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

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Titanium deoxidation equilibria between Ti and O in molten Fe–Cr and Fe–Cr–Ni alloys were investigated at temperatures of 1 823 to 1 923 K. Titanium oxides equilibrated with molten Fe–Cr and Fe–Cr–Ni alloys have been determined by EBSD (Electron Backscatter Diffraction) pattern analysis using FE-SEM (Field Emission Scanning Electron Microscope). Deoxidation product changes from Ti_2O_3 to Ti_3O_5 with decrease of Ti content in Fe–Cr and Fe–Cr–Ni alloys.

Binary interaction parameters of Redlich–Kister type polynomial between Cr and O was assessed by using the previous experimental result in the Fe–Cr–O system. Experimental result of titanium deoxidation in molten Fe–Cr alloy has been numerically analyzed by the excess Gibbs free energy change of mixing Fe–Cr–Ti–O system with Redlich–Kister type polynomial. Validity of evaluated parameters between Cr–O ($\Omega_{\text{Cr-O}}$) and Cr–Ti ($\Omega_{\text{Cr-Ti}}$) was confirmed by comparison with experimental result for Fe–Cr–Ni alloy.

Binary interaction parameters of Redlich–Kister type polynomial in present work were evaluated as follows,

$${}^0\Omega_{\text{Cr-O}} = -52\,870 - 24.10T \text{ J/mol} \quad (X_{\text{O}} < 0.0015, 1\,823 \leq T \leq 1\,923 \text{ K})$$

$${}^1\Omega_{\text{Cr-O}} = -498\,200 + 234.7T \text{ J/mol} \quad (X_{\text{O}} < 0.0015, 1\,823 \leq T \leq 1\,923 \text{ K})$$

$${}^0\Omega_{\text{Cr-Ti}} = 365\,700 - 206.3T \text{ J/mol} \quad (X_{\text{Ti}} < 0.003, 1\,823 \leq T \leq 1\,923 \text{ K})$$

$${}^1\Omega_{\text{Cr-Ti}} = 432\,900 - 208.8T \text{ J/mol} \quad (X_{\text{Ti}} < 0.003, 1\,823 \leq T \leq 1\,923 \text{ K})$$

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

1. Introduction

Titanium forms titanium oxide, carbide and nitride due to its strong affinity for C, N and O in steel. Addition of titanium in austenitic stainless steel enhances its corrosion resistance and welding property. Also, Cr equivalent of titanium in chromic stainless steel is 7.2¹⁾ and titanium is added to steel products in order to enhance its strength at high temperature.²⁾

Takahashi *et al.*³⁾ have reported the formation ability of titanium oxide and nitride using equilibrium relation among Ti, O and N in various stainless steels. Yoshikawa and Morita⁴⁾ experimented on titanium deoxidation in 18mass%Cr–8mass%Ni steel and thermodynamically analyzed the experimental result. However, analysis of titanium deoxidation products were done by EPMA. They determined that Ti_3O_5 was the stable oxide when the Ti content was lower than 0.238 mass% in Fe–Cr–Ni alloy and Ti_2O_3 was stable when the Ti content was higher than 0.238 mass%. In the report on the same alloy composition by Chino *et al.*,⁵⁾ determination of deoxidation product was done by XRD. They determined that Cr_2O_3 was the stable oxide when the Ti content was lower than 0.01 mass% in

Fe–Cr–Ni alloy, Ti_3O_5 was stable when Ti content was from 0.01 to 0.2 mass% and Ti_2O_3 was stable when Ti content was higher than 0.2 mass%. Those experimental results are shown in **Fig. 1** with titanium deoxidation result in pure Fe.⁶⁾ Both experimental results were different not only on oxygen contents at given Ti content, but also on the equilibrium titanium concentration range for each deoxidation product.

Titanium deoxidation equilibria in pure Fe and Fe–Ni alloy are reported by the present research group.^{6–8)} Thermodynamic equilibrium relation between Ti and O in Fe–Cr and Fe–Cr–Ni alloys are investigated in the present research to control deoxidation products in those alloys. Concentration of Cr was set lower than 40 mass% because of the difficulty of preparing good samples for oxygen analysis. Deoxidation experiments for Fe–20mass%Cr and Fe–20mass%Cr–10mass%Ni alloys were carried out at the temperature of 1 823 to 1 923 K in order to evaluate temperature dependence of titanium deoxidation equilibria in those alloys.

All titanium deoxidation products equilibrated with Fe–Cr and Fe–Cr–Ni alloys were determined by EBSD (Electron Backscatter Diffraction) pattern analysis of

Fig. 1. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe-18mass%Cr-8mass%Ni alloy at 1873 K.

metal/crucible interface using FE-SEM (Field Emission Scanning Electron Microscope).⁹⁾ The composition was also analyzed quantitatively with EDS by measuring the solid solubility of Fe, Cr and/or Ni oxides in Ti_3O_5 at metal/crucible interface.

Numerical analysis by Redlich-Kister type polynomial on titanium deoxidation of molten Fe-Ni alloy was carried out in order to extend applicable composition range of quadratic formalism in the previous report.⁸⁾ The experimental result of titanium deoxidation in molten Fe-Cr alloy has been numerically analyzed by applying Redlich-Kister type polynomial to the excess Gibbs free energy change of mixing for Fe-Cr-Ti-O system in the present work. In the sequence of numerical analysis, the interaction parameter between Cr and Ti ($\Omega_{\text{Cr-Ti}}$) of Redlich-Kister type polynomial was assessed using the experimental result in Fe-Cr-O system.¹⁰⁾ Also, binary interaction parameter of Redlich-Kister type polynomial between Cr and Ti ($\Omega_{\text{Cr-Ti}}$) was deduced. Finally, validity of those evaluated parameters was confirmed by comparing the present experimental results with the evaluated equilibrium relation between titanium and oxygen concentration in molten Fe-Cr-Ni alloy.

2. Experimental

Deoxidation of Fe-Cr and Fe-Cr-Ni alloys with titanium were carried out in a Ti_3O_5 crucible to fix the activity of titanium oxide and to avoid contamination of those alloy from crucible by induction furnace. Details of Ti_3O_5 crucible production and an experimental method of titanium deoxidation are given previous report.⁸⁾ Temperature of the melt was monitored by an infrared radiation pyrometer calibrated by the melting temperatures of Fe and Cu. The samples of Fe-Cr and Fe-Cr-Ni alloys were quenched by turning off the power of the furnace and impinging helium gas on the surface of the melt after the predetermined equilibrium time of 60 min and 90 min, respectively.

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 of 80 mass% acetic acid and 20 mass% perchloric acid was used for the electrolyte. The sample was ultrasonically cleaned in acetone and immediately supplied to O analysis by inert gas fusion infrared absorptionmetry to avoid effect of oxygen adsorption on the sample surface. Analysis of Cr, Ni, Fe

and Ti contents was conducted by induction coupled plasma emission spectrometry.

