Deoxidation Equilibria of Fe–Mn–Al Melt with Al₂O₃ or MnAl₂O₄ at 1 873 and 1 773 K

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(Received on March 31, 2020; accepted on June 5, 2020; J-STAGE Advance published date: July 13, 2020)

Deoxidation equilibria of Fe–Mn–Al melt with Al₂O₃ or MnAl₂O₄ were measured at 1 773 K. Composition of melts doubly-saturated with Al₂O₃ and MnAl₂O₄ were also measured using a crucible comprising these two phases at 1 873 or 1 773 K. Equilibria with each solid oxide were analyzed using Wagner’s Interaction Parameter Formalism (WIPF). In the case of Al₂O₃ saturation, Al deoxidation curve at 1 773 K was similar in shape to that at 1 873 K, and the equilibrium oxygen content was approximately 1/3 of that at 1 873 K. The deoxidation equilibria were reproduced using WIPF at the composition range above 0.1 mass%Al by using −0.32 as \( e^{0}_{O\text{Al}} \) and \( 10^{-13.4} \) as the equilibrium constant of Al₂O₃ dissolution reaction, both of which were determined through analysis of measured results for Fe–(20 to 30) mass% Mn melt. In the case of MnAl₂O₄ saturation, accurate values of equilibrium constant were not obtained because of the relatively significant influence of oxygen analysis error. On the contrary, using compositions doubly-saturated with Al₂O₃ and MnAl₂O₄, valid values of the equilibrium constant of MnAl₂O₄ dissolution reaction, \( 10^{-15.4} \) and \( 10^{-17.7} \) at 1 873 and 1 773 K, respectively, could be determined.

KEY WORDS: alumina; deoxidation; Fe–Mn melt; galaxite; thermodynamics.

1. Introduction

High-manganese steel comprising substantial amount of Mn (10 to 30 mass%) has both appropriate mechanical strength and ductility. In particular, twinning-induced plasticity (TWIP) steel, which comprises Mn (15 to 30 mass%) and Al (1.5 to 3 mass%), has garnered attention as the structural material for automobile construction.

To produce such steel grades, thermodynamic properties are necessary to improve the quality of steel. Figure 1 illustrates previous studies of deoxidation equilibria in high-manganese steel at 1 873 K.1–3) Equilibria of molten steel with Al₂O₃ and/or MnAl₂O₄ are needed because possible inclusion phases in such steel are Al₂O₃ and MnAl₂O₄. In Al₂O₃ saturated compositions, Paek et al.1) measured deoxidation equilibria for Fe–(15 to 21) mass%Mn–Al melt at 1 873 K, and calculated the deoxidation equilibria using the modified quasichemical model (MQM). In MnAl₂O₄ saturated compositions, Ogasawara et al.2) obtained the same measurement for Fe–(10 or 30) mass%Mn–Al melt at 1 873 K. Comparing these results, in the region of under 0.1 mass%Mn-Al measurement by Ogasawara et al. is significantly lower than the calculation by Paek et al. To verify the validity of these measurements, we3) measured deoxidation equilibria for Fe–(10, 20, or 30) mass%Mn–Al alloy with wide range of Al content (0.004 to 5.8 mass%) at 1 873 K.

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measurements indicated that equilibrium oxygen content is similar to other measurements in the entire Al content range. In most of the reports, experimental temperature is 1873 K because the secondary refining is performed at this temperature. However, manganese has a strong effect in decreasing the liquidus temperature of Fe–Mn alloy (approximately 1773 K for Fe–10 mass% Mn). The measurement under the melting point of pure iron is also important for consideration in the solidification process of high-manganese steel.

