Ti Deoxidation Equilibrium in Molten Fe–Ni Alloys at Temperatures between 1 823 to 1 923 K

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Equilibrium relation between $\overline{\text{Ti}}$ and $\overline{\text{O}}$ in molten Fe–Ni alloy has been investigated at 1 873 to 1 923 K. Ti oxide equilibrated with molten Fe–Ni alloy has been determined by EBSD (Electron Backscatter Diffraction) pattern analysis using FE-SEM (Field Emission Scanning Electron Microscope). The present results have been numerically analyzed by the excess Gibbs free energy change of mixing for the Fe–Ni–Ti–O system with Redlich–Kister type polynomial. Redlich–Kister type polynomial parameters concerning Ni and Ti were determined as follows,

$${}^0\Omega_{\text{Ni-Ti}} = 424\,280 - 270.40T \text{ J/mol } (X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K}),$$

$${}^1\Omega_{\text{Ni-Ti}} = -663\,380 + 313.15T \text{ J/mol } (X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K}).$$

KEY WORDS: thermodynamics; Ti deoxidation equilibrium; Fe–Ni alloy; Redlich–Kister polynomial; FE-SEM EBSD analysis.

1. Introduction

Titanium has been used as a deoxidizer due to its strong affinity with oxygen. Reliable thermodynamic information on Ti deoxidation equilibrium is important for inclusion control in clean steel and its alloy production processes. Fe–Ni alloy has been widely used such as special steel product like invar steel because of its low thermal expansion property at high temperature. Removal of non-metallic inclusion is required in steelmaking process to produce thin material for shadow mask of display. Also, nickel based alloys are used as materials of which high temperature strength and corrosion resistance are required. There are only a few researches on the equilibrium relation between Ti and O in molten Fe–Ni alloy.^{1,2)} Dashveskii *et al.*¹⁾ reported only estimated oxygen content in Fe–Ni alloy based on thermodynamic calculation using Wagner's parameter, and Yoshikawa and Morita²⁾ reported the experimental results where Ni content range was limited from 0.529 to 2.51 mass%. It was reported in previous researches^{3,4)} that the equilibrium titanium oxide varied from 'Ti₃O₅', Ti₂O₃ to 'TiO' by increasing Ti content in molten Fe–Ti alloy, and the equilibrium titanium oxide was 'Ti₃O₅' at lower titanium contents than 0.36 mass% Ti. Therefore, Ti deoxidation experiment was carried out in a Ti₃O₅ crucible in order to investigate the equilibrium between $\overline{\text{Ti}}$ and $\overline{\text{O}}$ in Fe–Ni alloy at 1 823 K, 1 873 K and 1 923 K in the present work.

Phase identification of formed titanium oxides at the metal/crucible interface was accomplished by automated indexing of EBSD technique.⁵⁾ The solid solubility of Fe and/or Ni in 'Ti₃O₅' crucible had been also analyzed quanti-

tatively by SEM-EDS.

Recently, some of the present authors have developed a method to express numerically deoxidation equilibrium for not only pure metals but also alloys. This model is based on Darken's quadratic formalism^{6,7)} and Redlich–Kister type polynomial^{8,9)} and the details are explained in the previous papers.^{10–13)} The numerical analysis on Ti deoxidation of molten Fe–Ni alloy has been carried out in the present work.

2. Experimental

Deoxidation of Fe–Ni alloy with titanium was carried out by induction furnace in a Ti₃O₅ crucible to fix the activity of titanium oxide as unity and to avoid contamination of Fe–Ni alloy with the other crucible material in this research. A schematic diagram of the experimental apparatus is given elsewhere.³⁾ Powder of Ti₃O₅ was made by reduction of anatase type TiO₂ with hydrogen, pressed into a crucible shape and then sintered at 1 823 K for 12 h. Weighted 50 g of electrolyte Fe and Ni with high purities (99.99%) were contained in the Ti₃O₅ crucible. The sample was melted at each given experimental temperature *i.e.* 1 823 K, 1 873 K or 1 923 K under dehydrated and deoxidized Ar + 3% H₂ stream of 100 mL/min, and titanium was added from the upper part of the furnace. The temperature of the melt was monitored by infrared radiation pyrometer calibrated by the melting points of Fe and Cu. The sample was quenched by turning off the power of the furnace and impinging helium gas on the surface of the melt after the pre-determined equilibrium time of 2 h.

