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 Ω_{i-j} 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 Wagner¹⁾ has been widely used to express the activity coefficients of solute in multi-component 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.

$$\ln \gamma_1 = \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3 \dots \dots (1)$$

$$\ln \gamma_2 = -2\alpha_{12} X_2 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_3 + \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3 + \ln \gamma_2^\circ \dots \dots (2)$$

$$\ln \gamma_3 = -2\alpha_{13} X_3 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_2 + \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3 + \ln \gamma_3^\circ \dots \dots (3)$$

Where X_i denotes mole fraction of component i , γ_i denotes the activity coefficient of component i , γ_i° denotes the activity coefficient of component i at infinite dilution, and α_{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 Wagner¹⁾ with Eq. (2).

$$\varepsilon_2^2 = -2\alpha_{12} \dots \dots (4)$$

$$\varepsilon_2^3 = \alpha_{23} - \alpha_{12} - \alpha_{13} \dots \dots (5)$$

$$\rho_2^2 = \alpha_{12} \dots \dots (6)$$

$$\rho_2^3 = \alpha_{13} \dots \dots (7)$$

$$\rho_2^{(2,3)} = \alpha_{12} + \alpha_{13} - \alpha_{23} \dots \dots (8)$$

Where ε_i^j and ρ_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, ΔG^{ex} , and partial molar excess Gibbs energy change, $\Delta \bar{G}_2^{\text{ex}}$, can be expressed as Eqs. (9) and (10), respectively.

$$\Delta G^{\text{ex}} = X_1 X_2 \{ {}^0\Omega_{1-2} + {}^1\Omega_{1-2}(X_1 - X_2) \} \dots \dots (9)$$

$$\begin{aligned}\Delta \bar{G}_2^{\text{ex}} &= RT \ln \gamma_2 \\ &= \Delta G^{\text{ex}} + (1 - X_2) \frac{\partial \Delta G^{\text{ex}}}{\partial X_2} \\ &= X_1^2 ({}^0\Omega_{1-2} - 3 {}^1\Omega_{1-2}) + X_1^3 (4 {}^1\Omega_{1-2}) \dots\dots\dots(10)\end{aligned}$$

Where ${}^0\Omega_{i-j}$ and ${}^1\Omega_{i-j}$ are binary interaction parameters. On the condition of $X_1 \cong 1$, the activity coefficient of component 2 will be γ_2° . Hence, the following relation can be obtained in the infinite dilute solution of 2.

$$RT \ln \gamma_2^\circ = {}^0\Omega_{1-2} + {}^1\Omega_{1-2} \dots\dots\dots(11)$$

The activity coefficient of component 2 in 1–2 binary system can be expressed as Eq. (12), using Darken's^{2,3)} quadratic formalism.

$$\ln \gamma_2 = \alpha_{12} X_1^2 + I \dots\dots\dots(12)$$

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.

$$\frac{\partial(RT \ln \gamma_2)}{\partial(X_1^2)} = RT \alpha_{12} \dots\dots\dots(13)$$

On the other hand, the following equation can be derived from partial differentiation of Eq. (10) with X_1^2 .

$$\frac{\partial(RT \ln \gamma_2)}{\partial(X_1^2)} = ({}^0\Omega_{1-2} - 3 {}^1\Omega_{1-2}) + 6 {}^1\Omega_{1-2} X_1 \dots\dots(14)$$

On the condition $X_1 \cong 1$, Eqs. (13) and (14) will be equivalent and the following relation will be obtained for infinite dilute solution.

$$RT \alpha_{12} = {}^0\Omega_{1-2} + 3 {}^1\Omega_{1-2} \dots\dots\dots(15)$$

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

$${}^0\Omega_{1-2} = RT \left(\frac{3}{2} \ln \gamma_2^\circ - \frac{1}{2} \alpha_{12} \right) \dots\dots\dots(16)$$

$${}^1\Omega_{1-2} = RT \left(-\frac{1}{2} \ln \gamma_2^\circ + \frac{1}{2} \alpha_{12} \right) \dots\dots\dots(17)$$

Quadratic formalism can be converted into Redlich–Kister type polynomial using ${}^0\Omega_{1-2}$ and ${}^1\Omega_{1-2}$ for dilute solution using Eqs. (16) and (17).

2.2. Standard State of Components

Pure substance is chosen 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.

$$a_{\text{O}} = P_{\text{O}_2}^{1/2} \dots\dots\dots(18)$$

The activity coefficient of oxygen at infinite dilution in metal is not unity as the case of Henrian standard state but γ_{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).

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

The Gibbs free energy change of Eq. (20) is identical to the Gibbs free energy of SiO_2 formation ($\Delta G_{\text{f, SiO}_2}^\circ$) 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_2 formation ($\Delta G_{\text{f, SiO}_2}^\circ$). Equation (19) and the Gibbs free energy of SiO_2 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.

$$\begin{aligned}\ln K_{\text{Si}} &= -\frac{\Delta G_{\text{f, SiO}_2}^\circ}{RT} \\ &= \ln a_{\text{SiO}_2} - \ln \gamma_{\text{Si}} - 2 \ln \gamma_{\text{O}} - \ln X_{\text{Si}} - 2 \ln X_{\text{O}} \\ &= -\ln \gamma_{\text{Si}} - 2 \ln \gamma_{\text{O}} - \ln X_{\text{Si}} - 2 \ln X_{\text{O}} (\because a_{\text{SiO}_2} = 1) \dots\dots(22)\end{aligned}$$

Where, the activity of SiO_2 is taken as unity, since deoxidation product is pure SiO_2 .

