Numerical Analysis on Si Deoxidation of Molten Fe–Ni and Ni–Co Alloys by Quadratic Formalism

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Relation between the activity coefficient expressed by Darken’s quadratic formalism and the excess Gibbs energy change of mixing described with Redlich–Kister type polynomial was discussed on Si deoxidation of Fe–Ni and Ni–Co alloys. The activity coefficients of Si and O in metal expressed by quadratic formalism have been converted into formula using interaction parameters \( \Omega_{ij} \) under the condition where concentration of Si and O are dilute.

Numerical analysis on Si deoxidation of molten Fe–Ni and Ni–Co alloy has been carried out. It has been found to be outstanding in the agreement of equilibrium Si and O contents in molten Fe–Ni and Ni–Co alloy analyzed in the present work with the experimental results. The deoxidation equilibrium of not only one component metal but also alloy can be analyzed numerically using the formula determined in the present work.

KEY WORDS: quadratic formalism; thermodynamics; activity; excess Gibbs energy; Redlich–Kister polynomial; deoxidation equilibrium; silicon; nickel; iron; cobalt.

1. Introduction

The equation proposed by Wagner\(^1\) has been widely used to express the activity coefficients of solute in multicomponent solutions. However, second order or higher terms must be added to represent the activity coefficients on the condition where solute contents are rich. Darken\(^2,3\) has proposed the quadratic formalism to express the activity coefficients that can be applied to higher solute content. The activity coefficients of solvent 1 and solute 2, 3 can be expressed for ternary solution by the following equations.

\[
\ln \gamma_i = \alpha_{12} X_1^2 + \alpha_{13} X_1^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_1 X_3 \quad \ldots \ldots \text{(1)}
\]

\[
\ln \gamma_2 = -2 \alpha_{12} X_2 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_3 + \alpha_{12} X_1^2 + \alpha_{13} X_1^2 + \ln \gamma_2^0 \quad \ldots \ldots \text{(2)}
\]

\[
\ln \gamma_3 = -2 \alpha_{13} X_3 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_1 + \alpha_{12} X_1^2 + \alpha_{13} X_1^2 + \ln \gamma_3^0 \quad \ldots \ldots \text{(3)}
\]

Where \( X_i \) denotes mole fraction of component \( i \), \( \gamma_i \) denotes the activity coefficient of component \( i \), \( \gamma_i^0 \) denotes the activity coefficient of component \( i \) at infinite dilution, and \( \alpha_{ij} \) is a constant that characterizes the thermodynamic property of \( i-j \) binary solution within the region of validity of equations at constant temperature and pressure, respectively.

The following relations can be obtained\(^2,3\) by comparing the equation proposed by Wagner\(^1\) with Eq. (2).

\[
\varepsilon_{12}^2 = -2 \alpha_{12} \quad \ldots \ldots \text{(4)}
\]

\[
\varepsilon_{13}^2 = \alpha_{13} - \alpha_{12} - \alpha_{13} \quad \ldots \ldots \text{(5)}
\]

\[
\rho_2 = \alpha_{12} \quad \ldots \ldots \text{(6)}
\]

\[
\rho_3 = \alpha_{13} \quad \ldots \ldots \text{(7)}
\]

\[
\rho_2^{\text{23}} = \alpha_{12} + \alpha_{13} - \alpha_{23} \quad \ldots \ldots \text{(8)}
\]

Where \( \varepsilon_i^2 \) and \( \rho_i^j \) are the first and the second order interaction coefficients, respectively.

Quadratic formalism includes all the first and the second order terms represented by Wagner’s formalism. Hence, the valid composition region that quadratic formalism stands is essentially wider than that where Wagner’s formalism are available. Numerical analysis on Si deoxidation of molten Ni and Ni–Cu alloy was conducted in our previous work.\(^4\) Numerical analysis on Si deoxidation of molten Fe–Ni and Ni–Co alloy utilizing quadratic formalism has been carried out in the present work.

