

Control of Oxygen Potential and Its Effect on Dephosphorization in Ferromanganese

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ABSTRACT

The relation of L_P and L_{Mn} with C content in ferromanganese was tested by means of equilibrium experiments of P, Mn in ferromanganese and BaO—BaF₂—MnO slag system. The results show that there exists in ferromanganese an optimum C content $[C]^*$ corresponding to maximum L_P and minimum L_{Mn} , which is closely related to P_{O_2} in the system and P activity in the alloy. The control limits of P_{O_2} in dephosphorization of ferromanganese is then analyzed. The theoretical limits and measures to improve ferromanganese dephosphorization with BaO—based slag are studied comprehensively based on previous research.

KEY WORDS Ferromanganese, dephosphorization
 P_{O_2} , activity

1 Introduction

The dephosphorization of ferroalloys is far more difficult than that of steels, while P content of ferroalloys has direct influence on that of steel products and therefore attracts special attention. The existing research is mainly focused on thermodynamic properties of various alloy melts and development of new slag system with high dephosphorization abilities.^[1-3] However, the significant influence of P_{O_2} and temperature on oxidizing dephosphorization, which seems to have been proved by previous research, was neglected. As for ferromanganese dephosphorization,

Mn and Fe share the similar properties. The activity of P in ferromanganese is less than in molten steel (With the same P contents), but it is not the sole key factor affecting ferromanganese dephosphorization. Ferromanganese has low melting point, suitable for low temperature dephosphorization. Therefore, another key factor affecting ferromanganese dephosphorization is P_{O_2} . For ferrochromium and some other alloys, P_{O_2} still plays an important role in dephosphorization even though its effects are sometimes ignored. In this paper, experiments were carried out to study the effect of P_{O_2} on oxidizing dephosphorization firstly, and then P_{O_2} control methods and control limits were theoretically analyzed. Finally, theoretical limits of oxidizing dephosphorization in ferromanganese underwent comprehensive analyses based on previous research.

2 Experiment and Result

The experiments were carried out in high temperature with silicomolybdenum rod furnace. And equilibrium experiments of P and Mn in ferromanganese melts and dephosphorization slag system was adopted. The alloy melt consisting of pure iron, electrolyzed manganese, ferrophosphorus and graphite powder are expressed as Mn(60%)—Fe—C(saturate)—P, in which contents of Mn, P are fixed and that of C are not. BaO(50%)—BaF₂(30%)—MnO₂(20%) slag system was mixed with BaO, BaF₂, and MnO₂ chemical reagents in proper proportion. The melt and slag were put together in MgO crucible and then in the furnace. The equilibrium experiment was held for 10h at 1673K. The sample was taken out and underwent chemical

chemical reagents in proper proportion. The melt and slag were put together in MgO crucible and then in the furnace. The equilibrium experiment was held for 10h at 1673K. The sample was taken out and underwent chemical analysis after experiment. The relation of L_P and L_{Mn} with C content was measured and shown in Fig. 1 and Fig. 2.

