Thermodynamics of Titanium and Oxygen Dissolved in Liquid Iron Equilibrated with Titanium Oxides

Jong-Jin PAK,¹⁾ Jong-Oh JO,¹⁾ Sun-In KIM,¹⁾ Wan-Yi KIM,¹⁾ Tae-In CHUNG,¹⁾ Seok-Min SEO,²⁾ Joo-Hyun PARK³⁾ and Dong-Sik KIM³⁾

1) Division of Materials and Chemical Engineering, Hanyang University, Ansan 426-791, Korea. E-mail: jjpark@hanyang.ac.kr

2) Formerly Graduate Student, Division of Materials and Chemical Engineering, Hanyang University. Now at SeAH Besteel Co., Ltd., Kunsan 573-711, Korea.

3) Technical Research Laboratories, POSCO, Pohang 790-690, Korea.

(Received on May 19, 2006; accepted on September 20, 2006)

The equilibrium relation of Ti and O dissolved in liquid iron saturated with solid titanium oxides was measured in the temperature range of 1 823 to 1 923 K. Pure Ti_2O_3 (s) phase was identified as the equilibrium deoxidation product for iron melts containing 0.25–4.75 mass% Ti. Using Wagner's formalism, the present results were thermodynamically analyzed to determine the equilibrium constant of Ti deoxidation reaction for the formation of pure Ti_2O_3 (s) and the first- and second-order interaction parameters between Ti and O given as follows in the temperature range of 1 823 to 1 923 K.

$$\begin{aligned} 2\text{Ti} + 3\text{O} &= \text{Ti}_2\text{O}_3 \text{ (s)} \quad (0.25 < \text{mass\% Ti} < 4.75) \\ \log K_{\text{Ti}_2\text{O}_3} &= 44\,238/T - 13.0 \\ e_{\text{O}}^{\text{Ti}} &= -1\,642/T + 0.3358, \quad e_{\text{Ti}}^{\text{O}} = -4\,915/T + 1.005 \\ r_{\text{O}}^{\text{Ti}} &= 0.0385, \quad r_{\text{Ti}}^{\text{O}} = -0.355 \end{aligned}$$

The equilibrium titanium oxide phase was identified as Ti_3O_5 (s) for iron melts containing 0.0012–0.25 mass% Ti at 1 873 K. The equilibrium constant of Ti deoxidation reaction for the formation of pure Ti_3O_5 (s) were estimated as follows.

$$\begin{aligned} 3\text{Ti} + 5\text{O} &= \text{Ti}_3\text{O}_5 \text{ (s)} \quad (0.0012 < \text{mass\% Ti} < 0.25) \\ \log K_{\text{Ti}_3\text{O}_5} &= 72\,813/T - 21.32 \end{aligned}$$

The activity coefficient of Ti in liquid iron at infinite dilution, $\gamma_{\text{Ti(s)}}^\circ$ was assessed as 0.011, 0.014 and 0.018 at 1 823 K, 1 873 K and 1 923 K, respectively.

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

1. Introduction

Titanium is added in many high grade steels to improve mechanical properties *via* the grain refinement during hot rolling. Also, Ti is an important alloying element in ferritic stainless steels to stabilize C and N, and hence to improve the intergranular corrosion resistance of the weld.¹⁾ Therefore, thermodynamics of Ti and O dissolved in liquid steel is very important for the precise control of Ti content in the steelmaking process.

Titanium is very reactive for O, and the titanium oxide as an equilibrium deoxidation product changes its chemical composition with Ti content in liquid steel.^{2–10)} Due to experimental difficulties, in spite of its importance, there are large discrepancies in thermodynamic data of the Ti deoxidation equilibria in liquid Fe–Ti–O system at 1 873 K previously reported.^{2–12)} Furthermore, the temperature dependencies of those data are not available.

In the present study, the deoxidation equilibrium between

Ti and O in liquid iron in contact with titanium oxide powder of a crucible form or in an Al_2O_3 crucible was studied in the temperature range of 1 823 to 1 923 K using a high frequency induction furnace. After each equilibration experiment, the titanium oxides near the oxide/metal interface were analyzed by the X-ray diffraction (XRD) and the electron probe micro-analyzer (EPMA) analysis for the phase identification and the composition analysis, respectively. The measured equilibrium relation of Ti and O in liquid iron was thermodynamically analyzed using Wagner's formalism¹³⁾ to determine the equilibrium constant of Ti deoxidation reaction in liquid iron for the formation of pure Ti_2O_3 (s) and the first- and second-order interaction parameters between Ti and O as a function of temperature. Using available thermochemical tables,^{14,15)} the equilibrium constant of Ti deoxidation reaction for the formation of pure Ti_3O_5 (s) and the activity coefficient of Ti in liquid iron at infinite dilution, $\gamma_{\text{Ti(s)}}^\circ$ were also assessed as a function of temperature.

2. Experimental Procedures

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

The reaction chamber consisted of a 80 mm OD quartz tube open at both ends and was connected to a gas delivery system. The flow rate of $\text{Ar}+3\text{vol}\%\text{H}_2$ gas mixture, which was dehydrated by magnesium perchlorate, was in the range of 100 to 150 mL/min. In order to remove any residual oxygen in the reaction chamber during heating, the mixture of Ti chips and MgO granules was packed in the space

Fig. 1. Schematic diagram of experimental system.