To control the inclusion phase in high-manganese steel, phase boundary of Al2O3 and MnAl2O4 is also necessary. Dimitrov et al.4) measured Al2O3/MnAl2O4 doubly-saturated compositions using a crucible comprising these two phases at 1823 and 1873 K. Although the calculation of these compositions using a chemical potential diagram6) are necessary to understand the reaction mechanism between Mn-containing inclusions and matrix metal during high temperature processing.14) In this study, deoxidation equilibria of molten Fe–Mn–Al alloy and Al2O3 or MnAl2O4 were measured at 1773 K. The range of manganese content was approximately 20 mass% in which the liquidus temperature of the alloy is approximately 1723 or 1673 K, respectively. The range of Al content was sufficiently wide to measure both Al and MnAl2O4 saturated compositions. Furthermore, Al2O3/MnAl2O4 doubly-saturated compositions were measured at 1773 or 1773 K. The obtained equilibrium compositions saturated with each solid phases were analyzed using Wagner’s Interaction Parameter Formalism (WIPF).

2. Experimental

2.1. Deoxidation Experiment

Schematic diagram of experimental apparatus is illustrated in Fig. 2. Electrolytic iron and reagent Mn chip were charged into an Al2O3 crucible (O.D. 38 mm, I.D. 34 mm, and height 45 mm). The total weight of the metal was approximately 40 g. The crucible was inserted into the glass tube (O.D. 54 mm, I.D. 50 mm, and length 300 mm), which was equipped in the 15 kW high-frequency induction furnace. Silica gel dried Ar gas was, deoxidized by Cu turnings at 773 K, and flowed into the glass tube (500 cm3/min). After melting of the Fe–Mn alloy, temperature was measured by inserting a B-type thermocouple with Al2O3 sheath into the melt, and controlled within ±5 K. Thereafter, Al wire or Fe–1 mass%Al alloy was added into the melt as a deoxidizer. The holding time of the melt was determined to be 60 min through preliminary experiments. Subsequently, the crucible was quenched by immersing it in water.

2.2. Measurement of Al2O3/MnAl2O4 Doubly-saturated Compositions

To achieve MnAl2O4 saturation, synthesis of MnAl2O4 was performed. Equimolar reagent grade Al2O3 and MnO powders were mixed. This mixture was charged into the Al2O3 crucible and heated at 1873 K in Ar atmosphere. After 24 h of heating, the crucible was removed and quenched through Ar gas blowing. The synthesized powder was identified to be the single phase of MnAl2O4 using X-ray diffraction (XRD) analysis. Approximately 1 g of MnAl2O4 powder was pressed into a tablet shape, and the tablet was attached to the bottom of the Al2O3 crucible using Al2O3 cement. Using this crucible made of Al2O3 and MnAl2O4, equilibrium experiments were conducted in a similar manner as described in Sec. 2.1. Temperature was controlled to be 1783 or 1773 ± 5 K.

2.3. Analyses

The obtained metal sample was cut into 0.2 to 1 g of specimens. During this time, all samples were collected more than 1 mm under the surface because separated oxides had accumulated near the surface. The specimens were polished and cleaned using ultrasonic in methanol before analyses.

Contents of Mn and Al were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). One specimen was dissolved into the acid mixture comprising 10 cm3 HNO3 and 5 cm3 HCl. This solution was filtrated and the filtrate was analyzed using ICP-OES. The total oxygen content was determined through inert gas fusion infrared absorptiometry. Three to five specimens were analyzed and the average value was determined to be the oxygen content. Though oxide inclusions contained in samples were minimized by holding the molten metal for 60 min as mentioned above, some inclusions may be inevitably entrapped in samples and result in the increased total oxygen content compared to soluble oxygen content. Identification of equilibrium phase was conducted through scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) observation. The interface of the metal/Al2O3 crucible or metal/MnAl2O4 tablet was polished and observed.

3. Results

3.1. Al–O Relationship in Fe–Mn–Al Melt at 1773 K

Results of deoxidation experiment at 1773 K is summarized in Table 1. The samples are classified by the Mn
content; A20 (18.02 to 23.31 mass% Mn) and A30 (31.06 to 34.48 mass% Mn). These compositions are illustrated in Fig. 3. Compared with the data at 1 873 K illustrated in Fig. 1, the shape of the deoxidation curve in this figure is similar. The minimum of the oxygen content exists at 1 to 2 mass% Al, and the slope of the oxygen content under 0.1 mass% Al is lower (negatively higher). The effect of manganese content on the oxygen content is insignificant at this temperature. The oxygen content at 1 773 K is approximately 1/3 of that at 1 873 K. In sample A20-1 and A30-1, all oxides in the sample were identified to be MnAl$_2$O$_4$ using SEM/EDS, and the MnAl$_2$O$_4$ layer was also observed on the surface of the Al$_2$O$_3$ crucible. These observation results are similar to those previously reported. 3)

