Deoxidation Equilibria among Mg, Al and O in Liquid Iron in the Presence of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ Spinel

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The deoxidation equilibria among Mg, Al and O in liquid iron in the presence of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel was studied at 1873 K by adding Al and Mg alloys into liquid iron in MgO and Al_2O_3 crucibles. From the experimental results, the equilibrium constant, K_{Mg} , for the reaction, $\text{MgO}(\text{s}) = \text{Mg} + \text{O}$, and the first- and second-order interaction parameters including cross-product terms between Mg and O have been determined. Using these thermodynamic parameters, the relations between a_{Mg} vs. a_{O} , a_{Mg} vs. a_{Al} in liquid iron could be well represented with respective oxide activities in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel. A stability diagram for MgO , $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 phases was constructed at 1873 K as a function of dissolved Mg, Al and O contents in liquid iron to examine the condition for the formation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel during the deoxidation process.

KEY WORDS: liquid iron; deoxidation equilibria; spinel; magnesium; aluminum.

1. Introduction

In the deoxidation process of liquid steel using aluminum, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel compound is often observed. This compound may remain in solidified steel as nonmetallic inclusions, and can create unfavorable effects on the physical properties of rolled steel products. The control of this spinel type nonmetallic inclusion requires a precise knowledge on thermodynamics of the Mg–Al–O deoxidation equilibrium in liquid iron.

There have been some investigations^{1–13)} on the Mg–O equilibrium in liquid iron. However, there are still considerable differences in the solubility product of Mg and O as well as the interaction parameters between these elements in liquid iron. The discrepancies can be attributed to errors in the chemical analyses of Mg and O, since the presence of deoxidation products in the iron sample would result in a serious error in determining extremely low contents of these elements. Another factor is the experimental difficulty in obtaining the Mg–O equilibrium in liquid iron due to a high vapor pressure of Mg.

In the present study, the deoxidation equilibria between Mg, Al and O in liquid iron in the presence of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel was investigated at 1873 K, using a specially designed high frequency induction furnace for a strong agitation of melt. Strong agitation of melt would result in a faster attainment of deoxidation equilibrium and a good separation of deoxidation products from iron melt. MgO

and Al_2O_3 crucibles were used to fix oxide activities in equilibrium with Mg, Al and O in iron melt. From the experimental data, the equilibrium constant of Mg deoxidation reaction, the first- and second-order interaction parameters including the cross-product terms between Mg and O in the presence of Al, were evaluated. The validity of these parameters was discussed by checking thermodynamic relations of Mg–Al–O co-deoxidation equilibria in liquid iron in the presence of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel.

2. Experimental Aspects

2.1. Apparatus and Procedure

An iron sample was melted by a high frequency induction furnace shown in Fig. 1. The induction coil was specially designed to give a dense electromagnetic flux going through the metallic charge in the crucible. The coil was formed from 6.35 mm OD thin walled copper tubing wrapped with glass fiber tape for insulation. The coil had 10 turns among which the outside 4 turns were tightly wound on the inside 6 turns in the same direction. This coil design was optimum to melt iron and provide a strong agitation of the melt using a 15 kW/50 kHz high frequency power generator.

The reaction chamber consisted of a 80 mm OD quartz tube open at both ends and connected to a gas delivery system. Two hundred grams of high purity electrolytic iron (99.99 mass%, 60 mass ppm O, <5 mass ppm N, 18 mass

Fig. 1. Schematic diagram of experimental furnace.

ppm C, <5 mass ppm Si, <7 mass ppm Ni, 1 mass ppm Al) contained in a MgO or Al₂O₃ crucible (OD: 40 mm, ID: 30 mm, H: 50 mm) together with MgO·Al₂O₃ spinel (0.2 g) was melted at 1873 K. In order to remove any residual oxygen in the reaction chamber during heating, the mixture of Ti chips and MgO granules was packed in the space between the inner and outer crucibles. The flow rate of Ar-3vol%H₂ gas mixture, which was dehydrated by magnesium perchlorate and deoxidized by Ti (873 K), was in the range of 100 to 150 ml/min. Temperature was measured by a two color pyrometer calibrated against the melting temperatures of pure copper and iron. The temperature reading of the pyrometer was connected to the PID controller of the induction furnace, hence to automatically adjust the power to keep the temperature of melt at 1873±2 K.

