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

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The equilibrium relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ 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 $\underline{\text{Ti}}$ and $\underline{\text{O}}$ in liquid Fe saturated with 'Ti₃O₅' and Ti₂O₃ at 1 823 K and 1 923 K for full understanding 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.

$$\log K_{\text{Ti}_2\text{O}_3} = -42\,940/T + 12.94, \quad (1\,823\text{ K} < T < 1\,923\text{ K}) \quad \begin{cases} -10.61, 0.28 < \text{mass\%Ti} < 4.89, \text{ at } 1\,823\text{ K} \\ -9.99, 0.40 < \text{mass\%Ti} < 6.22, \text{ at } 1\,873\text{ K} \\ -9.39, 0.52 < \text{mass\%Ti} < 2.79, \text{ at } 1\,923\text{ K} \end{cases}$$

$$e_{\text{O}}^{\underline{\text{Ti}}} = -701/T + 0.0344, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

$$\log K_{\text{'Ti}_3\text{O}_5\text{'}} = -68\,280/T + 19.95, \quad (1\,823\text{ K} < T < 1\,923\text{ K}) \quad \begin{cases} -17.50, 0.01 < \text{mass\%Ti} < 0.28, \text{ at } 1\,823\text{ K} \\ -16.52, 0.006 < \text{mass\%Ti} < 0.40, \text{ at } 1\,873\text{ K} \\ -15.56, 0.0045 < \text{mass\%Ti} < 0.52, \text{ at } 1\,923\text{ K} \end{cases}$$

$$e_{\text{O}}^{\underline{\text{Ti}}} = -701/T + 0.0344, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

$$\ln \gamma_{\text{Ti(l)}}^{\circ} = -20\,890/T + 6.228, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

$$e_{\text{Ti}}^{\underline{\text{Ti}}} = 212/T - 0.0640, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

$${}^0\Omega_{\text{Fe-Ti}} = -173\,600 + 51.76T/J, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

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 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 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 studies^{2–13)} 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 relation^{12,13)} between the concentration of $\underline{\text{Ti}}$ and $\underline{\text{O}}$ at 1 873 K is reproduced in **Fig. 1** with other researcher's works.^{2–13)} Substances in the

Fig. 1. Equilibrium relation between [mass% Ti] and [mass% O] in liquid Fe saturated with pure solid 'Ti₃O₅' after Cha *et al.*^{12,13} at 1 873 K with the various crucible materials.²⁻¹¹

parenthesis shows crucible materials used. Our equilibrium lines of thermodynamically analyzed results after Wagner's¹⁴ formalism and Darken's quadratic formalism^{15,16} with Redlich-Kister type polynomial^{17,18} are also shown by solid line in the Fig. 1.

In the previous results,^{12,13} the equilibrium relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ was evaluated only at 1 873 K. Therefore, thermodynamic parameters derived in our previous works^{12,13} do not include the temperature dependence of equilibrium relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ in liquid Fe. Reliable temperature dependencies of the thermodynamic information on Ti-O equilibrium in liquid iron are necessary for the precise control of Ti in steelmaking process. The present study was carried out for the temperature dependence of the equilibrium relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ 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 1 823 to 1 923 K as shown in Chap. 3.2, single quotation is utilized.) crucible was carried out with various Ti contents at 1 823 K and 1 923 K. The interface between Fe and 'Ti₃O₅' crucible was analyzed for identification of the equilibrium titanium oxides 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 results^{12,13} for temperature dependence evaluation of various thermodynamic values based on Wagner's¹⁴ formalism and Darken's quadratic formalism^{15,16} with Redlich-Kister type polynomial.^{17,18}

2. Experimental

Experimental equipment and procedure are essentially the same as the previous works.^{12,13} 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 1 773 K for 12 h. The

Fig. 2. Cross section of a sample together with metal and crucible.

produced 'Ti₃O₅' was ground for the homogenization and again reduced by H₂ at 1 773 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 1 823 K for 12 h under Ar-5%H₂ atmosphere.

A 'Ti₃O₅' crucible (Outer Diameter: 28 mm, Inner Diameter: 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 appropriate amount of Ti and Fe and was held for 60 min at 1 823 K and 1 923 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 rapidly after the attainment of equilibrium by switching off the power of the furnace and impinging He gas on the sample surface. The cooling rate during quench of the sample was about 30 K/s from 1 873 to 1 573 K. The quenched metal samples were cross-sectioned and observed with an optical microscope to find out titanium 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 chemical analyses.

The surface of samples was polished for $\underline{\text{O}}$ 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 0.5A. The $\underline{\text{O}}$ concentration in quenched samples was determined by an inert gas impulse infrared absorption spectroscopy. The concentration of $\underline{\text{Ti}}$ in the samples was determined by a high-frequency induction coupled plasma spectroscopy (ICP). All the formed oxide phases at the interface between melt and 'Ti₃O₅' crucible were analyzed by EBSD pattern analysis technique to identify the equilibrium titanium oxide phases. Solid solubility of Fe in Ti-oxide phases were analyzed quantitatively by EDAX analysis technique.

