9)} \\
r_{\text{O}} &= 2(M_j/M_i) r_{\text{O}} + (1/10^3) e_{\text{O}} + (M_i - M_j)/(2.3 \times 10^4 M_i) \quad \text{(10)}
\end{align*}
\]

where \(M_j\) and \(M_i\) represent atomic mass of component \(i\) and \(j\), respectively.

Applying Eqs. (8)–(10) to Al and O,

\[
\begin{align*}
e_{\text{Al}} &= 1.69 e_{\text{Al}} - 2.98 \times 10^{-3} \quad \text{(11)} \\
r_{\text{Al}} &= 1.19 r_{\text{Al}} - 0.01 e_{\text{Al}} + 1.77 \times 10^{-5} \quad \text{(12)} \\
r_{\text{O}} &= 3.37 r_{\text{O}} - 0.01 e_{\text{O}} + 2.98 \times 10^{-5} \quad \text{(13)}
\end{align*}
\]

The self-interaction parameters, \(e_{\text{Al}}\) and \(e_{\text{O}}\), \(r_{\text{Al}}\) and \(r_{\text{O}}\) are considered negligible, as they are much too small,11–13 Substitution of Eqs. (6) and (7) as well as Eqs. (11)–(13) in Eq. (5) yields Eq. (14).

\[
\log K_{\text{AO}} = \log K'_{\text{AO}} + e_{\text{Al}}[3[\%\text{Al}] + 3.38[\%\text{O}] - 0.0638[\%\text{Al}][\%\text{O}]) + r_{\text{Al}}[2[\%\text{Al}]^2 + 6.74[\%\text{Al}][\%\text{O}]) + r_{\text{O}}[2[\%\text{O}]^2 + 3.57[\%\text{Al}][\%\text{O}]) + (1.43 \times 10^{-4}[\%\text{Al}][\%\text{O}] - 5.96 \times 10^{-4}[\%\text{O}]) \quad \text{(14)}
\]

It is noted that the last term of the right hand side in the above equation is negligibly small, compared with other terms.

3.2. Interaction Parameters and Equilibrium Constant in Liquid Fe–36%Ni

Equilibrium chemical compositions of the metal obtained through experiment in present study are shown in Table 2, and graphically represented in Fig. 3. Included also in the figure are the data at 1873 K and 1973 K reported in the literature.5,6,12) The lines shown in Fig. 3 will be discussed later in Sec. 3.4. The present study was carried out in the wide range of aluminum concentration up to 1 mass% Al. It can be seen in the figure that there exists a solubility minimum of oxygen, that is, an optimum quantity of deoxidizer, which is well known phenomenon in strong deoxidation reactions. It is also seen that oxygen solubility increases with increasing temperature. It is interesting to note in Fig. 3 that Cho et al.2) reports that the deoxidation product of liquid Fe–50%Ni is very much the same as that in Fe–30%Ni. This appears to imply that variation of the deoxidation
product \((K_{\text{AO}})\) value is not sensitive to the change of nickel concentration at least in the concentration range of Fe–30\%Ni and Fe–50\%Ni. Katsuki et al.\(^6\) have reported much higher equilibrium oxygen values at 1873 K than Cho et al.\(^5\). Taking into account the data at 1973 K reported by Fujiwara et al.\(^1\) Cho et al.’s data may be considered more consistent.

