Equilibrium between Titanium and Oxygen in Liquid Fe–Ti Alloy Coexisted with Titanium Oxides at 1 873 K

Woo-Yeol CHA,¹⁾ Tetsuya NAGASAKA,²⁾ Takahiro MIKI,³⁾ Yasushi SASAKI³⁾ and Mitsutaka HINO³⁾

1) Graduate Student, Graduate School of Engineering, Tohoku University, 6-6-02 Aoba-yama, Aoba-ku, Sendai 980-8579 Japan.

2) Graduate School of Environmental Studies, Tohoku University, 6-6-11 Aoba-yama, Aoba-ku, Sendai 980-8579 Japan.

3) Department of Metallurgy, Graduate School of Engineering, Tohoku University, 6-6-02 Aoba-yama, Aoba-ku, Sendai 980-8579 Japan.

(Received on January 18 2006; accepted on March 14, 2006)

The equilibrium between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ has been investigated in molten Fe–Ti alloy saturated with various kinds of titanium oxides at 1 873 K. The present results have been thermodynamically analyzed applying Wagner's formalism as well as Darken's quadratic formalism with the excess Gibbs free energy change of mixing described by Redlich–Kister type polynomial. The equilibrium constants and the interaction parameters of Wagner's formalism were given as follows at 1 873 K in the present work.

$$\log K = -10.17, \quad e_{\text{O}}^{\text{Ti}} = -0.34$$

$$\log K = -16.86, \quad e_{\text{O}}^{\text{Ti}} = -0.34$$

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

$$\gamma_{\text{Ti(l)}}^{\circ} = 0.0090$$

The interaction parameters of Redlich–Kister type polynomial for molten Fe–Ti–O alloy were given by the following values at 1 873 K in the present work.

$${}^0\Omega_{\text{Fe–Ti}} = -73\,360/\text{J}$$

$${}^0\Omega_{\text{Ti–O}} = -1\,035\,900/\text{J}$$

The estimated results based on Wagner's formalism as well as Darken's quadratic formalism polynomials were well agreed with the experimental results which were observed between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ equilibrium contents in molten Fe–Ti alloy.

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

1. Introduction

Control of oxygen content in liquid iron is very important not only to remove impurities such as phosphorus and sulfur but also to improve the yield of valuable alloying elements such as Ti in steelmaking process. Ti is widely used as a strong deoxidizer due to its high affinity for oxygen. The most important thermodynamic information is the equilibrium relation between dissolved Ti and O in steel melt for the precise control of Ti in the steelmaking process. Fine titanium oxide can also be used to control for grain refinement with its dispersion in austenite grain.¹⁾

Due to such importance, huge number of studies^{2–26)} concerning the Ti and O equilibrium relation have been reported, where the Ti content in liquid iron has been up to 30 mass%.

There is huge scatter on Ti deoxidation equilibrium con-

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

Solid line in Fig. 1 denotes the recommended value at 1 873 K by the 19th Committee on Steelmaking, the Japan Society for the Promotion of Science (JSPS).²⁴⁾ The JSPS recommended value²⁴⁾ for the Fe–Ti–O system does not cover a wide concentration range of titanium because of experimental difficulties, and it is based on the experimental result by Suzuki and Sanbongi.¹⁹⁾ They measured the equi-

Fig. 1. Equilibrium relation between [mass%Ti] and [mass%O] in liquid Fe-Ti alloy at 1873 K with JSPS recommended values.²⁻²⁴⁾

librium between Ti and O in the range of 0.01–0.25 mass% Ti of Fe-Ti melt in a TiO_x ($0 < x < 1$) crucible. They found that the deoxidation product was ' Ti_3O_5 ' with small amount of iron, which depended on Ti content in liquid Fe-Ti alloy.

Most of other researchers²⁻²⁶⁾ conducted their experiments using a MgO , Al_2O_3 or CaO crucible, and they evaluated their results on the assumption of unit activity of titanium oxides. However, it is known that Al_2O_3 reacts with TiO_2 to form the intermediate compound $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ as reported by Lang *et al.*²⁷⁾ Al_2O_3 and Ti_2O_3 form a solid solution as reported by Belon and Forestier.²⁸⁾ MgO reacts with TiO_2 to form the intermediate compound $\text{MgO} \cdot \text{TiO}_2$, $\text{MgO} \cdot 2\text{TiO}_2$ and $2\text{MgO} \cdot \text{TiO}_2$ as reported by Woermann *et al.*²⁹⁾ Also, CaO reacts with TiO_2 to form the intermediate compound $\text{CaO} \cdot \text{TiO}_2$, $5\text{CaO} \cdot 4\text{TiO}_2$ and $3\text{CaO} \cdot 2\text{TiO}_2$ as reported by Tulgar.³⁰⁾ These facts indicate that the activity of each titanium oxide in equilibrium with molten Fe-Ti alloy is not always unity on their experimental conditions.

More reliable thermodynamic information on Ti-O equilibrium in liquid Fe is, therefore, necessary for the precise control of Ti in steelmaking process.

In the previous work,³¹⁾ ' Ti_3O_5 ' crucibles were equilibrated with the molten Fe-Ti alloy of various Ti contents at 1873 K. Different titanium oxide phases were formed at the interface between Fe-Ti alloy and ' Ti_3O_5 ' crucibles depending on Ti contents. The equilibrium titanium oxide phases were clearly identified by the automated indexing of electron backscatter diffraction (EBSD) pattern analysis.

Therefore, the measurements of equilibrium relation between Ti and O in the molten iron were carried out over the Ti concentration range from 0.0004 to 16.6 mass% with various kinds of titanium oxide at 1873 K in the present study. The measured equilibrium relation between Ti and O in the molten Fe-Ti alloy was thermodynamically analyzed based on Wagner's³²⁾ formalism and Darken's quadratic formalism^{33,34)} with Redlich-Kister type polynomial.^{35,36)}

2. Experimental

Experimental equipment and procedure are essentially the same as the previous work.³¹⁾ ' Ti_3O_5 ' crucibles were

manufactured by ourselves from ' Ti_3O_5 ' powder. ' Ti_3O_5 ' powder was produced by H_2 reduction of ' TiO_2 ' anatase (99.8% purity) powder at 1773 K for 12 h. ' Ti_3O_5 ' powder was formed in a crucible shape by rubber press and sintered at 1823 K for 12 h under $\text{Ar} + 5\% \text{H}_2$ atmosphere. A ' Ti_3O_5 ' crucible (outer diameter: 28 mm, inner diameter: 22 mm, height: 65 mm) charged with approximately 50 g of Fe-Ti alloy was set in a Al_2O_3 outer crucible in an induction furnace, and the metal was melted under dehydrated and deoxidized $\text{Ar} + 3\% \text{H}_2$ stream of 100 ml/min. The Fe-Ti alloy specimen was prepared by melting an appropriate amount of Ti and Fe and held for 60 min at 1873 K. Temperature measurement was conducted by an infrared radiation pyrometer, which was calibrated by the melting points of Fe and Cu. The melt and crucible were quenched after reaching equilibrium by switch-off and blowing He gas in the reaction chamber.