3. Experimental Results

Experimental results on the $\underline{\text{Ti}}$ - $\underline{\text{O}}$ equilibrium in liquid iron in coexistence with 'Ti₃O₅' and Ti₂O₃ are listed in Tables 1, 2 and 3. Figure 3 shows the equilibrium relation between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ concentrations at 1 823 K and 1 923 K observed in the present work together with other available literature values.^{3,6,8,10,11} Substances in the parenthesis shows crucible materials used. There is huge scatter on Ti deoxidation equilibrium relation in the literatures values.

The present results corresponded to those of Chino *et al.*⁶ with a Al₂O₃ crucible and Pak *et al.*¹¹ with a Al₂O₃ crucible of which inner wall was coated by mixture of Ti₂O₃ and TiO₂ powders (1 : 1 molar ratio). Recently, Pak *et*

Table 1. Experimental results on the Ti–O equilibrium in liquid iron saturated with various kinds of titanium oxides at 1 823 K.

	[mass% Ti]	[mass% O]	Fe/Ti ratio in Equilibrium Titanium Oxides	Equilibrium oxide by EBSD analysis
A-1	0.0027	0.0072	0.064	'Ti ₃ O ₅ '
A-2	0.0031	0.0051	0.057	'Ti ₃ O ₅ '
A-3	0.0605	0.0011	0.038	'Ti ₃ O ₅ '
A-4	0.1044	0.0009	0.016	'Ti ₃ O ₅ '
A-5	0.1969	0.0010	0.011	'Ti ₃ O ₅ '
B-1	0.3701	0.0005	-	Ti ₂ O ₃
B-2	0.4079	0.0007	-	Ti ₂ O ₃
B-3	0.5873	0.0007	-	Ti ₂ O ₃
B-4	0.7189	0.0005	-	Ti ₂ O ₃
B-5	0.7374	0.0007	-	Ti ₂ O ₃
B-6	1.092	0.0007	-	Ti ₂ O ₃
B-7	2.167	0.0010	-	Ti ₂ O ₃
B-8	2.252	0.0007	-	Ti ₂ O ₃
B-9	4.886	0.0039	-	Ti ₂ O ₃

Table 2. Experimental results on the Ti–O equilibrium in liquid iron saturated with various kinds of titanium oxides at 1 873 K.^{12,13)}

	[mass% Ti]	[mass% O]	Fe/Ti ratio in Equilibrium Titanium Oxides	Equilibrium oxide by EBSD analysis
C-1	0.0004	0.0230	0.159	'Ti ₃ O ₅ '
C-2	0.0005	0.0287	0.170	'Ti ₃ O ₅ '
C-3	0.0005	0.0114	0.176	'Ti ₃ O ₅ '
C-4	0.0007	0.0168	0.139	'Ti ₃ O ₅ '
C-5	0.0009	0.0173	0.129	'Ti ₃ O ₅ '
C-6	0.0014	0.0245	0.119	'Ti ₃ O ₅ '
C-7	0.0024	0.0181	0.091	'Ti ₃ O ₅ '
C-8	0.006	0.0103	0.041	'Ti ₃ O ₅ '
C-9	0.034	0.0028	0.020	'Ti ₃ O ₅ '
C-10	0.36	0.0013	0.015	'Ti ₃ O ₅ '
D-1	0.50	0.0008	-	Ti ₂ O ₃
D-2	0.87	0.0011	-	Ti ₂ O ₃
D-3	1.97	0.0010	-	Ti ₂ O ₃
D-4	2.17	0.0014	-	Ti ₂ O ₃
D-5	4.28	0.0028	-	Ti ₂ O ₃
D-6	6.22	0.0080	-	Ti ₂ O ₃
E-1	10.64	0.0164	-	'TiO'
E-2	14.13	0.0581	-	'TiO'
E-3	16.63	0.1036	-	'TiO'

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

	[mass% Ti]	[mass% O]	Fe/Ti ratio in Equilibrium Titanium Oxides	Equilibrium oxide by EBSD analysis
F-1	0.0045	0.0128	0.050	'Ti ₃ O ₅ '
F-2	0.0452	0.0049	0.032	'Ti ₃ O ₅ '
F-3	0.1035	0.0026	0.018	'Ti ₃ O ₅ '
F-4	0.1439	0.0021	0.018	'Ti ₃ O ₅ '
F-5	0.1734	0.0018	0.020	'Ti ₃ O ₅ '
F-6	0.1838	0.0023	0.021	'Ti ₃ O ₅ '
F-7	0.2120	0.0021	0.023	'Ti ₃ O ₅ '
F-8	0.2507	0.0030	0.021	'Ti ₃ O ₅ '
F-9	0.3924	0.0018	0.016	'Ti ₃ O ₅ '
F-10	0.5004	0.0017	0.014	'Ti ₃ O ₅ '
G-1	0.6765	0.0014	-	Ti ₂ O ₃
G-2	0.7802	0.0016	-	Ti ₂ O ₃
G-3	1.650	0.0017	-	Ti ₂ O ₃
G-4	2.786	0.0029	-	Ti ₂ O ₃