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.

$$\begin{aligned}\Delta G^{\text{ex}} &= X_{\text{Fe}} X_{\text{Si}} \{ {}^0\Omega_{\text{Fe-Si}} + {}^1\Omega_{\text{Fe-Si}} (X_{\text{Fe}} - X_{\text{Si}}) \} \\ &\quad + X_{\text{Fe}} X_{\text{O}} \{ {}^0\Omega_{\text{Fe-O}} + {}^1\Omega_{\text{Fe-O}} (X_{\text{Fe}} - X_{\text{O}}) \} + X_{\text{Si}} X_{\text{O}} \Omega_{\text{Si-O}} \\ &\quad \dots\dots\dots(23)\end{aligned}$$

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

$$\begin{aligned}\Delta \bar{G}_{\text{Si}}^{\text{ex}} &= RT \ln \gamma_{\text{Si}} \\ &= \Delta G^{\text{ex}} + (1 - X_{\text{Si}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Si}}} - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}}\end{aligned}$$

$$\begin{aligned}
 &= {}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1-X_{\text{Si}}) \\
 &+ {}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{Si}}-2X_{\text{Fe}}X_{\text{Si}}+2X_{\text{Si}}^2) \\
 &- {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}X_{\text{O}}-2{}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}X_{\text{O}}(X_{\text{Fe}}-X_{\text{O}}) \\
 &+ \Omega_{\text{Si-O}}X_{\text{O}}(1-X_{\text{Si}}) \dots\dots\dots(24)
 \end{aligned}$$

$$\begin{aligned}
 \Delta \bar{G}_{\text{O}}^{\text{ex}} &= RT \ln \gamma_{\text{O}} \\
 &= \Delta G^{\text{ex}} - X_{\text{Si}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Si}}} + (1-X_{\text{O}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\
 &= -{}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}X_{\text{Si}}-2{}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}X_{\text{Si}}(X_{\text{Fe}}-X_{\text{Si}}) \\
 &+ {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(1-X_{\text{O}}) \\
 &+ {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{O}}-2X_{\text{Fe}}X_{\text{O}}+2X_{\text{O}}^2) \\
 &+ \Omega_{\text{Si-O}}X_{\text{Si}}(1-X_{\text{O}}) \dots\dots\dots(25)
 \end{aligned}$$

Equation (26) can be deduced by substituting Eqs. (24) and (25) into Eq. (22).

$$\begin{aligned}
 &{}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1-3X_{\text{Si}})+{}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{Si}}-6X_{\text{Fe}}X_{\text{Si}}+6X_{\text{Si}}^2) \\
 &+ {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(2-3X_{\text{O}}) \\
 &+ {}^1\Omega_{\text{Fe-O}}2X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{O}}-3X_{\text{Fe}}X_{\text{O}}+3X_{\text{O}}^2) \\
 &+ \Omega_{\text{Si-O}}(2X_{\text{Si}}+X_{\text{O}}-3X_{\text{Si}}X_{\text{O}})+RT(\ln X_{\text{Si}}+2\ln X_{\text{O}}) \\
 &- \Delta G_{\text{f, SiO}_2}^{\circ} = 0 \dots\dots\dots(26)
 \end{aligned}$$

Equation (26) is the fundamental equation for numerical analysis of Si deoxidation in molten Fe. Experimental results reported by Matoba *et al.*,⁷⁾ Suzuki *et al.*,⁸⁾ Gokcen and Chipman,⁹⁾ Tszen-Tszi *et al.*,¹⁰⁾ Hilty and Crafts,¹¹⁾ Segawa *et al.*,¹²⁾ Shevtsov *et al.*¹³⁾ were utilized for analysis on Si deoxidation equilibrium of molten Fe. The binary interaction parameters ${}^0\Omega_{\text{Fe-O}}$, ${}^1\Omega_{\text{Fe-O}}$ 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 Chart²⁷⁾ 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.

$${}^0\Omega_{\text{Fe-O}} = -415\,700 + 139.5\,T/\text{J} \dots\dots\dots(27)$$

$${}^1\Omega_{\text{Fe-O}} = 298\,600 - 115.0\,T/\text{J} \dots\dots\dots(28)$$

$${}^0\Omega_{\text{Fe-Si}} = 1\,383\,000 - 751.0\,T/\text{J} \dots\dots\dots(29)$$

$${}^1\Omega_{\text{Fe-Si}} = -1\,574\,000 + 797.7\,T/\text{J} \dots\dots\dots(30)$$

$$\Delta G_{\text{f, SiO}_2}^{\circ} = -946\,300 + 197.7\,T/\text{J} \dots\dots\dots(31)$$

Equation (32) can be obtained by rearranging Eq. (26).

Fig. 1. Activity coefficient of silicon in molten Fe-Si alloys at 1873 K.²⁷⁾

Fig. 2. Relation between $2X_{\text{Si}}+X_{\text{O}}-3X_{\text{Si}}X_{\text{O}}$ and $Y_{\text{Si-O}}$.

$$\begin{aligned}
 Y_{\text{Si-O}} &= -{}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(2-3X_{\text{O}}) \\
 &- {}^1\Omega_{\text{Fe-O}}2X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{O}}-3X_{\text{Fe}}X_{\text{O}}+3X_{\text{O}}^2) \\
 &- {}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1-3X_{\text{Si}}) \\
 &- {}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{Si}}-6X_{\text{Fe}}X_{\text{Si}}+6X_{\text{Si}}^2) \\
 &- RT \ln X_{\text{Si}} - 2RT \ln X_{\text{O}} + \Delta G_{\text{f, SiO}_2}^{\circ} \\
 &= \Omega_{\text{Si-O}}(2X_{\text{Si}}+X_{\text{O}}-3X_{\text{Si}}X_{\text{O}}) \dots\dots\dots(32)
 \end{aligned}$$

By using the experimental results⁷⁻¹³⁾ and Eqs. (27)–(31) and taking $Y_{\text{Si-O}}$ in Eq. (32) as a vertical axis and

Fig. 3. Relation between silicon and oxygen concentration in molten Fe.

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

$$\Omega_{\text{Si-O}} = -388\,000 + 129.2\, T/J \quad \text{.....(33)}$$

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.

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-ya⁽³⁰⁾ were utilized for the analysis. Binary interaction parameters of Fe-Ni system reported by Tang⁽²⁸⁾ and that for Ni-O system obtained from the results of Sigworth *et al.*⁽²⁹⁾ are shown in the following.

$${}^0\Omega_{\text{Ni-Fe}} = -16\,911 + 5.1622\, T/J \quad \text{.....(34)}$$

$${}^1\Omega_{\text{Ni-Fe}} = -10\,180 + 4.146656\, T/J \quad \text{.....(35)}$$

$${}^0\Omega_{\text{Ni-O}} = -106\,500 + 44.80\, T/J \quad \text{.....(36)}$$

$${}^1\Omega_{\text{Ni-O}} = 35\,500 - 15.92\, T/J \quad \text{.....(37)}$$

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.

