Temperature Dependence of Ti Deoxidation Equilibria of Liquid Iron in Coexistence with ‘Ti₃O₅’ and Ti₂O₃

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The equilibrium relation between Ti and O in liquid Fe has been measured only at 1 873 K on the condition of various kinds of titanium oxides saturation in our previous paper. The present work deals with the equilibrium between Ti and O in liquid Fe saturated with ‘Ti₃O₅’ and Ti₂O₃ at 1 823 K and 1 923 K for full understanding of temperature dependence. Also, equilibrium phase changes of titanium oxides with various Ti contents in molten Fe have been identified as the equilibrium titanium oxides with electron backscatter diffraction (EBSD) pattern analysis technique. The present results have been thermodynamically evaluated combining with previous results on the various thermodynamic values as a function of temperature.

The equilibrium constants and the interaction parameters of Wagner’s formalism were given as a function of temperature in the present work as follows.

\[
\frac{K_{Ti,O_2}}{K_{Ti,O_5}} = 2^{Ti} + 3^{O} \quad \text{at 1 823 K}
\]

\[
\log K_{Ti,O_5} = -42.940/T + 12.94, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

\[
e_0^{Ti} = -701/T + 0.0344, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

\[
\log K_{Ti,O_3} = -68.280/T + 19.95, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

\[
e_0^{Ti} = -701/T + 0.0344, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

The Henry constant of Ti in liquid Fe was estimated as a function of temperature.

\[
\ln y^{Ti}_0 = -20.890/T + 6.228, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

The self-interaction parameter of Ti in liquid Fe was obtained as a function of temperature.

\[
e_2^{Ti} = 212/T - 0.0640, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

The interaction parameters of Redlich–Kister type polynomial for molten Fe–Ti–O alloy were given as the following values in the present work.

\[
\beta^{0}_{Ti-O} = -173600 + 51.76 T/J, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

\[
\gamma^{0}_{Ti-O} = -1 189 000 + 82.00 T/J, \quad (1 823 \text{ K} < T < 1 923 \text{ K})
\]

The estimated results based on Wagner’s formalism as well as Darken’s quadratic formalism with Redlich–Kister type polynomials agreed well with the experimental results at 1 823 to 1 923 K.

KEY WORDS: thermodynamics; Ti deoxidation equilibrium; interaction parameter; quadratic formalism; Redlich–Kister polynomial; phase equilibria; titanium oxides; electron backscatter diffraction.

1. Introduction

Control of oxygen content in liquid iron is very important not only for the removed of impurities such as phosphorus and sulfur but also for the improvement of 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 is the basic knowledge for the precise control of Ti in the steelmaking process. Furthermore, it is suggested that fine titanium oxides induce high density nucleation sites for the grain refinement technique in oxide metallurgy technology.¹)

Due to such importance, a huge number of studies²–¹³) concerning the Ti and O equilibrium relation have been reported, where the Ti content in liquid iron has been up to 30 mass%. Our previously measured relation¹²,¹³) between the concentration of Ti and O at 1 873 K is reproduced in Fig. 1 with other researcher’s works.²–¹³) Substances in the
and O was evaluated only at 1873 K. There-

i in liquid Fe. Reliable
concentration in
equilibrium in liquid
analysis by
in liquid Fe.
concentrations at 1823 K and 1923 K ob-

fore, thermodynamic parameters derived in our previous

tion on Ti–O equilibrium in liquid iron are necessary for

temperature dependencies of the thermodynamic informa-
tion between Ti and O in liquid Fe contained in a
‘Ti3O5’ crucible (Outer Diameter: 28 mm, Inner Diam-
crucible of which inner wall was coated by mixture of
produced ‘Ti3O5’ was ground for the homogenization and
again reduced by H2 at 1773 K for 12 h for the successful
production of ‘Ti3O5’ powder. ‘Ti3O5’ powder was pressed
into a crucible shape using rubber dye and sintered at
1823 K and 1923 K. The quenched metal samples were cross-sectioned
and observed with an optical microscope to find out tita-

In the previous results,12,13) the equilibrium relation
between Ti and O was evaluated only at 1873 K. There-
fore, thermodynamic parameters derived in our previous
works12,13) do not include the temperature dependence of
equilibrium relation between Ti and O in liquid Fe. Reliable
temperature dependencies of the thermodynamic informa-
tion on Ti–O equilibrium in liquid iron are necessary for
the precise control of Ti in steelmaking process. The pres-
ent study was carried out for the temperature dependence of
the equilibrium relation between Ti and O in liquid Fe.
In the present study, the measurement of the equilibrium
relation between Ti and O in liquid Fe contained in a
‘Ti3O5’ (Since Ti3O5 is non-stoichiometric compound at
1823 to 1923 K as shown in Chap. 3.2, single quotation is
utilized.) crucible was carried out with various Ti contents
at 1823 K and 1923 K. The interface between Fe and
‘Ti3O5’ crucible was analyzed for identification of the equi-
librium titanium oxide phases with the automated indexing of
electron backscatter diffraction (EBSD) pattern analysis
technique. The measured equilibrium relation between Ti
and O in the molten Fe was thermodynamically utilized
combining with the previous results12,13) for temperature de-
pendence evaluation of various thermodynamic values
based on Wagner’s14) formalism and Darken’s quadratic formalism15,16) with Redlich–Kister type polynomial17,18) are also shown by
solid line in the Fig. 1.

