Identification of Titanium Oxide Phases Equilibrated with Liquid Fe–Ti Alloy Based on EBSD Analysis

Woo-Yeol CHA,1) Takahiro MIKI,2) Yasushi SASAKI2) and Mitsutaka HINO2)

1) Graduate Student, Graduate School of Engineering, Tohoku University, 6-6-02 Aoba-yama, Aoba-ku, Sendai 980-8579 Japan.
2) 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)

There are huge quantities of uncertainties on the Ti deoxidation equilibrium constants and their interaction parameters in the literatures including the recommended values by the Japan Society for the Promotion of Science (JSPS). The main reason of such uncertainties among the previous works is due to the insufficient information of titanium oxide phase in equilibrium with liquid Fe–Ti alloy. The measurement of the equilibrium phase changes of titanium oxides with various Ti contents in molten Fe–Ti alloy has been carried out in the present study. Molten Fe–Ti alloys with various Ti contents have been equilibrated with ‘Ti3O5’ crucibles at 1 873 K. The kinds of Ti oxide at the interface of ‘Ti3O5’ crucible contacted with molten Fe–Ti alloys have been identified as the equilibrium titanium oxides with the electron backscatter diffraction (EBSD) pattern analysis technique. After the ‘Ti3O5’ crucible reacted with molten Fe–Ti alloys adequately and both of them were quenched.

The present result on the stable region of equilibrium titanium oxides with Ti contents in Fe–Ti alloy was in good agreement with the thermodynamically calculated results based on the free energies of titanium oxides formation and the activity of Ti in Fe–Ti alloy.

KEY WORDS: titanium deoxidation; thermodynamics; electron backscatter diffraction; 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 molten steel for the precise control of Ti in the steelmaking process. Also, fine titanium oxide can be used to control of grain refinement with its dispersion in austenite grain.11

In spite of such importance, there are huge uncertainties on the Ti deoxidation equilibrium constants and their interaction parameters in the literature values2–17) including the recommended values of the Japan Society for the Promotion of Science (JSPS).16 Furthermore, the equilibrium relation between the stable titanium oxides and Ti contents in molten Fe–Ti alloy are not established yet. The main reason of such uncertainties among the previous works is due to the ambiguity of titanium oxide phases in equilibrium with molten Fe–Ti alloy. The Ti–O equilibrium relation in molten iron must be established for each titanium oxide saturated condition. It is, therefore, very important to identify titanium oxide phases of the equilibrium titanium oxides coexisted with particular compositions of liquid Fe–Ti alloy. However, the Ti–O system is very complex as shown in Fig. 1.18 There are the stoichiometric compounds Ti3O5, TiO2 solid solution, a high-temperature congruently melting oxide Ti2O3, the incongruently melting oxide ‘Ti3O5’ and so called Magneli phases with the generalized formula Ti3nO2n−1 (n=4)19 in Ti–O system. It is also widely known that the liquid Fe–Ti alloy is in equilibrium with ‘TiO’, Ti2O3 and ‘Ti3O5’ depending on the Ti contents as shown in Fig. 2. As a consequence of the complexity of Fe–Ti–O system, it comes difficult to evaluate the equilibrium relation between dissolved Ti and O in molten Fe–Ti alloy.

Many researchers2–17) have been tried to identify the stable region of titanium oxides equilibrated with the molten Fe–Ti alloy with various Ti content using the XRD or the other equipments. It is summarized in Table 1. In this Table, the present results by EBSD analysis are also shown. This is discussed later.

Wentrup and Hieber2) investigated the Ti deoxidation equilibrium relation in molten iron quantitatively for the first time. They found the basic feature of Ti deoxidation that the produced titanium oxide depended on Ti content in melt. Evans and Sloman13) as well as Hadley and Derge14) investigated the deoxidation product using the XRD and optical microscopy. They also found that equilibrium titanium oxides depended on the Ti content of the melt. Chino et al.7) adopted the Peeling method for the sampling of the deoxidation products for identification. They determined that
Fig. 1. Phase diagram of Ti–O system.\(^{18}\)

Fig. 2. Schematic illustration of the phase relation among Fe–Ti alloy and titanium oxides at 1873 K.

