Activity of Phosphorus Oxide in $\text{CaO-MnO-SiO}_2\text{-PO}_{2.5}\text{(-MgO, Fe}_t\text{O)}$ Slags

Ahmad SOBANDI, Hiroshi G. KATAYAMA¹⁾ and Tadashi MOMONO¹⁾

Graduate School, Muroran Institute of Technology, Mizumoto-cho, Muroran, Hokkaido, 050-8585 Japan.

1) Department of Materials Science and Engineering, Muroran Institute of Technology, Mizumoto-cho, Muroran, Hokkaido, 050-8585 Japan.

(Received on January 29, 1998; accepted in final form on April 16, 1998)

The $\text{CaO-MnO-SiO}_2\text{-PO}_{2.5}\text{(-MgO, Fe}_t\text{O)}$ slags were equilibrated with liquid copper alloys in a molybdenum crucible under a flowing CO_2/H_2 atmosphere in the temperature range of 1 573 to 1 673 K.

The activity coefficient of $\text{PO}_{2.5}$, $\gamma_{\text{PO}_{2.5}}$, and the phosphate capacity, $C_{\text{PO}_4^{3-}} = (\% \text{PO}_4^{3-}) / p_{\text{P}_2}^{1/2} p_{\text{O}_2}^{5/4}$, of the slags were expressed as follows:

$$\log \gamma_{\text{PO}_{2.5}} = -2.59\{(\% \text{CaO}) + 0.33(\% \text{MnO}) + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_t\text{O}) - 0.77(\% \text{PO}_{2.5})\} / (\% \text{SiO}_2) + 1\,400/T - 5.75$$

$$\log C_{\text{PO}_4^{3-}} = 2.60\{(\% \text{CaO}) + 0.33(\% \text{MnO}) + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_t\text{O}) - 0.77(\% \text{PO}_{2.5})\} / (\% \text{SiO}_2) + 40\,400/T - 6.48$$

The phosphorus distributions between hot metal and the slag were examined, based on the thermodynamic data obtained in the present study. From comparison with the plant data, it was concluded that the thermodynamic data obtained in the present study are satisfactorily applicable to the thermodynamic assessment of hot metal pretreatment with high MnO slag.

KEY WORDS: thermodynamics; dephosphorization; high MnO slag; Cu-Mn-P alloy; hot metal; activity coefficient; phosphorus oxide; phosphate capacity.

1. Introduction

The thermodynamic properties of phosphorus in high MnO slags are important for the hot metal dephosphorization with steelmaking slag, especially from smelting reduction process of manganese ore using BOF.

In order to study the thermodynamic properties of phosphorus in high MnO slags by equilibrating with liquid copper, the interaction parameters between manganese and phosphorus as well as manganese itself in liquid copper were determined in the previous study.¹⁾

In this study, the thermodynamic property of phosphorus oxides in $\text{CaO-MnO-SiO}_2\text{-PO}_{2.5}\text{(-MgO, Fe}_t\text{O)}$ slags was investigated. The liquid Cu-Mn-P alloy was equilibrated with this slag in the temperature range from 1 573 to 1 673 K under flowing atmosphere of CO_2/H_2 gas mixtures with various proportions. The activity coefficients of $\text{PO}_{2.5}$ and the phosphate capacities of this slag were determined as a function of slag composition and temperature. Based on those data obtained, thermodynamic examination was made for the phosphorus distributions between hot metal and slag.

2. Experimental

2.1. Preparation of Samples

The copper-manganese alloys were prepared from copper and manganese metals with a high degree of purity. Those metals were premelted in a graphite crucible under the protection of argon for 1 h. Master slags of $\text{MnO-P}_2\text{O}_5$ and CaO-MnO-SiO_2 systems were prepared from reagent grade of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, CaCO_3 and SiO_2 , where their mixtures with desired proportions were calcined at 1 373 K for 3 h and then premelted at 1 673 K in a graphite crucible. In some of experiments, CaO, MgO and SiO_2 were added to the master slags to obtain the required slag compositions. High purity iron also was added to the copper alloy in order to study the effect of iron oxide in slag on the phosphorus distributions.

2.2. Experimental Apparatus and Procedure

The experimental apparatus is the same as that used in previous study.¹⁾ A vertical furnace with a mullite reaction tube and a SiC heating element was used. A molybdenum crucible (ID 18 mm, depth 28 mm) was used as the container of metal and slags. Temperature was measured by a R thermocouple installed at the bottom

of the molybdenum crucible. The experimental temperature was kept constant within ± 2 K at 1 573 to 1 673 K by a PID controller.

A copper–manganese alloy weighing about 20 g and a slag about 5 g, which were contained in a crucible, were hung slowly (about 3.3×10^{-4} m/s) to the hot zone in the reaction tube by a molybdenum wire and melted under CO_2/H_2 atmospheres at the flow rate of about 5×10^{-6} m³/s. Depending on experimental temperature, the holding time were decided as 30 h for 1 573 K, 24 h for 1 623 K and 20 h for 1 673 K. After the equilibrium was attained, the crucible was quickly withdrawn by a molybdenum wire and rapidly quenched by immersing the bottom of crucible into water under argon flushing.