In the present results,12,13) the equilibrium relation
between Ti and O in liquid Fe saturated with pure solid ‘Ti3O5’ after Cha et
al.12,13) at 1873 K with the various crucible materials.2–11)
parenthesis shows crucible materials used. Our equilibrium
lines of thermodynamically analyzed results after Wag-
ner’s14) formalism and Darken’s quadratic formalism15,16)
and Redlich–Kister type polynomial17,18) are also shown by

2. Experimental

Experimental equipment and procedure are essentially
the same as the previous works12,13) The ‘Ti3O5’ crucibles
were manufactured by ourselves from ‘Ti3O5’ powder as
follows. ‘TiO2’ anatase (99.8% purity) powder was reduced
to produce ‘Ti3O5’ powder by H2 at 1773 K for 12 h. The
produced ‘Ti3O5’ was ground for the homogenization and
again reduced by H2 at 1773 K for 12 h for the successful
production of ‘Ti3O5’ powder. ‘Ti3O5’ powder was pressed
into a crucible shape using rubber dye and sintered at
1823 K for 12 h under Ar–5%H2 atmosphere.

A ‘Ti3O5’ crucible (Outer Diameter: 22 mm, Inner Diam-
er: 22 mm, Height: 65 mm) charging with approximately
50 g of Fe–Ti alloy was set in an Al2O3 outer crucible and
the metal was melted under dehydrated and deoxidized
Ar+3%H2 stream of 100 ml/min with an induction furnace.
The Fe–Ti alloy specimen was prepared by melting an ap-
propriate amount of Ti and Fe and was held for 60 min at
1823 K and 1923 K. Temperature measurement was con-
ducted by an infrared radiation pyrometer, which was cali-
brated by the melting points of Fe and Cu. The melt
and crucible were quenched rapidly after the attainment of equi-
librium by switching off the power of the furnace and im-
pinging He gas on the sample surface. The cooling rate
during quench of the sample was about 30 K/s from 1873 to
1573 K. The quenched metal samples were cross-sectioned
and observed with an optical microscope to find out tita-
nium oxide inclusions. Cross section of a sample together with metal and ‘Ti3O5’ crucible is shown in Fig. 2. The central
part of metal sample was virtually clean without any noticeable inclusions, and the past was used for the chemi-

The surface of samples was polished for O analysis by
silicon carbide wet polishing papers (up to #1 500-grit) and
then electrically polished by the mixing solution (4:1) of
acetic acid (CH3COOH) and perchloric acid (HClO4) for
6 min with constant current of 0.5 A. The O concentration in
quenched samples was determined by an inert gas impulse
quenching He gas on the sample surface. The cooling rate dur-
ing quench of the sample was about 30 K/s from 1873 to
1573 K. The quenched metal samples were cross-sectioned
and observed with an optical microscope to find out tita-
nium oxide inclusions. Cross section of a sample together with metal and ‘Ti3O5’ crucible is shown in Fig. 2. The central
part of metal sample was virtually clean without any noticeable inclusions, and the past was used for the chemi-

The present results corresponded to those of Chino
et al.11) and Pak et al.1) with a Al2O3 crucible and Pak et al.11) with a Al2O3 crucible of which inner wall was coated by mixture of
‘Ti3O5’ and TiO2 powders (1:1 molar ratio). Recently, Pak et
al. determined the Ti deoxidation equilibrium in liquid iron as a function of temperature in contact with titanium oxide powder of a crucible formed in an Al₂O₃ crucible at 1 823 to 1 923 K using a high frequency induction furnace. They melted Fe containing from 0.0012 to 4.746 mass% Ti in an Al₂O₃ crucible, with inner wall coated by mixture of Ti₂O₃ and TiO₂ powders (1 : 1 molar ratio). They identified the stable region of titanium oxides equilibrated with the molten Fe of various Ti content using the XRD. They found that the first- and second-order interaction parameters should be introduced to express the activity coefficients of Ti and O. It will be discussed later.

However, Chino et al. did not cover a wide concentration range of titanium. They only measured low Ti concentration in liquid iron corresponding with ‘Ti₃O₅’ equilibrium region at 1 823 to 1 923 K. Pak et al. also did not measured the ‘Ti₃O₅’ equilibrium region at 1 823 K and 1 923 K. On the other hand, the present work has measured the wide range of Ti concentration in liquid iron coexisting with not only ‘Ti₃O₅’ but also Ti₂O₃ at 1 823 to 1 923 K.

### 3.1. Phase Identification of Titanium Oxides by EBSD Analysis

Many researchers have been tried to identify the stable region of titanium oxides equilibrated with the molten Fe with various Ti content using the XRD or the other equipments. However, there is huge uncertainty of identified equilibrium titanium oxides in the literatures. As a consequence of the complexity of Fe–Ti–O system, it is difficult to evaluate the equilibrium relation between dissolved Ti and O in molten Fe as mentioned in the previous works. EBSD patterns contain a large amount of information about the crystal structure. This crystallographic information is used to identify phases through the database of powder diffraction files. Fortunately, all of the crystal structure of titanium oxides are different each other. The identification of titanium oxide formed at the inner interface of the crucible can, therefore, be confirmed by EBSD analysis. A general introduction to EBSD is described in the previous work.

