1. Introduction

Titanium is added in many high grade steels to improve mechanical properties via the grain refinement during hot rolling. Also, Ti is an important alloying element in ferritic stainless steels to stabilize C and N, and hence to improve the intergranular corrosion resistance of the weld. Therefore, thermodynamics of Ti and O dissolved in liquid steel is very important for the precise control of Ti content in the steelmaking process.

Titanium is very reactive for O, and the titanium oxide as an equilibrium deoxidation product changes its chemical composition with Ti content in liquid steel. Due to experimental difficulties, in spite of its importance, there are large discrepancies in thermodynamic data of the Ti deoxidation equilibria in liquid Fe–Ti–O system at 1873 K previously reported. Furthermore, the temperature dependencies of those data are not available.

In the present study, the deoxidation equilibrium between Ti and O in liquid iron in contact with titanium oxide powders of a crucible form or in an Al₂O₃ crucible was studied in the temperature range of 1823 to 1923 K using a high frequency induction furnace. After each equilibration experiment, the titanium oxides near the oxide/metal interface were analyzed by the X-ray diffraction (XRD) and the electron probe micro-analyzer (EPMA) analysis for the phase identification and the composition analysis, respectively.

The measured equilibrium relation of Ti and O in liquid iron was thermodynamically analyzed using Wagner’s formalism to determine the equilibrium constant of Ti deoxidation reaction for the formation of pure Ti₂O₃ (s) and the first- and second-order interaction parameters between Ti and O given as follows in the temperature range of 1823 to 1923 K.

\[
2Ti + 3O = Ti_2O_3 (s) \quad (0.25 < \text{mass\% Ti} < 4.75)
\]

\[
\log K_{Ti_2O_3} = 44.238/T - 13.0
\]

\[
\phi_0^T = 1.642/T + 0.3358, \quad \phi_0^O = -4.915/T + 1.005
\]

\[
r_0^T = 0.0385, \quad r_0^O = -0.355
\]

The equilibrium titanium oxide phase was identified as Ti₃O₅ (s) for iron melts containing 0.0012–0.25 mass% Ti at 1873 K. The equilibrium constant of Ti deoxidation reaction for the formation of pure Ti₃O₅ (s) were estimated as follows.

\[
3Ti + 5O = Ti_3O_5 (s) \quad (0.0012 < \text{mass\% Ti} < 0.25)
\]

\[
\log K_{Ti_3O_5} = 72.813/T - 21.32
\]

The activity coefficient of Ti in liquid iron at infinite dilution, \( \gamma_{Ti,s}^\infty \) was assessed as 0.011, 0.014 and 0.018 at 1823 K, 1873 K and 1923 K, respectively.

KEY WORDS: liquid iron; deoxidation; titanium; oxygen; titanium oxides; equilibrium constant; interaction parameter.
2. Experimental Procedures

One hundred grams of high purity electrolytic iron (99.99% purity, 60 mass ppm O, <5 mass ppm N, 18 mass ppm C, <5 mass ppm Si, <7 mass ppm Ni, 1 mass ppm Al), contained in a mixture of solid Ti_2O_3 and TiO_2 powders (1:1 molar ratio, 99.9% and 99% purity, respectively) of a crucible form in an Al_2O_3 crucible (OD: 40 mm, ID: 30 mm, H: 50 mm), was melted using a 15 kW/30 kHz high frequency induction furnace as shown in Fig. 1. In some experiments, an Al_2O_3 crucible was used for melting the iron. In that case, a mixture of solid Ti_2O_3 and TiO_2 powders (1:1 molar ratio) was located at the bottom of Al_2O_3 crucible. Figure 2 shows the XRD pattern for a mixture of solid Ti_2O_3 and TiO_2 powders used in the present study.

The reaction chamber consisted of a 80 mm OD quartz tube open at both ends and was connected to a gas delivery system. The flow rate of Ar+3vol%H_2 gas mixture, which was dehydrated by magnesium perchlorate, was in the range of 100 to 150 mL/min. In order to remove any residual oxygen in the reaction chamber during heating, the mixture of Ti chips and MgO granules was packed in the space between the inner and outer Al_2O_3 crucibles. A detailed description of the experimental system is given in the previous article.16)

After melting the iron, sponge Ti (99.5% purity) metal, which was kept in a glass tube by a magnet, was dropped into liquid iron. The melt temperature was measured by a Pt/Pt–13mass%Rh thermocouple sheathed by a 5 mm OD quartz tube immersed in the melt. In order to minimize Si pick up in the melt by the reduction of quartz tube, the immersion depth and the time for temperature measurement were carefully controlled after Ti addition. Any possible influence of high frequency noise on the temperature reading was avoided by grounding the circuit of the thermocouple. Preliminary trials confirmed that no significant noise was detected, and the temperature fluctuation of iron melt could be controlled within 5 K during experiment. Strong agitation of melt by an induction furnace would result in a faster attainment of deoxidation equilibrium and a good separation of deoxidation products from the melt. The iron melts were equilibrated with titanium oxides for 1 h under an Ar+3vol%H_2 atmosphere at 1 823 K, 1 873 K and 1 923 K.