After melting the iron, Fe-5mass%Al (0.5 to 3 g) and Ni-10mass%Mg (1 to 2 g) alloys, which were kept in a glass tube by magnets, were dropped into liquid iron. When the fume arose, the temperature control was made by the manual adjustment of the output power level of the furnace. Preliminary trials confirmed that the temperature variation of iron melt during this period was within 5 K.

Figure 2 shows the variation of Al, Mg and O contents in iron melt with time after the Fe-Al and Ni-Mg alloys were added. All elements reach their equilibrium contents in about 20 min. Therefore, in all experiments, the melt was kept for 30 min after the alloy additions. After each experiment, the iron sample was quenched rapidly by helium gas blowing in the chamber, and followed by a water quenching. The quenched iron sample was cross-sectioned and examined with an optical microscope for the presence of non-metallic inclusions. The center part of iron sample was virtually clean without any noticeable inclusions, and was used for the chemical analyses.

2.2. Preparation of Additives

Fe-5mass%Al alloy was premelted in deoxidized argon atmosphere using an induction furnace. Ni-10mass%Mg alloy was prepared by melting high purity Ni (99.9 mass%) and Mg (99.9 mass%) in an alumina crucible enclosed in a capped graphite crucible.¹⁴⁾ The crucible was heated in a

Fig. 2. Variation of Mg, Al and O contents with time in liquid iron at 1873 K.

Fig. 3. X-ray diffraction pattern of MgO·Al₂O₃ spinel.

vertical resistance furnace with an alumina reaction tube. After holding the sample at a temperature a few degrees above the melting point of Mg (922 K) for 4 h, it was heated up to 1473 K at a rate of 2 K/min, and kept for 6 h.

For the preparation of stoichiometric MgO·Al₂O₃ spinel powder, the mixture of high purity (99.9 mass%) MgO and Al₂O₃ powders of the equi-molar ratio was melted in a fused Na₂CO₃ bath contained in a platinum crucible at 1273 K. The molten salt was quenched on a steel plate and powdered. The powder was heated in a graphite crucible at 1873 K for 4 h to evaporate Na₂CO₃ and obtain stoichiometric MgO·Al₂O₃ spinel powder. A small amount of carbon picked up in the powder during this process was removed by holding the powder in an ashing furnace at 1273 K for 12 h. **Figure 3** shows the XRD pattern of the MgO·Al₂O₃ spinel powder obtained.

2.3. Chemical Analyses

Recent reports by Inoue and Suito¹⁾ and Itoh *et al.*⁴⁾ describe details of chemical analysis method for determining very low contents of Mg, Al and O in iron sample. In the present study, the iron sample (0.5 g) was dissolved in 12 ml of HCl(1+1) and 3 ml of HNO₃(1+1) in a teflon tube of 25 ml capacity heated in a block heater at 353 K for 5 h. Water and all acids used were ultra pure grade. After dissolving the sample, the solution was transferred to the measuring flask (25 ml) using ultra pure water with filtration.

Virtually no residue was remained in the filter paper, and it was confirmed by the fusion method using ultra pure Na_2CO_3 for the analysis of acid-insoluble Mg and Al, which corresponded to oxide inclusions.

The content of Mg in sample solution was analyzed by inductively coupled plasma (ICP) spectroscopy. **Figure 4** shows the ICP intensities for Mg in standard solutions containing 0 to 100 mass ppb of Mg. The standard solution also contains 20 000 mass ppm of Fe in order to have the same condition as the sample solution. At a wavelength of 280.27 nm, the ICP intensity shows a perfect correlation with Mg content. The accuracy of Mg analysis in iron sample was 0.1 ± 0.02 mass ppm. The Al content in iron was analysed by the similar technique as Mg analysis. The oxygen content was measured with an accuracy of ± 1 mass ppm by inert gas fusion-infrared absorptiometry, using the standard sample of steel containing 6 ± 1 mass ppm oxygen.

3. Results Discussion

The experimental results of Mg, Al and O equilibration in iron melt at 1 873 K using MgO (MS) and Al_2O_3 (AS) crucibles are summarized in **Table 1**. As shown in **Fig. 5**, the SEM-EDS analysis on the inclusions formed near the melt surface confirmed the formation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel phase during Al and Mg deoxidation. Therefore, Mg, Al and O concentrations shown in Table 1 are the equilibrium contents in liquid iron for the relevant MgO and Al_2O_3 ac-

tivities in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel. **Figure 6** shows the phase diagram of $\text{MgO}-\text{Al}_2\text{O}_3$ binary system.¹⁵⁾ Itoh *et al.*¹⁶⁾ estimated the activity of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel as 0.64 at the solvus of the spinel phase with Al_2O_3 , and 0.96 at the solvus with MgO at 1 873 K. The MgO activity in the melt when saturated with both Al_2O_3 and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel at 1 873 K can then be calculated as 0.09 using following thermodynamic data.