Table 1. Relation among various kinds of equilibrium titanium oxides and titanium contents in liquid iron at 1873 K.\(^{2-17}\)

| Author          | Method | Titanium Oxides                                      |
|-----------------|--------|------------------------------------------------------|
| H. Wentrup\(^{11}\) | B      | 2FeO·TiO\(_2\)                                       |
| E. L. Evans\(^{11}\)       | B      | FeO·TiO\(_2\), FeO·TiO\(_3\), TiO\(_2\), TiO\(_2\) |
| R. L. Hadley\(^{4}\)        | B      | FeO·TiO\(_2\)                                       |
| B. K. Laudes\(^{11}\)       | A      | 2FeO·TiO\(_2\), TiO\(_2\)                           |
| Z. Bötké\(^{6}\)            |        | TiO\(_2\)                                           |
| H. Chino\(^{7}\)            | A      | TiO\(_2\) (anowsitelet)                             |
| K. Suzuki\(^{9}\)           | A      | TiO\(_2\)                                           |
| Y. Koźmima\(^{10}\)         | A      | TiO\(_2\) (anowsitelet)                             |
| V. I. Yavorskiy\(^{11}\)    | B      | TiO\(_2\)                                           |
| A. M. Smelley\(^{10}\)      | A      | TiO\(_2\) (anowsitelet)                             |
| V. I. Yavorskiy\(^{11}\)    | B      | TiO\(_2\)                                           |
| K. Suzuki\(^{14}\)          | A      | TiO\(_2\) (anowsitelet)                             |
| D. Janke\(^{15}\)           | A      | TiO\(_2\), TiO\(_3\)                               |
| JPS recommended value\(^{16}\) |        | TiO\(_2\)                                           |
| C.-T. Mutale\(^{17}\)       | C      | TiO\(_2\), TiO\(_3\)                               |
| Present work              | D      | TiO\(_2\) (anowsitelet)                             |

A: Measurement of equilibrium
B: X-ray diffraction of inclusions in ingot
C: X-ray diffraction of deoxidation products
D: TEM analysis of deoxidation products
E: EBSD analysis of metal/crucible interface for equilibrium oxides
‘Ti₂O₅’ was the stable equilibrium oxide when mass% Ti was between 0.001 to 0.16 and Ti₅O₅ was one when it was between 0.1 to 2.1 mass% Ti. Janke and Fischer\(^1\) reported ‘Ti₂O₅’ as the stable equilibrium oxides when mass% Ti was between 0.01 to 0.2 and Ti₂O₃ was one when it was between 0.2 to 2 mass% Ti. Smellie and Bell\(^2\) investigated the equilibrium between Ti and O in liquid iron using the ‘Ti₃O₅’ crucible. They controlled the oxygen partial pressure using H₂–H₂O gas mixture and determined that the equilibrium products were ‘Ti₃O₅’ when mass% Ti was between 0.001 to 0.16 and Ti₅O₅ was one when it was between 0.75 to 1.35 mass% Ti at 1898 K. Janke and Fischer\(^1\) reported ‘Ti₂O₅’ as the stable equilibrium oxides when mass% Ti was from 0.1 to 2 mass% Ti. The JSPS recommended values\(^6\) are based on the experimental results submitted by Suzuki and Sanbongi.\(^4\) They determined the concentration product by equilibrium measurements between Fe–Ti melt and a crucible consisted of titanium oxide (TiOₓ, 0<x<1) phases. In the range of important titanium content for commercial use, that is 0.01–0.25 mass% Ti, the equilibrium deoxidation product was ‘Ti₂O₅’ with small amount of iron content, which depended on Ti content in liquid Fe–Ti alloy.

The electron backscattering diffraction (EBSD) technique has significantly developed in recent years. The technique is most widely used for crystal orientation measurement, and it also provides a powerful tool for crystal phase identification. EBSD patterns are generated by inelastic interaction of the incident electron beam with the sample. Some of these electrons have the correct angular relationship with the planes for coherent scattering (Bragg diffraction). Each plane generates a band of diffracted electron intensity. These bands form a pattern (Kikuchi pattern) that reflects the crystal structure. These patterns can be used to determine the crystal structure.