Various Ti contents of molten Fe were equilibrated with a ‘Ti₃O₅’ crucible at 1 823 K and 1 923 K with the various crucible materials. TiO₁ and TiO₂ powders (1 : 1 molar ratio). They identified the stable region of titanium oxides equilibrated with the molten Fe of various Ti content using the XRD. They found that the first- and second-order interaction parameters should be introduced to express the activity coefficients of Ti and O. It will be discussed later.

Fig. 3. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe at 1 823 K and 1 923 K with the various crucible materials. 

| [mass% Ti] | [mass% O] | Equilibrium analysis |
|-----------|-----------|----------------------|
| F-1       | 0.0045    | 0.0281               |
| F-2       | 0.0452    | 0.0469               |
| F-3       | 0.1055    | 0.0325               |
| F-4       | 0.1439    | 0.0207               |
| F-5       | 0.1734    | 0.0168               |
| F-6       | 0.1830    | 0.0273               |
| F-7       | 0.2120    | 0.0211               |
| F-8       | 0.2507    | 0.0309               |
| F-9       | 0.3050    | 0.0168               |
| F-10      | 0.3504    | 0.0167               |
| G-1       | 0.4765    | 0.0141               |
| G-2       | 0.7002    | 0.0166               |
| G-3       | 1.650     | 0.0117               |
| G-4       | 2.789     | 0.0053               |

### Table 3. Experimental results on the Ti–O equilibrium in liquid iron saturated with various kinds of titanium oxides at 1 923 K.

![Fig. 3. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe at 1 823 K and 1 923 K with the various crucible materials.](image-url)
Figure 4 shows the EBSD analysis results for Ti$_3$O$_5$. In this experiment, Fe–0.677mass%Ti alloy was melted in a ‘Ti$_3$O$_5$’ crucible at 1923 K. The crystal structure of ‘Ti$_3$O$_5$’ away from the melt/crucible interface was high temperature type of anosovite ‘Ti$\textsubscript{3}O_5$’ based on the EBSD analysis result. Central part (white circle in ×50) was zoomed with 200 times for the precise analysis of equilibrium titanium oxide. ‘Ti$\textsubscript{3}O_5$’, reacted with Ti in the melt during experiment and then Ti$_2$O$_3$ was formed as new phase at the melt/crucible interface. The crystal structure of Ti$_2$O$_3$ is high temperature type of trigonal based on the EBSD analysis result. Central part (white circle in ×200) was zoomed with 3000 times for the precise analysis of equilibrium titanium oxide in the same manner. The newly formed equilibrium phase covered uniformly on the original crucible inner wall, and thickness of the layer between melt and crucible was very thin. The crystal structure of iron was delta(δ)-iron. These results mean that the melt and crucible was successfully quenched by He gas impinging in the present experimental method.

The present EBSD analysis results of phase equilibria between the titanium oxides and molten Fe–Ti alloys at 1823 to 1923 K are summarized in Tables 1, 2 and 3. It became clearly that titanium oxide phases in equilibrium with liquid Fe–Ti alloys changed with the Ti contents in the melt.

3.2. Solid Solubility of Fe in Ti-oxide Phases by EDAX Analysis

The results of line analysis and EDAX image of ‘Ti$_3$O$_5$’ crucible interface melted Fe–0.0027mass%Ti at 1823 K are presented in Fig. 5. The results of line analysis and EDAX image of Ti$_2$O$_3$ phase are presented in Fig. 6 at the interface between ‘Ti$_3$O$_5$’ crucible and Fe–1.65mass%Ti at 1923 K. No trace of Fe and other elements were detected by EDAX analysis at the metal/crucible interface after the experiments. The trace of Fe at ‘Ti$_3$O$_5$’ crucible interface was observed when Ti content was less than 0.197mass% at 1823 K in molten Fe as shown in Fig. 7.

Figure 7 shows the solid solubility of Fe in titanium oxides at 1823 to 1923 K observed in the present work together with the work by Hadley and Derge$^3$ who investigated the solid solubility of Fe in TiO$_2$ phase quantitatively for the first time. Hadley and Derge$^3$, Suzuki and San-
bongi,9) Chino et al.6) and Pak et al.11) were also pointed out the solid solubility of Fe in ‘Ti3O5’ phase. This means that the activity of ‘Ti3O5’ equilibrated with molten Fe is less than unity based on the present experimental results. When ‘Ti3O5’ crucible was equilibrated with 0.37–4.886 mass% Ti at 1 823 K and 0.5–6.22 mass% Ti at 1 873 K and 0.6765–2.786 mass% Ti at 1 923 K, ‘Ti3O5’ reacted with Ti in Fe melts and then equilibrium phase was changed from ‘Ti3O5’ to Ti3O5 based on the present EBSSD results. Therefore, ‘Ti2O3’ crucible could be used in order to fix the activity of Ti3O5 as unity.

The present EDAX analysis results of the solid solubility of Fe in titanium oxides at 1 823 to 1 923 K are summarized in Tables 1, 2 and 3 also in Fig. 7.

Thermodynamical evaluation was carried out using the experimental results of A-3 to A-5 in Table 1, C-8 to C-10 in Table 2 and F-1 to F-10 in Table 3, where the solid solubility of Fe in Ti3O5 phase was negligibly small as shown in the Fig. 7. Unit activity of ‘Ti3O5’ was assumed in these cases where the Fe/Ti ratio was less than 0.05.