### 3.2. Results of Al$_2$O$_3$/MnAl$_2$O$_4$ Doubly-saturated Experiment

Using the crucibles made of Al$_2$O$_3$ and MnAl$_2$O$_4$ as mentioned in Sec. 2.2, equilibrium experiments were conducted. The equilibrium compositions and observed phases are summarized in Table 2. The sample numbers are classified according to the temperature and Mn content. These compositions and equilibrium phases are illustrated in Fig. 4 at each temperature.

### Table 2. Results of Al$_2$O$_3$/MnAl$_2$O$_4$ doubly-saturated experiment.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Temp. (K)</th>
<th>Mn concentration (mass%)</th>
<th>Al concentration (mass%)</th>
<th>O concentration (mass%)</th>
<th>Equilibrium Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A20-1</td>
<td>1 873</td>
<td>21.79</td>
<td>0.005</td>
<td>0.00030</td>
<td>MnAl$_2$O$_4$</td>
</tr>
<tr>
<td>A20-2</td>
<td>22.54</td>
<td>0.011</td>
<td>0.00025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A20-3</td>
<td>23.31</td>
<td>0.159</td>
<td>0.00015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A20-4</td>
<td>22.81</td>
<td>0.492</td>
<td>0.00012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A20-5</td>
<td>22.95</td>
<td>1.050</td>
<td>0.00010</td>
<td>Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>A20-6</td>
<td>23.15</td>
<td>2.241</td>
<td>0.00008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A20-7</td>
<td>20.82</td>
<td>4.584</td>
<td>0.00019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A20-8</td>
<td>1 773</td>
<td>18.02</td>
<td>7.104</td>
<td>0.00106</td>
<td></td>
</tr>
<tr>
<td>A30-1</td>
<td>31.06</td>
<td>0.009</td>
<td>0.00019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A30-2</td>
<td>32.81</td>
<td>0.110</td>
<td>0.00008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A30-3</td>
<td>33.67</td>
<td>0.156</td>
<td>0.00013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A30-4</td>
<td>34.27</td>
<td>0.473</td>
<td>0.00016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A30-5</td>
<td>34.14</td>
<td>1.117</td>
<td>0.00007</td>
<td>Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>A30-6</td>
<td>33.40</td>
<td>2.226</td>
<td>0.00008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A30-7</td>
<td>34.48</td>
<td>4.569</td>
<td>0.00021</td>
<td></td>
<td></td>
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</tbody>
</table>

Fig. 3. Measured equilibrium relationship between Al and O contents and calculated curve using WIPF at 1 773 K.

Fig. 4. Relationship between Al and Mn contents and equilibrium phase at 1 873 or 1 773 K.
temperature. The solid lines are plotted using thermodynamic calculation software FactSage7.1. The compositions plotted by black-and-white lozenge are determined to be doubly-saturated. The BEC image and elemental mapping of metal/MnAl2O4 tablet of sample B10-2 are illustrated in Fig. 5(a). The MnAl2O4 tablet was partially reduced to Al2O3, and the metal was in contact with both Al2O3 and MnAl2O4. A similar phenomenon was observed at the interface between the Al2O3 crucible surface and metal, where some parts were covered by the MnAl2O4 phase while others were still Al2O3 as illustrated in Fig. 5(b). In samples B30-2 and C20-2, similar phenomena were observed.

The doubly-saturated compositions are lower in Al content than those calculated using FactSage7.1 and Paek et al.1) at 1 873 K. This tendency is similar to the measurement by Dimitrov et al.4) The doubly-saturated composition at 1 773 K exhibits a similar tendency as that at 1 873 K. However, only one point was obtained at this temperature. To strictly discuss the accuracy of those compositions, a measurement for a wider composition range is required.

