Equilibrium Relationships between Oxide Compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ with Iron at 1 873 K and Variations in Stable Oxides with Temperature

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It is important to determine the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and iron to avoid Al$_2$O$_3$ or MgO·Al$_2$O$_3$ formation and for inclusion control. In this study, the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron are investigated at 1 873 K. The phase-stability diagrams, which show the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron, are described. It is also important to know the oxides that newly form after solidification. Accordingly, the temperature-dependences of the stable compounds that newly form after solidification were investigated using the thermodynamic calculation software FactSage 6.1. Although the compounds formed after solidification are not necessarily the same as the equilibrium oxide compounds at 1 873 K, the correlation between them can be confirmed. In particular, under the unstable condition of MgAl$_2$O$_4$ at 1 873 K, it is found that the formation of MgAl$_2$O$_4$ could also be suppressed after solidification.

KEY WORDS: inclusion; deoxidation; equilibrium; oxide; iron; steelmaking.

1. Introduction

Nonmetallic inclusions in steel are mainly composed of deoxidation products, and they adversely affect the toughness, fatigability, and ductility of steel because of their high melting points and hardness. For example, it is very important to avoid the formation of Al$_2$O$_3$ and spinel (MgO·Al$_2$O$_3$) during the deoxidation of molten iron for high-grade wire and bearing steels. Several thermodynamic studies on the deoxidation equilibria of the Fe–Mg–Al–O and Fe–Ca–Mg–Al–O systems have been reported and the phase-equilibrium relationships between each oxide (or compound) and the composition of the solutes in molten iron have been clarified in the MgO–Al$_2$O$_3$ and CaO–MgO–Al$_2$O$_3$ systems.$^{1-3)}$

‘Oxide metallurgy’ is the control of inclusions and is used to improve the properties of steel.$^4)$ The toughness of steel can be improved by finely dispersing nonmetallic inclusions in the steel and by causing the inclusions to act as nuclei for ferrite production in grains. Titanium oxide finely dispersed in steel and complex deoxidation involving titanium are considered to be effective for the above-mentioned purpose.$^5)$ Determination of the equilibrium relationships between the oxide compounds in MgO–Al$_2$O$_3$–Ti$_2$O$_3$ and molten iron is important in avoiding Al$_2$O$_3$ or MgO·Al$_2$O$_3$ formation and for inclusion control.

In our previous work,$^6)$ we reported the equilibrium relationships between the oxide compounds in MgO–Al$_2$O$_3$–Ti$_2$O$_3$ and molten iron at 1 873 K. The formation of MgTi$_2$O$_5$ was confirmed as one of the equilibrium phases. However, there are insufficient thermodynamic data available on the formation of MgTi$_2$O$_5$. In this work, the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$ and molten iron are investigated at 1 873 K, and the equilibrium constant of the formation of MgTi$_2$O$_5$ from magnesium, titanium, and oxygen in molten iron and the interaction parameter of Mg on Ti in iron are derived. Using the derived values, we describe the phase-stability diagrams, which show the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron at 1 873 K. In inclusion control of steel, it is also important to know which oxides newly form after solidification. Accordingly, the variations in stable compounds with temperature are investigated using the thermodynamic calculation software FactSage 6.1.

2. Experimental

Ti$_2$O$_3$ was made using reagent grade TiO$_2$ (purity > 99%) and Ti (purity 98%) by mixing them in a molar ratio of 3:1. The mixture was put in an alumina crucible and the crucible was put in a carbon crucible with a lid and inserted in an electrical resistance furnace. The sample was held in the furnace for 18 h at 1 023 K under argon. After removal from the furnace, the compound was cooled under argon, and the formed Ti$_2$O$_3$ was then crushed to a powder before being
used for the following experiments.