Phosphorus, manganese and iron contents in copper were determined according to JIS analytical method (H 1241, H 1222 and H 1054). Ca, Mn, Mg, total Fe and P in slag were analyzed by ICP emission spectrometry, while SiO_2 was gravimetrically analyzed.

3. Results and Discussion

The chemical compositions of slag and metal phases are summarized in **Table 1**. The slags contained 4.83–36.8 mass% CaO, 25.2–53.9 mass% MnO, 21.9–45.7 mass% SiO_2 and 0.32–8.97 mass% $\text{PO}_{2.5}$. In some experiments they contained 1.89–7.12 mass% Fe_2O or 3.01–10.8 mass% MgO.

3.1. Predominant Phosphate Anion in CaO–MnO– SiO_2 – $\text{PO}_{2.5}$ Slag

Phosphorus species in the slag may consist of orthophosphate, PO_4^{3-} , and pyrophosphate, $\text{P}_2\text{O}_7^{4-}$ anions.^{2,3)} The dimerization of PO_4^{3-} to $\text{P}_2\text{O}_7^{4-}$ may be expressed as follows:

From the above reaction it is concluded that the dimer $\text{P}_2\text{O}_7^{4-}$ anion will be stabilized with increasing the phosphorus content of slag as well as with decreasing slag basicity. Tagaya *et al.*²⁾ found that a monomeric PO_4^{3-} anion was predominant up to 2 mass% of phosphorus in a CaO–CaF₂– SiO_2 slag doubly saturated with CaO and $3\text{CaO} \cdot \text{SiO}_2$ and in more basic slag such as 20mass% CaO–35mass% Na₂O–45mass% SiO_2 system it was the predominant species until the slag becomes saturated with $\text{Ca}_3(\text{PO}_4)_2$. On the other hand, Selin³⁾ investigated the phosphate anion for the MgO–saturated CaO– SiO_2 – Fe_2O system at 1 873 K and found that $\text{P}_2\text{O}_7^{4-}$ became more predominant at higher content of phosphorus oxide in slag.

In the present study, all phosphorus species were assumed to be $\text{PO}_{2.5}$ or PO_4^{3-} anion, because the phosphorus contents of MnO–CaO– SiO_2 – $\text{PO}_{2.5}$ slags were low to be 0.14–3.91 mass%.

3.2. Activity Coefficient of $\text{PO}_{2.5}$

The phosphorus equilibrium between liquid copper

Table 1. Experimental conditions and chemical compositions of liquid copper alloy and slag in equilibrium.

No.	Temp. / K	Po_2 / Pa	[%Mn]	[%P]	[%Fe]	(%CaO)	(%MnO)	(%SiO ₂)	(%PO _{2.5})	(%MgO)	(%Fe ₂ O)
1	1623	6.95×10^{-8}	1.24	0.026	0	19.6	48.8	21.9	8.97	0	0
2	1623	7.95×10^{-8}	0.904	0.110	0	14.5	51.2	27.6	4.90	0	0
3	1623	4.72×10^{-8}	0.555	0.236	0	9.51	53.3	36.3	1.86	0	0
4	1623	4.07×10^{-8}	0.380	0.219	0	4.83	53.9	39.3	0.32	0	0
5	1623	2.34×10^{-7}	0.694	0.022	0	24.4	40.8	25.7	8.87	0	0
6	1623	2.34×10^{-7}	0.242	0.117	0	18.4	42.1	31.8	7.91	0	0
7	1623	1.14×10^{-7}	0.673	0.045	0	21.2	42.8	27.0	8.68	0	0
8	1623	8.09×10^{-8}	1.19	0.017	0	33.4	30.6	25.6	8.78	0	0
9	1623	7.38×10^{-8}	0.743	0.071	0	27.8	34.1	29.8	7.78	0	0
10	1623	7.74×10^{-8}	0.370	0.206	0	23.2	36.0	34.0	6.61	0	0
11	1623	4.84×10^{-8}	0.242	0.384	0	19.0	37.3	40.6	3.86	0	0
12	1623	7.72×10^{-8}	0.936	0.036	0	36.8	25.2	31.2	8.12	0	0
13	1623	7.88×10^{-8}	0.508	0.075	0	32.4	28.1	32.3	7.38	0	0
14	1623	8.73×10^{-8}	0.264	0.231	0	29.3	29.4	36.8	6.30	0	0
15	1623	7.87×10^{-8}	0.165	0.347	0	22.9	29.6	40.7	3.96	0	0
16	1623	4.11×10^{-8}	0.949	0.035	0	30.3	32.1	33.5	2.56	0	0
17	1623	5.15×10^{-8}	0.694	0.061	0	27.3	33.7	37.0	2.23	0	0
18	1623	5.09×10^{-8}	0.395	0.137	0	22.9	35.1	40.3	1.37	0	0
19	1623	4.33×10^{-8}	0.267	0.221	0	18.2	35.5	45.7	0.64	0	0
20	1623	5.46×10^{-8}	1.10	0.033	0	19.8	44.1	27.4	4.83	3.01	0
21	1623	6.13×10^{-8}	1.15	0.024	0	19.1	42.0	26.5	4.68	5.78	0
22	1623	6.58×10^{-8}	1.11	0.017	0	19.3	40.8	26.7	4.85	8.34	0
23	1623	6.80×10^{-8}	1.07	0.017	0	18.8	38.0	26.1	5.03	10.8	0
24	1623	2.43×10^{-7}	0.310	0.072	0.770	17.7	42.1	31.8	4.37	0	1.89
25	1623	6.16×10^{-7}	0.175	0.030	1.20	18.2	39.1	34.3	4.50	0	3.99
26	1623	6.38×10^{-7}	0.147	0.046	1.77	18.6	35.9	34.0	4.43	0	5.57
27	1623	6.46×10^{-7}	0.123	0.079	2.43	19.7	31.4	34.6	3.98	0	7.12
28	1573	1.37×10^{-8}	0.928	0.062	0	21.1	45.6	30.2	2.50	0	0
29	1598	3.25×10^{-8}	0.919	0.044	0	21.2	46.2	31.1	2.56	0	0
30	1623	5.31×10^{-8}	1.08	0.051	0	20.7	44.6	30.9	2.29	0	0
31	1648	8.72×10^{-8}	1.19	0.050	0	21.1	44.4	31.8	2.39	0	0
32	1673	9.78×10^{-8}	1.65	0.089	0	21.6	43.0	32.6	2.07	0	0

