Formation Conditions of $\text{Mg}_2\text{TiO}_4$ and $\text{MgAl}_2\text{O}_4$ in Ti–Mg–Al Complex Deoxidation of Molten Iron

Hideki ONO,1) Keiji NAKAJIMA,2,3) Ryota MARUO,4) Shingo AGAWA5) and Tateo USAI1)

1) Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan. 2) Corporate Research & Development Laboratories, Sumitomo Metals Industries, Ltd., Japan. 3) Division of Applied Process Metallurgy, Department of Materials Science and Engineering, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden. 4) Formerly, Graduate Student, Graduate School of Engineering, Osaka University. Now at Nippon Steel Corporation, Japan. 5) Graduate Student, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.

(Received on December 25, 2008; accepted on February 23, 2009)

It is important to study the complex deoxidation equilibrium of molten iron in Ti–Mg–Al system from the view point of inclusion control. The equilibrium experiments between molten iron and TiO$_x$–MgO–Al$_2$O$_3$ slag and the thermodynamic calculation on the complex deoxidation are conducted at 1 973 K in the present study. The liquid phase region of TiO$_x$–MgO–Al$_2$O$_3$ system in equilibrium with molten iron is clarified at 1 973 K. The equilibrium compounds which are coexisted with the slag on the liquidus curve in the system are identified to be $\text{Mg}_2\text{TiO}_4$ and $\text{MgAl}_2\text{O}_4$. The equilibrium relation between the deoxidation products ($\text{Mg}_2\text{TiO}_4$ or $\text{MgAl}_2\text{O}_4$) and the composition of solute elements in steel is investigated, and the conditions that $\text{Mg}_2\text{TiO}_4$ forms instead of $\text{MgAl}_2\text{O}_4$ nor $\text{Al}_2\text{O}_3$ are examined in the complex deoxidation of Ti–Mg–Al system. When the aluminum content of molten iron is under 4 mass ppm, $\text{Mg}_2\text{TiO}_4$ forms over the wide concentration range. The concentration range of $\text{MgAl}_2\text{O}_4$ formation widens as the aluminum content of molten iron increases. It is necessary to increase Mg content and to decrease Al content in order to form $\text{Mg}_2\text{TiO}_4$ in the Ti–Mg–Al complex deoxidation of molten iron in the range Ti<0.01 mass%. However, it is difficult in the range of Ti>0.01 mass% to form $\text{Mg}_2\text{TiO}_4$.

KEY WORDS: inclusion; steelmaking; deoxidation; equilibrium.

1. Introduction

Nonmetallic inclusions in steel, which are mainly composed of deoxidation products, cause adverse effects on the toughness, fatigability and ductility of steel, because of their high melting-points and hardness. The frequency of inclusions observed in the fracture surface is shown in Fig. 1. In Fig. 1, it is found that a large number of inclusions observed in the fracture surface are Al$_2$O$_3$ and MgO·Al$_2$O$_3$. That is to say, it is very important to avoid the formation of Al$_2$O$_3$ and spinel (MgO·Al$_2$O$_3$) in the deoxidation process of high-grade wire and bearing steels, in particular. From this viewpoint, several thermodynamic studies have been reported on the deoxidation equilibria on the Fe–Mg–Al–O and Fe–Ca–Mg–Al–O systems, and the phase equilibrium relations among each oxide (or compound) and the composition of the solutes in molten iron has been clarified in MgO–Al$_2$O$_3$ and CaO–MgO–Al$_2$O$_3$ systems.2–4) The control of the oxidation reactions has been tried to improve the properties of steel, called ‘Oxide metallurgy’.5) It is known that the toughness of steel is improved by dispersing the nonmetallic inclusion finely in steel and by making it be acted as a product nucleus of ferrite in the grain. On the other hand, titanium oxide finely disperse in steel, and the complex deoxidation including titanium is considered to be effective in order to fulfill the above purpose. Accordingly, the complex deoxidation equilibrium of Fe–Ti–Mg–Al–O system is important from the view point of the avoidance of Al$_2$O$_3$ or MgO·Al$_2$O$_3$ formation and the inclusion control,
but the study on this system is very limited, and the phase equilibrium relations have not been clarified yet.

