Thermodynamic Assessment of Hot Metal and Steel Dephosphorization with MnO-containing BOF Slags

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The phosphorus distribution ratios between MnO (8–16 mass%)-containing CaO–SiO₂–Fe₂O slags and liquid iron were measured at 1873 K in a MgO crucible. The addition of MnO was found to reduce the phosphorus distribution ratio at a given total Fe content and (mass%CaO)/(mass%SiO₂) ratio. The equilibrium quotient of dephosphorization reaction, (mass%P)/{[mass%P]·(mass%T.Fe)^{5/2}}, the activity coefficient of P₂O₅, and that of Fe₂O in logarithmic form were formulated as a linear function of slag compositions. Based on these empirical formulas, the dephosphorization in hot metal and steel was thermodynamically assessed and the characteristics of double slag treatments were discussed from the mass balance relation between slag and metal with respect to phosphorus.

KEY WORDS: thermodynamics; dephosphorization; hot metal; steel; activity coefficient; P₂O₅; MnO; Fe₂O; slag recycle.

1. Introduction

For the effective dephosphorization of hot metal with CaO-based flux, fluorspar is added as a flux agent. However, the fluorine-containing slags in general cannot be utilized for road building or land-filled materials, because of the pollution problem of F[−] ion dissolution. In the new refining process using BOF converter,¹⁾ in which the slags obtained in decarburization furnace are recycled to the dephosphorization agent, it was confirmed that the total lime consumption was significantly reduced¹⁾ and the sufficient dephosphorization occurred by using the CaF₂-free flux with a low basicity of (mass%CaO)/(mass%SiO₂)=1–1.5.²⁾ It is also well established that manganese ore is added in decarburization period of dephosphorized hot metal.

In the aforementioned recent trend of hot metal dephosphorization, the knowledge of the effect of MnO on the dephosphorization is regarded as indispensable in view of the slag minimum and slag utilization. The present authors³⁾ previously reported the phosphorus distribution ratios between MnO-containing CaO–SiO₂–Fe₂O slags saturated with MgO and liquid iron, but the MnO level was in the small range of 0.6–5 mass%.

In this paper, the dephosphorization formulas were re-evaluated by using the phosphorus distribution ratios between MnO(8–16 mass%)-containing CaO–SiO₂–Fe₂O slags and liquid iron at 1873 K in a MgO crucible, coupled with the previous results^{3–6)} for the dephosphorization experiments and the effect of MnO addition on dephosphorization was studied. The hot metal dephosphorization was also considered by extrapolating

the data obtained at high temperatures between 1823 and 1923 K to a hot metal temperature. Furthermore, the characteristics of double slag treatments were discussed from the mass balance relation between slag and metal concerning phosphorus.

2. Effect of MnO on Steel Dephosphorization

2.1. Dephosphorization Formula

The present authors studied the phosphorus distribution between CaO–SiO₂–Fe₂O–P₂O₅ (<5 mass%) slags,^{3,5)} and CaF₂ (1–4 mass%)⁶⁾ or MnO (0.6–5 mass%)³⁾-containing CaO–SiO₂–Fe₂O–P₂O₅ (≤3 mass%) slags and liquid iron in a MgO crucible at 1823, 1873 and 1923 K. Using these results, they derived modified Balajiva-type⁷⁾ and Healy-type⁸⁾ dephosphorization formulas, in which not only the effect of CaO, but also that of other slag components was taken into consideration. Experimental method and the chemical compositions of the present slag and metal phases are given elsewhere.⁹⁾

A modified Balajiva-type formula⁷⁾ is given in Eq. (1) and the present results are plotted in Fig. 1.

$$\begin{aligned} \log(\%P_2O_5)/\{[\%P]^2 \cdot (\%FeO)^5\} \\ = 0.145[(\%CaO) + 0.3(\%MgO) - 0.5(\%P_2O_5) \\ + 0.3(\%MnO) + 1.2(\%CaF_2) - 0.2(\%Al_2O_3)] \\ + 22810/T - 20.51 \dots\dots\dots(1) \end{aligned}$$

The CaO-equivalency of MnO was determined as 0.3 in this study by the following method: The left-hand side term of Eq. (1) was calculated from the experimental data for (mass%P₂O₅), [mass%P] and (mass%Fe₂O)

Fig. 1. Balajiva-type dephosphorization formula.