Fig. 1. Relationship between $\log \gamma_{\text{PO}_{2.5}}$ and $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio at 1623 K.

and molten slag may be expressed as follows:

$$\begin{aligned} \log K_2 &= -35250/T + 14.36^{(4,5)} \\ &= \log [\% \text{P}] + \log f_{\text{P}} + 5/4 \log p_{\text{O}_2} - \log a_{\text{PO}_{2.5}} \end{aligned} \quad (3)$$

where K_2 is the equilibrium constant of Reaction (2), f_{P} is the activity coefficient of phosphorus in liquid copper relative to dilute solution of one mass% standard state, and $a_{\text{PO}_{2.5}}$ is the activity of $\text{PO}_{2.5}$ with reference to pure liquid $\text{PO}_{2.5}$.

The f_{P} value can be obtained by using Eq. (4):

$$\log f_{\text{P}} = e_{\text{P}}^{\text{Mn}} [\% \text{Mn}] + e_{\text{P}}^{\text{P}} [\% \text{P}] \quad (4)$$

where $e_{\text{P}}^{\text{P}} = 0^{(5)}$ and $e_{\text{P}}^{\text{Mn}} = -0.010$ at 1623 K.⁽¹⁾

By converting Eq. (3), the activity coefficient of $\text{PO}_{2.5}$, $\gamma_{\text{PO}_{2.5}}$ can be expressed as follows:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} &= -\log K_2 + \log f_{\text{P}} + \log [\% \text{P}] \\ &\quad + 5/4 \log p_{\text{O}_2} - \log X_{\text{PO}_{2.5}} \end{aligned} \quad (5)$$

where $X_{\text{PO}_{2.5}}$ is the mole fraction of $\text{PO}_{2.5}$ in slag.

3.2.1. Effect of $(\% \text{CaO})/(\% \text{SiO}_2)$ Ratio and MnO Contents

The effect of $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio as basicity index and MnO content of the slag on the activity coefficients of $\text{PO}_{2.5}$ is shown in Fig. 1. The $\log \gamma_{\text{PO}_{2.5}}$ values increased with decreasing the $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio at an approximately constant content of MnO, and increased with decreasing the MnO content at a constant $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio.

To derive the relationship between slag composition and $\log \gamma_{\text{PO}_{2.5}}$, the experimental data at 1623 K were arranged by means of the multiple linear regression method, according to the following algebraic sum and fractional expressions:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} &\propto (\% \text{CaO}) + \alpha (\% \text{MnO}) \\ &\quad + \beta (\% \text{PO}_{2.5}) - \chi (\% \text{SiO}_2) \end{aligned} \quad (6)$$

Fig. 2. Relationship between $\log \gamma_{\text{PO}_{2.5}}$ and $\{(\% \text{CaO}) + 0.33(\% \text{MnO}) - 0.77(\% \text{PO}_{2.5})\}/(\% \text{SiO}_2)$ at 1623 K.

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} &\propto \{(\% \text{CaO}) + \alpha' (\% \text{MnO}) \\ &\quad + \beta' (\% \text{PO}_{2.5})\}/(\% \text{SiO}_2) \end{aligned} \quad (7)$$

where α' , β' and χ are CaO-equivalent coefficients of MnO, $\text{PO}_{2.5}$ and SiO_2 , respectively.

As a result, it was found that the fractional expression (7) is superior to the algebraic sum expression (6) in accuracy and the following equation was obtained:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} &= -2.59\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ &\quad - 0.77(\% \text{PO}_{2.5})/(\% \text{SiO}_2)\} - 4.88 \end{aligned} \quad (8)$$

where the CaO-equivalent coefficients of MnO and $\text{PO}_{2.5}$ were determined to be 0.33 and -0.77 , respectively.