The concentration of O in the cut off from quenched samples was determined by an inert gas impulse infrared absorption spectroscopy. The surface of samples was polished for O analysis by silicon carbide wet polishing papers (up to #1500-grit) and then electrically polished by the solution of acetic acid (CH_3COOH) and perchloric acid (HClO_4) for 6 min with constant current of 0.5 A. The concentration of Ti in the samples was determined by a high-frequency induction coupled plasma spectroscopy (ICP). All the formed oxide phases at the interface between melts and ' Ti_3O_5 ' crucibles were analyzed by EBSD pattern analysis technique to identify the equilibrium titanium oxide phases. Solid solubility of Fe oxide in ' Ti_3O_5 ' phase was analyzed quantitatively by EDS.

3. Experimental Results

Experimental results are listed in Table 1. The previous³¹⁾ observed relation between Ti and O concentrations at 1873 K is reproduced in Fig. 2 with other researcher's works.^{2,4,6,7,10,12,15,19,22)} The present results corresponded to those of Suzuki and Sanbongi¹⁹⁾ who used a TiO_x ($0 < x < 1$) crucible and Janke and Fischer²²⁾ who used a ' TiO_2 ' crucible. The equilibrium lines of thermodynamic analyzed re-

Table 1. Experimental results on the Ti–O equilibrium in liquid iron saturated with various kinds of titanium oxides at 1873 K.³¹⁾

	[mass% Ti]	[mass% O]	Equilibrium oxide by EBSD analysis ³¹⁾
A-1	0.0004	0.0230	'Ti ₃ O ₅ '
A-2	0.0005	0.0287	'Ti ₃ O ₅ '
A-3	0.0005	0.0114	'Ti ₃ O ₅ '
A-4	0.0007	0.0168	'Ti ₃ O ₅ '
A-5	0.0009	0.0173	'Ti ₃ O ₅ '
A-6	0.0018	0.0250	'Ti ₃ O ₅ '
A-7	0.0026	0.0183	'Ti ₃ O ₅ '
A-8	0.0026	0.0198	'Ti ₃ O ₅ '
A-9	0.006	0.0103	'Ti ₃ O ₅ '
A-10	0.034	0.0028	'Ti ₃ O ₅ '
A-11	0.36	0.0013	'Ti ₃ O ₅ '
B-1	0.50	0.0008	Ti ₂ O ₃
B-2	0.87	0.0011	Ti ₂ O ₃
B-3	1.97	0.0010	Ti ₂ O ₃
B-4	2.17	0.0014	Ti ₂ O ₃
B-5	4.28	0.0028	Ti ₂ O ₃
B-6	6.22	0.0080	Ti ₂ O ₃
C-1	10.64	0.0164	'TiO'
C-2	14.13	0.0581	'TiO'
C-3	16.63	0.1034	'TiO'

sults by Wagner's³²⁾ formalism and Darken's quadratic formalism^{33,34)} with Redlich–Kister type polynomial^{35,36)} are also shown in the Fig. 2. This is discussing later.

The results of line analysis and EDS image of 'Ti₃O₅' crucible interface melted Fe–0.0026mass%Ti are presented in Fig. 3. The trace of Fe at 'Ti₃O₅' crucible interface was observed when Ti content was less than 0.36 mass% in molten Fe as shown in Fig. 4. Suzuki and Sanbongi¹⁹⁾ pointed out the solid solubility of Fe in 'Ti₃O₅' phase when Ti content was less than 0.25 mass% in molten Fe. Iwamoto *et al.*³⁷⁾ found the solid solution of 'Ti₃O₅' and 'FeO·2TiO₂' equilibrated with very low Ti concentration of Fe–Ti alloy.

Fig. 4. Solid solubility of Fe oxide in 'Ti₃O₅' phase at 1873 K. **Fig. 2.** Equilibrium relation between [mass%Ti] and [mass%O] in liquid Fe–Ti alloy at 1873 K with the various crucibles results.^{2–22)} **Fig. 3.** Line analysis and EDS image of Fe and Ti in the cross section of 'Ti₃O₅' crucible melted liquid Fe–0.0026mass% Ti at 1873 K.

Fig. 5. Line analysis and EDS image of Fe and Ti in the cross section of 'Ti₃O₅' crucible melted liquid Fe-0.5mass%Ti at 1873 K.

This means that the activity of 'Ti₃O₅' equilibrated with molten Fe (Ti<0.36 mass%) is less than unity based on the present experimental results. Suzuki and Sanbongi¹⁹⁾ also found that the solid solubility of Fe in 'Ti₃O₅' phase was negligibly small <1.2 mass% when Ti content was between 0.013–0.25 mass%.

Thermodynamical evaluation was carried out using the experimental results of A-9 to A-11 in Table 1, where the solid solubility of Fe iron in 'Ti₃O₅' phase was negligibly small as shown in the Fig. 4. Unit activity of 'Ti₃O₅' was assumed where the Fe/Ti ratio was less than 0.05 in these cases.

The results of line analysis and EDS image of Ti₂O₃ phase are presented in Fig. 5 at the interface between 'Ti₃O₅' crucible and Fe-0.5mass%Ti. No trace of Fe and other elements were detected by EDS analysis at the metal/crucible interface after the experiments. The same results also were observed for 'TiO' phase.

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

4. Discussion

Ti deoxidation results using other oxide crucibles such as MgO, Al₂O₃ had the possibility that the titanium oxide activity was not unity. The crucible materials reacted with titanium oxides and formed the intermediate compound or solid solution at the interface of crucibles. Therefore, only the present experimental results and those using titanium oxide crucibles^{4,15,19,22)} were used for the thermodynamic consideration as shown in Fig. 2.

