The Effect of Na_2O and Al_2O_3 on Dephosphorization of Molten Steel by High Basicity MgO Saturated $\text{CaO-FeO}_x\text{-SiO}_2$ 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 1823 K and 1873 K. The effect of Na_2O and Al_2O_3 addition and the activity of FeO and $\text{FeO}_{1.5}$ were also determined. The phosphate capacity for MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slag containing 0 to 5 mass% Al_2O_3 and 0 to 1.75 mass% Na_2O 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_2O_3 and 0 to 2.37 mass% Na_2O 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_2O_3 and 0 to 4.25 mass% Na_2O at 1823 K are in the range of $10^{17.84}$ to $10^{18.15}$.

The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system increases the phosphate capacity of the slags. Alumina in the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the phosphate capacity of the slags. The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the activity coefficients of FeO and $\text{FeO}_{1.5}$ and those of P_2O_5 . The activity coefficients of FeO and $\text{FeO}_{1.5}$ show that they all behave as an acidic oxide in MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system.

KEY WORDS: steelmaking; thermodynamics; phosphorus; MgO solubility; slag; $\text{MgO}_{\text{satd.}}\text{-CaO-FeO}_x\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ 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 Corporation¹⁾ 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 to 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_2O_3 , Na_2O , 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 $\text{CaO-Na}_2\text{O-SiO}_2\text{-FeO}_x$ slag at 1873 K in a MgO crucible under Ar atmo-

sphere. Miyata *et al.*⁴⁾ reported the results of hot metal dephosphorization with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ flux. 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_2O_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 $\text{CaO-Na}_2\text{O-SiO}_2\text{-CaF}_2$ slag doubly saturated with CaO and 3CaO-SiO_2 at 1573 K. They reported that the phosphorus partition ratio increases with increasing Na_2O content. The effect of Na_2O on dephosphorization is significantly large and phosphorus partition ratio increases ten-fold for an addition of only 2 mass% Na_2O . Park and Fruehan⁶⁾ reported that the phosphorus partition ratio increased 300 times when 3 mass% Na_2O were added into 50% $\text{CaO-40%Al}_2\text{O}_3\text{-10%SiO}_2$ slag in a graphite crucible at 1873 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 $\text{CaO-MgO-FeO}_x\text{-SiO}_2$ system at 1873 and 1823 K. They also investigated the effects of Na_2O addition (7 to 13 mass%) on phosphorus distribution between $\text{CaO-MgO-FeO}_x\text{-SiO}_2$ slags and liquid iron.⁸⁾ Kimura *et al.*⁹⁾ studied the activity of Na_2O in the

CaO–CaF₂–SiO₂ system doubly saturated with CaO and 3CaO·SiO₂ at 1423 to 1623 K. The relationship between the activity of Na₂O in both CaO–CaF₂–SiO₂ system and Na₂O–SiO₂ system was determined. Kimura *et al.*¹⁰⁾ measured the phosphorus partition ratio between CaO–K₂O–CaF₂–SiO₂ slags and carbon saturated iron and discussed the effects of Na₂O, BaO and K₂O addition to the CaO–CaF₂–SiO₂ system saturated with CaO and 3CaO·SiO₂ on phosphorus partition ratio at 1573 K. The enhancement of phosphorus partition ratio by the addition of Na₂O, BaO¹¹⁾ and K₂O was in the order K₂O, Na₂O and BaO.