Table 1. Experimental results on the equilibrium between titanium and oxygen concentration in molten Fe–Ni alloy at 1 873 K.

Heat No.	[mass% Ni]	[mass% Ti]	[mass% O]	Distinguished equilibrium oxides by EBSD analysis
D-1	18.99	0.0004	0.0089	Ti_3O_5
D-2	19.32	0.0008	0.0087	
D-3	18.26	0.0008	0.0191	
D-4	21.72	0.0009	0.0065	
D-5	18.48	0.0011	0.0135	
D-6	19.72	0.0013	0.0087	
D-7	19.56	0.0812	0.0021	
D-8	18.74	0.237	0.0015	
D-9	17.72	0.266	0.0009	
E-1	37.24	0.0014	0.0079	Ti_3O_5
E-2	37.87	0.0158	0.0038	
E-3	39.43	0.0813	0.0024	
E-4	39.48	0.310	0.0013	
F-1	56.67	0.0008	0.0114	Ti_3O_5
F-2	57.51	0.0089	0.0107	
F-3	61.68	0.0144	0.0051	
F-4	60.84	0.0166	0.0077	
F-5	58.86	0.183	0.0022	
F-6	62.50	0.260	0.0022	
G-1	79.16	0.0044	0.0072	Ti_3O_5
G-2	84.76	0.0165	0.0060	
G-3	75.85	0.101	0.0017	
G-4	74.09	0.230	0.0018	
G-5	78.72	0.685	0.0014	
H-1	99.94	0.0546	0.0023	Ti_3O_5
H-2	99.92	0.0750	0.0022	
H-3	99.87	0.128	0.0023	
H-4	99.82	0.182	0.0016	
H-5	99.78	0.217	0.0014	
H-6	99.65	0.348	0.0015	
H-7	99.54	0.459	0.0014	

The quenched sample was cut, polished by abrasive paper of SiC and then electrolytically-polished for 3 min under the condition of 5 V–0.5 A. Mixed acid, which contains 80 mass% acetic acid and 20 mass% perchloric acid, was used for electrolyte. The sample was ultrasonically cleaned in acetone and immediately supplied to oxygen analysis by inert gas fusion infrared absorptionmetry to avoid effect of oxygen adsorption on sample surface. Nickel, iron and titanium contents were analyzed by induction coupled plasma emission spectrometry.

All samples were analyzed by FE-SEM EBSD in order to determine deoxidation product coexisted with the alloy. The solid solubility of Fe and Ni oxide in the deoxidation product, titanium oxide phase, was also analyzed by EDS, quantitatively.

3. Experimental Results

Experimental results of the present work are listed in **Tables 1** and **2**, and the results are reproduced in **Fig. 1** to **Fig. 3** with the results in pure Fe.^{3,4)} The oxygen contents in Fe–Ni alloys are higher than those in pure Fe as shown in **Fig. 1**. Also, oxygen content at very low titanium concentration deviates lower from that extrapolated relation at high

Table 2. Experimental results on the equilibrium between titanium and oxygen concentration in molten Fe–40mass%Ni alloy and pure Ni at 1 823 K and 1 923 K.