*al.*¹¹⁾ 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

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.^{3–11)}

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.*⁶⁾ 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.*¹¹⁾ also did not measure 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^{2–11,19)} 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.¹²⁾ 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.¹²⁾

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.^{20,21)} 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.^{12,20,21)}

Various Ti contents of molten Fe were equilibrated with a 'Ti₃O₅' crucible at 1 823 K and 1 923 K in the present work. Different titanium oxide phase in equilibrium was formed at the interface between Fe–Ti alloy and the original 'Ti₃O₅' crucible depending on the Ti contents. Therefore, the titanium oxide formed at the interface between the Fe–Ti alloy and the 'Ti₃O₅' crucible must be identified to establish the Ti–O equilibrium relation.

Fig. 4. FE-SEM cross section image of crucible coexisted with liquid Fe-0.676mass%Ti alloy and its corresponding EBSD patterns at 1923 K.

Figure 4 shows the EBSD analysis results for Ti_2O_3 . In this experiment, Fe-0.677mass%Ti alloy was melted in a ' Ti_3O_5 ' crucible at 1923 K. The crystal structure of ' Ti_3O_5 ' away from the melt/crucible interface was high temperature type of anosovite ' Ti_3O_5 ' based on the EBSD analysis result. Central part (white circle in $\times 50$) was zoomed with 200 times for the precise analysis of equilibrium titanium oxide. ' Ti_3O_5 ' reacted with Ti in the melt during experiment and then Ti_2O_3 was formed as new phase at the melt/crucible interface. The crystal structure of Ti_2O_3 is high temperature type of trigonal based on the EBSD analysis result. Central part (white circle in $\times 200$) was zoomed with 3 000 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_3O_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_2O_3 phase are presented in Fig. 6 at the interface between ' Ti_3O_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 experi-

Fig. 5. Line analysis result and EDAX image of Fe and Ti in the cross section of ' Ti_3O_5 ' crucible melting liquid Fe-0.0027mass%Ti at 1823 K.

Fig. 6. Line analysis result and EDAX image of Fe and Ti in the cross section of ' Ti_3O_5 ' crucible melting liquid Fe-1.65mass%Ti at 1923 K.

Fig. 7. Solid solubility of Fe in ' Ti_3O_5 ' phase at 1823 to 1923 K.

ments. The trace of Fe at ' Ti_3O_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 Derge³⁾ who investigated the solid solubility of Fe in TiO_x 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% at 1 923 K, 'Ti₃O₅' reacted with Ti in Fe melts and then equilibrium phase was changed from 'Ti₃O₅' to Ti₂O₃ based on the present EBSD results. Therefore, 'Ti₃O₅' crucible could be used in order to fix the activity of Ti₂O₃ 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 and 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 crucibles^{3,5,9,10,12,13)} 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 formalism^{15,16)} combined with Redlich–Kister type polynomial,^{17,18)} and the two formalisms were compared and discussed. The equation by Wagner¹⁴⁾ 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^{15,16)} has proposed the quadratic formalism to express the activity coefficients that can be applied to higher solute content. Darken's quadratic formalism^{15,16)} was converted into Redlich–Kister type polynomial^{17,18)} 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–X–O system.

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

$$K = (h_{\text{Ti}}^x \cdot h_{\text{O}}^y) / a_{\text{Ti}_x\text{O}_y(\text{s})} = \{f_{\text{Ti}}^x [\% \text{Ti}]^x \cdot f_{\text{O}}^y [\% \text{O}]^y\} / a_{\text{Ti}_x\text{O}_y(\text{s})} \dots\dots(2)$$

where, K , a , h , f and $[\%i]$ 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_{Ti} and h_{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 Eqs. (3) and (4) if the second order interaction parameter r_{O}^{Ti} was ignored as a first approximation. A detailed introduction of equations is described in the

Fig. 8. Determining e_{O}^{Ti} , $\log K_{\text{Ti}_2\text{O}_3}$ and $\log K_{\text{Ti}_3\text{O}_5}$ in liquid Fe at 1 823 to 1 923 K.

previous work.¹³⁾

$$\begin{aligned} & 2e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + 3e_{\text{O}}^{\text{O}}[\% \text{O}] + 2 \log[\% \text{Ti}] \\ & \quad + 3 \log[\% \text{O}] - 0.0173[\% \text{O}] \\ & = e_{\text{O}}^{\text{Ti}}(-3[\% \text{Ti}] - 5.985[\% \text{O}]) + \log K_{\text{Ti}_2\text{O}_3} \dots\dots\dots(3) \end{aligned}$$

$$\begin{aligned} & 3e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + 5e_{\text{O}}^{\text{O}}[\% \text{O}] + 3 \log[\% \text{Ti}] \\ & \quad + 5 \log[\% \text{O}] - 0.026[\% \text{O}] \\ & = e_{\text{O}}^{\text{Ti}}(-5[\% \text{Ti}] - 8.978[\% \text{O}]) + \log K_{\text{Ti}_3\text{O}_5} \dots\dots\dots(4) \end{aligned}$$