We mixed the formed Ti$_2$O$_3$ powder and reagent grade MgO (purity > 99%) to obtain a total weight of 12 g. The initial compositions of the oxides are shown in Table 1. The mixture was put in an alumina crucible (O.D. 25 mm, I.D. 20 mm, height 35 mm), as shown in Fig. 1. High-purity electrolytic iron weighing about 6 g, which was deoxidized with H$_2$ at 1 873 K using an induction furnace, was then added to the mixture of oxides. The alumina crucible was put in a carbon crucible with a lid and was inserted in an electrical resistance furnace. The sample was heated to 1 273 K at a heating rate of 6.7 K/min under argon and then the temperature was maintained for 1 h. The sample was then heated to 1 873 K at a heating rate of 6.7 K/min under argon and kept at that temperature for 13 h. The sample was then removed from the furnace and cooled in an argon stream. After each experiment, the oxide compounds formed at the oxide/iron interface were identified by X-ray diffraction (XRD). The titanium and magnesium contents of the iron were analyzed by inductively coupled plasma (ICP) emission spectrometry. The oxygen content of the iron was analyzed by inert gas impulse infrared absorption spectroscopy. In order to suppress the effects of inclusion entrainment, the samples were analyzed more than twice for each element, and the content of each element was determined from the average of two or more analyzed values.

3. Results and Discussion

3.1. Experimental Results

The equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$ and molten iron were investigated at 1 873 K. XRD analysis was performed at the interface of the oxide and the iron after the experiments, and the results for samples No. 1 and No. 2 are shown in Fig. 2. The equilibrium phases were found to be MgO and MgTi$_2$O$_4$ for both samples. The equilibrium phases were also confirmed to be MgO and MgTi$_2$O$_4$ for the other samples. The dependences of the equilibrium phases on the initial composition of the oxides is shown in the MgO–Al$_2$O$_3$–Ti$_2$O$_3$ diagram in Fig. 3, together with previous results. The titanium, magnesium, and oxygen contents of the molten iron for each sample are shown in Table 1. We found that the oxygen content was almost constant and that the magnesium content was low, in the range 3–14 mass ppm.

3.2. Equilibrium Relationships between the Oxide Compounds in MgO–Ti$_2$O$_3$ and Iron

In this work, the formation of MgTi$_2$O$_4$ is confirmed as one of the equilibrium phases. First, the equilibrium constant for the formation of MgTi$_2$O$_4$ from magnesium, titanium, and oxygen in molten iron, and the interaction parameter of Mg on Ti in iron at 1 873 K are derived. The reaction of MgTi$_2$O$_4$ with molten iron is expressed by Eq. (1). The equilibrium constant for Eq. (1) can be expressed by Eq. (2) using the interaction parameters and the solute concentration.

\[
\text{MgTi}_2\text{O}_4 (s) = \text{Mg} + 2\text{Ti} + 4\text{O} \quad \text{........................................ (1)}
\]

\[
\log K_{MgTi_2O_4} = \log(h_{Mg} \cdot h_{Ti}^2 \cdot h_{O}^4 / \Delta_{MgTi_2O_4}) = \log f_{Mg} + \log(\%Mg) + 2\log f_{Ti} + 2\log(\%Ti) + 4\log f_{O} + 4\log(\%O) = \log(\%Mg) + 2\log(\%Ti) + 4\log(\%O) + (e_{Mg}^{Ti} + 2e_{Ti}^{Ti} + 4e_{O}^{Ti})[\%Ti] + (e_{Mg}^{Mg} + 2e_{Ti}^{Mg} + 4e_{O}^{Mg})[\%Mg] + (e_{Mg}^{O} + 2e_{Ti}^{O} + 4e_{O}^{O})[\%O] \quad \text{........................................ (2)}
\]
$a_i$ and $b_i$ denote the activity of $i$ relative to the pure solid and the activity of $j$ relative to a 1 mass% dilute solution, respectively; $[\% i]$ denotes the concentration of component $i$ in iron [mass%]. $f_i$ is the Henrian activity coefficient of component $i$ relative to the dilute solution and $e_i$ is the first-order interaction parameter of $i$ on $j$ in iron. The activity of MgTi$_2$O$_4$, $a_{MgTi_2O_4}$, is unity, assuming the existence of a pure solid. In Eq. (2), the values for the interaction parameters are already known except $e_{Mg}^{Mg}$ and $e_{Mg}^O$. Equation (2) is rearranged by transposing $\log K_{(1)}$ and the terms including $e_{Mg}^{Mg}$ and $e_{Mg}^O$ to the right-hand side, and Eq. (4) is derived using Eq. (3), which is a conversion equation for the interaction parameters. $M_i$ denotes the atomic weight of element $i$.