4. Discussion

Ti deoxidation results using other kinds of oxide crucibles such as MgO, Al2O3 had the possibility that the titanium oxide activity was not unity. The crucible materials react with titanium deoxidation products and form the intermediate compound or solid solution at the interface of crucibles. Therefore, only the present experimental results and those using titanium oxide crucibles3,9,10,12,13) shown in Figs. 1 and 3 are used for the thermodynamic consideration.

The calculation was carried out based on Wagner’s formalism14) and Darken’s quadratic formalism5,16) combined with Redlich–Kister type polynomial17,18) and the two formalisms were compared and discussed. The equation by Wagner14) has been widely used to express the activity coefficients when solute contents are rich. Darken15,16) has proposed the quadratic formalism to express the activity coefficients that can be applied to higher solute content. Darken’s quadratic formalism15,16) was converted into Redlich–Kister type polynomial17,18) using the excess Gibbs free energy change of mixing. It is useful to expand Darken’s quadratic formalism to multi-component alloy systems such as Fe–Ti–O–X system.

It is widely known that ‘TiO2’ forms extensive solid solution at 1 823 to 1 923 K. Thus, when ‘TiO2’ was formed as the Ti deoxidation product, the data did not utilize to evaluate thermodynamically in the present work, because the activity of ‘TiO2’ was not unity.

4.1. Thermodynamical Analysis by Wagner’s Formalism

4.1.1. Thermodynamics on 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 Ti3O5.

\[ \text{Ti}_3\text{O}_5(s) = 3\text{Ti}(l) + \text{O}_2(g) \] ...........................(1)

\[ K = \frac{h_0^{3\text{Ti}}}{h_0^{\text{Ti}_3\text{O}_5}}a_{\text{O}_2\text{r}} = \left(\frac{f_{\text{O}_2}^{\text{Ti}_3\text{O}_5}}{f_{\text{Ti}_3\text{O}_5}^{\text{Ti}_3\text{O}_5}}\right)^{\frac{3}{2}} \] ...........................(2)

where, \( K \), \( h_0 \), \( a \), \( h_0 \) and [%] denote the equilibrium constant, the Raoultian activity, the 1 mass% Henrian activity, the Henrian activity coefficient and concentration of i in liquid iron in mass%, respectively. The standard states of \( h_0 \) and \( h_0 \) 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 Eqs. (3) and (4) if the second order interaction parameter \( r_0^i \) was ignored as a first approximation. A detailed introduction of equations is described in the

Fig. 8. Determining \( e_{\text{Ti}_3\text{O}_5}^0 \), log \( K_{\text{Ti}_3\text{O}_5} \), and log \( K_{\text{Ti}_2\text{O}_3} \) in liquid Fe at 1 823 K.

previous work13)

\[ 2e_{\text{Ti}_3\text{O}_5}^{\text{Ti}}[\%\text{Ti}] + 3e_{\text{O}_2}^{\text{O}_2}[\%\text{O}] + 2\log[\%\text{Ti}] + 3\log[\%\text{O}] - 0.0173[\%\text{O}] = e_{\text{O}_2}^{\text{O}_2}(-3[\%\text{Ti}] - 5.985[\%\text{O}]) + \log K_{\text{Ti}_3\text{O}_5} \] ...........................(3)

\[ 3e_{\text{Ti}_3\text{O}_5}^{\text{Ti}}[\%\text{Ti}] + 5e_{\text{O}_2}^{\text{O}_2}[\%\text{O}] + 3\log[\%\text{Ti}] + 5\log[\%\text{O}] - 0.026[\%\text{O}] = e_{\text{O}_2}^{\text{O}_2}(-5[\%\text{Ti}] - 8.978[\%\text{O}]) + \log K_{\text{Ti}_3\text{O}_5} \] ...........................(4)

4.1.2. Determination of log \( K \), and \( e_{\text{Ti}_3\text{O}_5}^0 \)

The recommended values of the Japan Society for the Promotion of Science (JSPS)12) are adopted as \( e_{\text{Ti}_3\text{O}_5}^0 \) which are given by Eq. (5). Self-interaction parameter of Ti, \( e_{\text{Ti}_3\text{O}_5}^0 \), is derived from the multiple regression method with activity coefficient of Ti as described in the Sec. 4.1.4, are given by Eq. (6). This method is accompanied with iteration for the minimization of deviations.

\[ e_{\text{O}_2}^{\text{O}_2} - 1.750/T + 0.7622) \] ...........................(5)

\[ e_{\text{Ti}_3\text{O}_5}^0 = 212/T - 0.0640 \] ...........................(6)

The left hand sides of Eqs. (3) and (4) together with Eqs. (5) and (6) are plotted as vertical axis Y, and the term of \((-3[\%\text{Ti}] - 5.985[\%\text{O}]\)) and \((-5[\%\text{Ti}] - 8.978[\%\text{O}]\)) are taken as horizontal axis on the Ti2O3 and Ti3O5 saturated conditions at 1 823 to 1 923 K, respectively as shown in Fig. 8. The present thermodynamical evaluation was carried out by combining the previous experimental results12,13) and present experimental results of A-3 to A-5 in Table 1, C-8 to C-10 in Table 2 and F-1 to F-10 in Table 3 for ‘Ti3O5’ saturated condition and B-1 to B-9 in Table 1, D-1 to D-6 in Table 2 and G-1 to G-4 in Table 3 for Ti2O3 saturation.