Ishii and Fruehan¹²⁾ investigated the dephosphorization equilibria between liquid iron and highly basic CaO-based slags saturated with MgO at 1873 and 1843 K. However the influence of Na₂O on the dephosphorization of high basicity MgO saturated CaO–SiO₂–FeO_x 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–SiO₂–FeO_x slags and liquid steel has been measured in the present study. The effect of Al₂O₃ 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 MoSi₂ heating elements and a mullite reaction tube. Eight grams of electrolytic iron containing 0.0001 mass% P and 6 g of MgO–CaO–FeO_x–Al₂O₃–SiO₂ slags contained in a densely sintered pure MgO crucible (outer diameter 25, inner diameter 20, height 60 mm) were kept to equilibrium for 1 to 3 h at 1823 K and 1873 K, respectively. Several runs at 1823 K were conducted for 18 h. Since Na₂O is easy to evaporate, up to 20 mass% Na₂O was added to the slag initially in the form of sodium carbonate. The slag was prepared from reagent grade of SiO₂, Al₂O₃, MgO and FeO. The CaO was obtained from reagent grade of CaCO₃ chemicals decomposed at 1273 K in air. The temperature was controlled within ± 1 K using a B type thermocouple. The time for equilibration was determined by preliminary experiments. Equilibration was approached from both sides, dephosphorization and phosphorization of the metal by adding Fe–1.2mass%P alloy into metal and adding 3CaO·P₂O₅ into slag, respectively. Several sintered CaO pellets were dipped into slag for CaO saturation and remained undissolved CaO pellets were confirmed after experiments.

Oxygen partial pressure was controlled by reaction (1) controlling CO/CO₂ ratio. The moisture in CO₂ gas was removed by bubbling it through sulphuric acid and then passing through an anhydrous magnesium perchlorate column. CO gas was purified by bubbling it through sulphuric acid and then passing through the columns of soda lime and anhydrous magnesium perchlorate, respectively. The CO₂/CO ratios were 1/10 for the experiments at 1823 K and 1/18 for 1873 K respectively. The flow rates were 240 cm³/min at 1823 K and 270 cm³/min at 1873 K. The oxygen partial pressures calculated by reaction (1) are 6.40×10^{-5} Pa (6.32×10^{-10} atm) at 1823 K and 5.32×10^{-5} Pa (5.25×10^{-10} atm) at 1873 K, respectively.

$$\Delta G^\circ = -281\,000 + 85.23T \text{ J/mol}^{(13)} \dots\dots\dots(2)$$

The sample was taken out of the furnace and then quenched with argon stream. Phosphorus contents in both metal and slag were analyzed by molybdenum blue colorimetry. In the case that the phosphorus content in metal was below 0.0030 mass%, phosphorus molybdenum was extracted into isobutyl acetate, followed by colorimetry measurement. Oxygen content in metal was determined by LECO oxygen analyzer. CaO, MgO, Al₂O₃ and total iron content in slags were determined by ICP-AES spectrometry. FeO content in slags was determined by titration method and gravimetry was applied for SiO₂ analysis. Fe³⁺ content was obtained from total Fe and Fe²⁺ contents.

3. Results and Discussion

All experimental results were listed in **Tables 1** and **2**, including slag compositions for the MgO saturated CaO–SiO₂–FeO_x–Al₂O₃–Na₂O, MgO saturated CaO–SiO₂–FeO_x–Na₂O systems and metal. The slag compositions are also shown in the pseudo-ternary diagram (CaO+MgO+Na₂O)–(SiO₂+Al₂O₃+P₂O₅)–(FeO+Fe₂O₃) in **Fig. 1** together with the liquidus of CaO–SiO₂–FeO system after Muan *et al.*¹⁴⁾ and the liquidus of CaO–Al₂O₃–FeO system at 1873 K.