After each experiment, iron sample and crucible were quenched rapidly by helium gas of high flow rate (>50 L/min) blowing onto the melt surface. Figure 3 shows the iron sample contained in a crucible of sintered titanium oxide powder obtained after experiment. After each experiment, the titanium oxide layer near the oxide/metal interface was sampled and analyzed by the XRD for the phase identification. The EPMA analysis was also carried out for the composition analysis of the titanium oxide layer. In those experiments using Al_2O_3 crucibles with titanium oxide powder, the inner surface of Al_2O_3 crucible and the melt surface were examined by the SEM-EDS and analyzed by the thin film XRD for the identification of Ti deoxidation product.

The center part of metal sample was used for the chemical analysis of Ti, Al, Si and O. The metal sample (0.2 g) was dissolved in 15 mL of HCl(1+1) and 5 mL of HNO_3(1+1) in a glass beaker of 50 mL capacity heated in a water bath for 2 h. The leaching test of titanium oxide powders (Ti_2O_3 and Ti_3O_5) indicated that they were nearly insoluble in aqua regia solution heated in a water bath up to 12 h. After dissolving the sample, the solution was transferred to the measuring flask (100 mL) with filtration. Titanium, aluminum and silicon contents in sample solution were analyzed by the inductively coupled plasma-Auger electron spectroscopy (ICP-AES) technique using appropriate standard solutions containing the same amount of Fe (2 000 mass ppm) as sample solution. The oxygen content in metal sample was measured with an accuracy of ±1

![Fig. 1. Schematic diagram of experimental system.](image)

![Fig. 2. XRD pattern for a mixture of solid Ti_2O_3 and TiO_2 powders before melting the iron.](image)

![Fig. 3. Iron sample contained in a titanium oxide crucible.](image)
mass ppm by the inert gas fusion-infrared absorptiometry technique using the standard sample of steel containing 11±1 mass ppm oxygen.

3. Results and Discussion

3.1. Equilibrium Ti–O Relation and TiO\textsubscript{x} Phase Identification

The results of Ti deoxidation experiments for liquid iron in contact with titanium oxides are summarized in Table 1. Small amount of Si was picked up in the melt by the reduction of quartz tube immersed in the melt for the temperature measurement. When the melt was contained in an Al\textsubscript{2}O\textsubscript{3} crucible with titanium oxide powder at the bottom of the melt, small amount of Al was picked up. However, Al was not detected in the melt when the melt was contained in a crucible of titanium oxide powder.

Figure 4 shows the results of XRD analysis on the titanium oxide layers near the oxide/metal interface after the Ti deoxidation experiments. The XRD pattern for a mixture of solid Ti\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} powders shown in Fig. 2 has changed to new patterns of equilibrium titanium oxides. As shown in the figure, the equilibrium titanium oxide phase was identified as Ti\textsubscript{3}O\textsubscript{5} for Fe–Ti alloys containing from 0.0012 to 0.21 mass% Ti, and Ti\textsubscript{2}O\textsubscript{3} for alloys containing from 0.26 to 3.6 mass% Ti at 1 873 K. For an alloy containing 0.25 mass% Ti, the equilibrium oxide phase was a mixture of Ti\textsubscript{3}O\textsubscript{5} and Ti\textsubscript{2}O\textsubscript{3}. Therefore, the critical Ti content in liquid iron at which both Ti\textsubscript{3}O\textsubscript{5} and Ti\textsubscript{2}O\textsubscript{3} are the equilibrium oxide phases is experimentally determined as 0.25 mass% at 1873 K in the present study. The thermodynamic calculation of critical Ti content using the data obtained in the present study will be discussed later.