4.1.2. Determination of $\log K$, and e_{O}^{Ti}

The recommended values of the Japan Society for the Promotion of Science (JSPS)²²⁾ are adopted as e_{O}^{O} , which are given by Eq. (5). Self-interaction parameter of Ti, $e_{\text{Ti}}^{\text{Ti}}$, 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.

$$e_{\text{O}}^{\text{O}} = -1750/T + 0.76^{22)} \dots\dots\dots(5)$$

$$e_{\text{Ti}}^{\text{Ti}} = 212/T - 0.0640 \dots\dots\dots(6)$$

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 results^{12,13)} 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' saturation 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_{O}^{Ti} .

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 straight lines in Fig. 8 gave as the Ti deoxidation equilibrium constant $\log K_{\text{Ti}_2\text{O}_3}$, $\log K_{\text{Ti}_3\text{O}_5}$ and the interaction parameter e_{O}^{Ti} from the intercept at the Y axis and the slope based on the present and the other experimental data using Ti oxide crucible.^{3,5,9,10,12,13)}

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

$$\log K_{\text{Ti}_3\text{O}_5} = -68280/T + 19.95, \quad (1823 \text{ K} < T < 1923 \text{ K})$$

$$\begin{pmatrix} -17.50, 0.01 < \text{mass\%Ti} < 0.28, \text{ at } 1823 \text{ K} \\ -16.52, 0.006 < \text{mass\%Ti} < 0.40, \text{ at } 1873 \text{ K} \\ -15.56, 0.0045 < \text{mass\%Ti} < 0.52, \text{ at } 1923 \text{ K} \end{pmatrix} \dots\dots(7)$$

$$\log K_{\text{Ti}_2\text{O}_3} = -42940/T + 12.94, \quad (1823 \text{ K} < T < 1923 \text{ K})$$

$$\begin{pmatrix} -10.61, 0.28 < \text{mass\%Ti} < 4.89, \text{ at } 1823 \text{ K} \\ -9.99, 0.40 < \text{mass\%Ti} < 6.22, \text{ at } 1873 \text{ K} \\ -9.39, 0.52 < \text{mass\%Ti} < 2.79, \text{ at } 1923 \text{ K} \end{pmatrix} \dots\dots(8)$$

$$e_{\text{O}}^{\text{Ti}} = -701/T + 0.0344 \quad (1823 \text{ K} < T < 1923 \text{ K})$$

$$\begin{pmatrix} -0.35 \text{ at } 1823 \text{ K} \\ -0.34 \text{ at } 1873 \text{ K} \\ -0.33 \text{ at } 1923 \text{ K} \end{pmatrix} \dots\dots(9)$$

The derived first order interaction parameter, e_{O}^{Ti} , was -0.34 in 1873 K , and the Ti deoxidation equilibrium constants were -10.17 for Ti_2O_3 and -16.86 for Ti_3O_5 , respectively 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 deoxidation equilibrium constants is newly obtained as -9.99 for Ti_2O_3 and -16.52 for Ti_3O_5 at 1873 K , respectively in the present work.

Equations (7), (8) and (9) are compared with the literature values in Figs. 9, 10 and 11. The equilibrium constant on Ti_3O_5 determined in the present work is in good agree-

Fig. 9. Temperature dependence of $\log K_{\text{Ti}_3\text{O}_5}$ in liquid Fe at 1823 to 1923 K.

ment with that of Suzuki and Sanbongi⁹⁾ who considered the same solid solubility of Fe in Ti_3O_5 as the present work when they derived the equilibrium constant on Ti_3O_5 . However, they did not determine the temperature dependency of Ti deoxidation equilibrium constant of Ti_3O_5 . They also did not derived Ti deoxidation equilibrium constant of Ti_2O_3 . Gosh and Murthy²³⁾ and Pak *et al.*¹¹⁾ have conducted the thermodynamic estimation of Ti deoxidation constant activity of Ti_3O_5 . Chino *et al.*⁶⁾ pointed out the solid solubility of Fe in Ti_3O_5 . However, they did not consider the solid solubility of Fe in Ti_3O_5 when they derived the equilibrium constant on Ti_3O_5 . They assumed the activity of Ti_3O_5 is unity although the existence of the solid solubility of Fe in Ti_3O_5 .

The equilibrium constant on Ti_2O_3 determined in the

Fig. 10. Temperature dependence of $\log K_{\text{Ti}_2\text{O}_3}$ in liquid Fe at 1823 to 1923 K.

Fig. 11. Temperature dependence of e_{O}^{Ti} in liquid Fe at 1823 to 1923 K.

