Thermodynamics of O, N, and S in Liquid Fe Equilibrated with CaO-Al₂O₃-MgO Slags

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Nitrogen and S distribution ratios between CaO-Al₂O₃-MgO slags and liquid Fe were measured at 1873 K as a function of Al (or Mg, Ca) content in metal, using CaO, MgO, and Al₂O₃ crucibles. Based on the results for the solubility product of MgO, the equilibrium constant, $K_{Mg}$, for the reaction $MgO = Mg + O$ and the first-order interaction parameter, $\epsilon_{MgO}^0 (\epsilon_{Mg})$, were estimated to be $\log K_{Mg} = -7.8 \pm 0.2$ and $\epsilon_{MgO}^0 = -190 \pm 60 (\epsilon_{Mg} = -290 \pm 90)$, respectively. The activities of Al₂O₃ at the slag compositions double-saturated with CaO/MgO, MgO/Al₂O₃, and MgO·Al₂O₃/CaO·2Al₂O₃ components were obtained from the S distribution ratios between slag and metal, coupled with the reported values of sulfide capacities. Nitride capacities were also estimated from the N distribution ratios and the activities of Al₂O₃.

I. INTRODUCTION

In the production of Al-killed steel, Ca alloys are frequently used to modify alumina inclusions into liquid Ca aluminate inclusions for the purpose of improving castability during continuous casting and deformability at rolling temperature. In order to understand such a modification of inclusions, the thermodynamic relationships have been investigated using the published free energy data for the Fe-O-Ca-Al system.[1,2]

The fundamental studies on nonmetallic inclusions associated with Mg are considered to be necessary, since Mg in liquid steel, which comes from refractories or slags under strongly reducing conditions, affects the formation of inclusions in the calcium treatment of Al-killed steels.

Activities of components in CaO-Al₂O₃-MgO slags equilibrated with spinel, MgO·Al₂O₃, were thermodynamically evaluated at 1873 K by Kor.[3] Kalyanram and Bell[4] obtained activities of CaO at 1773 K in the S distribution ratios between gas and slag and estimated activities of MgO and Al₂O₃ using the Gibbs–Duhem equation. Sulfide capacities and N distribution ratios in this slag system were also measured at 1873 K by Hino et al.[5] and Wenz and Janke,[6] respectively.

The measured values for the equilibrium constant, $K_{Mg}$, for Mg deoxidation, MgO (s) = Mg + O at 1873 K (7.5 × 10⁻⁶, [7] 2.0 × 10⁻⁶ [8]), are about two orders of magnitude greater than those calculated from the thermodynamic data (2.9 × 10⁻⁹, [9] 3.09 × 10⁻⁸, [8] and 1.8 × 10⁻⁸ [10]). The reasons for this discrepancy have not been explained. There is only a reported value for the interaction parameter, $\epsilon_{MgO}^0 (\epsilon_{Mg})$, in the literature.[9]

The major objective of this research was to experimentally clarify the previously mentioned discrepancy. For this, the equilibrium constant, $K_{Mg}$, and the first-order interaction parameter, $\epsilon_{MgO}^0 (\epsilon_{Mg})$, were measured using the results of Mg and O contents in liquid Fe equilibrated with CaO-Al₂O₃-MgO slags at 1873 K. Additional objectives were (1) to estimate the activities of Al₂O₃ from the results for the S distribution ratios associated with the reported values for sulfide capacities[3] and (2) to obtain nitride capacities from the results for the N distribution ratios and activities of Al₂O₃.

II. EXPERIMENTAL

A. Procedure

A vertical resistance furnace with heating bars of LaCrO₃ was used. Twenty-five grams of high-purity electrolytic Fe starting with 500 to 1000 mass ppm O (C = 10 ppm, Ca < 1 ppm, Mg = 1 ppm, Si = 10 ppm, Al = 3 ppm) and 6 to 9 g of CaO-Al₂O₃-MgO slag were melted in CaO, MgO, and Al₂O₃ crucibles at 1873 K under deoxidized Ar flowing atmosphere. An appropriate amount of an Fe-2 (or 10) mass pct Al alloy was added from the top of the furnace by dropping. Immediately after, an appropriate amount of pure Mg metal (0.1 to 0.4 g) enclosed in a pure Fe capsule (o.d. 12 mm, i.d. 10 mm, height 10 mm) was immersed into liquid iron. Thereafter, the melts were stirred by an Al₂O₃ or MgO rod for 1 minute at 30 minute intervals. Finally, the melts were left for at least another hour without stirring for the purpose of eliminating oxide inclusions by flotation. Then, the crucible containing a sample was quenched rapidly in a He gas stream, followed by a water quenching.

Since only a very small amount of Mg dissolves into an Fe melt at 1873 K owing to high vapor pressure of Mg (approximately 19 atm), an Al-2 (or 20, 50) mass pct Mg alloy which was prepared by melting in a MgO crucible at 973 to 1073 K under deoxidized Ar flowing atmosphere was also used.

The amount of 0.05 g of a reagent grade AlN (or CaS) was mixed with master slags in the N (or S) distribution experiments.

B. Chemical Analysis

Details of chemical analysis were already described in previous reports.[11–14] The very low content of Mg and Ca in metal cannot be determined by the usual analytical method owing to the fluctuation of the blank value.

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test tube washed by HCl. Super special grade of HCl and HNO₃ and ultrapure water were used to lower and to stabilize the blank value.\textsuperscript{[13]} The analytical accuracy of the contents of Mg and Ca in metal was estimated to be 1 \( \pm \) 0.02 and 1 \( \pm \) 0.03 mass ppm, respectively.