Fig. 2. Healy-type dephosphorization formula at 1856-1898 K.

and the right-hand side of Eq. (1) except for the (%MnO) term was also calculated. Then, the CaO-equivalency of MnO was estimated from a slope in a plot of the difference between these two values versus MnO contents. More details are given elsewhere.³⁾ This value was different from that (0.6) reported in previous experiments,³⁾ in which the MnO contents were in the range of 0.6-5 mass%. The CaO-equivalency of Al_2O_3 was -0.2 from the estimation using the data of Winkler and Chipman⁴⁾ who used the slags containing 6-11 mass% Al_2O_3 .

A modified Healy-type dephosphorization formula³⁾ is given in Eq. (2) and the present and previous results^{3,4,7)} are plotted in Figs. 2 and 3.

$$\log \left(\frac{\%P}{\{[\%P] \cdot (\%T.Fe)^{5/2}\}} \right) = 0.0720 [(\%CaO) + 0.3(\%MgO) + 0.6(\%P_2O_5) + 0.2(\%MnO) + 1.2(\%CaF_2) - 0.5(\%Al_2O_3)] + 11570/T - 10.52 \quad (2)$$

Fig. 3. Healy-type dephosphorization formula at 1803-1843 and 1900-1945 K.

 Fig. 4. Phosphate capacity, C_p , as a function of slag composition on a mass percent base.

$$+ 0.2(\%MnO) + 1.2(\%CaF_2) - 0.5(\%Al_2O_3)] + 11570/T - 10.52 \quad (2)$$

The CaO-equivalency of MnO in Eq. (2) was obtained as 0.2 in this study by using the method similar to that mentioned above, although that obtained by using the slags with low contents of MnO was determined as 0.6.³⁾ The CaO-equivalency of Al_2O_3 was -0.5 from the estimation using the results of Winkler and Chipman.⁴⁾

Phosphate capacity, C_p , can be defined as follows:

$$C_p = (\%P)/(a_P \cdot a_O^{5/2}) \quad (3)$$

where a_i is the activity of i component relative to a dilute

Fig. 5. Activity coefficient of $P_2O_5(l)$ as a function of slag composition on a mole fraction base at 1856–1898 K.

Fig. 6. Activity coefficient of $P_2O_5(l)$ as a function of slag composition on a mole fraction base at 1803–1846 and 1900–1945 K.

solution of mass percent standard state.

The C_p value can be expressed as a function of slag composition on mass percent base. The values of the CaO-equivalency for slag components were determined from the present and previous^{3,5} results of slag-metal experiments, by using a multiple regression analysis as follows:

$$\log C_p = 0.0938[(\%CaO) + 0.50(\%MgO) + 0.30(\%Fe_2O) + 0.35(\%P_2O_5) + 0.46(\%MnO)] + 32500/T - 17.74 \quad (4)$$

The present and previous^{3,5} results are plotted in Fig. 4, indicating a good linearity.

2.2 Activity Coefficient of P_2O_5

Turkdogan and Pearson¹⁰ expressed the activity coefficient of P_2O_5 , $\gamma_{P_2O_5}$, calculated from Eq. (5) as a function of mole fraction of slag composition.

$$2P + 5O = P_2O_5(l) \quad (5)$$

$$\Delta G_5^\circ = -705400 + 556.5 T \text{ (J/mol)}$$

The following Turkdogan-type formula is derived by using the present and previous^{3–6} results:

$$\log \gamma_{P_2O_5} = -1.02(23X_{CaO} + 17X_{MgO} + 8X_{Fe_2O} - 26X_{P_2O_5} + 14X_{MnO} + 20X_{CaF_2} - 3X_{Al_2O_3}) - 23000/T + 9.49 \quad (6)$$

The coefficient of MnO in the present work was determined as 14, while that in previous report³ was determined as 13 by using the method similar to that used in Eq. (1). The coefficient of Al_2O_3 determined by the data of Winkler and Chipman⁴ was found to be -3 . The present and previous^{3,4} results are shown in Figs. 5 and 6.