The relationship between $\log \gamma_{\text{PO}_{2.5}}$ and slag basicity index of Eq. (8) is shown in Fig. 2. There is a good linear relationship.

3.2.2. Effect of MgO

The effect of MgO on $\log \gamma_{\text{PO}_{2.5}}$ was investigated concerning the slags containing 38.0–44.1 mass% MnO and 4.68–5.03 mass% $\text{PO}_{2.5}$ at $(\% \text{CaO})/(\% \text{SiO}_2) = 0.72$. Since MgO content of the slags was changed by the substitution of MgO for some of MnO, the $\log \gamma_{\text{PO}_{2.5}}$ values were plotted against the $(\% \text{MgO})/(\% \text{MnO})$ ratio of slag in Fig. 3. This result shows that MgO decreases the $\gamma_{\text{PO}_{2.5}}$ value to larger extent than MnO does so.

The value of CaO-equivalent coefficient of MgO was obtained by means of the linear regression method as 0.55. This value is higher than that for MnO.

3.2.3. Effect of Fe_2O_3

To examine the effect of Fe_2O_3 content of slag on the $\gamma_{\text{PO}_{2.5}}$ value, the liquid copper alloys containing iron as a source of Fe_2O_3 were equilibrated with the CaO–MnO– SiO_2 – $\text{PO}_{2.5}$ slags at 1623 K and $P_{\text{O}_2} = 2.43$ – 6.46×10^{-7} Pa. Since Fe_2O_3 content of slags was not determined, iron oxide of slags was assumed to be $\text{Fe}_{0.95}\text{O}$ by reference to the $(\% \text{Fe}^{3+})/(\% \text{Fe}^{2+})$ ratios reported by Ban-ya *et al.*⁽⁶⁾ for the Fe_2O_3 – SiO_2 –MnO slags at 1723 K. Based on this assumption, the content of Fe_2O_3 as $\text{Fe}_{0.95}\text{O}$ was calculated from total iron content of slags.

Fig. 3. Effect of (%MgO)/(%MnO) ratio on $\log \gamma_{\text{PO}_{2.5}}$ at 1623 K.

Fig. 4. Effect of (%FeO)/(%MnO) ratio on $\log \gamma_{\text{PO}_{2.5}}$ at 1623 K.

Since the interaction parameter (e_{P}^{Fe}) between phosphorus and iron in liquid copper was not reported, the effect of iron content on the activity of phosphorus in liquid copper alloys was neglected in computing the $\gamma_{\text{PO}_{2.5}}$ value.

The MnO content decreased with increasing the Fe_2O content, so that the $\log \gamma_{\text{PO}_{2.5}}$ values were plotted against the (% Fe_2O)/(%MnO) ratio of slag in Fig. 4. The solid line in the figure shows the change in the observed $\log \gamma_{\text{PO}_{2.5}}$ values with the (% Fe_2O)/(%MnO) ratio. The $\log \gamma_{\text{PO}_{2.5}}$ values increased with increasing the (% Fe_2O)/(%MnO) ratio. The broken line shows the change in the $\log \gamma_{\text{PO}_{2.5}}$ values calculated from Eq. (8), omitting the effect of Fe_2O . The comparison between values of solid and broken lines shows that Fe_2O has a capacity increasing the $\log \gamma_{\text{PO}_{2.5}}$ values. These results agree with those obtained by Pak and Fruehan⁷⁾ and Wrampelmeyer *et al.*⁸⁾ The CaO-equivalent coefficient of Fe_2O was determined by means of the linear regression method as -0.90 .

Fig. 5. Relationship between $\log \gamma_{\text{PO}_{2.5}}$ and $1/T$.

3.2.4. Effect of Temperature

The activity coefficient of $\text{PO}_{2.5}$ can be expressed as a function of temperature. In calculating the $\gamma_{\text{PO}_{2.5}}$ values at various temperatures from Eq. (5), the e_{P}^{Mn} values were estimated by the temperature function, $e_{\text{P}}^{\text{Mn}}(T) = (T'/T)e_{\text{P}}^{\text{Mn}}(T')$, where T' is the temperature (1623 K) at which the value was determined.¹⁾ Figure 5 shows the relationship between $\log \gamma_{\text{PO}_{2.5}}$ and $1/T$ for the slags containing 43.0–46.2 mass% MnO and 2.07–2.56 mass% $\text{PO}_{2.5}$ at (%CaO)/(%SiO₂) = 0.66–0.70. The following equation was obtained by means of the linear regression method:

$$\log \gamma_{\text{PO}_{2.5}} = -8.49 + 1400/T \quad \text{..... (9)}$$

The $\log \gamma_{\text{PO}_{2.5}}$ value decreased only slightly with increasing temperature.