Figure 5 shows the equilibrium relations between Ti and O dissolved in liquid iron at 1 873 K determined in the present study together with previous results\textsuperscript{3,6,8,10,11}. The oxygen solubility minimum was about 7.7 mass ppm at 0.625 mass% Ti, and the Ti–O relation was not much affected by whether using a titanium oxide crucible or an Al\textsubscript{2}O\textsubscript{3} crucible with titanium oxide powder at the bottom of the melt in the present study. As shown in the figure, the experimental results obtained by various equilibration techniques are widely dispersed. Fruehan\textsuperscript{11} measured the oxygen activity...
by the EMF method using ZrO$_2$(CaO) and ThO$_2$(Y$_2$O$_3$) electrolyte oxygen cells, and also determined the oxygen solubility by the sampling method in Fe–Ti melts at 1 873 K. He used ThO$_2$ and ZrO$_2$ crucibles for the containers of Fe–Ti melts. His oxygen solubility minimum was 33 mass ppm at 0.32 mass% Ti, and it is much higher than the others including the result of present study. The oxygen solubility data for Fe–Ti melts determined by Smellie and Bell$^6$ with Al$_2$O$_3$ and Ti$_3$O$_5$ crucibles, and Kojima et al.$^3$ with Al$_2$O$_3$, MgO and CaO crucibles are widely scattered. However, their data of lower oxygen content range are comparable to the data determined in the present study. Among those data, the results of present study are in good agreement with the studies by Janke and Fischer$^8$ and Cha et al.$^9,10$ who used sintered titanium oxide crucibles.

Janke and Fischer investigated the Ti deoxidation equilibrium in liquid iron at 1 873 K by the EMF method using a ZrO$_2$(CaO)–ThO$_2$(Y$_2$O$_3$) bielectrolyte oxygen cell also by the sampling method.$^8$ They measured the oxygen activity and the oxygen content in liquid iron containing from 0.001 to 8.8 mass% Ti contained in sintered titanium oxide crucibles. The calculated the Ti activity in Fe–Ti melts using the EMF data assuming the activities of titanium oxides are unity. In the present study, some trials were also made to measure the oxygen activity in Fe–Ti melts using a ZrO$_2$(CaO) electrolyte oxygen cell. After the cell measurement, the electrolyte/melt interface was analyzed by the SEM-EDS as shown in Fig. 6. At a Ti content of 0.395 mass% (Run 37), a pure titanium oxide was formed on the surface of the electrolyte. However, at about 0.18 mass% Ti content (Run 28), there was a solid solution layer of titanium oxide and zirconium oxide formed at the electrolyte–melt interface as shown in the figure. Therefore, the oxygen activity measured by the oxygen cell would be affected by the purity or activity of titanium oxides formed at the ZrO$_2$ electrolyte/melt interface depending on Ti content in Fe–Ti melts. For this reason, the oxygen activity measurement for Fe–Ti melts using ZrO$_2$ electrolyte was not carried out further in the present study.

Recently, Cha et al.$^9,10$ also studied the equilibrium between Ti and O in liquid Fe–Ti alloy contained in sintered Ti$_3$O$_5$ crucibles at 1 873 K. They emphasized the importance of identification of equilibrium titanium oxide phases formed at the interface between the crucibles and Ti containing iron melt. They identified the equilibrium titanium oxide phases of Ti$_2$O$_3$, TiO$_2$ and TiO formed at the interface as a function of Ti content in Fe–Ti melts with the electron backscatter diffraction (EBSD) pattern analysis at 1 873 K.$^9$ In the present study, the equilibrium titanium oxide phase was identified by the XRD analysis as Ti$_3$O$_5$ for alloys containing from 0.0012 to 0.25 mass% Ti, and Ti$_2$O$_3$ from 0.25 to 3.6 mass% Ti at 1 873 K. The purity or activity of equilibrium titanium oxides should be also considered for the accurate thermodynamic analysis of Ti deoxidation equilibria. Figure 7 shows the result of EPMA analysis on the TiO$_x$ crucible/metal interface (Run 7).
from other oxides of Fe, Si and Al. Suzuki et al.\(^7\) measured the solid solubility of FeO in synthetic titanium oxide crucibles after the equilibration with Fe–Ti melts at 1 873 K. They reported that there was no solubility of FeO in TiO and Ti\(_2\)O\(_3\), but there was an increasing solubility of FeO in titanium oxides of higher O/Ti ratio (1.67–2: Ti\(_3\)O\(_5\) and TiO\(_2\)) as shown in Fig. 8.\(^7\)

In the present study, some of Ti deoxidation experiments were carried out using Al\(_2\)O\(_3\) crucibles with titanium oxide powder located at the bottom of the crucible. Ti in the melt would react with Al\(_2\)O\(_3\) to dissolve some Al in the melt and form titanium oxides as following reaction:

\[
\frac{Ti}{3} + \frac{x}{3} Al_2O_3(s) = \frac{2x}{3} Al + TiO_2(s) \quad \text{...(1)}
\]