3.1. MgO Solubilities in the CaO–SiO₂–FeO_x–Al₂O₃–Na₂O and CaO–SiO₂–FeO_x–Na₂O Systems

The MgO concentration in CaO–SiO₂–FeO_x based slags was plotted against the ratio of [(mass%CaO)+(mass%Na₂O)]/[(mass%SiO₂)+(mass%Al₂O₃)+(mass%P₂O₅)] which presents the basicity of slags in **Fig. 2**. The data obtained by Shim and Ban-ya,¹⁵⁾ Suito *et al.*,^{7,8)} Ishii and Fruehan¹²⁾ were also shown in this figure. It can be seen that the solubility of MgO in CaO–SiO₂–FeO_x 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%Na₂O)]/[(mass%SiO₂)+(mass%Al₂O₃)+(mass%P₂O₅)] ratio is larger than 2, the MgO solubility of slag does not change too much. The influence of Al₂O₃ content to the MgO solubility was shown in **Fig. 3** comparing with the observed data of Ishii and Fruehan.¹²⁾ The MgO solubility increases with increasing of Al₂O₃ content. The present data agree reasonably well with those of Ishii and Fruehan¹²⁾ at 1873 K. The high MgO solubilities for the slags with 21.28 to 23.59 mass% Al₂O₃ kept at 1823 K for 18 h in present work are considered to be caused by relatively higher Na₂O and lower FeO_x contents in these slags as indicated in **Fig. 3**.

3.2. Phosphate Capacities of the MgO Saturated CaO–SiO₂–FeO_x–Al₂O₃–Na₂O and CaO–SiO₂–FeO_x–Na₂O Systems

Dephosphorization of steel by a metal–slag reaction can be expressed by Eq. (3)

Table 1. Experimental results for MgO saturated CaO–SiO₂–FeO_x–Al₂O₃–Na₂O slags at 1 823 K ($P_{O_2} = 6.40 \times 10^{-5}$ Pa).

No.	Slag composition (mass%)								Metal composition (mass%)		L_P Fe^{3+}/Fe^{2+}				
	(Na ₂ O)	(MgO)	(CaO)	(SiO ₂)	(Al ₂ O ₃)	(FeO)	(Fe ₂ O ₃)	(P ₂ O ₅)	[P]	[O]	$\frac{(mass\%P)}{[mass\%P]}$	$\frac{(mass\%)}{(mass\%)}$	$\log C_{PO_4^{3-}}$	γ_{FeO}	$\gamma_{FeO_{1.5}}$
1-1	2.37	5.53	25.01	3.56	4.14	47.64	10.36	1.39	0.00245	0.0862	247	0.196	18.62	1.96	0.201
1-2	0.17	5.61	30.27	4.20	5.00	42.52	10.44	1.80	0.00351	0.0972	224	0.221	18.57	2.22	0.201
1-3	1.65	5.24	26.27	2.95	4.32	48.10	10.00	1.48	0.00306	0.0949	211	0.187	18.55	1.94	0.208
1-4	0.76	5.24	27.89	3.78	4.52	45.98	10.12	1.70	0.00367	0.1016	202	0.198	18.53	2.04	0.206
1-5	4.25	7.44	26.70	5.97	22.05	27.07	5.56	0.943	0.00486	0.0836	84.8	0.185	18.15	3.40	0.368
1-6	1.84	8.06	26.48	6.07	21.70	29.87	5.08	0.903	0.00609	0.0833	64.7	0.153	18.03	3.09	0.404
1-7	1.14	8.92	26.20	5.29	21.28	31.88	4.36	0.928	0.00778	0.0995	52.1	0.123	17.94	2.91	0.473
1-8	0.10	13.01	28.64	3.91	23.59	25.05	4.69	1.01	0.00902	0.0756	49.0	0.168	17.91	3.79	0.450
1-9	0.08	11.82	28.57	5.09	23.42	24.78	5.30	0.945	0.00920	0.0814	44.9	0.193	17.87	3.81	0.396
1-10	0.17	13.68	27.50	6.01	22.49	25.16	4.05	0.942	0.00955	0.0846	43.0	0.145	17.86	3.81	0.526
1-11	0.18	12.55	27.27	5.03	22.17	27.14	4.73	0.930	0.00977	0.0826	41.5	0.157	17.84	3.50	0.446

Table 2. Experimental results for MgO saturated CaO–SiO₂–FeO_x–Al₂O₃–Na₂O slags at 1 873 K ($P_{O_2} = 5.32 \times 10^{-5}$ Pa).