2. Preparation of Numerical Analysis

2.1. Relation between Darken’s Quadratic Formalism and Redlich–Kister Type Polynomial

Quadratic formalism was converted into Redlich–Kister type polynomial\(^5,6\) to express the excess Gibbs energy change of mixing. This conversion was done because it would be easier to expand Darken’s quadratic formalism to multi-component alloy systems. The excess Gibbs energy change of mixing for 1–2 binary system, \( \Delta G^{\text{ex}} \), and partial molar excess Gibbs energy change, \( \Delta G^{\text{ex}}_{i} \), can be expressed as Eqs. (9) and (10), respectively.

\[
\Delta G^{\text{ex}} = X_1 X_2^0 \Omega_{1-2} + \Omega_{1-2} (X_1 - X_2) \quad \ldots \ldots \text{(9)}
\]
Quadratic formalism can be converted into Redlich–Kister combining Eqs. (11) and (15) as follows.

\[
\Delta G^\text{ex}_{2} = RT \ln \gamma_{2} = \Delta G^\text{ex} + (1 - X_{2}) \frac{\partial \Delta G^\text{ex}}{\partial X_{2}} = X_{1}^{2} \theta (\Omega_{1-2} - 3 \Omega_{1-2}) + X_{1}^{3} \Omega_{1-2} \quad \ldots \quad (10)
\]

Where \( \theta \Omega_{1-2} \) and \( \Omega_{1-2} \) are binary interaction parameters. On the condition of \( X_{1} = 1 \), the activity coefficient of component 2 will be \( \gamma_{2}^{O} \). Hence, the following relation can be obtained in the infinite dilute solution of 2.

\[
RT \ln \gamma_{2}^{O} = \theta \Omega_{1-2} + \Omega_{1-2} \quad \ldots \quad (11)
\]

The activity coefficient of component 2 in 1–2 binary system can be expressed as Eq. (12), using Darken’s quadratic formalism.

\[
\ln \gamma_{2} = \alpha_{1-2} X_{1}^{2} + I \quad \ldots \quad (12)
\]

Where \( I \) is a constant on the condition of constant temperature and pressure. Equation (12) is valid in the dilute solution of component 2. Multiplying gas constant, \( R \), and absolute temperature, \( T \), to both sides of Eq. (12) and partial differentiating with \( X_{1}^{2} \) gives us the following relation.

\[
\frac{\partial (RT \ln \gamma_{2})}{\partial (X_{1}^{2})} = RT \alpha_{1-2} \quad \ldots \quad (13)
\]

On the other hand, the following equation can be derived from partial differentiation of Eq. (10) with \( X_{1}^{2} \).

\[
\frac{\partial (RT \ln \gamma_{2})}{\partial (X_{1}^{2})} = 6 \theta \Omega_{1-2} + 6 \Omega_{1-2} \ldots \quad (14)
\]

On the condition \( X_{1} = 1 \), Eqs. (13) and (14) will be equivalent and the following relation will be obtained for infinite dilute solution.

\[
RT \alpha_{1-2} = \theta \Omega_{1-2} + \Omega_{1-2} \quad \ldots \quad (15)
\]

The binary interaction parameters can be obtained by combining Eqs. (11) and (15) as follows.

\[
\theta \Omega_{1-2} = RT \left( \frac{3}{2} \ln \gamma_{2}^{O} + \frac{1}{2} \alpha_{1-2} \right) \quad \ldots \quad (16)
\]

\[
\Omega_{1-2} = RT \left( - \frac{1}{2} \ln \gamma_{2}^{O} + \frac{1}{2} \alpha_{1-2} \right) \quad \ldots \quad (17)
\]

Quadratic formalism can be converted into Redlich–Kister type polynomial using \( \theta \Omega_{1-2} \) and \( \Omega_{1-2} \) for dilute solution using Eqs. (16) and (17).  

2.2. Standard State of Components

Pure substance is condensed as a standard state (Raoultian standard state) for condensed phases in the present work. It is general to select Henrian standard state for oxygen dissolved in pure melts. However, problems arise in case of alloys. The activity coefficients of oxygen in metal 1 and 2 are taken as unity to describe the activity coefficient of oxygen in 1–2 binary alloy by using Henrian standard state, and the effect of alloy component is compensated by interaction coefficients. When the oxygen activities using Henrian standard state in metal 1 and 2 are identical, the equilibrium oxygen partial pressure differs each other due to the difference of the Gibbs free energy change of oxygen dissolution into pure 1 and 2. Therefore, the Henrian standard state is not a universal reference in case of oxygen in alloy. Therefore, dissolved oxygen in the melt equilibrating with 101325 Pa (1 atm) oxygen gas has been selected as a standard state in the present work. The relation between the oxygen activity and oxygen partial pressure in this standard state can be expressed as follows.

\[
a_{O} = P_{O}^{1/2} \quad \ldots \quad (18)
\]

The activity coefficient of oxygen at infinite dilution in metal is not unity as the case of Henrian standard state but \( \gamma_{O}^{O} \). The oxygen activity or equilibrium oxygen partial pressure is, therefore, independent of the kind of metal solvent and can be expressed by utilizing this standard state.

