The effect of Fe_2O_3 Content on MgO Solubilities in Lime-based Slags

Sung-Mo JUNG¹⁾ and Dong-Joon MIN²⁾

1) Graduate Institute of Ferrous Technology, POSTECH, Pohang 790-784 Korea.

2) Department of Metallurgical Engineering, Yonsei University, Seoul 120-749 Korea.

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It was attempted to quantitatively elucidate the effect of Fe_2O_3 content on MgO solubilities in lime-based slags using the measured data of MgO solubility in the slags. The magnesia capacities of the lime-based liquid slags were nicely correlated with the optical basicities in case the ideal solution was assumed for the magnesiowustite saturation phase which is actually in equilibrium with the slags. The substitution of MgO for CaO in lime-based slags increased the activity coefficient of Fe_2O_3 for the constant activity of Fe_2O_3 , resulting in decreasing Fe_2O_3 content in the slags. It is believed that the Fe_2O_3 activities in metallurgical slags containing iron oxide play the decisive role in determining the MgO solubilities into the slags.

KEY WORDS: MgO solubility; magnesia capacity; optical basicity; activity; activity coefficient; interaction coefficient.

1. Introduction

A growing emphasis has been placed on improving steel-making processes for the production of ultra clean steels. The proper control of metallurgical slag properties and optimization of slag/metal reactions in Basic Oxygen Furnace (BOF) process are of great importance in the production of high grades of steels. BOF slags are usually multi-component, and are ultimately saturated with MgO because dolomite is charged into a converter to minimize the lining wear. It has been also 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.^{1,2)}

Several investigations have been carried out to find out

the solubility limit of MgO in lime-based slags containing iron oxide as shown in **Table 1**. The research about MgO solubility was initiated by Trömel *et al.*³⁾ in the 1960's. They found out that the $(\text{Fe}, \text{Mg})\text{O}$ phase was formed in the interface between liquid slag and the MgO crucible and they measured the iso- MgO solubility curves. Then, Shim and Ban-ya⁴⁾ reported that the MgO solubility limit decreases with increasing Fe_2O_3 content and slag basicity. Schürmann and Kolm⁵⁾ developed the numerical equations to describe the MgO contents of the magnesiowustite saturation surface in the pure quaternary system $\text{MgO}-\text{Fe}_2\text{O}_3-\text{CaO}-\text{SiO}_2$ at 1 600°C. Bergman⁶⁾ attempted to correlate the solubility of MgO in complex slags in equilibrium with magnesiowustite with the activity of MgO in the magnesiowustite phase. And Bergman⁶⁾ also described the magne-

Table 1. The experimental conditions of several investigations having dealt with MgO solubilities in metallurgical slags.

Authors	Slag systems	Temp(°C)	Remarks	References
Trömel <i>et al.</i>	$\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{MgO}$	1600	Slag-metal equilibrium	3)
Shim and Ban-ya	$\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{CaO}-\text{MgO}$	1600	Slag-metal equilibrium in MgO crucible	4)
Schürmann and Kolm	$\text{Fe}_2\text{O}_3-\text{MgO}-\text{CaO}-\text{SiO}_2$	1600	Slag-gas equilibrium	5)
Bergman	$\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{MgO}$	1600	To define magnesia capacity	6)
Jung <i>et al.</i>	$\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{MnO}-\text{MgO}$	1450	Slag-metal equilibrium in MgO crucible	7)
Jung	$\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{MnO}-\text{MgO}$ saturated with $2\text{CaO}-\text{SiO}_2$ and MgO	1600	Slag-metal equilibrium in MgO crucible	8)
Jung <i>et al.</i>	$\text{CaO}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{MnO}-\text{MgO}$ saturated with CaO and MgO	1600	Slag-metal equilibrium in MgO crucible	9)

sia capacity of liquid slag in terms of the slag's optical basicity. Jung and his coworkers examined the effects of slag composition and temperature on MgO solubilities using the data produced from the research topics about the thermodynamic behaviors of Mn oxide in several metallurgical slag systems.⁷⁻⁹⁾