$$e_{Mg}^{Mg} = e_{Mg}^O(M_{Ti} / M_{Mg}) + 0.434 \times 10^{-2} \left( (M_{Mg} - M_{Ti}) / M_{Mg} \right) \tag{3}$$

$$\log[\% Mg] + 2 \log[\% Ti] + 4 \log[\% O] + (2e_{Mg}^{Mg} + 4e_{O}^{Mg})[\% Ti]$$
$$+ (e_{Mg}^{Mg} + 4e_{O}^{Mg})[\% Mg] + (e_{O}^{Mg} + 2e_{Mg}^O + 4e_{O}^{O})[\% O]$$
$$+ 2 \times 0.434 \times 10^{-2} \left( (24.3 - 47.9) / 24.3 \right) [\% Mg]$$
$$= -e_{Mg}^{Mg} [\% Mg] + 2 \cdot 47.9 / 24.3 [\% Mg] + \log K_{(1)}$$
$$\tag{4}$$

The values for the left-hand side of Eq. (4) can be determined by substituting each interaction parameter and the experimental results of each solute content of the molten iron. The thermodynamic data used in this work are shown in Table 2. In Fig. 4, the values for the left-hand side of Eq. (4) are plotted against $([\% Mg] + 2 \cdot 47.9 / 24.3 [\% Mg])$, in accordance with Eq. (4). From the intercept and the slope in Fig. 4, the values for $\log K_{(1)}$ and $e_{Mg}^{Mg}$ are determined as follows:

$$\log K_{(1)} = -18.7 (±1.2) \tag{5}$$

$$e_{Mg}^{Mg} = -18.4 (±13.2) \tag{6}$$

The standard error of the value for $e_{Mg}^{Mg}$ is rather large, and this is considered to be caused by the low Mg content of the molten steel.

The phase-stability diagram of MgTi$_2$O$_4$, Ti$_2$O$_3$, and MgO is derived from the following equilibrium constants for the reaction of each compound with molten iron.

$$\text{MgTi}_2\text{O}_4 (s) = \text{Mg} + 2\text{Ti} + 4\text{O} \tag{1}$$
$$\log K_{(1)} = -18.7 \text{ (at 1 873 K)} \tag{5}$$

$$\text{Ti}_2\text{O}_3 (s) = 2\text{Ti} + 3\text{O} \tag{7}$$
$$\log K_{(7)} = -44.238 \text{ (at 1 873 K)} \tag{8}$$

$$\text{MgO (s) = Mg + O} \tag{9}$$
$$\log K_{(9)} = -30.760 \text{ (at 1 873 K)} \tag{10}$$

The equilibrium constants for Eqs. (7) and (9) are expressed by Eqs. (11) and (12), respectively, using the interaction parameters and the solute concentrations.

$$\log K_{(7)} = \log \left( h_{Mg}^{Mg} / a_{Mg, Ti} \right)$$
$$= 2 \log f_{Mg} + 2 \log[\% Ti] + 3 \log f_{O} + 3 \log[\% O] \tag{11}$$

$$\log K_{(9)} = \log \left( h_{Mg}^{Mg} / a_{Mg, O} \right)$$
$$= \log f_{Mg}^{O} + \log[\% Mg] + \log f_{O} + \log[\% O] \tag{12}$$

The doubly saturated curve with MgTi$_2$O$_4$ and Ti$_2$O$_3$ can be described by solving Eqs. (2) and (11), simultaneously. The thermodynamic data shown in Table 2 are used in the calculation. Similarly, the doubly saturated curve with MgTi$_2$O$_4$ and MgO can be described by solving Eqs. (2) and (12), simultaneously. The relationship between the Mg and Ti contents of the molten iron is shown in Fig. 5; the figure shows the stability regions of MgTi$_2$O$_4$, MgO, and Ti$_2$O$_3$ at 1 873 K. The calculated iso-oxygen curve is shown in Fig. 5, and the experimental results are also plotted in Fig. 5. The numerical values in the figure show the experimental results for the oxygen content of molten iron [mass ppm O]. From