3. Numerical Analysis on Si Deoxidation of Molten Fe

Si deoxidation reaction can be expressed by Eq. (19).

\[
\text{Si} + 2\text{O} = \text{SiO}_{2} (s) \quad \ldots \quad (19)
\]

This equation can be separated into following equations regarding that pure substance is chosen as a standard state (Raoultian standard state).

\[
\text{Si}(l) + \text{O}_{2}(g) = \text{SiO}_{2} (s) \quad \ldots \quad (20)
\]

\[
2\text{O} = \text{O}_{2}(g) \quad \ldots \quad (21)
\]

The Gibbs free energy change of Eq. (20) is identical to the Gibbs free energy of SiO formation \( \Delta G_{\text{ex}}^{\text{ex}} \) and that of Eq. (21) is zero due to the relationship of Eq. (18). Therefore, the Gibbs free energy change of Eq. (19) will be identical to the Gibbs free energy of SiO formation \( \Delta G_{\text{ex}}^{\text{ex}} \). Equation (19) and the Gibbs free energy of SiO formation can be utilized for Si deoxidation of any metal or alloy, and this is a great advantage. The equilibrium constant of Eq. (19), \( K_{Si} \), can be expressed as follows.

\[
\ln K_{Si} = - \frac{\Delta G_{\text{ex}}^{\text{ex}}}{RT} = \ln a_{SiO_{2}} - \ln \gamma_{Si} - 2 \ln \gamma_{O} - \ln X_{Si} - 2 \ln X_{O} \quad \ldots \quad (22)
\]

Where, the activity of SiO2 is taken as unity, since deoxidation product is pure SiO2.

The excess free energy change of mixing on Fe–Si–O ternary system can be expressed as Eq. (23) by using Redlich–Kister type polynomial.

\[
\Delta G^\text{ex} = X_{Fe} X_{Si} \left( \theta \Omega_{Fe-Si} + \Omega_{Fe-Si} \right) \quad \ldots \quad (23)
\]

The partial molar excess free energy change of Si and O can be derived as follows.

\[
\Delta G_{Si}^\text{ex} = RT \ln \gamma_{Si} = \Delta G^\text{ex} + (1 - X_{Si}) \frac{\partial \Delta G^\text{ex}}{\partial X_{Si}} - X_{O} \frac{\partial \Delta G^\text{ex}}{\partial X_{O}}
\]
interaction parameters 0 on Si deoxidization equilibrium of molten Fe. The binary parameters utilized in the present work are shown in the present evaluation shown by curve in Fig. 1. The results of EMF experiment were highly taken into account by curve in Fig. 1. The activity coefficient of Si in Ag phase differs widely among researchers. The activity coefficient of Si in molten Fe–Si alloy 16–26) has been taken from NIST-JANAF Thermochemical Tables. 15) Equation (26) is the fundamental equation for numerical analysis of Si deoxidation in molten Fe. Experimental results reported by Matoba et al., 9) Tszen-Tszi et al., 10) Hilty and Crafts, 11) Segawa et al., 12) Shevtsov et al. 13) were utilized for analysis on Si deoxidization equilibrium of molten Fe. The binary interaction parameters 00, 01 were obtained from the Gibbs free energy change of oxygen dissolution into molten Fe and the self-interaction coefficient of oxygen in molten Fe. 14) The Gibbs free energy of SiO2 formation has been taken from NIST-JANAF Thermochemical Tables. 15) The activity coefficient of Si in molten Fe–Si alloy16–26) compiled by Chart 27) is shown in Fig. 1. The results obtained from the equilibration of Si between Ag and Fe phase were omitted for evaluation because the activity coefficient of Si in Ag phase differs widely among researchers. The results of EMF experiment were highly taken into account in the present evaluation shown by curve in Fig. 1. The parameters utilized in the present work are shown below.

\[
\begin{align*}
0_0 & = -415700 + 139.5 T / J \\
1_0 & = 298600 - 115.0 T / J \\
0_1 & = 1338000 - 751.0 T / J \\
1_1 & = -1574000 + 797.7 T / J \\
\Delta G_{SiO2}^0 & = -946300 + 197.7 T / J
\end{align*}
\]

