1. Introduction

Control of oxygen content in liquid iron is very important not only to remove impurities such as phosphorus and sulfur but also to improve the yield of valuable alloying elements such as Ti in steelmaking process. Ti is widely used as a strong deoxidizer due to its high affinity for oxygen. The most important thermodynamic information is the equilibrium relation between dissolved Ti and O in steel melt for the precise control of Ti in the steelmaking process. Fine titanium oxide can also be used to control for grain refinement with its dispersion in austenite grain. 1) Due to such importance, huge number of studies 2–26) concerning the Ti and O equilibrium relation have been reported, where the Ti content in liquid iron has been up to 30 mass%.

There is huge scatter on Ti deoxidation equilibrium constants and interaction parameters in the literatures. Figure 1 shows the available literature values of the relation between Ti and O dissolved in liquid Fe–Ti alloy in the vicinity of 1 873 K.2,4,6,7,10,12,15,19,22) Substances in the parenthesis show the chemical kinds of crucible used. The main reason of such scatter among the previous works is due to the ambiguity of identification for titanium oxides in equilibrium with liquid Fe–Ti alloy. Each equilibrium titanium oxide phase would change with Ti content in liquid Fe–Ti alloy.

Solid line in Fig. 1 denotes the recommended value at 1 873 K by the 19th Committee on Steelmaking, the Japan Society for the Promotion of Science (JSPS). 24) The JSPS recommended value 24) for the Fe–Ti–O system does not cover a wide concentration range of titanium because of experimental difficulties, and it is based on the experimental result by Suzuki and Sanbongi. 19) They measured the equi-
librium between Ti and O in the range of 0.01–0.25 mass% Ti of Fe–Ti melt in a TiO$_x$ (0 < $x$ < 1) crucible. They found that the deoxidation product was ‘Ti$_3$O$_5$’ with small amount of iron, which depended on Ti content in liquid Fe–Ti alloy. Most of other researchers $^{2-26}$ conducted their experiments using a MgO, Al$_2$O$_3$ or CaO crucible, and they evaluated their results on the assumption of unit activity of titanium oxides. However, it is known that Al$_2$O$_3$ reacts with TiO$_2$ to form the intermediate compound Al$_2$O$_3$ · TiO$_2$ as reported by Lang $^{27}$ et al. Al$_2$O$_3$ and Ti$_2$O$_3$ form a solid solution as reported by Belon and Forestier. $^{28}$ MgO reacts with TiO$_2$ to form the intermediate compound MgO · TiO$_2$, MgO · 2TiO$_2$ and 2MgO · TiO$_2$ as reported by Woermann et al. $^{29}$ Also, CaO reacts with TiO$_2$ to form the intermediate compound CaO · TiO$_2$, 5CaO · 4TiO$_2$ and 3CaO · 2TiO$_2$ as reported by Tulgar. $^{30}$ These facts indicate that the activity of each titanium oxide in equilibrium with molten Fe–Ti alloy is not always unity on their experimental conditions. More reliable thermodynamic information on Ti–O equilibria in liquid Fe is, therefore, necessary for the precise control of Ti in steelmaking process.

In the previous work $^{31}$, ‘Ti$_3$O$_5$’ crucibles were equilibrated with the molten Fe–Ti alloy of various Ti contents at 1 873 K. Different titanium oxide phases were formed at the interface between Fe–Ti alloy and ‘Ti$_3$O$_5$’ crucibles depending on Ti contents. The equilibrium titanium oxide phases were clearly identified by the automated indexing of electron backscatter diffraction (EBSD) pattern analysis. Therefore, the measurements of equilibrium relation between Ti and O in the molten iron were carried out over the Ti concentration range from 0.01 to 16.6 mass% with various kinds of titanium oxide at 1 873 K in the present study. The measured equilibrium relation between Ti and O in the molten Fe–Ti alloy was thermodynamically analyzed based on Wagner’s formalism and Darken’s quadratic formalism $^{32,34}$ with Redlich–Kister type polynomial $^{35,36}$.

2. Experimental

Experimental equipment and procedure are essentially the same as the previous work. $^{31}$ ‘Ti$_3$O$_5$’ crucibles were manufactured by ourselves from ‘Ti$_3$O$_5$’ powder. ‘Ti$_3$O$_5$’ powder was produced by H$_2$ reduction of TiO$_2$ (99.8% purity) powder at 1 773 K for 12 h. ‘Ti$_3$O$_5$’ powder was formed in a crucible shape by rubber press and sintered at 1 823 K for 12 h under Ar/H$_2$ atmosphere. A ‘Ti$_3$O$_5$’ crucible (outer diameter: 28 mm, inner diameter: 22 mm, height: 65 mm) charged with approximately 50 g of Fe–Ti alloy was set in an Al$_2$O$_3$ outer crucible in an induction furnace, and the melt was charged with Ar/H$_2$ stream of 100 ml/min. The Fe–Ti alloy specimen was prepared by melting an appropriate amount of Ti and Fe and held for 60 min at 1 873 K. Temperature measurement was conducted by an infrared radiation pyrometer, which was calibrated by the melting points of Fe and Cu. The melt and crucible were quenched after reaching equilibrium by switch-off and blowing He gas in the reaction chamber.