The calculation was carried out based on Wagner's formalism³²⁾ and Darken's quadratic formalism^{33,34)} combined with Redlich–Kister type polynomial,^{35,36)} and the two formalisms were compared and discussed.

It is widely known that 'TiO' has relatively wide solid solution at 1873 K as shown in Fig. 6.³⁸⁾ Thus, 'TiO' can not be assumed as a line-compound.

Fig. 6. Phase diagram of Ti–O system.³⁸⁾

4.1. Thermodynamical Analysis by Wagner's Formalism

4.1.1. Thermodynamical Basis for Ti Deoxidation of Molten Fe

The chemical reaction between Ti and O in liquid iron and its equilibrium constant are given by Eqs. (1) and (2) under the presence of solid 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 Henrian activity, the Henrian activity coefficient and concentration of i in liquid iron (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 Eq. (3).

$$\begin{aligned} \log K = & x(\log f_{\text{Ti}}) + y(\log f_{\text{O}}) + x(\log [\% \text{Ti}]) \\ & + y(\log [\% \text{O}]) - \log a_{\text{Ti}_x\text{O}_y(\text{s})} \dots\dots\dots(3) \end{aligned}$$

Fig. 7. Relation of Eqs. (9), (10) for determining e_{O}^{Ti} and $\log K$ at 1873 K.

Each activity coefficient in Eq. (3) can be expressed by Eqs. (4) and (5).

$$\log f_{\text{Ti}} = e_{\text{Ti}}^{\text{O}}[\% \text{O}] + e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + r_{\text{Ti}}^{\text{O}}[\% \text{O}]^2 + r_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}]^2 + r_{\text{Ti}}^{\text{O,Ti}}[\% \text{O}][\% \text{Ti}] \quad (4)$$

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Ti}}[\% \text{Ti}] + e_{\text{O}}^{\text{O}}[\% \text{O}] + r_{\text{O}}^{\text{Ti}}[\% \text{Ti}]^2 + r_{\text{O}}^{\text{O}}[\% \text{O}]^2 + r_{\text{O}}^{\text{Ti,O}}[\% \text{Ti}][\% \text{O}] \quad (5)$$

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

$$e_{\text{Ti}}^{\text{Ti}} = 0.041 \quad (6)$$

$$e_{\text{O}}^{\text{O}} = -1750/T + 0.76 \quad (7)$$

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

$$e_{\text{Ti}}^{\text{O}} = 2.993e_{\text{O}}^{\text{Ti}} - 0.00865 \quad (8)$$

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

$$2e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + 3e_{\text{O}}^{\text{O}}[\% \text{O}] + 2\log[\% \text{Ti}] + 3\log[\% \text{O}] - 0.0173[\% \text{O}] = e_{\text{O}}^{\text{Ti}}(-3[\% \text{Ti}] - 5.985[\% \text{O}]) + \log K_{\text{Ti}_2\text{O}_3} \quad (9)$$

$$3e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + 5e_{\text{O}}^{\text{O}}[\% \text{O}] + 3\log[\% \text{Ti}] + 5\log[\% \text{O}] - 0.026[\% \text{O}] = e_{\text{O}}^{\text{Ti}}(-5[\% \text{Ti}] - 8.978[\% \text{O}]) + \log K_{\text{Ti}_3\text{O}_5} \quad (10)$$

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

The left hand sides of Eqs. (9) and (10) 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 in Fig. 7 on the Ti_2O_3 and Ti_3O_5 saturated conditions, respective-

ly. Thermodynamical evaluation was carried out using only the previous experimental results³¹ of B-1 to B-6 for Ti_2O_3 and A-9 to A-11 for Ti_3O_5 in Table 1. Good linear relation was observed for each titanium oxide. It means that Eqs. (9) and (10) can well express the equilibrium relation between Ti and O up to 6.5 mass% of Ti in molten Fe at Ti_3O_5 and Ti_2O_3 saturation and the second order interaction parameters such as r_{O}^{Ti} can be omitted.

The interaction between Ti and O is the same as in the region where Ti and O contents are not so large. However, the Ti deoxidation equilibrium constant is different for each kind of Ti deoxidation product. Regression analysis to a straight line in Fig. 7 gave the Ti deoxidation equilibrium constant $\log K$ and the interaction parameter e_{O}^{Ti} from the intercept at the Y axis and the slope based on the present experimental data and the others using Ti oxide crucible.^{4,15,19,22} The obtained first order interaction, e_{O}^{Ti} , parameter 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.

The interaction parameters determined in the present study are compared with previous results³⁻²⁴ in Table 2. The present interaction parameter, -0.34 , and deoxidation equilibrium constant of Ti_3O_5 , -16.86 , are in good agreement with that of Suzuki and Sanbongi.¹⁹ However, they did not determine the Ti deoxidation equilibrium constant of Ti_2O_3 . The present Ti deoxidation equilibrium constant of Ti_2O_3 , -10.17 , is in good agreement with the values of -10.43 obtained by Janke and Fischer²² and -10.39 obtained by Bůžek¹⁴ at 1873 K.

The estimated relation between equilibrium Ti and O content in molten Fe based on Wagner's formalism³² are shown in Fig. 2 with the experimental results. This equilibrium line was drawn using the estimated values in the present work. The results by Darken's formalism^{33,34} with Redlich-Kister^{35,36} type polynomial is also shown in this figure. This is discussed later.

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

Activity coefficient $\gamma_{\text{Ti}}^{\text{O}}$ is evaluated from the derived Ti deoxidation equilibrium constant $\log K$. Ti deoxidation