Equation (26) can be obtained by rearranging Eq. (26).
4. Numerical Analysis on Si Deoxidation of Molten Fe–Ni and Ni–Co Alloys

In case of analyzing numerically Si deoxidation of molten Fe–Ni alloy, binary interaction parameters of Fe–Ni, Ni–Si, and Ni–O systems must be additionally considered with the binary interaction parameters used for the numerical analysis of Si deoxidation in molten Fe. The excess Gibbs free energy change of mixing for Fe–Ni binary alloy reported by Tang,28 the Gibbs free energy change of oxygen dissolution into molten Ni and self-interaction parameter of oxygen in molten Ni reported by Sigworth et al.29 were used to determine the binary interaction parameters of Fe–Ni and Ni–O systems, respectively. Experimental results for Si deoxidation of molten Fe–Ni alloys reported by Ishii and Ban-ya30 were utilized for the analysis. Binary interaction parameters of Fe–Ni system reported by Tang30 and that for Ni–O system obtained from the results of Sigworth et al.29 are shown in the following.

\[ \Omega_{\text{Ni,Fe}}^{0} = -16\,911 + 5.1622\,T/J \]

Equations (34) and (35) are valid for any composition of Fe–Ni binary, while Eqs. (36) and (37) are valid in the dilute region of O in molten Ni.

The excess Gibbs free energy change for Ni–Fe–Si–O quaternary system can be expressed as follows.

\[
\Delta G^{\text{ex}} = X_{\text{Ni}} X_{\text{Fe}} (\theta_{\text{Ni,Fe}}^{0}) \Omega_{\text{Ni,Fe}}^{0} (X_{\text{Ni}} - X_{\text{Fe}}) + X_{\text{Ni}} X_{\text{Si}} (\theta_{\text{Ni,Si}}^{0}) \Omega_{\text{Ni,Si}}^{0} (X_{\text{Ni}} - X_{\text{Si}}) + X_{\text{Ni}} X_{\text{O}} (\theta_{\text{Ni,O}}^{0}) \Omega_{\text{Ni,O}}^{0} (X_{\text{Ni}} - X_{\text{O}})
\]

The partial molar excess free energy change of Si and O can be derived as follows.

\[
\Delta G_{\text{Si}}^{\text{ex}} = \Delta G^{\text{ex}} - X_{\text{Fe}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Fe}}} + (1 - X_{\text{Si}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Si}}} - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}}
\]

\[
\Delta G_{\text{O}}^{\text{ex}} = RT \ln \gamma_{\text{O}}
\]

Relation between silicon and oxygen concentration in molten Fe.

\[
2X_{\text{Si}} + X_{\text{O}} = 3X_{\text{Si}} X_{\text{O}} \text{ as a horizontal axis, } \Omega_{\text{Si-O}} \text{ can be derived from the slope of the regression line. The results are shown in Fig. 2. The results of Hilty and Crafts\textsuperscript{11} are not shown in the figure due to large scatter. Liner relations have been observed at each temperature, and } \Omega_{\text{Si-O}} \text{ was determined as follows.}
\]

\[
\Omega_{\text{Si-O}} = -388\,000 + 129.2\,T/J \]

The relation between equilibrium Si and O content in molten Fe compared with the results of researchers is shown in Fig. 3. The present result agrees extremely well with their experimental results and was confirmed that the parameters determined in the present work is suitable.
The following relation can be obtained by substituting Eqs. (39) and (40) into Eq. (22).