Fig. 2. XRD pattern for a mixture of solid Ti_2O_3 and TiO_2 powders before melting the iron.

between the inner and outer Al_2O_3 crucibles. A detailed description of the experimental system is given in the previous article.¹⁶⁾

After melting the iron, sponge Ti (99.5 % purity) metal, which was kept in a glass tube by a magnet, was dropped into liquid iron. The melt temperature was measured by a Pt/Pt-13mass%Rh thermocouple sheathed by a 5 mm OD quartz tube immersed in the melt. In order to minimize Si pick up in the melt by the reduction of quartz tube, the immersion depth and the time for temperature measurement were carefully controlled after Ti addition. Any possible influence of high frequency noise on the temperature reading was avoided by grounding the circuit of the thermocouple. Preliminary trials confirmed that no significant noise was detected, and the temperature fluctuation of iron melt could be controlled within 5 K during experiment. Strong agitation of melt by an induction furnace would result in a faster attainment of deoxidation equilibrium and a good separation of deoxidation products from the melt. The iron melts were equilibrated with titanium oxides for 1 h under an $\text{Ar}+3\text{vol}\%\text{H}_2$ atmosphere at 1 823 K, 1 873 K and 1 923 K.

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

The center part of metal sample was used for the chemical analysis of Ti, Al, Si and O. The metal sample (0.2 g) was dissolved in 15 mL of $\text{HCl}(1+1)$ and 5 mL of $\text{HNO}_3(1+1)$ in a glass beaker of 50 mL capacity heated in a water bath for 2 h. The leaching test of titanium oxide powders (Ti_2O_3 and Ti_3O_5) indicated that they were nearly insoluble in aqua regia solution heated in a water bath up to 12 h. After dissolving the sample, the solution was transferred to the measuring flask (100 mL) with filtration. Titanium, aluminum and silicon contents in sample solution were analyzed by the inductively coupled plasma-Auger electron spectroscopy (ICP-AES) technique using appropriate standard solutions containing the same amount of Fe (2 000 mass ppm) as sample solution. The oxygen content in metal sample was measured with an accuracy of ± 1

Fig. 3. Iron sample contained in a titanium oxide crucible.

Table 1. The experimental results of Ti and O equilibration in iron melt.

Test No.	Temp. (K)	Crucible	[%Ti]	[%Si]	[%Al]	[O]ppm	Equilibrium phase
1	1873	TiO _x	0.0012	0.0679	—	64.7	Ti ₃ O ₅
2			0.0024	0.0607	—	45.8	
3			0.0100	0.0815	—	28.9	
4			0.1502	0.0685	—	12	Ti ₂ O ₃
5			0.2601	0.0532	—	10	
6			0.5168	0.0289	—	9	
7			1.470	0.0301	—	10.5	Ti ₃ O ₅
8		Al ₂ O ₃ (TiO _x)	0.0057	0.0226	—	30.7	
9			0.0059	0.0214	—	38.2	
10			0.0276	0.0197	—	21.1	
11			0.0291	0.0211	—	20.2	
12			0.0332	0.0259	—	21	
13			0.0369	0.0222	—	19.9	
14			0.0395	0.0429	—	16.9	
15			0.0476	0.0021	0.0022	16.5	
16			0.0493	0.0034	0.0014	15.2	
17			0.0535	0.0220	—	17.4	
18			0.0811	0.0143	0.0020	13.3	
19			0.0885	0.0022	0.0024	9.3	
20			0.0888	0.0429	0.0024	10.8	
21			0.0934	0.0498	0.0008	10.7	
22			0.1022	0.0220	0.0003	9.50	
23			0.1119	0.0165	0.0006	10.9	
24			0.1185	0.0325	0.0043	10.3	
25			0.1245	0.0478	0.0007	9	
26			0.1469	0.0235	0.0080	11	
27			0.1656	0.0390	0.0029	8.7	
28			0.1782	0.0296	0.0038	11.5	
29			0.1903	0.0334	0.0034	10.9	
30			0.1925	0.0155	0.0036	10.8	
31			0.2153	0.0221	0.0055	9.6	
32			0.2576	0.0168	0.0113	8.5	
33	1823	TiO _x	0.3034	0.0140	0.0059	8.8	Ti ₃ O ₅ , Ti ₂ O ₃
34			0.3140	0.0205	0.0076	10	
35			0.3321	0.0191	0.0087	8.8	
36			0.3562	0.0170	0.0049	9.6	
37			0.3949	0.0186	0.0093	9.2	
38			0.4503	0.0279	0.0041	9.2	
39			0.5189	0.0324	0.0040	8.7	
40			0.6248	0.0293	0.0045	7.7	
41			0.6514	0.0113	0.0044	8	
42			0.9378	0.0246	0.0038	9.3	
43			1.762	0.0125	0.0130	12.5	
44			2.766	0.0110	0.0100	19.1	
45			3.612	0.0150	0.0120	26.5	
46	1923	TiO _x	0.5947	0.0216	—	5.1	Ti ₂ O ₃
47			0.6179	0.0262	—	5.2	
48			0.9308	0.0142	—	6.1	
49			1.772	0.0176	—	10.6	
50			2.845	0.0277	—	13.8	
51			3.839	0.0744	—	19.9	
52			4.451	0.0336	—	28	
53	1923	TiO _x	0.4213	0.0562	—	13.2	Ti ₃ O ₅
54			0.4365	0.0423	—	13.3	
55			0.5945	0.0183	—	12.7	
56			0.9429	0.0323	—	14.6	
57			1.140	0.0299	—	14.9	
58			1.564	0.0685	—	21.1	
59			2.622	0.0863	—	26.8	
60			3.644	0.0311	—	42.7	
61			4.746	0.0633	—	53.6	

* TiO_x powder at the bottom of Al₂O₃ Crucible

mass ppm by the inert gas fusion-infrared absorptiometry technique using the standard sample of steel containing 11 ± 1 mass ppm oxygen.