Fig. 12. Equilibrium relation between [%Ti] and [%O] in liquid Fe at 1823 to 1923 K.

present work is in good agreement with that of Yavoytskiy *et al.*²⁶⁾ The equilibrium constant of Ti_2O_3 determined in the present work differs from Pak *et al.*¹¹⁾ Only Gosh and Murthy²³⁾ conducted the thermodynamic assessment on Ti deoxidation constant of Ti_2O_3 .

The interaction parameter, e_{Ti}^{O} , determined in the present work differs from most of the literature values and is in good agreement with that of Suzuki and Sanbongi⁹⁾ and Kulikov.²⁹⁾ The estimated relation between equilibrium Ti and O contents in molten Fe based on Wagner's formalism¹⁴⁾ are shown in Fig. 12 with the experimental results. This equilibrium line was drawn using the estimated values in the present work. The results by Darken's formalism^{15,16)} with Redlich-Kister^{17,18)} type polynomial is also shown in this figure. These results of Ti equilibrium relation of two formalisms will be discussed and compared in Chap. 4.2.

4.1.3. Determination of $\gamma_{\text{Ti(l)}}^{\text{O}}$

Activity coefficient of Ti in liquid Fe, $\gamma_{\text{Ti(l)}}^{\text{O}}$, is evaluated from the derived Ti deoxidation equilibrium constant $\log K$. Ti deoxidation equilibrium constant of -9.99 on Ti_2O_3 gives $\Delta G_{(10)1873\text{K}}^{\text{O}}$ as the Eq. (11) at 1873 K.

$$\Delta G_{(10)1873\text{K}}^{\text{O}} = -RT \ln K_{(10)} = 358\,000 \text{ J} \dots \dots \dots (11)$$

The Gibbs free energies of Ti_2O_3 formation, Ti fusion, and oxygen dissolution in molten Fe are shown by Eqs. (12), (13) and (14) at 1873 K after NIST-JANAF Thermochemical Tables³⁰⁾ and JSPS recommendation.²²⁾

Equation (15) is obtained by combining Eqs. (11) with Eqs. (12), (13) and (14).

Gibbs energy of Ti dissolution, $\Delta G_{(15)1873\text{K}}^{\text{O}}$, is shown by the following Eq. (16).

$$\Delta G_{(15)1873\text{K}}^{\text{O}} = RT \ln \left(\frac{\gamma_{\text{Ti(l)}}^{\text{O}} \times M_{\text{Fe}}}{100 \times M_{\text{Ti}}} \right) \dots \dots \dots (16)$$

Where, M_{Fe} and M_{Ti} denote the molecular weight of Fe and Ti, respectively. The activity coefficient $\gamma_{\text{Ti(l)}}^{\text{O}}$ can, therefore,

Fig. 13. Temperature dependence of $\gamma_{\text{Ti}}^{\text{O}}$ in liquid Fe at 1823 to 1923 K.

be calculated as 0.0073 at 1873 K by substituting $\Delta G_{(15)1873\text{K}}^{\text{O}}$ into the Eq. (16). The derived activity coefficient, $\gamma_{\text{Ti(l)}}^{\text{O}}$, was 0.0090 in 1873 K in our previous work.¹³⁾ However, the activity coefficient was reevaluated as 0.0073 in the present work as mentioned in Sec. 4.1.2.

$$\frac{\exp \left(\frac{\Delta G_{(15)1873\text{K}}^{\text{O}}}{RT} \right) \times 100 \times M_{\text{Ti}}}{M_{\text{Fe}}} = \gamma_{\text{Ti(l)}}^{\text{O}} = 0.0073 \dots (17)$$

The deoxidation equilibrium constant corresponding to ' Ti_3O_5 ' was used for the same calculation, and almost same value of 0.0069 was obtained at 1873 K as $\gamma_{\text{Ti(l)}}^{\text{O}}$. It is expected that this difference originates in the accuracy of Gibbs free energy of ' Ti_3O_5 ' formation and existence of the solid solubility of Fe in ' Ti_3O_5 '.

The temperature functions of the activity coefficient, $\ln \gamma_{\text{Ti(l)}}^{\text{O}}$, determined in the present work was given by Eq. (18).

$$\gamma_{\text{Ti(l)}}^{\text{O}} = -20\,890/T + 6.228 \quad (1823 \text{ K} < T < 1923 \text{ K})$$

$$\left(\begin{array}{l} \gamma_{\text{Ti(l)}}^{\text{O}} = 0.0054 \text{ at } 1823 \text{ K} \\ \gamma_{\text{Ti(l)}}^{\text{O}} = 0.0073 \text{ at } 1873 \text{ K} \\ \gamma_{\text{Ti(l)}}^{\text{O}} = 0.0097 \text{ at } 1923 \text{ K} \end{array} \right) \dots \dots \dots (18)$$

Equation (18) is compared with the literature values in Fig. 13. Recently, Bouchard and Bale,³⁶⁾ Jonsson³⁸⁾ and Dumitrescu and Hillert³⁹⁾ were thermodynamically assessed Fe-Ti binary system with literature values. Previous values vary more than one order from 0.004 to 0.050, and most of them are about one order larger than ours. However, the activity coefficient, $\gamma_{\text{Ti(l)}}^{\text{O}}$, determined in the present work is in good agreement with the values of 0.0071 obtained by Suzuki *et al.*⁸⁾ and 0.0070 obtained by Averin²⁸⁾ at 1873 K.