2.3 Activity Coefficient of Fe_2O

Activity coefficients of Fe_2O relative to the liquid standard state were calculated by using the present and

Fig. 7. Activity coefficient of $Fe_2O(l)$ as a function of slag composition on a mass percent at 1849–1898 K.

previous^{3–5,11} results for the slag-metal experiments.

$$Fe(l) + O = Fe_2O(l) \quad (7)$$

$$\Delta G_7^\circ = -116100 + 48.79 T \text{ (J/mol)}^{12}$$

Logarithm of activity coefficient of Fe_2O was expressed as a function of slag composition on a mass percent base by the following formula, in which the values of CaO-equivalency were determined by a multiple regression analysis.

$$\log \gamma_{Fe_2O} = -0.0202[(\%CaO) + 0.93(\%MgO) + 1.07(\%Fe_2O) + 1.14(\%MnO) + 0.35(\%SiO_2) + 0.03(\%P_2O_5) + 1.01(\%Al_2O_3)] + 2.053 \quad (8)$$

Fig. 8. Activity coefficient of $\text{Fe}_2\text{O}_3(l)$ as a function of slag composition on a mass percent base at 1803–1846 and 1900–1945 K.

Fig. 9. Phosphorus distribution ratio, L_p , plotted against total Fe content as a function of MnO content at 1873 and 1923 K.

The temperature dependence of $\log \gamma_{\text{Fe}_2\text{O}_3}$ was not observed in the range of 1803 to 1945 K. The present and previous^{3-5,11} results are plotted in Figs. 7 and 8.

It should be emphasized that logarithms of the equilibrium quotients of the dephosphorization reactions such as Eqs. (1), (2) and (4), $\log \gamma_{\text{P}_2\text{O}_5}$ (Eq. (6)) and $\log \gamma_{\text{Fe}_2\text{O}_3}$ (Eq. (8)) could be expressed empirically as a linear function of slag composition, but these formulas can be applied only for the CaO–SiO₂–Fe₂O₃ slags saturated with MgO, which contain limited contents of MnO, P₂O₅, CaF₂ and/or Al₂O₃.

2.4. Phosphorus Distribution Ratio

By using Eq. (2), logarithms of phosphorus distribution ratio $L_p \{=(\text{mass}\% \text{P})/[\text{mass}\% \text{P}]\}$ or $L'_p \{=(\text{mass}\% \text{P}_2\text{O}_5)/[\text{mass}\% \text{P}]\}$ at 1873 and 1923 K are

Fig. 10. Phosphorus distribution ratio, L_p , plotted against MnO content as a function of CaO/SiO₂ ratio on a mass percent base at 1873 and 1923 K.

plotted against the total Fe contents as a function of MnO content in Fig. 9 for the typical BOF slag composition $\{(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)=3.5, (\text{mass}\% \text{MgO})=5, (\text{mass}\% \text{Al}_2\text{O}_3)=2 \text{ and } (\text{mass}\% \text{P}_2\text{O}_5)=3 \text{ on a mass percent base}\}$. The $\log L_p$ values increase drastically up to the $(\text{mass}\% \text{T.Fe})=10-15$ at a given MnO content and reach the maximum without respect to the MnO content. It can be seen that the values of $L_p > 100$ can be obtained at 1923 K by the addition of $(\text{mass}\% \text{MnO}) \leq 10$ in the range of $(\text{mass}\% \text{T.Fe})=8-25$.

The relations between $\log L_p$ and $(\text{mass}\% \text{MnO})$, which were calculated from Eq. (2) for the $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$ ratios of 2, 3 and 4 are shown in Fig. 10. The L_p values decrease linearly with an increase in the MnO content at constant $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$ ratio. The value of $L_p > 100$ can be obtained at 1923 K by adding MnO up to 9 mass% to the slags with the $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$ ratio ≥ 3 . The plant data¹³ are also included by the hatched area, indicating a similar trend and lower L_p values.

3. Effect of MnO on Hot Metal Dephosphorization

The dephosphorization reaction in practical hot metal treatment is known to be controlled by the oxygen potential close to that determined by the Fe/(Fe₂O₃) equilibrium, which is much higher than that by the C/CO equilibrium. It should be noted, however, that the equilibrium phosphorus distribution ratio between Fe₂O₃-containing slags and hot metal cannot be determined in the slag-metal laboratory experiment with remaining the Fe₂O₃ level constant, because of the reduction of Fe₂O₃ in slag by carbon. Therefore, in order to obtain the phosphorus distribution ratios between Fe₂O₃-containing slags and hot metal, those between slags and liquid iron obtained at high temperatures must be extrapolated to the temperature of hot metal treatment. In this case, the extrapolated L_p value must be converted to the value of L_p^h for the hot metal by using the following equation.