3. Results and Discussion

3.1. Equilibrium Ti–O Relation and TiO_x Phase Identification

The results of Ti deoxidation experiments for liquid iron in contact with titanium oxides are summarized in **Table 1**. Small amount of Si was picked up in the melt by the reduc-

Fig. 4. XRD patterns for titanium oxide layers near the TiO_x crucible/metal interface.

tion of quartz tube immersed in the melt for the temperature measurement. When the melt was contained in an Al₂O₃ crucible with titanium oxide powder at the bottom of the melt, small amount of Al was picked up. However, Al was not detected in the melt when the melt was contained in a crucible of titanium oxide powder.

Figure 4 shows the results of XRD analysis on the titanium oxide layers near the oxide/metal interface after the Ti deoxidation experiments. The XRD pattern for a mixture of solid Ti₂O₃ and TiO₂ powders shown in Fig. 2 has changed to new patterns of equilibrium titanium oxides. As shown in the figure, the equilibrium titanium oxide phase was identified as Ti₃O₅ for Fe–Ti alloys containing from 0.0012 to 0.21 mass% Ti, and Ti₂O₃ for alloys containing from 0.26 to 3.6 mass% Ti at 1873 K. For an alloy containing 0.25 mass% Ti, the equilibrium oxide phase was a mixture of Ti₃O₅ and Ti₂O₃. Therefore, the critical Ti content in liquid iron at which both Ti₃O₅ and Ti₂O₃ are the equilibrium oxide phases is experimentally determined as 0.25 mass% at 1873 K in the present study. The thermodynamic calculation of critical Ti content using the data obtained in the present study will be discussed later.

Figure 5 shows the equilibrium relations between Ti and O dissolved in liquid iron at 1873 K determined in the present study together with previous results.^{3,6,8,10,11)} The oxygen solubility minimum was about 7.7 mass ppm at 0.625 mass% Ti, and the Ti–O relation was not much affected by whether using a titanium oxide crucible or an Al₂O₃ crucible with titanium oxide powder at the bottom of the melt in the present study. As shown in the figure, the experimental results obtained by various equilibration techniques are widely dispersed. Fruehan¹¹⁾ measured the oxygen activity

Fig. 5. Equilibrium relation between [%Ti] and [%O] in liquid iron at 1873 K together with previous results.

by the EMF method using $\text{ZrO}_2(\text{CaO})$ and $\text{ThO}_2(\text{Y}_2\text{O}_3)$ electrolyte oxygen cells, and also determined the oxygen solubility by the sampling method in Fe–Ti melts at 1873 K. He used ThO_2 and ZrO_2 crucibles for the containers of Fe–Ti melts. His oxygen solubility minimum was 33 mass ppm at 0.32 mass% Ti, and it is much higher than the others including the result of present study. The oxygen solubility data for Fe–Ti melts determined by Smellie and Bell⁶⁾ with Al_2O_3 and Ti_3O_5 crucibles, and Kojima *et al.*³⁾ with Al_2O_3 , MgO and CaO crucibles are widely scattered. However, their data of lower oxygen content range are comparable to the data determined in the present study. Among those data, the results of present study are in good agreement with the studies by Janke and Fischer⁸⁾ and Cha *et al.*^{9,10)} who used sintered titanium oxide crucibles.

Janke and Fischer investigated the Ti deoxidation equilibrium in liquid iron at 1873 K by the EMF method using a $\text{ZrO}_2(\text{CaO})$ – $\text{ThO}_2(\text{Y}_2\text{O}_3)$ bielectrolyte oxygen cell also by the sampling method.⁸⁾ They measured the oxygen activity and the oxygen content in liquid iron containing from 0.001 to 8.8 mass% Ti contained in sintered titanium oxide crucibles. They calculated the Ti activity in Fe–Ti melts using the EMF data assuming the activities of titanium oxides are unity. In the present study, some trials were also made to measure the oxygen activity in Fe–Ti melts using a $\text{ZrO}_2(\text{CaO})$ electrolyte oxygen cell. After the cell measurement, the electrolyte/melt interface was analyzed by the SEM-EDS as shown in Fig. 6. At a Ti content of 0.395 mass% (Run 37), a pure titanium oxide was formed on the surface of the electrolyte. However, at about 0.18 mass% Ti content (Run 28), there was a solid solution layer of titanium oxide and zirconium oxide formed at the electrolyte–melt interface as shown in the figure. Therefore, the oxygen activity measured by the oxygen cell would be affected by the purity or activity of titanium oxides formed at the ZrO_2 electrolyte/melt interface depending on Ti content in Fe–Ti melts. For this reason, the oxygen activity measurement for Fe–Ti melts using ZrO_2 electrolyte was not carried out further in the present study.

Recently, Cha *et al.*^{9,10)} also studied the equilibrium between Ti and O in liquid Fe–Ti alloy contained in sintered Ti_3O_5 crucibles at 1873 K. They emphasized the impor-

[wt% Ti]	0.18	0.395
SEM		
Ti		
Zr		
Fe		
Reaction product	TiO_x - ZrO_2 solid solution	Pure TiO_x

Fig. 6. SEM-EDS analysis results on the ZrO_2 electrolyte/melt interface.