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

3. Experimental Results

Titanium deoxidation experimental results in molten Fe-Cr and Fe-Cr-Ni alloys are listed in **Tables 1** and **2** and the results are reproduced in **Figs. 2** to **5** with the results in molten pure Fe.^{6,7)} The curves in Figs. 2 to 5 show the calculated relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ based on analysis by Redlich-Kister type polynomial and they will be discussed in Chap. 4. It is shown in Fig. 2 that the oxygen contents at the constant titanium concentration in molten Fe-Cr alloys are higher than those in molten pure Fe. Also, oxygen content at very low titanium concentration deviates lower from that extrapolated relation at high titanium region. It is shown in Fig. 3 that the oxygen content increases with increasing temperature at constant titanium concentration in molten Fe-20mass%Cr alloy. Behavior of oxygen content at low titanium concentration region and effect of temperature in Fe-Cr-Ni alloy were similar to those in Fe-Cr alloy as shown in Figs. 4 and 5. The experimental results of the present work were similar to those of Yoshikawa and Morita⁴⁾ from Fig. 4.

It is reported that the chemicals of equilibrium titanium oxide change with titanium content in metal and the equilibrium oxides can be determined by EBSD analysis.^{6,7)} In our previous report, the quenched interface between Fe-Ni alloy and Ti_3O_5 crucible was analyzed by EBSD and Ti deoxidation product was confirmed to be Ti_3O_5 .⁸⁾ An example of the EBSD analysis results for Ti_3O_5 crucible equilibrated with Fe-18.6mass%Cr-0.157mass%Ti alloy at 1873 K is shown in **Fig. 6(a)**. The crystal structure of Ti_3O_5 crucible was confirmed to be anosovite modified orthorhombic by automated indexing of EBSD method from Fig. 6(a). However, in the case of Fe-19.9mass%Cr-0.418mass%Ti as shown in Fig. 6(b), the equilibrium oxide was confirmed to be Ti_2O_3 of trigonal structure. All samples in the present experiment were analyzed by EBSD method and those results were also listed in **Tables 1** and **2**.

It is reported in previous report that the solubility of iron and/or nickel oxide in ' Ti_3O_5 ' phase increases with decrease of content of Ti in Fe-Ti and Fe-Ni-Ti alloys.⁶⁻⁸⁾ Suzuki and Sanbongi¹¹⁾ measured the solubility of iron oxide in synthesized titanium oxide crucible after equilibration with molten Fe-Ti alloy at 1873 K and reported that the solubility of iron oxide in titanium oxides increased with increase of oxygen to titanium ratio at the range between 1.67 and 2. Therefore, the quenched interface between Fe-Cr and Fe-Cr-Ni alloys and Ti_3O_5 crucible was analyzed using SEM-EDS in order to confirm solid solubility of Fe, Cr and/or Ni oxide in ' Ti_3O_5 ' phase in the present work. The SEM-EDS analysis of ' Ti_3O_5 ' crucible interface contacted with Fe-18.6mass%Cr-0.157mass%Ti and Fe-16.9mass%Cr-0.0627mass%Ti at 1873 K are shown in **Fig. 7** as representative examples. Solubility of Fe and/or Cr oxide in Ti_3O_5 phase at low Ti content in Fe-Cr alloy was

Table 1. Experimental results of titanium deoxidation equilibrium for liquid Fe–Cr alloy at 1 823 to 1 923 K.

Heat No.	Experimental Temperature	[mass% Cr]	[mass% Ti]	[mass% O]	Distinguished equilibrium oxides by EBSD analysis
1	1873K	20.6	0.0076	0.0127	Ti ₃ O ₅ (Anovosite)
2		19.2	0.0403	0.0062	
3		16.9	0.0627	0.0081	
4		20.0	0.0645	0.0060	
5		18.6	0.0777	0.0033	
6		18.6	0.157	0.0035	
7		19.9	0.418	0.0023	Ti ₂ O ₃ (Trigonal)
8		35.7	0.0110	0.0311	Ti ₃ O ₅ (Anovosite)
9		34.9	0.0335	0.0121	
10		39.6	0.0350	0.0334	
11		39.7	0.0437	0.0194	
12		40.2	0.153	0.0071	Ti ₂ O ₃ (Trigonal)
13		41.0	0.389	0.0047	
14	1823K	22.0	0.0078	0.0052	Ti ₃ O ₅ (Anovosite)
15		21.8	0.0176	0.0042	
16		19.1	0.0807	0.0024	
17	1923K	21.8	0.028	0.0114	Ti ₃ O ₅ (Anovosite)
18		20.0	0.0064	0.0228	
19		21.4	0.078	0.0116	

Table 2. Experimental results of titanium deoxidation equilibrium for liquid Fe–Cr–Ni alloy at 1 823 to 1 923 K.

Heat No.	Experimental Temperature	[mass% Cr]	[mass% Ni]	[mass% Ti]	[mass% O]	Distinguished equilibrium oxides by EBSD analysis
20	1873K	17.6	7.92	0.0028	0.0123	Ti ₃ O ₅ (Anovosite)
21		16.4	8.08	0.0049	0.0194	
22		19.0	10.48	0.0070	0.0169	
23		19.7	9.81	0.0506	0.0079	
24		19.6	9.76	0.0710	0.0064	
25		14.3	7.34	0.0766	0.0052	
26		17.5	12.58	0.0189	0.0054	Ti ₂ O ₃ (Trigonal)
27		19.9	10.15	0.7850	0.0019	Ti ₃ O ₅ (Anovosite)
28		38.7	19.76	0.0049	0.0350	
29		34.5	20.23	0.0074	0.0550	
30		38.8	18.69	0.0573	0.0175	
31		38.9	19.39	0.2410	0.0112	Ti ₂ O ₃ (Trigonal)
32		38.6	19.54	0.2750	0.0074	
33	1823K	19.4	10.14	0.0895	0.0019	Ti ₃ O ₅ (Anovosite)
34		16.2	8.39	0.0064	0.0103	
35		19.0	9.98	0.0681	0.0030	
36	1923K	16.8	8.36	0.0064	0.0150	Ti ₃ O ₅ (Anovosite)
37		18.1	9.36	0.167	0.0137	

confirmed. Critical titanium content in the alloy that solubility of Fe and/or Cr oxide in ‘Ti₃O₅’ was observed increased with increase of Cr content in the alloy as shown in Fig. 2. Temperature dependence of Fe and/or Cr oxide solu-

bility in ‘Ti₃O₅’ phase is shown in Fig. 3. Critical titanium content where of Fe and/or Cr oxides started to solve in ‘Ti₃O₅’ was observed at higher titanium content at higher temperature. Solid solubility of Fe, Cr and/or Ni oxides in

Fig. 2. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe-Cr alloy compared with that in pure Fe⁽⁶⁾ by at 1873 K.

Fig. 3. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe-20mass%Cr alloy compared with that in pure Fe^(6,7) at 1823 to 1923 K.

Fig. 4. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe-Cr-Ni alloy compared with that in pure Fe⁽⁶⁾ at 1873 K.