4. Discussion

4.1. Equilibrium of Fe–Mn–Al Melt and Al2O3 at 1 773 K

Using the experimental data presented in Table 1, equilibria of Fe–Mn–Al melt and Al2O3 are discussed. We3) considered manganese as part of a solvent and analyzed the equilibrium constant of Eq. (1) introducing interaction coefficients as follows:

$$\text{Al}_2\text{O}_3(s) = 2\text{Al}(\text{mass})\% \text{ in Fe} - x\%\text{Mn} \quad + 3\text{O}(\text{mass})\% \text{ in Fe} - x\%\text{Mn}$$

Here, the standard state of Al2O3 is pure solid Al2O3 and that of Al or O is 1 mass% Henrian standard state in Fe-x mass%Mn melt. If manganese is considered to be a solute, the analysis will not be successful. This is because the effect of manganese content on the change of oxygen content is insignificant as illustrated in Figs. 1 and 3. Hence, manganese is considered to be a part of the solvent in this study as well.

To express the deoxidation equilibria, interaction coefficients are introduced and Eq. (1) is expressed as Eq. (2) because the melt is equilibrated with Al2O3 as follows:

$$\log[\%\text{Al}] = 2\log[\%\text{Al}] + \left(2e_{\text{Al}}^{\text{Al}} + 3e_{\text{Al}}^{\text{O}}\right)[\%\text{Al}]$$

$$+ 3\log[\%\text{O}] + \left(2e_{\text{O}}^{\text{Al}} + 3e_{\text{O}}^{\text{O}}\right)[\%\text{O}]$$

Here, $K_1$ is the equilibrium constant of Eq. (1), and $e_i$ is the first-order interaction coefficient in Fe-x mass%Mn melt. Using the equation proposed by Lupis et al.,15) Eq. (2) is written as Eq. (3) as follows:

$$\log[\%\text{Al}]^2[\%\text{O}] + 2e_{\text{Al}}^{\text{Al}}[\%\text{Al}] + 3e_{\text{Al}}^{\text{O}}[\%\text{O}]$$

$$= -(3[\%\text{Al}] + 3.38[\%\text{O}])e_{\text{Al}}^{\text{Al}} + \log K_1$$

Fig. 5. BEC image and elemental mapping of the metal/MnAl2O4 tablet interface in Fe–9.829 mass%Mn–0.003 mass%Al–0.00165 mass%O alloy (B10-2). (Online version in color.)
Interaction coefficients in Fe melt are listed in Table 3 as a function of temperature. The interaction coefficients are determined from the data obtained in this study because those in Fe–Mn melt are not reported. Plotting the left side of Eq. (3) as vertical axis and $3\%$Al as horizontal axis, $-e_O^3$ and $\log K_4$ at 1773 K can be obtained as the slope and intercept, respectively. For the calculation, self-interaction coefficients $e_O^3$ and $e_{Al}^3$ in Fe–Mn melt are assumed to be equal to those in the Fe melt. These values at 1773 K have not been measured because this temperature is below the melting point of pure iron. Hence in this study, the function of temperature described in Table 3 was assumed to be able to be extrapolated to 1773 K.

The plot of Eq. (3) is illustrated in Fig. 6. Although the plot is classified according to manganese content, the analysis was conducted with all results because its effect on oxygen content is insignificant. The line plotted in Fig. 6 is the result of linear regression, which results in $-0.32$ as $e_{Al}^3$ and $-13.4$ as $\log K_4$ at 1773 K. The deoxidation curve calculated using these values is plotted in Fig. 3. The solid curve is the result of linear regression, which results in $-0.32$ as $e_{Al}^3$ and $-13.4$ as $\log K_4$ at 1773 K. The deoxidation curve calculated using these values is plotted in Fig. 3. The solid curve represents the region where Al$_2$O$_3$ saturation is confirmed, whereas the dashed curve denotes the region where MnAl$_2$O$_4$ may saturate. Compared to the measurement, the curve accurately reproduced the experimental results in the Al content range over 0.1 mass%. On the contrary, the calculated value is higher than the measurements at the range below 0.1 mass%Al. In low Al content range, the deoxidation curve plotted using WIPF is nearly similar to the straight line with a slope of $-2/3$, which is thermodynamically valid. However, the experimental results exhibit a less steep slope than $-2/3$ at the concentration range below 0.1 mass% Al. Therefore, the experimental results cannot be reproduced using WIPF at a range below 0.1 mass%Al.