Therefore, it is important to give a consideration for the equilibrium titanium oxide phase which may be formed at the interface between Al\(_2\)O\(_3\) crucibles and Fe–Ti melt. The inner surface of Al\(_2\)O\(_3\) crucibles were examined by the SEM-EDS after the Ti deoxidation experiments. However, no reaction layer was observed on the surface of Al\(_2\)O\(_3\) crucible. Instead, there was a thin titanium oxide layer formed on the surface of the melt when the Ti content was higher than 0.2 mass% in Fe–Ti melt. Figure 9 shows the SEM-EDS analysis results on the titanium oxide layers formed on the melt surface and Al\(_2\)O\(_3\) crucible/melt interface for the melt containing 1.76 mass% Ti (Run 43). The oxide layers were virtually pure titanium oxide phases free from other constituents. The thin film XRD analysis on top oxide layer identified the deoxidation product as Ti\(_2\)O\(_3\) as shown in Fig. 10. Therefore, considering the results in Figs. 7, 9 and 10, it can be concluded that pure solid Ti\(_2\)O\(_3\) is the equilibrium deoxidation product for Fe–Ti melts at Ti contents higher than 0.25 mass% at 1 873 K, regardless of using a titanium oxide crucible or an Al\(_2\)O\(_3\) crucible with titanium oxide powder at the bottom of the melt in the present study.

### 3.2. Thermodynamics of Ti Deoxidation in Liquid Iron for Ti\(_2\)O\(_3\) Formation

The deoxidation reaction of Ti to form Ti\(_2\)O\(_3\) in liquid iron and its equilibrium constant can be expressed by Eqs. (2) and (3):

\[
2Ti + 3O = Ti_2O_3(s) \quad \text{...(2)}
\]

\[
\log K_{Ti_2O_3} = \log (\frac{\gamma_{Ti_2O_3}}{h_{O_2}^3}) \quad \text{...(3)}
\]

\[
\log K_{Ti_2O_3} = \log (\frac{\gamma_{Ti_2O_3}}{h_{O_2}^3}) = \log (\frac{\gamma_{Ti_2O_3}}{f_{O_2}^{3} [\%Ti]^{2} [\%O]}) \quad \text{...(3)}
\]

---

Fig. 8. The solid solubility of FeO in titanium oxide at 1 873 K.

Fig. 9. SEM-EDS analysis results of TiO\(_x\) layer formed on the melt surface at 1 873 K (Run 43).

Fig. 10. Thin film XRD patterns for TiO\(_x\) layer formed on the melt surface at 1 873 K (Run 43).
where $K_{TiO_2}$, $a_{TiO_2}$, $h_i$ and $f_i$ are the equilibrium constant, the Raoultian activity, the Henrian activity and the Henrian activity coefficient, respectively. The standard states of $h_i$ and $f_i$ are their infinitely dilute solution in liquid iron, and that of $a_{TiO_2}$ is pure solid Ti$_2$O$_3$. The activity coefficients of Ti and O in liquid iron can be expressed by Wagner’s relation using the first- and second-order interaction parameters.

\[
\log f_{Ti} = e^{[Ti]}_i/h_i + r^{[Ti]}_{0,1}[%Ti] + r^{[O]}_{0,1}[%O] + r^{[Ti,1]}_{0,1}[%Ti][%O] \\
\log f_{O} = e^{[O]}_i/h_i + r^{[Ti]}_{0,1}[%Ti] + r^{[O]}_{0,1}[%O] + r^{[Ti,1]}_{0,1}[%Ti][%O] \\
\]

Using only the first-order interaction parameters and the Lupis’ reciprocal relationship between $e^{[Ti]}_i$ and $e^{[O]}_i$, Eq. (3) can be rewritten as the following relation:

\[ -\log K_{TiO_2} + \log a_{TiO_2} = -2\log e^{[Ti]}_i + \log K_{TiO_2} \]  

\[ = e^{[O]}_i(2[\%O] + 1.002[\%Ti]) + \log K_{TiO_2} \]  

