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 Ti2O3 to Ti3O5 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,

\[ \begin{align*}
\Omega_{\text{Cr-O}} &= -52 870 - 24.10 T \text{ J/mol (} X_O = 0.0015, 1 823 \leq T \leq 1 923 \text{ K) } \\
\Omega_{\text{Cr-Ti}} &= -498 200 + 234.77 T \text{ J/mol (} X_O = 0.0015, 1 823 \leq T \leq 1 923 \text{ K) } \\
\Omega_{\text{Cr-Ti}} &= 365 700 - 206.3 T \text{ J/mol (} X_Ti = 0.003, 1 823 \leq T \leq 1 923 \text{ K) } \\
\Omega_{\text{Cr-Ti}} &= 432 900 - 208.8 T \text{ J/mol (} X_Ti = 0.003, 1 823 \leq T \leq 1 923 \text{ K) }
\end{align*} \]

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 7.2) and titanium is added to steel products in order to enhance its strength at high temperature.3)

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 Ti2O3 was the stable oxide when the Ti content was lower than 0.238 mass% in Fe–Cr–Ni alloy and Ti3O5 was stable when 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 Cr2O3 was the stable oxide when the Ti content was lower than 0.01 mass% in Fe–Cr–Ni alloy, Ti3O5 was stable when Ti content was from 0.01 to 0.2 mass% and Ti2O3 was stable when Ti content was higher than 0.2 mass%.

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
metal/crucible interface using FE-SEM (Field Emission Scanning Electron Microscope). The composition was also analyzed quantitatively with EDS by measuring the solid solubility of Fe, Cr and/or Ni oxides in Ti$_3$O$_5$ 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. 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 ($\Omega_{Cr,Ti}$) of Redlich–Kister type polynomial was assessed using the experimental result in Fe–Cr–O system. Also, binary interaction parameter of Redlich–Kister type polynomial between Cr and Ti ($\Omega_{Cr,Ti}$) 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$_3$O$_5$ crucible to fix the activity of titanium oxide and to avoid contamination of those alloy from crucible by induction furnace. Details of Ti$_3$O$_5$ crucible production and an experimental method of titanium deoxidation are given previous report. 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. The curves in Figs. 2 to 5 show the calculated relation between Ti and 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–Ti alloy as shown in Figs. 4 and 5. The experimental results of the present work were similar to those of Yoshikawa and Morita 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. In our previous report, the quenched interface between Fe–Ni alloy and Ti$_3$O$_5$ crucible was analyzed by EBSD and Ti deoxidation product was confirmed to be Ti$_3$O$_5$. An example of the EBSD analysis results for Ti$_3$O$_5$ 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$_3$O$_5$ crucible was confirmed to be an asbestos 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$_3$O$_5$ 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$_3$O$_5$ phase increases with decrease of content of Ti in Fe–Ti and Fe–Ni–Ti alloys. Suzuki and Sanbongi 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$_3$O$_5$ crucible was analyzed using SEM-EDS in order to confirm solid solubility of Fe, Cr and/or Ni oxide in Ti$_3$O$_5$ phase in the present work. The SEM-EDS analysis of Ti$_3$O$_5$ 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$_3$O$_5$ phase at low Ti content in Fe–Cr alloy was
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 solubility 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