3.2.5. Derivation of Empirical Equation for the Activity Coefficient of $\text{PO}_{2.5}$ Including Slag Composition and Temperature

The activity coefficient of $\text{PO}_{2.5}$ for the CaO–MnO–SiO₂– $\text{PO}_{2.5}$ slag containing MgO and Fe_2O can be expressed as a function of slag composition and temperature as mentioned above. Consequently the following relationship was obtained by means of the linear regression method:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} = & -2.59\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ & + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_2\text{O}) \\ & - 0.77(\% \text{PO}_{2.5})\}/(\% \text{SiO}_2) + 1400/T - 5.75 \end{aligned} \quad \text{..... (10)}$$

where the CaO-equivalent coefficients of slag components and the temperature dependence of $\log \gamma_{\text{PO}_{2.5}}$ were fixed at the values described above.

Figure 6 shows the correlation between the observed values of $\log \gamma_{\text{PO}_{2.5}}$ and the values calculated from Eq. (10). There is a good correlation with the correlation coefficient (R^2) of 0.96.

3.3. Phosphate Capacity

Based on Reaction (11), Wagner⁹⁾ defined the phosphate capacity ($C_{\text{PO}_4^{3-}}$), which is considered to be the

Fig. 6. Correlation between the observed values of $\log \gamma_{\text{PO}_{2.5}}$ and the values calculated from Eq. (10).

Fig. 7. Relationship between $\log C_{\text{PO}_4^{3-}}$ and slag basicity index, B , at 1623 K.

dephosphorization power of slag as Eq. (12):

$$C_{\text{PO}_4^{3-}} \equiv \frac{(\% \text{PO}_4^{3-})}{p_{\text{P}_2}^{1/2} p_{\text{O}_2}^{5/4}} = \frac{K_{11} a_{\text{O}^{2-}}^3}{f_{\text{PO}_4^{3-}}} \quad \text{..... (12)}$$

where $(\% \text{PO}_4^{3-})$ and $f_{\text{PO}_4^{3-}}$ are the mass% and activity coefficient of PO_4^{3-} anion in slag, $a_{\text{O}^{2-}}$ is the activity of O^{2-} anion in slag, p_{P_2} is the partial pressure of P_2 gas in equilibrium with phosphorus in metal, and K_{11} is the equilibrium constant of Reaction (11).

The partial pressure of P_2 gas can be evaluated from the phosphorus content in liquid copper and the following thermodynamic data.

$$\underline{P}_{\text{in Cu}} = 1/2 \text{P}_2(\text{g}) \quad \text{..... (13)}$$

$$\log K_{13} = -6260/T + 0.0285^5$$

$$= 1/2 \log p_{\text{P}_2} - \log [\% \text{P}] - \log f_{\text{P}} \quad \text{..... (14)}$$

where f_{P} can be obtained by using Eq. (4).

Fig. 8. Relationship between $\log C_{\text{PO}_4^{3-}}$ and $1/T$.

The phosphate capacity is only dependent on slag composition and temperature. Figure 7 shows the $C_{\text{PO}_4^{3-}}$ value at 1623 K as a function of the same basicity index as that determined in the arrangement of $\log \gamma_{\text{PO}_{2.5}}$ (Eq. (10)). The following equation was obtained by means of the linear regression method:

$$\log C_{\text{PO}_4^{3-}} = 2.60\{(\% \text{CaO}) + 0.33(\% \text{MnO}) + 0.55(\% \text{MgO}) - 0.90(\% \text{FeO}) - 0.77(\% \text{PO}_{2.5})\} / (\% \text{SiO}_2) + 18.41 \quad \text{... (15)}$$

The $\log C_{\text{PO}_4^{3-}}$ value increased linearly with increasing the basicity index at a constant temperature. This result agrees with the indication of Eq. (12); that is, $C_{\text{PO}_4^{3-}}$ increases with increasing slag basicity ($a_{\text{O}^{2-}}$) and with decreasing $f_{\text{PO}_4^{3-}}$ at a constant temperature.

The phosphate capacity shows the ability of slag to absorb phosphorus. It is the intrinsic property of a given slag, irrespective of the kind of liquid metal used for its measurement. Therefore, the present values can be utilized in investigating the dephosphorization characteristic of various metals, such as liquid steel, hot metal, liquid copper and so on.

The temperature dependence of $C_{\text{PO}_4^{3-}}$ is shown in Fig. 8 for the same slags as in Fig. 5, and is expressed by the following equation:

$$\log C_{\text{PO}_4^{3-}} = -3.72 + 40400/T \quad \text{..... (16)}$$

The $C_{\text{PO}_4^{3-}}$ values decreased with increasing temperature. This shows that dephosphorization reaction is exothermic. Neglecting temperature dependence of $a_{\text{O}^{2-}}$ and $f_{\text{PO}_4^{3-}}$, the relationship between phosphate capacity of slag and temperature can be derived by using the following van't Hoff's equation:

$$\frac{\partial(\log C_{\text{PO}_4^{3-}})}{\partial(1/T)} = -\frac{\Delta H^\circ}{2.303R} \quad \text{..... (17)}$$

where ΔH° is the standard enthalpy change for dephosphorization reaction.

From the slope of line shown in Fig. 8, the ΔH° value was obtained to be -774 kJ/mol . This value and those reported by other investigators are given in Table 2 for

Table 2. The standard enthalpy change of reaction: $1/2 \text{P}_2(\text{g}) + 5/4 \text{O}_2(\text{g}) = \text{PO}_{2.5}(\text{l})$.

