The Effect of Na$_2$O and Al$_2$O$_3$ on Dephosphorization of Molten Steel by High Basicity MgO Saturated CaO–FeO$_x$–SiO$_2$ Slag

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Highly basic CaO based slags saturated with MgO have been studied with respect to the phosphate capacity by measuring the phosphorous distribution ratio between slag and metal under controlled oxygen partial pressure at 1 823 K and 1 873 K. The effect of Na$_2$O and Al$_2$O$_3$ addition and the activity of FeO and FeO$_{1.5}$ were also determined. The phosphate capacity for MgO saturated CaO–FeO$_x$–SiO$_2$ slag containing 0 to 5 mass% Al$_2$O$_3$ and 0 to 1.75 mass% Na$_2$O at 1 873 K are in the range of 10$^{18.37}$ to 10$^{19.00}$ and that containing 4.1 to 5.0 mass% Al$_2$O$_3$ and 0 to 2.37 mass% Na$_2$O at 1 823 K are in the range of 10$^{18.63}$ to 10$^{18.62}$.

For the slags containing 21.28 to 23.59 mass% Al$_2$O$_3$ and 0 to 4.25 mass% Na$_2$O at 1 823 K are in the range of 10$^{18.53}$ to 10$^{18.62}$. The addition of Na$_2$O to the MgO saturated CaO–FeO$_x$–SiO$_2$ system increases the phosphate capacity of the slags. Alumina in the MgO saturated CaO–FeO$_x$–SiO$_2$ system decreases the phosphate capacity of the slags. The activity coefficients of FeO and FeO$_{1.5}$ show that they all behave as an acidic oxide in MgO saturated CaO–FeO$_x$–SiO$_2$ system.

KEY WORDS: steelmaking; thermodynamics; phosphorus; MgO solubility; slag; MgO$_{satd.}$–CaO–FeO$_x$–SiO$_2$–Al$_2$O$_3$–Na$_2$O system; phosphate capacity.

1. Introduction

There is an increasing demand for lower phosphorus steels. Hot metal dephosphorization is commonly applied in Japan and some special processes were proposed for high efficiency dephosphorization of molten steel in order to minimize the amount of steelmaking slags, for example, the Zero Slag Process developed by NKK Corporation$^1$ and the MURC process developed by Nippon Steel Corporation$^2$. On the other hand, ladle dephosphorization is also an alternative to obtain lower phosphorus steels by using special fluxes. Usually calcium fluoride has been commonly added into steelmaking slags to increase the solubility of CaO and to improve the kinetics of desulfurization and dephosphorization. Considering the toxicity of fluorides to the health of human being, developing a dephosphorization process with CaF$_2$-free slags is becoming an urgent demand. So it is necessary to clarify the influences of another additives to the dephosphorization reaction between metal and slags.