'Ti₃O₅' phase was also analyzed by SEM-EDS and those results are shown in Figs. 4 and 5. Solid solubility of Fe, Cr and/or Ni oxide in 'Ti₃O₅' phase coexisting with liquid Fe-Cr-Ni alloy was also observed at low titanium content. The dependences of Cr and Ni contents of the alloy and temperature on critical titanium content that solid solubility of Fe, Cr and/or Ni oxides was observed were similar to the results of Fe-Cr alloy.

It was assumed in the present work that the activity of

Fig. 5. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe-20mass%Cr-10mass%Ni alloy compared with that in pure Fe^(6,7) at 1823 to 1923 K.

(a)

(b)

Fig. 6. FE-SEM EBSD cross section image of quenched crucibles coexisted with liquid (a) Fe-18.6mass%Cr-0.157mass%Ti and (b) Fe-19.9mass%Cr-0.418mass%Ti alloy at 1873 K.

Ti₃O₅ was unity when the solubility of Fe and Cr oxides in 'Ti₃O₅' phase was lower than $(X_{\text{Fe}} + X_{\text{Cr}})/X_{\text{Ti}}$ (in 'Ti₃O₅' solid solution)=0.05. Only the experimental data that satisfy this condition were used for thermodynamic analysis in Chap. 4.

4. Discussion

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

(a)

(b)

Fig. 7. SEM EDS analysis result of Fe and/or Cr oxide in Ti_3O_5 crucible near the interface with (a) Fe-18.6mass%Cr-0.157mass%Ti and (b) Fe-16.9mass%Ni-0.0627mass%Ti alloy at 1873 K.

formalism to multi-component alloy systems. Miki and Hino^{12,13)} have reported the numerical analysis on Si deoxidation in various alloys by quadratic formalism.

The final objective of the present research is to evaluate the Ti deoxidation equilibria in Fe-Cr-Ni alloy as shown in **Fig. 8**. Redlich-Kister type interaction parameters between Fe-Ti, Ti-O and Ni-Ti were reported in previous research based on experimental data of Ti deoxidation in pure Fe and Fe-Ni alloy from 1823 to 1923 K.⁶⁻⁸⁾ The objectives of the present research are to deduce Redlich-Kister type interaction parameters between Cr and Ti by using the present experimental results and to evaluate the validity of deduced parameters by comparing analyzed relation between Ti and O in Fe-Cr-Ni alloy with the experimental results. However, reexamination of the previous derived parameters between Cr and O is needed in analysis about Fe-Cr-Ti-O quaternary system, and those parameters are re-deduced from reported results between Cr and O in pure Fe.¹⁰⁾ Calculation was repeated until analysis results agreed with the experimental results and the final analyzed results were described in this research.

In the present research, pure liquid substances were chosen as a standard state for condensed phases in the present numerical analysis, *i.e.* Raoultian standard state. In case of oxygen, hypothetically dissolved oxygen in the melt equilibrating with 101325 Pa (1 atm) oxygen gas had been se-

Fig. 8. Flow chart of numerical analysis in the present research.

lected as the standard state.^{12,13)}

4.1. Numerical Analysis on Equilibrium between Cr and O in Pure Fe

Ito *et al.*¹⁰⁾ have reported the equilibrium relation between Cr and O in pure Fe. The stable oxide changes with Cr content in pure Fe and $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ is the stable in the Cr content region lower than about 6 to 7 mass% and Cr_2O_3 is stable at higher content of Cr. In the case that stable oxide is Cr_2O_3 , namely higher than 6 to 7 mass% of Cr content, formation reaction of Cr_2O_3 can be expressed by Eq. (1).

By choosing Cr standard state as pure liquid substance, 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 change of Cr_2O_3 formation ($\Delta G_{\text{f,Cr}_2\text{O}_3}^\circ$) and twice of the Gibbs free energy change of fusion of chromium ($2\Delta G_{\text{fus,Cr}}^\circ$). From the chosen standard state of oxygen as hypothetically dissolved state in the melt equilibrated with 101325 Pa (1 atm) oxygen gas, the Gibbs free energy change 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, $K_{\text{Cr}_2\text{O}_3}$, of Eq. (1) can be expressed as follows,

$$\begin{aligned} \ln K_{\text{Cr}_2\text{O}_3} &= - \frac{(-\Delta G_{\text{f,Cr}_2\text{O}_3}^\circ + 2\Delta G_{\text{fus,Cr}}^\circ)}{RT} \\ &= -\ln a_{\text{Cr}_2\text{O}_3} + 2\ln \gamma_{\text{Cr}} + 3\ln \gamma_{\text{O}} + 2\ln X_{\text{Cr}} + 3\ln X_{\text{O}} \\ &= 2\ln \gamma_{\text{Cr}} + 3\ln \gamma_{\text{O}} + 2\ln X_{\text{Cr}} + 3\ln X_{\text{O}} \end{aligned}$$

$$(\because a_{\text{Cr}_2\text{O}_3} = 1) \dots\dots\dots(4)$$

where, γ_i and X_i denote the Raoultian activity coefficient and mole fraction of component *i*, respectively. The activity of Cr_2O_3 in Eq. (1) was taken as unity, because the stable oxide was pure Cr_2O_3 at higher content of Cr than 6.7 mass%. The Gibbs free energy change of Cr_2O_3 formation ($\Delta G_{\text{f,Cr}_2\text{O}_3}^\circ$) and the Gibbs free energy change of fusion of chromium ($\Delta G_{\text{fus,Cr}}^\circ$) in Eq. (4) were taken from NIST-

JANAF Thermochemical Tables.¹⁴⁾

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

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

where, Ω_{i-j} is binary interaction parameters of Redlich–Kister type polynomial between component i and j .

The partial molar excess free energy change of Cr and O in Fe–Cr–O system can be derived as Eqs. (6) and (7), respectively.

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

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

Following equation can be deduced by substituting the partial molar excess free energy change of titanium and oxygen of Eq. (6) and (7) into Eq. (4).

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

where, binary interaction parameters of Redlich–Kister type polynomial in Eq. (8) were reported as follows;

$$\begin{aligned} {}^0\Omega_{\text{Fe-Cr}} &= -17737 + 7.996546T/\text{J} \\ (0 < X_{\text{Fe}} < 1, 1823 \leq T \leq 1923 \text{ K})^{15)} \dots \dots \dots (9) \end{aligned}$$

$$\begin{aligned} {}^1\Omega_{\text{Fe-Cr}} &= 1331/\text{J} \\ (0 < X_{\text{Fe}} < 1, 1823 \leq T \leq 1923 \text{ K})^{15)} \dots \dots \dots (10) \end{aligned}$$

$$\begin{aligned} {}^0\Omega_{\text{Fe-O}} &= -415700 + 139.5T/\text{J} \\ (X_{\text{O}} \leq 0.004, 1823 \leq T \leq 1973 \text{ K})^{12,13)} \dots \dots \dots (11) \end{aligned}$$

$$\begin{aligned} {}^1\Omega_{\text{Fe-O}} &= 298600 - 115.0T/\text{J} \\ (X_{\text{O}} \leq 0.004, 1823 \leq T \leq 1973 \text{ K})^{12,13)} \dots \dots \dots (12) \end{aligned}$$

$$\begin{aligned} {}^0\Omega_{\text{Cr-O}} &= -688900 + 302.8T/\text{J} \\ (X_{\text{O}} < 0.0015, 1823 \leq T \leq 1973 \text{ K})^{12,13)} \dots \dots \dots (13) \end{aligned}$$

$$\begin{aligned} {}^1\Omega_{\text{Cr-O}} &= 1770000 - 951.2T/\text{J} \\ (X_{\text{O}} < 0.0015, 1823 \leq T \leq 1973 \text{ K})^{12,13)} \dots \dots \dots (14) \end{aligned}$$