No.	Slag composition (mass%)								Metal composition (mass%)		L_P Fe^{3+}/Fe^{2+}				
	(Na ₂ O)	(MgO)	(CaO)	(SiO ₂)	(Al ₂ O ₃)	(FeO)	(Fe ₂ O ₃)	(P ₂ O ₅)	[P]	[O]	$\frac{(mass\%P)}{[mass\%P]}$	$\frac{(mass\%)}{(mass\%)}$	$\log C_{PO_4^{3-}}$	γ_{FeO}	$\gamma_{FeO_{1.5}}$
2-1	0.93	4.10	38.43	3.76	-	41.86	9.15	1.77	0.00123	0.0600	629	0.197	19.00	1.34	0.100
2-2	1.75	3.33	35.13	2.74	-	42.87	12.71	1.46	0.00115	0.0655	554	0.267	18.95	1.29	0.071
2-3	0.98	3.98	35.74	3.53	-	43.01	11.08	1.68	0.00136	0.0687	538	0.232	18.93	1.29	0.082
2-4	0.26	4.81	37.99	3.57	-	40.21	11.15	2.02	0.00178	0.0688	493	0.250	18.90	1.40	0.082
2-5	1.21	5.07	37.85	2.74	3.34	39.76	8.49	1.56	0.00148	0.0556	459	0.192	18.87	1.41	0.107
2-6	0.83	4.97	38.92	2.61	3.52	39.14	8.36	1.66	0.00170	0.0566	425	0.192	18.83	1.43	0.109
2-7	0.09	4.58	39.23	4.00	-	39.54	10.41	2.14	0.00222	0.0722	422	0.237	18.83	1.42	0.088
2-8	0.11	6.30	41.04	5.04	4.99	29.56	8.53	1.79	0.00188	0.0541	416	0.260	18.82	1.87	0.106
2-9	0.12	5.91	41.35	3.58	4.16	35.37	7.53	1.98	0.00221	0.0626	391	0.192	18.79	1.60	0.122
2-10	0.12	5.46	41.27	3.70	4.22	35.56	7.69	1.98	0.00222	0.0538	389	0.195	18.79	1.59	0.119
2-11	0.83	5.02	34.17	2.67	4.19	40.13	11.10	1.89	0.00263	0.0784	313	0.249	18.70	1.37	0.081
2-12	0.09	6.83	29.87	4.30	4.41	37.67	14.84	1.47	0.00244	0.0679	263	0.355	18.62	1.46	0.060
2-13	0.10	6.44	30.59	4.07	4.43	36.66	14.90	1.53	0.00308	0.0821	217	0.366	18.54	1.48	0.059
2-14	0.17	7.11	27.06	4.13	4.28	42.73	13.71	1.53	0.00455	0.0809	147	0.289	18.37	1.29	0.066

Fig. 1. Experimental slag compositions.

where $\underline{\quad}$ and $(\quad)$ 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).

$$C_{PO_4^{3-}} \equiv \frac{(mass\%PO_4^{3-})}{P_2^{1/2} \cdot P_{O_2}^{4/5}} = K_4 \frac{a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}} \quad \dots\dots\dots(5)$$

where $a_{O^{2-}}$, P_i , $f_{PO_4^{3-}}$ and K_4 are the activity of oxide ion, partial pressure of i , activity coefficient of PO_4^{3-} and equilibrium constant of Eq. (4), respectively.

Fig. 2. Change of the MgO solubilities with the ratio $[(\text{mass}\% \text{CaO}) + (\text{mass}\% \text{Na}_2\text{O})] / [(\text{mass}\% \text{SiO}_2) + (\text{mass}\% \text{Al}_2\text{O}_3) + (\text{mass}\% \text{P}_2\text{O}_5)]$ of $\text{CaO}-\text{FeO}_x-\text{SiO}_2$ slags containing Na_2O and Al_2O_3 .

Fig. 3. Effect of Al_2O_3 content to the MgO solubility in $\text{CaO}-\text{FeO}_x-\text{SiO}_2$ slag.