Fig. 7. EPMA analysis results on the TiO_x crucible/metal interface (Run 7).

tance of identification of equilibrium titanium oxide phases formed at the interface between the crucibles and Ti containing iron melt. They identified the equilibrium titanium oxide phases of Ti_3O_5 , Ti_2O_3 and TiO formed at the interface as a function of Ti content in Fe–Ti melts with the electron backscatter diffraction (EBSD) pattern analysis at 1873 K.⁹⁾ In the present study, the equilibrium titanium oxide phase was identified by the XRD analysis as Ti_3O_5 for alloys containing from 0.0012 to 0.25 mass% Ti, and Ti_2O_3 from 0.25 to 3.6 mass% Ti at 1873 K. The purity or activity of equilibrium titanium oxides should be also considered for the accurate thermodynamic analysis of Ti deoxidation equilibria. Figure 7 shows the result of EPMA analysis on the crucible/metal interface after the Ti deoxidation experiment at 1.47 mass% Ti content (Run 7). The oxide layer was virtually a pure titanium oxide phase free

from other oxides of Fe, Si and Al. Suzuki *et al.*⁷⁾ measured the solid solubility of FeO_l in synthetic titanium oxide crucibles after the equilibration with Fe–Ti melts at 1873 K. They reported that there was no solubility of FeO_l in TiO and Ti_2O_3 , but there was an increasing solubility of FeO_l in titanium oxides of higher O/Ti ratio (1.67–2: Ti_3O_5 and TiO_2) as shown in Fig. 8.⁷⁾

In the present study, some of Ti deoxidation experiments were carried out using Al_2O_3 crucibles with titanium oxide powder located at the bottom of the crucible. Ti in the melt would react with Al_2O_3 to dissolve some Al in the melt and form titanium oxides as following reaction;

Therefore, it is important to give a consideration for the equilibrium titanium oxide phase which may be formed at the interface between Al_2O_3 crucibles and Fe–Ti melt. The inner surface of Al_2O_3 crucibles were examined by the SEM-EDS after the Ti deoxidation experiments. However, no reaction layer was observed on the surface of Al_2O_3 crucible. Instead, there was a thin titanium oxide layer formed on the surface of the melt when the Ti content was higher than 0.2 mass% in Fe–Ti melt. Figure 9 shows the SEM-EDS analysis results on the titanium oxide layers formed on the melt surface and Al_2O_3 crucible/melt interface for the

Fig. 8. The solid solubility of FeO_l in titanium oxide at 1873 K.

melt containing 1.76 mass% Ti (Run 43). The oxide layers were virtually pure titanium oxide phases free from other constituents. The thin film XRD analysis on top oxide layer identified the deoxidation product as Ti_2O_3 as shown in Fig. 10. Therefore, considering the results in Figs. 7, 9 and 10, it can be concluded that pure solid Ti_2O_3 is the equilibrium deoxidation product for Fe–Ti melts at Ti contents higher than 0.25 mass% at 1873 K, regardless of using a titanium oxide crucible or an Al_2O_3 crucible with titanium oxide powder at the bottom of the melt in the present study.

3.2. Thermodynamics of Ti Deoxidation in Liquid Iron for Ti_2O_3 Formation

The deoxidation reaction of Ti to form Ti_2O_3 in liquid iron and its equilibrium constant can be expressed by Eqs. (2) and (3):

$$\begin{aligned} \log K_{\text{Ti}_2\text{O}_3} &= \log(a_{\text{Ti}_2\text{O}_3} / h_{\text{Ti}}^2 \cdot h_{\text{O}}^3) \\ &= \log(a_{\text{Ti}_2\text{O}_3} / f_{\text{Ti}}^2 \cdot [\% \text{Ti}]^2 \cdot f_{\text{O}}^3 \cdot [\% \text{O}]^3) \quad \text{.....(3)} \end{aligned}$$

Fig. 10. Thin film XRD patterns for TiO_x layer formed on the melt surface at 1873 K (Run 43).

Fig. 9. SEM-EDS analysis results of TiO_x layer formed on the melt surface at 1873 K (Run 43).

Table 2. Interaction parameters used in the present study.

	1873K	Temp. Dependency	Reference
e_{Ti}^{Ti}	0.048	-	8
e_{Ti}^{Al}	0.048	1873~1973K	18
e_{Ti}^{Si}	-0.0256	177.5/T-0.12	20
e_O^O	-0.17	-1750/T+0.76	2
e_O^{Al}	-1.17	-	2
e_O^{Si}	-0.066	1823~1923K	2

where $K_{Ti_2O_3}$, $a_{Ti_2O_3}$, h_i and f_i are the equilibrium constant, the Raoultian activity, the Henrian activity and the Henrian activity coefficient, respectively. The standard states of h_{Ti} and h_O are their infinitely dilute solution in liquid iron, and that of $a_{Ti_2O_3}$ is pure solid Ti_2O_3 . The activity coefficients of Ti and O in liquid iron can be expressed by Wagner's relation¹³⁾ using the first- and second-order interaction parameters.