Recently, the concept of optical basicity has taken significant interest and it has been applied to several metallurgical parameters. And it has been found to be an excellent measure by applying it to capacities of metallurgical data in previous works.¹⁰⁻¹²⁾ Therefore, it was considered that the slag's magnesia capacity could be correlated with the optical basicity in order to give a succinct description of the MgO solubility in the relevant slag systems. In particular, it is still unclear how the Fe₂O content in liquid slags thermodynamically affects the MgO solubility. As previously mentioned, it is well known that magnesiowustite, a solid solution of FeO in MgO, is formed at the slag/MgO crucible interface.³⁾ That is, the actual saturation phase in equilibrium with steelmaking slags is the magnesiowustite, (Fe₂O, MgO) as shown in Fig. 1. In the present study, the attempts were also made to quantitatively elucidate the effect of iron oxide on the MgO solubility in the lime-based slags in terms of the interaction coefficients of Fe₂O and MgO.

2. Theoretical Background

2.1. MgO Solubility Limit

The solubility limit of a component in a liquid slag is determined by the actual saturation phase. The dissolution reaction of MgO into liquid slag can be described by Eq. (1) and the equilibrium constant of reaction (1) can be expressed by Eq. (2) where the activity of MgO in magnesiowustite is with respect to pure solid MgO. As shown in Eq. (4), the MgO solubility in liquid slags is strongly affected by the MgO activity in magnesiowustite which is actual saturation phase and the activity of O²⁻, slag basicity. In other words, the MgO solubility limit can be inversely proportional to the O²⁻ activity, slag basicity, for some fixed value of MgO activity in magnesiowustite assuming that the equilibrium constant of Eq. (1), $K_{Mg^{2+}}$, and the activity coefficients of Mg²⁺, $f_{Mg^{2+}}$ are constant in the slag compositions investigated:

$$MgO_{\text{magnesiowustite}} = (Mg^{2+})_{\text{slag}} + (O^{2-})_{\text{slag}} \dots\dots\dots(1)$$

$$K_{Mg^{2+}} = \frac{a_{Mg^{2+}} \cdot a_{O^{2-}}}{a_{MgO}} \dots\dots\dots(2)$$

$$(\text{mass\% Mg}^{2+}) = a_{MgO} \cdot \frac{K_{Mg^{2+}}}{f_{Mg^{2+}} \cdot a_{O^{2-}}} \dots\dots\dots(3)$$

Fig. 1. Schematic diagram of slag/metal reaction in BOF process and the magnesiowustite saturation phase formed at slag/refractory interface.³⁾

$$\begin{aligned} (\text{mass\% MgO}) &= (\text{mass\% Mg}^{2+}) \cdot \frac{MW_{MgO}}{MW_{Mg}} \\ &= a_{MgO} \cdot \frac{K_{Mg^{2+}}}{f_{Mg^{2+}} \cdot a_{O^{2-}}} \cdot \frac{MW_{MgO}}{MW_{Mg}} \dots\dots\dots(4) \end{aligned}$$

where MW_i is the molecular weight of component i .

2.2. Measurement of Fe₂O Activity

As previously described, the MgO solubility in liquid slag is significantly affected by the MgO activity in magnesiowustite, which is dominated by the Fe₂O activity in the saturation phase. Thus, the information about the Fe₂O activity in magnesiowustite is of great importance because the Fe₂O activity in magnesiowustite and liquid slag is identical in case the magnesiowustite is the actual saturation phase in equilibrium with liquid slag. The current authors have previously investigated the thermodynamic behaviors of manganese oxide in the CaO-SiO₂-Fe₂O-Al₂O₃-MnO-MgO_{sat}¹³⁾ by equilibrating the liquid slag with liquid silver and solid iron in a MgO crucible. And they also did the similar research for CaO-SiO₂-Fe₂O-MnO¹⁴⁾ slags in equilibrium with liquid silver in a Fe crucible. In those studies, the Fe₂O activity in the slags in equilibrium with solid Fe were determined by Eq. (5).