\[ 0 \Omega_{\text{Ni-Si}} \Delta S_{\text{Ni-Si}} (1 - 3X_{\text{Si}}) + 0 \Omega_{\text{Ni-Si}} \Delta S_{\text{Ni-Si}} (X_{\text{Ni}} - 2X_{\text{Si}} - 6X_{\text{Ni}}X_{\text{Si}} + 6X_{\text{Si}}^2) 
+ 0 \Omega_{\text{Ni-O}} \Delta S_{\text{Ni-O}} (2 - 3X_{\text{O}}) 
+ 1 \Omega_{\text{Ni-O}} 2X_{\text{Ni}} (X_{\text{Ni}} - 2X_{\text{O}} - 3X_{\text{Ni}}X_{\text{O}} + 3X_{\text{O}}^2) 
+ 0 \Omega_{\text{Fe-Si}} \Delta S_{\text{Fe-Si}} (1 - 3X_{\text{Si}}) + 1 \Omega_{\text{Fe-Si}} \Delta S_{\text{Fe-Si}} (X_{\text{Fe}} - 2X_{\text{Si}} - 6X_{\text{Fe}}X_{\text{Si}} + 6X_{\text{Si}}^2) 
+ 0 \Omega_{\text{Fe-O}} \Delta S_{\text{Fe-O}} (2 - 3X_{\text{O}}) + 1 \Omega_{\text{Fe-O}} 2X_{\text{Fe}} (X_{\text{Fe}} - 2X_{\text{O}} - 3X_{\text{Fe}}X_{\text{O}} + 3X_{\text{O}}^2) 
+ 0 \Omega_{\text{Si-O}} \Delta S_{\text{Si-O}} (2X_{\text{Si}} + 3X_{\text{O}} - 3X_{\text{Si}}X_{\text{O}}) 
- 3^3 \Omega_{\text{Ni-Fe}} X_{\text{Ni}} X_{\text{Fe}} - 6^1 \Omega_{\text{Ni-Fe}} X_{\text{Ni}} X_{\text{Fe}} (X_{\text{Ni}} - X_{\text{Fe}}) + RT \ln X_{\text{Ni}} + 2RT \ln X_{\text{O}} - \Delta G_{\text{Ni-SiO}} = 0 \] .................(41)
Rearranging Eq. (41) derives Eq. (42).

\[ Y_{\text{Ni-Si}} = \frac{1}{X_{\text{Ni}} (1 - 3X_{\text{Si}})} (-^6 \Omega_{\text{Fe-Si}} X_{\text{Fe}} (1 - 3X_{\text{Si}}) 
- ^1 \Omega_{\text{Fe-Si}} X_{\text{Fe}} (X_{\text{Fe}} - 2X_{\text{Si}} - 6X_{\text{Fe}}X_{\text{Si}} + 6X_{\text{Si}}^2) 
- ^0 \Omega_{\text{Fe-O}} X_{\text{Fe}} (2 - 3X_{\text{O}}) 
- ^1 \Omega_{\text{Fe-O}} X_{\text{Fe}} (X_{\text{Fe}} - 2X_{\text{O}} - 3X_{\text{Fe}}X_{\text{O}} + 3X_{\text{O}}^2) 
- ^0 \Omega_{\text{Ni-O}} X_{\text{Ni}} (2 - 3X_{\text{O}}) 
- ^1 \Omega_{\text{Ni-O}} X_{\text{Ni}} (X_{\text{Ni}} - 2X_{\text{O}} - 3X_{\text{Ni}}X_{\text{O}} + 3X_{\text{O}}^2) 
- ^0 \Omega_{\text{Si-O}} X_{\text{Si}} (2X_{\text{Si}} + 3X_{\text{O}} - 3X_{\text{Si}}X_{\text{O}}) 
+ ^3 \Omega_{\text{Ni-Fe}} X_{\text{Ni}} X_{\text{Fe}} 
+ 6^1 \Omega_{\text{Ni-Fe}} X_{\text{Ni}} X_{\text{Fe}} (X_{\text{Ni}} - X_{\text{Fe}}) 
- RT \ln X_{\text{Ni}} - 2RT \ln X_{\text{O}} + \Delta G_{\text{Ni-SiO}}) 
= ^6 \Omega_{\text{Ni-Si}} + ^1 \Omega_{\text{Ni-Si}} X_{\text{Ni}} - 2X_{\text{Si}} - 6X_{\text{Ni}}X_{\text{Si}} + 6X_{\text{Si}}^2 
\frac{1}{1 - 3X_{\text{Si}}} \] .................(42)

By utilizing Eqs. (27)–(31), (33)–(37) and experimental results reported by Ishii and Ban-ya\(^{[10]}\) and taking \(Y_{\text{Ni-Si}}\) in Eq. (42) as a vertical axis and \((X_{\text{Ni}} - 2X_{\text{Si}} - 6X_{\text{Ni}}X_{\text{Si}} + 6X_{\text{Si}}^2)/(1 - 3X_{\text{Si}})\) as a horizontal axis, \(^6 \Omega_{\text{Ni-Si}}\) and \(^1 \Omega_{\text{Ni-Si}}\) can be determined from the intercept and the slope of the regressed line, respectively. The results are shown in Fig. 4 and the following relations has been obtained from the regression.

\[ ^6 \Omega_{\text{Ni-Si}} = -1388000 + 661.1 T/J \] .................(43)
\[ ^1 \Omega_{\text{Ni-Si}} = 931500 - 495.5 T/J \] .................(44)

Apparent Si deoxidation product of molten Fe–Ni alloy determined in the present work are shown with the results reported by Ishii and Ban-ya\(^{[10]}\) in Fig. 5. The present result agrees well with their experimental results in the whole region of the alloy.