Heat No.	[mass% Ni]	[mass% Ti]	[mass% O]	Distinguished equilibrium oxides by EBSD analysis
I-1	36.65	0.0019	0.0055	Ti_3O_5
I-2	36.18	0.156	0.0013	
I-3	39.29	0.523	0.0012	
J-1	99.95	0.0499	0.0022	Ti_3O_5
J-2	99.89	0.111	0.0012	
J-3	99.43	0.570	0.0006	

(a) at 1823K

Heat No.	[mass% Ni]	[mass% Ti]	[mass% O]	Distinguished equilibrium oxides by EBSD analysis
K-1	37.80	0.0076	0.0130	Ti_3O_5
K-2	41.35	0.214	0.0049	
K-3	41.40	0.373	0.0046	
L-1	99.89	0.106	0.0037	Ti_3O_5
L-2	99.75	0.247	0.0026	
L-3	99.45	0.547	0.0021	

(b) at 1923K

Fig. 1. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe–Ni alloy at 1 873 K. **Fig. 2.** Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe–40mass%Ni alloy compared with that in pure Fe at 1 823 to 1 923 K.

Fig. 3. Equilibrium relation between [mass% Ti] and [mass% O] in pure Ni alloy compared with that in pure Fe at 1 823 to 1 923 K.

titanium region. The oxygen content increases with increasing temperature at constant titanium concentration for in Fe–40mass%Ni alloy and pure Ni as shown in Figs. 2 and 3. The curves in Figs. 1 to 3 show the calculated relation between Ti and O based on analysis by Redlich–Kister type polynomial and it will be discussed in Chap. 4.

It is reported that the equilibrium titanium oxide changes with titanium content in metal and the equilibrium oxide can be determined by EBSD analysis.^{3,4)} The interface between Fe–Ni alloy and Ti_3O_5 crucible was analyzed by EBSD for all samples. One example of the EBSD analysis results for Ti_3O_5 crucible equilibrated with Fe–17.72 mass%Ni–0.266mass%Ti is shown in Fig. 4. The crystal structure of Ti_3O_5 was confirmed to be anosovite named modified orthorhombic by automated indexing of EBSD method. All alloy samples were confirmed to coexist with Ti_3O_5 by EBSD analysis in the present experiment.

It is reported that solid solubility of Fe in ' Ti_3O_5 ' phase increases with decrease of content of Ti in Fe–Ti alloy at very low titanium region.^{3,4)} Suzuki and Sanbongi¹⁴⁾ measured the solubility of iron in synthetic titanium oxide crucible after equilibration with Fe–Ti alloy at 1 873 K and reported that the solubility of iron in titanium oxides increased with increase of oxygen to titanium ratio at the range between 1.67 and 2. Therefore, the interface between Fe–Ni alloy and Ti_3O_5 crucible was analyzed using SEM-EDS in the present work in order to confirm the solid solubility of Fe and/or Ni oxide in ' Ti_3O_5 ' phase. Figure 5 shows SEM-EDS analysis of Ti_3O_5 crucible interface contacted with Fe–17.72mass%Ni–0.266mass%Ti and Fe–21.72mass%Ni–0.0009mass%Ti at 1 873 K as representative examples. It is confirmed that there is the solubility of Fe and/or Ni oxide in ' Ti_3O_5 ' phase at lower titanium content in Fe–Ni alloy. The titanium content limit where solubility of Fe and/or Ni in ' Ti_3O_5 ' is observed increases with increase of Ni content in the alloy as shown in Fig. 1. Temperature dependence of the solubility of Fe and/or Ni in ' Ti_3O_5 ' phase is shown in Fig. 2. Solid solubility of Fe and/or Ni in ' Ti_3O_5 ' is observed at higher titanium content as temperature is higher. However, no temperature dependence is observed in the solubility of Fe and/or Ni in ' Ti_3O_5 ' phase in the case of pure Ni as shown in Fig. 3.

It is assumed in the present work that the activity of

Fig. 4. FE-SEM EBSD cross section image of quenched Ti_3O_5 crucible coexisting with liquid Fe–17.72mass%Ni–0.266mass%Ti at 1 873 K.

Fig. 5. SEM EDS analysis result of Fe and/or Ni in Ti_3O_5 crucible near the interface with Fe–17.72mass%Ni–0.266mass%Ti and Fe–21.72mass%Ni–0.0009mass%Ti alloys at 1 873 K.