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

$$\log f_O = e_O^O[\%O] + r_O^O[\%O]^2 + e_O^{Ti}[\%Ti] + r_O^{Ti}[\%Ti]^2 + r_O^{Ti,O}[\%Ti][\%O] \quad (5)$$

Using only the first-order interaction parameters and the Lupis' reciprocal relationship¹⁷⁾ between e_{Ti}^O and e_O^{Ti} , Eq. (3) can be rewritten as the following relation:

$$-\log K'_{Ti_2O_3} + \log a_{Ti_2O_3} - \sum 2e_{Ti}^k[\%k] - \sum 3e_O^l[\%l] = e_{Ti}^O(2[\%O] + 1.002[\%Ti]) + \log K_{Ti_2O_3} \quad (6)$$

Where $K'_{Ti_2O_3}$ ($=[\%Ti]^2 \cdot [\%O]^3$) is the apparent equilibrium constant, k and l represent elements other than O and Ti, respectively, and the value of $a_{Ti_2O_3}$ is unity in the present study. When Al and Si are present in liquid iron, the interaction parameters of those elements on Ti and O should be also considered. The interaction parameters used in the present study are summarized in **Table 2**.^{2,8,18-20)}

Figure 11 shows a plot for the relation expressed by Eq. (6) using the present experimental data for iron melts containing 0.26–0.94 mass% Ti at 1 873 K. It is apparent from the figure that the data points determined at different Ti contents show a good linear relationship. The value of $\log K_{Ti_2O_3}$ obtained by extrapolating the line is found to be approximately 10.62 at 1 873 K. The values of $\log K_{Ti_2O_3}$ at 1 873 K previously reported are in the range of 9.9–11.69 as shown in **Table 3**.^{2-8,10-12,21,22)} Among those values, the present data is in good agreement with the values of 10.39 determined by Búžek⁵⁾ and 10.43 determined by Janke and Fischer⁸⁾ at 1 873 K.

The value of e_{Ti}^O can be obtained from the slope of the line as -1.62 , and e_O^{Ti} as -0.541 using the reciprocal relationship.¹⁷⁾ The recommended value of the Japan Society for the Promotion of Science (JSPS)²⁾ for e_{Ti}^O is -1.12 at 1 873 K taken from the data reported by Fruehan.¹¹⁾ However, considering a rough estimation of e_{Ti}^O from the non-linear plot of $\log f_O$ vs. Ti content over a wide composition range of 0.02–12.5 mass% Ti, this value does not seem to

Fig. 11. Relation of Eq. (6) to determine e_{Ti}^O and $\log K_{Ti_2O_3}$ values.**Table 3.** $\log K$ of Ti deoxidation and interaction parameters of Ti and O in liquid iron at 1 873 K.

Equilibrium Phase	$\log K$	e_O^{Ti}	r_O^{Ti}	Reference
Ti_2O_3	18.71	-		21
Ti_2O_3	11.53	-		
Ti_3O_5	19.26	-1.0		22
Ti_2O_3	11.69	-0.42		
Ti_3O_5	17.4	-0.37		3
Ti_2O_3	9.90	-0.65		4
Ti_3O_5	17.56	-4.79		5
Ti_2O_3	10.39	-0.75		
Ti_3O_5	18.5	-5.0		6
Ti_3O_5	*16.10	-0.31		7
Ti_3O_5	17.13	-		8
Ti_2O_3	10.43	-		
Ti_3O_5	16.86	-0.34		10
Ti_2O_3	10.17	-		
-	-	*-1.12		11
-	-	-0.6	0.031	12
Ti_3O_5	17.56	-0.541	0.0385	Present study
Ti_2O_3	10.62			

* JSPS recommended values(Ref. 2)

be a reliable one to use. Sigworth and Elliott recalculated the first- and second-order interaction parameters of e_{Ti}^O and r_{Ti}^O using Fruehan's experimental data¹¹⁾ as -0.6 and 0.031 at 1 873 K, respectively, and compiled them in their thermodynamic data of liquid dilute iron alloys.¹²⁾

In the present study, the equilibrium relations between Ti and O in liquid iron at temperatures other than 1 873 K were also measured. **Figure 12** compares the Ti–O relations measured at 1 823 K and 1 923 K using titanium oxide crucibles for iron melts containing 0.42–4.75 mass% Ti together with data obtained at 1 873 K. The equilibrium titanium oxide phases at this Ti concentration range at 1 823 K and 1 923 K were all identified as pure solid Ti_2O_3 . By the same procedure using Eq. (6), the equilibrium constants for the reaction (2) and the first-order interaction parameters between Ti and O at 1 823 K and 1 923 K can be also determined as shown in Fig. 11.

Figure 13 shows the temperature dependences of $\log K_{Ti_2O_3}$ and e_{Ti}^O values determined in the present study, and they can be expressed as Eqs. (7) and (8) in the temperature range of 1 823 to 1 923 K.

Fig. 12. Relations between [%Ti] and [%O] in liquid iron at 1823, 1873 and 1923 K.

$$\log K_{\text{Ti}_2\text{O}_3} = 44\,238/T - 13.0 \quad (7)$$

$$e_{\text{O}}^{\text{Ti}} = -1642/T + 0.3358 \quad \text{or} \quad e_{\text{Ti}}^{\text{O}} = -4915/T + 1.005 \quad (8)$$

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

$$\begin{aligned} & -\log K_{\text{Ti}_2\text{O}_3} - \log K'_{\text{Ti}_2\text{O}_3} + \log a_{\text{Ti}_2\text{O}_3} \\ & - 2 \sum e_{\text{Ti}}^k [\%k] - \sum e_{\text{O}}^l [\%l] + 0.00414 [\% \text{Ti}] [\% \text{O}] \\ & - e_{\text{Ti}}^{\text{O}} (2 [\% \text{O}] + 1.002 [\% \text{Ti}] - 0.03 [\% \text{Ti}] [\% \text{O}]) \\ & = r_{\text{Ti}}^{\text{O}} (2 [\% \text{O}]^2 + 2.005 [\% \text{Ti}] [\% \text{O}]) \\ & + r_{\text{O}}^{\text{Ti}} (3 [\% \text{Ti}]^2 + 11.97 [\% \text{Ti}] [\% \text{O}]) \quad (9) \end{aligned}$$