The activity coefficient of Si in molten Ni determined from Eqs. (4), (11), (15), (43) and (44) is shown with literature values\(^{[20,31-33]}\) in Fig. 6. The activity coefficient of Si at infinite dilution determined in the present result is very close to the value reported by Schwerdtfeger and Engell.\(^{[33]}\) It was confirmed that deoxidation equilibrium of molten alloy can be expressed utilizing quadratic formalism from the above analysis.

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**Fig. 4.** Relation between \(Y_{\text{Ni-Si}}\) and \((X_{\text{Ni}} - 2X_{\text{Si}} - 6X_{\text{Ni}}X_{\text{Si}} + 6X_{\text{Si}}^2)/(1 - 3X_{\text{Si}})\).

\[ [X_{\text{Si}}] \times 10^5 \]

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**Fig. 5.** Relation between alloy composition and Si deoxidation product.

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**Fig. 6.** Activity coefficient of silicon in molten Ni–Si alloys.
The values for $\Omega_{\text{Ni-Si}}$ and $\Omega_{\text{Ni-Si}}$ determined in the present work differ from the previous work. However, the activity of Si in molten Ni that can be determined from the present and previous work are almost identical. The authors believe that the same value of $\Omega_{\text{Ni-Si}}$ and $\Omega_{\text{Ni-Si}}$ can be applied to any alloy systems. Reassessment of $\Omega_{\text{Ni-Si}}$ and $\Omega_{\text{Ni-Si}}$ is necessary in the near future.

Si deoxidation equilibrium of molten Ni–Co alloy was also analyzed by substituting Co for Fe in Eq. (42). The experimental results of Ishii and Ban-ya and the following parameters were utilized to determine $\Omega_{\text{Co-Si}}$ and $\Omega_{\text{Co-Si}}$:

$$\Omega_{\text{Co-Si}} = -92250 + 10.35 T / J$$  \hspace{1cm} (45)

$$\Omega_{\text{Co-Si}} = 30750 - 3.45 T / J$$  \hspace{1cm} (46)

$$\Omega_{\text{Ni-Co}} = 1331 / J$$  \hspace{1cm} (47)

Temperature dependence of $\Omega_{\text{Co-Si}}$ and $\Omega_{\text{Co-Si}}$ were obtained from the intercept and the slope of Fig. 7 as follows.

$$\Omega_{\text{Co-Si}} = 520500 - 297.5 T / J$$  \hspace{1cm} (48)

$$\Omega_{\text{Co-Si}} = -1142000 + 579.8 T / J$$  \hspace{1cm} (49)

Apparent Si deoxidation product of molten Ni–Co alloy determined in the present work are shown with the results reported by Ishii and Ban-ya in Fig. 8. The present result agrees extremely well with their experimental results in the whole region of the alloy.

![Fig. 8. Relation between alloy composition and Si deoxidation product.](image_url)

**Table 1.** Binary interaction parameters utilized and determined in the present work.

| Parameter       | Value (J)     | Region of validity | Literature |
|-----------------|---------------|--------------------|------------|
| $\Omega_{\text{Co}}$ | $-415700 + 1395 T$ | $X_{\text{Co}} = 0.0000$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Co}}$ | $298500 - 1150 T$ | $X_{\text{Co}} = 0.0000$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $1383000 - 751 T$ | $X_{\text{Ni}} = 0.040$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Co}}$ | $-1574000 + 797 T$ | $X_{\text{Co}} = 0.040$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $-388000 + 129.2 T$ | $X_{\text{Ni}} = 0.0040$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Co}}$ | $-16911 + 5.162 T$ | $0<X_{\text{Co}}<1$, $1823 \text{K}/1993$ | Tang (21) |
| $\Omega_{\text{Ni}}$ | $-10180 + 4.146 T$ | $0<X_{\text{Ni}}<1$, $1823 \text{K}/1993$ | Tang (21) |
| $\Omega_{\text{Co}}$ | $35500 - 15.92 T$ | $X_{\text{Co}} = 0.00060$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $-138800 + 661.1 T$ | $X_{\text{Ni}} = 0.040$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Co}}$ | $931500 - 495.5 T$ | $X_{\text{Co}} = 0.040$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $-92260 + 10.33 T$ | $X_{\text{Ni}} = 0.00045$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Co}}$ | $30750 - 3.45 T$ | $X_{\text{Co}} = 0.00045$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $1331$ | $0<X_{\text{Co}}<1$, $1823 \text{K}/1993$ | Guillermet (20) |
| $\Omega_{\text{Co}}$ | $520500 - 297.3 T$ | $X_{\text{Co}} = 0.012$, $1823 \text{K}/1993$ | Present work |
| $\Omega_{\text{Ni}}$ | $-1142000 + 579.8 T$ | $X_{\text{Ni}} = 0.012$, $1823 \text{K}/1993$ | Present work |
5. Numerical Analysis on Si Deoxidation of Molten Ni