$$\Delta G_5^\circ = 263440 - 208.0T \quad (\text{J/mol})^{15)} \dots\dots\dots(6)$$

The activity of Fe₂O, a_{Fe_2O} , is calculated by Eq. (7) using the equilibrium constant of Eq. (5), K_5 because the activity of solid Fe is unity in the experimental temperatures investigated. The activity of Fe₂O is with respect to pure liquid iron oxide in equilibrium with pure δ iron in Eq. (7). As can be expected from Eq. (7), the activity of Fe₂O will increase with increasing the partial pressure ratio of CO₂ to CO, that is, with increasing the oxygen partial pressure in the current system.

$$a_{Fe_2O} = (p_{CO_2} / p_{CO}) \cdot K_5 \dots\dots\dots(7)$$

3. Results and Discussion

3.1. Correlation of Magnesia Capacity with Optical Basicity

According to Richardson and Fincham's proposal,¹⁶⁾ the sulphide capacity was defined to be a measurement of the capacity of a slag to hold sulfur and it was reasonably correlated with optical basicity of the slag. The optical basicity concept was first introduced and applied to metallurgy by Duffy *et al.*¹⁷⁾ The values of optical basicities for the pure oxides are directly correlated with the Pauling electronegativity and the equivalent fraction of components and are listed in Table 2.¹⁸⁾ In Table 1, the relative basicity of CaO, MgO and MnO are compared in order. Based on the optical

Table 2. Theoretical optical basicities from Pauling electronegativity of pure oxides.¹⁸⁾

Oxide	CaO	SiO ₂	Fe ₂ O	Al ₂ O ₃	MgO	MnO	P ₂ O ₅
Optical basicity	1.0	0.48	0.51	0.61	0.78	0.59	0.40

Fig. 2. Logarithms of the magnesia capacities derived from Eq. (9) as a function of the optical basicity of the steelmaking slags. Experimental data from Jung *et al.*⁷⁾ (a) using the MgO activity by Hahn and Muan,¹⁹⁾ (b) using the MgO activity by Sakawa *et al.*²⁰⁾ (c) using the MgO activity by ideal solution assumption.

Fig. 3. Saturation solubilities of MgO in liquid slags, in equilibrium with magnesio-wustite, calculated from slag composition and oxygen partial pressure as compared to the experimental data from Jung *et al.*⁷⁾ (a) using the MgO activity by Hahn and Muan,¹⁹⁾ (b) using the MgO activity by Sakawa *et al.*²⁰⁾ (c) using the MgO activity by ideal solution assumption.

basicities in Table 1, it is possible to calculate the optical basicity, Λ , for metallurgical slags of any composition involving these oxides by Eq. (8):

$$\Lambda = \sum X_i \Lambda_i \quad \text{.....(8)}$$

where Λ_i is the optical basicity of the pure oxide and X_i is the equivalent cation fraction, *i.e.* the molar fractions of cations multiplied by the number of oxygens in the respective component.

From MgO dissolution into slag, the slag ability to retain Mg^{2+} was defined as magnesia capacity, for the MgO activity in magnesio-wustite as represented by Eq. (9).⁶⁾ The magnesio-wustite is formed at slag/crucible interface and the MgO solubility in liquid slag is ultimately limited by (Fe_7O , MgO) solid solution which is a kind of intermediate phase formed in the interface.

$$C_{Mg^{2+}} = \frac{(\text{mass}\% \text{Mg}^{2+})}{a_{MgO}} = \frac{K_{Mg^{2+}}}{f_{Mg^{2+}} \cdot a_{O^{2-}}} \quad \text{.....(9)}$$