$$\begin{aligned} \Delta G^{\text{ex}} = & X_{\text{Ni}}X_{\text{Fe}}\{ {}^0\Omega_{\text{Ni-Fe}} + {}^1\Omega_{\text{Ni-Fe}}(X_{\text{Ni}} - X_{\text{Fe}}) \} \\ & + X_{\text{Ni}}X_{\text{Si}}\{ {}^0\Omega_{\text{Ni-Si}} + {}^1\Omega_{\text{Ni-Si}}(X_{\text{Ni}} - X_{\text{Si}}) \} \\ & + X_{\text{Ni}}X_{\text{O}}\{ {}^0\Omega_{\text{Ni-O}} + {}^1\Omega_{\text{Ni-O}}(X_{\text{Ni}} - X_{\text{O}}) \} \\ & + X_{\text{Fe}}X_{\text{Si}}\{ {}^0\Omega_{\text{Fe-Si}} + {}^1\Omega_{\text{Fe-Si}}(X_{\text{Fe}} - X_{\text{Si}}) \} \\ & + X_{\text{Fe}}X_{\text{O}}\{ {}^0\Omega_{\text{Fe-O}} + {}^1\Omega_{\text{Fe-O}}(X_{\text{Fe}} - X_{\text{O}}) \} + X_{\text{Si}}X_{\text{O}}\Omega_{\text{Si-O}} \quad \text{.....(38)} \end{aligned}$$

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

$$\begin{aligned} \Delta \bar{G}_{\text{Si}}^{\text{ex}} = & RT \ln \gamma_{\text{Si}} \\ = & \Delta G^{\text{ex}} - X_{\text{Fe}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Fe}}} \\ & + (1 - X_{\text{Si}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Si}}} - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ = & {}^0\Omega_{\text{Ni-Si}}X_{\text{Ni}}(1 - X_{\text{Si}}) \\ & + {}^1\Omega_{\text{Ni-Si}}X_{\text{Ni}}(X_{\text{Ni}} - 2X_{\text{Si}} - 2X_{\text{Ni}}X_{\text{Si}} + 2X_{\text{Si}}^2) \\ & + {}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1 - X_{\text{Si}}) \\ & + {}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}} - 2X_{\text{Si}} - 2X_{\text{Fe}}X_{\text{Si}} + 2X_{\text{Si}}^2) \\ & - {}^0\Omega_{\text{Ni-O}}X_{\text{Ni}}X_{\text{O}} - 2{}^1\Omega_{\text{Ni-O}}X_{\text{Ni}}X_{\text{O}}(X_{\text{Ni}} - X_{\text{O}}) \\ & - {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}X_{\text{O}} - 2{}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}X_{\text{O}}(X_{\text{Fe}} - X_{\text{O}}) \\ & + \Omega_{\text{Si-O}}X_{\text{O}}(1 - X_{\text{Si}}) - {}^0\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}} \\ & - 2{}^1\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}}(X_{\text{Ni}} - X_{\text{Fe}}) \quad \text{.....(39)} \end{aligned}$$

$$\begin{aligned} \Delta \bar{G}_{\text{O}}^{\text{ex}} = & RT \ln \gamma_{\text{O}} \\ = & \Delta G^{\text{ex}} - X_{\text{Fe}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Fe}}} - X_{\text{Si}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Si}}} \\ & + (1 - X_{\text{O}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ = & -{}^0\Omega_{\text{Ni-Si}}X_{\text{Ni}}X_{\text{Si}} - 2{}^1\Omega_{\text{Ni-Si}}X_{\text{Ni}}X_{\text{Si}}(X_{\text{Ni}} - X_{\text{Si}}) \\ & - {}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}X_{\text{Si}} - 2{}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}X_{\text{Si}}(X_{\text{Fe}} - X_{\text{Si}}) \\ & + {}^0\Omega_{\text{Ni-O}}X_{\text{Ni}}(1 - X_{\text{O}}) \\ & + {}^1\Omega_{\text{Ni-O}}X_{\text{Ni}}(X_{\text{Ni}} - 2X_{\text{O}} - 2X_{\text{Ni}}X_{\text{O}} + 2X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(1 - X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(X_{\text{Fe}} - 2X_{\text{O}} - 2X_{\text{Fe}}X_{\text{O}} + 2X_{\text{O}}^2) \\ & + \Omega_{\text{Si-O}}X_{\text{Si}}(1 - X_{\text{O}}) \\ & - {}^0\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}} - 2{}^1\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}}(X_{\text{Ni}} - X_{\text{Fe}}) \quad \text{.....(40)} \end{aligned}$$

The following relation can be obtained by substituting Eqs. (39) and (40) into Eq. (22).

$$\begin{aligned}
 & {}^0\Omega_{\text{Ni-Si}}X_{\text{Ni}}(1-3X_{\text{Si}}) + {}^0\Omega_{\text{Ni-Si}}X_{\text{Ni}}(X_{\text{Ni}}-2X_{\text{Si}}-6X_{\text{Ni}}X_{\text{Si}}+6X_{\text{Si}}^2) \\
 & + {}^0\Omega_{\text{Ni-O}}X_{\text{Ni}}(2-3X_{\text{O}}) \\
 & + {}^1\Omega_{\text{Ni-O}}2X_{\text{Ni}}(X_{\text{Ni}}-2X_{\text{O}}-3X_{\text{Ni}}X_{\text{O}}+3X_{\text{O}}^2) \\
 & + {}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1-3X_{\text{Si}}) + {}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{Si}}-6X_{\text{Fe}}X_{\text{Si}}+6X_{\text{Si}}^2) \\
 & + {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(2-3X_{\text{O}}) + {}^1\Omega_{\text{Fe-O}}2X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{O}}-3X_{\text{Fe}}X_{\text{O}}+3X_{\text{O}}^2) \\
 & + \Omega_{\text{Si-O}}(2X_{\text{Si}}+X_{\text{O}}-3X_{\text{Si}}X_{\text{O}}) \\
 & - 3^0\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}} - 6^1\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}}(X_{\text{Ni}}-X_{\text{Fe}}) \\
 & + RT\ln X_{\text{Si}} + 2RT\ln X_{\text{O}} - \Delta G_{\text{f, SiO}_2}^\circ = 0 \dots\dots\dots(41)
 \end{aligned}$$

Rearranging Eq. (41) derives Eq. (42).