The concentration of O in the cut off from quenched samples was determined by an inert gas impulse infrared absorption spectroscopy. The surface of samples was polished with SiC wet polishing papers (up to #1500-grit) and then electrically polished by the solution of acetic acid (CH$_3$COOH) and perchloric acid (HClO$_4$) for 6 min with constant current of 0.5 A. All the formed oxide phases at the interface between melts and ‘Ti$_3$O$_5$’ crucibles were analyzed by EBSD pattern analysis technique to identify the equilibrium titanium oxide phases. Solid solubility of Fe oxide in ‘Ti$_3$O$_5$’ phase was analyzed quantitatively by EDS.

3. Experimental Results

Experimental results are listed in Table 1. The previous $^{31}$ observed relation between Ti and O concentrations at 1 873 K is reproduce in Fig. 2 with other researcher’s works $^{2,4,6,7,10,12,15,19,22}$ The present results corresponded to those of Suzuki and Sanbongi $^{19}$ who used a TiO$_x$ (0 < $x$ < 1) crucible and Janke and Fischer $^{22}$ who used a TiO$_2$ crucible. The equilibrium lines of thermodynamic analyzed re-
The results of line analysis and EDS image of ‘Ti₃O₅’ crucible interface melted Fe–0.0026 mass% Ti are presented in Fig. 3. The trace of Fe at ‘Ti₃O₅’ crucible interface was observed when Ti content was less than 0.36 mass% in molten Fe as shown in Fig. 4. Suzuki and Sanbongi \(^{19}\) pointed out the solid solubility of Fe in ‘Ti₃O₅’ phase when Ti content was less than 0.25 mass% in molten Fe. Iwamoto et al. \(^{37}\) found the solid solution of ‘Ti₃O₅’ and ‘FeO · 2TiO₂’ equilibrated with very low Ti concentration of Fe–Ti alloy.

### Table 1

| [mass% Ti] | [mass% O] | Equilibrium oxide by EBSD analysis
|------------|-----------|----------------------------------|
| A-1        | 0.0004    | ‘Ti₃O₅’                          |
| A-2        | 0.0005    | ‘Ti₃O₅’                          |
| A-3        | 0.0005    | ‘Ti₃O₅’                          |
| A-4        | 0.0007    | ‘Ti₃O₅’                          |
| A-5        | 0.0009    | ‘Ti₃O₅’                          |
| A-6        | 0.0018    | ‘Ti₃O₅’                          |
| A-7        | 0.0026    | ‘Ti₃O₅’                          |
| A-8        | 0.0026    | ‘Ti₃O₅’                          |
| A-9        | 0.006     | ‘Ti₃O₅’                          |
| A-10       | 0.034     | ‘Ti₃O₅’                          |
| A-11       | 0.36      | ‘Ti₃O₅’                          |
| B-1        | 0.50      | TiO₂                             |
| B-2        | 0.87      | TiO₂                             |
| B-3        | 1.97      | TiO₂                             |
| B-4        | 2.17      | TiO₂                             |
| B-5        | 4.28      | TiO₂                             |
| B-6        | 6.22      | TiO₂                             |
| C-1        | 10.64     | TiO’                             |
| C-2        | 14.13     | TiO’                             |
| C-3        | 16.63     | TiO’                             |

**Fig. 2.** Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe–Ti alloy at 1873 K with the various crucibles results.\(^2\)\(^{–}\)\(^{22}\)

**Fig. 3.** Line analysis and EDS image of Fe and Ti in the cross section of ‘Ti₃O₅’ crucible melted liquid Fe–0.0026 mass% Ti at 1873 K.

**Fig. 4.** Solid solubility of Fe oxide in ‘Ti₃O₅’ phase at 1873 K.
This means that the activity of ‘Ti₂O₅’ equilibrated with molten Fe (Ti:<0.36 mass%) is less than unity based on the present experimental results. Suzuki and Sanbogii also found that the solid solubility of Fe in ‘Ti₂O₅’ phase was negligibly small (<1.2 mass%) when Ti content was between 0.013~0.25 mass%.

Thermodynamical evaluation was carried out using the experimental results of A-9 to A-11 in Table 1, where the solid solubility of Fe iron in ‘Ti₂O₅’ phase was negligibly small as shown in the Fig. 4. Unit activity of ‘Ti₂O₅’ was assumed where the Fe/Ti ratio was less than 0.05 in these cases.