For dephosphorization process without CaF$_2$ addition, Al$_2$O$_3$, Na$_2$O, MnO, MgO etc. are added into CaO base slags with high basicity and high FeO to decrease the melting temperature, increase fluidity, and improve the dephosphorization ability of the slags. Usui et al.$^3$ studied the phosphorization of molten steel with CaO–Na$_2$O–SiO$_2$–FeO$_x$ slag at 1 873 K in a MgO crucible under Ar atmosphere. Miyata et al.$^4$ reported the results of hot metal dephosphorization with CaO–SiO$_2$–Al$_2$O$_3$–FeO$_x$. It was found that the addition of small amount alumina can improve the fluidity of high CaO/SiO$_2$ slags and increase phosphorus partition ratio. In the case of CaO/SiO$_2$ (in mass%)=1.9 with 5% Al$_2$O$_3$ addition, an apparent phosphorus partition ratio of 310 and dephosphorization rate of 91% were obtained. Muraki et al.$^5$ measured the phosphorus partition ratio for the CaO–Na$_2$O–SiO$_2$–CaF$_2$ slag doubly saturated with CaO and 3CaO·SiO$_2$ at 1 573 K. They reported that the phosphorus partition ratio increases with increasing Na$_2$O content. The effect of Na$_2$O on dephosphorization is significantly large and phosphorus partition ratio increases ten-fold for an addition of only 2 mass% Na$_2$O. Park and Fruehan$^6$ reported that the phosphorus partition ratio increased 300 times when 3 mass% Na$_2$O were added into 50%CaO–40%Al$_2$O$_3$–10%SiO$_2$ slag in a graphite crucible at 1 873 K under CO atmosphere. In case of processing in an ladle with basic refractory, such as MgO, dolomite, the ladle slag would be saturated with MgO. Suito et al.$^7$ studied the phosphorus distribution between liquid iron and MgO saturated slag of the CaO–MgO–FeO$_x$–SiO$_2$ system at 1 873 and 1 823 K. They also investigated the effects of Na$_2$O addition (7 to 13 mass%) on phosphorus distribution between CaO–MgO–FeO$_x$–SiO$_2$ slags and liquid iron.$^8$ Kimura et al.$^9$ studied the activity of Na$_2$O in the
CaO–CaF$_2$–SiO$_2$ system doubly saturated with CaO and 3CaO·SiO$_2$ at 1 423 to 1 623 K. The relationship between the activity of Na$_2$O in both CaO–CaF$_2$–SiO$_2$ system and Na$_2$O–SiO$_2$ system was determined. Kimura et al.\textsuperscript{10} measured the phosphorus partition ratio between CaO–K$_2$O–CaF$_2$–SiO$_2$ slags and carbon saturated iron and discussed the effects of Na$_2$O, BaO and K$_2$O addition to the CaO–CaF$_2$–SiO$_2$ system saturated with CaO and 3CaO·SiO$_2$ on phosphorus partition ratio at 1 573 K. The enhancement of phosphorus partition ratio by the addition of Na$_2$O, BaO\textsuperscript{10} and K$_2$O was in the order K$_2$O, Na$_2$O and BaO.

Ishii and Fruehan\textsuperscript{12} investigated the dephosphorization equilibria between liquid iron and highly basic CaO-based slags saturated with MgO at 1 873 and 1 843 K. However, the influence of Na$_2$O on the dephosphorization of high basicity MgO saturated CaO–SiO$_2$–FeO$_2$ slags has not been reported. Due to the importance of sodium oxide on dephosphorization reaction in steelmaking process, the phosphorus partition ratio between MgO saturated highly basic CaO–SiO$_2$–FeO$_2$ slags and liquid steel has been measured in the present study. The effect of Al$_2$O$_3$ in this system on phosphorus removal was also investigated.

2. Experimental

The chemical equilibration technique was employed in the present study. The experiments were carried out in an electric resistance furnace with MoSi$_2$ heating elements and a mullite reaction tube. Eight grams of electrolytic iron containing 0.0001 mass% P and 6 g of MgO–CaO–FeO$_2$–Al$_2$O$_3$–SiO$_2$ mullite reaction tube. Eight grams of electrolytic iron were dipped into slag for CaO saturation and remained undisolved. CaO pellets were confirmed after experiments. The MgO concentration in CaO–SiO$_2$–FeO$_2$–Al$_2$O$_3$–SiO$_2$ slags was determined by ICP-AES spectrometry. FeO content in slags was determined by titration and gravimetry was applied for SiO$_2$ analysis. Fe$^{3+}$ content was obtained from total Fe and Fe$^{2+}$ contents.