Therefore, the equilibrium Mg–O relation in liquid iron should vary with MgO activity in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel.

Figure 7 shows the Mg deoxidation equilibrium data obtained in the present study together with previous results.^{1,4,6,8)} The experimental results obtained by various equilibration techniques are widely dispersed. The data in a low Mg concentration range (0.1–10 mass ppm) were obtained by the addition of Mg or Mg alloys into liquid iron.^{1,4)} Inoue and Suito¹⁾ equilibrated the Al and Mg deoxidized liquid iron with $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$ slags of known MgO activities using a vertical resistance furnace. Itoh *et al.*⁴⁾ added Mg into inductively stirred melts in MgO crucibles to study Mg–O equilibrium in liquid iron. They equilibrated iron melts with solid MgO crucibles without slags. The solid curve in Fig. 7 is the relation of equilibrium

Fig. 4. ICP intensities for Mg in Fe-rich standard solutions.

Table 1. Experimental results of Mg, Al and O equilibration in iron melt at 1 873 K.

(mass ppm)							
MgO/ $\text{MgO} \cdot \text{Al}_2\text{O}_3$ sat. (MS)				$\text{Al}_2\text{O}_3/\text{MgO} \cdot \text{Al}_2\text{O}_3$ sat. (AS)			
No.	Mg	Al	O	No.	Mg	Al	O
1	1.89	194.7	4.6	13	0.40	435.6	3.8
2	0.69	278.6	7.2	14	0.16	107.3	7.5
3	2.14	9.34	16.3	15	1.16	2242	2.8
4	2.26	203.5	5.4	16	0.13	174.4	5.6
5	8.76	105.4	1.8	17	0.73	877.5	4.3
6	3.35	70.7	8.4	18	0.56	644.9	4.2
7	9.94	857.0	1.4	19	0.15	208.0	4.8
8	5.86	598.6	1.3	20	0.26	194.9	7.0
9	7.69	208.2	1.5	21	0.58	235.9	3.6
10	0.68	33.6	7.8	22	1.64	398.5	1.5
11	1.51	176.8	7.0				
12	11.22	162.0	4.2

Fig. 5. SEM image and EDS analysis of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusion formed in liquid iron.

 Fig. 6. Phase diagram of the MgO-Al₂O₃ binary system.¹⁵⁾

Fig. 7. Relation between Mg and O contents in liquid iron at 1873 K.

Mg-O content in liquid iron at MgO saturation calculated using the thermodynamic data obtained by Itoh *et al.*⁴⁾ In the present study, MgO·Al₂O₃ spinel was used as an equilibrium phase, and it can be seen that the equilibrium Mg-O relation in liquid iron varies with MgO activities.

The data in a high Mg concentration range (10–900 mass ppm) were measured by the dissolution equilibrium of Mg vapor in liquid iron.^{6,8)} In their experiments, however, it was not clear if the melts were free from MgO inclusions at such high Mg concentrations.

The deoxidation equilibrium of Mg is represented by Eq. (2), and the equilibrium constant, K_{Mg} is expressed by Eq. (3):

$$K_{\text{Mg}} = \frac{a_{\text{Mg}} \cdot a_{\text{O}}}{a_{\text{MgO}}} = \frac{f_{\text{Mg}} [\% \text{Mg}] \cdot f_{\text{O}} [\% \text{O}]}{a_{\text{MgO}}} \quad \text{.....(3)}$$

where a_{Mg} and a_{O} are the activities of Mg and O, respective-

ly, and their standard states are their infinitely dilute solution in liquid iron.