Table 2. e_{O}^{Ti} and $\log K$ of Ti deoxidation at 1 873 K.⁵⁻²⁴⁾

Researchers	Equilibrium Titanium Oxide	e_{O}^{Ti}	$\log K$	Remark
J. Chipman ⁵⁾ ('60)	'TiO'	-0.187	-	1627 °C Estimated
H. Chino et al. ⁶⁾ ('66)	'Ti ₃ O ₅ ' (containing Fe)	-	-18.74	
K. Suzuki et al. ⁷⁾ ('67)	Ti ₂ O ₃ 'TiO ₂ '	-0.158	-6.50	
V. Averin ⁸⁾ ('67)	-	-0.60	-	Fe-5%Cr melts
Y. Kojima et al. ¹⁰⁾ ('69)	'Ti ₃ O ₅ ' Ti ₂ O ₃	-0.37	-17.4	-
K. Segawa et al. ¹¹⁾ ('69)	'Ti ₃ O ₅ ' (containing Fe)	-	-18.71	Estimated for Ti ₂ O ₃
	Ti ₂ O ₃	-	-11.53	
R. J. Fruehan ¹²⁾ ('70)	-	-1.12	-	EMF
V. I. Yavovskiy et al. ¹³⁾ ('71)	Ti ₂ O ₃	-0.65	-9.90	
Z. Bůžek ¹⁴⁾ ('71)	'Ti ₃ O ₅ ' Ti ₂ O ₃	-4.79 -0.75	-17.56 -10.39	
A. M. Smellie and B. H. Bell ¹⁵⁾ ('72)	'Ti ₃ O ₅ ' (containing Fe)	-5.0	-18.5	
V. I. Yavovskiy et al. ¹⁷⁾ ('74)	'Ti ₃ O ₅ ' Ti ₂ O ₃	-	-15.46 -8.04	
K. Suzuki and K. Sanbongi ¹⁹⁾ ('75)	'Ti ₃ O ₅ ' (containing Fe)	-0.31	-16.10	
Kulikov. IS. ²⁰⁾ ('75)	-	-0.30	-	
D. Janke and W. A. Fischer ²²⁾ ('76)	'Ti ₃ O ₅ ' Ti ₂ O ₃		-17.13 -10.43	EMF
A. Ghosh and G. V. R. Murthy ²³⁾ ('86)	'Ti ₃ O ₅ ' Ti ₂ O ₃	-1.0 -0.42	-19.26 -11.69	Estimated
JSPS recommended value ²⁴⁾ ('88) K. Suzuki and K. Sanbongi ('75)	'Ti ₃ O ₅ ' (containing Fe)	-	-16.10	
Present work	'Ti ₃ O ₅ ' Ti ₂ O ₃	-0.34 -0.34	-16.86 -10.17	EBS analysis ³¹⁾

Table 3. $\gamma_{\text{Ti}}^{\circ}$ at 1 873 K.³⁻²⁶⁾

Researchers	$\gamma_{\text{Ti}}^{\circ}$	Procedure
J. Chipman ³⁾ ('50)	0.050	Estimated
J. Chipman ⁵⁾ ('60)	0.011	Estimated from Hadley's data
H. Chino et al. ⁶⁾ ('66)	0.033	Thermodynamic evaluation using experimental data
K. Suzuki et al. ⁷⁾ ('67)	0.0071	Thermodynamic evaluation using experimental data
V. Averin ⁸⁾ ('67)	0.007	Not given
K. Sawamura and T. Hana ⁹⁾ ('68)	0.029	Vapour pressure measurement
R. J. Fruehan ¹²⁾ ('70)	0.038	EMF measurement
A. M. Smellie and B. H. Bell ¹⁵⁾ ('72)	0.050	Estimated from experimental data
Z. Morita et al. ¹⁶⁾ ('73)	0.004	Thermodynamic calculation
S. Wagner and G. R. Pierre ¹⁸⁾ ('74)	0.068	Knudsen Cell Mass Spectrometry
K. Suzuki and K. Sanbongi ¹⁹⁾ ('75)	0.016	Thermodynamic evaluation using experimental data
T. Furukawa and E. Kato ²¹⁾ ('75)	0.018	Knudsen Cell Mass Spectrometry
JSPS recommended value ²⁴⁾ ('88) (T. Furukawa and E. Kato)	0.018	-
D. Bouchard and C. W. Bale ²⁵⁾ ('95)	0.043	Estimated from experimental data
H. Y. Choi et al. ²⁶⁾ (2005)	0.018	EMF measurement
Present work	0.0090	Thermodynamic evaluation using experimental data

equilibrium constant -10.17 on Ti_2O_3 gives $\Delta G_{1873\text{K}}^{\circ}$ as the Eq. (12) at 1 873 K.

$$\Delta G_{11}^{\circ} = -RT \ln K = 364\,670/\text{J} \quad (1\,873\text{K}) \dots \dots \dots (12)$$

The Gibbs free energy of Ti_2O_3 formation and the free energy of oxygen dissolution in molten Fe are shown by the Eqs. (13) and (14) at 1 873 K after the NIST-JANAF Thermochemical Tables⁴⁰⁾ and JSPS recommended values.²⁴⁾

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

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

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

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

into the Eq. (16).

$$\frac{\exp \left(\frac{\Delta G_{15}^{\circ}}{RT} \right) \times 100 \times M_{\text{Ti}}}{M_{\text{Fe}}} = \gamma_{\text{Ti}}^{\circ} = 0.0090 \dots \dots (17)$$

The deoxidation equilibrium constant corresponded to ' Ti_3O_5 ' was used for the same calculation, and the same value of 0.0090 was obtained at 1 873 K as $\gamma_{\text{Ti}}^{\circ}$. Suzuki and Sanbongi¹⁹⁾ estimated the activity coefficient of Ti using their experimental results. However, their estimated value was changed with titanium concentration.

$\gamma_{\text{Ti}}^{\circ}$ determined in the present work is compared with previous results³⁻²⁶⁾ in **Table 3**. Previous values vary more than one order from 0.004 to 0.050, most of them are about one order larger than ours. However, the value of 0.0090 is in good agreement with the values of 0.011 obtained by Chipman⁵⁾ and 0.0071 obtained by Suzuki et al.⁷⁾ at 1 873 K.