The results of line analysis and EDS image of Ti₂O₃ phase are presented in Fig. 5 at the interface between ‘Ti₂O₅’ crucible and Fe–0.5mass%Ti. No trace of Fe and other elements were detected by EDS analysis at the metal/crucible interface after the experiments. The same results also were observed for ‘TiO’ phase.

When ‘Ti₃O₇’ crucible was equilibrated with 0.5–6.2 mass% Ti, ‘Ti₃O₅’ reacted with Ti in Fe melts and then equilibrium phase was changed from ‘Ti₃O₅’ to Ti₂O₃. Therefore, ‘Ti₃O₅’ crucible could be used in order to fix the activity of Ti₂O₃ as unity when Ti content (0.5–6.2 mass%) in liquid Fe.

4. Discussion

Ti deoxidation results using other oxide crucibles such as MgO, Al₂O₃ had the possibility that the titanium oxide activity was not unity. The crucible materials reacted with titanium oxides and formed the intermediate compound or solid solution at the interface of crucibles. Therefore, only the present experimental results and those using titanium oxide crucibles⁴,¹⁵,¹⁹,²² were used for the thermodynamic consideration as shown in Fig. 2.

The calculation was carried out based on Wagner’s formalism³² and Darken’s quadratic formalism³³,³⁴ combined with Redlich–Kister type polynomial.³⁵,³⁶ and the two formalisms were compared and discussed.

It is widely known that ‘TiO’ has relatively wide solid solution at 1873 K as shown in Fig. 6. Thus, ‘TiO’ can not be assumed as a line-compound.

4.1. Thermodynamical Analysis by Wagner’s Formalism

4.1.1. Thermodynamical Basis for Ti Deoxidation of Molten Fe

The chemical reaction between Ti and O in liquid iron and its equilibrium constant are given by Eqs. (1) and (2) under the presence of solid Ti₂O₅.

\[
\text{Ti}_x\text{O}_y(s) = x\text{Ti} + y\text{O} \quad \text{...............(1)}
\]

\[
K = (h^{\text{Ti}}_i, h^{\text{O}}_i)/a_{\text{Ti},(\text{i},\text{g})} = f^{\text{Ti}}_i[f^{\text{O}}_i]^{f^{\text{O}}_i}/a_{\text{Ti},(\text{i},\text{g})} \quad \text{...............(2)}
\]

Where, \( K \), \( a \), \( f \) and [\%] denote the equilibrium constant, the Raoultian activity, the Henrian activity, the Henrian activity coefficient and concentration of \( i \) in liquid iron (mass%), respectively. The standard states of \( h_\text{Ti} \) and \( h_\text{O} \) in Eq. (2) are infinite dilute solutions for Ti and O in liquid iron. Taking the logarithm of both sides and rearrangement of Eq. (2) gives Eq. (3).

\[
\log K = x(\log f_i) + y(\log f_i) + x(\log [\%\text{Ti}])
\]

\[
+ y(\log [\%\text{O}]) - \log a_{\text{Ti},(\text{i},\text{g})} \quad \text{...............(3)}
\]
Each activity coefficient in Eq. (3) can be expressed by Eqs. (4) and (5).

\[
\log f_i = e_{i1}^O [\%O] + e_{iTi}^O [\%Ti] + r_{i11}^O [\%O]^2 + r_{iTi}^O [\%Ti]^2 + r_{iTiO}^O [\%O][\%Ti]
\]

\[
\log f_0 = e_0^{Ti}[\%Ti] + e_0^{O}[\%O] + r_{01}^{Ti}[\%Ti]^2 + r_{0O}^O [\%O]^2 + r_{0TiO}^O [\%Ti][\%O]
\]

Where, \(e_i^O\), \(e_{ij}^O\) and \(r_{ij}^O\) denote the first order, second order interaction parameters between \(i\) and \(j\) and cross product term, respectively. It was assumed that second order parameter and cross product term could be ignored in the present work and \(a_{Ti,O}(s)\) was unity because \(Ti_2O_3\) is considered as pure solid. The recommended values of the Japan Society for the Promotion of Science (JSPS)\(^{24}\) were adopted as \(e_{iTi}^O\) and \(e_0^O\), which were given by Eqs. (6) and (7).

\[
e_{iTi}^O = 0.041 \quad \text{..........................(6)}
\]

\[
e_0^O = -1750/T + 0.76 \quad \text{..........................(7)}
\]

The relation between \(e_{iTi}^O\) and \(e_0^O\) is thermodynamically derived by Eq. (8).\(^{39}\)

\[
e_{iTi}^O = 2.993e_0^O - 0.00865 \quad \text{..........................(8)}
\]

Equations (9) and (10) can be derived from combining Eqs. (3) to (8) if the second order interaction parameter \(r_{0TiO}^O\) was ignored as a first approximation.

