Solubility of MgO in CaO–SiO₂–MnO Slags

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1. Introduction

The control of metallurgical slag properties and optimization of slag/metal reactions in the BOF process are of prime importance in the production of high grades of steels. In practice, the BOF slags are usually multi-component, and MgO containing dolomite is charged into a converter to minimize the lining wear, which leads to formation of the BOF slag saturated with MgO. It is widely known that MgO additions have great influences on the slag refining capacity and physical properties, consequently, on the ultimate steel productivity with high demand for high-performance usage.

Manganese is one of the most important alloying elements used during the production of several steel grades because it significantly improves the mechanical properties of steels. Due to higher manganese levels required than are presently achieved in current steelmaking process, manganese ore is practiced in an oxygen steelmaking (OSM) converter to increase the Mn content in steel. Therefore, there have been growing concerns about the lime-manganese (FeMn). Also, direct addition of less expensive manganese is added to steel in ladles usually in the form of ferro-manganese (FeMn). In such experiments, MgO was brought into equilibrium with molten copper in a MgO crucible. The activity of MnO in slags was determined by measuring Mn and temperature on MgO solubility were investigated using MgO. In the present study, the effects of slag composition on MgO solubility elucidating the slag refining behavior of Mn oxide. In such experiments, MgO crucibles are usually used as vessels to hold the metallurgical slags, whose compositions are ultimately saturated with MgO. In the present study, the effects of slag composition and temperature on MgO solubility were investigated using the experimental data produced in the measurement of Mn oxide activity in the simplest lime-based slags containing MnO, CaO–SiO₂–MnO slags. And it was attempted to derive a correlation between the MgO solubility and optical basicity.

2. Experimental

2.1. Experimental Procedure

A SiC-resistor furnace with a mullite tube (72 mm-OD, 66 mm-ID, and 1000 mm-length) were used in the experiments as shown in Fig. 1. A Pt–Pt/13 pct Rh thermocouple mounted outside the mullite tube was employed to measure the temperature, which was controlled within the range of ±2 K using a PID controller. The oxygen partial pressure was controlled by a CO/CO₂ gas mixture using a gas mixing pump (Woestoff GmbH, 5M201/a-F), and CO and CO₂ were dried by H₂SO₄ and silica gel in advance. The mixing gas was blown onto the MgO crucible containing 5 g of Cu and 10 g of slag powder through alumina lance in the temperature range of 1 623 to 1 723 K. A preliminary experiment indicated 12 h was required for the equilibrium to be reached. Then the crucible was quickly withdrawn from the furnace and rapidly quenched in an Ar gas stream. The metallic copper which had separated from the slag and the slag sample were collected for the chemical analyses.

2.2. Measurement of the MnO Activity

A slag containing manganese oxide was brought into equilibrium with molten copper in a MgO crucible. The activity of MnO in slags was determined by measuring Mn content in Cu in equilibrium with the slags in a CO/CO₂ gas mixture. This equilibrium is represented by Eq. (1):

$$\text{Mn} (l) + \text{CO}_2 (g) = \text{MnO} (s) + \text{CO} (g)$$

$$\Delta G^\circ = -125 600 + 2.607 (\mu \text{mol})^3$$

With knowledge of the activity coefficient of manganese oxides in copper, the activity of MnO, $a_{\text{MnO}}$, is calculated by Eq. (3) using the equilibrium constant of Eq. (1), $K_t$.

$$a_{\text{MnO}} = \gamma_{\text{MnO}} \cdot X_{\text{MnO}} \cdot (\text{P}_{\text{CO}}/\text{P}_{\text{CO}_2}) \cdot K_t$$

where $\gamma_{\text{MnO}}$ and $X_{\text{MnO}}$ are the activity coefficient and mole fraction of Mn in Cu, respectively.

3. Results and Discussion

3.1. Effect of Slag Composition on MgO Solubility

Figures 2 and 3 show the effect of slag composition on MgO solubility. In Fig. 2, the MgO solubility decreases from 14 to 2.6 mass% as the slag basicity, (mass%CaO)/(mass%SiO₂), increases. It also decreases from 9.7 to 6.5 mass% as the MnO content increases from 8 to 36 mass% with the slag basicity maintained at 0.9 in Fig. 3, this can be explained by Eqs. (4) to (7). In particular, the MgO solubility is inversely proportional to the activity of O²⁻, slag basicity, as shown in Eq. (7) assuming that the
The results also indicate that the degree of decreasing MgO solubility caused by increasing MnO is considerably smaller than that by increasing slag basicity. This indirectly shows that the CaO-equivalent of MnO is lower than that of MgO, which can be explained by the relative basicity of oxides in terms of optical basicity.

\[ \text{MgO} = \text{Mg}^{2+} + \text{O}^2^- \] (4)
\[ K_{\text{Mg}^{2+}} = \frac{a_{\text{Mg}^{2+}} \cdot a_{\text{O}^2^-}}{a_{\text{MgO}}} \] (5)
\[ (\% \text{Mg}^{2+}) = a_{\text{MgO}} \cdot \frac{K_{\text{Mg}^{2+}}}{f_{\text{Mg}^{2+}} \cdot a_{\text{O}^2^-}} \] (6)
\[ (\% \text{MgO}) = a_{\text{MgO}} \cdot \frac{K_{\text{Mg}^{2+}}}{f_{\text{Mg}^{2+}} \cdot a_{\text{O}^2^-}} \cdot \frac{M_{\text{MgO}}}{M_{\text{Mg}}} \] (7)

A solubility limit of a component in a slag system is influenced by the actual saturation phase. For the basic lime-based slags examined in this study, highly dense and electrically sintered MgO crucibles were used forming a solid solution of MnO in MgO at the slag/crucible interface. Accordingly, the solubility of MgO is limited by the saturation of the slag with (Mg, Mn)O solid solution and it is related to the activity of MgO by Eq. (7). In Eq. (7), the activity of MgO can be described as a function of the MnO activity using the Gibbs–Duhem equation or by assuming the (Mg, Mn)O solid solution to be an ideal solution at the temperatures investigated in this study.

In the present work, MgO solubilities were measured for the slag composition of MnO (8 to 36 mass%) with a slag basicity of 0.9 at an oxygen partial pressure of $5.1 \times 10^{-9}$ atm. As shown in Fig. 5, the MgO solubility increases from 5 to 11 mass% as the temperature increases from 1623 to 1723 K, and their temperature dependence can be formulated by Eq. (8):
The relation between the logarithm of the MgO solubility and optical basicity is similar to that for steelmaking slags by Bergman. The MgO solubility values in the present study are lower than those estimated for steelmaking slags at the same optical basicities. The reason behind is that the MgO solubility were measured at lower temperatures for the present slags containing no iron oxide, and this has a major influence on the MgO solubility in steelmaking slags.

3.3. Correlation of MgO Solubility with Optical Basicity

The concept of the optical basicity was introduced and applied to metallurgy by Duffy et al. The values of optical basicities for the pure oxides are directly correlated with the Pauling electronegativity and the equivalent fraction of basicities for the pure oxides.9) In Table 1, the relative basicity of oxides based on the optical basicity concept. In addition, the temperature dependence of the MgO solubility was obtained. The relationship between the logarithm of the MgO solubility and optical basicity was empirically formulated and compared to those of the values obtained from basic steelmaking slags. This study confirms that the optical basicity can be applied to estimate the MgO solubility in the metallurgical slags, which may enhance the slag properties control in attempts to achieve higher productivity of steel grades.

**REFERENCES**