Good linear relation was observed for each titanium oxide and temperature. It means that Eqs. (3) and (4) can well express the equilibrium relation between Ti and O in molten Fe at ‘Ti3O5’ and Ti2O3 saturation without the second order interaction parameters such as \( r_0^i \).

The interaction between Ti and O is the same 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
gave as the Ti deoxidation equilibrium constant
\( \log K_{\text{Ti}_3\text{O}_5} \), \( \log K_{\text{Ti}_2\text{O}_3} \), and the interaction pa-
\( e_{\text{O} \text{Ti}} \) from the intercept at the Y axis and the slope
based on the present and the other experimental data using
Ti oxide crucible.3,9,10,12,13]

The temperature functions of equilibrium constant
\( \log K_{\text{Ti}_3\text{O}_5} \), \( \log K_{\text{Ti}_2\text{O}_3} \) and the first order interaction parameter,
\( e_{\text{O} \text{Ti}} \) determined in the present work are given by Eqs. (7),
(8) and (9).

\[
\log K_{\text{Ti}_3\text{O}_5} = -68.280 / T + 19.95, \quad (1823 \text{ K} < T < 1923 \text{ K})
\]
\[
\begin{align*}
-17.50, & \quad 0.01<\text{mass}\%\text{Ti}<0.28, \quad \text{at } 1823 \text{ K} \\
-16.52, & \quad 0.006<\text{mass}\%\text{Ti}<0.40, \quad \text{at } 1873 \text{ K} \\
-15.56, & \quad 0.0045<\text{mass}\%\text{Ti}<0.52, \quad \text{at } 1923 \text{ K}
\end{align*}
\]

(7)

\[
\log K_{\text{Ti}_2\text{O}_3} = -42.940 / T + 12.94, \quad (1823 \text{ K} < T < 1923 \text{ K})
\]
\[
\begin{align*}
-10.61, & \quad 0.28<\text{mass}\%\text{Ti}<4.89, \quad \text{at } 1823 \text{ K} \\
-9.99, & \quad 0.40<\text{mass}\%\text{Ti}<6.22, \quad \text{at } 1873 \text{ K} \\
-9.39, & \quad 0.52<\text{mass}\%\text{Ti}<2.79, \quad \text{at } 1923 \text{ K}
\end{align*}
\]

(8)

\[
e_{\text{O} \text{Ti}} = -701 / T + 0.0344, \quad (1823 \text{ K} < T < 1923 \text{ K})
\]
\[
\begin{align*}
-0.35 & \quad \text{at } 1823 \text{ K} \\
-0.34 & \quad \text{at } 1873 \text{ K} \\
-0.33 & \quad \text{at } 1923 \text{ K}
\end{align*}
\]

(9)

The derived first order interaction parameter, \( e_{\text{O} \text{Ti}} \), was
\(-0.34\) in 1873 K, and the Ti deoxidation equilibrium constants were
\(-10.17\) for \( \text{Ti}_2\text{O}_3 \) and \(-16.86\) for \( \text{Ti}_3\text{O}_5 \), re-
spectively in our previous work.13 In the present work, Ti
deoxidation equilibrium constants was reevaluated taking
account of present results and previous results.12,13 Ti deox-
idation equilibrium constants is newly obtained as
\(-9.99\) for \( \text{Ti}_2\text{O}_3 \) and \(-16.52\) for \( \text{Ti}_3\text{O}_5 \) at 1873 K, respectively in
the present work.

Equations (7), (8) and (9) are compared with the litera-
\( \text{Fig. 9. Temperature dependence of } \log K_{\text{Ti}_2\text{O}_3} \text{ in liquid Fe at}
1823 \text{ to } 1923 \text{ K.}
\)

\( \text{Fig. 10. Temperature dependence of } \log K_{\text{Ti}_3\text{O}_5} \text{ in liquid Fe at}
1823 \text{ to } 1923 \text{ K.}
\)

\( \text{Fig. 11. Temperature dependence of } e_{\text{O} \text{Ti}} \text{ in liquid Fe at 1823 to}
1923 \text{ K.}
\)
The equilibrium line was drawn using the estimated values of SuZuki and Sanbongi. The work differs from most of the literature values and is in good agreement with that of Yavoskiy et al. Only Gosh and Murthy conducted the thermodynamic assessment on Ti deoxidation constant of TiO3.

Equation (15) is obtained by combining Eqs. (11) with Eqs. (12), (13) and (14). The interaction parameter, ϵO, determined in the present work differs from most of the literature values and is in good agreement with that of Yavoskiy et al. Only Gosh and Murthy conducted the thermodynamic assessment on Ti deoxidation constant of TiO3.