As can be seen in Eq. (9), the magnesia capacity is evaluated by the MgO activity in magnesio-wustite and the MgO content in liquid slag. Thus, one should consider the method of obtaining the activity value of MgO in magnesio-wustite. Hahn and Muan¹⁹⁾ reported the relationship represented by Eq. (10) by plotting a_{MgO} against a_{FeO} using the activities of FeO and MgO in magnesio-wustite at 1100 and 1300°C. And Sakawa *et al.*²⁰⁾ calculated the activity of

MgO by using the Gibbs–Duhem equation and found that the activity of MgO in the range was expressed by Eq. (11). Additionally, the ideal solution assumption for magnesio-wustite was adopted in the current study as shown in Eq. (12).

$$a_{MgO} = 1 - 0.224 \cdot a_{FeO} - 0.467 \cdot a_{FeO}^2 \quad \text{.....(10)}$$

$$a_{MgO} = 1 - 0.73 \cdot a_{FeO}^{20)} \quad \text{.....(11)}$$

$$a_{MgO} = 1 - a_{FeO} \quad \text{.....(12)}$$

Using the three different relationships between the activities of MgO and Fe_7O , the relations between magnesia capacity and optical basicity of the experimental data employed were derived. Starting with the result of Hahn and Muan¹⁹⁾ to that by ideal solution, it was noticed that the linearity of the regression line improved toward that by ideal solution as shown in Fig. 2. And the relations between magnesia capacity and optical basicity were then tested by plotting the calculated values of MgO solubility against the experimental values. Similarly, the linearity of the regression line was enhanced toward that by the ideal solution assumption for magnesio-wustite in Fig. 3. Therefore, it was confirmed that the ideal solution assumption for $MgO-Fe_7O$ solid solution is reasonably convincing in dealing with the evaluation of the MgO activity for MgO dissolution into slags.

Fig. 4. Relationship between Fe_2O_3 concentration and oxygen partial pressure in $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-MnO}$ slag and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MnO-MgO}_{\text{sat}}$ slag equilibrated with solid Fe.

3.2. Effect of MgO Substitution for CaO on Fe_2O_3 Activity

The current authors have previously investigated the thermodynamic behaviors of manganese oxide in the $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-MnO-MgO}_{\text{sat}}$ ¹³⁾ and $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-MnO}$ ¹⁴⁾ slags. As shown in Fig. 4, the Fe_2O_3 content in $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-MnO-MgO}_{\text{sat}}$ slags is smaller than that in the $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-MnO}$ slags at the identical oxygen partial pressure. It is believed that this results from the effect of MgO on the activity coefficient of Fe_2O_3 . That is, the activity of Fe_2O_3 is constant at some oxygen partial pressure by Eq. (7). This means that the activity coefficient of Fe_2O_3 increases with substituting MgO for CaO for the constant activity of Fe_2O_3 as indicated by Eq. (13):

$$a_{\text{Fe}_2\text{O}_3} = \gamma_{\text{Fe}_2\text{O}_3} \cdot X_{\text{Fe}_2\text{O}_3} \quad (13)$$

$$\frac{\partial \ln \gamma_{\text{Fe}_2\text{O}_3}}{\partial X_{\text{MgO}}} = \epsilon_{\text{Fe}_2\text{O}_3}^{\text{MgO}} \quad (14)$$

where X_i indicates the mole fraction of component i in slag, and a_i and γ_i represent the activity and activity coefficient of component i with respect to Raoultian standard state, respectively. The effect of MgO on activity coefficient of Fe_2O_3 can be expressed by the interaction coefficient of MgO on Fe_2O_3 as shown in Eq. (14), which is positive in this case. That is, increasing MgO content in slag could enhance the activity coefficient of Fe_2O_3 , resulting in decreasing Fe_2O_3 content for the constant activity of Fe_2O_3 . The current result is compared with the previous research findings by Shim and Ban-ya.⁴⁾ They reported that the Fe_2O_3 activity in $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ slags showed larger values than those in $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-MgO}$ slags and that the activity of Fe_2O_3 increased with substituting MgO for CaO in $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-MgO}$ slags. The results can be understood as follows. The substitution of MgO for CaO in lime-based slags will actually increase the activity coefficient of Fe_2O_3 more significantly compared with the less enhancement of Fe_2O_3 activity, resulting in decreasing Fe_2O_3 content in the slags.