$$\begin{aligned}
 Y_{\text{Ni-Si}} &= \frac{1}{X_{\text{Ni}}(1-3X_{\text{Si}})} \{ -{}^0\Omega_{\text{Fe-Si}}X_{\text{Fe}}(1-3X_{\text{Si}}) \\
 & - {}^1\Omega_{\text{Fe-Si}}X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{Si}}-6X_{\text{Fe}}X_{\text{Si}}+6X_{\text{Si}}^2) \\
 & - {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(2-3X_{\text{O}}) \\
 & - {}^1\Omega_{\text{Fe-O}}2X_{\text{Fe}}(X_{\text{Fe}}-2X_{\text{O}}-3X_{\text{Fe}}X_{\text{O}}+3X_{\text{O}}^2) \\
 & - {}^0\Omega_{\text{Ni-O}}X_{\text{Ni}}(2-3X_{\text{O}}) \\
 & - {}^1\Omega_{\text{Ni-O}}2X_{\text{Ni}}(X_{\text{Ni}}-2X_{\text{O}}-3X_{\text{Ni}}X_{\text{O}}+3X_{\text{O}}^2) \\
 & - \Omega_{\text{Si-O}}(2X_{\text{Si}}+X_{\text{O}}-3X_{\text{Si}}X_{\text{O}}) + 3^0\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}} \\
 & + 6^1\Omega_{\text{Ni-Fe}}X_{\text{Ni}}X_{\text{Fe}}(X_{\text{Ni}}-X_{\text{Fe}}) \\
 & - RT\ln X_{\text{Si}} - 2RT\ln X_{\text{O}} + \Delta G_{\text{f, SiO}_2}^\circ \} \\
 & = {}^0\Omega_{\text{Ni-Si}} + {}^1\Omega_{\text{Ni-Si}} \frac{X_{\text{Ni}}-2X_{\text{Si}}-6X_{\text{Ni}}X_{\text{Si}}+6X_{\text{Si}}^2}{1-3X_{\text{Si}}} \dots\dots\dots(42)
 \end{aligned}$$

By utilizing Eqs. (27)–(31), (33)–(37) and experimental results reported by Ishii and Ban-ya³⁰⁾ 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, ${}^0\Omega_{\text{Ni-Si}}$ 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

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

and the following relations has been obtained from the regression.

$${}^0\Omega_{\text{Ni-Si}} = -1\,388\,000 + 661.1\,T/\text{J} \dots\dots\dots(43)$$

$${}^1\Omega_{\text{Ni-Si}} = 931\,500 - 495.5\,T/\text{J} \dots\dots\dots(44)$$

Apparent Si deoxidation product of molten Fe–Ni alloy determined in the present work are shown with the results reported by Ishii and Ban-ya³⁰⁾ 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.

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

Fig. 6. Activity coefficient of silicon in molten Ni–Si alloys.

The values for ${}^0\Omega_{\text{Ni-Si}}$ and ${}^1\Omega_{\text{Ni-Si}}$ determined in the present work differs from the previous work.⁴⁾ 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 ${}^0\Omega_{\text{Ni-Si}}$ and ${}^1\Omega_{\text{Ni-Si}}$ can be applied to any alloy systems. Reassessment of ${}^0\Omega_{\text{Ni-Si}}$ and ${}^1\Omega_{\text{Ni-Si}}$ 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-ya³⁴⁾ and the following parameters were utilized to determine ${}^0\Omega_{\text{Co-Si}}$ and ${}^1\Omega_{\text{Co-Si}}$

$${}^0\Omega_{\text{Co-O}} = -92\,260 + 10.35\,T/J^{35)} \dots\dots\dots(45)$$

$${}^1\Omega_{\text{Co-O}} = 30\,750 - 3.45\,T/J^{35)} \dots\dots\dots(46)$$

$${}^0\Omega_{\text{Ni-Co}} = 1\,331/J^{36)} \dots\dots\dots(47)$$

Temperature dependence of ${}^0\Omega_{\text{Co-Si}}$ and ${}^1\Omega_{\text{Co-Si}}$ were obtained from the intercept and the slope of Fig. 7 as follows.

$${}^0\Omega_{\text{Co-Si}} = 520\,500 - 297.5\,T/J \dots\dots\dots(48)$$

$${}^1\Omega_{\text{Co-Si}} = -1\,142\,000 + 579.8\,T/J \dots\dots\dots(49)$$

Fig. 7. Relation between $Y_{\text{Co-Si}}$ and $(X_{\text{Co}} - 2X_{\text{Si}} - 6X_{\text{Co}}X_{\text{Si}} + 6X_{\text{Si}}^2)/(1 - 3X_{\text{Si}})$.

Fig. 8. Relation between alloy composition and Si deoxidation product.

Apparent Si deoxidation product of molten Ni-Co alloy determined in the present work are shown with the results reported by Ishii and Ban-ya³⁴⁾ in Fig. 8. The present result agrees extremely well with their experimental results in the whole region of the alloy.

Fig. 9. Relation between silicon and oxygen concentration in molten Ni.