4.1.4. Determination of $e_{\text{Ti}}^{\text{Ti}}$

The excess free energy change of mixing on Fe-Ti binary system can be expressed as Eq. (19).

$$\Delta G^{\text{ex}} = X_{\text{Fe}} X_{\text{Ti}} \{ {}^0\Omega_{\text{Fe-Ti}} + {}^1\Omega_{\text{Fe-Ti}} (X_{\text{Fe}} - X_{\text{Ti}}) \} \dots\dots\dots(19)$$

Redlich–Kister^{17,18)} type parameter of ${}^0\Omega_{\text{Fe-Ti}}$ is obtained from the Henry constant of $\gamma_{\text{Ti(l)}}$ as Eq. (20) because of a negligible quantity of ${}^1\Omega_{\text{Fe-Ti}}$ as described in the session 4.1.3 at 1 873 K.

$${}^0\Omega_{\text{Fe-Ti}} = RT \ln \gamma_{\text{Ti(l)}}^{\circ} = -76\,630/\text{J} \dots\dots\dots(20)$$

The partial molar excess Gibbs free energy change, $\Delta \bar{G}_{\text{Ti(l)}}^{\text{ex}}$, can be express as Eq. (21) in Fe–Ti binary system,

$$\begin{aligned} \Delta \bar{G}_{\text{Ti(l)}}^{\text{ex}} &= RT \ln \gamma_{\text{Ti(l)}} \\ &= \Delta G^{\text{ex}} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} \\ &= {}^0\Omega_{\text{Fe-Ti}} - 2 {}^0\Omega_{\text{Fe-Ti}} X_{\text{Ti}} + {}^0\Omega_{\text{Fe-Ti}} X_{\text{Ti}}^2 \\ &= -76\,630 + 153\,260 X_{\text{Ti}} - 76\,630 X_{\text{Ti}}^2 \dots\dots\dots(21) \end{aligned}$$

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 1 873 K for T leads to the following Eq. (22).

$$\ln \gamma_{\text{Ti(l)}} = -4.9206 + 9.8412 X_{\text{Ti}} - 4.9206 X_{\text{Ti}}^2 \dots\dots\dots(22)$$

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

$$\varepsilon_{\text{Ti}}^{\text{Ti}} = \lim_{\substack{X_{\text{Fe}} \rightarrow 1 \\ X_{\text{Ti}} \rightarrow 0}} \left(\frac{\partial \ln \gamma_{\text{Ti(l)}}}{\partial X_{\text{Ti}}} \right) = 9.841 \dots\dots\dots(23)$$

Self-interaction coefficient of Ti based on mass percentage can be estimated derived after Lupis⁴⁰⁾ by utilizing the following relation, in which M_1 denotes the molecular weight of the solvent and M_j denote the molecular weight of solute of “j”.

$$\varepsilon_i^j = 230 \frac{M_j}{M_1} e_i^j + \frac{M_1 - M_j}{M_1} \dots\dots\dots(24)$$

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

$$\begin{aligned} e_{\text{Ti}}^{\text{Ti}} &= 212.2/T - 0.06400 \quad (1\,823\,\text{K} < T < 1\,923\,\text{K}) \\ &\quad \begin{pmatrix} 0.0524 \text{ at } 1\,823\,\text{K} \\ 0.0492 \text{ at } 1\,873\,\text{K} \\ 0.0463 \text{ at } 1\,923\,\text{K} \end{pmatrix} \dots\dots\dots(25) \end{aligned}$$

Equation (25) is compared with the literature values in Fig. 14. The self-interaction coefficient of Ti, $e_{\text{Ti}}^{\text{Ti}}$, determined in the present work differs from most of the literature values except for good agreement with that of Janke and Fischer,⁵⁾ Suzuki *et al.*⁸⁾ and Kim *et al.*⁴¹⁾ at 1 873 K.

4.2. Thermodynamic Analysis by Quadratic Formalism with Redlich–Kister Type Polynomial^{41–44)}

Thermodynamic analysis for Ti deoxidation of molten Fe is essentially the same as the previous work.¹³⁾ Ti deoxidation reaction is expressed by Eq. (26).

This equation is separated into the following two equations.

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

Fig. 14. Temperature dependence of self-interaction parameter of titanium in liquid Fe at 1 823 to 1 923 K.