Using the apparent equilibrium constant, K'_{Mg} ($= [\% \text{Mg}] \cdot [\% \text{O}]$), the first-order interaction parameter, e_{O}^{Mg} , and Lupis' reciprocal relationship between e_{O}^{Mg} and e_{Mg}^{O} , Eq. (3) can be rewritten as the following relation:

$$\begin{aligned} \log K'_{\text{Mg}} - \log a_{\text{MgO}} + \sum e_{\text{Mg}}^k [\% k] + \sum e_{\text{O}}^l [\% l] \\ = -e_{\text{O}}^{\text{Mg}} ([\% \text{Mg}] + 1.52 [\% \text{O}]) + \log K_{\text{Mg}} \quad \text{.....(4)} \end{aligned}$$

where k and l represent elements other than O and Mg, respectively. When Al is present in liquid iron, e_{O}^{Al} ($= -3.9$ at 1873 K)¹⁸⁾ and $e_{\text{Mg}}^{\text{Al}}$ ($= -0.12$ at 1873 K)¹⁹⁾ should be considered. The values of $e_{\text{Mg}}^{\text{Mg}}$ and e_{O}^{O} in liquid iron at 1873 K are known as 0⁴⁾ and -0.2 ,¹⁸⁾ respectively. In this work, 1 to 2 g of Ni-10mass%Mg alloy was added into 200 g of iron melt. Considering the low values of e_{O}^{Ni} ($= -0.006$)¹⁸⁾ and $e_{\text{Mg}}^{\text{Ni}}$ ($= -0.012$)¹²⁾ at 1873 K, the effect of nickel on O and

Mg can be neglected.

Figure 8 shows a plot for the relation expressed by Eq. (4) using the present experimental data given in Table 1. It is apparent from the figure that the data points determined at different MgO activities and Al contents show a good linear relationship. The value of $\log K_{\text{Mg}}$ obtained by extrapolating the line is found to be approximately -7.24 . The value of e_{O}^{Mg} can be obtained from the slope of the line as -266 , and e_{Mg}^{O} as -404 using the reciprocal relationship.

Figure 9 compares the same relation expressed by Eq. (4) for different author's results over a wide range of $([\% \text{Mg}] + 1.52[\% \text{O}])$. The data obtained at the high range of $([\% \text{Mg}] + 1.52[\% \text{O}])$, especially the Mg vapor equilibration data^{6,8)} do not show the relationship described above, and would give different values of $\log K_{\text{Mg}}$ and e_{O}^{Mg} . It should be emphasized that those values obtained at extremely low range of Mg and O contents dissolved in liquid iron is thermodynamically meaningful to determine the first-order interaction parameters.

Due to a strong interaction between Mg and O in liquid iron, the higher order interaction parameters should be also considered. When the activity coefficients, f_i in Eq. (3) are expressed by Wagner's relation using the first- and second-

Fig. 8. A plot for the Mg–O relation expressed by Eq. (4).

order interaction parameters, the following relation can be derived by means of Lupis' relation.^{20,21)}

$$\begin{aligned} \log K_{\text{Mg}} - \log K'_{\text{Mg}} + \log a_{\text{MgO}} - \sum e_{\text{Mg}}^k [\%k] + \sum e_{\text{O}}^l [\%l] \\ - e_{\text{O}}^{\text{Mg}} ([\% \text{Mg}] + 1.52[\% \text{O}] - 0.025[\% \text{Mg}][\% \text{O}]) \\ = r_{\text{O}}^{\text{Mg}} ([\% \text{Mg}]^2 + 3.04[\% \text{Mg}][\% \text{O}]) \\ + r_{\text{Mg}}^{\text{O}} ([\% \text{O}]^2 + 1.32[\% \text{Mg}][\% \text{O}]) \end{aligned} \quad (5)$$

where k and l represent the same meanings as in Eq. (4), and $\log K_{\text{Mg}}$ and e_{O}^{Mg} were determined previously as -7.24 and -266 , respectively.

All terms in Eq. (5) are known values except the second-order interaction parameters, r_{O}^{Mg} and r_{Mg}^{O} . Therefore, these parameters can be determined from the relation between Mg and O contents measured in the present experiment as shown in **Fig. 10**. The values of r_{O}^{Mg} and r_{Mg}^{O} determined by a regression analysis are $-40\,000$ and $527\,000$, respectively.

Fig. 10. A plot for the relation of Eq. (5) for determining $\gamma_{\text{O}}^{\text{Mg}}$ and $\gamma_{\text{Mg}}^{\text{O}}$.

Fig. 9. The Mg–O relations in liquid iron obtained by various investigators.