No.	Slag system	Temperature range (K)	ΔH° (kJ/mol)	Authors
1.	BaO-based slag	1 448–1 573	– 528	Hara <i>et al.</i> ¹³⁾
2.	BaO-based slag	1 573–1 673	– 1 107	Liu <i>et al.</i> ¹⁴⁾
3.	BaO-based slag	1 473–1 623	– 1 350	Tabuchi <i>et al.</i> ¹⁵⁾
4.	Na ₂ O-based slag	1 473–1 623	– 761	Tsukihashi <i>et al.</i> ¹¹⁾
5.	CaO-based slag	1 448–1 623	– 723–– 787	Yang <i>et al.</i> ¹⁰⁾
6.	CaO–MnO–SiO ₂	1 573–1 673	– 774	Present work
7.	$1/2 \text{P}_2 + 5/4 \text{O}_2 = 1/2 \text{P}_2\text{O}_5(\text{l})$		– 767	Turkdogan <i>et al.</i> ¹²⁾

Fig. 9. Correlation between the observed values of $\log C_{\text{PO}_3^{3-}}$ and the values calculated from Eq. (18).

comparison. The present value is in good agreement with those obtained by Yang *et al.*¹⁰⁾ for CaO-based slag and by Tsukihashi *et al.*¹¹⁾ for Na₂O-based slag as well as the theoretical value reported by Turkdogan and Pearson.¹²⁾ Comparing with the enthalpy change for BaO-based slag, the present value is somewhat lower than the value by Hara *et al.*,¹³⁾ but considerably higher than those obtained by Liu *et al.*¹⁴⁾ and Tabuchi and Sano.¹⁵⁾

The phosphate capacity of slag can be expressed as a function of slag composition and temperature. The following relationship was obtained by means of the linear regression method:

$$\begin{aligned} \log C_{\text{PO}_3^{3-}} = & 2.60\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ & + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_t\text{O}) \\ & - 0.77(\% \text{PO}_{2.5})\}/(\% \text{SiO}_2) \\ & + 40\,400/T - 6.48 \quad \dots(18) \end{aligned}$$

where the temperature dependence of $\log C_{\text{PO}_3^{3-}}$ was assumed to be equal to that of Eq. (16). Figure 9 shows the correlation between the observed values of $\log C_{\text{PO}_3^{3-}}$ and the values calculated from Eq. (18). The correlation is satisfactory.

3.4. Activity of Fe_tO

The activity of Fe_tO in the CaO–MnO–Fe_tO–SiO₂–PO_{2.5} slags can be obtained by using the following equations:

Fig. 10. Relationship between $a_{\text{Fe}_t\text{O}}$ and mol% Fe_tO at 1 623 K.

$$\log K_{19} = -14\,290/T + 4.421^{4,16)} \quad \dots(20)$$

$$\begin{aligned} \log a_{\text{Fe}_t\text{O}} = & t\{\log[\% \text{Fe}] + e_{\text{Fe}}^{\text{Fe}}[\% \text{Fe}] + e_{\text{Fe}}^{\text{Mn}}[\% \text{Mn}] \\ & + e_{\text{Fe}}^{\text{P}}[\% \text{P}]\} + 1/2 \log p_{\text{O}_2} - \log K_{19} \quad \dots(21) \end{aligned}$$

where e_{Fe}^i is the interaction parameter between Fe and i in liquid copper. The value for $e_{\text{Fe}}^{\text{Fe}}$ is reported as -0.029 at 1 823 K,¹⁶⁾ but the values of $e_{\text{Fe}}^{\text{Mn}}$ and e_{Fe}^{P} are unknown. Thus, the terms of $e_{\text{Fe}}^{\text{Mn}}[\% \text{Mn}]$ and $e_{\text{Fe}}^{\text{P}}[\% \text{P}]$ were neglected, because of relatively low contents of manganese and phosphorus in the metal.

Figure 10 shows the activity of Fe_tO plotted against the mole fraction of Fe_tO, $X_{\text{Fe}_t\text{O}}$, at 1 623 K. The $a_{\text{Fe}_t\text{O}}$ values showed positive deviation from ideal behavior, and the following relationship was obtained:

$$a_{\text{Fe}_t\text{O}} = 1.76 X_{\text{Fe}_t\text{O}} \quad \dots(22)$$

3.5. Examination of Phosphorus Distribution between Hot Metal and CaO–MnO–MgO–Fe_tO–SiO₂–PO_{2.5} Slags

The dephosphorizing capability of slags can be expressed as the phosphate capacity which is dependent only on temperature and slag composition. By using the phosphate capacity of slags, the experimental results of the phosphorus distributions obtained under different oxygen partial pressures or with different metals can be connected directly with each other. Based on the present

data of the phosphorus equilibria between liquid copper alloys and CaO–MnO–SiO₂–PO_{2.5}–(MgO, Fe₂O) slags at temperature of 1 573 to 1 673 K along with the available thermodynamic data, the phosphorus distributions between hot metal and the slags were examined.