Table 2. Interaction parameters used in the present study.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Temp. Dependency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^{[Ti]}_i$</td>
<td>0.048</td>
<td>-</td>
</tr>
<tr>
<td>$e^{[O]}_i$</td>
<td>0.048</td>
<td>1873–1973K</td>
</tr>
<tr>
<td>$e^{[Ti]}_l$</td>
<td>0.0037</td>
<td>-</td>
</tr>
<tr>
<td>$e^{[O]}_l$</td>
<td>-0.0256</td>
<td>177.5/K–0.12</td>
</tr>
<tr>
<td>$e^{[Ti]}_o$</td>
<td>-0.17</td>
<td>-1750/T–0.76</td>
</tr>
<tr>
<td>$e^{[O]}_o$</td>
<td>-1.17</td>
<td>-</td>
</tr>
<tr>
<td>$e^{[O]}_2$</td>
<td>-0.066</td>
<td>1823–1923K</td>
</tr>
</tbody>
</table>

where $K_{TiO_2}$, $a_{TiO_2}$, $h_i$ and $f_i$ and are the equilibrium constant, the Raoultian activity, the Henrian activity and the Henrian activity coefficient, respectively. The standard states of $h_i$ and $f_i$ are their infinitely dilute solution in liquid iron, and that of $a_{TiO_2}$ is pure solid Ti$_2$O$_3$. The activity coefficients of Ti and O in liquid iron can be expressed by Wagner’s relation using the first- and second-order interaction parameters.

\[
\log f_{Ti} = e^{[Ti]}_i/h_i + r^{[Ti]}_{0,1}[%Ti] + r^{[O]}_{0,1}[%O] + r^{[Ti,1]}_{0,1}[%Ti][%O] \\
\log f_{O} = e^{[O]}_i/h_i + r^{[Ti]}_{0,1}[%Ti] + r^{[O]}_{0,1}[%O] + r^{[Ti,1]}_{0,1}[%Ti][%O] \\
\]

Using only the first-order interaction parameters and the Lupis’ reciprocal relationship between $e^{[Ti]}_i$ and $e^{[O]}_i$, Eq. (3) can be rewritten as the following relation:

\[ -\log K_{TiO_2} + \log a_{TiO_2} = -2\log e^{[Ti]}_i + \log K_{TiO_2} \]  

\[ = e^{[O]}_i(2[\%O] + 1.002[\%Ti]) + \log K_{TiO_2} \]  

Where $K_{TiO_2} (= [%Ti]^2 [\%O]^2)$ is the apparent equilibrium constant, $k$ and $l$ represent elements other than O and Ti, respectively, and the value of $a_{TiO_2}$ is unity in the present study. When Al and Si are present in liquid iron, the interaction parameters of those elements on Ti and O should be also considered. The interaction parameters used in the present study are summarized in Table 2.\(^{2,3,8,18–20}\)

Figure 11 shows a plot for the relation expressed by Eq. (6) using the present experimental data for iron melts containing 0.26–0.94 mass% Ti at 1873 K. It is apparent from the figure that the data points determined at different Ti contents show a good linear relationship. The value of $\log K_{TiO_2}$ obtained by extrapolating the line is found to be approximately 10.62 at 1873 K. The values of $\log K_{TiO_2}$ at 1873 K previously reported are in the range of 9.9–11.69 as shown in Table 3.\(^{2,8,10-12,21,22}\) Among those values, the present data is in good agreement with the values of 10.39 determined by Büüzki\(^{23}\) and 10.43 determined by Janke and Fischer\(^{24}\) at 1873 K.

The value of $e^{[O]}_i$ can be obtained from the slope of the line as $-1.62$, and $e^{[O]}_i$ as $-0.541$ using the reciprocal relationship.\(^{17}\) The recommended value of the Japan Society for the Promotion of Science (JSPS)\(^{3}\) for $e^{[O]}_i$ is $-1.12$ at 1873 K taken from the data reported by Fruehan.\(^{11}\) However, considering a rough estimation of $e^{[O]}_i$ from the nonlinear plot of $\log f_{O}$ vs. Ti content over a wide composition range of 0.02–12.5 mass% Ti, this value does not seem to be a reliable one to use. Sigworth and Elliott recalculated the first- and second-order interaction parameters of $e^{[O]}_i$ and $r^{[O]}_{0,1}$ using Fruehan’s experimental data as $-0.6$ and $0.031$ at 1873 K, respectively, and compiled them in their thermodynamic data of liquid dilute iron alloys.\(^{12}\)

In the present study, the equilibrium relations between Ti and O in liquid iron at temperatures other than 1873 K were also measured. Figure 12 compares the Ti–O relations measured at 1823 K and 1923 K using titanium oxide crucibles for iron melts containing 0.42–4.75 mass% Ti together with data obtained at 1873 K. The equilibrium titanium oxide phases at this Ti concentration range at 1823 K and 1923 K were all identified as pure solid Ti$_2$O$_3$. By the same procedure using Eq. (6), the equilibrium constants for the reaction (2) and the first-order interaction parameters between Ti and O at 1823 K and 1923 K can be also determined as shown in Fig. 11.