Figure 9(a) shows analyzed results of equilibrium relation between Cr and O in pure Fe using binary interaction parameter of Eqs. (9) to (14) for Eq. (8). From Fig. 9(a), there is discrepancy between the analyzed results and the experimental results after Itoh *et al.*¹⁰⁾ Its difference becomes larger with increase of Cr content and experimental temperature. Binary interaction parameters of Redlich–Kister type polynomial of Eqs. (13) and (14) were deduced by Si deoxidation experimental results in Fe–Cr, and Fe–Cr–Ni alloys. Those parameters were reevaluated based on experimental results by Itoh *et al.*¹⁰⁾ in the following. In order to deduce these parameters, Eq. (15) can be expressed by rearranging Eq. (8).

$$\begin{aligned} Y_{\text{Cr-O}} &= -\frac{1}{3X_{\text{Cr}} + 2X_{\text{O}} - 5X_{\text{Cr}}X_{\text{O}}} [X_{\text{Fe}} {}^0\Omega_{\text{Fe-Cr}}(2 - 5X_{\text{Cr}}) \\ &\quad + 2X_{\text{Fe}} {}^1\Omega_{\text{Fe-Cr}}(X_{\text{Fe}} - 2X_{\text{Cr}} - 5X_{\text{Fe}}X_{\text{Cr}} + 5X_{\text{Cr}}^2) \\ &\quad + X_{\text{Fe}} {}^0\Omega_{\text{Fe-O}}(3 - 5X_{\text{O}}) \\ &\quad + X_{\text{Fe}} {}^1\Omega_{\text{Fe-O}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2) \\ &\quad + 2RT \ln X_{\text{Cr}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{f,Cr}_2\text{O}_3}^{\circ}] \\ &= {}^0\Omega_{\text{Cr-O}} + {}^1\Omega_{\text{Cr-O}} \\ &\quad \times \frac{(3X_{\text{Cr}}^2 - 2X_{\text{O}}^2 - 2X_{\text{Cr}}X_{\text{O}} - 10X_{\text{Cr}}^2X_{\text{O}} + 10X_{\text{Cr}}X_{\text{O}}^2)}{(3X_{\text{Cr}} + 2X_{\text{O}} - 5X_{\text{Cr}}X_{\text{O}})} \\ &\dots \dots \dots (15) \end{aligned}$$

Fig. 9. Equilibrium relation between [mass% Cr] and [mass% O] in molten Fe at 1823 to 1923 K¹⁰⁾ with numerical analysis results by Redlich–Kister type polynomial by using binary interaction parameter of (a) literature values¹³⁾ and (b) present research.

It is possible to determine both ${}^0\Omega_{\text{Cr-O}}$ and ${}^1\Omega_{\text{Cr-O}}$ simultaneously from Eq. (15). However, these parameters were determined separately to improve the accuracy in the present work. Binary interaction parameter of Redlich–Kister type polynomial between Cr and O, ${}^0\Omega_{\text{Cr-O}}$ in Eq. (15) was derived from interaction parameter reported by Itoh *et al.*¹⁰⁾ They determined e_{O}^{Cr} as Eq. (16) and $\varepsilon_{\text{O}}^{\text{Cr}}$ could be derived using Eq. (17) as Eq. (18).

$$e_{\text{O}}^{\text{Cr}} = -123/T + 0.034$$

(mass%Cr < 46, 1 823 ≤ T ≤ 1 923 K).....(16)

$$\varepsilon_{\text{O}}^{\text{Cr}} = 230 \frac{M_{\text{Cr}}}{M_{\text{Fe}}} e_{\text{O}}^{\text{Cr}} + \frac{(M_{\text{Fe}} - M_{\text{Cr}})}{M_{\text{Fe}}} \dots\dots\dots(17)$$

$$\varepsilon_{\text{O}}^{\text{Cr}} = \varepsilon_{\text{Cr}}^{\text{O}} = -26\,340.2/T + 7.35$$

($X_{\text{Cr}} < 0.47$, 1 823 ≤ T ≤ 1 923 K).....(18)

Also, $\varepsilon_{\text{Cr}}^{\text{O}}$ could be derived as follows from Eq. (6).

$$\begin{aligned} \varepsilon_{\text{Cr}}^{\text{O}} &= \lim_{X_{\text{Fe}} \rightarrow 1} \left(\frac{\partial \ln \gamma_{\text{Cr}}}{\partial X_{\text{O}}} \right) \\ &= \frac{1}{RT} (-{}^0\Omega_{\text{Fe-Cr}} - 2{}^1\Omega_{\text{Fe-Cr}} - {}^0\Omega_{\text{Fe-O}} - 2{}^1\Omega_{\text{Fe-O}} \\ &\quad + 2{}^0\Omega_{\text{Cr-O}}) \dots\dots\dots(19) \end{aligned}$$

${}^0\Omega_{\text{Cr-O}}$ was derived from Eq. (18) by substituting Eqs. (9) to (12) and (18) into Eq. (15) and the result was as follows.

$${}^0\Omega_{\text{Cr-O}} = -52\,870 - 24.10T \text{ J/mol}$$

($X_{\text{O}} < 0.0015$, 1 823 ≤ T ≤ 1 923 K).....(20)

After substituting Eqs. (9) to (12) and (18) and experimental results of Itoh *et al.*¹⁰⁾ into Eq. (15), unknown parameter ${}^1\Omega_{\text{Cr-O}}$ can be deduced from the slope of the regressed line. It is shown Fig. 10. Evaluated binary interaction parameter of Redlich–Kister type polynomial between Cr and O is as follows.

$${}^1\Omega_{\text{Cr-O}} = -498\,200 + 234.7T \text{ J/mol}$$

($X_{\text{O}} < 0.0015$, 1 823 ≤ T ≤ 1 923 K).....(21)

The regressed line in Fig. 10 was determined according the flow chart shown in Fig. 8. Not only $\Omega_{\text{Cr-O}}$ but also $\Omega_{\text{Cr-Ti}}$, explained in the following, was determined. Therefore, the line may not totally agree with the plots in Fig. 10. Figure 9(b) shows equilibrium relation between Cr and O in pure Fe which is analyzed using Eqs. (20) and (21). Equilibrium relation between Cr and O using binary interaction parameters of Eqs. (20) and (21) deduced in the present work was more suitable than the analysis using Eqs. (13) and (14) from comparison of Fig. 9(b) with Fig. 9(a).