The activity of phosphorus in liquid iron can be evaluated from the following thermodynamic data.

$$\begin{aligned} \log K_{23} &= \log f_{\text{P}} + \log [\% \text{P}] - 1/2 \log p_{\text{P}_2} \\ &= 6383/T + 1.006^{17)} \quad (24) \end{aligned}$$

where K_{23} is the equilibrium constant for Reaction (23) and f_{P} is the activity coefficient of phosphorus in liquid iron relative to one mass% standard state.

The activity coefficient of phosphorus (f_{P}) in the Mn-containing Fe–C_{sat} alloy was estimated between 1 573 and 1 673 K by Shim *et al.*¹⁸⁾ as follows:

$$\log f_{\text{P}} = -0.0029[\% \text{Mn}] - \frac{386}{T} + 0.891 \quad (25)$$

where the self interaction of phosphorus, e_{P}^{P} , was neglected because its content was low enough.

Therefore, the phosphorus distribution between hot metal and slag can be estimated using the present values of phosphate capacity which were measured by equilibrating the slag with liquid copper alloy.

$$\begin{aligned} \log L_{\text{P}} &= \log \frac{(\% \text{P})}{[\% \text{P}]_{\text{in HM}}} \\ &= \log C_{\text{PO}_4^{3-}} + \frac{5}{4} \log p_{\text{O}_2} + \log f_{\text{P}} - \log K_{23} \\ &\quad - \log \frac{M_{\text{PO}_4^{3-}}}{M_{\text{P}}} \quad (26) \end{aligned}$$

where $[\% \text{P}]_{\text{in HM}}$ is the mass% of phosphorus in hot metal, and $M_{\text{PO}_4^{3-}}$ and M_{P} are the formula weight of PO_4^{3-} and atomic weight of P, respectively.

The phosphate capacity for the CaO–MnO–SiO₂–PO_{2.5}–MgO–FeO slags is represented as a function of slag composition and temperature, as shown by Eq. (18). By combining Eq. (26) with Eq. (18), the values of L_{P} between hot metal and slag can be obtained at various slag compositions, temperatures and oxygen partial pressures.

The dephosphorization reaction in practical hot metal pretreatment is known to be controlled by the oxygen potential close to that determined by the Fe/Fe₂O equilibrium, which is much higher than that by the C/CO equilibrium.¹⁹⁾ Thus, the oxygen partial pressure was calculated by using the equilibrium constant, K_{27} , for Reaction (27):

$$\begin{aligned} \log K_{27} &= -12360/T + 2.50^{4)} \\ &= 1/2 \log P_{\text{O}_2} + \log a_{\text{Fe}}^{\text{l}} - \log a_{\text{Fe}_2\text{O}} \quad (28) \end{aligned}$$

where a_{Fe} is the activity of iron with reference to pure liquid iron. The value for a_{Fe} in Fe–C_{sat} melt at 1 623 K was assumed to be 0.65 by referring to the data reported by Elliott *et al.*²⁰⁾ The ' t ' value was assumed to be 0.95

Fig. 11. Relationship between $\log(\% \text{P})/[\% \text{P}]_{\text{in HM}}$ and $(\% \text{Fe}_2\text{O})$ at various $(\% \text{CaO})/(\% \text{SiO}_2)$ ratios at 1 623 K.

Fig. 12. Relationship between $\log(\% \text{P})/[\% \text{P}]_{\text{in HM}}$ and $(\% \text{MnO})$ at various $(\% \text{CaO})/(\% \text{SiO}_2)$ ratios at 1 623 K.

as described above. The values for $a_{\text{Fe}_2\text{O}}$ at 1 623 K were estimated from the relationship between $a_{\text{Fe}_2\text{O}}$ and the mole fraction of Fe₂O, which was derived in the present study as shown in Fig. 10.

Figure 11 shows the relationship between the $\log L_{\text{P}}$ values and the Fe₂O content at 1 623 K for the slags containing 10 mass% MnO, 5 mass% MgO and 5 mass% PO_{2.5} with the constant $(\% \text{CaO})/(\% \text{SiO}_2)$ ratios of 1 to 2. The $\log L_{\text{P}}$ values at 1 623 K increased with increasing the $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio at a given Fe₂O content. They increased with increasing the Fe₂O content at a given $(\% \text{CaO})/(\% \text{SiO}_2)$ ratio, but they had the tendency to decrease slightly in higher Fe₂O content at the $(\% \text{CaO})/(\% \text{SiO}_2)$ ratios higher than 1.5. These results are similar to those assessed thermodynamically by Suito and Inoue¹⁹⁾ concerning the hot metal dephosphorization with MnO-containing BOF slags.

The effect of the MnO content on the $\log L_{\text{P}}$ value at 1 623 K is shown in Fig. 12 for the slags containing 10 mass% Fe₂O, 5 mass% MgO and 5 mass% PO_{2.5} with the constant $(\% \text{CaO})/(\% \text{SiO}_2)$ ratios of 1 to 2. The $\log L_{\text{P}}$ values increased gradually with increasing the MnO

content, while they decreased in the thermodynamic assessment of hot metal dephosphorization by Suito and Inoue.¹⁹⁾ The reason for this is not obvious.