The equilibrium constant and interaction parameters on Mg deoxidation reaction determined in the present study are summarized in **Table 2**, together with the values reported previously.^{3,4,7-13} The values of $r_{\text{O}}^{\text{Mg},\text{O}}$ and $r_{\text{Mg}}^{\text{Mg},\text{O}}$ in Table 2 were obtained using the following relationships derived by Lupis *et al.*²¹:

$$r_{\text{O}}^{\text{Mg},\text{O}} = 2 \left(\frac{M_{\text{O}}}{M_{\text{Mg}}} \right) r_{\text{Mg}}^{\text{O}} + 0.01e_{\text{O}}^{\text{O}} - 0.01e_{\text{O}}^{\text{Mg}} \dots\dots\dots(6)$$

$$r_{\text{Mg}}^{\text{Mg},\text{O}} = 2 \left(\frac{M_{\text{Mg}}}{M_{\text{O}}} \right) r_{\text{O}}^{\text{Mg}} + 0.01e_{\text{Mg}}^{\text{Mg}} - 0.015e_{\text{O}}^{\text{Mg}} \dots\dots\dots(7)$$

From Eq. (3), the following relation is derived using K_{Mg} :

$$\log K_{\text{Mg}} - \log a_{\text{O}} + \log a_{\text{MgO}} = \log a_{\text{Mg}} \dots\dots\dots(8)$$

Figure 11 shows the relation expressed by Eq. (8) for the data shown in Fig. 7 using the values of K_{Mg} and interaction parameters determined in the present study. Good correlations are observed for the data of present study and Inoue *et al.*'s,¹¹ in which $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ – MgO slags, respectively, were used as equilibrium phases. The equilibrium Mg–O data determined by Mg vapor dissolution experiments^{6,8} do not follow the thermodynamic relation expressed by Eq. (8).

Figure 12 shows the relation of Al and O contents in liq-

uid iron obtained in the present study. The measured values are in good agreement with calculated lines. The lines were calculated using the activity values of Al_2O_3 in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel determined from Eq.(1), the Gibbs free energy change of Al deoxidation reaction given by Eq. (9), and the interaction parameters given in the thermodynamic data.¹⁸

$$\Delta G_T^\circ = 1\,202\,000 - 386.3T \quad (\text{J/mol})^{18}$$

From reactions (2) and (9), the following relation between $\log a_{\text{Mg}}$ and $\log a_{\text{Al}}$ can be derived.

$$\log a_{\text{Mg}} = \frac{2}{3} \log a_{\text{Al}} + \log(a_{\text{MgO}} / a_{\text{Al}_2\text{O}_3}^{1/3}) + \log(K_{\text{Mg}} / K_{\text{Al}}^{1/3}) \dots\dots\dots(10)$$

The lines shown in **Fig. 13** were obtained by substituting the respective values of oxide activities in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel and the equilibrium constants of reactions (2) and

Table 2. Deoxidation equilibria of Mg in liquid iron at 1 873 K.

	$\log K_{\text{Mg}}$	e_{O}^{Mg}	e_{Mg}^{O}	$\gamma_{\text{O}}^{\text{Mg}}$	$\gamma_{\text{Mg}}^{\text{O}}$	$\gamma_{\text{O}}^{\text{MgO}}$	$\gamma_{\text{Mg}}^{\text{MgO}}$
Thermodynamic calculation							
Kulikov ¹⁰	-8.54	-160	-243				
Gorobetz ¹¹	-9.24	-250	-380				
Turkdogan ⁹	-7.74						
Experimental							
Teplitskii <i>et al.</i> ¹³	-5.12						
Nadif <i>et al.</i> ¹²	-5.70						
Han <i>et al.</i> ⁸	-6.03	-106	-161				
Itoh <i>et al.</i> ⁴	-6.8	-280	-430	-20,000	350,000	462,000	-61,000
Ohta <i>et al.</i> ³	-7.86	-300	-460	16,000	37,000	48,000	48,000
Seo <i>et al.</i> ⁷	-7.21	-370	-560	5,900	145,000	191,400	17,940
Present study	-7.24	-266	-404	-40,000	527,000	696,000	-122,000

Fig. 11. Thermodynamic relation of Mg deoxidation reaction in liquid iron at 1 873 K.

Fig. 12. Relation between Al and O contents in liquid iron at 1 873 K.

Fig. 13. Relation between $\log a_{\text{Al}}$ and $\log a_{\text{Mg}}$ in liquid iron for oxide activities in $\text{MgO} \cdot \text{Al}_2\text{O}_3$.