4.2. Numerical Analysis on Ti Deoxidation Equilibrium in Molten Fe–Cr and Fe–Cr–Ni Alloys

It was confirmed that Ti deoxidation product changes from Ti_2O_3 to Ti_3O_5 with decrease of Ti content in Fe–Cr and Fe–Cr–Ni alloys from FE-SEM EBSD results. In the low Ti content region in Fe–Cr alloy, Ti_3O_5 was deoxidation product and Ti deoxidation reaction can be expressed by Eq. (22).

Fig. 10. Relation between $Y_{\text{Cr-O}}$ and $(3X_{\text{Cr}}^2 - 2X_{\text{Cr}}X_{\text{O}} - 10X_{\text{Cr}}^2X_{\text{O}} + 10X_{\text{Cr}}X_{\text{O}}^2)/(3X_{\text{Cr}} + 2X_{\text{O}} - 5X_{\text{Cr}}X_{\text{O}})$ in Fe–Cr–O system at 1 823 to 1 923 K.

If the same standard state are chosen as mentioned in numerical analysis equilibrium between Cr and O in pure Fe, Eq. (22) can be divided into Eqs. (23) and (24) as follows.

The Gibbs free energy change of Eq. (23) is identical to the summation the minus value of the Gibbs free energy change of Ti_3O_5 formation ($\Delta G_{\text{f,Ti}_3\text{O}_5}^\circ$) and the triple of Gibbs free energy change of fusion of titanium ($3\Delta G_{\text{fus,Ti}}^\circ$). From the chosen standard state of oxygen as hypothetically dissolved state in the melt equilibrated with 101 325 Pa (1 atm) oxygen gas, the Gibbs free energy change of Eq. (24) is zero. As a result, the Gibbs free energy change of Eq. (22) is identical to that of Eq. (23).

The equilibrium constant of Eq. (19), $K_{\text{Ti}_3\text{O}_5}$, can be expressed as follows,

$$\begin{aligned} \ln K_{\text{Ti}_3\text{O}_5} &= - \frac{(-\Delta G_{\text{f,Ti}_3\text{O}_5}^\circ + 3\Delta G_{\text{fus,Ti}}^\circ)}{RT} \\ &= -\ln a_{\text{Ti}_3\text{O}_5} + 3\ln \gamma_{\text{Ti}} + 5\ln \gamma_{\text{O}} + 3\ln X_{\text{Ti}} + 5\ln X_{\text{O}} \\ &= 3\ln \gamma_{\text{Ti}} + 5\ln \gamma_{\text{O}} + 3\ln X_{\text{Ti}} + 5\ln X_{\text{O}} \\ &(\because a_{\text{Ti}_3\text{O}_5} = 1) \dots\dots\dots(25) \end{aligned}$$

The activity of Ti_3O_5 in Eq. (25) was taken as unity, because deoxidation product is pure Ti_3O_5 in the present work and the Gibbs free energy change of Ti_3O_5 formation ($\Delta G_{\text{f,Ti}_3\text{O}_5}^\circ$) and the Gibbs free energy change of fusion of titanium ($\Delta G_{\text{fus,Ti}}^\circ$) in Eq. (25) were taken from NIST-JANAF Thermochemical Tables.¹⁴⁾

In the case of high Ti content in Fe–Cr alloy, Ti_2O_3 was confirmed to be equilibrium titanium deoxidation product. Deoxidation reaction and the equilibrium constant can be expressed by Eqs. (26) and (27).

$$\begin{aligned}\ln K_{\text{Ti}_2\text{O}_3} &= - \frac{(-\Delta G_{\text{f,Ti}_2\text{O}_3}^\circ + 3\Delta G_{\text{fus,Ti}}^\circ)}{RT} \\ &= -\ln a_{\text{Ti}_2\text{O}_3} + 2\ln \gamma_{\text{Ti}} + 3\ln \gamma_{\text{O}} + 2\ln X_{\text{Ti}} + 3\ln X_{\text{O}} \\ &= 2\ln \gamma_{\text{Ti}} + 3\ln \gamma_{\text{O}} + 2\ln X_{\text{Ti}} + 3\ln X_{\text{O}} \\ (\because a_{\text{Ti}_2\text{O}_3} &= 1) \dots\dots\dots(27)\end{aligned}$$

The excess free energy change of mixing in Fe–Cr–Ti–O system using Redlich–Kister type polynomial can be expressed as Eq. (28).

$$\begin{aligned}\Delta G^{\text{ex}} &= X_{\text{Fe}}X_{\text{Cr}}\{^0\Omega_{\text{Fe–Cr}} + ^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}})\} \\ &+ X_{\text{Fe}}X_{\text{Ti}}\{^0\Omega_{\text{Fe–Ti}} + ^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - X_{\text{Ti}})\} \\ &+ X_{\text{Fe}}X_{\text{O}}\{^0\Omega_{\text{Fe–O}} + ^1\Omega_{\text{Fe–O}}(X_{\text{Fe}} - X_{\text{O}})\} \\ &+ X_{\text{Cr}}X_{\text{Ti}}\{^0\Omega_{\text{Cr–Ti}} + ^1\Omega_{\text{Cr–Ti}}(X_{\text{Cr}} - X_{\text{Ti}})\} \\ &+ X_{\text{Cr}}X_{\text{O}}\{^0\Omega_{\text{Cr–O}} + ^1\Omega_{\text{Cr–O}}(X_{\text{Cr}} - X_{\text{O}})\} \\ &+ X_{\text{Ti}}X_{\text{O}}\{^0\Omega_{\text{Ti–O}} + ^1\Omega_{\text{Ti–O}}(X_{\text{Ti}} - X_{\text{O}})\} \\ &+ X_{\text{Fe}}\Delta G_{\text{fus,Fe}}^\circ + X_{\text{Cr}}\Delta G_{\text{fus,Cr}}^\circ + X_{\text{Ti}}\Delta G_{\text{fus,Ti}}^\circ \dots\dots(28)\end{aligned}$$

where, $\Delta G_{\text{fus,Ti}}^\circ$ and $\Delta G_{\text{fus,Cr}}^\circ$ are the Gibbs free energy of fusion of titanium and chromium, respectively.