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

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Experimental Temperature</th>
<th>[mass% Cr]</th>
<th>[mass% Ti]</th>
<th>[mass% O]</th>
<th>Distinguished equilibrium oxides by EBSD analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1873K</td>
<td>20.6</td>
<td>0.0076</td>
<td>0.0127</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>2</td>
<td>1873K</td>
<td>19.2</td>
<td>0.0403</td>
<td>0.0062</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1873K</td>
<td>18.9</td>
<td>0.0627</td>
<td>0.0081</td>
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</tr>
<tr>
<td>4</td>
<td>1873K</td>
<td>20.0</td>
<td>0.0645</td>
<td>0.0060</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1873K</td>
<td>18.6</td>
<td>0.0777</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1873K</td>
<td>18.6</td>
<td>0.157</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1873K</td>
<td>19.9</td>
<td>0.418</td>
<td>0.0023</td>
<td>Ti₃O₅ (Trigonal)</td>
</tr>
<tr>
<td>8</td>
<td>1873K</td>
<td>35.7</td>
<td>0.0110</td>
<td>0.0311</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>9</td>
<td>1873K</td>
<td>34.9</td>
<td>0.0335</td>
<td>0.0121</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>10</td>
<td>1873K</td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>1873K</td>
<td>39.7</td>
<td>0.0457</td>
<td>0.0194</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1873K</td>
<td>40.2</td>
<td>0.153</td>
<td>0.0071</td>
<td>Ti₃O₅ (Trigonal)</td>
</tr>
<tr>
<td>13</td>
<td>1873K</td>
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<td>0.389</td>
<td>0.0047</td>
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</tr>
<tr>
<td>14</td>
<td>1823K</td>
<td>22.0</td>
<td>0.0078</td>
<td>0.0052</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>15</td>
<td>1823K</td>
<td>21.8</td>
<td>0.0176</td>
<td>0.0042</td>
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<tr>
<td>16</td>
<td>1823K</td>
<td>19.1</td>
<td>0.0807</td>
<td>0.0024</td>
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</tr>
<tr>
<td>17</td>
<td>1923K</td>
<td>21.8</td>
<td>0.028</td>
<td>0.0114</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>18</td>
<td>1923K</td>
<td>20.0</td>
<td>0.0064</td>
<td>0.0228</td>
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</tr>
<tr>
<td>19</td>
<td>1923K</td>
<td>21.4</td>
<td>0.078</td>
<td>0.0116</td>
<td></td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Experimental Temperature</th>
<th>[mass% Cr]</th>
<th>[mass% Ni]</th>
<th>[mass% Ti]</th>
<th>[mass% O]</th>
<th>Distinguished equilibrium oxides by EBSD analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1873K</td>
<td>17.6</td>
<td>7.92</td>
<td>0.0028</td>
<td>0.0123</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>21</td>
<td>1873K</td>
<td>16.4</td>
<td>8.08</td>
<td>0.0049</td>
<td>0.0194</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1873K</td>
<td>19.0</td>
<td>10.48</td>
<td>0.0070</td>
<td>0.0169</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>1873K</td>
<td>19.7</td>
<td>9.81</td>
<td>0.0506</td>
<td>0.0079</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>1873K</td>
<td>19.6</td>
<td>9.76</td>
<td>0.0710</td>
<td>0.0064</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1873K</td>
<td>14.3</td>
<td>7.34</td>
<td>0.0766</td>
<td>0.0052</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1873K</td>
<td>17.5</td>
<td>12.58</td>
<td>0.0189</td>
<td>0.0054</td>
<td>Ti₃O₅ (Trigonal)</td>
</tr>
<tr>
<td>27</td>
<td>1873K</td>
<td>19.9</td>
<td>10.15</td>
<td>0.7850</td>
<td>0.0019</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>28</td>
<td>1873K</td>
<td>38.7</td>
<td>19.76</td>
<td>0.0049</td>
<td>0.0350</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>29</td>
<td>1873K</td>
<td>34.5</td>
<td>20.23</td>
<td>0.0074</td>
<td>0.0550</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>30</td>
<td>1873K</td>
<td>38.8</td>
<td>18.69</td>
<td>0.0573</td>
<td>0.0175</td>
<td>Ti₃O₅ (Trigonal)</td>
</tr>
<tr>
<td>31</td>
<td>1873K</td>
<td>38.9</td>
<td>19.39</td>
<td>0.2410</td>
<td>0.0112</td>
<td>Ti₃O₅ (Trigonal)</td>
</tr>
<tr>
<td>32</td>
<td>1873K</td>
<td>38.6</td>
<td>19.54</td>
<td>0.2750</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>1823K</td>
<td>19.4</td>
<td>10.14</td>
<td>0.0895</td>
<td>0.0019</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>34</td>
<td>1823K</td>
<td>16.2</td>
<td>8.39</td>
<td>0.0064</td>
<td>0.0103</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1823K</td>
<td>19.0</td>
<td>9.98</td>
<td>0.0681</td>
<td>0.0030</td>
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</tr>
<tr>
<td>36</td>
<td>1923K</td>
<td>16.8</td>
<td>8.36</td>
<td>0.0064</td>
<td>0.0150</td>
<td>Ti₃O₅ (Anovosite)</td>
</tr>
<tr>
<td>37</td>
<td>1923K</td>
<td>18.1</td>
<td>9.36</td>
<td>0.167</td>
<td>0.0137</td>
<td></td>
</tr>
</tbody>
</table>
The ‘Ti$_3$O$_5$’ 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 ‘Ti$_3$O$_5$’ 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 Ti$_3$O$_5$ was unity when the solubility of Fe and Cr oxides in ‘Ti$_3$O$_5$’ phase was lower than \[
\left( \frac{X_{Fe}}{X_{Ti}} \right)^{0.05}.
\]