\[
2e_{iTi}^O[\%Ti]+3e_0^O[\%O]+2\log[\%Ti]+3\log[\%O]-0.0173[\%O] = e_0^O(-3[\%Ti]-5.985[\%O]) + \log K_{Ti_2O_3} \quad \text{..........................(9)}
\]

\[
3e_{iTi}^O[\%Ti]+5e_0^O[\%O]+3\log[\%Ti]+5\log[\%O]-0.026[\%O] = e_0^O(-5[\%Ti]-8.978[\%O]) + \log K_{Ti_2O_3} \quad \text{..........................(10)}
\]

4.1.2. Determination of \(\log K\) and \(e_{iTi}^O\)

The left hand sides of Eqs. (9) and (10) are plotted as vertical axis \(Y\), and the term of \((-3[\%Ti]-5.985[\%O])\) and \((-5[\%Ti]-8.978[\%O])\) are taken as horizontal axis in Fig. 7 on the \(Ti_2O_3\) and ‘\(Ti_3O_5\)’ saturated conditions, respectively. Thermodynamical evaluation was carried out using only the previous experimental results\(^{11}\) of B-1 to B-6 for \(Ti_2O_3\) and A-9 to A-11 for ‘\(Ti_3O_5\)’ in Table 1. Good linear relation was observed for each titanium oxide. It means that Eqs. (9) and (10) can well express the equilibrium relation between \(Ti\) and \(O\) up to 6.5 mass\(\%\) of Ti in molten Fe at ‘\(Ti_2O_3\)’ and ‘\(Ti_3O_5\)’ saturation and the second order interaction parameters such as \(r_{0TiO}^O\) can be omitted.

The interaction between Ti and O is the same as in the region where Ti and O contents are not so large. However, the Ti deoxidation equilibrium constant is different for each kind of Ti deoxidation product. Regression analysis to a straight line in Fig. 7 gave the Ti deoxidation equilibrium constant \(\log K\) and the interaction parameter \(e_0^O\) from the intercept at the \(Y\) axis and the slope based on the present experimental data and the others using Ti oxide crushive.\(^{4,15,19,22}\) The obtained first order interaction, \(e_{iTi}^O\) parameter was –0.34 in 1 873 K, and the Ti deoxidation equilibrium constants were –10.17 for \(Ti_2O_3\) and –16.86 for ‘\(Ti_3O_5\)’, respectively.

The interaction parameters determined in the present study are compared with previous results\(^3 - 24\) in Table 2. The present interaction parameter, –0.34, and deoxidation equilibrium constant of ‘\(Ti_3O_5\)’, –16.86, are in good agreement with that of Suzuki and Sanbongi.\(^{19}\) However, they did not determine the Ti deoxidation equilibrium constant of \(Ti_2O_3\). The present Ti deoxidation equilibrium constant of \(Ti_2O_3\), –10.17, is in good agreement with the values of –10.43 obtained by Janke and Fischer\(^{22}\) and –10.39 obtained by Bůžek\(^{41}\) at 1 873 K.

The estimated relation between equilibrium \(Ti\) and \(O\) content in molten Fe based on Wagner’s formalism\(^{22}\) are shown in Fig. 2 with the experimental results. This equilibrium line was drawn using the estimated values in the present work. The results by Darken’s formalism\(^{33,34}\) with Redlich–Kister\(^{35,36}\) type polynomial is also shown in this figure. This is discussing later.

4.1.3. Determination of \(r_{0TiO}^O\)

Activity coefficient \(r_{0TiO}^O\) is evaluated from the derived Ti deoxidation equilibrium constant \(\log K\). Ti deoxidation
equilibrium constant $-10.17$ on TiO$_3$ gives $\Delta G^\circ_{1873K}$ as the Eq. (12) at 1 873 K.

$\text{Ti}_2\text{O}_3(s) = 2\text{Ti}(l) + 3\text{O}_2(g)$..........................(11)

$\Delta G^\circ_{1873K} = -RT \ln K = 364 670/J$ (1 873 K).........(12)

The Gibbs free energy of TiO$_3$ formation and the free energy of oxygen dissolution in molten Fe are shown by the Eqs. (13) and (14) at 1 873 K after the NIST-JANAF Thermochemical Tables$^{40)$ and JSPS recommended values.$^{24)$

$2\text{Ti}(l) + 3/2 \text{O}_2(g) = \text{Ti}_2\text{O}_3(s)$, $\Delta G^\circ_{1873K} = -1 020 330/J$ (at 1 873 K).........(13)

$1/2 \text{O}_2(g) = \text{O}_{1\text{mass} \%}$

$\Delta G^\circ_{1873K} = -123 460/J$ (at 1 873 K).........(14)

Equation (15) is obtained by combining the Eq. (11) with the Eqs. (13) and (14).

Ti(l)=$\text{Ti}_{1\text{mass} \%}$  $\Delta G^\circ_{1873K} = -142 640/J$ (at 1 873 K) ... (15)

Free energy of Ti dissolution is shown by the following Eq. (16).