In the present study, the liquid phase region of TiO$_2$–MgO–Al$_2$O$_3$ system in equilibrium with molten iron is investigated at 1 973 K. The equilibrium relation between the deoxidation products (Mg$_2$TiO$_4$ or MgAl$_2$O$_4$) and the composition of solute elements in steel is investigated, and the conditions that Mg$_2$TiO$_4$ forms instead of MgAl$_2$O$_4$ nor Al$_2$O$_3$ are examined in the complex deoxidation of Ti–Mg–Al system.

2. Experimental

An induction furnace was used for the deoxidation of high-purity electrolytic iron. The electrolytic iron in an alumina crucible was preliminary deoxidized in H$_2$ for over an hour at 1 873 K and was used in the following experiments. The slag was made by mixing the reagent grade of TiO$_2$ (purity $>$99%), MgO (purity $>$99%) and Al$_2$O$_3$ (purity 99.6%). The initial slag composition was set to the liquidus region in the TiO$_2$–MgO–Al$_2$O$_3$ phase diagram FactSage5. 4. 1. The calculated phase diagram for TiO$_2$–MgO–Al$_2$O$_3$ system at 1 973 K is described in Fig. 2. The initial slag composition is shown in Table 1 and is also plotted in Fig. 2.

Sixteen gram of the deoxidized iron and the reagent grade of TiO$_2$, MgO and Al$_2$O$_3$ slag totally weighing 8 g were put in a magnesia or an alumina crucible, and the crucible was inserted in a carbon crucible with a carbon lid. The experiments were carried out by using a multipurpose electric resistance furnace, of which the heating element is carbon. After the sample was set in the furnace, the inner space of the furnace was decompressed to 8 Pa and was switched to an inert atmosphere by introducing an argon gas. By carrying out this operation repeatedly 2 time, the inside of the furnace was kept to be an argon gas atmosphere (0.011 to 0.013 MPa). Then, the sample was heated to 1 973 K according to the heat pattern shown in Fig. 3. The sample was equilibrated in the furnace by being held for 3 h in an argon atmosphere at 1 973 K. The sample was quickly cooled in the furnace by switching off the button of the power supply. After each experiment, metal and slag in the crucible were divided, and the Ti, Mg and Al contents of metal and slag and the O content of metal were analyzed by an inductively coupled plasma emission spectrometry (ICP) and an inert gas impulse infrared absorption spectroscopy, respectively.

The compound in equilibrium with metal and slag was identified for each sample as follows: The oxide layer formed at the interface of metal and MgO (or Al$_2$O$_3$) crucible was mainly identified. The viscosity of the metal interface was analyzed by using FE-SEM/EDS, EMPA and Micro focus XRD. In the FE-SEM/EDS and EPMA analysis, the point analysis was carried out from the interface of metal/crucible at the bottom part of sample to the inside of the crucible at the interval of a few μm, and the contents of Mg, Ti, Al and Fe were analyzed. The thin oxide layer which adhered to the metal surface was also analyzed by XRD. In the Micro focus XRD analysis, the compound which form at the metal/crucible interface of the square region of 10×10 μm was analyzed.
3. Results