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

	Values (J)	Region of validity	Literature
${}^0\Omega_{\text{Fe-O}}$	$-415700 + 139.5T$	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$	Present work
${}^1\Omega_{\text{Fe-O}}$	$298600 - 115.0T$	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$	Present work
${}^0\Omega_{\text{Fe-Si}}$	$1383000 - 751.0T$	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$	Present work
${}^1\Omega_{\text{Fe-Si}}$	$-1574000 + 797.7T$	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$	Present work
$\Omega_{\text{Si-O}}$	$-388000 + 129.2T$	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1973$	Present work
${}^0\Omega_{\text{Ni-Fe}}$	$-16911 + 5.1622T$	$0 < X_{\text{Fe}} < 1, 1823 \leq T \leq 1973$	Tang ²⁸⁾
${}^1\Omega_{\text{Ni-Fe}}$	$-10180 + 4.146656T$	$0 < X_{\text{Fe}} < 1, 1823 \leq T \leq 1973$	Tang ²⁸⁾
${}^0\Omega_{\text{Ni-O}}$	$-106500 + 44.80T$	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$	Present work
${}^1\Omega_{\text{Ni-O}}$	$35500 - 15.92T$	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$	Present work
${}^0\Omega_{\text{Ni-Si}}$	$-1388000 + 661.1T$	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$	Present work
${}^1\Omega_{\text{Ni-Si}}$	$931500 - 495.5T$	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$	Present work
${}^0\Omega_{\text{Co-O}}$	$-92260 + 10.35T$	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$	Present work
${}^1\Omega_{\text{Co-O}}$	$30750 - 3.45T$	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$	Present work
${}^0\Omega_{\text{Ni-Co}}$	1331	$0 < X_{\text{Co}} < 1, 1823 \leq T \leq 1923$	Guillemet ³⁶⁾
${}^0\Omega_{\text{Co-Si}}$	$520500 - 297.5T$	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$	Present work
${}^1\Omega_{\text{Co-Si}}$	$-1142000 + 579.8T$	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$	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-ya³⁴⁾ 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's¹⁾ 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
$\gamma_{\text{O}}^{\circ} \exp\left(-\frac{14100}{T} + 2.95\right)$	0.0103	$1823 \leq T \leq 1953$
$\gamma_{\text{Si}}^{\circ} \exp\left(-\frac{23000}{T} + 5.62\right)$	0.00130	$1823 \leq T \leq 1953$
$\gamma_{\text{Ni}}^{\circ} \exp\left(-\frac{810}{T} + 0.122\right)$	0.733	$1823 \leq T \leq 1973$
$\epsilon_{\text{Si}}^{\text{Si}} \frac{803000}{T} - 395$	33.8	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\epsilon_{\text{Si}}^{\text{O}} \frac{297000}{T} - 157$	1.42	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\epsilon_{\text{Si}}^{\text{Ni}} \frac{569000}{T} - 296$	7.95	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\epsilon_{\text{O}}^{\text{O}} - \frac{115000}{T} + 49.4$	-12.2	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\epsilon_{\text{O}}^{\text{Ni}} - \frac{59400}{T} + 25.2$	-6.47	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\epsilon_{\text{Ni}}^{\text{Ni}} - \frac{3280}{T} + 1.75$	0	$1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{\text{Si}} - \frac{402000}{T} + 198$	-16.9	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{O}} \frac{57700}{T} - 24.7$	6.11	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{\text{Ni}} \frac{1640}{T} - 0.875$	0	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{Si}} - \frac{402000}{T} + 198$	-16.9	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{O}} \frac{57700}{T} - 24.7$	6.11	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{Ni}} \frac{1640}{T} - 0.875$	0	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{\text{Si}} - \frac{402000}{T} + 198$	-16.9	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{\text{O}} \frac{57700}{T} - 24.7$	6.11	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{\text{Ni}} \frac{1640}{T} - 0.875$	0	$1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{(\text{Si}, \text{O})} - \frac{297000}{T} + 157$	-1.42	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{(\text{Si}, \text{Ni})} - \frac{569000}{T} + 296$	-7.95	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{(\text{O}, \text{Si})} - \frac{297000}{T} + 157$	-1.42	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{O}}^{(\text{O}, \text{Ni})} - \frac{59400}{T} - 25.2$	6.47	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{Si})} - \frac{569000}{T} + 296$	-7.95	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{O})} - \frac{59400}{T} - 25.2$	6.47	$X_{\text{O}} < 0.00080, 1823 \leq T \leq 1953$

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
$\gamma_{\text{O}}^{\circ} \exp\left(-\frac{8540}{T} + 3.47\right)$	0.338	$1823 \leq T \leq 1973$
$\gamma_{\text{Si}}^{\circ} \exp\left(-\frac{54900}{T} + 19.9\right)$	0.0000830	$1823 \leq T \leq 1973$
$\gamma_{\text{Fe}}^{\circ} \exp\left(-\frac{3260}{T} + 1.12\right)$	0.538	$1823 \leq T \leq 1973$
$\gamma_{\text{Co}}^{\circ} \exp\left(\frac{160}{T}\right)$	1.09	$1823 \leq T \leq 1923$
$\epsilon_{\text{Si}}^{\text{Si}} - \frac{338000}{T} + 199$	17.9	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\epsilon_{\text{Si}}^{\text{O}} - \frac{216000}{T} + 115$	-0.0636	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\epsilon_{\text{Si}}^{\text{Fe}} - \frac{565000}{T} + 295$	-7.02	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\epsilon_{\text{Si}}^{\text{Co}} - \frac{519000}{T} + 273$	-4.28	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\epsilon_{\text{O}}^{\text{O}} 0.712$	0.712	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\epsilon_{\text{O}}^{\text{Fe}} \frac{63500}{T} - 26.5$	7.40	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\epsilon_{\text{O}}^{\text{Co}} - \frac{161}{T} + 0.356$	0.270	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1923$
$\epsilon_{\text{Fe}}^{\text{Fe}} \frac{11400}{T} - 4.23$	1.86	$1823 \leq T \leq 1973$
$\epsilon_{\text{Co}}^{\text{Co}} - \frac{320}{T}$	-0.171	$1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{\text{Si}} \frac{169000}{T} - 99.3$	-8.96	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{\text{O}} - 0.356$	-0.356	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{Fe}}^{\text{Fe}} - \frac{5710}{T} + 2.12$	-0.930	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{\text{Co}} \frac{160}{T}$	0.0855	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{\text{Si}} \frac{169000}{T} - 99.3$	-8.96	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{\text{O}} - 0.356$	-0.356	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{\text{Fe}} - \frac{5710}{T} + 2.12$	-0.930	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{\text{Co}} \frac{160}{T}$	0.0855	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1923$
$\rho_{\text{Fe}}^{\text{Si}} \frac{169000}{T} - 99.3$	-8.96	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\rho_{\text{Fe}}^{\text{O}} - 0.356$	-0.356	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{Fe}}^{\text{Fe}} - \frac{5710}{T} + 2.12$	-0.930	$1823 \leq T \leq 1973$
$\rho_{\text{Co}}^{\text{Si}} \frac{169000}{T} - 99.3$	-8.96	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1923$
$\rho_{\text{Co}}^{\text{O}} - 0.356$	-0.356	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1923$
$\rho_{\text{Co}}^{\text{Co}} \frac{160}{T}$	0.0855	$1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{(\text{Si}, \text{O})} \frac{216000}{T} - 115$	0.0636	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{(\text{Si}, \text{Fe})} - \frac{565000}{T} - 295$	7.02	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{(\text{Si}, \text{Co})} \frac{519000}{T} - 273$	4.28	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{(\text{O}, \text{Si})} \frac{216000}{T} - 115$	0.0636	$X_{\text{Si}} < 0.040, X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{(\text{O}, \text{Fe})} - \frac{63500}{T} + 26.5$	-7.40	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{O}}^{(\text{O}, \text{Co})} \frac{161}{T} - 0.356$	-0.270	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1923$
$\rho_{\text{Fe}}^{(\text{Fe}, \text{Si})} \frac{565000}{T} - 295$	7.02	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1973$
$\rho_{\text{Fe}}^{(\text{Fe}, \text{O})} - \frac{63500}{T} + 26.5$	-7.40	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1973$
$\rho_{\text{Co}}^{(\text{Co}, \text{Si})} \frac{519000}{T} - 273$	4.28	$X_{\text{Si}} < 0.040, 1823 \leq T \leq 1923$
$\rho_{\text{Co}}^{(\text{Co}, \text{O})} \frac{161}{T} - 0.356$	-0.270	$X_{\text{O}} < 0.00060, 1823 \leq T \leq 1923$