Figure 13 shows the temperature dependences of $\log K_{TiO_2}$ and $e^{[O]}_i$ values determined in the present study, and they can be expressed as Eqs. (7) and (8) in the temperature range of 1823 K to 1923 K.
In the preceding discussion, the first order $e_O^{Ti}$ values were determined from the experimental data of Ti and O relation for the melts containing 0.26–1.77 mass% Ti. At a higher Ti concentration in liquid iron, higher order interaction parameters should be considered. If the second-order interaction parameters are also considered in Eqs. (4) and (5), Eq. (3) can be rewritten as the following relation:

\[ \log K_{Ti,O_3} = 44238/T - 13.0 \]  \hspace{1cm} (7)

\[ e_O^{Ti} = -1642/T + 0.3358 \quad \text{or} \quad e_O^{O} = -4915/T + 1.005 \]  \hspace{1cm} (8)

In the preceding discussion, the first order $e_O^{Ti}$ values were determined from the experimental data of Ti and O relation for the melts containing 0.26–1.77 mass% Ti. At a higher Ti concentration in liquid iron, higher order interaction parameters should be considered. If the second-order interaction parameters are also considered in Eqs. (4) and (5), Eq. (3) can be rewritten as the following relation:

\[
- \log K_{Ti,O_3} = -\log K'_{Ti,O_3} + \log a_{Ti,O_3} \\
- 2 \sum e'^{Ti}[k] - 2 \sum e'^{O}[l] + 0.00414[\%Ti][\%O] \\
- e_O^{O}(2[\%O] + 1.002[\%Ti] - 0.03[\%Ti][\%O]) \\
= r^{Ti}_{O}(2[\%O]^2 + 2.005[\%Ti][\%O]) \\
+ r^{O}_{O}(3[\%Ti]^2 + 11.97[\%Ti][\%O]) \\ 
\]  \hspace{1cm} (9)

where $k$ and $l$ represent the same meanings as in Eq. (6), and $K'_{Ti,O_3}$ and $a_{Ti,O_3}$ were determined previously as Eqs. (7) and (8), respectively. The values of $r^{Ti}_{O}$ and $r^{O}_{O}$ are assumed as zero in the present study. The cross product terms of $r^{Ti,O}_{O}$ and $r^{O,O}_{Ti}$ can be expressed as a function of $r^{Ti}_{Ti}$ and $r^{O}_{O}$, respectively, using the following relationships:\n
\[ r^{Ti,O}_{O} = 2 \left( \frac{M_{Ti}}{M_{O}} \right) r^{Ti}_{Ti} + 0.01 e^{Ti}_{Ti} - 0.01 e^{O}_{O} \]  \hspace{1cm} (10)

\[ r^{O,O}_{Ti} = 2 \left( \frac{M_{O}}{M_{Ti}} \right) r^{O}_{O} + 0.01 e^{O}_{O} - 0.01 e^{Ti}_{Ti} \]  \hspace{1cm} (11)

Therefore, all terms in Eq. (9) are known values except the second-order interaction parameters, $r^{Ti}_{Ti}$ and $r^{O}_{O}$. These parameters can be determined from the experimental data of Ti and O relation for the melts containing 1.47–4.75 mass% Ti. Figure 14 shows the relation of Eq. (9) in which both sides are divided by the term $(2[\%O]^2 + 2.005[\%Ti][\%O])$ at 1823, 1873 and 1923 K. The temperature dependence of the relation was negligible. The values of and determined by a linear regression analysis are 0.0385 and 0.355, respectively. The second-order $r^{Ti}_{Ti}$ value of 0.0385 is in good agreement with the value of 0.031 at 1873 K reported by Sigworth and Elliott.\n
The values of interaction parameters between Ti and O and the equilibrium constant for the reaction (2) determined in the present study are summarized in Table 4. Using the thermodynamic parameters determined in the present study, the Ti deoxidation product for the formation of pure solid Ti$_2$O$_3$ in Fe–Ti–O melt can be derived as Eq. (12).

\[
\log[\%Ti]^2[\%O]^3 = -\left(44238/T - 13.0\right) \\
- (-4915/T + 1.005)(2[\%O] + 1.002[\%Ti]) \\
- 2(e^{Ti}_{Ti}[\%Ti] + r^{Ti}_{O}[\%O]^2 + r^{O,O}_{Ti}[\%Ti][\%O]) \\
- 3(e^{O}_{O}[\%O] + r^{O}_{O}[\%Ti]^2 + r^{Ti,O}_{O}[\%Ti][\%O]) \\
\]  \hspace{1cm} (12)