The slag composition after the experiments is shown in Table 2 and is plotted on the TiO$_2$–MgO–Al$_2$O$_3$ diagram at 1973 K in Fig. 4, which is described by regarding the value for $X$ of TiO$_X$ as to be 2. From Fig. 4, it is clarified the liquidus curve of TiO$_2$–MgO–Al$_2$O$_3$ in equilibrium with molten iron at 1973 K. The liquidus curve described from the experimental results is much different from the calculated one from Fact Sage 5.4.1, which is shown by the dotted curve in Fig. 4. One of the causes of this discrepancy is considered to be the solid solution of MgAl$_2$O$_4$. It is known that MgAl$_2$O$_4$ has a relatively wide solid solution range at high temperature. Taking the solubility of Al$_2$O$_3$ or MgO in MgAl$_2$O$_4$ into consideration, the phase diagram is described as shown in Fig. 4 at 1973 K from the present experimental results. As another cause of this discrepancy, the variation of titanium valence in the slag phase is considered. As the kind of titanium oxide, only TiO$_2$ (Ti$^{4+}$) is taken into account in the calculation. However, in the present experiments, the oxide phase is in equilibrium with molten iron, and the coexistence of Ti$_2$O$_3$ (Ti$^{3+}$) and TiO$_2$ (Ti$^{4+}$) is expected in the slag. In the present experiments, the titanium content of molten iron is from 8 to 88 [mass ppm Ti]. In this titanium concentration range, the kind of titanium oxide is reported to be Ti$_2$O$_3$ or Ti$_4$O$_7$ in Fe–Ti–O system at 1873 K. Accordingly, although the coexistence of Ti$_2$O$_3$ (Ti$^{3+}$) and TiO$_2$ (Ti$^{4+}$) in the slag phase is also expected in the present study, the experimental results are plotted by regarding all the titanium oxides as to be TiO$_2$ in Fig. 4, as a matter of convenience.

Subsequently, the results of the identification of the equilibrium oxide phase are shown. On the whole, the results of FE-SEM/EDS and EPMA analysis are in reasonable agreement with each other. As examples, the results of the FE-SEM/EDS analysis for No. 1 and 24 are shown in Figs. 5 and 6. The analysis points are also shown in Figs. 5 and 6. From Fig. 5, the equilibrium phase for No. 1 is considered to be Mg$_2$TiO$_4$. From Fig. 6, the sample of No. 24 is expected to be in equilibrium with both MgAl$_2$O$_4$ and Al$_2$O$_3$. Subsequently, the results of XRD and Micro focus XRD for No. 11 are shown in Figs. 7 and 8, respectively. From these

![Table 2](image)

The composition of slag and metal after experiments.

![Fig. 4](image)

The equilibrium slag compositions after experiments at 1973 K.

![Fig. 5](image)

The result of FE-SEM/EDS analysis of the oxide layer formed at the vicinity of the metal for No. 1 sample.

![Fig. 6](image)

The result of FE-SEM/EDS analysis of the oxide layer formed at the vicinity of the metal for No. 24 sample.
The formation of Mg$_2$TiO$_4$ is also considered for several through 20, which are conducted by using MgO crucible, the other hand, from the initial slag composition in the present study, the formation of Mg$_2$TiO$_4$ is more possible than the sample is in equilibrium with MgAl$_2$O$_4$. On the other hand, the XRD patterns for both Mg$_2$TiO$_4$ and MgTiO$_4$ compounds are almost identical, and it is difficult to distinguish MgTiO$_4$ from Mg$_2$TiO$_4$. On the other hand, from the initial slag composition in the present study, the formation of Mg$_2$TiO$_4$ is more possible than MgTiO$_4$ as the equilibrium compound. Through these analyses, it is considered that the samples of No. 1 through 20 are in equilibrium with Mg$_2$TiO$_4$. With regard to the experiments which are conducted by using Al$_2$O$_3$ crucible, the samples of No. 21, 22 and 29 are identified to be in equilibrium with MgAl$_2$O$_4$. On the other hand, the coexistence of Al$_2$O$_3$ or Al$_2$TiO$_5$ with MgAl$_2$O$_4$ is identified for the samples of No. 24 through 28.

4. Discussion

In the complex deoxidation of molten iron with Mg–Ti–Al at 1 973 K, the formation of Mg$_2$TiO$_4$ and MgAl$_2$O$_4$ was confirmed. The formation conditions of these compounds are considered from the present results.