Values of \(e_{\text{Al}}^O\), \(r_{\text{Al}}^O\), \(r_{\text{Al}}^O\) and \(\log K_{\text{AO}}\) in Fe–36\%Ni can be obtained from the Eq. (14) by regression analysis using the experimental data of the present study and these are,

\[
e_{\text{Al}}^O = -3.8, \quad r_{\text{Al}}^O = 0.9, \quad r_{\text{Al}}^O = 700, \quad \log K_{\text{AO}} = -13.2
\]

From Eqs. (11)–(13),

\[
e_{\text{Al}}^O = -6.4, \quad r_{\text{Al}}^O = 3.1, \quad r_{\text{Al}}^O = 833
\]

### 3.3. Estimation of Thermodynamic Data

If the second order interaction parameter terms between aluminum and oxygen become negligible in Eq. (14), \(\log K_{\text{AO}}\) can be simplified as follows:

\[
\log K_{\text{AO}} = \log K_{\text{AO}} - 3e_{\text{Al}}^O ([\%\text{Al}] + 1.124[\%\text{O}]) .... (15)
\]

In deriving the above equation, the term, \(-0.0638\cdot[\%\text{Al}][\%\text{O}]\), was eliminated as well since the term was also originated from expressions of the second order interaction parameters in Eqs. (12) and (13).

Figure 4 shows a graphical expression of Eq. (15) using experimental data obtained in the present study, where \(\log K_{\text{AO}}\) is related against the \(3([\%\text{Al}] + 1.124[\%\text{O}])\). The result shows a non-linear relationship and hence indicates that the equilibrium between aluminum and oxygen in liquid Fe–36\%Ni cannot be explained by first order interaction parameters alone, in particular, in the high concentration range of aluminum. By use of Eq. (14), on the other hand, the plot of \(\log K_{\text{AO}} + r_{\text{Al}}^O \cdot 3([\%\text{Al}] + 6.74([\%\text{Al}] + [\%\text{O}])\cdot r_{\text{Al}}^O \cdot (2([\%\text{O}] + 3.57[\%\text{Al}][\%\text{O}])

\[3([\%\text{Al}] + 1.124[\%\text{O}] - 0.0213[\%\text{Al}][\%\text{O}]\) results in an excellent linear relationship as shown in Fig. 5. This result indicates that the equilibrium calculation between aluminum and oxygen in liquid Fe–36\%Ni requires the second order interaction parameters as well as the first order ones especially for high aluminum concentration range.

If the concentration of a solute is dilute enough, it is customary to use only first order interaction parameters for the activity calculation of solutes. In this case, however, validity of use of the first order interaction parameters alone has to be confirmed, otherwise the second order interaction pa-
The activity coefficient of oxygen given by Eq. (7), for instance, may be reduced to the following equation by ignoring the self-interaction parameter terms like $e_{O}^O$ and $r_{O}^O$:

$$\log f_{O}/H_{11005} = e_{O}^Al[%Al]/H_{11001} + r_{O}^Al[%Al]/H_{11001}$$

The concentration limit of aluminum below which use of first order interaction parameter, $e_{O}^Al$, alone suffices for the calculation of $f_{O}$ can be readily determined simply by plotting $\log f_{O}$ against $[%Al]$ according to Eq. (16). As can be seen in Fig. 6, the plot of $\log f_{O}$ against $[%Al]$ shows a linear relationship up to 0.1% of aluminum. This implies that use of the first order interaction parameters alone is sufficient below 0.1% of aluminum, above which higher order parameters are required to be included in the activity calculation.

At low aluminum concentration range ($[%Al]<0.1$), $\log K_{AO}$ were re-plotted against $3([%Al]+1.124[O])$ in the range of $[%Al]<0.1$ in liquid Fe–36%Ni at 1773 K.

The concentration limit of aluminum below which use of first order interaction parameter, $e_{O}^Al$, alone suffices for the calculation of $f_{O}$ can be readily determined simply by plotting $\log f_{O}$ against $[%Al]$ according to Eq. (16). As can be seen in Fig. 6, the plot of $\log f_{O}$ against $[%Al]$ shows a linear relationship up to 0.1% of aluminum. This implies that use of the first order interaction parameters alone is sufficient below 0.1% of aluminum, above which higher order parameters are required to be included in the activity calculation.