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In Fig. 12, the solid lines shown in the Ti concentration range higher than 0.25 mass% are the calculated equilibrium Ti–O relations in liquid iron for the formation of Ti₂O₃(s) at 1823, 1873 and 1923 K using Eq. (12), assuming the activity of Ti₂O₃(s) as unity. The calculated relations well represent the experimental results obtained over a wide range of Ti content. The dotted lines shown in the same Ti concentration range are the calculated Ti–O relations using only the first order interaction parameters. The dotted lines show a good correlation with the experimental results at Ti contents less than 1 mass%. However, they deviate from the experimental results significantly at higher Ti contents.

From the temperature dependence of equilibrium constant for the Ti deoxidation reaction expressed as Eq. (7), the following Gibbs free energy change for the reaction (2) can be derived in the temperature range of 1823 to 1923 K.

$$\Delta G_2 = -845928 + 248.67T \text{ J/mol} \quad \text{(13)}$$

The standard Gibbs free energy change for the formation of Ti₂O₃(s) is given by NIST-JANAF\textsuperscript{14}) as Eq. (15).

$$\Delta G_0^o_{2Ti} = -1502126 + 258.087T \text{ J/mol} \quad \text{(15)}$$

Combination of Eqs. (13), (15) and the free energy change data for the dissolution of oxygen in liquid iron\textsuperscript{13}) given as Eq. (17) would give the free energy change for the dissolution of Ti in liquid iron as Eq. (19).

$$1/2 O_2(g) = O \quad \text{(16)}$$

$$\Delta G_{16} = -117122 - 2.88T \text{ J/g·atom} \quad \text{(17)}$$

$$\text{Ti} (s) = Ti \quad \text{(18)}$$

$$\Delta G_{18} = -152416 + 9.07T \text{ J/g·atom} \quad \text{(19)}$$

From Eq. (19), one would be able to calculate the value of $\gamma^\circ_{Ti}$, the activity coefficient of Ti in liquid iron at infinite dilution, as 0.011, 0.014 and 0.018 at 1823 K, 1873 K and 1923 K, respectively. Table 5 compares these values together with previous results.\textsuperscript{2,22–24)}

### Table 4. The equilibrium constants and interaction parameters determined in the present study.

<table>
<thead>
<tr>
<th>$e^o_{Ti}$</th>
<th>$e^o_{O_2}$</th>
<th>$\beta^0_{Ti}$</th>
<th>$\beta^0_{O_2}$</th>
<th>$\log K_{Ti}$</th>
<th>$\log K_{O_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.541</td>
<td>-1.620</td>
<td>0.0385</td>
<td>-0.355</td>
<td>10.62</td>
<td>17.56</td>
</tr>
<tr>
<td>-1.620</td>
<td>-1.620</td>
<td>0.0385</td>
<td>-0.355</td>
<td>10.62</td>
<td>17.56</td>
</tr>
</tbody>
</table>

In the present study, the equilibrium titanium oxide phase was identified as Ti₃O₅ for iron melts containing from 0.0012 to 0.25 mass% Ti at 1873 K. The standard Gibbs free energy change for the formation of pure solid Ti₃O₅ is given by NIST-JANAF\textsuperscript{14}) as Eq. (21).

$$3\text{Ti} (s) + 5/2 O_2(g) = Ti_3O_5(s) \quad \text{(20)}$$

Combination of Eqs. (17), (19) and (21) would give the free energy change for Ti deoxidation reaction in liquid iron to form Ti₃O₅(s) as:

$$\Delta G_{22} = -1392344 + 407.7T \text{ J/g·atom} \quad \text{(23)}$$

Therefore, the Ti deoxidation product for the formation of pure solid Ti₃O₅ in Fe–Ti–O melt can be derived as Eq. (24).

$$\log[\%Ti]^{1/3}[\%O]^5 = - (728.13/T - 21.32)$$

From Eq. (19), one would be able to calculate the value of $\gamma^\circ_{Ti}$, the activity coefficient of Ti in liquid iron at infinite dilution, as 0.011, 0.014 and 0.018 at 1823 K, 1873 K and 1923 K, respectively. Table 5 compares these values together with previous results.\textsuperscript{2,22–24)}
lier, Suzuki and Sanbongi\textsuperscript{71} found that there was a significant solubility of FeO in titanium oxides with O/Ti ratio higher than 1.67 (Ti$_3$O$_5$) after the equilibration with liquid iron containing low Ti contents. Recently, Cha \textit{et al.}\textsuperscript{29} also found that the solid solubility of FeO in Ti$_3$O$_5$ phase increased significantly when the Ti content in liquid iron decreased below 0.01 mass% at 1 873 K. Therefore, such deviation at low Ti contents in the present study can be explained by the activity of Ti$_3$O$_5$ being less than unity due to the solid solution of FeO in Ti$_3$O$_5$ phase.