Fig. 11. Effects of temperature and oxygen potential on the phosphorus distribution ratio.

$$\log L_p^h = \log L_p + e_p^c \cdot [\%C] + r_p^c \cdot [\%C]^2 \quad \dots\dots (9)$$

where e_p^c and r_p^c represent the first-order (0.126) and the second-order (0.014) interaction parameters,¹⁴⁾ respectively.

The values of L_p^h at 1623 K and those of L_p at 1923 K for the BOF slag $\{(\%MgO)=5, (\%MnO)=4, (\%Al_2O_3)=2 \text{ and } (\%P_2O_5)=3 \text{ on a mass percent base}\}$ were obtained by using Eq. (2) and plotted against the $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)$ ratio as a function of the total Fe content in the left-hand side of Fig. 11. The L_p^h values at 1623 K for hot metal were calculated from Eq. (9) by using the values for the interaction parameters e_p^c and r_p^c and the content of carbon (4.77 mass%¹⁵⁾) saturated at 1623 K. It is obvious from the left-hand side of Fig. 11 that the decrease in the temperature of 300 K enhances the L_p values in the order of 10^2 . In practical operation, however, the carbon is not saturated and the oxygen potential is not so high as that determined by the Fe/(Fe₂O) equilibrium. Furthermore, the L_p^h and L_p values are more strongly dependent on the $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)$ ratio rather than the total Fe level. The solid lines in Fig. 11 correspond to the liquid region predicted from the CaO-SiO₂-Fe₂O phase diagram. Although the liquid region may be larger than these solid lines due to the presence of other slag components, it seems to be difficult to increase the $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)$ ratio more than 1.5 in the range of $(\text{mass}\%T.Fe) \leq 30$ without adding flux agent such as CaF₂.

The values of L_p^h for the oxygen potential controlled by the Fe/(Fe₂O) equilibrium were calculated at 1623 K by using Eqs. (2) and (9). Those for the oxygen potential controlled by the C/CO ($P_{CO}=1 \text{ atm}$) equilibrium were calculated by using Eq. (4). The values for L_p^h at Fe/(Fe₂O) equilibrium were not determined by using Eq. (4), since the estimation of oxygen potential from the γ_{FeO} value, which was extrapolated from the data at 1803–1945 K, could not be accurately made. These values are plotted against the $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)$ ratio as a function of the total Fe content in the left-hand side of Fig. 11. It can be seen that in hot metal dephosphorization the control of oxygen

Fig. 12. Phosphorus distribution ratio plotted against total Fe content as a function of MnO content at 1623 K.

potential as close as that by the Fe/(Fe₂O) equilibrium is more important than the increase in the $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)$ ratio. The control of oxygen potential can be made much easier in combined blowing converter where top and bottom gas flow rates can be varied. Knowledge of the effect of MnO on the L_p^h values in hot metal dephosphorization become significant, when the BOF slags with high MnO content, which is increased by the addition of manganese ore, is considered to be recycled to hot metal dephosphorization.

Figure 12 shows the relation between the L_p^h values and the total Fe contents as a function of MnO content for the BOF slag $\{(\%MgO)=3, (\%Al_2O_3)=1, (\%P_2O_5)=6 \text{ and } (\%CaO)/(\%SiO_2) \text{ ratio}=1 \text{ or } 2 \text{ on a mass percent base}\}$. These relations were calculated from Eqs. (2) and (9) at $[\text{mass}\%C]=3.5$, although the liquid region of these flux compositions are not certain at present. The L_p^h values increase with an increase in total Fe up to about 15 mass%, irrespective to the MnO content. The results of L_p^h in a 6 ton converter,²⁾ which are represented by a shaded area, are significantly lower than those in this study. This is due to the lower oxygen potential, compared with that determined by the Fe/(Fe₂O) equilibrium in the present work. It should be pointed out, however, that the value of about $L_p^h=100$ was obtained at the slag composition with a low basicity of $(\text{mass}\%CaO)/(\text{mass}\%SiO_2)=0.9\text{--}1.1$ and $(\text{mass}\%T.Fe)=10$, using a 6 ton converter.²⁾

4. Optimum Slag Volume in Dephosphorization

From the mass balance relation between slag and metal, the following relation with respect to phosphorus can be derived:

$$[\%P]_1 = [\%P]_0 / (1 + L_1 \cdot W_1 \times 10^{-3}) \quad \dots\dots (10)$$

where $[\%P]_0$ is the initial phosphorus content, $[\%P]_1$ is the phosphorus content after a treatment, L_1 is the phosphorus distribution ratio L_p and W_1 is the flux

consumption (kg/t metal).