Ti_3O_5 is unity when the solubility of Fe and Ni in ' Ti_3O_5 ' phase is lower than $(X_{\text{Fe}} + X_{\text{Ni}})/X_{\text{Ti}}$ (in ' Ti_3O_5 ' solid solution)=0.05. Only the experimental data that satisfy this condition are used for thermodynamic analysis in Chap. 4.

4. Discussion

Conversion of Darken's quadratic formalism into Redlich–Kister type polynomial was used to expand the

quadratic formalism to multi-component alloy systems. Miki and Hino¹⁰⁻¹³⁾ have reported the numerical analysis on Si deoxidation in various alloys by the quadratic formalism.

In the present research, pure liquid substances are chosen as standard states for condensed phases in the present numerical analysis, *i.e.* Raoultian standard state. In case of oxygen, hypothetical dissolved oxygen in the melt equilibrating with 101 325 Pa (1 atm) oxygen gas is selected as the standard state.¹⁰⁻¹³⁾

Ti deoxidation reaction can be expressed by Eq. (1).

By choosing Ti and O standard states as mentioned above, Eq. (1) can be divided into Eqs. (2) and (3) as follows.

The Gibbs free energy change of Eq. (2) is identical to the summation of the minus value of the Gibbs free energy of Ti_3O_5 formation ($\Delta G_{\text{f},\text{Ti}_3\text{O}_5}^\circ$) and three times value of the Gibbs free energy of fusion of titanium ($3\Delta G_{\text{fus},\text{Ti}}^\circ$). Also, chosen standard stage of oxygen as hypothetical dissolve state in the melt equilibrium with 101 325 Pa (1 atm) oxygen gas, the Gibbs free energy of Eq. (3) is zero. As the result, the Gibbs free energy change of Eq. (1) is identical to that of Eq. (2).

The equilibrium constant, $K_{\text{Ti}_3\text{O}_5}$, of Eq. (2) can be expressed as follows,

$$\begin{aligned} \ln K_{\text{Ti}_3\text{O}_5} &= - \frac{(-\Delta G_{\text{f},\text{Ti}_3\text{O}_5}^\circ + 3\Delta G_{\text{fus},\text{Ti}}^\circ)}{RT} \\ &= -\ln a_{\text{Ti}_3\text{O}_5} + 3\ln \gamma_{\text{Ti}} + 5\ln \gamma_{\text{O}} + 3\ln X_{\text{Ti}} + 5\ln X_{\text{O}} \\ &= 3\ln \gamma_{\text{Ti}} + 5\ln \gamma_{\text{O}} + 3\ln X_{\text{Ti}} + 5\ln X_{\text{O}} \quad (\because a_{\text{Ti}_3\text{O}_5} = 1) \end{aligned} \dots\dots\dots(4)$$

where, γ_i and X_i denote the Raoultian activity coefficient and mole fraction of component i , respectively. The activity of Ti_3O_5 in Eq. (4) is taken as unity, because deoxidation product is pure Ti_3O_5 in the present work and the Gibbs free energy of Ti_3O_5 formation ($\Delta G_{\text{f},\text{Ti}_3\text{O}_5}^\circ$) and Gibbs free energy of fusion of titanium ($\Delta G_{\text{fus},\text{Ti}}^\circ$) in Eq. (4) are taken from NIST-JANAF Thermochemical Tables.¹⁵⁾

The excess free energy change of mixing in Fe–Ni–Ti–O system can be expressed as Eq. (5) using Redlich–Kister type polynomial.