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,³⁷⁾ where “1” denotes the matrix.

$$\varepsilon_i^j = 230 \frac{M_j}{M_1} e_i^j + \frac{M_1 - M_j}{M_1} \dots\dots\dots(50)$$

$$\rho_i^j = \frac{230}{M_1^2} [100M_j^2 r_i^j + M_j(M_1 - M_j)e_i^j] + \frac{1}{2} \left(\frac{M_1 - M_j}{M_1} \right)^2 \dots\dots\dots(51)$$

$$\rho_i^{(j,k)} = \frac{230}{M_1^2} [100M_j M_k r_i^{(j,k)} + M_j(M_1 - M_k)e_i^j]$$

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
$\gamma_{\text{O}}^{\text{O}}$ $\exp\left(-\frac{7400}{T} + 0.830\right)$	0.0442	$1823 \leq T \leq 1923$
$\gamma_{\text{Si}}^{\text{O}}$ $\exp\left(-\frac{74800}{T} + 34.0\right)$	0.00259	$1823 \leq T \leq 1923$
$\gamma_{\text{Ni}}^{\text{O}}$ $\exp\left(\frac{160}{T}\right)$	1.09	$1823 \leq T \leq 1923$
$\varepsilon_{\text{Si}}^{\text{Si}}$ $\frac{699000}{T} - 347$	26.3	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\varepsilon_{\text{Si}}^{\text{O}}$ $\frac{303000}{T} - 158$	3.78	$X_{\text{Si}} < 0.012, X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\varepsilon_{\text{Si}}^{\text{Ni}}$ $\frac{518000}{T} - 273$	4.11	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\varepsilon_{\text{O}}^{\text{O}}$ 0	0	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\varepsilon_{\text{O}}^{\text{Ni}}$ $-\frac{159}{T} - 0.356$	-0.441	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\varepsilon_{\text{Ni}}^{\text{Ni}}$ $-\frac{320}{T}$	-0.171	$1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{\text{Si}}$ $-\frac{349000}{T} + 173$	-13.2	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{\text{O}}$ 0	0	$X_{\text{Si}} < 0.012, X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{\text{Ni}}$ $\frac{160}{T}$	0.0855	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{\text{Si}}$ $-\frac{349000}{T} + 173$	-13.2	$X_{\text{Si}} < 0.012, X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{\text{O}}$ 0	0	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{\text{Ni}}$ $\frac{160}{T}$	0.0855	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{Ni}}^{\text{Si}}$ $-\frac{349000}{T} + 173$	-13.2	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\rho_{\text{Ni}}^{\text{O}}$ 0	0	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{Ni}}^{\text{Ni}}$ $\frac{160}{T}$	0.0855	$1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{(\text{Si}, \text{O})}$ $-\frac{303000}{T} + 158$	-3.78	$X_{\text{Si}} < 0.012, X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{Si}}^{(\text{Si}, \text{Ni})}$ $-\frac{518000}{T} + 273$	-4.11	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{(\text{O}, \text{Si})}$ $-\frac{303000}{T} + 158$	-3.78	$X_{\text{Si}} < 0.012, X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{O}}^{(\text{O}, \text{Ni})}$ $\frac{159}{T} - 0.356$	0.441	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{Si})}$ $-\frac{518000}{T} + 273$	-4.11	$X_{\text{Si}} < 0.012, 1823 \leq T \leq 1923$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{O})}$ $\frac{159}{T} - 0.356$	0.441	$X_{\text{O}} < 0.000045, 1823 \leq T \leq 1923$

$$+ M_k(M_1 - M_j)e_i^k] + \frac{(M_1 - M_j)(M_1 - M_k)}{M_1^2} \dots\dots\dots(52)$$

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
$\frac{1}{2} \text{O}_2(\text{g}) = \text{O}(\text{1 mass\%})$ -117000-3.39T / J	-123000/J	$1823 \leq T \leq 1953$
$\text{Si}(\text{l}) = \text{Si}(\text{1 mass\%})$ -191000+14.2T / J	-164000/J	$1823 \leq T \leq 1953$
$\text{Ni}(\text{l}) = \text{Ni}(\text{1 mass\%})$ -6730-37.7T / J	-77300/J	$1823 \leq T \leq 1973$
$\varepsilon_{\text{Si}}^{\text{Si}}$ $\frac{6940}{T} - 3.41$	0.295	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\varepsilon_{\text{Si}}^{\text{O}}$ $\frac{4510}{T} - 2.39$	0.0179	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\varepsilon_{\text{Si}}^{\text{Ni}}$ $\frac{2350}{T} - 1.22$	0.0347	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\varepsilon_{\text{O}}^{\text{Si}}$ $\frac{2570}{T} - 1.36$	0.0121	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\varepsilon_{\text{O}}^{\text{O}}$ $-\frac{1750}{T} + 0.739$	-0.195	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\varepsilon_{\text{O}}^{\text{Ni}}$ $-\frac{246}{T} + 0.104$	-0.0273	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\varepsilon_{\text{Ni}}^{\text{Si}}$ $\frac{4920}{T} - 2.56$	0.0668	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\varepsilon_{\text{Ni}}^{\text{O}}$ $-\frac{94.3}{T} + 0.0389$	-0.0114	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\varepsilon_{\text{Ni}}^{\text{Ni}}$ $-\frac{13.6}{T} + 0.00724$	-0.0000211	$1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{\text{Si}}$ $-\frac{138}{T} + 0.0677$	-0.00718	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{\text{O}}$ $-\frac{81.7}{T} + 0.0463$	0.00268	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{\text{Ni}}$ $\frac{0.110}{T} - 0.0000583$	4.29×10^{-7}	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{Si}}$ $-\frac{94.5}{T} + 0.168$	0.118	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{O}}$ $\frac{74.1}{T} - 0.0316$	0.00796	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{O}}^{\text{Ni}}$ $\frac{0.0670}{T} - 0.000036$	-3.29×10^{-7}	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{\text{Si}}$ $-\frac{118}{T} + 0.0593$	-0.00370	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{\text{O}}$ $\frac{32.9}{T} - 0.0142$	0.00337	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{\text{Ni}}$ $\frac{0.0708}{T} - 0.000037$	3.20×10^{-10}	$1823 \leq T \leq 1973$
$\rho_{\text{Si}}^{(\text{Si}, \text{O})}$ $-\frac{307}{T} + 0.156$	-0.00791	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{Si}}^{(\text{Si}, \text{Ni})}$ $-\frac{66.7}{T} + 0.0348$	-0.000811	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\rho_{\text{O}}^{(\text{O}, \text{Si})}$ $-\frac{136}{T} + 0.0739$	0.00129	[mass%Si]<2.0, [mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{O}}^{(\text{O}, \text{Ni})}$ $\frac{13.9}{T} - 0.00586$	0.00156	[mass%O]<0.023, $1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{Si})}$ $-\frac{44.3}{T} + 0.0230$	-0.000652	[mass%Si]<2.0, $1823 \leq T \leq 1953$
$\rho_{\text{Ni}}^{(\text{Ni}, \text{O})}$ $\frac{8.87}{T} - 0.00380$	0.000936	[mass%O]<0.023, $1823 \leq T \leq 1953$