The final P content after dephosphorization treatments of n times can be written from Eq. (10) as

$$[\%P]_n = [\%P]_0 / \{(1 + L_1 \cdot W_1 \times 10^{-3}) \cdot \dots \cdot (1 + L_n \cdot W_n \times 10^{-3})\} \quad \dots \dots \dots (11)$$

where L_n and W_n are the phosphorus distribution ratio, L_p , and the flux consumption (kg/t metal) at the dephosphorization treatments of n times.

Total flux consumption can be calculated from Eq. (11) in the hot metal and steel dephosphorization where phosphorus is reduced from 0.10 to 0.015 mass% after the treatments of 1 to 4 times. For the purpose of simplicity, the assumptions such as $L_1 = L_2 = L_3 = L_4$ and $W_1 = W_2 = W_3 = W_4$ are made. The results for $L_p = 50$, 100 and 200 are shown in Fig. 13. It is clear that the considerable reduction of total flux consumption can be possible in multiple treatments and, in particular, the degree of the reduction is the greatest in the case of double treatments. The reduction of phosphorus from 0.10 to 0.015 mass% for single treatment by the flux with $L_p = 100$ requires 57 kg/t, whereas that for double

treatments by the same flux requires 32 kg/t. This implies that almost the same total flux consumption at a given degree of dephosphorization can be obtained in the double treatments (63 kg/t) by the flux with $L_p = 50$ and in the single treatment (57 kg/t) by the flux with $L_p = 100$.

In decarburization period, the slag volume as well as the total Fe content has to be decreased as much as possible from the aspects of the refractory erosion, the phosphorus reversion in deoxidation after tapping, the manganese ore addition and so on. However, as is clear in Fig. 13, the steel dephosphorization coupled with hot metal dephosphorization is favorable in view of the minimization of the flux consumption. Furthermore, the flux with high L_p value such as about 200 is not available in the CaF_2 -free hot metal dephosphorization, thus leading to the increase in the flux consumption. On the basis of the above-mentioned reasons, the hot metal dephosphorization coupled with steel one is considered to be of crucial importance.

In the left-hand side of Fig. 14, the phosphorus contents after hot metal treatment, $[\%P]_f^h$, are plotted against the flux consumption in the case of the initial P level, $[\%P]_i^h = 0.10$. Similarly, in the right-hand side of Fig. 14, the P contents before steel dephosphorization, $[\%P]_i^s$, are plotted on the same scale of $[\%P]_f^h$ against the flux consumption in the case of the final P content, $[\%P]_f^s = 0.015$. As shown in the left-hand side diagram, the $[\%P]_f^h$ values do not decrease linearly with increasing the flux consumption. Accordingly, about 15 kg/t (ac in Fig. 14) is required in the hot metal dephosphorization of using the flux with $L_p^h = 100$, when phosphorus is reduced from 0.10 to 0.04 mass%. On the other hand, 57 kg/t is required, when phosphorus is reduced from 0.10 to 0.015 mass%. The $[\%P]_i^s$ values increase linearly with an increase in the flux consumption, when the final P content, $[\%P]_f^s$, is fixed as 0.015, as shown in the right-hand side diagram. The P content of 0.04 mass% after hot metal dephosphorization by the flux with $L_p^h = 100$ can be reduced to 0.015 mass% in steel dephosphorization by using the flux with $L_p = 100$ (bc: 17 kg/t). In this double dephos-

Fig. 13. Effect of treatment times on the total flux consumption.

Fig. 14. Material balance in hot metal and steel dephosphorization.

phosphorization process, total flux consumption is reduced about 32 kg/t, whereas that in single process in hot metal or steel requires about 57 kg/t.