4.2. Thermodynamic Analysis by Quadratic Formalism with Redlich-Kister Type Polynomial⁴¹⁻⁴³⁾

The equation by Wagner³²⁾ has been widely used to express the activity coefficients of solutes in multi-component solutions. However, the second order or higher terms must be added to represent the activity coefficients when solute contents are rich. Darken^{33,34)} has proposed the quadratic formalism to express the activity coefficients that can be applied to higher solute content. The activity coefficients of solvent 1 and solute 2, 3 are expressed for ternary solution by the following equations.

$$\ln \gamma_1 = \alpha_{12}X_2^2 + \alpha_{13}X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3 \dots \dots (18)$$

$$\ln \gamma_2 = \ln \gamma_2^\circ - 2\alpha_{12}X_2 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_3 + \alpha_{12}X_2^2 + \alpha_{13}X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3, \dots (19)$$

$$\ln \gamma_3 = \ln \gamma_3^\circ - 2\alpha_{13}X_3 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_2 + \alpha_{12}X_2^2 + \alpha_{13}X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3, \dots (20)$$

Where X_i , γ_i , γ_i° , α_{ij} denote mole fraction of component i , the activity coefficient of component i , the Henry constant, interaction between i and j in their binary solution at constant temperature and pressure, respectively. The following relations are obtained⁴¹⁻⁴³⁾ by comparing the equations by Wagner³²⁾ with Eq. (19).

$$\varepsilon_2^\circ = -2\alpha_{12}, \dots (21)$$

$$\varepsilon_2^3 = \alpha_{23} - \alpha_{12} - \alpha_{13}, \dots (22)$$

$$\rho_2^2 = \alpha_{12}, \dots (23)$$

$$\rho_2^3 = \alpha_{13}, \dots (24)$$

$$\rho_2^{(2,3)} = \alpha_{12} + \alpha_{13} - \alpha_{23}, \dots (25)$$

Where ε_j^i and ρ_j^i are the first and the second order interaction coefficients between i and j , respectively.

Quadratic formalism was converted into Redlich–Kister type polynomial^{35,36)} using the excess Gibbs free energy change of mixing. This conversion was done by Miki and Hino⁴¹⁻⁴³⁾ because it was useful to expand Darken's quadratic formalism to multi-component alloy systems. The excess Gibbs free energy change of mixing for 1–2 binary system is expressed as Eq. (26) by Redlich–Kister type polynomial.^{35,36)}

$$\Delta G^{\text{ex}} = X_1X_2\{^0\Omega_{1-2} + ^1\Omega_{1-2}(X_1 - X_2)\}, \dots (26)$$

The following equations are obtained in the infinite dilute solution of component 2.⁴¹⁻⁴³⁾

$$RT \ln \gamma_2^\circ = ^0\Omega_{1-2} + ^1\Omega_{1-2}, \dots (27)$$

$$RT \alpha_{12} = ^0\Omega_{1-2} + 3^1\Omega_{1-2}, \dots (28)$$

The binary interaction parameters can be obtained by combining Eqs. (27) and (28) as follows.⁴¹⁻⁴³⁾

$$^0\Omega_{1-2} = RT \left(\frac{3}{2} \ln \gamma_2^\circ - \frac{1}{2} \alpha_{12} \right), \dots (29)$$

$$^1\Omega_{1-2} = RT \left(-\frac{1}{2} \ln \gamma_2^\circ + \frac{1}{2} \alpha_{12} \right), \dots (30)$$

Quadratic formalism can be converted into Redlich–Kister type polynomial using $^0\Omega_{1-2}$ and $^1\Omega_{1-2}$ for dilute solution with Eqs. (29) and (30).⁴¹⁻⁴³⁾

Pure substance is chosen as a standard state (Raoultian standard state) for condensed phases in the present work. On the other hand, dissolved oxygen in the melt equilibrating with 101 325 Pa (1 atm) oxygen gas is selected as a standard state in the present work.⁴¹⁻⁴³⁾ The relation between the oxygen activity and oxygen partial pressure can be expressed as follows in this standard state.

$$a_{\text{O}} = P_{\text{O}_2}^{1/2}, \dots (31)$$

4.2.1. Thermodynamic Analysis on Ti Deoxidation

Ti deoxidation reaction is expressed by Eq. (32).

This equation is separated into the following two equations.

The Gibbs free energy change of Eq. (33) is identical to the Gibbs free energy of Ti_xO_y formation ($\Delta G_{\text{f}, \text{Ti}_x\text{O}_y}^\circ$) and that of Eq. (34) is zero due to the relation of Eq. (31). Therefore, the Gibbs free energy change of Eq. (32) is identical to the minus value of Ti_xO_y formation free energy ($\Delta G_{\text{f}, \text{Ti}_x\text{O}_y}^\circ$), which is utilized for Ti deoxidation of any kinds of metal or alloy, and this has a great advantage. The equilibrium constant of Eq. (32), K_{Ti} , can be expressed as follows.

$$\begin{aligned} \ln K_{\text{Ti}} &= -\frac{\Delta G_{\text{f}, \text{Ti}_x\text{O}_y}^\circ}{RT} \\ &= x \ln \gamma_{\text{Ti}} + y \ln \gamma_{\text{O}} + x \ln X_{\text{Ti}} + y \ln X_{\text{O}} - \ln a_{\text{Ti}_x\text{O}_y} \\ &= x \ln \gamma_{\text{Ti}} + y \ln \gamma_{\text{O}} + x \ln X_{\text{Ti}} + y \ln X_{\text{O}} \quad (\because a_{\text{Ti}_x\text{O}_y} = 1) \end{aligned} \dots (35)$$

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

The excess free energy change of mixing in Fe–Ti–O ternary system is expressed as Eq. (36) using Redlich–Kister type polynomial,^{35,36)} where $^1\Omega_{\text{Ti–O}}$ term was neglected.

$$\begin{aligned} \Delta G^{\text{ex}} &= X_{\text{Fe}}X_{\text{Ti}}\{^0\Omega_{\text{Fe–Ti}} + ^1\Omega_{\text{Fe–Ti}}(X_{\text{Fe}} - X_{\text{Ti}})\} \\ &\quad + X_{\text{Fe}}X_{\text{O}}\{^0\Omega_{\text{Fe–O}} + ^1\Omega_{\text{Fe–O}}(X_{\text{Fe}} - X_{\text{O}})\} + X_{\text{Ti}}X_{\text{O}}^0\Omega_{\text{Ti–O}} \end{aligned} \dots (36)$$

The partial molar excess free energy changes of Ti and O are derived as follows.