EBSD patterns contain a large amount of information about the crystal structure. It is possible to use this information for determination of the phase space group from the symmetry elements contained in the pattern. Table 2 shows the crystal structures of titanium oxides. Fortunately, all of the crystal structure of each titanium oxide are different each other. The identification of titanium oxide at the inner interface of the crucible can, therefore, be confirmed by EBSD analysis.

A general introduction to EBSD is described everywhere.\(^20,21\) The identification of the titanium oxides was generally carried out at 25 kV accelerating voltage and emission beam current of approximately 93 μA in this study. A carbon coating was necessary to avoid charging of the sample. Computer assisted indexing of EBSD pattern is now well developed and commercially available, and the identification of titanium oxides phases can be automatically carried out. FE-SEM fitted with an Orientation Imaging Microscopy (OIM\(^7\)) system was used in the present study.

### Table 2. Crystal structure of titanium oxides.\(^24\)

| Oxides | Crystal Structure |
|--------|------------------|
| Ti₂O₅ | 0 – 130 K: crystal I, Triclinic Structure |
|       | 130 – 150 K: crystal II, Triclinic Structure |
|       | 150 – 1950 K: crystal III, Triclinic Structure |
|       | Above 1950 K: Liquid |
| Ti₅O₅ | 0 – 450 K: crystal, alpha, Monoclinic Structure |
|       | 450 – 2050 K: crystal, beta, Pseudobrookelite type with slight monoclinic distortion |
|       | Above 2050 K: Liquid |
| Ti₂O₃ | 0 – 470 K: crystal, alpha, Trigonal Structure |
|       | 470 – 2115 K: crystal, beta, Trigonal Structure |
|       | Above 2115 K: Liquid |
| TiO₂ | 0 – 1265 K: crystal, alpha, Monoclinic Structure |
|       | 1265 – 2023 K: crystal, beta, Cubic NaCl-type Structure |
|       | Above 2023 K: Liquid |

#### 3. Experimental

#### 3.1. Fabrication of ‘Ti₂O₅’ Crucible

Figure 3 shows the schematic diagram of the Ti–oxide crucible handcraft. The equipment consists of high purity alumina reaction chamber (outer diameter: 80 mm, inner diameter: 70 mm, height: 1000 mm) and three heating zone type electric resistance furnace. The temperature was monitored by Pt–13%Pt/Rh thermocouple located just below the crucible and controlled by the other three thermocouples which were inserted between heating element and the reaction tube.

Reagent ‘TiO₂’ anatase was chosen as the starting mater-
ial for the production of pure ‘Ti$_3$O$_5$’ powder. The ‘TiO$_2$’ anatase (99.8% purity) of 80 g was loaded in a high purity alumina crucible (outer diameter: 60 mm, inner diameter: 50 mm, height: 150 mm) and placed in the hot zone of a vertical furnace. The ‘TiO$_2$’ anatase was heated in a dehydrated and deoxidized Ar atmosphere. After a sample reached the desired temperature, Ar gas was switched to the H$_2$ gas. As it was found in preliminary experiments that the time required for the reduction to the ‘Ti$_3$O$_5$’ was 6 h at 1 773 K. ‘TiO$_2$’ anatase (99.8% purity) powder was reduced to produce ‘Ti$_3$O$_5$’ powder by H$_2$ at 1 773 K for 12 h. The produced ‘Ti$_3$O$_5$’ was ground for the homogenization and again reduced by H$_2$ at 1 773 K for 12 h for the successful production of ‘Ti$_3$O$_5$’ powder. The average size of fabricated ‘Ti$_3$O$_5$’ powder was 50.6 $\mu$m. ‘Ti$_3$O$_5$’ powder contacted to the wall of Al$_2$O$_3$ crucible was abandoned to avoid any contamination from Al$_2$O$_3$ crucible. The remained center part of ‘Ti$_3$O$_5$’ powder was examined using the SEM-EDS technique and XRD analysis and Al$_2$O$_3$ could not be detected in the powder.

The rubber press with CIP (Cold Isostatic Press) was chosen for production of ‘Ti$_3$O$_5$’ crucible. The compressed green ‘Ti$_3$O$_5$’ crucibles were sintered in Ar/H$_2$ stream of 100 mL/min. Temperature measurement was conducted by the infrared radiation pyrometer, which was calibrated by the melting points of Fe and Cu. The melts was quenched rapidly by switching off the power and helium gas blowing into the reaction chamber after given reaction time. 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. The center part of metal sample was virtually clean without any noticeable inclusions and was used for the chemical analyses.