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
formalism to multi-component alloy systems. Miki and Hino\textsuperscript{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 1 823 to 1 923 K.\textsuperscript{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.\textsuperscript{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, \textit{i.e.} Raoultian standard state. In case of oxygen, hypothetically dissolved oxygen in the melt equilibrating with 101 325 Pa (1 atm) oxygen gas had been selected as the standard state.\textsuperscript{12,13}

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

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

$$\text{Cr}_2\text{O}_3(s) = 2\text{Cr}(l) + 3\text{O}_2(g) \quad \text{(1)}$$

By choosing Cr standard state as pure liquid substance, Eq. (1) can be divided into Eqs. (2) and (3) as follows.

$$\text{Cr}_2\text{O}_3(s) = 2\text{Cr}(l) + \frac{3}{2}\text{O}_2(g) \quad \text{(2)}$$

$$\frac{3}{2}\text{O}_2(g) = 3\text{O} \quad \text{(3)}$$

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$_2$O$_3$ formation ($\Delta G^\circ_{\text{fus,Cr}_2\text{O}_3}$) and twice of the Gibbs free energy change of fusion of chromium (2$\Delta G^\circ_{\text{fus, Cr}}$). 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. (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,

$$\ln K_{\text{Cr}_2\text{O}_3} = - \frac{-\Delta G^\circ_{\text{fus,Cr}_2\text{O}_3} + 2\Delta G^\circ_{\text{fus, Cr}}}{RT}$$

$$= - \ln \alpha_{\text{Cr}_2\text{O}_3} + 2\ln \gamma_C + 3\ln \gamma_O + 2\ln X_{\text{Cr}} + 3\ln X_O$$

$$= 2\ln \gamma_C + 3\ln \gamma_O + 2\ln X_{\text{Cr}} + 3\ln X_O$$

$$= 1 \quad \text{(4)}$$

where, $\gamma_i$ and $X_i$ denote the Raoultian activity coefficient and mole fraction of component $i$, respectively. The activity of Cr$_2$O$_3$ in Eq. (1) was taken as unity, because the stable oxide was pure Cr$_2$O$_3$ at higher content of Cr than 6.7 mass\%. The Gibbs free energy change of Cr$_2$O$_3$ formation ($\Delta G^\circ_{\text{fus,Cr}_2\text{O}_3}$) and the Gibbs free energy change of fusion of chromium ($\Delta G^\circ_{\text{fus, Cr}}$) in Eq. (4) were taken from NIST-
The excess Gibbs free energy change of mixing for Fe–Cr–O system using Redlich–Kister type polynomial can be expressed as Eq. (5).

$$\Delta G_{ex} = X_{Fe} \phi_{Fe-Cr} + X_{Cr} \phi_{Cr-O} - X_{O} \phi_{O}$$

where, $\phi_{i,j}$ 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.

$$\Delta G_{ex}^{C_i} = RT \ln \gamma_i$$

$$\Delta G_{ex}^{O_j} = RT \ln \gamma_j$$

where, $\gamma_i$ and $\gamma_j$ are activity coefficients of element $i$ and $j$.

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).

$$X_{Fe} \phi_{Fe-Cr} (2 - 5X_Cr) + X_{Fe} \phi_{Fe-Cr}(X_{Fe} - 2X_Cr) + X_{Cr} \phi_{Cr-O}(X_{Fe} - X_Cr) + X_{Cr} \phi_{Cr-O}$$

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

$$\phi_{Fe-Cr} = -17737 + 799654673J$$

$$\phi_{Cr-O} = -1731 + 139573J$$

$$\phi_{O} = -688900 + 302873J$$

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.

The experimental results after Itoh et al.\(^{10}\) in the following. In order to deduce these parameters, Eq. (15) can be expressed by rearranging Eq. (8).

$$\gamma_{Cr} = \frac{1}{X_{Cr}(X_{Fe} - X_{Cr})}$$

Fig. 9 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.

$$\gamma_{Cr} = \frac{1}{X_{Cr}(X_{Fe} - X_{Cr})}$$

The experimental results after Itoh et al.\(^{10}\) in the following: In order to deduce these parameters, Eq. (15) can be expressed by rearranging Eq. (8).

$$\gamma_{Cr} = \frac{1}{X_{Cr}(X_{Fe} - X_{Cr})}$$

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).

$$X_{Fe} \phi_{Fe-Cr}(2 - 5X_Cr) + X_{Fe} \phi_{Fe-Cr}(X_{Fe} - 2X_Cr - 5X_{Fe}X_Cr + 5X_Cr^2) + X_{Cr} \phi_{Cr-O}(3 - 5X_O) + X_{Cr} \phi_{Cr-O}(3X_{Fe} - 6X_O - 10X_{Fe}X_O + 10X^2_O)$$