$$\begin{aligned} \Delta \bar{G}_{\text{Ti}}^{\text{ex}} &= RT \ln \gamma_{\text{Ti}} = \Delta G^{\text{ex}} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} - X_{\text{O}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= ^0\Omega_{\text{Fe–Ti}}X_{\text{Fe}}(1 - X_{\text{Ti}}) \\ &\quad + ^1\Omega_{\text{Fe–Ti}}X_{\text{Fe}}(X_{\text{Fe}} - 2X_{\text{Ti}} - 2X_{\text{Fe}}X_{\text{Ti}} + 2X_{\text{Ti}}^2) \\ &\quad - ^0\Omega_{\text{Fe–O}}X_{\text{Fe}}X_{\text{O}} - 2^1\Omega_{\text{Fe–O}}X_{\text{Fe}}X_{\text{O}}(X_{\text{Fe}} - X_{\text{O}}) \\ &\quad + ^0\Omega_{\text{Ti–O}}X_{\text{O}}(1 - X_{\text{Ti}}), \dots (37) \end{aligned}$$

$$\begin{aligned} \Delta \bar{G}_{\text{O}}^{\text{ex}} &= RT \ln \gamma_{\text{O}} = \Delta G^{\text{ex}} - X_{\text{Ti}} \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{Ti}}} + (1 - X_{\text{O}}) \frac{\partial \Delta G^{\text{ex}}}{\partial X_{\text{O}}} \\ &= -^0\Omega_{\text{Fe–Ti}}X_{\text{Fe}}X_{\text{Ti}} - 2^1\Omega_{\text{Fe–Ti}}X_{\text{Fe}}X_{\text{Ti}}(X_{\text{Fe}} - X_{\text{Ti}}) \\ &\quad + ^0\Omega_{\text{Fe–O}}X_{\text{Fe}}(1 - X_{\text{O}}) \\ &\quad + ^1\Omega_{\text{Fe–O}}X_{\text{Fe}}(X_{\text{Fe}} - 2X_{\text{O}} - 2X_{\text{Fe}}X_{\text{O}} + 2X_{\text{O}}^2) \\ &\quad + ^0\Omega_{\text{Ti–O}}X_{\text{Ti}}(1 - X_{\text{O}}), \dots (38) \end{aligned}$$

The following equation can be obtained from Eq. (35) for

Ti₂O₃.

$$\Delta G_{f, \text{Ti}_2\text{O}_3}^\circ = -2RT \ln \gamma_{\text{Ti}} - 3RT \ln \gamma_{\text{O}} - 2RT \ln X_{\text{Ti}} - 3RT \ln X_{\text{O}} \quad (39)$$

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

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

The following equation is also obtained from Eq. (35) for 'Ti₃O₅'.

$$\Delta G_{f, \text{Ti}_3\text{O}_5}^\circ = -3RT \ln \gamma_{\text{Ti}} - 5RT \ln \gamma_{\text{O}} - 3RT \ln X_{\text{Ti}} - 5RT \ln X_{\text{O}} \quad (41)$$

Equation (42) is derived by substituting Eqs. (37) and (38) into Eq. (41).

$$\begin{aligned} & {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3+8X_{\text{Ti}}) \\ & + {}^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{Ti}}+16X_{\text{Fe}}X_{\text{Ti}}-16X_{\text{Ti}}^2) \\ & + {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5+8X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5X_{\text{Fe}}+10X_{\text{O}}+16X_{\text{Fe}}X_{\text{O}}-16X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Ti-O}}(-5X_{\text{Ti}}-3X_{\text{O}}+8X_{\text{Ti}}X_{\text{O}}) \\ & + RT(-3 \ln X_{\text{Ti}} - 5 \ln X_{\text{O}}) - \Delta G_{f, \text{Ti}_3\text{O}_5}^\circ = 0 \quad (42) \end{aligned}$$

Equations (40) and (42) are the fundamental equation for thermochemical 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 Gibb free energy change of oxygen dissolution into molten Fe and the self-interaction coefficient of oxygen in molten Fe.⁴³⁾ The Gibbs free energy of Ti_xO_y formation has been adopted from NIST-JANAF Thermochemical Tables.⁴⁰⁾ Redlich-Kister type parameter of ${}^0\Omega_{\text{Fe-Ti}}$ was estimated from the activity coefficient of γ_{Ti}^0 as described in the Sec. 4.1.3 assumed that ${}^1\Omega_{\text{Fe-Ti}}$ was negligible at 1 873 K.

The parameters referred in the present work are shown below.

$${}^0\Omega_{\text{Fe-O}} = -415\,400 + 142.4T/\text{J} \quad (1\,823-1\,973\text{ K})^{43)} \quad (43)$$

$${}^1\Omega_{\text{Fe-O}} = 298\,300 - 117.8T/\text{J} \quad (1\,823-1\,973\text{ K})^{43)} \quad (44)$$

$${}^0\Omega_{\text{Fe-Ti}} = -73\,360\text{ J} \quad \text{at } 1\,873\text{ K} \quad (45)$$

$$\Delta G_{f, \text{Ti}_2\text{O}_3}^\circ = -1\,520\,750 + 267.2T/\text{J} \quad (1\,750-1\,950\text{ K}) \quad (46)$$

$$\Delta G_{f, \text{Ti}_3\text{O}_5}^\circ = -2\,464\,580 + 434.9T/\text{J} \quad (1\,750-1\,950\text{ K}) \quad (47)$$

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

For Ti₂O₃,

$$\begin{aligned} Y_{\text{Ti}_2\text{O}_3} &= {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-3+5X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{O}}+10X_{\text{Fe}}X_{\text{O}}-10X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-2+5X_{\text{Ti}}) \\ & + 2^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-X_{\text{Fe}}+2X_{\text{Ti}}+5X_{\text{Fe}}X_{\text{Ti}}-5X_{\text{Ti}}^2) \\ & - 2RT \ln X_{\text{Ti}} - 3RT \ln X_{\text{O}} - \Delta G_{f, \text{Ti}_2\text{O}_3}^\circ \\ & = {}^0\Omega_{\text{Ti-O}}(3X_{\text{Ti}}+2X_{\text{O}}-5X_{\text{Ti}}X_{\text{O}}) \quad (48) \end{aligned}$$

For 'Ti₃O₅',

$$\begin{aligned} Y_{\text{Ti}_3\text{O}_5} &= {}^0\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5+8X_{\text{O}}) \\ & + {}^1\Omega_{\text{Fe-O}}X_{\text{Fe}}(-5X_{\text{Fe}}+10X_{\text{O}}+16X_{\text{Fe}}X_{\text{O}}-16X_{\text{O}}^2) \\ & + {}^0\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3+8X_{\text{Ti}}) \\ & + {}^1\Omega_{\text{Fe-Ti}}X_{\text{Fe}}(-3X_{\text{Fe}}+6X_{\text{Ti}}+16X_{\text{Fe}}X_{\text{Ti}}-16X_{\text{Ti}}^2) \\ & - 3RT \ln X_{\text{Ti}} - 5RT \ln X_{\text{O}} - \Delta G_{f, \text{Ti}_3\text{O}_5}^\circ \\ & = {}^0\Omega_{\text{Ti-O}}(5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}) \quad (49) \end{aligned}$$