The phosphate capacity was calculated from the PO_4^{3-} 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.

$$\frac{1}{2} \text{P}_2(\text{g}) = \text{P}(\text{mass}\% \text{ in Fe}) \quad \text{.....(6)}$$

$$\Delta G^\circ = -157\,700 + 5.4T \text{ J/mol}^{(16)} \quad \text{.....(7)}$$

In the present study, the oxygen partial pressure was con-

Fig. 4. Effect of Na_2O content on the phosphorus partition between MgO saturated $\text{CaO}-\text{FeO}_x-\text{SiO}_2-\text{Al}_2\text{O}_3$ system and liquid iron.

trolled 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.

$$\frac{1}{2} \text{O}_2(\text{g}) = \text{O}(\text{mass}\%) \quad \text{.....(8)}$$

$$\Delta G^\circ = -117\,110 - 3.39T \text{ J/mol}^{(17)} \quad \text{.....(9)}$$

$$\log f_{\text{O}} = e_{\text{O}}^{\text{O}} [\text{mass}\% \text{O}] + e_{\text{O}}^{\text{P}} [\text{mass}\% \text{P}] \quad \text{.....(10)}$$

$$e_{\text{O}}^{\text{O}} = -\frac{1750}{T} + 0.76^{(18)} \quad \text{.....(11)}$$

$$e_{\text{O}}^{\text{P}} = 0.07^{(17)} \quad \text{.....(12)}$$

Phosphorus partition ratio of the MgO saturated $\text{CaO}-\text{SiO}_2-\text{FeO}_x-\text{Al}_2\text{O}_3-\text{Na}_2\text{O}$ and $\text{CaO}-\text{SiO}_2-\text{FeO}_x-\text{Na}_2\text{O}$ systems are shown in Fig. 4. The results obtained by Suito and Inoue⁸⁾ in $\text{CaO}-\text{SiO}_2-\text{FeO}_x-\text{Na}_2\text{O}$ systems at 1823 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 $\text{CaO}-\text{SiO}_2-\text{FeO}_x-\text{Al}_2\text{O}_3-\text{Na}_2\text{O}$ slag and liquid iron increases with increasing of ratio $[(\text{mass}\% \text{CaO}) + (\text{mass}\% \text{Na}_2\text{O})] / [(\text{mass}\% \text{SiO}_2) + (\text{mass}\% \text{Al}_2\text{O}_3) + (\text{mass}\% \text{P}_2\text{O}_5)]$. The phosphorus partition ratio in all cases increases with the increasing of Na_2O content. Due to the lower silica contents (2.6 to 6.1 mass%) in slags, it is very difficult to increase the Na_2O yield at 1873 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 Inoue⁸⁾ at 1823 K.

In order to investigate the effect of Al_2O_3 addition on phosphorus removal, the values of phosphorus partition

Fig. 5. Effect of Al_2O_3 substitution for SiO_2 on phosphorus partition between MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slags and liquid iron.

Fig. 6. Change of phosphate capacities with CaO contents in MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slags.

ratio were plotted against the $X_{\text{Al}_2\text{O}_3}/(X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2})$ ratio in mole fraction along with Ishii and Fruehan's¹²⁾ results in Fig. 5. 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 $\text{CaO-SiO}_2\text{-FeO}_x$ 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_2O 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 pre-

Fig. 7. The influence of FeO contents to the phosphate capacities of MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slags.

sent study is $10^{19.00}$. The present results agree well with those of Ishii and Fruehan's¹²⁾ in the same range of slag composition and temperature. The data for the slags with 4 to 5 mass% alumina containing Na_2O 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 Inoue⁸⁾ in MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ 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_2O_5 , $\gamma_{\text{P}_2\text{O}_5}$, in slag can be calculated by using Eqs. (13) to (15)

$$\text{P}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) = \text{P}_2\text{O}_5(\text{l}) \dots\dots\dots(13)$$

$$\Delta G^\circ = -1534\,000 + 506.4T \text{ J/mol}^{(19,20)} \dots\dots\dots(14)$$

$$\gamma_{\text{P}_2\text{O}_5} = \frac{K_{13} \cdot P_{\text{P}_2} \cdot P_{\text{O}_2}^{5/2}}{X_{\text{P}_2\text{O}_5}} \dots\dots\dots(15)$$