$$\begin{aligned} \Delta G^{\text{ex}} &= X_{\text{Fe}}X_{\text{Ni}}\{^0\Omega_{\text{Fe-Ni}} + ^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}} - X_{\text{Ni}})\} \\ &+ X_{\text{Fe}}X_{\text{Ti}}\{^0\Omega_{\text{Fe-Ti}} + ^1\Omega_{\text{Fe-Ti}}(X_{\text{Fe}} - X_{\text{Ti}})\} \\ &+ X_{\text{Fe}}X_{\text{O}}\{^0\Omega_{\text{Fe-O}} + ^1\Omega_{\text{Fe-O}}(X_{\text{Fe}} - X_{\text{O}})\} \\ &+ X_{\text{Ni}}X_{\text{Ti}}\{^0\Omega_{\text{Ni-Ti}} + ^1\Omega_{\text{Ni-Ti}}(X_{\text{Ni}} - X_{\text{Ti}})\} \\ &+ X_{\text{Ni}}X_{\text{O}}\{^0\Omega_{\text{Ni-O}} + ^1\Omega_{\text{Ni-O}}(X_{\text{Ni}} - X_{\text{O}})\} \\ &+ X_{\text{Ti}}X_{\text{O}}\{^0\Omega_{\text{Ti-O}} + \Delta G_{\text{fus},\text{Ti}}^\circ \cdot X_{\text{Ti}}\} \dots\dots\dots(5) \end{aligned}$$

where, Ω_{i-j} is binary interaction parameters of Redlich–

Kister type polynomial between component i and j .

The partial molar excess energy change of Ti and O in Fe–Ni–Ti–O alloy can be derived as following Eqs. of (6) and (7), respectively.

$$\begin{aligned} \Delta G_{\text{Ti}}^{\text{ex}} &= RT \ln \gamma_{\text{Ti}} \\ &= \Delta G^{\text{ex}} - X_{\text{Ni}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ni}}} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= -X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} - 2X_{\text{Fe}}X_{\text{Ni}}^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}} - X_{\text{Ni}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe-Ti}}(1 - X_{\text{Ti}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe-Ti}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 2X_{\text{Fe}}X_{\text{Ti}} + 2X_{\text{Ti}}^2) \\ &- X_{\text{Fe}}X_{\text{O}}^0\Omega_{\text{Fe-O}} - 2X_{\text{Fe}}X_{\text{O}}^1\Omega_{\text{Fe-O}}(X_{\text{Fe}} - X_{\text{O}}) \\ &+ X_{\text{Ni}}^0\Omega_{\text{Ni-Ti}}(1 - X_{\text{Ti}}) \\ &+ X_{\text{Ni}}^1\Omega_{\text{Ni-Ti}}(X_{\text{Ni}} - 2X_{\text{Ti}} - 2X_{\text{Ni}}X_{\text{Ti}} + 2X_{\text{Ti}}^2) \\ &- X_{\text{Ni}}X_{\text{O}}^0\Omega_{\text{Ni-O}} - 2X_{\text{Ni}}X_{\text{O}}^1\Omega_{\text{Ni-O}}(X_{\text{Ni}} - X_{\text{O}}) \\ &+ X_{\text{O}}^0\Omega_{\text{Ti-O}}(1 - X_{\text{Ti}}) + \Delta G_{\text{fus},\text{Ti}}^\circ \dots\dots\dots(6) \end{aligned}$$

$$\begin{aligned} \Delta G_{\text{O}}^{\text{ex}} &= RT \ln \gamma_{\text{O}} \\ &= \Delta G^{\text{ex}} - X_{\text{Ni}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ni}}} - X_{\text{Ti}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} + (1 - X_{\text{O}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= -X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} - 2X_{\text{Fe}}X_{\text{Ni}}^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}} - X_{\text{Ni}}) \\ &- X_{\text{Fe}}X_{\text{Ti}}^0\Omega_{\text{Fe-Ti}} - 2X_{\text{Fe}}X_{\text{Ti}}^1\Omega_{\text{Fe-Ti}}(X_{\text{Fe}} - X_{\text{Ti}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe-O}}(1 - X_{\text{O}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe-O}}(X_{\text{Fe}} - 2X_{\text{O}} - 2X_{\text{Fe}}X_{\text{O}} + 2X_{\text{O}}^2) \\ &- X_{\text{Ni}}X_{\text{Ti}}^0\Omega_{\text{Ni-Ti}} - 2X_{\text{Ni}}X_{\text{Ti}}^1\Omega_{\text{Ni-Ti}}(X_{\text{Ni}} - X_{\text{Ti}}) \\ &+ X_{\text{Ni}}^0\Omega_{\text{Ni-O}}(1 - X_{\text{O}}) \\ &+ X_{\text{Ni}}^1\Omega_{\text{Ni-O}}(X_{\text{Ni}} - 2X_{\text{O}} - 2X_{\text{Ni}}X_{\text{O}} + 2X_{\text{O}}^2) \\ &+ X_{\text{Ti}}^0\Omega_{\text{Ti-O}}(1 - X_{\text{O}}) \dots\dots\dots(7) \end{aligned}$$