Table 2. Mass percentage interaction parameters for Fe-Ti-Mg-Al-O at 1 873 K.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>$e_i^j$</th>
<th>Reference</th>
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<tr>
<td>Ti</td>
<td>Ti</td>
<td>0.048</td>
<td>Janke et al. 70</td>
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<tr>
<td>Ti</td>
<td>Al</td>
<td>0.0037</td>
<td>Yanchang et al. 10</td>
</tr>
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<td>Ti</td>
<td>Mg</td>
<td>-36.3</td>
<td>Present work</td>
</tr>
<tr>
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<td>O</td>
<td>-1.619</td>
<td>Pak et al. 7</td>
</tr>
<tr>
<td>Al</td>
<td>Ti</td>
<td>0.004</td>
<td>Yanchang et al. 10</td>
</tr>
<tr>
<td>Al</td>
<td>Al</td>
<td>0.038</td>
<td>Satoh et al. 31</td>
</tr>
<tr>
<td>Al</td>
<td>Mg</td>
<td>-0.13</td>
<td>Sigworth et al. 8</td>
</tr>
<tr>
<td>Al</td>
<td>O</td>
<td>-1.867</td>
<td>Satoh et al. 31</td>
</tr>
<tr>
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<td>Ti</td>
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<td>O</td>
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Fig. 5, it is found that the calculation is in reasonable agreement with the experimental results. As a titanium oxide that can be in equilibrium with molten iron, Ti$_2$O$_3$ is also generally considered under conditions of high oxygen content (or low titanium content). Here, the calculation is conducted for conditions under which Ti$_3$O$_5$ is not formed.

With respect to inclusion control of steel, it is also important to know which oxides newly form after solidification. Accordingly, variations in the stable compounds with temperature are investigated using the thermodynamic calculation software FactSage 6.1. The initial metal composition was determined from the phase-stability diagram described in this work, which is shown in Fig. 6. The initial metal composition is also shown in Table 3 with the calculation conditions. Fact 53 and FSstel are used as the thermodynamic databases for pure substances and solutions, respectively. The equilibrium phase at 1 873 K is MgO for Nos. 1 and 2, MgTi$_2$O$_4$ for No. 3, and Ti$_2$O$_3$ for Nos. 4 and 5. The calculation was conducted at intervals of 50 K from 1 673 K to 1 873 K, and the temperature dependences of the newly formed stable compounds are shown in Figs. 7–9. In Fig. 7, the variations in the formed compounds with the initial composition (Ti and Mg contents) of the metal are compared at a fixed initial oxygen content of 15 mass ppm. The formation of titanium oxide (Ti$_3$O$_5$ or Ti$_2$O$_3$) is observed below 1 773 K for each condition, and Ti$_2$O$_3$ begins to form at higher temperatures as the titanium content increases. For Nos. 3 and 4, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed. In contrast, for No. 1, the equilibrium phase at 1 873 K is MgO, but the formation of MgO is not confirmed. Similarly, in Figs. 8 and 9, the variations in the formed compounds with the initial metal composition are compared at a fixed initial titanium content of 708 mass ppm and at a fixed initial magnesium content of 2.09 mass ppm, respectively. From Fig. 8, it is found that the formation of titanium oxide is prevented as the magnesium content increases, and in the case of No. 2, the formation of the same compound as the equilibrium phase at 1 873 K, i.e., MgO, is confirmed after solidification. From Fig. 9, it is found that the formation of Mg$_2$TiO$_4$ is prevented and Ti$_2$O$_3$ begins to form at higher temperatures as the titanium content increases. In the case of No. 5, the formation of the same compound as the equilibrium phase at 1 873 K, i.e., Mg$_2$TiO$_4$, is confirmed after solidification. The validity of the thermodynamic data for the solutes in solid iron used for the above calculation cannot be verified. In this work, it is found that there is a strong affinity between Ti and Mg in molten iron. If this strong affinity is also present in solid iron, this suggests that Ti$_2$O$_3$ is easier to form than Mg$_2$TiO$_4$ in the above calculation.

### 3.3. Equilibrium Relationships between the Oxide Compounds in MgO–Al$_2$O$_3$–Ti$_2$O$_3$ and Iron

The phase-stability diagram of Ti$_2$O$_3$, MgTi$_2$O$_4$, and MgAl$_2$O$_4$ is derived from the following equilibrium constants for the reaction of each compound with molten iron.