Figure 6 shows that variation of the Ti and O content with reaction time after addition of Fe–Ti alloy into molten Fe. They reached constant values after 30 min holding, and they reached to the equilibrium condition so that the metal specimen held for 60 min after addition of Fe–Ti alloy into molten Fe and quenched was used to analyze Ti and O content in the all of the experiments.

The concentration of O in the quenched samples was determined by an inert gas impulse infrared absorption spectroscopy. The Fe–Ti melt samples were cut into 1 g of cubic...
shape by using a fine cutter. The surface of samples was polished using silicon carbide wet polishing papers (up to #1500-grit) and then electrically polished using the solution of acetic acid (CH₃COOH) and perchloric acid (HClO₄) for 6 min with constant current of 0.5A for O analysis. After any polishing step the samples were applied to a supersonic cleaning.

The concentration of Ti in the quenched samples was determined by a high-frequency induction coupled plasma spectroscopy (ICP). The surface of samples was polished by using silicon carbide wet polishing papers (up to #1500-grit) for Ti analysis. The samples were applied to a supersonic cleaning after any polishing step. The metallic samples (0.2–0.5 g) were dissolved in 30 mL of HCl (1+1) at 353 K for 6 h. Water and acids used were ultra pure grades. The diluted solution was filtrated by 5B filter paper after dissolving the sample. No residue was remained in the filter paper.

### 3.3. Sample Preparation for EBSD Observation

One of the most important requirements in using the EBSD for identification of titanium oxides structure is the sample’s surface preparation. The electron beam interaction depth is approximately 10 nm, and this layer must be relatively strain free and clean to obtain the pattern. The interface of the titanium oxide crucible contacted with Fe–Ti sample was cut into cubic shape (5×5×5 mm) by using a fine cutter and then mounted. For SEM and EBSD analysis, the surface of samples were polished by using silicon carbide wet polishing papers (up to #1500-grit) and then polished by using alumina dry polishing paper (up to #4000-grit), and finally, mechanically polished using 1 μm diameter of diamond paste and 0.03 μm diameter of colloidal silica suspended solution to remove any surface damage and most of the strain on surface layer. The samples were applied to a supersonic cleaning after any polishing step. The finally polished samples were applied for carbon coating. EBSD technique was applied to all samples to identification of equilibrium titanium oxides phases and Fe solid solubility in ‘TiₓOᵧ’ phase was analyzed quantitatively by EDS.

### 4. Results

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

Various Ti contents of molten Fe–Ti alloy were melted in ‘TiₓOᵧ’ crucibles at 1 873 K in the present work. Different equilibrium titanium oxide phase was formed at the interface between Fe–Ti alloy and the original ‘TiₓOᵧ’ crucibles depending on the Ti contents. Therefore, the titanium oxide formed at the interface between the Fe–Ti alloy and the ‘TiₓOᵧ’ crucibles must be identified to establish the Ti–O equilibrium relation.

The XRD analysis of the equilibrium titanium oxides formed at the metal/crucible interface after the experiment is generally quite difficult because the formed titanium oxides layer is a thin film at the metal/crucible interface. As the XRD diffraction method provides the average information of selected volume of samples, it would be misleading information of titanium oxides.

If the SEM-EDS was used for the identification of titanium oxides at crucible interface, it is easily misleading and the ratio of O/Ti may be deviated from that of equilibrium titanium oxides since the accuracy of oxygen detecting by SEM-EDS is too low. In fact, the O/Ti ratio of ‘TiₓOᵧ’ (1.76) by SEM-EDS was quite different from the correct ratio of 1.67 as shown in Fig. 7. The same deviation was also observed for other titanium oxides.

The widely used applicable technique for the identification of micrometer-sized phases with the transmission electron microscope (TEM) requires the preparation of electron transparent samples that is very difficult and time intensive. Furthermore, the extracting method of the titanium oxide particles from the solidified steel in an ethanol included strongly oxidizing solution of iodine affects the oxidation state of titanium in its oxide.