For Fe–Ni–Ti–O system, Eq. (8) can be deduced by substituting the partial molar excess free energy change of titanium and oxygen of Eqs. (6) and (7) into Eq. (4).

$$\begin{aligned} &-8X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} - 16X_{\text{Fe}}X_{\text{Ni}}^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}} - X_{\text{Ni}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe-Ti}}(3 - 8X_{\text{Ti}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe-Ti}}(3X_{\text{Fe}} - 6X_{\text{Ti}} - 16X_{\text{Fe}}X_{\text{Ti}} + 16X_{\text{Ti}}^2) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe-O}}(5 - 8X_{\text{O}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe-O}}(5X_{\text{Fe}} - 10X_{\text{O}} - 16X_{\text{Fe}}X_{\text{O}} + 16X_{\text{O}}^2) \\ &+ X_{\text{Ni}}^0\Omega_{\text{Ni-Ti}}(3 - 8X_{\text{Ti}}) \\ &+ X_{\text{Ni}}^1\Omega_{\text{Ni-Ti}}(3X_{\text{Ni}} - 6X_{\text{Ti}} - 16X_{\text{Ni}}X_{\text{Ti}} + 16X_{\text{Ti}}^2) \\ &+ X_{\text{Ni}}^0\Omega_{\text{Ni-O}}(5 - 8X_{\text{O}}) \\ &+ X_{\text{Ni}}^1\Omega_{\text{Ni-O}}(5X_{\text{Ni}} - 10X_{\text{O}} - 16X_{\text{Ni}}X_{\text{O}} + 16X_{\text{O}}^2) \\ &+ ^0\Omega_{\text{Ti-O}}(5X_{\text{Ti}} + 3X_{\text{O}} - 8X_{\text{Ti}}X_{\text{O}}) + 3RT \ln X_{\text{Ti}} \\ &+ 5RT \ln X_{\text{O}} - \Delta G_{\text{f},\text{Ti}_3\text{O}_5}^\circ = 0 \dots\dots\dots(8) \end{aligned}$$

Equation (9) can be obtained by rearranging Eq. (8).

$$\begin{aligned}
Y_{\text{Ni-Ti}} = & \frac{1}{X_{\text{Ni}}(3-8X_{\text{Ti}})} \times \{-8X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} \\
& -16X_{\text{Fe}}X_{\text{Ni}}^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}}-X_{\text{Ni}}) \\
& +X_{\text{Fe}}^0\Omega_{\text{Fe-Ti}}(3-8X_{\text{Ti}}) \\
& +X_{\text{Fe}}^1\Omega_{\text{Fe-Ti}}(3X_{\text{Fe}}-6X_{\text{Ti}}-16X_{\text{Fe}}X_{\text{Ti}}+16X_{\text{Ti}}^2) \\
& +X_{\text{Fe}}^0\Omega_{\text{Fe-O}}(5-8X_{\text{O}}) \\
& +X_{\text{Fe}}^1\Omega_{\text{Fe-O}}(5X_{\text{Fe}}-10X_{\text{O}}-16X_{\text{Fe}}X_{\text{O}}+16X_{\text{O}}^2) \\
& +X_{\text{Ni}}^0\Omega_{\text{Ni-O}}(5-8X_{\text{O}}) \\
& +X_{\text{Ni}}^1\Omega_{\text{Ni-O}}(5X_{\text{Ni}}-10X_{\text{O}}-16X_{\text{Ni}}X_{\text{O}}+16X_{\text{O}}^2) \\
& +^0\Omega_{\text{Ti-O}}(5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}) \\
& +3RT \ln X_{\text{Ti}}+5RT \ln X_{\text{O}}-\Delta G_{\text{Ti,Ti}_2\text{O}_3}^\circ\} \\
= & ^0\Omega_{\text{Ni-Ti}}+^1\Omega_{\text{Ni-Ti}} \frac{3X_{\text{Ni}}-6X_{\text{Ti}}-16X_{\text{Ni}}X_{\text{Ti}}+16X_{\text{Ti}}^2}{3-8X_{\text{Ti}}} \dots\dots\dots(9)
\end{aligned}$$