- \[ \text{MgTi}_2\text{O}_4 (s) = \text{Mg} + 2\text{Ti} + 4\text{O} \] .......................... (1)
- \[ \log K_{(1)} = -18.7 \text{ (at 1 873 K)} \] .................................. (5)
- \[ \text{Ti}_2\text{O}_3 (s) = 2\text{Ti} + 3\text{O} \] ................................. (7)
- \[ \log K_{(7)} = -10.6 \text{ (at 1 873 K)} \] .................................. (8)
- \[ \text{MgAl}_2\text{O}_4(s) = \text{Mg} + 2\text{Al} + 4\text{O} \] .......................... (13)

![Fig. 5. Stability regions of MgTi$_2$O$_4$, MgO, and Ti$_2$O$_3$ at 1 873 K.](image)

![Fig. 6. Initial metal compositions plotted on the stability diagram of the oxide compounds in MgO–Ti$_2$O$_3$ with molten iron at 1 873 K.](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal contents [mass ppm]</th>
<th>Databases</th>
<th>Solution species</th>
<th>Final Conditions</th>
<th>The equilibrium phase at 1 873 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
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<tr>
<td>1</td>
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<td>15</td>
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<td>5</td>
<td>2 430</td>
<td>2.09</td>
<td>10</td>
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</tr>
</tbody>
</table>
The equilibrium constants for Eqs. (1), (7), and (13) are expressed by Eqs. (15), (16), and (17), respectively, using the interaction parameters and the solute concentrations.

\[
\log K_{(13)} = \log(h_{Mg}^1 \cdot h_{O}^2 / a_{MgTiO_3}) = 21.41 - \frac{80 980}{T^0} = -21.8 \text{ (at 1873 K)}
\]

\[
\log K_{(7)} = \log(h_{Ti}^1 \cdot h_{Mg}^1 / a_{TiO_3}) = 2 \log f_{Ti} + 2 \log[\% Ti] + 3 \log f_{O} + 3 \log[\% O]
\]

\[
\log K_{(13)} = \log(h_{Mg}^1 \cdot h_{Al}^1 \cdot h_{O}^2 / a_{MgAl_2O_4}) = 4 \log f_{Al} + 4 \log[\% O] = \log[\% Mg] + 2 \log[\% Al] + 4 \log[\% O]
\]

The doubly saturated curve for Ti$_2$O$_3$ and MgTi$_2$O$_4$ can be obtained by solving Eqs. (15) and (16) simultaneously. Similarly, the doubly saturated curves for Ti$_2$O$_3$ and MgAl$_2$O$_4$ and MgTi$_2$O$_4$ and MgAl$_2$O$_4$ can be obtained by solving Eqs. (16) and (17) or Eqs. (15) and (17), respectively. The relationships among the four elements (Ti, Mg, Al, and O) in molten iron need to be considered. By fixing the content of one component, the relationships among the other three components can be determined from the two equilibrium equations. The relationship between the Al and Ti contents of molten iron was calculated at 1873 K using Eqs. (15)–(17) and the interaction parameters shown in Table 2. The phase-stability regions of MgTi$_2$O$_4$, MgAl$_2$O$_4$, and Ti$_2$O$_3$ when [mass ppm Mg] = 3 are shown in Fig. 10 together with our previous experimental results. 6) The numerical values near the open and closed circles show the oxygen content [mass ppm O]. The calculated iso-oxygen curves are also shown in Fig. 10. Overall, we found that the obtained experimental results are in reasonable agreement with the calculated results. When the titanium content of the molten iron is more than 0.1 mass%, Ti$_2$O$_3$ forms, and this is independent of the aluminum concentration. When the titanium con-

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tent is less than 0.1 mass%, MgAl$_2$O$_4$ forms at Al mass% values above 0.003, and the region of MgAl$_2$O$_4$ formation widens as the titanium content of the molten iron decreases. It is necessary to lower the Al content to at least below Al mass% = 0.003 and to adjust the Ti content to within an appropriate concentration range so that MgTi$_2$O$_4$ can form when [mass ppm Mg] = 3.