where k and l represent the same meanings as in Eq. (6), and $\log K_{\text{Ti}_2\text{O}_3}$ and e_{Ti}^{O} were determined previously as Eqs. (7) and (8), respectively. The values of r_{Ti}^{O} and r_{O}^{Ti} are assumed as zero in the present study. The cross product terms of r_{Ti}^{O} and r_{Ti}^{O} can be expressed as a function of r_{O}^{Ti} and r_{O}^{Ti} , respectively, using the following relationships¹⁷⁾:

$$r_{\text{Ti}}^{\text{Ti},\text{O}} = 2 \left(\frac{M_{\text{Ti}}}{M_{\text{O}}} \right) r_{\text{O}}^{\text{Ti}} + 0.01 e_{\text{Ti}}^{\text{Ti}} - 0.01 e_{\text{Ti}}^{\text{O}} \quad (10)$$

$$r_{\text{O}}^{\text{Ti},\text{O}} = 2 \left(\frac{M_{\text{O}}}{M_{\text{Ti}}} \right) r_{\text{Ti}}^{\text{O}} + 0.01 e_{\text{O}}^{\text{Ti}} - 0.01 e_{\text{O}}^{\text{O}} \quad (11)$$

Therefore, all terms in Eq. (9) are known values except the second-order interaction parameters, r_{O}^{Ti} and r_{Ti}^{O} . These parameters can be determined from the experimental data of Ti and O relation for the melts containing 1.47–4.75 mass% Ti. Figure 14 shows the relation of Eq. (9) in which both sides are divided by the term $(2 [\% \text{O}]^2 + 2.005 [\% \text{Ti}] [\% \text{O}])$ at 1823, 1873 and 1923 K. The temper-

Fig. 13. Temperature dependences of $\log K_{\text{Ti}_2\text{O}_3}$ and e_{O}^{Ti} values.

Fig. 14. Relation of Eq. (9) to determine r_{O}^{Ti} and r_{Ti}^{O} values.

ature dependence of the relation was negligible. The values of and determined by a linear regression analysis are 0.0385 and -0.355 , respectively. The second-order r_{O}^{Ti} value of 0.0385 is in good agreement with the value of 0.031 at 1873 K reported by Sigworth and Elliott.¹²⁾

The values of interaction parameters between Ti and O and the equilibrium constant for the reaction (2) determined in the present study are summarized in Table 4. Using the thermodynamic parameters determined in the present study, the Ti deoxidation product for the formation of pure solid Ti_2O_3 in Fe–Ti–O melt can be derived as Eq. (12).

$$\begin{aligned} & \log [\% \text{Ti}]^2 [\% \text{O}]^3 \\ & = -(44\,238/T - 13.0) \\ & - (-4915/T + 1.005)(2 [\% \text{O}] + 1.002 [\% \text{Ti}]) \\ & - 2(e_{\text{Ti}}^{\text{Ti}} [\% \text{Ti}] + r_{\text{O}}^{\text{Ti}} [\% \text{O}]^2 + r_{\text{Ti}}^{\text{Ti},\text{O}} [\% \text{Ti}] [\% \text{O}]) \\ & - 3(e_{\text{O}}^{\text{O}} [\% \text{O}] + r_{\text{O}}^{\text{O}} [\% \text{Ti}]^2 + r_{\text{O}}^{\text{Ti},\text{O}} [\% \text{Ti}] [\% \text{O}]) \quad (12) \end{aligned}$$

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

	1873K	Temp. Dependency
e_{O}^{Ti}	-0.541	-1642/T + 0.3358
e_{Ti}^{O}	-1.620	-4915/T + 1.005
r_{O}^{Ti}	0.0385	1823~1923K
r_{Ti}^{O}	-0.355	1823~1923K
$\log K_{\text{Ti}_2\text{O}_3}$	10.62	44238/T-13.0
$\log K_{\text{Ti}_3\text{O}_5}$	17.56	72813/T-21.32

In Fig. 12, the solid lines shown in the Ti concentration range higher than 0.25 mass% are the calculated equilibrium Ti–O relations in liquid iron for the formation of Ti_2O_3 (s) at 1 823, 1 873 and 1 923 K using Eq. (12), assuming the activity of Ti_2O_3 (s) as unity. The calculated relations well represent the experimental results obtained over a wide range of Ti content. The dotted lines shown in the same Ti concentration range are the calculated Ti–O relations using only the first order interaction parameters. The dotted lines show a good correlation with the experimental results at Ti contents less than 1 mass%. However, they deviate from the experimental results significantly at higher Ti contents.

From the temperature dependence of equilibrium constant for the Ti deoxidation reaction expressed as Eq. (7), the following Gibbs free energy change for the reaction (2) can be derived in the temperature range of 1 823 to 1 923 K.

$$\Delta G_2 = -845\,928 + 248.6T \text{ J/mol} \quad \text{.....(13)}$$

The standard Gibbs free energy change for the formation of Ti_2O_3 (s) is given by NIST-JANAF¹⁴⁾ as Eq. (15).

$$\Delta G_{14}^\circ = -1\,502\,126 + 258.08T \text{ J/mol}^{14)} \quad \text{.....(15)}$$

Combination of Eqs. (13), (15) and the free energy change data for the dissolution of oxygen in liquid iron¹⁵⁾ given as Eq. (17) would give the free energy change for the dissolution of Ti in liquid iron as Eq. (19).

$$\Delta G_{16} = -117\,122 - 2.88T \text{ J/g} \cdot \text{atom}^{15)} \quad \text{.....(17)}$$

$$\Delta G_{18} = -152\,416 + 9.07T \text{ J/g} \cdot \text{atom} \quad \text{.....(19)}$$

From Eq. (19), one would be able to calculate the value of γ_{Ti}° , the activity coefficient of Ti in liquid iron at infinite dilution, as 0.011, 0.014 and 0.018 at 1 823 K, 1 873 K and 1 923 K, respectively. **Table 5** compares these values together with previous results.^{2,22–24)}

Table 5. Henrian activity coefficient of Ti, γ_{Ti}° in liquid iron at 1 873 K.