Generally, WIPF is applicable for the dilute solution. However, the above analysis indicates the inapplicability of WIPF at the Al content range below 0.1 mass%. A similar Al composition dependency of O content was also observed in our previous study as illustrated in Fig. 1, regardless the experimental temperature, whereas the oxygen contents at 1773 K was approximately 1/3 of those at 1873 K as already mentioned. The inapplicability of reported interaction parameters, $e_{Al}^3$ and $e_O^3$, for pure Fe melt at a temperature range above 1823 K, for the Fe-based melt containing a substantial quantity of Mn at 1773 K might be the possible reason for this inconsistency between the measured and calculated values. However, this is currently unclear.

4.2. Equilibrium of Fe–Mn–Al melt and MnAl$_2$O$_4$

Using the experimental data presented in Tables 1 and 2 and previous data, equilibrium of Fe–Mn–Al melt and MnAl$_2$O$_4$ are discussed. Equilibrium with MnAl$_2$O$_4$ is written as Eqs. (4) and (5) in the same manner as Sec. 4.1 as follows:

$$\text{MnAl}_2\text{O}_4(s) = \text{Mn(mass\% in Fe)} + 2\text{Al(mass\% in Fe)} + 4\text{O(mass\% in Fe)} \quad \ldots \quad (4)$$

$$\log K_4 = \log[\%\text{Mn}] + \left(\frac{\text{Mn} + 2\text{Mn}}{\text{Al} + 4\text{O}}\right)[\%\text{Mn}]$$

$$+ 2\log[\%\text{Al}] + \left(\frac{\text{Al} + 2\text{Al}}{\text{Al} + 4\text{O}}\right)[\%\text{Al}] \quad \ldots \quad (5)$$

$$+ 4\log[\%\text{O}] + \left(\frac{\text{O} + 2\text{O}}{\text{Al} + 4\text{O}}\right)[\%\text{O}]$$

Here, the standard state of MnAl$_2$O$_4$ is pure solid MnAl$_2$O$_4$ and that of Mn, Al, or O is 1 mass% Henrian standard state in the Fe melt. Manganese is considered to be a solute because it is involved in the reaction. In this formula, all values in Table 3 can be used because the solvent is pure Fe. To investigate the effect of manganese content on the deoxidation equilibria, $e_{Al}^M$ and $\log K_4$ are determined from the data obtained in this study.

We can write Eq. (5) as Eq. (6) in the same manner as Eq. (3) as follows:

$$\log[\%\text{Mn}] \left(\%\text{Al}\right)^2 \left(\%\text{O}\right)^4 + \left(\frac{\text{Mn} + 2\text{Mn}}{\text{Al} + 4\text{O}}\right)[\%\text{Mn}]$$

$$+ \left(\frac{\text{Al} + 2\text{Al}}{\text{Al} + 4\text{O}}\right)[\%\text{Al}] + \left(\frac{\text{O} + 2\text{O}}{\text{Al} + 4\text{O}}\right)[\%\text{O}] \quad \ldots \quad (6)$$

$$= \left(-4\%\text{Mn} + 3.44\%\text{O}\right) e_{Al}^M + \log K_4$$

Plotting the left side of Eq. (6) as vertical axis and $4\%\text{Mn} + 3.44\%\text{O}$ as horizontal axis, $-e_O^3$ and $\log K_4$ can be obtained as the slope and intercept, respectively. The result of the plot at each temperature is illustrated in Fig. 7. From this figure, $e_{Al}^M$ is calculated to be $-0.009$ and $-0.007$ at 1873 and 1773 K, respectively. The value of $\log K_4$ is calculated to be $-16.3$ and $-18.6$ at 1873 and 1773 K, respectively.