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

$$\phi_{Fe-Cr} = -17737 + 799654673J$$

$$\phi_{Cr-O} = -1731 + 139573J$$

$$\phi_{O} = -688900 + 302873J$$

Fig. 9. Equilibrium relation between [mass% Cr] and [mass% O] in molten Fe at 1823 to 1923 K with numerical analysis results by Redlich–Kister type polynomial by using binary interaction parameter of (a) literature values\(^{12}\) and (b) present research.
It is possible to determine both $^0\Omega_{\text{Cr}-\text{O}}$ and $^1\Omega_{\text{Cr}-\text{O}}$ 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, $^0\Omega_{\text{Cr}-\text{O}}$ in Eq. (15) was derived from interaction parameter reported by Itoh et al.\textsuperscript{10} They determined $e_{\text{Cr}}^0$ as Eq. (16) and $e_{\text{O}}^0$ could be derived using Eq. (17) as Eq. (18).

$$e_{\text{O}}^0 = -123/T + 0.034$$

(mass%Cr<46, $1823 \leq T \leq 1923$ K)................(16)

$$e_{\text{Cr}}^0 = 230 \frac{M_{\text{Cr}}}{M_{\text{Fe}}} e_{\text{Cr}}^0 + \frac{(M_{\text{Fe}} - M_{\text{Cr}})}{M_{\text{Fe}}}$$

(19)

Also, $e_{\text{Cr}}^0$ could be derived as follows from Eq. (6).

$$e_{\text{Cr}}^0 = \frac{\partial \ln \gamma_{\text{Cr}}}{\partial \alpha_{\text{O}}}$$

$$\frac{1}{RT} (0^{\text{Fe-Cr}}_2 - 2^1\Omega_{\text{Fe-Cr}} - 0^{\text{Fe-O}} - 2^1\Omega_{\text{Fe-O}}$$

$$+ 2^{0}\Omega_{\text{Cr-O}})$$

(20)

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

$$^{0}\Omega_{\text{Cr-O}} = -1230 - 24.107 J/mol$$

($X_{\text{Cr}} < 0.047$, $1823 \leq T \leq 1923$ K)..............(20)

After substituting Eqs. (9) to (12) and (18) and experimental results of Itoh et al.\textsuperscript{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.

$$^1\Omega_{\text{Cr-O}} = -498 200 + 234.77 T J/mol$$

($X_{\text{Cr}} < 0.0015$, $1823 \leq T \leq 1923$ K)..............(21)

The regressed line in Fig. 10 was determined according the flow chart shown in Fig. 8. Not only $^{0}\Omega_{\text{Cr-O}}$ but also $^{1}\Omega_{\text{Cr-O}}$, 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$_2$O$_3$ to TiO$_2$ 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, TiO$_2$ was deoxidation product and Ti deoxidation reaction can be expressed by Eq. (22).

$$\text{TiO}_2(s) = 2\text{Ti} + 3\text{O}$$

(22)
\[ \ln K_{\text{Ti,O}} = \frac{-\Delta G_{\text{Ti,O}}^0 + 3\Delta G_{\text{Fe,Ti}}^0}{RT} = -\ln \gamma_{\text{Ti}} + 2\ln \gamma_{\text{O}} + 2\ln X_{\text{Ti}} + 3\ln X_{\text{O}} = 2\ln \gamma_{\text{Ti}} + 3\ln \gamma_{\text{O}} + 2\ln X_{\text{Ti}} + 3\ln X_{\text{O}} \]

\[ (\cdot a_{\text{Ti,O}} = 1) \quad \cdots (27) \]

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

\[ \Delta G = k_{\text{Ti}} \frac{\partial \Delta G}{\partial X_{\text{Ti}}} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G}{\partial X_{\text{Ti}}} = -X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} = -X_{\text{O}} \frac{\partial \Delta G}{\partial X_{\text{O}}} \]

where, \( \Delta G_{\text{Fe,Ti}}^0 \) and \( \Delta G_{\text{Fe,Ti}}^0 \) 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.

\[ \Delta G_{\text{Ti,O}}^0 = RT \ln \gamma_{\text{Ti}} \]

\[ \Delta G_{\text{Fe,Ti}}^0 = RT \ln \gamma_{\text{Fe}} \]

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.