The partial molar excess free energy change of Ti and O in Fe–Cr–Ti–O alloy can be derived as following Eqs. of (29) and (30), respectively.

$$\begin{aligned}\overline{\Delta G_{\text{Ti}}^{\text{ex}}} &= RT \ln \gamma_{\text{Ti}} \\ &= \Delta G^{\text{ex}} - X_{\text{Cr}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Cr}}} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} \\ &\quad - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= -X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} - 2X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &\quad + X_{\text{Fe}}^0\Omega_{\text{Fe–Ti}}(1 - X_{\text{Ti}}) \\ &\quad + X_{\text{Fe}}^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 2X_{\text{Fe}}X_{\text{Ti}} + 2X_{\text{Ti}}^2) \\ &\quad - X_{\text{Fe}}X_{\text{O}}^0\Omega_{\text{Fe–O}} - 2X_{\text{Fe}}X_{\text{O}}^1\Omega_{\text{Fe–O}}(X_{\text{Fe}} - X_{\text{O}}) \\ &\quad + X_{\text{Cr}}^0\Omega_{\text{Cr–Ti}}(1 - X_{\text{Ti}}) \\ &\quad + X_{\text{Cr}}^1\Omega_{\text{Cr–Ti}}(X_{\text{Cr}} - 2X_{\text{Ti}} - 2X_{\text{Cr}}X_{\text{Ti}} + 2X_{\text{Ti}}^2) \\ &\quad - X_{\text{Cr}}X_{\text{O}}^0\Omega_{\text{Cr–O}} - 2X_{\text{Cr}}X_{\text{O}}^1\Omega_{\text{Cr–O}}(X_{\text{Cr}} - X_{\text{O}}) \\ &\quad + X_{\text{O}}^0\Omega_{\text{Ti–O}}(1 - X_{\text{Ti}}) + \Delta G_{\text{fus,Ti}}^\circ \dots\dots\dots(29)\end{aligned}$$

$$\begin{aligned}\overline{\Delta G_{\text{O}}^{\text{ex}}} &= RT \ln \gamma_{\text{O}} \\ &= \Delta G^{\text{ex}} - X_{\text{Cr}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Cr}}} - X_{\text{Ti}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} + (1 - X_{\text{O}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= -X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} - 2X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &\quad - X_{\text{Fe}}X_{\text{Ti}}^0\Omega_{\text{Fe–Ti}} - 2X_{\text{Fe}}X_{\text{Ti}}^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - X_{\text{Ti}}) \\ &\quad + X_{\text{Fe}}^0\Omega_{\text{Fe–O}}(1 - X_{\text{O}}) \\ &\quad + X_{\text{Fe}}^1\Omega_{\text{Fe–O}}(X_{\text{Fe}} - 2X_{\text{O}} - 2X_{\text{Fe}}X_{\text{O}} + 2X_{\text{O}}^2) \\ &\quad - X_{\text{Cr}}X_{\text{Ti}}^0\Omega_{\text{Cr–Ti}} - 2X_{\text{Cr}}X_{\text{Ti}}^1\Omega_{\text{Cr–Ti}}(X_{\text{Cr}} - X_{\text{Ti}}) \\ &\quad + X_{\text{Cr}}^0\Omega_{\text{Cr–O}}(1 - X_{\text{O}}) \\ &\quad + X_{\text{Cr}}^1\Omega_{\text{Cr–O}}(X_{\text{Cr}} - 2X_{\text{O}} - 2X_{\text{Cr}}X_{\text{O}} + 2X_{\text{O}}^2) \\ &\quad + X_{\text{Ti}}^0\Omega_{\text{Ti–O}}(1 - X_{\text{O}}) \dots\dots\dots(30)\end{aligned}$$

For Fe–Cr–Ti–O system, Eqs. (31) and (32) can be deduced by substituting the partial molar excess free energy change of titanium and oxygen of Eq. (29) and (30) into Eqs. (25) and (27), respectively.

$$\begin{aligned}&-8X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} - 16X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–Ti}}(3 - 8X_{\text{Ti}}) + X_{\text{Fe}}^1\Omega_{\text{Fe–Ti}}(3X_{\text{Fe}} - 6X_{\text{Ti}} \\ &- 16X_{\text{Fe}}X_{\text{Ti}} + 16X_{\text{Ti}}^2) + X_{\text{Fe}}^0\Omega_{\text{Fe–O}}(5 - 8X_{\text{O}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe–O}}(5X_{\text{Fe}} - 10X_{\text{O}} - 16X_{\text{Fe}}X_{\text{O}} + 16X_{\text{O}}^2) \\ &+ X_{\text{Cr}}^0\Omega_{\text{Cr–Ti}}(3X_{\text{Cr}} - 6X_{\text{Ti}} - 16X_{\text{Cr}}X_{\text{Ti}} \\ &- 16X_{\text{Cr}}X_{\text{O}} + 16X_{\text{O}}^2) + X_{\text{Cr}}^1\Omega_{\text{Cr–Ti}}(5X_{\text{Cr}} - 10X_{\text{O}} \\ &- 16X_{\text{Cr}}X_{\text{O}} + 16X_{\text{O}}^2) + ^0\Omega_{\text{Ti–O}}(5X_{\text{Ti}} + 3X_{\text{O}} - 8X_{\text{Ti}}X_{\text{O}}) \\ &+ 3RT \ln X_{\text{Ti}} + 5RT \ln X_{\text{O}} - \Delta G_{\text{f,Ti}_2\text{O}_3}^\circ = 0 \dots\dots\dots(31)\end{aligned}$$

$$\begin{aligned}&-5X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} - 10X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–Ti}}(2 - 5X_{\text{Ti}}) + 2X_{\text{Fe}}^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 5X_{\text{Fe}}X_{\text{Ti}} \\ &+ 5X_{\text{Ti}}^2) + X_{\text{Fe}}^0\Omega_{\text{Fe–O}}(3 - 5X_{\text{O}}) + X_{\text{Fe}}^1\Omega_{\text{Fe–O}}(3X_{\text{Fe}} - 6X_{\text{O}} \\ &- 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2) + X_{\text{Cr}}^0\Omega_{\text{Cr–Ti}}(2 - 5X_{\text{Ti}}) \\ &+ 2X_{\text{Cr}}^1\Omega_{\text{Cr–Ti}}(X_{\text{Cr}} - 2X_{\text{Ti}} - 5X_{\text{Cr}}X_{\text{Ti}} + 5X_{\text{Ti}}^2) \\ &+ X_{\text{Cr}}^0\Omega_{\text{Cr–O}}(3 - 5X_{\text{O}}) + X_{\text{Cr}}^1\Omega_{\text{Cr–O}}(3X_{\text{Cr}} - 6X_{\text{O}} - 10X_{\text{Cr}}X_{\text{O}} \\ &+ 10X_{\text{O}}^2) + ^0\Omega_{\text{Ti–O}}(3X_{\text{Ti}} + 2X_{\text{O}} - 5X_{\text{Ti}}X_{\text{O}}) + 2RT \ln X_{\text{Ti}} \\ &+ 3RT \ln X_{\text{O}} - \Delta G_{\text{f,Ti}_2\text{O}_3}^\circ = 0 \dots\dots\dots(32)\end{aligned}$$

Equations (33) and (34) can be obtained by rearranging Eqs. (31) and (32), respectively.