101 325 Pa (1 atm) oxygen gas is selected as a standard state in the present work.^{13,42–44)} The relation between the oxygen activity and oxygen partial pressure can be expressed as follows in this standard state.

$$a_{\text{O}} = (P_{\text{O}_2}/P^{\circ})^{1/2} \dots\dots\dots(29)$$

The Gibbs energy change of the reaction for Eq. (26) is identical to the minus value of the Gibbs energy of formation for Ti_xO_y ($-\Delta G_{\text{f,Ti}_x\text{O}_y}^{\circ}$) 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 Ti_xO_y ($-\Delta G_{\text{f,Ti}_x\text{O}_y}^{\circ}$), 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,

$$\begin{aligned} \ln K_{\text{Ti}} &= \frac{\Delta G_{\text{f,Ti}_x\text{O}_y}^{\circ}}{RT} \\ &= x \ln \gamma_{\text{Ti}} + y \ln \gamma_{\text{O}} + x \ln X_{\text{Ti}} + y \ln X_{\text{O}} - \ln a_{\text{Ti}_x\text{O}_y} \\ &= x \ln \gamma_{\text{Ti}} + y \ln \gamma_{\text{O}} + x \ln X_{\text{Ti}} + y \ln X_{\text{O}} \quad (\because a_{\text{Ti}_x\text{O}_y} = 1) \end{aligned} \dots\dots\dots(30)$$

where, the activity of Ti_xO_y is taken as unity in the present work.

The following equation can be obtained from Eq. (30) for Ti_2O_3 .

$$\begin{aligned} \Delta G_{\text{f,Ti}_2\text{O}_3}^{\circ} &= 2RT \ln \gamma_{\text{Ti}} + 2RT \ln \gamma_{\text{O}} \\ &\quad + 2RT \ln X_{\text{Ti}} + 3RT \ln X_{\text{O}} \dots\dots\dots(31) \end{aligned}$$

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.¹³⁾

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

The following equation is also obtained from Eq. (30) for ‘ Ti_3O_5 ’.

$$\Delta G_{f, \text{Ti}_2\text{O}_3}^\circ = 3RT \ln \gamma_{\text{Ti}} + 5RT \ln \gamma_{\text{O}} + 3RT \ln X_{\text{Ti}} + 5RT \ln X_{\text{O}} \dots \dots \dots (33)$$

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⁾

$$\begin{aligned} & {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3+8X_{\text{Ti}}) \\ & + {}^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{Ti}}+16X_{\text{Fe}}X_{\text{Ti}}-16X_{\text{Ti}}^2) \\ & + {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5+8X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5X_{\text{Fe}}+10X_{\text{O}}+16X_{\text{Fe}}X_{\text{O}}-16X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Ti-O}}(-5X_{\text{Ti}}-3X_{\text{O}}+8X_{\text{Ti}}X_{\text{O}}) \\ & + RT(-3 \ln X_{\text{Ti}}-5 \ln X_{\text{O}}) + \Delta G_{f, \text{Ti}_2\text{O}_3}^\circ = 0 \dots \dots \dots (34) \end{aligned}$$

Equations (32) and (34) are the fundamental equation for thermodynamic analysis of Ti deoxidation in molten Fe. The binary interaction parameters, ${}^0\Omega_{\text{Fe-O}}$ and ${}^1\Omega_{\text{Fe-O}}$, 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 Ti_2O_3 was adopted from NIST-JANAF Thermochemical Tables.²⁹⁾ Redlich-Kister type parameter of ${}^0\Omega_{\text{Fe-Ti}}$ was estimated from the negligible. Although the derived Redlich-Kister type parameter of ${}^0\Omega_{\text{Fe-Ti}}$ was $-73\,360/\text{J}$ in 1873 K in our previous work.^{12,13)} Redlich-Kister type parameter of ${}^0\Omega_{\text{Fe-Ti}}$ is reevaluated as $-76\,630/\text{J}$ in the present work as mentioned in Sec. 4.1.2.

The parameters referred in the present work are shown below.

$${}^0\Omega_{\text{Fe-O}} = -415\,400 + 142.4T/\text{J} \quad (1\,823\,\text{K} < T < 1\,973\,\text{K})^{44)} \dots \dots \dots (35)$$

$${}^1\Omega_{\text{Fe-O}} = 298\,300 - 117.8T/\text{J} \quad (1\,823\,\text{K} < T < 1\,973\,\text{K})^{44)} \dots \dots \dots (36)$$

$${}^0\Omega_{\text{Fe-Ti}} = -173\,600 + 51.76T/\text{J} \quad (1\,823\,\text{K} < T < 1\,923\,\text{K}) \dots \dots \dots (37)$$

$$\Delta G_{f, \text{Ti}_2\text{O}_3}^\circ = -1\,521\,000 + 267.2T/\text{J} \quad (1\,730\,\text{K} < T < 1\,930\,\text{K})^{29)} \dots \dots \dots (38)$$

$$\Delta G_{f, \text{Ti}_3\text{O}_5}^\circ = -2\,465\,000 + 434.9T/\text{J} \quad (1\,730\,\text{K} < T < 1\,930\,\text{K})^{29)} \dots \dots \dots (39)$$