The plant data²¹⁾ obtained using 6t converter at 1623 K were also pictured by the hatched area in Figs. 11 and 12, where the slags contained 1.1–11.5 mass% MnO, 1.8–13.1 mass% MgO and 0.7–8.3 mass% PO_{2.5} at (%CaO)/(%SiO₂)=1.4–1.6. They are significantly lower than the log L_P values estimated in the present study. This is due to the lower oxygen potential, compared with that determined by the Fe/Fe₂O equilibrium, as considered by Suito and Inoue.¹⁹⁾

4. Conclusions

Phosphorus equilibria between liquid copper alloys and the CaO–MnO–SiO₂–P₂O₅–(FeO, MgO) slags were investigated by equilibrating with CO₂–H₂ mixtures with different proportions in the temperature range of 1573 to 1673 K. The results are summarized as follows:

(1) An empirical expression for the activity coefficient of PO_{2.5} in slag was obtained as follows:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} = & -2.59\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ & + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_t\text{O}) \\ & - 0.77(\% \text{PO}_{2.5})\}/(\% \text{SiO}_2) + 1400/T - 5.75 \end{aligned}$$

(2) The phosphate capacity, $C_{\text{PO}_4^{3-}} = (\% \text{PO}_4^{3-}) / (p_{\text{P}_2}^{1/2} p_{\text{O}_2}^{5/4})$, of the slags was expressed by the following equation:

$$\begin{aligned} \log C_{\text{PO}_4^{3-}} = & 2.60\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ & + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_t\text{O}) \\ & - 0.77(\% \text{PO}_{2.5})\}/(\% \text{SiO}_2) + 40400/T - 6.48 \end{aligned}$$

The standard enthalpy change for dephosphorization reaction was found to be –774 kJ/mol.

(3) The phosphorus distributions between hot metal and the CaO–MnO–SiO₂–PO_{2.5}–MgO–Fe_tO slags were examined at 1623 K, based on the thermodynamic data obtained in the present study. It was assumed that the

oxygen partial pressure can be controlled according to Fe_tO/Fe equilibrium. From comparison with the plant data, it was concluded that the thermodynamic data obtained in the present study are satisfactorily applicable to the thermodynamic assessment of hot metal pretreatment with high MnO slag.

REFERENCES

- 1) Ahmad Sobandi, H. G. Katayama and T. Momono: *ISIJ Int.*, **37** (1997), 1043.
- 2) A. Tagaya, H. Chiba, F. Tsukihashi and N. Sano: *Metall. Trans. B*, **22B** (1991), 499.
- 3) R. Selin: Proc. 3rd Int. Conf. on Molten Slags and Fluxes, The Inst. of Metals, London, (1989), 317.
- 4) I. Barin: Thermochemical Data of Pure Substances, VHC Verlagsgesellschaft mbH, Weinheim, (1989), 271; 272; 560; 650; 900; 1117.
- 5) M. Iwase, E. Ichise and N. Yamada: *Steel Res.*, **56** (1985), 319.
- 6) S. Ban-ya, M. Hino and N. Yuge: *Tetsu-to-Hagané*, **71** (1985), 853.
- 7) J. J. Pak and R. J. Fruchan: *Metall. Trans. B*, **22B** (1991), 39.
- 8) J. C. Wrampelmeyer, S. Dimitrov and D. Janke: *Steel Res.*, **60** (1989), 539.
- 9) C. Wagner: *Metall. Trans. B*, **6B** (1975), 405.
- 10) Y. Yang, A. McLean, I. D. Sommerville and R. McKague: *Steel Res.*, **66** (1995), 103.
- 11) F. Tsukihashi, F. Matsumoto, T. Hyodo, M. Yukinobu and N. Sano: *Tetsu-to-Hagané*, **71** (1985), 823.
- 12) E. T. Turkdogan and J. Pearson: *J. Iron Steel Inst.*, **175** (1953), 398.
- 13) T. Hara, F. Tsukihashi and N. Sano: *Tetsu-to-Hagané*, **76** (1990), 352.
- 14) X. Liu, O. Wijk, R. Selin and J. O. Edstrom: *Steel Res.*, **66** (1995), 96.
- 15) S. Tabuchi and N. Sano: *Tetsu-to-Hagané*, **71** (1985), 689.
- 16) G. K. Sigworth and J. F. Elliott: *Can. Metall. Q.*, **13** (1974), 455.
- 17) G. K. Sigworth and J. F. Elliott: *Met. Sci.*, **8** (1974), 298.
- 18) S. C. Shim, K. Morita and N. Sano: *Steel Res.*, **65** (1994), 523.
- 19) H. Suito and R. Inoue: *ISIJ Int.*, **35** (1995), 258.
- 20) J. F. Elliott, M. Gleiser and V. Ramakrishna: Thermochemistry for Steelmaking, Vol. II, Addison-Wesley, Massachusetts, (1963), 501.
- 21) Y. Ogawa, M. Yano, M. Matsuo and Y. Demote: *CAMP-ISIJ*, **6** (1993), 1074.