The phosphorus contents after single treatment by the flux with $L_p=100$ and 200 (broken lines) and that after double treatments by the flux with $L_p=100$ (solid line) are plotted against the total flux consumption in Fig. 15, in which the initial P content is 0.10 mass%. When the flux with $L_p^h=200$ is used in single treatment of hot metal dephosphorization to reduce the P level from 0.10 to 0.015 mass%, the CaF_2 -containing flux must be used. In this case, however, the flux consumption is small about 28 kg/t. Similarly, when the flux with $L_p=200$ is used in single treatment of steel dephosphorization to reduce the same degree, the flux without MnO and $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2) \geq 3$ is required, as shown in Fig. 10. However, although the L_p value of 100 can be obtained in the flux with $(\text{mass}\% \text{MnO})=9$, $(\text{mass}\% \text{T.Fe})=10$ and $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)=3$ on a mass percent base, the flux consumption in single treatment requires about 57 kg/t. Therefore, for the purpose of the CaF_2 -free

Fig. 15. Relation between phosphorus content and total flux consumption in single and double treatments.

Fig. 16. Material balance in hot metal dephosphorization when BOF slag is recycled.

refining, the flux with $L_p^h=100$ which consists of the $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)=1$, $(\text{mass}\% \text{MnO}) \leq 20$ and $(\text{mass}\% \text{T.Fe}) \geq 6$, as shown in Fig. 12, is used in hot metal dephosphorization and the flux with $L_p=100$ which consists of $(\text{mass}\% \text{MnO}) \leq 10$, $(\text{mass}\% \text{T.Fe})=8-25$ and $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)=3.5$ on a mass percent base, as shown in Fig. 9, is used in steel dephosphorization. In such double slag treatments, 32 kg/t of the flux consumption is needed to decrease $[\%P]_i^h=0.10$ to $[\%P]_f^s=0.015$.

Hot metal dephosphorization by using the recycled slag after steel dephosphorization as a part or whole will be discussed subsequently. The mass balance relation in this case can be written as

$$[\%P]_i^h + \{(\%P_2O_5)^R/2.29\} \cdot W^R \times 10^{-3} = [\%P]_f^h \cdot (1 + L_p^h \cdot W_{\text{flux}}^h \times 10^{-3}) \quad \dots\dots\dots(12)$$

where $(\%P_2O_5)^R$ and W^R are the P_2O_5 content in recycled slag and the amount of the recycled slag (kg/t hot metal), respectively.

The mass balance relation in steel dephosphorization can be written as

$$[\%P]_i^s = [\%P]_f^s (1 + L_p^s \cdot W_{\text{flux}}^s \times 10^{-3}) = [\%P]_f^s + \{(\%P_2O_5)^s_f/2.29\} \cdot W_{\text{flux}}^s \times 10^{-3} \quad \dots\dots\dots(13)$$

where $(\%P_2O_5)^s_f$ and W_{flux}^s are the P_2O_5 content in slag after dephosphorization and the flux consumption (kg/t steel), respectively.

The relations between $[\%P]_i^s$ and $(\%P_2O_5)^s_f$ or L_p in Eq. (13) are plotted as a function of W_{flux}^s (20, 40 and 60 kg/t) in the right-hand side of Fig. 16. In this calculation, the value of $[\%P]_f^s$ is fixed as 0.015 mass%. By using the flux of $L_p=90$ with $W_{\text{flux}}^s=20$ kg/t, the phosphorus level after hot metal dephosphorization, $[\%P]_f^h$ ($=[\%P]_i^s$) must be lowered to 0.042 from $[\%P]_i^h=0.10$ and the P_2O_5 content after steel dephosphorization, $(\%P_2O_5)^s_f$, is calculated to be about 3 mass%.

When the slag after steel dephosphorization is recycled to the hot metal dephosphorization, the relations between

$[\%P]_f^h$ and $W_{flux}^h (\geq W^R)$ were calculated by using Eq. (12). The results for $L_p^h=100$ and 200 are plotted by solid lines in the left-hand side of Fig. 16. The result for no recycle of BOF slag, which is calculated by Eq. (12) for $W^R=0$ is shown by broken line. When the hot metal dephosphorization is carried out by the recycled slag of $L_p^h=100$ with $W^R (=W_{flux}^h)=20$ kg/t, the initial phosphorus in hot metal, $[\%P]_i^h=0.10$ can be lowered to 0.042 (point a). Similarly, by using the recycled slag of $L_p^h=100$ with $W^R (=W_{flux}^h)=40$ kg/t or the flux of $L_p^h=100$ with $W_{flux}^h=40$ kg/t which is the sum of $W^R=20$ kg/t plus new flux of 20 kg/t, the phosphorus can be reduced from 0.10 to 0.022 mass% (point b). After the hot metal dephosphorization using the flux of $L_p^h=100$ with $W_{flux}^h \geq 57$ kg/t (point c) or the flux of $L_p^h=200$ with $W_{flux}^h \geq 29$ kg/t (point d), dephosphorization is unnecessary in steel.