4.1. Determination of Thermodynamic Data on the Equilibrium of Mg$_2$TiO$_4$ and Molten Iron at 1 973 K

The reaction of molten iron and Mg$_2$TiO$_4$ is expressed by Eq. (1). The equilibrium constant of Eq. (1) is represented by Eq. (2).

$$
\text{Mg}_2\text{TiO}_4(s) = 2\text{Mg} + \text{Ti} + 4\text{O} \quad \text{(1)}
$$

$$
\log K_{(i)} = \log(a_{\text{Mg}}^2 \cdot a_{\text{Ti}} \cdot a_{\text{O}}^4 / a_{\text{Mg}_2\text{TiO}_4}) \quad \text{(2)}
$$

where $a_{\text{Mg}_2\text{TiO}_4}$ and $a_{i}$ ($i=$ Mg, Ti or O) denote the activity of Mg$_2$TiO$_4$ relative to the pure solid and the activity of $i$ relative to the dilute solution of 1 mass%, respectively. The activity of Mg$_2$TiO$_4$ is set to be unity by assuming the existence of the pure solid. The values for the equilibrium constant of Eq. (1) and the interaction parameter between Mg and Ti in melt iron are determined from the present experimental results at 1 973 K. The activity of Mg, Ti and O in Eq. (2) can be rewritten as Eq. (3), using the activity coefficient and the solute content of molten iron. The activity coefficient can be written by Eq. (4) from Wagner’s equation, using the interaction parameters and the solute contents of molten iron.

$$
\log f_i = \sum_j e_i^{[\%j]} + \sum_j \sum_k r_{jk}^{[\%j][\%k]} + \cdots \quad \text{(3)}
$$

$$
\log f_i = \sum_j e_i^{[\%j]} + \sum_j \sum_k r_{jk}^{[\%j][\%k]} + \cdots \quad \text{(4)}
$$

where $[\%i, j or k]$ denotes the concentration of component $i, j$ or $k$ in molten iron [mass%], $f_i$ the Henrian activity coefficient of component $i$ relative to the dilute solution, $e_i^{[\%j]}$ and $r_{jk}^{[\%j][\%k]}$ the first and the second order interaction parameters of $i$ on $j$ in molten iron, respectively. Equation (5) is derived from Eq. (2), using Eqs. (3) and (4). When the magnesium deoxidation equilibrium of molten iron is considered, it is reported that it is necessary to introduce the second order interaction parameters including cross product terms for the strong affinity between Mg and O. According to the interaction parameters between Mg and O, the second order terms are also considered in the present study.

$$
\log K_{(i)} = 2 \log f_{\text{Mg}} + 2 \log[\%\text{Mg}] + \log f_{\text{Ti}} + \log[\%\text{Ti}] + 4 \log[\%\text{O}]
$$

$$
= 2 \log[\%\text{Mg}] + \log[\%\text{Ti}] + 4 \log[\%\text{O}]
$$

$$
+ 2 e_{\text{Mg}}^{\text{Ti}}[\%\text{Ti}] + 2 e_{\text{Mg}}^{\%\text{Mg}}[\%\text{Mg}] + 2 e_{\text{Mg}}^{\%\text{Al}}[\%\text{Al}]
$$

$$
+ 2 e_{\text{Mg}}^{0}[\%\text{O}] + 2 r_{\text{Mg}}^{0}[\%\text{O}][\%\text{O}] + 2 r_{\text{Mg}}^{0}[\%\text{Mg}][\%\text{O}]
$$

$$
+ e_{\text{Ti}}^{0}[\%\text{Ti}] + e_{\text{Mg}}^{\text{Ti}}[\%\text{Mg}] + e_{\text{Al}}^{\%\text{Ti}}[\%\text{Al}]
$$

$$
+ e_{\text{Mg}}^{\%\text{O}}[\%\text{O}] + 4 e_{\text{O}}^{\text{Ti}}[\%\text{Ti}] + 4 e_{\text{Mg}}^{\%\text{Mg}}[\%\text{Mg}]
$$