$\Delta G^\circ_{1873K} = RT \ln \left( \frac{\gamma_{\text{Ti}} \times M_{\text{Fe}}}{100 \times M_{\text{Ti}}} \right)$ ......................(16)

Where, $M_{\text{Fe}}$ and $M_{\text{Ti}}$ denote the molecular weight of Fe and Ti. The activity coefficient $\gamma_{\text{Ti}}$ can, therefore, be calculated as 0.0090 at 1 873 K by substituting $\Delta G^\circ_{1873K}$ of the Eq. (15) into the Eq. (16).

$\exp \left( \frac{\Delta G^\circ_{1873K}}{RT} \right) \times \frac{100}{M_{\text{Ti}}} = \frac{\gamma_{\text{Ti}}}{M_{\text{Fe}}} = 0.0090$ ......(17)

The deoxidation equilibrium constant corresponded to ‘TiO$_3$’ was used for the same calculation, and the same value of 0.0090 was obtained at 1 873 K as $\gamma_{\text{Ti}}$. Suzuki and Sanbongi$^{19)$ estimated the activity coefficient of Ti using their experimental results. However, their estimated value was changed with titanium concentration. $\gamma_{\text{Ti}}$ determined in the present work is compared with previous results$^{3–26)$ in Table 3. Previous values vary more than one order from 0.004 to 0.050, most of them are about one order larger than ours. However, the value of 0.0090 is in good agreement with the values of 0.011 obtained by Chipman$^5)$ and 0.0071 obtained by Suzuki et al.$^7)$ at 1 873 K.

### 4.2. Thermodynamic Analysis by Quadratic Formalism with Redlich–Kister Type Polynomial$^{41–43)$

The equation by Wagner$^{32)$ has been widely used to express the activity coefficients of solutes in multi-component solutions. However, the second order or higher terms must be added to represent the activity coefficients when solute contents are rich. Darken$^{33,34)$ has proposed the quadratic formalism to express the activity coefficients that can be applied to higher solute content. The activity coefficients of solvent 1 and solute 2, 3 are expressed for ternary solution by the following equations.

$\ln \gamma_i = \alpha_{i1} X_1^2 + \alpha_{i2} X_2^2 + (\alpha_{i1} + \alpha_{i3} - \alpha_{i2}) X_1 X_3$ ......(18)
\[
\ln \gamma_2 = \ln \gamma_2^0 - 2\alpha_{12}X_2^0 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_1X_3
\\]
\[
+ \alpha_{12}^2X_1^2 + \alpha_{13}X_1^0 + (\alpha_{13} + \alpha_{23} - \alpha_{12})X_2X_3....(19)
\]
\[
\ln \gamma_3 = \ln \gamma_3^0 - 2\alpha_{12}X_3^0 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_1X_3
\\]
\[
+ \alpha_{12}^2X_1^2 + \alpha_{13}X_1^0 + (\alpha_{13} + \alpha_{23} - \alpha_{12})X_2X_3....(20)
\]

Where \( X_r, \gamma_r, \gamma_r^0, \alpha_q \) denote mole fraction of component \( i \), the activity coefficient of component \( i \), the Henry constant, interaction between \( i \) and \( j \) in their binary solution at constant temperature and pressure, respectively. The following relations are obtained \(^{31-43} \text{by comparing the equations by Wagner}^{33} \text{with Eq. (19).}
\]
\[
\varepsilon_i^0 = -2\alpha_{12} \ldots(21)
\]
\[
\varepsilon_j^0 = \alpha_{23} - \alpha_{12} - \alpha_{13} \ldots(22)
\]
\[
\rho_2^0 = \alpha_{12} \ldots(23)
\]
\[
\rho_1^0 = \alpha_{13} \ldots(24)
\]
\[
\rho_{23}^{(2,3)} = \alpha_{12} + \alpha_{13} - \alpha_{23} \ldots(25)
\]

Where \( \varepsilon_i^0 \) and \( \rho_i^0 \) are the first and the second order interaction coefficients between \( i \) and \( j \), respectively.

Quadradic formalism was converted into Redlich–Kister type polynomial \(^{35,36} \text{using the excess Gibbs free energy change of mixing. This conversion was done by Miki and Hino}^{41-43} \text{because it was useful to expand Darken’s quadradic formalism to multi-component alloy systems. The excess Gibbs free energy change of mixing for 1–2 binary system is expressed as Eq. (26) by Redlich–Kister type polynomial.}^{35,36}\n\]
\[
\Delta G^{ex}_{\infty} = X_1X_2[\rho_{12}^0 + 3\rho_{12}1][X_1 - X_2] \ldots(26)
\]

The following equations are obtained in the infinite dilute solution of component 2.\(^{41-43}\n\]
\[
RT \ln \gamma_2^0 = \rho_{12}^0 + 3\rho_{12}1 \ldots(27)
\]
\[
RT \alpha_{12} = \rho_{12}^0 + 3\rho_{12}1 \ldots(28)
\]