\[ -8X_{\text{Fe}}X_{\text{Cr}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} = -16X_{\text{Fe}}X_{\text{Cr}} \frac{\partial \Delta G}{\partial X_{\text{Cr}}} + X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} \]

\[ +X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} + (3 - 8X_{\text{Fe}}) + X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} + 3X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} = -16X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} + 16X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} + 16X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} \]

\[ +X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} + (3 - 8X_{\text{Fe}}) + X_{\text{Fe}} \frac{\partial \Delta G}{\partial X_{\text{Fe}}} + 3X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} + 16X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} + 16X_{\text{Fe}}X_{\text{Cr}}X_{\text{Ti}}X_{\text{O}} \]

Binary interaction parameter of Eqs. (9) to (12), \( \Omega_{\text{Fe,Ti}} \), \( \Omega_{\text{Fe,O}} \), and \( \Omega_{\text{Cr,O}} \) in the present research were utilized for Eqs. (33) and (34). Unknown parameters \( \Omega_{\text{Cr,Ti}} \) and \( \Omega_{\text{Ti,O}} \) 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.
The regressed line in Fig. 11 was determined according to the flow chart in Fig. 8. As explained before, both \( \Omega_{\text{Fe-O}} \) and \( \Omega_{\text{Cr-Ti}} \) were simultaneously determined and the line may not totally agree with the plots in Fig. 11.

The estimated equilibrium relation between Ti and O concentration in Fe–Cr alloys at 1 823 to 1 923 K is shown in Figs. 2 and 3 based on Redlich-Kister type polynomial parameters. The calculated result agrees well with experimental results in the whole composition region of the alloy.

Final objective of the present research is to evaluate Ti deoxidation equilibria in Fe–Cr–Ni–Ti alloy and to verify the application range of binary interaction parameters of Redlich–Kister type polynomial of Ni–Ti\(^{19}\) and Cr–Ti. Estimated equilibrium relation between Ti and O in Fe–Cr–Ni alloy expressed by using Redlich–Kister type polynomial was compared with titanium deoxidation experimental results.

In order to predict the properties of matrix made by Fe–Cr–Ni, interaction parameter of Redlich–Kister type polynomial among Fe, Cr and Ni, \( \Omega_{\text{Fe-Cr-Ni}} \) should be considered. The details are given by Hillert\(^{19}\) and the excess free energy change of mixing in Fe–Cr–Ni–Ti–O system using Redlich–Kister type polynomial can be expressed as Eq. (37).

\[
\Delta G_{\text{ex}} = X_{\text{Fe}} \gamma_{\text{Fe}} \left( \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Fe}}} \right) + X_{\text{Cr}} \gamma_{\text{Cr}} \left( \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Cr}}} \right) + X_{\text{Ni}} \gamma_{\text{Ni}} \left( \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Ni}}} \right) + X_{\text{O}} \gamma_{\text{O}} \left( \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{O}}} \right) + X_{\text{Ti}} \gamma_{\text{Ti}} \left( \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Ti}}} \right)
\]

The partial molar excess free energy change of Ti and O in Fe–Cr–Ni alloy can be derived as Eqs. (38) and (39), respectively.

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

\[
\Delta G_{\text{O}}^{\text{ex}} = \Delta G_{\text{ex}} - X_{\text{Fe}} \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Fe}}} - X_{\text{Cr}} \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Cr}}} - X_{\text{Ni}} \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{Ni}}} - X_{\text{O}} \frac{\partial \Delta G_{\text{ex}}}{\partial x_{\text{O}}}
\]

The partial molar excess free energy change of Ti and O in Fe–Cr–Ni–Ti–O system, Eqs. (40) and (41) can be deduced by substituting the partial molar excess free energy change of titanium and oxygen of Eq. (38) and (39) into Eqs. (25) and (27), respectively.
+X_{Fe}^{-1}\Omega_{Fe-O}(5X_{Fe}-10X_{Cr}-16X_{Fe}X_{O}+16X_{O}^{2})
-8X_{Cr}X_{Ni}\Omega_{Cr-Ni}(16X_{Cr}X_{Ni}-X_{Cr}X_{Ni})
+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(3-5X_{Ni})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}(3-8X_{Ni}+X_{Ni}X_{Cr}-3X_{Ni}-6X_{Cr})
-16X_{Cr}X_{Ni}+16X_{Ni}^{5}+X_{Cr}X_{Ni}\Omega_{Cr-Ni}(5-8X_{Ni})
+X_{Cr}X_{Ni}\Omega_{O}(5X_{Cr}-10X_{Cr}X_{Ni}+16X_{O}^{2})
+X_{Ni}X_{Cr}\Omega_{Ni-Cr}