γ_{Ti}°	Method	Reference
0.011	Estimated from Hadley's data	23
0.033	Thermodynamic evaluation using experimental data	24
0.038	EMF	11
0.050	Estimated from experimental data	6
0.016	Thermodynamic evaluation using experimental data	7
*0.018	Knudsen Cell Mass Spectrometry	25
0.018	EMF	26
0.009	Thermodynamic evaluation using experimental data	10
0.011 at 1823K 0.014 at 1873K 0.018 at 1923K	Thermodynamic evaluation using experimental data	Present study

* JSPS recommended values(Ref. 2)

3.3. Thermodynamic Assessment of Ti Deoxidation Reaction for Ti_3O_5 Formation

In the present study, the equilibrium titanium oxide phase was identified as Ti_3O_5 for iron melts containing from 0.0012 to 0.25 mass% Ti at 1 873 K. The standard Gibbs free energy change for the formation of pure solid Ti_3O_5 is given by NIST-JANAF¹⁴⁾ as Eq. (21).

$$\Delta G_{20}^\circ = -2\,435\,202 + 420.5T \text{ J/mol}^{14)} \quad \text{.....(21)}$$

Combination of Eqs. (17), (19) and (21) would give the free energy change for Ti deoxidation reaction in liquid iron to form Ti_3O_5 (s) as:

$$\Delta G_{22} = -1\,392\,344 + 407.7T \text{ J/g} \cdot \text{atom} \quad \text{.....(23)}$$

Therefore, the Ti deoxidation product for the formation of pure solid Ti_3O_5 in Fe–Ti–O melt can be derived as Eq. (24).

$$\begin{aligned} \log[\% \text{Ti}]^3 [\% \text{O}]^5 &= -(72\,813/T - 21.32) \\ &\quad - (4\,915/T + 1.005) \cdot (3[\% \text{O}] + 1.67[\% \text{Ti}]) \\ &\quad - 3(e_{\text{Ti}}^{\text{Ti}} [\% \text{Ti}] + r_{\text{Ti}}^{\text{O}} [\% \text{O}]^2 + r_{\text{Ti}}^{\text{TiO}} [\% \text{Ti}][\% \text{O}]) \\ &\quad - 5(e_{\text{O}}^{\text{O}} [\% \text{O}] + r_{\text{O}}^{\text{Ti}} [\% \text{Ti}]^2 + r_{\text{O}}^{\text{TiO}} [\% \text{Ti}][\% \text{O}]) \\ &\quad \text{.....(24)} \end{aligned}$$

In Fig. 12, the solid lines shown in the Ti concentration range lower than 0.25 mass% are the calculated equilibrium Ti–O relations in liquid iron for the formation of Ti_3O_5 (s) at 1 823, 1 873 and 1 923 K using Eq. (24), assuming the activity of Ti_3O_5 (s) as unity. However, it can be seen that the experimental results of Ti–O relation at 1 873 K deviate from the calculated relation at the same temperature. The deviation becomes more significant when Ti content decreases below 0.01 mass% in liquid iron. As discussed ear-

lier, Suzuki and Sanbongi⁷⁾ found that there was a significant solubility of FeO_l in titanium oxides with O/Ti ratio higher than 1.67 (Ti_3O_5) after the equilibration with liquid iron containing low Ti contents. Recently, Cha *et al.*⁹⁾ also found that the solid solubility of FeO_l in Ti_3O_5 phase increased significantly when the Ti content in liquid iron decreased below 0.01 mass% at 1 873 K. Therefore, such deviation at low Ti contents in the present study can be explained by the activity of Ti_3O_5 being less than unity due to the solid solution of FeO_l in Ti_3O_5 phase.

3.4. Critical Ti Content in Liquid Iron for Ti_2O_3 and Ti_3O_5 Formation

In the present study, the critical Ti content in liquid iron at which both Ti_3O_5 and Ti_2O_3 coexisted was experimentally determined as 0.25 mass% at 1 873 K. Cha *et al.*⁹⁾ recently estimated the critical Ti content in liquid iron for coexistence of Ti_3O_5 and Ti_2O_3 phases as 0.526 at 1 873 K using the standard free energies of titanium oxide formation¹⁴⁾ and their activity data of Ti in liquid iron at 1 873 K.¹⁰⁾

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

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

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

$$\begin{aligned} \log K_{24} &= \log(a_{\text{Ti}_2\text{O}_3}^5 / h_{\text{Ti}} \cdot a_{\text{Ti}_3\text{O}_5}^3) \\ &= -\log h_{\text{Ti}} = -(\log f_{\text{Ti}} + \log[\% \text{Ti}]) \\ &= -(e_{\text{Ti}}^{\text{Ti}}[\% \text{Ti}] + e_{\text{Ti}}^{\text{O}}[\% \text{O}] + \log[\% \text{Ti}]) \dots\dots(26) \end{aligned}$$

Where the activities of both Ti_3O_5 and Ti_2O_3 are assumed to be unity, the value of $e_{\text{Ti}}^{\text{Ti}}$ used in this study is 0.048^{8,18)} at 1 823–1 873 K, and the effect of oxygen on the Ti activity is assumed to be negligible due to its extremely small content. The critical Ti contents satisfying the Eq. (26) can be calculated as 0.33, 0.36 and 0.39 mass% at 1 823, 1 873 and 1 923 K, respectively. They are also shown in Fig. 12. The critical Ti content of 0.36 mass% Ti estimated at 1 873 K is slightly higher than 0.25 mass% Ti determined experimentally in the present study.