The relationship between $\gamma_{\text{P}_2\text{O}_5}$ and (mass% Na_2O) are shown in Fig. 8. The addition of Na_2O in the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ systems lowers the $\gamma_{\text{P}_2\text{O}_5}$ values. The same tendency was observed by Suito and Inoue⁸⁾ 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 $\text{CaO-FeO}_x\text{-SiO}_2$ system were also plotted for comparison. The solid and dashed line were linear fit results from data

Fig. 8. Effect of Na₂O content on the activity coefficient of P₂O₅ in MgO saturated CaO-FeO_x-SiO₂-Al₂O₃ slags.

Fig. 9. Relationship between phosphate capacities and the optical basicity of slags.

obtained by Suito *et al.*⁷⁾ at 1873 and 1823 K, respectively. The dot dashed line was drawn by using the Eq. (16) summarized by Mori²²⁾ at 1873 K.

$$\log C_{\text{PO}_4^{3-}} = 17.55A + 5.72 \quad \text{.....(16)}$$

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-SiO₂-FeO_x System Containing Na₂O and Al₂O₃

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

Fig. 10. Relationship between the activity coefficients of FeO(l) and FeO_{1.5}(s) and the mole fraction of SiO₂.

$$\Delta G^\circ = -256\,000 + 53.68T \text{ J/mol}^{13)} \quad \text{.....(18)}$$

$$\Delta G^\circ = -407\,000 + 125T \text{ J/mol}^{13)} \quad \text{.....(20)}$$

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

$$\gamma_{\text{FeO}} = \frac{K_{17} \cdot P_{\text{O}_2}^{1/2}}{X_{\text{FeO}}} \quad \text{.....(21)}$$

$$\gamma_{\text{FeO}_{1.5}} = \frac{K_{19} \cdot P_{\text{O}_2}^{3/4}}{X_{\text{FeO}_{1.5}}} \quad \text{.....(22)}$$

where γ_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_{1.5} is solid FeO_{1.5}.

Figure 10 shows the relationship between the activity coefficient of FeO and FeO_{1.5} and mole fraction of SiO₂ for the present study and those previously reported.^{7,8,12)} Both activity coefficients increased with increasing of SiO₂ content in the slags. For MgO saturated highly basic slags as in present study and those of Ishii and Fruehan,¹²⁾ this tendency is also observed. This means that both FeO and FeO_{1.5} behave as an acidic oxide. It should be noted that in Fig. 10 the slags with Na₂O addition have lower $\gamma_{\text{FeO}_{1.5}}$ values, as reported by Suito and Inoue.⁸⁾

In Fig. 11, the activity coefficients of FeO obtained in

Fig. 11. Change of activity coefficients of FeO(l) with the ratio of mole fraction of $(\text{CaO} + \text{MgO} + \text{Na}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$.

present study and previous investigators for MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ systems with or without Na_2O or Al_2O_3 addition were plotted against the ratio of mole fraction of $(\text{CaO} + \text{MgO} + \text{Na}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$. 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 in the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ systems with or without Na_2O or Al_2O_3 addition behaves as an acidic oxide.

3.4. Industrial Significance

MgO saturated highly basic $\text{CaO-FeO}_x\text{-SiO}_2$ slags have very good ability for dephosphorization. Instead of using highly basic $\text{CaO-FeO}_x\text{-SiO}_2$ slags containing CaF_2 , phosphorus distribution ratio greater than 500 are possible by using slags free of alumina and with 1 to 2 mass% Na_2O 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_2O , 5 mass% MgO, 36 mass% CaO, 4 mass% SiO_2 and 54 mass% FeO_x 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_2O and Al_2O_3 addition and the activity of FeO and $\text{FeO}_{1.5}$ were also determined. The results are summarized as follows:

The phosphate capacity for MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slag containing 0 to 5 mass% Al_2O_3 and 0 to

1.75 mass% Na_2O 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_2O_3 and 0 to 2.37 mass% Na_2O 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_2O_3 and 0 to 4.25 mass% Na_2O at 1823 K are in the range of $10^{17.84}$ to $10^{18.15}$.