The relation between equilibrium Si and O content in molten Ni was calculated utilizing the equations that Ni was substituted for Fe in Eq. (26), Eqs. (31), (33), (36), (37), (43) and (44) to confirm that the parameters determined in the present work was appropriate. The relation is shown with the results reported by Ishii and Ban-ya\(^{34}\) in Fig. 9. The Si deoxidation equilibrium of molten Ni can be expressed by utilizing the parameters obtained in the present work.

The binary interaction parameters utilized and determined in the present work are summarized in Table 1 with the composition range of validity. The activity coefficients of elements in molten Fe, Ni and Co at infinite dilution and Wagner’s\(^{11}\) interaction coefficients based on mole fractions.

Table 2. Activity coefficients of elements at infinite dilution and interaction coefficients based on mole fractions in molten Fe.

| Temperature Function | Value at 1873K | Region of Validity |
|----------------------|----------------|-------------------|
| \(\gamma_{i}^{12} \)  | 0.0103         | 1823 ≤ T ≤ 1953  |
| \(\gamma_{i}^{12} \)  | 0.0013         | 1823 ≤ T ≤ 1953  |
| \(\gamma_{i}^{12} \)  | 0.733          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.331          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.740          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.420          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.510          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.240          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.140          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.040          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.040          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.040          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.040          | 1823 ≤ T ≤ 1953  |

Table 3. Activity coefficients of elements at infinite dilution and interaction coefficients based on mole fractions in molten Ni.

| Temperature Function | Value at 1873K | Region of Validity |
|----------------------|----------------|-------------------|
| \(\gamma_{i}^{12} \)  | 0.338          | 1823 ≤ T ≤ 1953  |
| \(\gamma_{i}^{12} \)  | 0.000080       | 1823 ≤ T ≤ 1953  |
| \(\gamma_{i}^{12} \)  | 0.538          | 1823 ≤ T ≤ 1953  |
| \(\gamma_{i}^{12} \)  | 0.093          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 17.9           | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | -0.0636        | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | -7.02          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.72           | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 0.270          | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | 1.86           | 1823 ≤ T ≤ 1953  |
| \(\omega_{i}^{12} \)  | -0.171         | 1823 ≤ T ≤ 1953  |

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in molten Fe, Ni and Co derived from Eqs. (4)–(8), (11), (15) and the binary interaction parameters are shown in Tables 2 to 4. Also, the free energy change of dissolution in molten Fe, Ni and Co and interaction coefficients based on mass percents are shown in Tables 5 to 7. The interaction coefficients were converted by utilizing the following relations derived by Lupis,\textsuperscript{37} where “I” denotes the matrix.

\[ e_j' = 230 \frac{M_{j'}}{M_j} e_j + \frac{M_j - M_{j'}}{M_j} \]  

\[ \rho_{j'} = \frac{230}{M_j^2} [100M_{j'}^2 e_j' + M_j(M_j - M_{j'})e_j'] + 1 \frac{M_j - M_{j'}}{M_j}^2 \]  

\[ \rho_{j'}^{(j,k)} = \frac{230}{M_j^2} [100M_{j'}M_{j''} e_{j,k} + M_j^2(M_j - M_{j''})e_j'] \]  

Table 4. Activity coefficients of elements at infinite dilution and interaction coefficients based on mole fractions in molten Co.