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Equations (15) and (16) at 1873 K after NIST-JANAF Thermochimical Tables and JSPS recommendation. The temperature functions of the activity coefficient, ln γTi(l), determined in the present work was given by Eq. (18).

\[
\gamma_{Ti(l)}^0 = \frac{\exp \left( \frac{AG_{1873K}^{Ti(l)}}{RT} \right) \times M_{Ti}}{M_{Fe}} = 0.0073
\]  

The temperature functions of the activity coefficient, ln γTi(l), determined in the present work was given by Eq. (18).

\[
\gamma_{Ti(l)}^0 = 20890/T + 6.228 \quad (1823 K < T < 1923 K)
\]

Equation (18) is compared with the literature values in Fig. 13. Recently, Bouchard and Bale, Jonsson and Dumitrescu and Hillert were thermodynamically assessed the solid solubility of Fe in TiO3. They are expected that this difference originates in the accuracy of Gibbs free energy of TiO3 formation and existence of the solid solubility of Fe in TiO3.

The temperature functions of the activity coefficient, ln γTi(l), determined in the present work was given by Eq. (18).

\[

\gamma_{Ti(l)}^0 = 0.0054 \quad (1823 K < T < 1923 K)
\]

Equation (18) is compared with the literature values in Fig. 13. Recently, Bouchard and Bale, Jonsson and Dumitrescu and Hillert were thermodynamically assessed the solid solubility of Fe in TiO3. They are expected that this difference originates in the accuracy of Gibbs free energy of TiO3 formation and existence of the solid solubility of Fe in TiO3.

The temperature functions of the activity coefficient, ln γTi(l), determined in the present work was given by Eq. (18).

\[

\gamma_{Ti(l)}^0 = 0.0054 \quad (1823 K < T < 1923 K)
\]
\( \Delta G^{\infty} = X_{Fe}X_{Ti} \left( \Omega_{Fe-Ti} + 1 \right) \) (19)  

Redlich–Kister (17, 18) type parameter of \( \Omega_{Fe-Ti} \) is obtained from the Henry constant of \( \gamma_{Ti}^{\infty} \) as Eq. (20) because of a negligible quantity of \( \Omega_{Fe-Ti}^{2} \) as described in the session 4.1.3 at 1873 K.  

\( \Omega_{Fe-Ti} = RT \ln \gamma_{Ti}^{\infty} = -76.630 J \) ...

The partial molar excess Gibbs free energy change, \( \Delta G_{Ti}^{\infty} \), can be express as Eq. (21) in Fe–Ti binary system,  

\[ \Delta G_{Ti}^{\infty} = \frac{RT}{\gamma_{Ti}^{\infty}} \ln \gamma_{Ti}^{\infty} = \Delta G^{\infty} \left( 1 - X_{Ti} \right) \]  

\[ = \Delta G^{\infty} + \left( 1 - X_{Ti} \right) \frac{\partial \Delta G^{\infty}}{\partial X_{Ti}} \]  

\[ = \Omega_{Fe-Ti}^{2} X_{Ti}^2 + \Omega_{Fe-Ti} X_{Ti} \]  

\[ = -76.630 + 153.260 X_{Ti} - 76.630 X_{Ti}^2 \]  

where \( R \) is gas constant and \( T \) is absolute temperature. Division of both sides of the Eq. (21) by \( RT \), followed by the substitution of 1 at 1873 K for \( T \) leads to the following Eq. (22).  

\[ \ln \gamma_{Ti}^{\infty} = -4.9206 + 9.8412 X_{Ti} - 4.9206 X_{Ti}^2 \]  

The partial differentialation of Eq. (22) for \( X_{Ti} \) results in the self-interaction coefficient of Ti based on mole fraction as follows:  

\[ \varepsilon_{Ti}^T = \lim_{X_{Ti} \to 0} \left( \frac{\partial \ln \gamma_{Ti}^{\infty}}{\partial X_{Ti}} \right) = 9.841 \]  

Self-interaction coefficient of Ti based on mass percentage can be estimated derived after Lippel (40) by utilizing the following relation, in which \( M_{s} \) denotes the molecular weight of the solvent and \( M_{i} \) denote molecular weight of solute of \( i^{th} \).  

\[ \varepsilon_{Ti}^I = 230 \frac{M_{s}}{M_{i}} \frac{M_{i} - M_{s} - M_{Fe}}{M_{Ti}} \]  

The temperature function of Ti self-interaction coefficient based on mass percentage, \( \varepsilon_{Ti}^T \), determined in the present work are given by Eqs. (25).  

\[ \varepsilon_{Ti}^T = 212.2 / T - 0.06400 \quad (1823 K < T < 1923 K) \]  

\[ 0.0524 \text{ at } 1823 K \]  

\[ 0.0492 \text{ at } 1873 K \]  

\[ 0.0463 \text{ at } 1923 K \]  

Equation (25) is compared with the literature values in Fig. 14. The self-interaction coefficient of Ti, \( \varepsilon_{Ti}^T \), determined in the present work differs from most of the literature values except for good agreement with that of Janke and Fischer (21) Suzuki et al. (24) and Kim et al. (24) at 1873 K.  