The N content in metal and slag was analyzed within 1 \( \pm \) 0.2 mass ppm by the newly developed method of ion chromatography after extracting N as ammonia from a sample solution by the Kjeldahl method.\textsuperscript{[13]}

The O content was measured with an accuracy of 1 \( \pm \) 0.7 mass ppm by inert gas fusion-infrared absorptionmetry,\textsuperscript{[14]} using the standard sample of steel containing 3.4 mass ppm O, which was supplied by the Iron and Steel Institute of Japan, Tokyo. The S content in metal and slag was analyzed within 2 \( \pm \) 0.2 and 200 \( \pm \) 3 mass ppm, respectively, by O gas fusion-infrared absorptiometry, using the standard sample of steel containing 1.9 mass ppm S.

III. RESULTS AND DISCUSSION

The chemical compositions of slag and metal phases obtained in the N and S distribution experiments are given in Tables I and II, respectively. The slag compositions designated by marks A to D are indicated in the CaO-Al₂O₃-MgO\textsuperscript{-} phase diagram, as shown in Figure 1.

A. Time for Attainment of Equilibrium

The contents of elements in the metal phase are plotted against time in Figure 2, in which the experiments were carried out by initially adding pure Mg. The data points at 20 and 40 minutes were obtained in the experiments where the stirring was made only once immediately after the Mg addition. It can be seen that a short time is sufficient for equilibrium to be attained. The equilibration times for the present experiments using CaO, MgO, and Al₂O₃ crucibles were chosen to be 90 to 120 minutes, 120 to 180 minutes, and 180 minutes, respectively.

B. Equilibrium Relation in Metal Phase

Total O content is plotted against total Al content in logarithmic scale in Figure 3. Total Al content represents the sum of the acid-soluble and acid-insoluble Al concentrations which correspond to the dissolved Al in metal and Al-containing inclusions, respectively. It is assumed in the present study that the inclusions which were observed to be less than 1 \( \mu \)m by scanning electron microscopy were precipitated during solidification. The open circles shown in Figure 3 correspond to the results obtained in the experiments where the equilibrium of Mg was approached by adding an Fe-Al alloy, that is, the forward reaction in Eq. [1]:

\[
2/3\text{Al} + (\text{MgO}) = 1/3(\text{Al}_2\text{O}_3) + \text{Mg} \quad [1]
\]

The results expressed by other marks were obtained by adding a pure Mg or Mg-Al alloy, that is, the backward reaction in Eq. [1]. It can be seen from Figure 3 that the results approached from either side are in good agreement.

The values for the activity of Al₂O₃ were calculated from the present results of the S distribution ratio, \( L_S = \text{(mass pct S)/[mass pct S]} \), and those of sulfide capacity, \( C_S = \text{(mass pct S) \cdot P_{S_2}/P_{S_2}} \), using the equilibrium constants \( K_{\text{Al}} \), for the reaction 2/3\text{Al} + 1/2\text{O}_2 = 1/3\text{Al}_2\text{O}_3\text{,}^{[16,17]} \) and \( K_S \), for the reaction \( \text{1/2S}_2 = \text{S} \),\textsuperscript{[17]} as well as the respective interaction parameters given in Table III. The solid lines for slags A, C, and D in Figure 3 were obtained by the iterative method, using the activity of Al₂O₃, the values for \( \Delta G_S \text{[16,17]} \) for Reaction [2], and the respective interaction parameters\textsuperscript{[17]} listed in Table III.

\[
2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 (s) \quad [2]
\]

\[
\Delta G_S^0 = -1,202,000 + 386.3T \text{J/mol}^{[16,17]}
\]

The estimation of the activity of Al₂O₃ will be discussed in Section III–E.

The line for slag B was obtained by the following method: the activities of Al₂O₃ were calculated from Eq. [2], using the Al and O contents and the respective interaction parameters.\textsuperscript{[13]} Then, using the average value for activity of Al₂O₃, the line was calculated by a method similar to those used for slags A, C, and D. The experimental data points for slag A are different from the calculated line. This is not due to the error limit of the analytical method for O (1 \( \pm \) 0.7 mass ppm) but due to the fact that the values for \( e_O^A \) and \( e_O^M \) were not taken into account in the calculation.

Relations between \( \text{log [mass pct Al]} vs \text{log [mass pct Mg]} \), \( \text{log [mass pct Al]} vs \text{log [mass pct Ca]} \), and \( \text{log [mass pct Ca]} vs \text{log [mass pct Mg]} \) are shown in Figures 4 through 6, respectively. It is clear that the results obtained by N distribution experiments are in close agreement with those in S distribution experiments.

C. Equilibrium Constant of Mg
Deoxidation and Interaction Parameter

The deoxidation equilibrium for Mg is expressed in Eq. [3]:

\[
\text{MgO (s) = Mg + O} \quad [3]
\]

Using the equilibrium constant, \( K_{\text{Mg}} = a_{\text{Mg}} \cdot a_{\text{O}}/a_{\text{MgO}} \), for Reaction [3], the apparent equilibrium constant, \( K_{\text{Mg}} = [\text{mass pct Mg}] / [\text{mass pct O}] \), and the first-order interaction parameter, \( e_{\text{O}} = (\text{M_{mg}/M_o}) \cdot e_{\text{O}}^\text{Mg} \), \( M \) denotes the atomic weight of element \( i \), the following relation is derived:

\[
\text{log } K_{\text{Mg}} - \log a_{\text{MgO}} + \Sigma e_i [\text{mass pct j}] + \Sigma e_i [\text{mass pct k}] = -e_{\text{O}} [\text{mass pct Mg}] + (M_{\text{mg}}/M_o) [\text{mass pct O}] + \log K_{\text{Mg}} \quad [4]
\]