At low aluminum concentration range ($[%Al]<0.1$), $\log K_{AO}$ were re-plotted against $3([%Al]+1.124[O])$ in Fig. 7. For the effect of temperature on equilibrium constant, the reported data of Cho et al.\textsuperscript{15} (1873 K) and Fujiwara et al.\textsuperscript{15} (1973 K) are re-estimated and listed in the Table 3 together with the present work. The data of Cho et al.\textsuperscript{15} are in fact for the alloy of not Fe–36%Ni, but Fe–30%Ni. As discussed earlier with Fig. 3, however, they reported the deoxidation product of for Fe–50%Ni being very much the same as that for Fe–30%Ni. This assures that use of their data for Fe–30%Ni in place of Fe–36%Ni at 1873 K does not introduce unacceptable inaccuracy in determining the effect of temperature. Figure 8 gives an Arrhenius plot of $\log K_{AO}$ against temperature and it shows an excellent linear relationship. The following equation, Eq. (17), is the linear regression of the data:

$$\log K_{AO}/H_{11005} = 0.58 - 24460/T \quad (1773 K \leq T \leq 1973 K)$$

### Table 3. Equilibrium constants in liquid Fe–Ni alloys.

| Authors                | $\log K_{AO}$ | Temperature (K) | Remarks          |
|------------------------|---------------|-----------------|-----------------|
| Fujiwara et al.\textsuperscript{15} | -11.8         | 1973            | Fe-36%Ni *      |
| Cho and Suito\textsuperscript{15} | -12.5         | 1873            | Fe-30%Ni *      |
| Present study          | -13.2         | 1773            | Fe-36%Ni        |

* Calculated in this study with the reported data.

3.4. Deoxidation Equilibrium of Aluminum in Liquid Fe–36%Ni

The activity of Al was obtained by two different methods, namely, one by using experimentally determined aluminum concentration and its activity coefficient calculated by Eq. (7), and the other by using the following equation.

$$2 \log a_{Al} = \log K_{AO} - 3 \log a_{O}$$

The aluminum activities obtained by the above two meth-
ods are compared in Fig. 9. It is clearly seen that the aluminum activities calculated by the former method (denoted by $a_{Al}^{(direct)}$) are in excellent agreement with the ones obtained by the latter method (denoted by $a_{Al}^{(indirect)}$).

Deoxidation equilibrium relationship between aluminum and oxygen at 1773 K was computed using Eq. (14) and the results are included in Fig. 3 in the form of a solid curve. The relationships at other temperatures of 1873 K and 1973 K are also included, which were estimated from the results at 1773 K by employing regular solution approximation. It is clearly seen that the calculated line at each temperature is in good accordance with the experimental data within experimental uncertainty.

4. Conclusions

Thermodynamics of aluminum deoxidation equilibrium in Fe–36%Ni alloy was studied by using a cold crucible. The following conclusions were derived from the present results:

1) Interaction parameters, $e_{O}^{Al}$, $r_{O}^{Al}$, $e_{Al}^{O}$, $r_{Al}^{O}$, $r_{Al,O}^{Al}$ and $r_{O}^{Al,O}$ for Fe–36%Ni base were determined in the range of $[\%Al]<1$:

$$e_{O}^{Al} = -3.8, \quad r_{O}^{Al} = 0.9,$$
$$e_{Al}^{O} = -6.4, \quad r_{Al}^{O} = 700,$$
$$r_{Al,O}^{Al} = 3.1, \quad r_{O}^{Al,O} = 833$$

The temperature dependence of the equilibrium constant was obtained in the range of $1773 \leq T \leq 1973$ K by using reported data and present results as follows:

$$\log K_{AO} = 0.58 - 24460/T$$

2) The equilibrium relationship between aluminum and oxygen contents in Fe–36%Ni alloys calculated by using the first and second order interaction parameters as well as the equilibrium constant determined in this study were in good agreement with the experimental results. The deoxidation equilibrium of aluminum in Fe–36%Ni could thermodynamically be described in the range of $[\%Al]<1$.

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