$$\begin{aligned}Y_{\text{Ti}_2\text{O}_3} &= - \frac{1}{X_{\text{Cr}}(2 - 5X_{\text{Ti}})} \{-5X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} \\ &- 10X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–Ti}}(2 - 5X_{\text{Ti}}) \\ &+ 2X_{\text{Fe}}^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 5X_{\text{Fe}}X_{\text{Ti}} + 5X_{\text{Ti}}^2) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–O}}(3 - 5X_{\text{O}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe–O}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2) \\ &+ X_{\text{Cr}}^0\Omega_{\text{Cr–O}}(3 - 5X_{\text{O}}) \\ &+ X_{\text{Cr}}^1\Omega_{\text{Cr–O}}(3X_{\text{Cr}} - 6X_{\text{O}} - 10X_{\text{Cr}}X_{\text{O}} + 10X_{\text{O}}^2) \\ &+ ^0\Omega_{\text{Ti–O}}(3X_{\text{Ti}} + 2X_{\text{O}} - 5X_{\text{Ti}}X_{\text{O}}) \\ &+ 2RT \ln X_{\text{Ti}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{f,Ti}_2\text{O}_3}^\circ\} \\ &= ^0\Omega_{\text{Cr–Ti}} + ^1\Omega_{\text{Cr–Ti}} \frac{2(X_{\text{Cr}} - 2X_{\text{Ti}} - 5X_{\text{Cr}}X_{\text{Ti}} + 5X_{\text{Ti}}^2)}{2 - 5X_{\text{Ti}}} \\ &\dots\dots\dots(33)\end{aligned}$$

$$\begin{aligned}Y_{\text{Ti}_2\text{O}_3} &= - \frac{1}{X_{\text{Cr}}(2 - 5X_{\text{Ti}})} \{-5X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe–Cr}} \\ &- 10X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe–Cr}}(X_{\text{Fe}} - X_{\text{Cr}}) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–Ti}}(2 - 5X_{\text{Ti}}) \\ &+ 2X_{\text{Fe}}^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 5X_{\text{Fe}}X_{\text{Ti}} + 5X_{\text{Ti}}^2) \\ &+ X_{\text{Fe}}^0\Omega_{\text{Fe–O}}(3 - 5X_{\text{O}}) \\ &+ X_{\text{Fe}}^1\Omega_{\text{Fe–O}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2) \\ &+ X_{\text{Cr}}^0\Omega_{\text{Cr–O}}(3 - 5X_{\text{O}}) \\ &+ X_{\text{Cr}}^1\Omega_{\text{Cr–O}}(3X_{\text{Cr}} - 6X_{\text{O}} - 10X_{\text{Cr}}X_{\text{O}} + 10X_{\text{O}}^2) \\ &+ ^0\Omega_{\text{Ti–O}}(3X_{\text{Ti}} + 2X_{\text{O}} - 5X_{\text{Ti}}X_{\text{O}}) \\ &+ 2RT \ln X_{\text{Ti}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{f,Ti}_2\text{O}_3}^\circ\} \\ &= ^0\Omega_{\text{Cr–Ti}} + ^1\Omega_{\text{Cr–Ti}} \frac{2(X_{\text{Cr}} - 2X_{\text{Ti}} - 5X_{\text{Cr}}X_{\text{Ti}} + 5X_{\text{Ti}}^2)}{2 - 5X_{\text{Ti}}} \\ &\dots\dots\dots(34)\end{aligned}$$

Binary interaction parameter of Eqs. (9) to (12), $\Omega_{\text{Fe–Ti}}^{(7)}$, $\Omega_{\text{Ti–O}}^{(7)}$, $\Omega_{\text{Fe–Cr}}^{(15)}$, $\Omega_{\text{Fe–O}}^{(13)}$ and $\Omega_{\text{Cr–O}}$ in the present research were utilized for Eqs. (33) and (34). Unknown parameters $^0\Omega_{\text{Cr–Ti}}$ and $^1\Omega_{\text{Cr–Ti}}$ were determined by utilizing experimental results in Table 1, where the activity of titanium oxide were regarded as unity for Fe–Cr–Ti–O system. The result is shown in Fig. 11.

Following binary interaction parameters of Redlich–Kister type polynomial between Cr and Ti were obtained from the intercept and the slope at 1 823 to 1 923 K.

$$\begin{aligned}
 &+X_{\text{Fe}}^1\Omega_{\text{Fe-O}}(5X_{\text{Fe}}-10X_{\text{O}}-16X_{\text{Fe}}X_{\text{O}}+16X_{\text{O}}^2) \\
 &-8X_{\text{Cr}}X_{\text{Ni}}^0\Omega_{\text{Cr-Ni}}-16X_{\text{Cr}}X_{\text{Ni}}^1\Omega_{\text{Cr-Ni}}(X_{\text{Cr}}-X_{\text{Ni}}) \\
 &+X_{\text{Cr}}^0\Omega_{\text{Cr-Ti}}(3-8X_{\text{Ti}})+X_{\text{Cr}}^1\Omega_{\text{Cr-Ti}}(3X_{\text{Cr}}-6X_{\text{Ti}} \\
 &-16X_{\text{Cr}}X_{\text{Ti}}+16X_{\text{Ti}}^2)+X_{\text{Cr}}^0\Omega_{\text{Cr-O}}(5-8X_{\text{O}}) \\
 &+X_{\text{Cr}}^1\Omega_{\text{Cr-O}}(5X_{\text{Cr}}-10X_{\text{O}}-16X_{\text{Cr}}X_{\text{O}}+16X_{\text{O}}^2) \\
 &+X_{\text{Ni}}^0\Omega_{\text{Ni-Ti}}(3-8X_{\text{Ti}})+X_{\text{Ni}}^1\Omega_{\text{Ni-Ti}}(3X_{\text{Ni}}-6X_{\text{Ti}} \\
 &-16X_{\text{Ni}}X_{\text{Ti}}+16X_{\text{Ti}}^2)+X_{\text{Ni}}^0\Omega_{\text{Ni-O}}(5-8X_{\text{O}}) \\
 &+X_{\text{Ni}}^1\Omega_{\text{Ni-O}}(5X_{\text{Ni}}-10X_{\text{O}}-16X_{\text{Ni}}X_{\text{O}}+16X_{\text{O}}^2) \\
 &+{}^0\Omega_{\text{Ti-O}}(5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}) \\
 &-8X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ni}}^1(2{}^0\Omega_{\text{Fe-Cr-Ni}}+3X_{\text{Fe}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}} \\
 &+3X_{\text{Cr}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}}+3X_{\text{Ni}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}}) \\
 &+3RT\ln X_{\text{Ti}}+5RT\ln X_{\text{O}}-\Delta G_{\text{Fe-Ti}_2\text{O}_3}^0=0 \dots\dots\dots(40)
 \end{aligned}$$