On the other hand, the phase identification of formed ti-
tanium oxides at the metal/crucible interface is easily accomplished by EBSD technique. This crystallographic information is used to identify phases through the database of powder diffraction files.

Figure 8 shows the EBSD analysis results for ‘Ti$_3$O$_5$’. The ‘Ti$_3$O$_5$’ crucible was equilibrated with Fe–0.0004 mass% Ti alloy. The crystal structure of ‘Ti$_3$O$_5$’ was anosovite named by modified orthorhombic.

Figure 9 shows the EBSD analysis results for Ti$_2$O$_3$. In this experiment, Fe–2mass%Ti alloy was melted in a ‘Ti$_3$O$_5$’ crucible. ‘Ti$_3$O$_5$’ reacted with Ti in the melt during experiment and then Ti$_2$O$_3$ formed as new phase at the melt/crucible interface. The newly formed equilibrium phase covered uniformly on the original crucible wall and the thickness of layer between melt and crucible was found to be from 50 to 100 µm. The crystal structure of Ti$_2$O$_3$ is trigonal.

Figure 10 shows the EBSD analysis results for TiO. Fe–16.6mass%Ti alloy was formed at the interface. The crystal structure of TiO is cubic. However, the Ti$_4$O$_7$ phase was not observed for the variation of Ti contents from 0.0004 to 16.6 mass% in the metal.

Measured result is nearly the same as that reported by Suzuki and Sanbongi as shown in Table 1. They investigated the equilibrium between molten Fe–Ti alloy and crucible consisted of titanium oxide (TiO$_x$ (0<x<1)). The present EBSD analysis results of phase equilibria between the various kinds of titanium oxides and molten Fe–Ti alloys at 1873 K are shown in Fig. 11 and Table 1. It became clearly that titanium oxide phases in equilibrium with liquid Fe–Ti alloys changed with the Ti contents in the melt.

5. Discussion

5.1. Estimation on the Stable Region of Each Titanium Oxide Equilibrated with Liquid Fe–Ti Alloy

The critical Ti contents in Fe–Ti melt where two kinds of titanium oxide phases coexisted were determined experimentally by EBSD technique in the previous session. It is also possible to estimate the critical Ti contents theoretically if the standard free energy of each titanium oxide forma-
tion and the activity of Ti as a function of Ti content in liquid Fe–Ti alloy were known. The accuracy of the estimated critical Ti contents depends on the reliability of thermodynamic values. The critical Ti concentration was evaluated in this session based on the available literature values, and the calculated result was compared with that obtained by EBSD analysis in the present work.

The critical Ti concentration where ‘Ti$_3$O$_5$’ coexisted with Ti$_2$O$_3$ was firstly examined. The standard free energies of titanium oxide formation from Ti(l) are given by NIST-JANAF Thermochemical Tables$^{24}$ as Eqs. (1) to (4).

$$3\text{Ti(l)} + 5/2 \text{O}_2(g) = \text{Ti}_2\text{O}_3(s)$$ \hspace{1cm} \text{(1)}

$$\Delta G^o_1 = -2464.580 + 434.977T/2$$ \hspace{1cm} \text{(1750–1950 K)} \hspace{1cm} \text{(2)}

$$2\text{Ti(l)} + 3/2 \text{O}_2(g) = \text{Ti}_2\text{O}_3(s)$$ \hspace{1cm} \text{(3)}

$$\Delta G^o_2 = -1520.750 + 267.27T/2$$ \hspace{1cm} \text{(1750–1950 K)} \hspace{1cm} \text{(4)}

Combination of Eqs. (1) and (3) gives Eq. (5).

$$5\text{Ti}_2\text{O}_3(s) = 3\text{Ti}_2\text{O}_3(s) + \text{Ti(l)}$$ \hspace{1cm} \text{(5)}

Equilibrium constant of Eq. (5) is expressed by Eq. (7).

$$K_{(5)} = \left( a^0_{\text{Ti}_2\text{O}_3} \times a_{\text{Ti}} \right) / \left( a^0_{\text{Ti}_2\text{O}_3} \right)$$ \hspace{1cm} \text{(7)}

The liquid Fe–Ti alloy is in equilibrium with both Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ at the critical Ti concentration. ‘Ti$_3$O$_5$’ coexisted with Ti$_2$O$_3$ was assumed as a line-compound in this calculation. Therefore, the activities of both oxide phases are assumed to be unity. The equilibrium constant of Eq. (5) can be simplified as Eq. (8) in such a limited case.