The binary interaction parameters can be obtained by combining Eqs. (27) and (28) as follows.\(^{41-43}\n\]
\[
\rho_{12}^0 = \frac{\rho_{12}1}{RT} \left( \frac{3}{2} \ln \gamma_2^0 - \frac{1}{2} \alpha_{12} \right) \ldots(29)
\]
\[
\rho_{12}1 = \frac{\alpha_{12}}{RT} \left( -\frac{1}{2} \ln \gamma_2^0 + \frac{1}{2} \alpha_{12} \right) \ldots(30)
\]

Quadradic formalism can be converted into Redlich–Kister type polynomial using \( \rho_{12}^0 \) and \( \rho_{12}1 \) for dilute solution with Eqs. (29) and (30).\(^{41-43}\n
Pure substance is chosen as a standard state (Raoultian standard state) for condensed phases in the present work. On the other hand, dissolved oxygen in the melt equilibrating with 1013.25 Pa (1 atm) oxygen gas is selected as a standard state in the present work.\(^{41-43}\n
The relation between the oxygen activity and oxygen partial pressure can be expressed as follows in this standard state.
\[
a_o = P_0^{1,2} \ldots(31)
\]

4.2.1. Thermodynamic Analysis on Ti Deoxidation

Ti deoxidation reaction is expressed by Eq. (32).
\[
\text{Ti}_2\text{O}_3(s) = x\text{Ti}(l) + y\text{O}_2(g) \ldots(32)
\]

This equation is separated into the following two equations.
\[
\text{Ti}_2\text{O}_3(s) = x\text{Ti}(l) + y/2 \text{O}_2(g) \ldots(33)
\]
\[
y\Omega = y/2 \text{O}_2(g) \ldots(34)
\]

The Gibbs free energy change of Eq. (33) is identical to the Gibbs free energy of Ti\text{O}_3 formation (\( \Delta G^0_{\text{Ti,O}} \)) and that of Eq. (34) is zero due to the relation of Eq. (31). Therefore, the Gibbs free energy change of Eq. (32) is identical to the minus value of Ti\text{O}_3 formation free energy (\( \Delta G^0_{\text{Ti,O}} \)), which is utilized for Ti deoxidation of any kinds of metal or alloy, and this has a great advantage. The equilibrium constant of Eq. (32), \( K_{\text{eq}} \), can be expressed as follows.
\[
\ln K_{\text{eq}} = - \frac{\Delta G^0_{\text{Ti,O}}}{RT}
\]
\[
= x \ln \gamma_2 + y \ln \gamma_0 + x \ln X_2 + y \ln X_0 - \ln K_{\text{Ti,O}} \ldots(35)
\]
\[
\text{Where, the activity of Ti}_2\text{O}_3 \text{is taken as unity in the present work.}
\]

The excess free energy change of mixing in Fe–Ti–O ternary system is expressed as Eq. (36) using Redlich–Kister type polynomial \(^{35,36} \) where \( \Omega_{\text{Ti,O}} \) term was neglected.
\[
\Delta G^{ex}_{\infty} = X_1X_2[\rho_{12}^0 + 3\rho_{12}1][X_1 - X_2] + X_1X_0[\rho_{12}^0 + 3\rho_{12}1][X_1 - X_2] + X_2X_0 \rho_{12}^0 \Omega_{\text{Ti,O}} \ldots(36)
\]

The partial molar extra free energy changes of Ti and O are derived as follows.
\[
\Delta G_{\text{Ti}}^{ex} = RT \ln \gamma_2 = \Delta G^{ex} - (1 - X_1) \frac{\partial \Delta G^{ex}}{\partial X_1} \frac{\partial \Delta G^{ex}}{\partial X_0} - X_0 \frac{\partial \Delta G^{ex}}{\partial X_0} \ldots(37)
\]
\[
\Delta G_{\text{O}}^{ex} = RT \ln \gamma_0 = \Delta G^{ex} - X_0 \frac{\partial \Delta G^{ex}}{\partial X_1} \frac{\partial \Delta G^{ex}}{\partial X_0} - (1 - X_0) \frac{\partial \Delta G^{ex}}{\partial X_0} \ldots(38)
\]

The following equation can be obtained from Eq. (35) for
\[
\alpha_{12} = P_0^{1,2} \ldots(31)
\]
\[ \Delta G_{\text{Fe}-\text{Ti}_2\text{O}_3}^{\circ} = -2RT \ln \gamma_{\text{Fe}} - 3RT \ln \gamma_{\text{O}} - 2RT \ln x_{\text{Fe}} - 3RT \ln x_{\text{O}} \]

Equation (39)

Equation (40) is obtained by substituting Eqs. (37) and (38) into Eq. (39).