Fig. 5. Comparison of Fe_2O_3 activities among Fe_2O_3 -containing slags doubly saturated with $2\text{CaO} \cdot \text{SiO}_2$ and MgO, CaO and MgO and saturated with CaO at 1600°C.

3.3. Effect of Fe_2O_3 Content on MgO Solubility

As previously reported,^{8,9)} the Fe_2O_3 activities were measured along the slag compositions doubly saturated with $2\text{CaO} \cdot \text{SiO}_2$ and MgO, and CaO and MgO, respectively. As can be seen in Fig. 5, the Fe_2O_3 activities almost remain unchanged and the values are about 0.3 on average in the Fe_2O_3 concentration investigated, and the MgO activities can be calculated to be about 0.7 in case the ideal solution assumption was applied to magnesiowustite solid solution, (Fe_2O_3 , MgO). That is, as the Fe_2O_3 content in liquid slags increases, the Fe_2O_3 activities in the slags are constant, which are equivalent to those in the magnesiowustite phase. Similarly, the MgO activities in the saturation phase and in liquid slag are the same and constant. As previously demonstrated, because the interaction coefficient of MgO on Fe_2O_3 is positive as shown in Eq. (14), the interaction coefficient of Fe_2O_3 on MgO is also positive by Eq. (15). That is, the activity coefficient of MgO in the slags will increase with increasing Fe_2O_3 content, resulting in decreasing MgO content in the slags for almost constant activities of MgO by Eq. (16).

$$\frac{\partial \ln \gamma_{\text{MgO}}}{\partial X_{\text{Fe}_2\text{O}_3}} = \epsilon_{\text{MgO}}^{\text{Fe}_2\text{O}_3} = \epsilon_{\text{Fe}_2\text{O}_3}^{\text{MgO}} \quad (15)$$

$$a_{\text{MgO}} = \gamma_{\text{MgO}} \cdot X_{\text{MgO}} \quad (16)$$

The understandings obtained by Eqs. (15) and (16) can be confirmed by the previous experimental data reported by Trömel *et al.*³⁾ That is, the MgO solubility decreases with increasing Fe_2O_3 content in $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3\text{-MgO}$ slag system at 1600°C as shown in Fig. 6. The change of MgO solubility affected by Fe_2O_3 content reported to date can quantitatively be explained based on the findings and thermodynamic relations obtained in this work. Therefore, it is believed that the Fe_2O_3 activity should precisely be controlled in metallurgical slags containing iron oxide because it plays the decisive role in dominating the MgO solubility into the slags.

Fig. 6. Central projection of the magnesiowustite saturation surface on the base system $\text{CaO-SiO}_2\text{-FeO}$. The dashed lines indicate the solubility limit of MgO in the liquid slag in mass%.²²⁾

4. Conclusions

The experimental results previously obtained were analyzed in terms of the MgO solubility and the following conclusions were obtained from the findings:

(1) It was confirmed that the ideal solution assumption for $\text{Fe}_2\text{O}_3\text{-MgO}$ solid solution is reasonably convincing in dealing with MgO dissolution into slags.

(2) The activity coefficient of Fe_2O_3 increases with substituting MgO for CaO for the constant activity of Fe_2O_3 .

(3) The MgO content in metallurgical slags containing iron oxide decreases with increasing Fe_2O_3 concentration for almost constant activities of MgO because the interaction coefficient of Fe_2O_3 on MgO is positive.

(4) It was quantitatively clarified that the Fe_2O_3 activities in the metallurgical slags have the greatest influence on the MgO solubility.

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