$$K_{(5)} = \exp(-\Delta G^o_5 / RT) = a_{\text{Ti}_3\text{O}_5} = \gamma_{\text{Ti}_3\text{O}_5} \times X_{\text{Ti}_3\text{O}_5}$$ \hspace{1cm} \text{(8)}

Assumed that the effect of oxygen on the activity of Ti in Fe–Ti–O was negligible due to its small content, the Ti content satisfying the Eq. (8) can be calculated from activities of the constituents in liquid Fe–Ti binary.

The activity of Ti in Fe–Ti melt can be evaluated based on the reported parameters in Redlich–Kister$^{25,26}$ type polynomial. The excess free energy change of mixing on Fe–Ti binary system can be expressed as Eq. (9).

$$\Delta G^o_{ex} = X_{\text{Fe}}X_{\text{Ti}}^3 \Omega_{\text{Fe}-\text{Ti}} + \Omega_{\text{Fe}-\text{Ti}} X_{\text{Fe}} - X_{\text{Ti}}$$ \hspace{1cm} \text{(9)}

Redlich–Kister$^{25,26}$ type parameter of $\Omega_{\text{Fe}-\text{Ti}}$ was obtained from the Henry constant of $\gamma_{\text{Fe}}^o$ as Eq. (10) with a negligible quantity of $\Omega_{\text{Fe}-\text{Ti}}$ at 1873 K, which was determined by Cha et al.$^{27}$

$$\Omega_{\text{Fe}-\text{Ti}} = RT \ln \gamma_{\text{Fe}}^o = -73360 / J$$ \hspace{1cm} \text{(10)}

The partial molar excess Gibbs free energy change $\Delta G^o_{ex_{(Ti)}}$ can be expressed as Eq. (11) in Fe–Ti binary system.

$$\Delta G^o_{ex_{(Ti)}} = RT \ln \gamma_{\text{Ti}}^o$$

$$= \Delta G^o_{ex} + (1 - X_{\text{Ti}}) \frac{\partial \Delta G^o_{ex}}{\partial X_{\text{Ti}}}$$

$$\begin{align*}
&= \Omega_{\text{Fe}-\text{Ti}} - \frac{\partial \Omega_{\text{Fe}-\text{Ti}}}{\partial X_{\text{Fe}}} X_{\text{Fe}} + \frac{\partial \Omega_{\text{Fe}-\text{Ti}}}{\partial X_{\text{Ti}}} X_{\text{Ti}}^2 \\
&= -73360 + 146720 X_{\text{Fe}} - 73360 X_{\text{Ti}}^2 / J \hspace{1cm} \text{(11)}
\end{align*}$$

where $R$ is gas constant and $T$ is absolute temperature. Divided both sides of the Eq. (11) by $RT$, and substituted 1873 K for $T$, the following Eq. (12) is obtained.

$$\ln \gamma_{\text{Ti}}^o = -4.7105 + 9.4210 X_{\text{Fe}} - 4.7105 X_{\text{Ti}}^2$$ \hspace{1cm} \text{(12)}

Using the Eqs. (8) and (12), the critical Ti content can be calculated from the activity of Ti in liquid Fe–Ti binary system. The critical Ti concentration where ‘Ti$_3$O$_5$’ coexisted with Ti$_2$O$_3$ was estimated as 0.526 mass%.

Similar consideration was made on the coexistence of Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ with liquid Fe–Ti alloy. When the reaction of Eq. (13) takes place, the free energy change is given by Eq. (14).

$$7\text{Ti}_3\text{O}_5(s) = 5\text{Ti}_2\text{O}_3(s) + \text{Ti(l)}$$ \hspace{1cm} \text{(13)}

$$\Delta G^o_7 = 127680 + 59.977 / 2$$ \hspace{1cm} \text{(1750–1950 K)} \hspace{1cm} \text{(14)}

Since the activities of ‘Ti$_3$O$_5$’ and Ti$_2$O$_3$ are both unity when the liquid Fe–Ti alloy is doubly saturated with these oxides, the equilibrium constant of Eq. (13) equals the Ti activity in liquid iron as Eq. (15).

$$K_{(13)} = \exp(-\Delta G^o_7 / RT) = a_{\text{Ti}_3\text{O}_5} = \gamma_{\text{Ti}_3\text{O}_5} X_{\text{Ti}_3\text{O}_5}$$ \hspace{1cm} \text{(15)}

The critical Ti concentration corresponding to coexistence of Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ was calculated to be 0.002 mass% according to this thermodynamic consideration.