\[ 0 \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} X_{\text{Fe}} (-2 + 5X_{\text{Ti}}) + 2 \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} X_{\text{Fe}} (-3 + 5X_{\text{Ti}}) + \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} (-3X_{\text{Fe}} + 6X_{\text{O}} + 10X_{\text{Fe}}X_{\text{Ti}} - 5X_{\text{O}}^2) + \Omega_{\text{Ti}-\text{O}} (-3X_{\text{Fe}} - 2X_{\text{O}} + 5X_{\text{Fe}}X_{\text{O}}) + RT (-2 \ln X_{\text{Fe}} - 3 \ln X_{\text{O}}) - \Delta G_{\text{Fe}-\text{Ti}_2\text{O}_3}^{\circ} = 0 \]

Equation (40)

Equations (40) and (42) are the fundamental equation for thermochemical analysis of Ti deoxidation in molten Fe. The binary interaction parameters, \( \Omega_{\text{Fe}-\text{O}} \) and \( \Omega_{\text{Ti}-\text{O}} \), were obtained from the Gibb free energy change of oxygen dissolution into molten Fe and the self-interaction coefficient of oxygen in molten Fe.\(^{43}\) The Gibbs free energy of TiO\(_2\) formation has been adopted from NIST-JANAF Thermochemical Tables.\(^{40}\) Redlich–Kister type parameter of \( \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} \) was estimated from the activity coefficient of \( \gamma_{\text{Ti}_2\text{O}_3} \) as described in the Sec. 4.1.3 assumed that \( \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} \) was negligible at 1873 K.

The parameters referred in the present work are shown below.

\[ 0 \Omega_{\text{Fe}-\text{O}} = -415400 + 142.47T / \text{J} \quad (1823–1973 \text{ K})^{43} \]

\[ 1 \Omega_{\text{Fe}-\text{O}} = 298300 - 117.87T / \text{J} \quad (1823–1973 \text{ K})^{43} \]

\[ 0 \Omega_{\text{Fe}-\text{Ti}} = -73360 \text{ J} \quad \text{at} \ 1873 \text{ K} \]

\[ \Delta G_{\text{Fe}-\text{Ti}_2\text{O}_3}^{\circ} = -1520750 + 267.2T / \text{J} \quad (1750–1950 \text{ K}) \]

\[ \Delta G_{\text{Fe}-\text{O}}^{\circ} = -2464580 + 434.9T / \text{J} \quad (1750–1950 \text{ K}) \]

\[ \Delta G_{\text{Ni}-\text{O}}^{\circ} = -1035900 \text{ J} \quad \text{at} \ 1873 \text{ K} \]

Equations (48), (49) are obtained by rearranging Eqs. (40), (42).

For Ti\(_2\)O\(_3\),

\[ Y_{\text{Ti}_2\text{O}_3}^{\circ} = -0 \Omega_{\text{Fe}-\text{O}} X_{\text{Fe}} (-5 + 8X_{\text{Ti}}) + \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} (-3X_{\text{Fe}} + 6X_{\text{O}} + 10X_{\text{Fe}}X_{\text{O}} - 16X_{\text{Ti}}^2) + \Omega_{\text{Fe}-\text{Ti}_2\text{O}_3} (-3X_{\text{Fe}} + 10X_{\text{O}} + 16X_{\text{Fe}}X_{\text{Ti}} - 16X_{\text{O}}^2) + \Omega_{\text{Ti}-\text{O}} (-5X_{\text{Fe}} - 2X_{\text{O}} + 5X_{\text{Fe}}X_{\text{O}}) + RT (-3 \ln X_{\text{Fe}} - 5 \ln X_{\text{O}}) - \Delta G_{\text{Fe}-\text{Ti}_2\text{O}_3}^{\circ} = 0 \]

Equation (49)

Equations (48) or (49) are plotted as a vertical axis with the term of \( 5X_{\text{Ti}} + 3X_{\text{O}} - 8X_{\text{Fe}}X_{\text{O}} \) and \( 3X_{\text{Ti}} + 2X_{\text{O}} - 5X_{\text{Fe}}X_{\text{O}} \) as a horizontal axis in Fig. 8 using the present experimental results and other researcher’s results using titanium oxide crucible\(^{13,19,22}\) and values of Eqs. (43)–(47). \( \Omega_{\text{Ti}_2\text{O}_3} \) is evaluated from the slope of the regressed line through the origin in this figure. \( \Omega_{\text{Ti}_2\text{O}_3} \) was determined as follows.

\[ 0 \Omega_{\text{Ti}_2\text{O}_3} = -1035900 / \text{J} \quad \text{at} \ 1873 \text{ K} \]

The equilibrium relation between Ti and O contents in molten Fe is compared with the experimental results by other researchers in Fig. 2. This equilibrium line was drawn using the Eqs. (40) from (47), the Gibb free energy of TiO\(_2\) formation (referred from NIST-JANAF Thermochemical Tables\(^{40}\)) and estimated parameters, Eq. (50), in the present work.