$$\begin{aligned}
 &-5X_{\text{Fe}}X_{\text{Cr}}^0\Omega_{\text{Fe-Cr}}-10X_{\text{Fe}}X_{\text{Cr}}^1\Omega_{\text{Fe-Cr}}(X_{\text{Fe}}-X_{\text{Cr}}) \\
 &-5X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}}-10X_{\text{Fe}}X_{\text{Ni}}^1\Omega_{\text{Fe-Ni}}(X_{\text{Fe}}-X_{\text{Ni}}) \\
 &+X_{\text{Fe}}^0\Omega_{\text{Fe-Ti}}(2-5X_{\text{Ti}})+2X_{\text{Fe}}^1\Omega_{\text{Fe-Ti}}(X_{\text{Fe}}-2X_{\text{Ti}} \\
 &-5X_{\text{Fe}}X_{\text{Ti}}+5X_{\text{Ti}}^2)+X_{\text{Fe}}^0\Omega_{\text{Fe-O}}(3-5X_{\text{O}}) \\
 &+X_{\text{Fe}}^1\Omega_{\text{Fe-O}}(3X_{\text{Fe}}-6X_{\text{O}}-10X_{\text{Fe}}X_{\text{O}}+10X_{\text{O}}^2) \\
 &-5X_{\text{Cr}}X_{\text{Ni}}^0\Omega_{\text{Cr-Ni}}-10X_{\text{Cr}}X_{\text{Ni}}^1\Omega_{\text{Cr-Ni}}(X_{\text{Cr}}-X_{\text{Ni}}) \\
 &+X_{\text{Cr}}^0\Omega_{\text{Cr-Ti}}(2-5X_{\text{Ti}})+2X_{\text{Cr}}^1\Omega_{\text{Cr-Ti}}(X_{\text{Cr}}-2X_{\text{Ti}} \\
 &-5X_{\text{Cr}}X_{\text{Ti}}+5X_{\text{Ti}}^2)+X_{\text{Cr}}^0\Omega_{\text{Cr-O}}(3-5X_{\text{O}}) \\
 &+X_{\text{Cr}}^1\Omega_{\text{Cr-O}}(3X_{\text{Cr}}-6X_{\text{O}}-10X_{\text{Cr}}X_{\text{O}}+10X_{\text{O}}^2) \\
 &+X_{\text{Ni}}^0\Omega_{\text{Ni-Ti}}(2-5X_{\text{Ti}})+2X_{\text{Ni}}^1\Omega_{\text{Ni-Ti}}(X_{\text{Ni}}-2X_{\text{Ti}} \\
 &-5X_{\text{Ni}}X_{\text{Ti}}+5X_{\text{Ti}}^2)+X_{\text{Ni}}^0\Omega_{\text{Ni-O}}(3-5X_{\text{O}}) \\
 &+X_{\text{Ni}}^1\Omega_{\text{Ni-O}}(3X_{\text{Ni}}-6X_{\text{O}}-10X_{\text{Ni}}X_{\text{O}}+10X_{\text{O}}^2) \\
 &+{}^0\Omega_{\text{Ti-O}}(3X_{\text{Ti}}+2X_{\text{O}}-5X_{\text{Ti}}X_{\text{O}}) \\
 &-5X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ni}}^1(2{}^0\Omega_{\text{Fe-Cr-Ni}}+3X_{\text{Fe}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}} \\
 &+3X_{\text{Cr}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}}+3X_{\text{Ni}}\cdot{}^1\Omega_{\text{Fe-Cr-Ni}}) \\
 &+2RT\ln X_{\text{Ti}}+3RT\ln X_{\text{O}}-\Delta G_{\text{Fe-Ti}_2\text{O}_3}^0=0 \dots\dots\dots(41)
 \end{aligned}$$

Following ternary parameter was given for titanium de-oxidation equilibrium in Fe–Cr–Ni alloy by Miettinen.²¹⁾

$$\begin{aligned}
 \Omega_{\text{Fe-Cr-Ni}} &= {}^0\Omega_{\text{Fe-Cr-Ni}} + {}^1\Omega_{\text{Fe-Cr-Ni}}X_{\text{Fe}} + {}^1\Omega_{\text{Fe-Cr-Ni}}X_{\text{Cr}} \\
 &+ {}^1\Omega_{\text{Fe-Cr-Ni}}X_{\text{Ni}} \\
 &= (90\,000 - 50T) - 10\,000X_{\text{Fe}} + 40\,000X_{\text{Cr}} \\
 &- 30\,000X_{\text{Ni}}/J \quad (1\,823 \leq T \leq 1\,923\text{ K}) \dots\dots\dots(42)
 \end{aligned}$$

The equilibrium relation between Ti and O concentration in Fe–Cr–Ni alloy at 1 823 to 1 923 K based on calculation of Redlich–Kister type polynomial parameters between Ni–Ti ($\Omega_{\text{Ni-Ti}}$)⁸⁾ and Cr–Ti ($\Omega_{\text{Cr-Ti}}$) was reproduced in Figs. 4 and 5. Calculated results agree well with experimental results in the composition region of the alloy treated in the present work. Hence, deduced binary interaction parameters of Redlich–Kister type polynomial between Ni–Ti and Cr–Ti were valid for titanium deoxidation equilibrium of Fe–Cr–Ni alloy for wide composition range.

5. Conclusions

Ti deoxidation experiments of Fe–Cr and Fe–Cr–Ni alloys were carried out at 1 823 to 1 923 K using Ti_3O_5 crucible and the Ti deoxidation products equilibrated with the alloys were analyzed by FE-SEM EBSD. Chemical change of titanium deoxidation product in Fe–Cr and Fe–Cr–Ni alloys from Ti_2O_3 to Ti_3O_5 was confirmed with decrease with

titanium content in those alloys. Numerical analysis was done in order to estimate deoxidation relation between Ti and O in wide composition range of Fe–Cr and Fe–Cr–Ni alloys using Redlich–Kister type polynomial deduced based on titanium deoxidation experimental results. The binary interaction parameters of Redlich–Kister type polynomial between Cr and O are reevaluated in sequence of numerical analysis on titanium deoxidation equilibrium in Fe–Cr alloy.

Validity of deduced binary interaction parameters in Fe–Cr–Ni alloy was confirmed by comparison with experimental results. The following binary interaction parameters of Redlich–Kister type polynomial were obtained.

$$\begin{aligned}
 {}^0\Omega_{\text{Cr-O}} &= -52\,870 - 24.10T/\text{J/mol} \\
 (X_{\text{O}} < 0.0015, 1\,823 \leq T \leq 1\,923\text{ K})
 \end{aligned}$$

$$\begin{aligned}
 {}^1\Omega_{\text{Cr-O}} &= -498\,200 + 234.7T/\text{J/mol} \\
 (X_{\text{O}} < 0.0015, 1\,823 \leq T \leq 1\,923\text{ K})
 \end{aligned}$$

$$\begin{aligned}
 {}^0\Omega_{\text{Cr-Ti}} &= 365\,700 - 206.3T/\text{J/mol} \\
 (X_{\text{Ti}} < 0.003, 1\,823 \leq T \leq 1\,923\text{ K})
 \end{aligned}$$

$$\begin{aligned}
 {}^1\Omega_{\text{Cr-Ti}} &= 432\,900 - 208.8T/\text{J/mol} \\
 (X_{\text{Ti}} < 0.003, 1\,823 \leq T \leq 1\,923\text{ K})
 \end{aligned}$$

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