3.4. Critical Ti Content in Liquid Iron for Ti$_3$O$_5$ and Ti$_2$O$_3$ Formation

In the present study, the critical Ti content in liquid iron at which both Ti$_3$O$_5$ and Ti$_2$O$_3$ coexisted was experimentally determined as 0.25 mass% at 1 873 K. Cha \textit{et al.}\textsuperscript{19} recently estimated the critical Ti content in liquid iron for co-existence of Ti$_3$O$_5$ and Ti$_2$O$_3$ phases as 0.526 at 1 873 K using the standard free energies of titanium oxide formation\textsuperscript{18} and their activity data of Ti in liquid iron at 1 873 K.\textsuperscript{10}

From Eqs. (13) and (23), the following Gibbs free energy change for the reaction (25) can be derived.

$$ \Delta G_{24} = -52 \text{ 608} + 19.9 T \text{ J} / \text{g \ atom} \quad \text{(25)} $$

Equilibrium constant of Eq. (24) can be expressed as

$$ \log K_{24} = \log(a_{T_i^{O_0}}^{5} / h_{T_i} \cdot a_{T_i^{O_0}}^{1}) 
= -\log h_{T_i} = -(\log f_{T_i} + \log[\%\text{Ti}]) 
= -(\epsilon_{T_i}^{O_0}[\%\text{Ti}] + c_{T_i}^{O}[\%\text{O}] + \log[\%\text{Ti}]) \quad \text{(26)} $$

Where the activities of both Ti$_3$O$_5$ and Ti$_2$O$_3$ are assumed to be unity, the value of $\epsilon_{T_i}^{O_0}$ used in this study is 0.048\textsuperscript{18} at 1 823–1 873 K, and the effect of oxygen on the Ti activity is assumed to be negligible due to its extremely small content. The critical Ti contents satisfying the Eq. (26) can be calculated as 0.33, 0.36 and 0.39 mass% at 1 823, 1 873 and 1 923 K, respectively. They are also shown in Fig. 12. The critical Ti content of 0.36 mass% Ti estimated at 1 873 K is slightly higher than 0.25 mass% Ti determined experimentally in the present study.

4. Conclusions

The relation of Ti and O dissolved in liquid iron equilibrated with solid titanium oxides has been determined in the temperature range of 1 823 to 1 923 K. The equilibrium titanium oxide phase was identified as Ti$_3$O$_5$ for Fe–Ti alloys containing from 0.0012 to 0.21 mass% Ti, and Ti$_2$O$_3$ for alloys containing from 0.26 to 3.6 mass% Ti at 1 873 K. The critical Ti content in liquid iron at which both Ti$_3$O$_5$ and Ti$_2$O$_3$ coexisted was experimentally determined as 0.25 mass% at 1 873 K. The equilibrium constants of Ti deoxidation reactions for the formation of pure solid Ti$_2$O$_3$ and Ti$_3$O$_5$, and the first- and second-order interaction parameters between Ti and O in liquid iron were determined as a function of temperature given by the following equa-

$$ 2T_i + 3O = T_i_{2}O_3 (s) \quad (0.25 < \text{mass}\% T_i < 4.75) $$

$$ \log K_{T_iO_3} = 44.238 / T - 13.0 $$

$$ 3T_i + 5O = T_i_3O_5 (s) \quad (0.0012 < \text{mass}\% T_i < 0.25) $$

$$ \log K_{T_i_3O_5} = 72.813 / T - 21.32 $$

$$ \epsilon_{T_i}^{O_0} = -1642 / T + 0.3358, \quad c_{T_i}^{O} = -4.915 / T + 1.005 $$

$$ r_{T_i}^{O_0} = 0.0385, \quad r_{T_i}^{O} = -0.355 $$

In addition, the activity coefficient of Ti in liquid iron at infinite dilution, $\gamma_{T_i}^{SSO}$ was assessed as 0.011, 0.014 and 0.018 at 1 823 K, 1 873 K and 1 923 K, respectively.

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