When the broken line (no recycling) of $L_p^h=100$ is compared with that of a solid line (recycling) of $L_p^h=100$, it can be seen that the P_2O_5 content in recycled slag does not influence the relation between $[\%P]_i^h$ and W_{flux}^h . This clearly demonstrates that the use of the recycled slag and the double slag treatments reduce the total flux consumption to considerable degree. It should be pointed out that for the high value of L_p^h such as 100 in the hot metal dephosphorization without using CaF_2 as a flux agent, the oxygen potential must be controlled as close as possible to that determined by the $Fe/(Fe_2O)$ equilibrium.

5. Conclusions

By using the formulas for modified Healy-type dephosphorization and phosphate capacity along with the mass balance relation, the hot metal and steel dephosphorization with MnO -containing slags was thermodynamically assessed in view of the use of the CaF_2 -free flux and of the minimum slag volume. The following conclusions were derived:

(1) The phosphorus distribution ratios between $MnO(8-16 \text{ mass\%})$ -containing MgO_{sat} - CaO - SiO_2 -

Fe_2O slags and liquid iron at 1873 K decreased with MnO content at a given total Fe content and $(\text{mass\%}CaO)/(\text{mass\%}SiO_2)$ ratio.

(2) The phosphorous distribution ratios increased considerably with an increase in the $(\text{mass\%}CaO)/(\text{mass\%}SiO_2)$ ratio rather than the increase in total Fe content. However, in hot metal dephosphorization, the oxygen potential was found to be most influential factor and should be controlled as close as possible to that by the $Fe/(Fe_2O)$ equilibrium.

(3) By using the flux with a low basicity of the $(\text{mass\%}CaO)/(\text{mass\%}SiO_2)$ ratio=1-2, phosphorus can be reduced to a satisfactory degree in hot metal dephosphorization. In this case, however, steel dephosphorization should be coupled in view of the minimization of the slag volume.

REFERENCES

- 1) K. Yoshida, I. Yamazaki, Y. Tozaki, N. Aoki, J. Yoshiyama and K. Arai: *Tetsu-to-Hagane*, **76** (1990), 1817.
- 2) Y. Ogawa, M. Yano, M. Matsuo and Y. Demote: *CAMP-ISIJ*, **6** (1993), 1074.
- 3) H. Suito and R. Inoue: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 40.
- 4) T. B. Winkler and J. Chipman: *Trans. AIME*, **167** (1946), 111.
- 5) H. Suito, R. Inoue and M. Takada: *Trans. Iron Steel Inst. Jpn.*, **21** (1981), 250.
- 6) H. Suito and R. Inoue: *Trans. Iron Steel Inst. Jpn.*, **22** (1982), 869.
- 7) K. Balajiva, A. G. Quarrell and P. Vajragupta: *J. Iron Steel Inst.*, **153** (1946), 115.
- 8) G. W. Healy: *J. Iron Steel Inst.*, **208** (1970), 664.
- 9) H. Suito and R. Inoue: *ISIJ Int.*, **35** (1995), 266.
- 10) E. T. Turkdogan and J. Pearson: *J. Iron Steel Inst.*, **173** (1953), 217.
- 11) R. Inoue, H. Suito and M. Ohtani: *Bull. Res. Inst. Miner. Dressing. Metall., Tohoku University*, **42** (1986), 25.
- 12) H. Suito and R. Inoue: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 301.
- 13) J. Nakajima, H. Goto, N. Ogibayashi and M. Nasu: *CAMP-ISIJ*, **4** (1991), 277.
- 14) H. G. Hadrys, M. G. Froberg and J. F. Elliott: *Metall. Trans.*, **1** (1970), 1867.
- 15) F. Neumann, H. Schenck and W. Patterson: *Giesserei*, **23** (1959), 1217.