4.2. Thermodynamic Analysis by Quadratic Formalism with Redlich–Kister Type Polynomials (11–44)  

Thermodynamic analysis for Ti deoxidation of molten Fe is essentially the same as the previous work (11). Ti deoxidation reaction is expressed by Eq. (26).  

\[ Ti_{x}O_{y} = xTi + yO \]  

This equation is separated into the following two equations.  

\[ TiO_{x} = xTi + y/2 O_{2} \]  

Pure substance is chosen as a standard state (Raoultian standard state) for condensed phases in the present work, while dissolved oxygen in the melt equilibrated with 101 325 Pa (1 atm) oxygen gas is selected as a standard state in the present work (11, 22, 24). The relation between the oxygen activity and oxygen partial pressure can be expressed as follows in this standard state.  

\[ \alpha_{O_{2}} = (P_{O_{2}} / P_{O_{2}}^\infty)^{1/2} \]  

The Gibbs energy change of the reaction for Eq. (26) is identical to the minus value of the Gibbs energy of formation for \( TiO_{x} \) and that of Eq. (28) is zero due to the relation of Eq. (29). Therefore, the Gibbs energy change of the reaction for Eq. (26) is identical to the minus value of the Gibbs energy of formation for TiO, which is utilized for Ti deoxidation of any kinds of metal or alloy, and this has a great advantage. The equilibrium constant of Eq. (26), \( K_{Ti} \), can be expressed as follows,  

\[ \ln K_{Ti} = \frac{\Delta G_{TiO_{x}}}{RT} \]  

\[ = x \ln \gamma_{Ti}^x + y \ln \gamma_{O_{2}} + y \ln \gamma_{O_{2}} - \ln \alpha_{TiO_{x}} \]  

\[ = x \ln \gamma_{Ti}^x + y \ln \gamma_{O_{2}} + y \ln \gamma_{O_{2}} \]  

\[ \alpha_{TiO_{x}} = 1 \]  

\[ \alpha_{TiO_{x}} = 1 \]  

where, the activity of \( TiO_{x} \) is taken as unity in the present work.  

The following equation can be obtained form Eq. (30) for \( Ti_{x}O_{y} \),  

\[ \Delta G_{Ti_{x}O_{y}} = 2R \ln \gamma_{Ti}^x + 2RT \ln \gamma_{O_{2}} + 2RT \ln X_{Ti} + 2RT \ln X_{O_{2}} \]  

Equation (32) is obtained by substituting the partial molar excess Gibbs energy changes of Ti and O into Eq. (31). A detailed introduction of equations is described in the previous work (11).  

The following equation is also obtained form Eq. (30) for \( Ti_{x}O_{y} \).
\[ \Delta G_{T_i,T_iO_i} = 3RT \ln \gamma_Ti + 5RT \ln \gamma_{O_i} + 3RT \ln X_{T_i} + 5RT \ln X_{O_i} \]..............(33)

Equation (34) is derived by substituting the partial molar excess free energy changes of Ti and O into Eq. (33). A detailed introduction of equations is described in the previous work.13)

\[ 0 \Omega_{Fe–Ti}X_F = (-3 + 8X_{Ti}) \]
\[ + \Omega_{Fe–Ti}X_F = (-3X_{Fe} + 6X_{Ti} + 16X_{Fe}X_{Ti} - 16X_{Ti}^2) \]
\[ + \Omega_{Fe–O}X_F = (-5 + 8X_{Ti}) \]
\[ + \Omega_{Fe–O}X_F = (-5X_{Fe} + 10X_{Ti} + 16X_{Fe}X_{Ti} - 16X_{Ti}^2) \]
\[ + \Omega_{Ti–O}X_F = (-5X_{Ti} - 3X_{O} + 8X_{Ti}X_{O}) \]
\[ + RT(3 \ln X_{Ti} - 5 \ln X_{O}) + \Delta G_{T_i,T_iO_i} = 0 \]..............(34)

Equations (32) and (34) are the fundamental equation for thermodynamic analysis of Ti deoxidation in molten Fe. The binary interaction parameters, \( \Omega_{Fe–Ti} \) and \( \Omega_{Fe–O} \), were obtained from the Gibbs energy of oxygen dissolution into molten Fe and the self-interaction coefficient of oxygen in molten Fe.\(^{44} \) The Gibbs energy of formation of TiO\(_2\) was adopted from NIST-JANAF Thermochemical Tables.\(^{29} \) Redlich–Kister type parameter of \( \Omega_{Fe–Ti} \) was estimated from the negligible. Although the derived Redlich–Kister type parameter of \( \Omega_{Fe–Ti} \) was \(-73360/1 \) in 1873 K in our previous work.\(^{12,13} \) Redlich–Kister type parameter of \( \Omega_{Fe–Ti} \) is reevaluated as \(-76630/1 \) in the present work as mentioned in Sec. 4.1.2.

The parameters referred in the present work are shown below.

\[ 0 \Omega_{Fe–O} = -415400 + 142.47T \]
\[ \ln X_{Fe} - \ln X_{O} = 298300 - 1187.71 \]
\[ \ln X_{Fe} - \ln X_{O} = -173600 + 51.767T \]
\[ \ln X_{Fe} - \ln X_{O} = -173600 + 51.767T \]
\[ \Delta G_{T_i,T_iO_i} = -1521000 + 267.27T \]
\[ \Delta G_{T_i,T_iO_i} = -2465000 + 434.97T \]
\[ \ln X_{Ti} = 1730K < T < 1930K \]..............(35)

Equations (40) and (41) are obtained by rearranging Eqs. (32) and (34).