Table 6. Activity coefficients of elements at infinite dilution and interaction coefficients based on mass percents in molten Ni.

	Temperature Function	Value at 1873K	Region of Validity
$\frac{1}{2} \text{O}_2(\text{g}) = \text{O}(\text{1mass}\%)$	$-71000 + 1.37T / \text{J}$	-68400/J	$1823 \leq T \leq 1973$
$\text{Si}(\text{l}) = \text{Si}(\text{1mass}\%)$	$-456000 + 133T / \text{J}$	-207000/J	$1823 \leq T \leq 1973$
$\text{Fe}(\text{l}) = \text{Fe}(\text{1mass}\%)$	$-27100 - 28.6T / \text{J}$	-80700/J	$1823 \leq T \leq 1973$
$\text{Co}(\text{l}) = \text{Co}(\text{1mass}\%)$	$1330 - 38.3T / \text{J}$	-70400/J	$1823 \leq T \leq 1923$
$e_{\text{Si}}^{\text{Si}}$	$-\frac{3070}{T} + 1.80$	0.161	[mass%Si]<1.9, $1823 \leq T \leq 1973$
e_{Si}^{O}	$-\frac{3450}{T} + 1.82$	-0.0220	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
$e_{\text{Si}}^{\text{Fe}}$	$-\frac{2580}{T} + 1.35$	-0.0275	[mass%Si]<1.9, $1823 \leq T \leq 1973$
$e_{\text{Si}}^{\text{Co}}$	$-\frac{2370}{T} + 1.25$	-0.0153	[mass%Si]<1.9, $1823 \leq T \leq 1973$
e_{O}^{Si}	$-\frac{1860}{T} + 0.987$	-0.00606	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
e_{O}^{O}	0	0	[mass%O]<0.016, $1823 \leq T \leq 1973$
e_{O}^{Fe}	$\frac{290}{T} - 0.121$	0.0338	[mass%O]<0.016, $1823 \leq T \leq 1973$
e_{O}^{Co}	$-\frac{0.735}{T} + 0.00141$	0.00102	[mass%O]<0.016, $1823 \leq T \leq 1923$
$e_{\text{Fe}}^{\text{Si}}$	$-\frac{5130}{T} + 2.68$	-0.0589	[mass%Si]<1.9, $1823 \leq T \leq 1973$
e_{Fe}^{O}	$\frac{1010}{T} - 0.434$	0.105	[mass%O]<0.016, $1823 \leq T \leq 1973$
$e_{\text{Fe}}^{\text{Fe}}$	$\frac{52.1}{T} - 0.0193$	0.00852	$1823 \leq T \leq 1973$
$e_{\text{Co}}^{\text{Si}}$	$-\frac{4720}{T} + 2.48$	-0.0400	[mass%Si]<1.9, $1823 \leq T \leq 1973$
e_{Co}^{O}	$-\frac{2.57}{T} - 0.00592$	-0.00729	[mass%O]<0.016, $1823 \leq T \leq 1923$
$e_{\text{Co}}^{\text{Co}}$	$-\frac{1.46}{T} - 0.000214$	-0.000993	$1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{Si}}$	$\frac{65.5}{T} - 0.0385$	-0.00353	[mass%Si]<1.9, $1823 \leq T \leq 1973$
r_{Si}^{O}	$\frac{92.1}{T} - 0.0489$	0.000272	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{Si}}^{\text{Fe}}$	$\frac{1.04}{T} - 0.000587$	-0.0000317	[mass%Si]<1.9, $1823 \leq T \leq 1973$
$r_{\text{Si}}^{\text{Co}}$	$\frac{1.18}{T} - 0.000616$	0.0000140	[mass%Si]<1.9, $1823 \leq T \leq 1923$
r_{O}^{Si}	$\frac{52.4}{T} - 0.0296$	-0.00162	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
r_{O}^{O}	-0.000363	-0.000363	[mass%O]<0.016, $1823 \leq T \leq 1973$
r_{O}^{Fe}	$-\frac{0.422}{T} + 0.000400$	0.000175	[mass%O]<0.016, $1823 \leq T \leq 1973$
r_{O}^{Co}	$\frac{0.0802}{T} - 7.48 \times 10^{-7}$	0.0000421	[mass%O]<0.016, $1823 \leq T \leq 1923$
$r_{\text{Fe}}^{\text{Si}}$	$\frac{88.0}{T} - 0.218$	-0.171	[mass%Si]<1.9, $1823 \leq T \leq 1973$
r_{Fe}^{O}	$-\frac{27.0}{T} + 0.0112$	-0.00322	[mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{Fe}}^{\text{Fe}}$	$-\frac{0.301}{T} + 0.000112$	-0.0000487	$1823 \leq T \leq 1973$
$r_{\text{Co}}^{\text{Si}}$	$\frac{83.5}{T} - 0.216$	-0.171	[mass%Si]<1.9, $1823 \leq T \leq 1923$
r_{Co}^{O}	$\frac{0.0686}{T} - 0.000205$	-0.000168	[mass%O]<0.016, $1823 \leq T \leq 1923$
$r_{\text{Co}}^{\text{Co}}$	$\frac{0.00838}{T} + 5.27 \times 10^{-8}$	4.53×10^{-6}	$1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{(Si, O)}}$	$\frac{116}{T} - 0.106$	-0.0441	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{Si}}^{\text{(Si, Fe)}}$	$\frac{83.6}{T} - 0.0438$	0.000834	[mass%Si]<1.9, $1823 \leq T \leq 1973$
$r_{\text{Si}}^{\text{(Si, Co)}}$	$\frac{76.8}{T} - 0.0405$	0.000504	[mass%Si]<1.9, $1823 \leq T \leq 1923$
$r_{\text{O}}^{\text{(O, Si)}}$	$\frac{122}{T} - 0.0648$	0.000336	[mass%Si]<1.9, [mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{O}}^{\text{(O, Fe)}}$	$-\frac{18.4}{T} + 0.00766$	-0.00216	[mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{O}}^{\text{(O, Co)}}$	$\frac{0.0465}{T} - 0.000103$	-0.0000782	[mass%O]<0.016, $1823 \leq T \leq 1923$
$r_{\text{Fe}}^{\text{(Fe, Si)}}$	$\frac{56.0}{T} - 0.0293$	0.000599	[mass%Si]<1.9, $1823 \leq T \leq 1973$
$r_{\text{Fe}}^{\text{(Fe, O)}}$	$-\frac{12.5}{T} + 0.00517$	-0.00150	[mass%O]<0.016, $1823 \leq T \leq 1973$
$r_{\text{Co}}^{\text{(Co, Si)}}$	$\frac{51.8}{T} - 0.0273$	0.000356	[mass%Si]<1.9, $1823 \leq T \leq 1923$
$r_{\text{Co}}^{\text{(Co, O)}}$	$\frac{0.0671}{T} - 0.0000567$	-0.0000209	[mass%O]<0.016, $1823 \leq T \leq 1923$