3. Results and Discussion

All experimental results were listed in Tables 1 and 2, including slag compositions for the MgO saturated CaO–SiO$_2$–FeO$_2$–Al$_2$O$_3$–Na$_2$O, MgO saturated CaO–SiO$_2$–FeO$_2$–Al$_2$O$_3$–Na$_2$O systems and metal. The slag compositions are also shown in the pseudo-ternary diagram (CaO+MgO+Na$_2$O)–SiO$_2$–Al$_2$O$_3$–FeO$_2$ in Fig. 1 together with the liquidus of CaO–SiO$_2$–FeO$_2$ system after Muan et al.\textsuperscript{14} and the liquidus of CaO–Al$_2$O$_3$–FeO$_2$ system at 1 873 K.

3.1. MgO Solubilities in the CaO–SiO$_2$–FeO$_2$–Al$_2$O$_3$–Na$_2$O and CaO–SiO$_2$–FeO$_2$–Na$_2$O Systems

The MgO concentration in CaO–SiO$_2$–FeO$_2$ based slags was plotted against the ratio of [(mass%CaO)/(mass%Na$_2$O)]/[mass%SiO$_2$] + [mass%Al$_2$O$_3$] + [mass%P$_2$O$_5$] which presents the basicity of slags in Fig. 2. The results obtained by Shim and Ban-ya\textsuperscript{15}, Suito et al.\textsuperscript{7,8} and Ishii and Fruehan\textsuperscript{12} were also shown in this figure. It can be seen that the solubility of MgO in CaO–SiO$_2$–FeO$_2$ systems obtained by different authors are in good agreement with each other. The MgO content decreases when the basicity of slags increases. It also decreases with the increasing of FeO content. When the [(mass%CaO)/(mass%Na$_2$O)]/[mass%SiO$_2$] + [mass%Al$_2$O$_3$] + [mass%P$_2$O$_5$] ratio is larger than 2, the MgO solubility of slag does not change much. The influence of Al$_2$O$_3$ content to the MgO solubility was shown in Fig. 3 comparing with the observed data of Ishii and Fruehan.\textsuperscript{12} The MgO solubility increases with increasing of Al$_2$O$_3$ content. The present data agree reasonably well with those of Ishii and Fruehan\textsuperscript{12} at 1 873 K. The high MgO solubilities for the slags with 21.28 to 23.59 mass% Al$_2$O$_3$ kept at 1 823 K for 18 h in present work are considered to be caused by relatively higher Na$_2$O and lower FeO$_2$ contents in these slags as indicated in Fig. 3.

3.2. Phosphate Capacities of the MgO Saturated CaO–SiO$_2$–FeO$_2$–Al$_2$O$_3$–Na$_2$O and CaO–SiO$_2$–FeO$_2$–Na$_2$O Systems

Dephosphorization of steel by a metal–slag reaction can be expressed by Eq. (3)
where _ and ( ) denote the component in metal and slag, respectively. According to reaction (4), the ability of a slag to contain phosphorus as a phosphate ion is defined by the phosphate capacity as expressed by Eq. (5).

\[
P + \frac{5}{2} O + \frac{3}{2} (O^{2-}) = (PO_{4}^{3-}) \quad \text{-------------------(3)}
\]

where _ and ( ) denote the component in metal and slag, respectively. According to reaction (4), the ability of a slag to contain phosphorus as a phosphate ion is defined by the phosphate capacity as expressed by Eq. (5).

\[
\frac{1}{2} P_{2}(g) + \frac{5}{4} O_{2}(g) + \frac{3}{2} O^{2-} = PO_{4}^{3-} \quad \text{-----------(4)}
\]

\[
C_{PO_{4}^{3-}} = \frac{\text{(mass\%PO}_{4}^{3-})}{P^{0.5},PO_{4}^{3-}} = K_{4} a_{PO_{4}^{3-}}^{1/2} \quad \text{-----------(5)}
\]

where \( a_{PO_{4}^{3-}}, P_{r}, f_{PO_{4}^{2-}} \) and \( K_{4} \) are the activity of oxide ion, partial pressure of \( P_{r} \), activity coefficient of \( PO_{4}^{3-} \), and equilibrium constant of Eq. (4), respectively.
The phosphate capacity was calculated from the PO$_4^{3-}$/H$_2$O content in slag. Oxygen partial pressure was controlled by reaction (1) in the system. Partial pressure of phosphorus can be calculated from the phosphorus content of iron using Eqs. (6) and (7) assuming Henry’s law.