Figure 12 shows the corresponding calculated Ti contents when each ‘Ti$_3$O$_5$’, Ti$_2$O$_3$, TiO, Ti$_2$O$_3$ coexists with liquid Fe–Ti alloy at 1873 K.

As it is well known that ‘TiO’ has wide solid solution region at 1873 K as shown in Fig. 1, ‘TiO’ can not be considered as a line-compound. Therefore, the critical Ti content in coexistence of Ti$_2$O$_3$ with ‘TiO’ could not be evaluated, because the activity of ‘TiO’ could not be assumed to be unity.

The same consideration is available on the stable region of titanium oxides corresponding to various Ti contents also using the Thermochemical Data of Pure Substance by I. Barin$^{28}$ and Thermochernical Properties of Inorganic Substances by O. Kubaschewski$^{29}$ as shown in Table 3.

All calculated results are shown in Table 3. Three calculated critical Ti contents in coexistence of Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ were agreed fairly each other and also with that by EBSD analysis results in the present work as shown in Fig. 12.

‘Ti$_3$O$_5$’ phase was stable more than the Ti content of 0.0004 from the EBSD analysis. However, the calculated critical Ti contents coexisted with Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ were agreed fairly each other and also with that by EBSD analysis results in the present work as shown in Fig. 12.

‘Ti$_3$O$_5$’ phase was stable more than the Ti content of 0.0004 from the EBSD analysis. However, the calculated critical Ti contents coexisted with Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ were agreed fairly each other and also with that by EBSD analysis results in the present work as shown in Fig. 12.

‘Ti$_3$O$_5$’ phase was stable more than the Ti content of 0.0004 from the EBSD analysis. However, the calculated critical Ti contents coexisted with Ti$_2$O$_3$ and ‘Ti$_3$O$_5$’ were agreed fairly each other and also with that by EBSD analysis results in the present work as shown in Fig. 12.
In the present work, the interface of ‘Ti₃O₅’ crucible equilibrated with 0.0018 mass% Ti was analyzed by SEM-EDS, and the Fe content in ‘Ti₃O₅’ was found to be 11.25 at%. This result was reasonably corresponding to the result of Iwamoto et al.10) and Suzuki and Sanbongi.14) Iwamoto et al.10) found the solid solution of ‘Ti₃O₅’ and ‘FeO · 2TiO₂’ equilibrated with very low Ti concentration of Fe–Ti alloy. Suzuki and Sanbongi14) also found that the deoxidation product was ‘Ti₃O₅’ with small amount of iron, in which contents depended on Ti contents in liquid Fe–Ti alloy. Therefore, the activity of ‘Ti₃O₅’ cannot be considered to be unity when the Ti concentration is very low. It is, therefore, necessary to carry out the measurement of ‘Ti₃O₅’ activity in ‘Ti₃O₅’–iron oxide solid solution in future to confirm the present estimation.

6. Conclusions

Various Ti contents of molten Fe–Ti alloy were melted in a ‘Ti₃O₅’ crucible at 1 873 K in the present work. Different titanium oxide phases depending on the Ti contents were formed at the interface between Fe–Ti alloy and ‘Ti₃O₅’ crucible. The formed titanium oxide at the interface was clearly identified with EBSD automated analysis technique. The following conclusions were obtained based on these measurements.

(1) ‘Ti₂O₃’ (Anosovite) was equilibrated with Fe–0.0004–0.36 mass% Ti molten alloy
(2) Ti₂O₃ (Trigonal) was equilibrated with Fe–0.5–6.2 mass% Ti molten alloy
(3) ‘TiO’ (NaCl type Cubic) was equilibrated with Fe–10.6–16.6 mass% Ti molten alloy

The equilibrium titanium oxide phases depended on the Ti contents in the molten Fe–Ti alloy. The critical Ti content coexisted with Ti₂O₃ and ‘TiO’ was in good agreement with the calculated result based on the free energies of titanium oxides formation and the activity of Ti in Fe–Ti alloy.