The composition doubly-saturated using Al$_2$O$_3$ and MnAl$_2$O$_4$ was calculated from the thermodynamic values

<table>
<thead>
<tr>
<th>Table 3. Interaction coefficients as a function of temperature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e'_O$</td>
</tr>
<tr>
<td>$0.76 - \frac{1.750}{T}$</td>
</tr>
<tr>
<td>$80.5$</td>
</tr>
<tr>
<td>$1.90 - \frac{5.750}{T}$</td>
</tr>
<tr>
<td>$3.21 - \frac{9.720}{T}$</td>
</tr>
<tr>
<td>$e'_Mn$</td>
</tr>
<tr>
<td>$e'_Mn$</td>
</tr>
<tr>
<td>$e'_O$</td>
</tr>
</tbody>
</table>
determined in this study. When the iron equilibrates with both Al2O3 and MnAl2O4, Eqs. (4) and (7) are satisfied.

\[
\text{Al}_2\text{O}_3(s) = 2\text{Al(mass\% in Fe)} + 3\text{O(mass\% in Fe)} \quad (7)
\]

Combining Eqs. (4) and (7), the doubly-saturated state is expressed using Eqs. (8) and (9) as follows:

\[
\begin{align*}
4\text{Al}_2\text{O}_3(s) + 3\text{Mn(mass\% in Fe)} &= 3\text{MnAl}_2\text{O}_4(s) + 2\text{Al(mass\% in Fe)} \quad (8) \\
3\log[\%\text{Mn}] + (2\varepsilon^{\text{Mn}} - 3\varepsilon^{\text{Al}})[\%\text{Al}] + (2\varepsilon^{\text{O}} - 3\varepsilon^{\text{Mn}})[$\%\text{O}]) &= -\log K_8 \quad (9)
\end{align*}
\]

Here, \(K_8\) is the equilibrium constant of Eq. (8).

Equilibrium constant of Eq. (7) is recommended as Eq. (10). Note that this value is different from \(K_1\) because the solvent is pure Fe.

\[
\log K_7 = -\frac{64 000}{T} + 20.57(1823 \leq T \leq 2023 \text{ K}) \quad (10)
\]

From Eq. (10) and \(K_4\) determined in this study, we can obtain \(K_8\) as Eq. (11) as follows:

\[
\log K_8 = 4\log K_7 - 3\log K_4 \quad (11)
\]

The doubly-saturated compositions were calculated as a function of Mn and Al contents from Eq. (9). The member containing [%O] was ignored because it is significantly smaller than \(K_8\). The solid line in Fig. 8 represents the result of the calculation at 1 873 K. Compared with the results measured in this study and reported by Dimitrov et al., the calculated line does not reproduce these points. The line reproducing these results shown by the broken line in Fig. 8 is given when \(\log K_4 = -15.4\). This value was obtained from the results of this study. Using the data of Dimitrov et al. including points out of the Al content range in this figure, a similar value of \(\log K_4 = -15.6\) was obtained. Assuming that Eq. (10) can be extrapolated to 1 773 K, a similar calculation was performed and \(\log K_8\) was determined to be -17.7 at 1 773 K.

The value of \(\log K_4\) obtained from all MnAl2O4 saturated compositions using Eq. (6) and that obtained from Al2O3/MnAl2O4 doubly-saturated compositions using Eq. (9) are different. Although the values should be evaluated, reports for the equilibrium of iron and MnAl2O4 are few. Therefore, the thermodynamic value of Eq. (12) is calculated from the result of this study because there are several reports of this reaction.

\[
\text{Al}_2\text{O}_3(s) + \text{MnO(s)} = \text{MnAl}_2\text{O}_4(s) \quad (12)
\]