Table 7. Activity coefficients of elements at infinite dilution and interaction coefficients based on mass percents in molten Co.

	Temperature Function	Value at 1873K	Region of Validity
$\frac{1}{2} \text{O}_2(\text{g}) = \text{O}(\text{1mass}\%)$	$-61500 - 20.5T / \text{J}$	-99900/J	$1823 \leq T \leq 1923$
$\text{Si}(\text{l}) = \text{Si}(\text{1mass}\%)$	$-622000 + 251T / \text{J}$	-152000/J	$1823 \leq T \leq 1923$
$\text{Ni}(\text{l}) = \text{Ni}(\text{1mass}\%)$	$1330 - 38.3T / \text{J}$	-70400/J	$1823 \leq T \leq 1923$
$e_{\text{Si}}^{\text{Si}}$	$\frac{6050}{T} - 3.01$	0.220	[mass%Si]<0.60, $1823 \leq T \leq 1923$
e_{Si}^{O}	$\frac{4610}{T} - 0.0109$	2.45	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
$e_{\text{Si}}^{\text{Ni}}$	$\frac{2150}{T} - 1.13$	0.0179	[mass%Si]<0.60, $1823 \leq T \leq 1923$
e_{O}^{Si}	$\frac{2620}{T} - 1.37$	0.0288	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
e_{O}^{O}	-0.0109	-0.0109	[mass%O]<0.0013, $1823 \leq T \leq 1923$
e_{O}^{Ni}	$-\frac{0.659}{T} - 0.00127$	-0.00162	[mass%O]<0.0013, $1823 \leq T \leq 1923$
$e_{\text{Ni}}^{\text{Si}}$	$\frac{4490}{T} - 2.37$	0.0272	[mass%Si]<0.60, $1823 \leq T \leq 1923$
e_{Ni}^{O}	$-\frac{2.42}{T} - 0.0163$	-0.0176	[mass%O]<0.0013, $1823 \leq T \leq 1923$
$e_{\text{Ni}}^{\text{Ni}}$	$-\frac{133}{T} + 0.000204$	-0.0708	$1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{Si}}$	$-\frac{120}{T} + 0.0597$	-0.00437	[mass%Si]<0.60, $1823 \leq T \leq 1923$
r_{Si}^{O}	$-\frac{115}{T} + 0.000137$	-0.0613	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{Ni}}$	$\frac{1.02}{T} - 0.000531$	0.0000136	[mass%Si]<0.60, $1823 \leq T \leq 1923$
r_{O}^{Si}	$-\frac{86.2}{T} + 0.0434$	-0.00262	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
r_{O}^{O}	-0.0251	-0.0251	[mass%O]<0.0013, $1823 \leq T \leq 1923$
r_{O}^{Ni}	$\frac{0.00601}{T} - 6.45 \times 10^{-7}$	2.56×10^{-6}	[mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{Ni}}^{\text{Si}}$	$-\frac{105}{T} + 0.0533$	-0.00276	[mass%Si]<0.60, $1823 \leq T \leq 1923$
r_{Ni}^{O}	$\frac{0.0604}{T} + 0.000271$	0.000303	[mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{Ni}}^{\text{Ni}}$	$-\frac{0.0562}{T} + 4.79 \times 10^{-8}$	-0.0000300	$1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{(Si, O)}}$	$-\frac{289}{T} + 0.123$	-0.0313	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{Si}}^{\text{(Si, Ni)}}$	$-\frac{61.2}{T} + 0.0323$	-0.000375	[mass%Si]<0.60, $1823 \leq T \leq 1923$
$r_{\text{O}}^{\text{(O, Si)}}$	$-\frac{157}{T} + 0.0820$	-0.00182	[mass%Si]<0.60, [mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{O}}^{\text{(O, Ni)}}$	$\frac{0.0395}{T} - 0.0000199$	1.19×10^{-6}	[mass%O]<0.0013, $1823 \leq T \leq 1923$
$r_{\text{Ni}}^{\text{(Ni, Si)}}$	$-\frac{39.3}{T} + 0.0214$	0.000418	[mass%Si]<0.60, $1823 \leq T \leq 1923$
$r_{\text{Ni}}^{\text{(Ni, O)}}$	$\frac{3.34}{T} - 0.0000592$	0.00172	[mass%O]<0.0013, $1823 \leq T \leq 1923$

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 converted into Wagner's interaction coefficients.

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