$$
+ 4 e_{\text{Mg}}^{0}[\%\text{Al}] + 4 e_{\text{Mg}}^{0}[\%\text{O}] + 4 r_{\text{Mg}}^{0}[\%\text{Mg}]^2
$$

$$
+ 4 r_{\text{Mg}}^{0}[\%\text{Mg}][\%\text{O}]
$$

$$
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
The values for the left-hand side of Eq. (7) can be determined by substituting each interaction parameter and the experimental results of each solute content of molten iron. The values for the left-hand side of Eq. (7) are plotted against (2[\%Ti]/[\%Mg]) in Fig. 9 in accordance with Eq. (7). From the slope and the intercept in Fig. 9, the values for $e_{Mg}^{Ti}$ and log $K_{ij}$ are determined respectively as follows:

$$e_{Mg}^{Ti} = -135, \quad \log K_{ii} = -20.9 \quad (at \ 1973 \ K) \quad ....(8)$$

The thermodynamic data used in the present study are shown in Table 3. However, the data shown in Table 3 are the values at 1973 K. Accordingly, the values are converted to those at 1973 K by using Eq. (9) and are used in the present calculation.

$$e_{_{Mg,Ti}}^{i} \cdot T = e_{_{Mg,Ti}}^{i} \cdot T' \quad .........(9)^{11}$$

where $T$ and $e_{_{Mg,Ti}}^{i}$ denote the temperature (K) and the interaction parameter of $i$ on $j$ in molten iron at $T$ (K), respectively.

### 4.2. Description of the Doubly Saturated Curve with Mg$_3$TiO$_4$ and MgAl$_2$O$_4$

In order to investigate the formation conditions of Mg$_3$TiO$_4$ and MgAl$_2$O$_4$, the doubly saturated curve with Mg$_3$TiO$_4$ and MgAl$_2$O$_4$ is calculated, using the thermodynamic data derived in Sec. 4.1.

The reaction of Mg$_3$TiO$_4$ with molten iron is expressed by Eq. (1). The equilibrium constant for Eq. (1) is written by Eq. (2). The value derived in Sec. 4.1 is used as the equilibrium constant for Eq. (1). The reaction of MgAl$_2$O$_4$ with molten iron and the equilibrium constant are expressed by Eqs. (10) and (11), respectively.

$$\text{MgAl}_2\text{O}_4(s) = \text{Mg} + 2\text{Al} + 4\text{O} \quad ...........(10)$$

$$\log K_{(10)} = \log(a_{\text{Mg}} \cdot a_{\text{Al}}^2 \cdot a_{\text{O}}^4 / a_{\text{MgAl}_2\text{O}_4}) \quad ...........(11)$$

The equilibrium constant for Eq. (10) is derived from the data on the deoxidation equilibria of Mg and Al. The deoxidation reactions of molten iron with Mg and Al are represented by Eqs. (12) and (14), respectively. The equilibrium constants for Eqs. (12) and (14) are represented by Eqs. (13) and (15), respectively.

$$\text{MgO(s)} = \text{Mg} + \text{O} \quad ...........(12)$$

$$\log K_{(12)} = -38.067 / T + 12.46^{(12)} = -7.86 \quad (at \ 1873 \ K)$$

$$= -6.84 \quad (at \ 1973 \ K) \quad ...........(13)$$

$$\text{Al}_2\text{O}_3(s) = 2\text{Al} + 3\text{O} \quad ...........(14)$$

$$\log K_{(14)} = 20.18 - 62.80042 / T^{19} = -13.35 \quad (at \ 1873 \ K)$$

$$= -11.66 \quad (at \ 1973 \ K) \quad ...........(15)$$

The formation reaction of MgAl$_2$O$_4$ and the equilibrium constant are expressed as Eqs. (16) and (17), respectively.