4. Conclusions

The relation of Ti and O dissolved in liquid iron equilibrated with solid titanium oxides has been determined in the temperature range of 1 823 to 1 923 K. The equilibrium titanium oxide phase was identified as Ti_3O_5 for Fe–Ti alloys containing from 0.0012 to 0.21 mass% Ti, and Ti_2O_3 for alloys containing from 0.26 to 3.6 mass% Ti at 1 873 K. The critical Ti content in liquid iron at which both Ti_3O_5 and Ti_2O_3 coexist was experimentally determined as 0.25 mass% at 1 873 K. The equilibrium constants of Ti deoxidation reactions for the formation of pure solid Ti_2O_3 and Ti_3O_5 , and the first- and second-order interaction parameters between Ti and O in liquid iron were determined as a function of temperature given by the following equa-

tions.

$$\log K_{\text{Ti}_2\text{O}_3} = 44\,238/T - 13.0$$

$$\log K_{\text{Ti}_3\text{O}_5} = 72\,813/T - 21.32$$

$$e_{\text{O}}^{\text{Ti}} = -1\,642/T + 0.3358, \quad e_{\text{Ti}}^{\text{O}} = -4\,915/T + 1.005$$

$$r_{\text{O}}^{\text{Ti}} = 0.0385, \quad r_{\text{Ti}}^{\text{O}} = -0.355$$

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

Acknowledgments

The present work was financially supported by POSCO (Grant No.: 2004Z021). The authors also wish to thank Mr. Gil-Yeol Ryu, RIST, Pohang for help with the analysis by EPMA.

REFERENCES

- 1) Y. D. Lee and S. H. Park: *J. Korean Inst. Met. Mater.*, **31** (1993), 984.
- 2) Steelmaking Data Sourcebook; The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Gordon and Breach Science Publishers, New York, (1988), 165.
- 3) Y. Kojima, M. Inoue and J. Ohi: *Arch. Eisenhüttenwes.*, **40** (1969), 667.
- 4) V. I. Yavoykii, L. B. Kosterev, A. A. Ayub and L. N. Rastorguev: *Russ. Metall.*, **2** (1971), 33.
- 5) Z. Bůžek: Proc. Int. Symp. On Metall. Chem. Application in ferrous Metallurgy, University Of Sheffield, United Kingdom, 2, (1971), 173.
- 6) A. M. Smellie and B. H. Bell: *Can. Metall. Q.*, **11** (1972), 351.
- 7) K. Suzuki and K. Sanbongi: *Trans. Iron Steel Inst. Jpn.*, **15** (1975), 618.
- 8) D. Janke and W. A. Fischer: *Arch. Eisenhüttenwes.*, **47** (1976), 195.
- 9) W. Y. Cha, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **46** (2006), 987.
- 10) W. Y. Cha, T. Nagasaka, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **46** (2006), 996.
- 11) R. J. Fruehan: *Metall. Trans.*, **1** (1970), 3403.
- 12) G. K. Sigworth and J. F. Elliott: *Met. Sci.*, **8** (1974), 298.
- 13) C. Wagner: Thermodynamics of Alloys, Addison-wesley Press, Cambridge, Mass., (1952), 47.
- 14) NIST-JANAF Thermochemical Tables, 4th ed., Amer. Chem. Soc., Westerville, Ohio, (1998).
- 15) E. T. Turkdogan: Physical Chemistry of High Temperature Technology, Academic Press, New York, (1980), 81.
- 16) W. G. Seo, W. H. Han, J. S. Kim and J. J. Pak: *ISIJ Int.*, **43** (2003), 201.
- 17) C. H. P. Lupis and J. F. Elliott: *Acta Metall.*, **14** (1966), 529.
- 18) W. Y. Kim, J. O. Jo, S. I. Kim, T. I. Chung, J. G. Kang and J. J. Pak: Hanyang University, Ansan, Korea, unpublished research, (2006).
- 19) G. Yuanchang and W. Changchen: *Metall. Trans. B.*, **21B** (1990), 543.
- 20) J. J. Pak, J. T. Yoo, Y. S. Jeong, S. J. Tae, S. M. Seo, D. S. Kim and Y. D. Lee: *ISIJ Int.*, **45** (2005), 23.
- 21) K. Segawa, E. Tsunetomi, Y. Nakamura and H. Chino: *Trans. Iron Steel Inst. Jpn.*, **9** (1969), 89.
- 22) A. Ghosh and G. V. R. Murthy: *Trans. Iron Steel Inst. Jpn.*, **26** (1986), 628.
- 23) J. Chipman: *Trans. Met. Sci. AIME.*, **218** (1960), 767.
- 24) H. Chino, Y. Nakamura, E. Tsunetomi and K. Segawa: *Tetsu-to-Hagané*, **52** (1966), 959.
- 25) T. Furukawa and E. Kato: *Tetsu-to-Hagané*, **61** (1975), 3060.
- 26) H. Y. Choi, W. E. Slye, R. J. Fruehan and R. C. Nunnington: *Metall. Mater. Trans. B.*, **36B** (2005), 537.