Acknowledgments

The authors wish to thank Dr. H. Itoh (Yoshizawa Lime Ind. Co.) for the great help for the processing of ‘Ti₃O₅’ crucible and Dr. T. Nagasaka, Professor of Tohoku University, for his great help and encouragement. The present work was financially supports from 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) E. Ll. Evans and H. A. Sloman: J. Iron Steel Inst., 74 (1953), 318.
4) R. L. Hadley and G. Derge: Trans. Met. Soc. AIME, 203 (1955), 55.
5) B. K. Liaudis and A. M. Samarin: Dokl. Akad. Nauk SSSR, 101 (1955), 325.
6) Z. Bužek and A. Hutla: Sb. V ed. Pr. Vys. Sk. Vysoké Výučné Ústavy, 181 (1965), 379.
7) H. Chino, Y. Nakamura, E. Tsunetomi and K. Segawa: Tetsu-to-Hagané, 52 (1966), 959.
8) K. Suzuki, Y. Ohmori and K. Sanbongi: Bull. Res. Inst. Miner. Dressing Metall., Tohoku Univ., 23 (1967), 137.
9) Y. Kojima, M. Inoye and J. Ohi: Acta Mater., 40 (1969), 667.
10) N. Iwamoto, H. Yoshida and A. Adachi: Tetsu-to-Hagané, 56 (1970), 1646.
11) V. I. Yavovskiy, L. B. Kosterev, A. A. Ayub and L. N. Rostorguyev: Russ. Metall., 2 (1971), 33.
12) A. M. Smellie and H. B. Bell: Can. Metall. Q., 11 (1972), No. 2.
351.
13) V. I. Yavoyskiy, L. P. Vladimirov, V. P. Luzgin, N. M. Kopitsa and E. B. Teplitskiy: *Russ. Metall.*, 2 (1974), 10.
14) K. Suzuki and K. Sanbongi: *Trans. Iron Steel Inst. Jpn.*, 15 (1975), 618.
15) D. Janke and W. A. Fischer: *Arch. Eisenhüttenwes.*, 47 (1976), 195.
16) 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).
17) C.-T. Mutale, A. S. Tuling and S. M. C. Verryn: Proc. of The VII Int. Conf. on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, Johannesburg, (2004), 293.
18) M. Pajunen and J. Kivilahti: *Z. Metallkd.*, 83 (1992), No. 1, 17.
19) P. Waldner and G. Eriksson: *Calphad*, 23 (1999), 189.
20) Electron Backscatter Diffraction in Materials Science, ed. by A. J. Schwartz et al., Kulwer Academic/Plenum Publisher, New York, (2000).
21) Y. Sasaki, K. Ohkawara, M. Iguchi, K. Ishii and M. Hino: *ISIJ Int.*, 45 (2005), No. 4, 582.
22) K. Takahashi and M. Hino: *High Temp. Mater. Process.*, 19 (2000), 1.
23) M. B. Saddik: Ph. D. Thesis, Tohoku University, Japan, (2004).
24) NIST-JANAF Thermochemical Tables, 4th ed., ed. by M. W. Chase, Jr, J. Phys. Chem. Ref. Data, (1998).
25) M. Hillert and L.-I. Staffanson: *Acta Chem. Scand.*, 24 (1970), 3618.
26) N. Saunders and A. P. Miodownik: *Calphad* (Calculation of Phase Diagrams.), A Comprehensive Guide, (Pergamon, Oxford, 1988), 91.
27) W. Y. Cha, T. Nagasaka, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, 46 (2006), No. 7, 996.
28) Thermochemical Data of Pure Substances, ed. by I. Barin, VCH, Weinheim, (1993).
29) Thermochemical Properties of Inorganic Substances, 2nd ed., ed. by O. Knacke, O. Kubaschewski and K. Hesselmann, Springer-Verlag, Berlin, (1991).
30) S. Andersson, B. Collen, U. Kuxlenstierna and A. Magnusli: *Acta Chem. Scand.*, 11 (1957), 1641.
31) R. J. Fruehan: *Metall. Trans.*, 1 (1970), 3403.