4.3. Comparison of Wagner’s Formalism with Quadratic Formalism and Redlich–Kister Type Polynomial

The estimated equilibrium curves based on each formalism\(^{52–56}\) show excellent agreement with the present experimental results as shown in Fig. 2. However, the curve based on Redlich–Kister type polynomial is likely to more precisely expresses the equilibrium relation between Ti and O contents in molten Fe than that based on Wagner’s formalism because Redlich–Kister type polynomial includes the higher order terms, too. The interaction parameters in Redlich–Kister type polynomial are easily converted into Wagner’s interaction parameters as shown in Eqs. (21) to (30).\(^{41–47}\) Table 4 shows the comparison of the Wagner’s interaction coefficients based on mass percent as concentration in molten Fe obtained in Sec. 4.1.2 with those derived from Redlich–Kister type polynomial parameters with Eqs. (21)–(25), (27), (28), (43)–(47), (50), (51)–(53). Redlich–
Kister type polynomial parameters are converted into the interaction coefficients based on mass percents by utilizing the following relations derived after Lupis,39) where $M_1$ denote the molecular weight of the solvent and $M_i$ denote the molecular weight of element of “$i$”.

\[
e_{ij} = 230 \frac{M_i}{M_1} e_{ij} + \frac{M_i - M_j}{M_1} \tag{51}
\]

\[
\rho_{ij} = \frac{230}{M_1^2} [100M_j e_{ij} + M_j(M_i - M_j)e_{ij}] + \frac{1}{2} \left( \frac{M_i - M_j}{M_1} \right)^2 \tag{52}
\]

\[
\rho_{ij}^{(j,k)} = \frac{230}{M_1^2} [100M_i M_k e_{ij}^{(j,k)} + M_j(M_i - M_j)e_{ij}] + M_k (M_i - M_j)e_{ij} + \frac{(M_i - M_j)(M_i - M_k)}{M_1^2} \tag{53}
\]

The converted first order interaction parameters derived from Redlich–Kister type polynomial parameters are identical to the Wagner’s interaction parameters obtained in Sec. 4.1.2 as shown in Table 4. However, second order interaction parameters by Wagner’s formalism could not be determined from the present experimental results due to the lack of experimental accuracy. On the other hand, Darken’s quadratic formalism includes all of the first and the second order terms represented by Wagner’s formalism. Hence, the concentration range of solutes that quadratic formalism can cover is essentially wider than that by Wagner’s formalism. The Redlich–Kister type polynomial parameters are universal for any alloy systems. Figure 9 shows the interrelation among the Henry constant, the interaction parameters and the thermodynamical parameters in the two formalisms.

It was affirmed from the present thermodynamic analysis that the Ti deoxidation equilibrium of molten Fe could be quantitatively expressed with high accuracy using the quadratic formalisms.

5. Conclusions

The equilibrium relation between dissolved Ti and O was observed in liquid Fe–0.0004 to 16.6 mass% Ti alloy saturated with solid titanium oxides at 1 873 K. The equilibrium constant of Ti deoxidation and the interaction parameters of Wagner’s formalism between Ti and O in liquid Fe satura-
ed with titanium oxides were given by the following equations.

\[
\text{Ti}_2\text{O}_3(s) = 2\text{Ti} + 3\text{O} \quad (0.5 < \text{mass}\%\text{Ti} < 6.2)
\]

log \(K_{\text{Ti}} = -10.17, \quad e_{\text{O}}^{\text{Ti}} = -0.34\)

\[
'\text{Ti}_2\text{O}_3'(s) = 3\text{Ti} + 5\text{O} \quad (0.0004 < \text{mass}\%\text{Ti} < 0.36)
\]

log \(K_{\text{Ti}} = -16.86, \quad e_{\text{O}}^{\text{Ti}} = -0.34\)

The Henry constant of Ti in liquid Fe was assessed at 1 873 K as follows.

\[
\gamma_{\text{H}}^{\text{Ti}} = 0.0090
\]

The interaction parameters of Redlich–Kister type polynomial between Ti(l) and O in molten Fe saturated with titanium oxides were given by the following values in the present work.

\[
\begin{align*}
\theta_{\text{O}}^{\text{Fe-Ti}} &= -73.360 / \text{J}, \quad \theta_{\text{Ti}}^{\text{O}} = -1 035 900 / \text{J} \\
\end{align*}
\]

Ti deoxidation equilibrium of molten Fe could be quantitatively expressed using binary interaction parameters determined on the basis of the quadratic formalism with high accuracy compared to the Wagner’s formalism because of the applicable parameters to wide composition range in the quadratic formalism. Redlich–Kister type polynomial parameters determined in the present work was useful to any composition such as Fe–Ti–X–O system. The parameters determined in the present work can easily convert from the quadratic formalism and Redlich–Kister type polynomial formalism into Wagner’s interaction coefficients.

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