$\Omega_{\text{Fe-Ti}}$,⁴⁾ $\Omega_{\text{Ti-O}}$,⁴⁾ $\Omega_{\text{Ni-O}}$,¹¹⁾ $\Omega_{\text{Fe-Ni}}$,¹⁶⁾ $\Omega_{\text{Fe-O}}$ ¹⁷⁾ in Eq. (9) were obtained from literature values and unknown parameters *i.e.* $^0\Omega_{\text{Ni-Ti}}$ and $^1\Omega_{\text{Ni-Ti}}$ were determined by the present experimental results where activity of titanium deoxidation oxide can regard as unity in the present system. Determined result which is done from the intercept and the slope of the regressed line by applying the least-square method to Eq. (9) is given in Fig. 6. As the result, following binary interaction parameters of Redlich–Kister type polynomial between Ni and Ti could be obtained at 1 823 to 1 923 K.

$$\begin{aligned}
^0\Omega_{\text{Ni-Ti}} = & 424\,280 - 270.40T \text{ J/mol} \\
(X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K}) \dots\dots\dots(10)
\end{aligned}$$

Fig. 6. Relation between $Y_{\text{Ni-Ti}}$ and $(3X_{\text{Ni}}-6X_{\text{Ti}}-16X_{\text{Ni}}X_{\text{Ti}}+16X_{\text{Ti}}^2)/(3-8X_{\text{Ti}})$ in liquid Fe–Ni alloy at 1 823 to 1 923 K.

$$\begin{aligned}
^1\Omega_{\text{Ni-Ti}} = & -663\,380 + 313.15T \text{ J/mol} \\
(X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K}) \dots\dots\dots(11)
\end{aligned}$$

The analyzed relation between Ti and O concentration in Fe–Ni alloys at 1 873 K was reproduced in Figs. 1 to 3 with experimental data. The calculated results agree well with the experimental results in the whole composition region except for alloy composition coexisting with ‘Ti₃O₅’ solid solutions containing Fe and Ni.

5. Conclusions

Ti deoxidation experiment of Fe–Ni alloy was carried out at 1 823 to 1 923 K using Ti₃O₅ crucible and the Ti deoxidation product equilibrated with the alloy was analyzed by FE-SEM EBSD. Numerical analysis was done in order to estimate deoxidation relation between Ti and O in wider composition range of Ni in Fe–Ni alloy by using Redlich–Kister type polynomial. Following binary interaction parameters of Redlich–Kister type polynomial could be obtained.

$$\begin{aligned}
^0\Omega_{\text{Ni-Ti}} = & 424\,280 - 270.40T \text{ J/mol} \\
(X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K})
\end{aligned}$$

$$\begin{aligned}
^1\Omega_{\text{Ni-Ti}} = & -663\,380 + 313.15T \text{ J/mol} \\
(X_{\text{Ti}} < 0.003, 1\,823 \text{ K} \leq T \leq 1\,923 \text{ K})
\end{aligned}$$

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