$$\text{MgAl}_2\text{O}_4(s) = \text{MgO(s)} + \text{Al}_2\text{O}_3(s) \quad ...........(16)$$

$$\log K_{(16)} = -0.329 - 982.24 / T^{14} = -0.86 \quad (at \ 1873 \ K)$$

$$= -0.83 \quad (at \ 1973 \ K) \quad ...........(17)$$

By combining Eqs. (13), (15) and (17), the equilibrium constant for Eq. (10) can be derived as follows:

$$e_{_{Mg,Ti}}^{i} \cdot T = e_{_{Mg,Ti}}^{i} \cdot T' \quad .........(9)^{11}$$

where $T$ and $e_{_{Mg,Ti}}^{i}$ denote the temperature (K) and the interaction parameter of $i$ on $j$ in molten iron at $T$ (K), respectively.

### Table 3. The mass percent interaction parameters of Fe–Ti–Mg–Al–O system at 1873 K.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>k</th>
<th>literature</th>
<th>$e_{ij}^1$</th>
<th>$r_{ij}^1$</th>
<th>$r_{ij}^{10}$</th>
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<tbody>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>Ti</td>
<td>Junkes et al.</td>
<td>0.048</td>
<td>0.0007</td>
<td>unknown</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>Al</td>
<td>Yanchang et al.</td>
<td>0.004</td>
<td>0.0094</td>
<td>unknown</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>O</td>
<td>Pak et al.</td>
<td>-1.62</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Al</td>
<td>Ti</td>
<td>Ti</td>
<td>Yanchang et al.</td>
<td>0.004</td>
<td>0.0094</td>
<td>unknown</td>
</tr>
<tr>
<td>Al</td>
<td>Ti</td>
<td>Al</td>
<td>Sigworth et al.</td>
<td>0.045</td>
<td>0.0094</td>
<td>unknown</td>
</tr>
<tr>
<td>Al</td>
<td>Ti</td>
<td>O</td>
<td>Sigworth et al.</td>
<td>-0.13</td>
<td>0.0094</td>
<td>unknown</td>
</tr>
<tr>
<td>Mg</td>
<td>Ti</td>
<td>Al</td>
<td>Sigworth et al.</td>
<td>-0.12</td>
<td>0.0094</td>
<td>unknown</td>
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<tr>
<td>Mg</td>
<td>Ti</td>
<td>Mg</td>
<td>Sigworth et al.</td>
<td>0</td>
<td>0</td>
<td>48000</td>
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<tr>
<td>Mg</td>
<td>Ti</td>
<td>O</td>
<td>Olita et al.</td>
<td>-460</td>
<td>37000</td>
<td>unknown</td>
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<tr>
<td>O</td>
<td>Ti</td>
<td>Ti</td>
<td>Pak et al.</td>
<td>-0.54</td>
<td>0.0094</td>
<td>unknown</td>
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<tr>
<td>O</td>
<td>Ti</td>
<td>Al</td>
<td>Sigworth et al.</td>
<td>-3.85</td>
<td>0.0094</td>
<td>unknown</td>
</tr>
<tr>
<td>O</td>
<td>Ti</td>
<td>Mg</td>
<td>Olita et al.</td>
<td>-300</td>
<td>16000</td>
<td>48000</td>
</tr>
<tr>
<td>O</td>
<td>Ti</td>
<td>O</td>
<td>Sigworth et al.</td>
<td>-0.2</td>
<td>0</td>
<td>unknown</td>
</tr>
</tbody>
</table>
The equilibrium constants for Eqs. (1) and (10) are expressed by Eqs. (19) and (20), respectively, using the interaction parameters and the concentration of solutes.