$$\Delta G^0 = -157700 + 5.4T \text{ J/mol}^{(6)} \quad (7)$$

In the present study, the oxygen partial pressure was controlled by CO/CO$_2$ equilibrium. On the other hand, since the oxygen contents of iron were determined, the oxygen partial pressures were calculated by using Eqs. (8) to (12). The oxygen partial pressures calculated from CO/CO$_2$ ratio were compared with those obtained from oxygen contents in metal and both are in good agreement.

$$\Delta G^0 = -117110 - 3.39T \text{ J/mol}^{(7)} \quad (9)$$

$$\log fO = eO^0 [\text{mass%O}] + eO^p [\text{mass%P}] \quad (10)$$

$$eO^0 = \frac{1750}{T} + 0.76^{(8)} \quad (11)$$

$$eO^p = 0.07^{(7)} \quad (12)$$

Phosphorus partition ratio of the MgO saturated CaO–FeO$_x$–SiO$_2$–Al$_2$O$_3$–Na$_2$O systems are shown in Fig. 4. The results obtained by Suito and Inoue$^8$ in CaO–FeO$_x$–SiO$_2$–Na$_2$O systems at 1 823 K were also plotted in this figure. The experimental data are separated into several groups depending on the slag compositions. Generally the phosphorus partition ratio between MgO saturated CaO–FeO$_x$–SiO$_2$–Al$_2$O$_3$ slag and liquid iron increases with increasing ratio \((\text{mass%CaO})/\text{mass%Na}_2\text{O})/\text{mass%SiO}_2/\text{mass%Al}_2\text{O}_3/\text{mass%P}_2\text{O}_5\). The phosphorus partition ratio in all cases increases with the increasing of Na$_2$O content. Due to the lower silica contents (2.6 to 6.1 mass%) in slags, it is very difficult to increase the Na$_2$O yield at 1 873 K. The lower the alumina contents, the higher the phosphorus partition ratios. The maximum phosphorus partition ratio of 629 was obtained in the slag doubly saturated with lime and magnesio-wustite without alumina. The same tendency was observed from the results by Suito and Inoue$^8$ at 1 823 K.

In order to investigate the effect of Al$_2$O$_3$ addition on phosphorus removal, the values of phosphorus partition
The phosphorus partition ratio values decrease when the ratio of alumina in acidic oxides increases and they decrease rapidly when this ratio exceeds 0.66.

The relationship between phosphate capacities and the CaO content in the MgO saturated CaO–SiO$_2$–FeO$_x$ system are shown in Fig. 6. The phosphate capacity increases with increasing of CaO contents in all cases. However, for slags either containing lower SiO$_2$ contents and Na$_2$O addition as in present study, lower silica and high lime contents as in Ishii and Fruehan’s work, or sodium oxide addition, as in Suito and Inoue’s work, the phosphate capacities become higher. The maximum phosphate capacity obtained in present study is $10^{19.00}$. The present results agree well with those of Ishii and Fruehan’s$^{12}$ in the same range of slag composition and temperature. The data for the slags with 4 to 5 mass% alumina containing Na$_2$O at 1823 K in present study also agree well with Suito and Inoue’s results.

The influence of FeO contents in slag to the phosphate capacities is shown in Fig. 7. The phosphate capacities increased with increasing of FeO content to about 40 mass% and decreased when FeO content exceeded about 40%. The results obtained by Suito and Inoue in MgO saturated CaO–FeO$_x$–SiO$_2$ system show this tendency more obviously. Phosphate capacities show maximum value at 40 mass% of FeO because high FeO contents diluted the concentration of CaO, which performs a main role in dephosphorization.