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

\[ Y_{Ti,O_3} = \Omega_{Fe–O}X_F = (-3 + 3X_{O}) \]
\[ + \Omega_{Fe–O}X_F = (-3X_{Fe} + 6X_{Ti} + 10X_{Fe}X_{Ti} - 10X_{Ti}^2) \]
\[ + \Omega_{Fe–O}X_F = (-5 + 8X_{Ti}) \]
\[ + \Omega_{Fe–O}X_F = (-5X_{Fe} + 10X_{Ti} + 16X_{Fe}X_{Ti} - 16X_{Ti}^2) \]
\[ - 2RT \ln X_{Ti} - 3RT \ln X_{O} + \Delta G_{T_i,T_iO_i} = 0 \]
\[ \ln X_{Ti} = 3X_{Ti} + 2X_{O} - 5X_{Ti}X_{O} \]..............(40)

For TiO\(_2\),

\[ Y_{Ti,O_2} = \Omega_{Fe–O}X_F = (-3 + 5X_{O}) \]
\[ + \Omega_{Fe–O}X_F = (-3X_{Fe} + 6X_{Ti} + 10X_{Fe}X_{Ti} - 10X_{Ti}^2) \]
\[ + \Omega_{Fe–O}X_F = (-5 + 8X_{Ti}) \]
\[ + \Omega_{Fe–O}X_F = (-5X_{Fe} + 10X_{Ti} + 16X_{Fe}X_{Ti} - 16X_{Ti}^2) \]
\[ - 3RT \ln X_{Ti} - 5RT \ln X_{O} + \Delta G_{T_i,T_iO_i} = 0 \]
\[ \ln X_{Ti} = 3X_{Ti} + 2X_{O} - 5X_{Ti}X_{O} \]..............(41)

Equations (40) and (41) are obtained by rearranging Eqs. (35)–(39) in Eq. (40) or (41) is plotted as a function of \( 3X_{Ti} + 2X_{O} - 5X_{Ti}X_{O} \) or Ti–O relation in Eqs. (40) and (41) for determining \( 0 \Omega_{Ti,0} \) at 1823 to 1923 K.

The equilibrium relation between \( Ti \) and \( O \) contents in molten Fe at 1873 K is compared with the experimental results by other researchers in Fig. 1. This equilibrium line was drawn using the Eqs. (32) to (39), the Gibbs energy of formation for TiO\(_2\) (referred from NIST-JANAF Thermochemical Tables\(^{29} \)) and the estimated parameters, Eq. (42), in the present work.

The estimated equilibrium curves based on Wagner’s\(^{14} \) formalism and Darken’s quadratic formalism\(^{15,16} \) with Redlich–Kister type polynomial\(^{17,18} \) show excellent agreement with the present experimental results as shown in Fig. 12. However, the curve based on Redlich–Kister type polynomial\(^{17,18} \) is likely to more precisely express the equilibrium relation between \( Ti \) and \( O \) contents in molten Fe than that based on Wagner’s\(^{14} \) formalism because Redlich–Kister type polynomial\(^{17,18} \) includes the higher order terms, too. Second order interaction parameters by Wagner’s\(^{14} \) 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\(^{15,16} \) includes all of the first and the second order terms represented by Wagner’s\(^{14} \) formalism as mentioned in the previous works.\(^{13} \) The concentration range of solutes, which Darken’s quadratic formalism\(^{15,16} \) can cover, is essentially wider than that by Wagner’s\(^{14} \) formalism. The Redlich–Kister type polynomial\(^{17,18} \) parameters are universal for any alloy systems. Redlich–Kister type polynomial parameters determined in the present work was useful to any composition such as Fe–Ti–X–O system. 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 formalism.
5. Conclusions

The equilibrium relation between dissolved Ti and O has been determined in liquid Fe saturated with \(\text{T}_2\text{O}_3\) and \(\text{Ti}_2\text{O}_3\) at 1823 K and 1923 K. The equilibrium phase changes of titanium oxides with various Ti contents in molten Fe has been identified with the electron backscatter diffraction (EBSD) pattern analysis technique in the present study.

The equilibrium constant of Ti deoxidation and the interaction parameters of Wagner’s formalism between Ti and O in liquid Fe saturated with titanium oxides were given as a function of temperature in the present work as follows.

\[ \log K_{\text{Ti}_2\text{O}_3} = -42,940/T + 12.94, \quad (1823 \text{ K} < T < 1923 \text{ K}) \]
\[ e^0_{\text{Ti}} = -701/T + 0.0344, \quad (1823 \text{ K} < T < 1923 \text{ K}) \]

The Henry constant of Ti in liquid Fe was assessed as a function of temperature as follows.

\[ \log K_{\text{Ti}_2\text{O}_3} = -68,280/T + 19.95, \quad (1823 \text{ K} < T < 1923 \text{ K}) \]
\[ e^0_{\text{Ti}} = -701/T + 0.0344, \quad (1823 \text{ K} < T < 1923 \text{ K}) \]

The self-interaction parameter of Ti in liquid Fe was assessed as a function of temperature as follows.

\[ \log K_{\text{Ti}_2\text{O}_3} = -17.50, 0.01<\text{mass}\%\text{Ti}<0.28, \quad (1823 \text{ K}) \]
\[ -16.52, 0.006<\text{mass}\%\text{Ti}<0.40, \quad (1873 \text{ K}) \]
\[ -15.56, 0.0045<\text{mass}\%\text{Ti}<0.52, \quad (1923 \text{ K}) \]

The derived temperature dependency of the thermodynamic information on Ti–O equilibrium in liquid Fe in the present work can be utilized for the precise control of Ti in steelmaking process.

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