Equilibrium constant of Eq. (12) can be calculated by combining the equilibrium constant of the dissolution reaction of each oxide in molten Fe. Dissolution reactions of MnAl2O4 and Al2O3 are shown in Eqs. (4) and (7), respectively. The case of MnO is reported by Takahashi et al. as Eqs. (13) and (14) as follows:

\[
\begin{align*}
\text{MnO(s)} &= \text{Mn(mass\% in Fe)} + \text{O(mass\% in Fe)} \quad (13) \\
\log K_{13} &= \frac{-11 900}{T} + 5.10(1823 \leq T \leq 1923 \text{ K}) \quad (14)
\end{align*}
\]

Equilibrium constant of Eq. (12), \(\log K_{12}\), can be calculated from Eq. (15), and the standard Gibbs energy change of Eq. (12) is obtained:

\[
\log K_{12} = \log K_7 + \log K_{13} - \log K_4 \quad (15)
\]

Figure 9 illustrates the standard Gibbs energy change of Eq. (13) compared with other studies. The open lozenges represent the value calculated from the \(\log K_4\) value from all MnAl2O4 saturated compositions, and the solid lozenges show the value calculated from Al2O3/MnAl2O4 doubly-saturated compositions only. Among these studies, Dimitrov et al. and Kim et al. measured the value from the equilibrium experiment of molten Fe and MnAl2O4. Values shown by the solid lozenges are close to those reported by Dimitrov et al. and Kim et al., whereas the values shown by open lozenges are lower than other values. Its reason would be the uncertainty of the oxygen analysis. The values shown by open lozenges are calculated from Eq. (6), which contains the member of log[%O]. It implies that the analysis error of oxygen content has a significant influence on the subsequent calculations. In fact, the linearity of Fig. 7 is inappropriate especially at 1 773 K. On the contrary, the values shown by solid lozenges are calculated from Eq. (9) in which the member containing [%O] is significantly lower than log

\[
\begin{align*}
\text{Determination of } \varepsilon^{\text{Mn}} \text{ and } \varepsilon^{\text{Al}} \text{ in } \text{Fe}-(10 \text{ to } 30) \text{ mass\% Mn melt at } 1 873 \text{ or } 1 773 \text{ K.}
\end{align*}
\]
smaller than others. Thus, the influence of analysis error of oxygen content is insignificant. The difference of values shown by solid and open lozenges is approximately 30 kJ/mol. Converting its difference into oxygen content, it corresponds to approximately 1.8 times in oxygen content. In this study, the range of oxygen content is mostly from 1 to 10 mass ppm. In this oxygen content region, a difference of 1.8 times is likely to appear. In conclusion, thermodynamic values obtained from Al₂O₃/MnAl₂O₄ doubly-saturated compositions are valid because the analysis error of oxygen content can be ignored. However, only one point was available for the analysis at 1773 K. To obtain more reliable values, further measurements in wider composition ranges are needed.

5. Conclusions

Deoxidation equilibria of Fe–Mn–Al melt with Al₂O₃ or MnAl₂O₄ were measured at 1773 K, and compositions of melts doubly-saturated with Al₂O₃ and MnAl₂O₄ were measured at 1873 or 1773 K. The following results were obtained:

(1) Al deoxidation curve at 1773 K is similar in shape to that at 1873 K, and the equilibrium oxygen content is approximately 1/3 of that at 1873 K.

(2) The compositions of melts doubly-saturated with Al₂O₃ and MnAl₂O₄ at 1873 K are lower in Al content than other calculations, but exhibit a similar tendency to Dimitrov et al.⁴

(3) In Fe–(20 to 30) mass%Mn melt, the interaction coefficient εₒ is ~ 0.32 and the equilibrium constant of Al₂O₃ dissolution reaction is 10⁻¹³.4 at 1773 K. These values reproduced the measured results using WIPF especially in the concentration range above 0.1 mass%Al.

(4) The equilibrium constants of MnAl₂O₄ dissolution reaction are determined from the compositions doubly-saturated with Al₂O₃ and MnAl₂O₄ as 10⁻¹⁵.4 and 10⁻¹⁷.7 at 1873 and 1773 K, respectively. These values are considered to be accurate because the influence of the analysis error of oxygen content is insignificant.

Acknowledgment

This research was supported by the 31st research grant from Hitachi Metals · Materials Science Foundation. Authors greatly appreciate the financial support.

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