The activity coefficient of P$_2$O$_5$, $g_{P_2O_5}$, in slag can be calculated by using Eqs. (13) to (15)

$$\Delta G^o = -1534000 + 506.47T \text{ J/mol}^{19,20} \quad \text{...(14)}$$

$$g_{P_2O_5} = K_{13} \cdot P_{O_{2}} \cdot P_{O_{2}}^{5/2} \quad \text{...(15)}$$

The relationship between $g_{P_2O_5}$ and (mass%Na$_2$O) are shown in Fig. 8. The addition of Na$_2$O in the MgO saturated CaO–FeO$_x$–SiO$_2$ system lowers the $g_{P_2O_5}$ values. The same tendency was observed by Suito and Inoue as shown in this figure.

Previous researchers correlated the theoretical optical basicity with the phosphate capacity of the slags$^{8,12,21-24}$. In order to compare the present result with those of previous investigators, the theoretical optical basicity was applied and the values for the optical basicities were taken from the literature$^{25}$. The relationship between phosphate capacities in logarithmic form and optical basicity is shown in Fig. 9. Data obtained by previous researchers in MgO saturated CaO–FeO$_x$–SiO$_2$ system were also plotted for comparison. The solid and dashed line were linear fit results from data.
obtained by Suito et al.\textsuperscript{7)} at 1 873 and 1 823 K, respectively. The dot dashed line was drawn by using the Eq. (16) summarized by Mori\textsuperscript{22)} at 1 873 K.

\[
\log C_{\text{PO}_4}^\text{O} / H_{\text{1} 1\text{002}/H_{\text{1} 1\text{005}}} = 17.55 + 5.72 \quad \text{..........................}(16)
\]

The phosphate capacities in logarithmic form show a linear relationship with optical basicity even though the phosphate capacity scatters within one order of magnitude.

### 3.3. Activity Coefficients of Iron Oxides in the MgO Saturated CaO–SiO\textsubscript{2}–FeO\textsubscript{x} System Containing Na\textsubscript{2}O and Al\textsubscript{2}O\textsubscript{3}

The reactions of formation of iron oxides are expressed as follows:

\[
\text{Fe} + \frac{1}{2} \text{O}_2 (g) = \text{FeO} (l) \quad \text{..........................}(17)
\]

\[
\Delta G^\text{o} = -256000 + 53.68T \text{ J/mol}\textsuperscript{13)} \quad \text{..........................}(18)
\]

\[
\text{Fe} + \frac{3}{4} \text{O}_2 (g) = \text{FeO}_{1.5} (s) \quad \text{..........................}(19)
\]

\[
\Delta G^\text{o} = -407000 + 125T \text{ J/mol}\textsuperscript{13)} \quad \text{..........................}(20)
\]

The activity coefficients of iron oxides are given by Eqs. (21) and (22).

\[
\gamma_{\text{FeO}} = \frac{K_{\text{FeO}} \cdot P_{\text{O}_2}^{1/2}}{X_{\text{FeO}}} \quad \text{..........................}(21)
\]

\[
\gamma_{\text{FeO}_{1.5}} = \frac{K_{\text{FeO}_{1.5}} \cdot P_{\text{O}_2}^{3/4}}{X_{\text{FeO}_{1.5}}} \quad \text{..........................}(22)
\]

where \( \gamma_i \) is the activity coefficient of \( i \) and \( X_i \) is mole fraction of \( i \). The standard state of FeO is stoichiometric liquid FeO and that of FeO\textsubscript{1.5} is solid FeO\textsubscript{1.5}.