$Y_{\text{Ti}_2\text{O}_3}$, $Y_{\text{Ti}_3\text{O}_5}$ in Eq. (48) or (49) are plotted as a vertical axis with the term of $5X_{\text{Ti}}+3X_{\text{O}}-8X_{\text{Ti}}X_{\text{O}}$ and $3X_{\text{Ti}}+2X_{\text{O}}-5X_{\text{Ti}}X_{\text{O}}$ as a horizontal axis in **Fig. 8** using the present experimental results and other researcher's results using titanium oxide crucible^{4,15,19,22)} and values of Eqs. (43)–(47). ${}^0\Omega_{\text{Ti-O}}$ is evaluated from the slope of the regressed line through the origin in this figure. ${}^0\Omega_{\text{Ti-O}}$ was determined as follows.

$${}^0\Omega_{\text{Ti-O}} = -1\,035\,900/\text{J} \quad \text{at } 1\,873\text{ K} \quad (50)$$

The equilibrium relation between Ti and O contents in molten Fe is compared with the experimental results by other researchers in Fig. 2. This equilibrium line was drawn using the Eqs. (40) from (47), the Gibbs free energy of Ti_xO_y formation (referred from NIST-JANAF Thermochemical Tables⁴⁰⁾) and estimated parameters, Eq. (50), in the present work.

4.3. Comparison of Wagner's Formalism with Quadratic Formalism and Redlich-Kister Type Polynomial

The estimated equilibrium curves based on each formalism^{32–36)} show excellent agreement with the present experimental results as shown in Fig. 2. However, the curve based on Redlich-Kister type polynomial is likely to more precisely expresses the equilibrium relation between Ti and O contents in molten Fe than that based on Wagner's formalism because Redlich-Kister type polynomial includes the higher order terms, too. The interaction parameters in Redlich-Kister type polynomial are easily converted into Wagner's interaction parameters as shown in Eqs. (21) to (30).^{41–43)} **Table 4** shows the comparison of the Wagner's interaction coefficients based on mass percent as concentration in molten Fe obtained in Sec. 4.1.2 with those derived from Redlich-Kister type polynomial parameters with Eqs. (21)–(25), (27), (28), (43)–(47), (50), (51)–(53). Redlich–

 Fig. 8. Relation of Eqs. (48), (49) for determining ${}^0\Omega_{\text{Ti-O}}$ at 1873 K.

 Table 4. Wagner's formalism³²⁾ interaction parameters and those of derived from the corresponding Redlich-Kister^{35,36)} type polynomial parameters.

	e_{O}^{Ti}	e_{Ti}^{O}	$e_{\text{Ti}}^{\text{Ti}}$	e_{O}^{O}	$\gamma_{\text{O}}^{\text{Ti}}$	$\gamma_{\text{Ti}}^{\text{O}}$	$\gamma_{\text{Ti}}^{\text{Ti}}$	$\gamma_{\text{O}}^{\text{O}}$	$\gamma_{\text{O}}^{(\text{Ti},\text{O})}$	$\gamma_{\text{Ti}}^{(\text{O},\text{Ti})}$	log K
1	-0.34	-1.0261	0.041 ⁴⁾	-0.17 ⁴⁾	-	-	-	-	-	-	-16.86 (Ti_3O_5) -10.17 (Ti_2O_3)
2	-0.34	-1.0261	0.047	-0.175	0.00003	0.00284	-0.000036	0.000709	0.02071	0.012459	-

 1: Wagner's formalism³²⁾ interaction parameters.

 2: Wagner's formalism³²⁾ interaction parameters converted from Redlich-Kister^{35,36)} parameters.

Kister type polynomial parameters are converted into the interaction coefficients based on mass percents by utilizing the following relations derived after Lupis,³⁹⁾ where M_1 denote the molecular weight of the solvent and M_i denote the molecular weight of element of "i".

$$\varepsilon_i^j = 230 \frac{M_j}{M_1} e_i^j + \frac{M_1 - M_j}{M_1} \dots (51)$$

$$\rho_i^j = \frac{230}{M_1^2} [100M_j^2 r_i^j + M_j(M_1 - M_j)e_i^j] + \frac{1}{2} \left(\frac{M_1 - M_j}{M_1} \right)^2 \dots (52)$$

$$\rho_i^{(j,k)} = \frac{230}{M_1^2} [100M_j M_k r_i^{(j,k)} + M_j(M_1 - M_k)e_i^j + M_k(M_1 - M_j)e_i^k] + \frac{(M_1 - M_j)(M_1 - M_k)}{M_1^2} \dots (53)$$

The converted first order interaction parameters derived from Redlich-Kister type polynomial parameters are identical to the Wagner's interaction parameters obtained in Sec. 4.1.2 as shown in Table 4. However, second order interaction parameters by Wagner's formalism could not be determined from the present experimental results due to the lack of experimental accuracy. On the other hand, Darken's quadratic formalism includes all of the first and the second order terms represented by Wagner's formalism. Hence, the concentration range of solutes that quadratic formalism can

Fig. 9. Interrelation of thermodynamic parameters.

cover is essentially wider than that by Wagner's formalism. The Redlich-Kister type polynomial parameters are universal for any alloy systems. Figure 9 shows the interrelation among the Henry constant, the interaction parameters and the thermodynamical parameters in the two formalisms.

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

5. Conclusions

The equilibrium relation between dissolved Ti and O was observed in liquid Fe-0.0004 to 16.6 mass% Ti alloy saturated with solid titanium oxides at 1873 K. The equilibrium constant of Ti deoxidation and the interaction parameters of Wagner's formalism between Ti and O in liquid Fe saturat-

ed with titanium oxides were given by the following equations.

$$\log K = -10.17, \quad e_{\text{O}}^{\text{Ti}} = -0.34$$

$$\log K = -16.86, \quad e_{\text{O}}^{\text{Ti}} = -0.34$$

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

$$\gamma_{\text{Ti}}^{\circ} = 0.0090$$

The interaction parameters of Redlich–Kister type polynomial between Ti(l) and Q in molten Fe saturated with titanium oxides were given at 1 873 K by the following values in the present work.

$${}^0\Omega_{\text{Fe-Ti}} = -73\,360/\text{J}, \quad {}^0\Omega_{\text{Ti-O}} = -1\,035\,900/\text{J}$$

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

Acknowledgments

The authors wish to thank Dr. H. Itoh (Yoshizawa Lime Ind. Co.) for the great help for the processing of 'Ti₃O₅' crucible. The present work was financially supported by the Japanese Government Ministry of Education, Culture, Sports, Science and Technology and the 21st COE Program in Tohoku University Materials Research Center.