| Temperature Function | Value at 1873K | Region of Validity |
|----------------------|----------------|-------------------|
| \( y_{O}^{a} \) | \( \frac{7400 + 0.830}{T} \) | 0.0442 | 1823°C–17923 |
| \( y_{O}^{a} \) | \( \frac{74800 + 34.0}{T} \) | 0.00259 | 1823°C–17923 |
| \( y_{O}^{a} \) | \( \frac{699000}{T} \) | 1.09 | 1823°C–17923 |
| \( e_{O}^{a} \) | \( \frac{699000}{T} \) | 26.3 | 1823°C–17923 |
| \( e_{O}^{a} \) | \( \frac{303000}{T} \) | 3.78 | 1823°C–17923 |
| \( e_{O}^{a} \) | \( \frac{518000}{T} \) | 4.11 | 1823°C–17923 |
| \( e_{O}^{a} \) | \( \frac{159}{T} \) | -0.356 | 1823°C–17923 |
| \( e_{O}^{a} \) | \( \frac{320}{T} \) | -0.171 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{349000}{T} \) | -13.2 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{0}{T} \) | 0.0855 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{349000}{T} \) | -13.2 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{160}{T} \) | 0.0855 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{349000}{T} \) | -13.2 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{160}{T} \) | 0.0855 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{349000}{T} \) | -13.2 | 1823°C–17923 |
| \( \rho_{O}^{a} \) | \( \frac{160}{T} \) | 0.0855 | 1823°C–17923 |

It was confirmed from the present numerical analysis that the Si deoxidation equilibrium of molten Fe, Ni and Fe–Ni, Ni–Co alloys could be quantitatively expressed with high accuracy by utilizing quadratic formalism.

Table 5. Activity coefficients of elements at infinite dilution and interaction coefficients based on mass percents in molten Fe.

| Temperature Function | Value at 1873K | Region of Validity |
|----------------------|----------------|-------------------|
| \( \frac{1}{2} N_{[O]} = [O_{(mass%) \times 1000} - 3.3971]/J \) | -21000001/J | 1823°C–17953 |
| \( \frac{1}{2} N_{[O]} = [O_{(mass%) \times 1000} + 14.271]/J \) | -1640000001/J | 1823°C–17953 |
| \( \frac{1}{2} N_{[O]} = [O_{(mass%) \times 1000} - 27.771]/J \) | -7730000001/J | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{6400}{T} \) | 3.41 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{4510}{T} \) | 2.39 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{2350}{T} \) | 1.122 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{2357}{T} \) | 1.122 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{4920}{T} \) | 2.56 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{943}{T} \) | 0.0389 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{15.6}{T} \) | 0.00724 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{138}{T} \) | 0.0677 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{81.7}{T} \) | 0.0463 | 1823°C–17953 |
| \( e_{O}^{a} \) | \( \frac{0.110}{T} \) | 0.0000583 | 4.29×10\textsuperscript{-7} |
| \( e_{O}^{a} \) | \( \frac{94.5}{T} \) | 0.104 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{74.1}{T} \) | 0.0316 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{0.0670}{T} \) | 0.000036 | \( 3.20×10\textsuperscript{-7} \) |
| \( e_{O}^{a} \) | \( \frac{112}{T} \) | 0.0593 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{32.9}{T} \) | 0.0412 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{0.0708}{T} \) | 0.000037 | 3.20×10\textsuperscript{-7} |
| \( e_{O}^{a} \) | \( \frac{307}{T} \) | 0.156 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{66.7}{T} \) | 0.0348 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{136}{T} \) | 0.0739 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{13.9}{T} \) | 0.00586 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{44.3}{T} \) | 0.00320 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |
| \( e_{O}^{a} \) | \( \frac{8.87}{T} \) | 0.00380 | \( [O_{(mass%) \times 1000} - 20.271]/J \) |

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The Redlich–Kister parameters should have uniform values that do not depend with type of alloy system. The authors will apply the present method to other systems and confirm its universality in the future.

### 6. Conclusion

Deoxidation equilibrium of molten Fe, Ni and Fe–Ni,
Ni–Co alloys can be quantitatively expressed by binary interaction parameters determined on basis of the quadratic formalism. The Gibbs energy of formation of deoxidation product can be utilized by selecting dissolved oxygen in the melt equilibrating with 101325 Pa (1 atm) oxygen gas as a standard state to analyze numerically deoxidation equilibria of metal and its alloy. The parameters determined in the present work can easily be converted into Wagner's interaction coefficients.

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