The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system increases the phosphate capacity of the slags. Alumina in the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the phosphate capacity of the slags and increases the MgO solubility in the slags.

The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the activity coefficients of FeO, $\text{FeO}_{1.5}$ and P_2O_5 . The activity coefficients of FeO and $\text{FeO}_{1.5}$ show that they all behave as an acidic oxide in MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system.

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REFERENCES

- 1) H. Kagechika: *NKK Tech. Rep.*, **88** (2003), 6.
- 2) Y. Ogawa, M. Yano, S. Kitamura and H. Hirata: *Tetsu-to-Hagane*, **87** (2001), 21.
- 3) T. Usui, K. Yamada, Y. Miyashita, H. Tanabe, M. Hanmyo and Y. Miyawaki: The 9th Japan-USSR Joint Symposium on Physical Chem. Metall., ISIJ, Tokyo, (1983), 179.
- 4) M. Miyata, S. Fukagawa, K. Shinme and H. Li: *CAMP-ISIJ*, **8** (1995), 101.
- 5) M. Muraki, H. Fukushima and N. Sano: *Trans. Iron Steel Inst. Jpn.*, **25** (1985), 1025.
- 6) J. J. Park and R. J. Fruehan: *Metall. Mater. Trans. B*, **22B** (1991), 39.
- 7) H. Suito, R. Inoue and M. Takada: *Trans. Iron Steel Inst. Jpn.*, **21** (1981), 250.
- 8) H. Suito and R. Inoue: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 47.
- 9) H. Kimura, F. Tsukihashi and N. Sano: *Metall. Mater. Trans. B*, **26B** (1995), 553.
- 10) H. Kimura and F. Tsukihashi: *Tetsu-to-Hagane*, **83** (1997), 689.
- 11) F. Tsukihashi, M. Nakamura, T. Orimoto and N. Sano: *Tetsu-to-Hagane*, **76** (1990), 1664.
- 12) H. Ishii and R. J. Fruehan: *Iron Steelmaker*, **24** (1997), 47.
- 13) E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, (1980), 7.
- 14) A. Muan and E. F. Osborn: *Phase Equilibria among Oxides in Steelmaking*, Addison-Wesley Publishing Co., Inc., Reading, (1965), 113.
- 15) J.-D. Shim and S. Ban-ya: *Tetsu-to-Hagane*, **67** (1981), 1735.
- 16) M. Yamamoto, K. Yamada, L. Meshkov and E. Kato: *Tetsu-to-Hagane*, **66** (1980), 2032.
- 17) The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking: *Steelmaking Data Sourcebook*, Gordon and Breach Science Publishers, New York, (1988), 279, 288.
- 18) H. Sakao and K. Sano: *J. Jpn. Inst. Met.*, **23** (1959), 671.
- 19) E. T. Turkdogan and J. P. Pearson: *J. Iron Steel Inst.*, **175** (1953), 393.
- 20) F. D. Richardson and J. H. E. Jeffes: *J. Iron Steel Inst.*, **160** (1948), 261.
- 21) D. R. Gaskell: *Trans. Iron Steel Inst. Jpn.*, **22** (1982), 997.
- 22) T. Mori: *Trans. Jpn. Inst. Met.*, **25** (1984), 761.
- 23) K. Kunisada and H. Iwai: *Trans. Iron Steel Inst. Jpn.*, **27** (1987), 332.
- 24) A. Bergaman and A. Gustafsson: *Steel Res.*, **59** (1988), 281.
- 25) *Slag Atlas*, 2nd Ed., ed by Verein Deutscher Eisenhüttenleute, Verlag Stahleisen GmbH, Düsseldorf, (1995), 616.