REFERENCES

- 1) J.-S. Byun, J.-H. Shim, Y. W. Cho and D. N. Lee: *Acta Mater.*, **51** (2003), 1593.
- 2) H. Wentrup and G. Hieber: *Arch. Eisenhüttenwes.*, **13** (1939), 69.
- 3) Basic Open Hearth Steelmaking, ed. by J. Chipman, John Wiley & Sons, New York, (1950).
- 4) R. L. Hadley and G. Derge: *Trans. Met. Soc. AIME*, **203** (1955), 55.
- 5) J. Chipman: *Trans. Met. Soc., AIME*, **218** (1960), 217.
- 6) H. Chino, Y. Nakamura, E. Tsunetomi and K. Segawa: *Tetsu-to-Hagané*, **52** (1966), 959.
- 7) K. Suzuki, Y. Ohmori and K. Sanbongi: *Bull. Res. Inst. Miner. Dressing Met., Tohoku Univ.*, **23** (1967), 137.
- 8) V. V. Averin: Proc. 1st Japan-USSR Joint Symp. on Physical Chemistry of Metallurgical Process, ISIJ, Tokyo, (1967), 84.
- 9) K. Sawamura and T. Hanai: The 20th Kyushu Branch Meeting on the Iron and Steel Inst. of Japan, (1968)
- 10) Y. Kojima, M. Inoue and J. Ohi: *Arch. Eisenhüttenwes.*, **40** (1969), 667.
- 11) K. Segawa, E. Tsunetomi, Y. Nakamura and H. Chino: *Trans. Iron Steel Inst. Jpn.*, **9** (1969), 89.
- 12) R. J. Fruehan: *Metall. Trans.*, **1** (1970), 3403.
- 13) V. I. Yavoiskii, L. B. Kosterev, A. A. Ayub and L. N. Rastorguev: *Russ. Metall.*, **2** (1971), 33.
- 14) Z. Bužek and A. Hutla: *Sb. Věd. Pr. Vys. Šk. Báňské vostrave Rocnik XI, rok. cislo 3, rada hutnicka, clanek*, **181** (1965), 379.
- 15) A. M. Smellie and H. B. Bell: *Can. Metall. Q.*, **11** (1972), No. 2, 351.
- 16) Z. Morita, Y. Iwanaga, S. Hamada and A. Adachi: *Tetsu-to-Hagané*, **52** (1973), 214.
- 17) V. I. Yavoiskii, L. P. Vladimirov, V. P. Luzgin, N. M. Kopitsa and E. B. Teplitskiy: *Russ. Metall.*, **2** (1974), 10.
- 18) S. Wagner and G. R. ST. Pierre: *Metall. Trans.*, **5** (1974), 887.
- 19) K. Suzuki and K. Sanbongi: *Trans. Iron Steel Inst. Jpn.*, **15** (1975), 618.
- 20) I. S. Kulikov: Deoxidation of Metals. M, Metallurgiya, (1975), 183.
- 21) T. Furukawa and E. Kato: *Tetsu-to-Hagané*, **61** (1975), 3060.
- 22) D. Janke and W. A. Fischer: *Arch. Eisenhüttenwes.*, **47** (1976), 195.
- 23) A. Ghosh and G. V. R. Murthy: *Trans. Iron Steel Inst. Jpn.*, **26** (1986), 628.
- 24) Steelmaking Data Sourcebook, Gordon and Breach Science Publishers, ed. by The Japan Society for Promotion of Science, The 19th Committee in Steelmaking, New York, NY, (1988).
- 25) D. Bouchard and C. W. Bale: *Metall. Mater. Trans. B.*, **26B** (1995), 467.
- 26) H. Y. Choi, W. E. Slye, R. J. Fruehan and R. C. Nunnington: *Metall. Mater. Trans. B.*, **36B** (2005), 537.
- 27) S. M. Lang, C. L. Fillmore, L. H. Maxwell: *J. Res. Natl. Bur. Stand.*, RP 231648, **4** (1952), 298.
- 28) L. Belon and H. Forestier: *C. R. Acad. Sci.*, **258** (1964), No. 17, 4284.
- 29) E. Woermann, B. Brezny and A. Muan: *Am. J. Sci.*, **267A** (1969), 463.
- 30) H. E. Tulgar: *Istanbul Tek. Univ. Bul.*, **29** (1976), No. 1, 111.
- 31) W. Y. Cha, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **46** (2006), No. 7, 987.
- 32) C. Wagner: Thermodynamics of Alloys, Addison-Wesley, Cambridge, MA, (1952).
- 33) L. S. Darken: *Trans. Met. Soc. AIME*, **239** (1967), 80.
- 34) L. S. Darken: *Trans. Met. Soc. AIME*, **239** (1967), 90.
- 35) M. Hillert and L.-I. Staffanson: *Acta Chem. Scand.*, **24** (1970), 3618.
- 36) N. Saunders and A. P. Miodownik: Calphad (Calculation of Phase Diagrams.), A Comprehensive Guide, Pergamon, Oxford, (1988), 91.
- 37) N. Iwamoto, H. Yoshida and A. Adachi: *Tetsu-to-Hagané*, **56** (1970), 1646.
- 38) M. Pajunen and J. Kivilahti: *Z. Metallkd.*, **83** (1992), No. 1, 17.
- 39) C. H. P. Lupis: Chemical Thermodynamics of Materials, ed. by Prentice Hall, London, (1993), 255.
- 40) NIST-JANAF Thermochemical Tables, 4th ed., ed. by M. W. Chase, Jr., J. Phys. Chem. Ref. Data, (1998).
- 41) T. Miki, F. Ishii and M. Hino: *Mater. Trans.*, **44**, (2003), No. 9, 1817.
- 42) T. Miki and M. Hino: *ISIJ Int.*, **44**, (2004), No. 11, 1800.
- 43) T. Miki and M. Hino: *ISIJ Int.*, **45**, (2005), No. 12, 1848.