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

For Ti_2O_3 ,

$$\begin{aligned} Y_{\text{Ti}_2\text{O}_3} &= {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-3+5X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{O}}+10X_{\text{Fe}}X_{\text{O}}-10X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-2+5X_{\text{Ti}}) \\ & + 2{}^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-X_{\text{Fe}}+2X_{\text{Ti}}+5X_{\text{Fe}}X_{\text{Ti}}-5X_{\text{Ti}}^2) \\ & - 2RT \ln X_{\text{Ti}} - 3RT \ln X_{\text{O}} + \Delta G_{f, \text{Ti}_2\text{O}_3}^\circ \\ & = {}^0\Omega_{\text{Ti-O}}(3X_{\text{Ti}}+2X_{\text{O}}-5X_{\text{Ti}}X_{\text{O}}) \dots \dots \dots (40) \end{aligned}$$

For ' Ti_3O_5 ',

$$\begin{aligned} Y_{\text{Ti}_3\text{O}_5} &= {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5+8X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5X_{\text{Fe}}+10X_{\text{O}}+16X_{\text{Fe}}X_{\text{O}}-16X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3+8X_{\text{Ti}}) \\ & + {}^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{Ti}}+16X_{\text{Fe}}X_{\text{Ti}}-16X_{\text{Ti}}^2) \\ & - 3RT \ln X_{\text{Ti}} - 5RT \ln X_{\text{O}} + \Delta G_{f, \text{Ti}_3\text{O}_5}^\circ \\ & = {}^0\Omega_{\text{Ti-O}}(5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}) \dots \dots \dots (41) \end{aligned}$$

$Y_{\text{Ti}_2\text{O}_3}$ or $Y_{\text{Ti}_3\text{O}_5}$ using values of Eqs. (35)–(39) in Eq. (40) or (41) is plotted as a function of $3X_{\text{Ti}}+2X_{\text{O}}-5X_{\text{Ti}}X_{\text{O}}$ or

Fig. 15. Relation in Eqs. (40) and (41) for determining ${}^0\Omega_{\text{Ti-O}}$ at 1823 to 1923 K.

$5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}$ in Fig. 15 using the present experimental results and other researcher's results using titanium oxide crucible.^{3,5,9,10,12,13)} ${}^0\Omega_{\text{Ti-O}}$ is evaluated from the slope of the regressed line through the origin in this figure. ${}^0\Omega_{\text{Ti-O}}$ was determined as a function of temperature and was given by Eq. (42).

$${}^0\Omega_{\text{Ti-O}} = -1\,189\,000 + 82.00T/\text{J} \quad (1\,823\,\text{K} < T < 1\,923\,\text{K}) \dots \dots \dots (42)$$

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 Ti_2O_3 (referred from NIST-JANAF Thermochemical Tables²⁹⁾) and the estimated parameters, Eq. (42), in the present work.

The estimated equilibrium curves based on Wagner's¹⁴⁾ 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's¹⁴⁾ formalism because Redlich-Kister type polynomial^{17,18)} includes the higher order terms, too. Second order interaction parameters by Wagner's¹⁴⁾ 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's¹⁴⁾ 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's¹⁴⁾ 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 ' Ti_3O_5 ' and Ti_2O_3 at 1 823 K and 1 923 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.

$$\log K_{\text{Ti}_2\text{O}_3} = -42\,940/T + 12.94, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

$$\left(\begin{array}{l} -10.61, 0.28 < \text{mass\%Ti} < 4.89, \text{ at } 1\,823\text{ K} \\ -9.99, 0.40 < \text{mass\%Ti} < 6.22, \text{ at } 1\,873\text{ K} \\ -9.39, 0.52 < \text{mass\%Ti} < 2.79, \text{ at } 1\,923\text{ K} \end{array} \right)$$

$$e_{\text{O}}^{\text{Ti}} = -701/T + 0.0344, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

$$\log K_{\text{Ti}_3\text{O}_5} = -68\,280/T + 19.95, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

$$\left(\begin{array}{l} -17.50, 0.01 < \text{mass\%Ti} < 0.28, \text{ at } 1\,823\text{ K} \\ -16.52, 0.006 < \text{mass\%Ti} < 0.40, \text{ at } 1\,873\text{ K} \\ -15.56, 0.0045 < \text{mass\%Ti} < 0.52, \text{ at } 1\,923\text{ K} \end{array} \right)$$

$$e_{\text{O}}^{\text{Ti}} = -701/T + 0.0344, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

$$\ln \gamma_{\text{Ti(l)}}^{\circ} = -20\,890/T + 6.228, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

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

The interaction parameters of Redlich–Kister type polynomial between Ti(l) and O in molten Fe saturated with titanium oxides were given as a function of temperature in the present work as follows.

$${}^0\Omega_{\text{Fe-Ti}} = -173\,600 + 51.76T/J, \quad (1\,823\text{ K} < T < 1\,923\text{ K})$$

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

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 steel-making process.

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