As described in Section 4.1, the temperature dependences of the newly formed stable compounds are investigated using the thermodynamic calculation software FactSage 6.1 for the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron. The initial metal compositions were determined from the phase-stability diagram described in this work, as shown in Fig. 11. The initial metal compositions are also shown in Table 4 with the calculation conditions. Fact 53 and FSstel are used as the thermodynamic databases for pure substances and solutions, respectively. The calculation was conducted at intervals of 50 K from 1 673 K to 1 873 K. The variations in the formed compounds with the initial composition (Ti and Mg contents) of the metal are compared in Fig. 12 at a fixed initial oxygen content of 15 mass ppm. From Fig. 12, it is found that the formation of MgAl$_2$O$_4$ is prevented as the titanium content increases, and, for both No. 2 and No. 4, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. Moreover, in the case of No. 2, the formation of a complex oxide, (FeO)$_2$(TiO$_2$), is confirmed. Similarly, in Figs. 13 and 14, the variations in the formed compounds with the initial metal composition are compared at a fixed initial titanium content of 168 mass ppm and at a fixed initial aluminum content of 6.68 mass ppm, respectively. From Fig. 13, it is found that MgAl$_2$O$_4$ forms with increasing aluminum content. From Fig. 14, it is found that the formation of MgAl$_2$O$_4$ is prevented and formation of Ti$_2$O$_3$ is confirmed as the titanium content increases. In cases No. 1 and No. 5, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. From these calculations, although the compound formed after solidification is not necessarily in accordance with the equilibrium oxide compound at 1 873 K, a correlation between them can be confirmed. In particular, formation of MgAl$_2$O$_4$ outside the stable region at 1 873 K is not confirmed. Under the unstable conditions for MgAl$_2$O$_4$ at 1 873 K in the phase-stability diagram shown in Fig. 11, it is found that the MgAl$_2$O$_4$ formation is also suppressed after solidification.

4. Conclusions

The equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron are investigated at 1 873 K. It is important to know which new oxides are formed after solidification. Accordingly, the variations in the formed compounds with the initial composition (Ti and Mg contents) of the metal are compared in Fig. 12 at a fixed initial oxygen content of 15 mass ppm. From Fig. 12, it is found that the formation of MgAl$_2$O$_4$ is prevented as the titanium content increases, and, for both No. 2 and No. 4, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. Moreover, in the case of No. 2, the formation of a complex oxide, (FeO)$_2$(TiO$_2$), is confirmed. Similarly, in Figs. 13 and 14, the variations in the formed compounds with the initial metal composition are compared at a fixed initial titanium content of 168 mass ppm and at a fixed initial aluminum content of 6.68 mass ppm, respectively. From Fig. 13, it is found that MgAl$_2$O$_4$ forms with increasing aluminum content. From Fig. 14, it is found that the formation of MgAl$_2$O$_4$ is prevented and formation of Ti$_2$O$_3$ is confirmed as the titanium content increases. In cases No. 1 and No. 5, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. From these calculations, although the compound formed after solidification is not necessarily in accordance with the equilibrium oxide compound at 1 873 K, a correlation between them can be confirmed. In particular, formation of MgAl$_2$O$_4$ outside the stable region at 1 873 K is not confirmed. Under the unstable conditions for MgAl$_2$O$_4$ at 1 873 K in the phase-stability diagram shown in Fig. 11, it is found that the MgAl$_2$O$_4$ formation is also suppressed after solidification.

Table 4. Initial metal compositions and calculation conditions for equilibrium of oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and iron.

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal contents [mass ppm]</th>
<th>Databases</th>
<th>Solution species</th>
<th>Final Conditions</th>
<th>The equilibrium phase at 1 873 K</th>
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<td>Base-Phase T [K]</td>
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with temperature in the formed compounds after solidification are investigated using the thermodynamic calculation software FactSage 6.1. The conclusions are as follows.

(1) The equilibrium constant of the reaction of MgTi$_2$O$_4$ with molten iron and the interaction parameter of Mg on Ti at 1873 K are determined as follows:

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

$$\log K = -18.7 \ (\pm 1.2)$$

$$\epsilon_{\text{Mg}}^{\text{Ti}} = -18.4 \ (\pm 13.2)$$

(2) The phase-stability diagram, which show the equilibrium relationships between the oxide compounds in MgO–Ti$_2$O$_3$–Al$_2$O$_3$ and molten iron, is derived at 1873 K [mass ppm Mg] = 3. When the titanium content of the molten iron is more than 0.1 mass%, Ti$_2$O$_3$ forms, and this is independent of the aluminum concentration. When the titanium content is less than 0.1 mass%, MgAl$_2$O$_4$ forms at Al mass% values above 0.003 and the region of MgAl$_2$O$_4$ formation widens as the titanium content of the molten iron decreases.

(3) Although the compound formed after solidification is not necessarily in accordance with the equilibrium oxide compound at 1873 K, the correlation between them can be confirmed. In particular, under the unstable conditions for MgAl$_2$O$_4$ at 1873 K, it is found that its formation is suppressed after solidification.

REFERENCES