\[
\log K_{(1)} = 2\log[\%Mg] + \log[\%Ti] + 4\log[\%O] + (2\varepsilon_{\text{Ti}}^{\text{Mg}} + e_{\text{Ti}}^{\text{Mg}} + 4e_{\text{O}}^{\text{Mg}})[\%Ti] \\
+ (2\varepsilon_{\text{Mg}}^{\text{Ti}} + e_{\text{Mg}}^{\text{Ti}} + 4e_{\text{O}}^{\text{Ti}})[\%Mg] \\
+ (2\varepsilon_{\text{Mg}}^{\text{Al}} + e_{\text{Al}}^{\text{Mg}} + 4e_{\text{O}}^{\text{Al}})[\%Al] \\
+ (2e_{\text{Mg}}^{\text{O}} + e_{\text{O}}^{\text{Mg}} + 4e_{\text{O}}^{\text{O}})[\%O] \\
+ 2r_{\text{Mg}}^{\text{O}}[\%O]^2 + 4r_{\text{Mg}}^{\text{Mg}}[\%Mg]^2 \\
+ (4e_{\text{Mg}}^{\text{Mg}} + 2e_{\text{Mg}}^{\text{O}})[\%Mg][\%O] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \lod
be 0.5 at a fixed aluminum content of 4, 8 and 12 mass ppm, respectively. The numerical values in these figures show the experimental results of the oxygen content of molten iron, [mass ppm O]. The oxygen contents of several samples are not much in agreement with the calculated iso-oxygen curves. One of the causes of this discrepancy is considered to be the sensitivity of the oxygen content to the aluminum content of molten iron, which is divided into 3 levels ([mass ppm Al]<5, 5< [mass ppm Al]<10, 10<[mass ppm Al]) in the present study. From Figs. 13 through 15, the formation condition of Mg$_2$TiO$_4$ is considered in the Ti–Mg–Al complex deoxidation of molten iron at 173 K. When the aluminum content of molten iron is under 5 mass ppm, Mg$_2$TiO$_4$ forms over the wide region including the lower titanium concentration range. On the other hand, as the aluminum content of molten iron increasing, the region of MgAl$_2$O$_4$ formation widens. Accordingly, not only the higher titanium content of molten iron but also comparatively higher magnesium content of molten iron is needed in order to form Mg$_2$TiO$_4$.

5. Conclusions

The equilibrium experiments between molten iron and TiO$_X$–MgO–Al$_2$O$_3$ slag and the thermodynamic calculation on the complex deoxidation of molten iron in Ti–Mg–Al system are conducted at 173 K. The conclusions are as follows

(1) The liquid phase region of TiO$_X$–MgO–Al$_2$O$_3$ system in equilibrium with molten iron is clarified at 173 K. The equilibrium compounds which are coexisted with the slag on the liquidus curve in the system are identified to be Mg$_2$TiO$_4$ and MgAl$_2$O$_4$.

(2) The equilibrium constant of the reaction of Mg$_2$TiO$_4$ with molten iron and the interaction parameter of Mg on Ti at 173 K is determined as follows:

$$\log K^{(e)}_{\text{Mg}_2\text{TiO}_4} = -20.9 \quad \text{(at 173 K)}$$

$$\epsilon_{\text{Mg}}^{\text{Ti}} = -135 \quad \text{(at 173 K)}$$

(3) The phase diagram which shows the stability region of Mg$_2$TiO$_4$ and MgAl$_2$O$_4$ is shown in the Ti–Mg–Al complex deoxidation of molten iron at 173 K, and the formation conditions of Mg$_2$TiO$_4$ and MgAl$_2$O$_4$ are investigated. When the aluminum content of molten iron is under 4 mass ppm, Mg$_2$TiO$_4$ forms over the wide concentration range. The concentration range of MgAl$_2$O$_4$ formation widens as the aluminum content of molten iron increases. It is necessary to increase Mg content and to decrease Al content in order to form Mg$_2$TiO$_4$ in the Ti–Mg–Al complex deoxidation of molten iron in the range Ti<0.01 mass%. However, it is difficult in the range of Ti>0.01 mass% to form Mg$_2$TiO$_4$.

Acknowledgment

The authors gratefully gratitude to Mr. H. Takada, Sumitomo Metal Industries, Ltd., for his great technical assistance in the present work.

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