(9). The data points obtained from the present Mg–Al deoxidation experiments agree well with the lines calculated from Eq. (10). These results suggest that the co-deoxidation equilibria among Mg, Al and O in liquid iron in the presence of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel has been attained, and the thermodynamic parameters determined are well established.

The curves in Fig. 14 are proposed equilibrium relations of Mg–O content in liquid iron at MgO saturation at 1873 K, calculated using the thermodynamic data obtained from the present study. When Al is present in liquid iron, Al decreases the activity coefficients of Mg and O, and hence would shift the equilibrium Mg–O relation curve upward. The dotted curve is for the melt containing 0.25 mass% of Al. The equilibrium Mg–O data of present study obtained at different Al contents (<0.25 mass%) fall reasonably well within these curves. Considering the effect of Al, it is interesting to see that the data of Itoh *et al.*,⁴⁾ who measured the Mg–O relation without Al addition, show higher O contents than Inoue and Suito's data¹⁾ measured with Al additions. Figure 15 shows the equilibrium Mg–O relation curves for iron melt saturated with both $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 ($a_{\text{MgO}}=0.09$). The equilibrium Mg–O data

Fig. 14. Proposed equilibrium relations of Mg–O content in liquid iron ($a_{\text{MgO}}=1$) and the observed values at 1873 K.

Fig. 15. Proposed equilibrium Mg–O relations ($a_{\text{MgO}}=0.09$) and the observed values at 1873 K.

Fig. 16. Stability diagram of MgO, MgO·Al₂O₃ and Al₂O₃ as a function of Mg, Al and O contents in liquid iron at 1873 K.

obtained with Al additions in the present study fall within the curves calculated for the melt containing Al.

During the Al deoxidation of liquid steel in contact with MgO saturated slags or MgO lining, Al₂O₃, MgO and/or MgO·Al₂O₃ spinel can form as deoxidation products in melt. The thermodynamic parameters obtained in the present study can be used to examine the stability of these oxides as a function of Mg and Al contents in liquid iron as shown in Fig. 16. The boundary lines between MgO and MgO·Al₂O₃, and between MgO·Al₂O₃ and Al₂O₃ can be calculated using Eqs. (11) and (12), respectively.

$$\Delta G_{1873\text{K}}^\circ = 271\,309 \quad (\text{J/mol})$$

$$\Delta G_{1873\text{K}}^\circ = -393\,708 \quad (\text{J/mol})$$

The free energy changes of Eqs. (11) and (12) were derived from the equilibrium constant of Mg deoxidation determined in the present study, and those of Eqs. (1) and (9). Using the equilibrium constants of Eqs. (11) and (12), the interaction parameters between Mg, Al and O and the activity values of oxides at the phase boundaries,¹⁶⁾ the relation of equilibrium Mg, Al and O contents at the boundary lines can be evaluated.

For a given O level, the equilibrium phase changes in the order of MgO, MgO·Al₂O₃ and Al₂O₃ with increasing Al content. At the Al level higher than 15 mass ppm in liquid iron, the MgO·Al₂O₃ phase appears at [mass ppm O]=15 and [mass ppm Mg]=0.1 at 1873 K. With a further increase in Al content, the equilibrium Mg content to form MgO·Al₂O₃ phase decreases at a constant O level. For an example, the tire cord steel is deoxidized with Si and Mn, and the O level in liquid steel is 15–30 mass ppm. If the Al con-

tent in liquid steel increases to a level above 15 mass ppm during the dissolution of ferroalloys containing some Al or by the reduction of Al₂O₃ in refractory, the MgO·Al₂O₃ spinel would easily form and become harmful inclusions in steel products.

4. Conclusions

The Mg–Al–O equilibrium in liquid iron was studied at 1873 K by deoxidizing the melt with Fe–Al and Ni–Mg alloys, which was equilibrated with MgO·Al₂O₃ spinel in MgO and Al₂O₃ crucibles. The main findings of this study can be summarized as follows.

(1) The equilibrium constant of Mg deoxidation, the first- and second-order interaction parameters including cross-product terms between Mg and O have been determined.

(2) Using these thermodynamic parameters, the relations between a_{Mg} vs. a_{O} , a_{Mg} vs. a_{Al} in liquid iron could be well represented with respective oxide activities in MgO·Al₂O₃ spinel.

(3) A stability phase diagram of MgO–MgO·Al₂O₃–Al₂O₃ was constructed at 1873 K as a function of dissolved Mg, Al and O contents in liquid iron to examine the condition for MgO·Al₂O₃ spinel formation.

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