Figure 10 shows the relationship between the activity coefficient of FeO and FeO\textsubscript{1.5} and mole fraction of SiO\textsubscript{2} for the present study and those previously reported.\textsuperscript{7,8,12)} Both activity coefficients increased with increasing of SiO\textsubscript{2} content in the slags. For MgO saturated highly basic slags as in present study and those of Ishii and Fruehan,\textsuperscript{12)} this tendency is also observed. This means that both FeO and FeO\textsubscript{1.5} behave as an acidic oxide. It should be noted that in Fig. 10 the slags with Na\textsubscript{2}O addition have lower \( \gamma_{\text{FeO}_{1.5}} \) values, as reported by Suito and Inoue.\textsuperscript{8)}

In Fig. 11, the activity coefficients of FeO obtained in
present study and previous investigators for MgO saturated CaO–FeO$_x$SiO$_2$ systems with or without Na$_2$O or Al$_2$O$_3$ addition were plotted against the ratio of mole fraction of (CaO+MgO+Na$_2$O)/(SiO$_2$+Al$_2$O$_3$). The solid line is the profile of the present data. The activity coefficient of FeO decreased drastically with increasing the ratio of basic oxides to acidic oxides. This phenomenon supports that FeO decreases the activity coefficients of FeO, FeO$_{1.5}$ and P$_2$O$_5$. The activity coefficients of FeO and FeO$_{1.5}$ show that they all behave as an acidic oxide in MgO saturated CaO–FeO$_x$–SiO$_2$ system.

### 3.4. Industrial Significance

MgO saturated highly basic CaO–FeO$_x$–SiO$_2$ slags have very good ability for dephosphorization. Instead of using highly basic CaO–FeO$_x$–SiO$_2$ slags containing Fe$_2$O$_3$, phosphorus distribution ratio greater than 500 are possible by using slags free of alumina and with 1 to 2 mass% Na$_2$O addition according to the results of present study. In the case of steel tapped from a basic oxygen furnace with 0.010 mass% P in the metal and 0.7 mass% P in the slag, if the carry-over slag is 5 kg per ton steel and 10 kg of flux is added to give a slag containing 1 mass% Na$_2$O, 5 mass% MgO, 36 mass% CaO, 4 mass% SiO$_2$ and 54 mass% FeO at 1873 K, the final phosphorus content will be about 16 ppm.

### 4. Conclusions

Highly basic CaO based slags saturated with MgO have been studied with respect to the phosphate capacity by measuring the phosphorus partition ratio between slag and metal under controlled oxygen partial pressure at 1823 K and 1873 K, respectively. The effect of Na$_2$O and Al$_2$O$_3$ addition and the activity of FeO and FeO$_{1.5}$ were also determined. The results are summarized as follows:

The phosphate capacity for MgO saturated CaO–FeO$_x$–SiO$_2$ slag containing 0 to 5 mass% Al$_2$O$_3$ and 0 to 1.75 mass% Na$_2$O at 1873 K are in the range of 10$^{18.37}$ to 10$^{19.00}$ and that containing 4.1 to 5.0 mass% Al$_2$O$_3$ and 0 to 2.37 mass% Na$_2$O at 1823 K are in the range of 10$^{18.53}$ to 10$^{18.62}$. For the slags containing 21.28 to 23.59 mass% Al$_2$O$_3$ and 0 to 4.25 mass% Na$_2$O at 1823 K are in the range of 10$^{17.86}$ to 10$^{18.15}$.

The addition of Na$_2$O to the MgO saturated CaO–FeO$_x$–SiO$_2$ system increases the phosphorus capacity of the slags. Alumina in the MgO saturated CaO–FeO$_x$–SiO$_2$ system decreases the phosphorus capacity of the slags and increases the MgO solubility in the slags.

The addition of Na$_2$O to the MgO saturated CaO–FeO$_x$–SiO$_2$ system decreases the activity coefficients of FeO, FeO$_{1.5}$ and P$_2$O$_5$. The activity coefficients of FeO and FeO$_{1.5}$ show that they all behave as an acidic oxide in MgO saturated CaO–FeO$_x$–SiO$_2$ system.

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