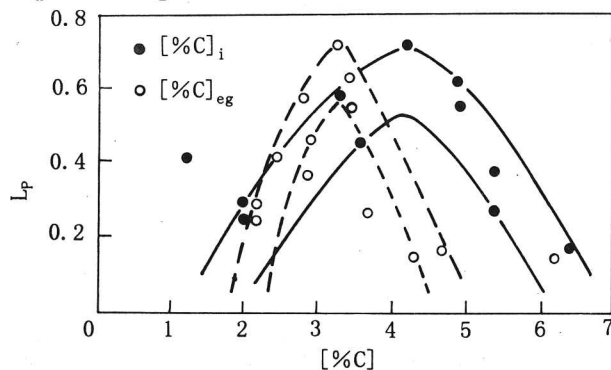


Fig. 1 Relationship between L_P and $[\%C]_i$, $[\%C]_{eg}$

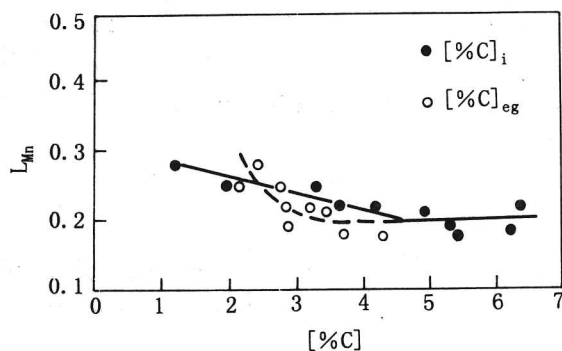


Fig. 2 Relationship between L_{Mn} and $[\%C]_i$, $[\%C]_{eg}$

The results show that L_P is in parabolic change with contents of both equilibrium $[C]_{eq}$. And relevant initial $[C]_i$, with peak as maximum L_P which corresponds to optimum $[C]^*$. It can be seen in Fig. 1 that $[C]^*$ and $[C]_i^*$ are around 3.20% and 4.20% respectively. When $[C] < [C]^*$, L_P will increase with $[C]$ and reach the maximum value until $[C] = [C]^*$. When $[C] > [C]^*$, L_P decreases with $[C]$. It is also shown in Fig. 1 that average carbon loss during ferromanganese dephosphorization is about 1%.

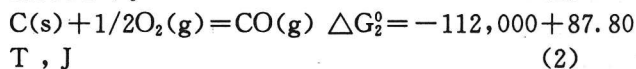
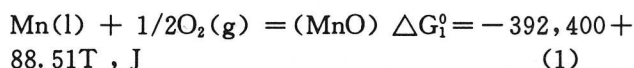
The relation of L_{Mn} with $[C]$ is not as evident as that of L_P , but similar change law can still be seen (Fig. 2). L_{Mn} will decrease with the increase of $[C]$ and reach minimum value until $[C] = [C]^*$. Further increase of $[C]$ has almost no effect on L_{Mn} . In addition, $[C]^*$

corresponding to L_{Mn} and L_P are absolutely the same by comparing Fig. 1 with Fig. 2.

3 Discussion

3.1 Effect of oxygen potential on dephosphorization

The change law of L_P and L_{Mn} with $[C]$ shown in Fig. 1 and Fig. 2 has close relation with P_{O_2} in the ferromanganese dephosphorization system. Temporary P_{O_2} in reacting area might be increased by adding oxidizing agent and improving oxygen blowing, but equilibrium P_{O_2} is determined by equilibrium relations of various elements with oxygen in the melts. The P_{O_2} in this system is dependent of the following reactions;



It should be noted that there are no data on activities of components in Mn-based slag and standard states. By combining Eq. (1) and (2), the follows are obtained

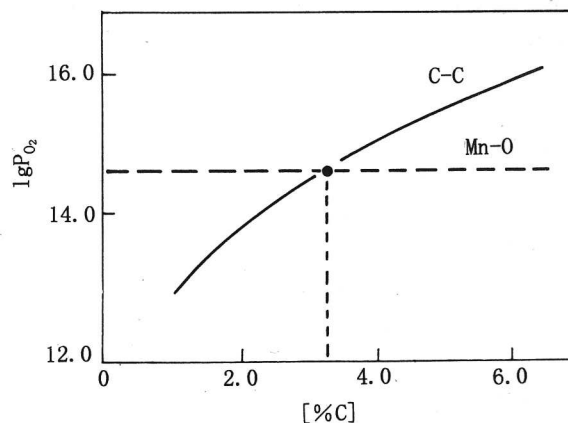
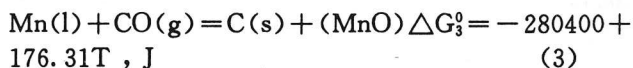


Fig. 3 The relationship between oxygen potential of Mn-O, C-O equilibria and $[C]$

When Eq. (3) reaches equilibrium, $\Delta G_3^0 = 0$, namely P_{O_2} controlled by C is equal to that by Mn, Then the follow is obtained

$$\ln K_3 = \ln \frac{a_{\text{MnO}} \cdot a_{\text{C}}}{a_{\text{Mn}}} = -1.406 \quad (4)$$

Where $\ln K_3$ is derived from ΔG_3° based on $T = 1673\text{K}$ and $P_\infty = 1\text{atm}$.

It is reported in Ref. [4] that a_{Mn} suitable for this system is 0.18. MnO_2 makes up 20% of this dephosphorization slag and its molar fraction X_{MnO} is obtained as 0.352 after converted into MnO . Fig. 2 shows that MnO content in the system saw no change after reaching equilibrium.

$$\ln r_{\text{C}} = -1.635 + 10.889X_{\text{C}} + 1.467X_{\text{Fe}} \quad [1]$$

The above equation is substituted into (4) and X_{C} is obtained as 0.135 from Eq. (3). Then $[\text{C}]$ is calculated as 3.3% after conversion. All those are in agreement with experimental results shown in Fig. 1–2. It means that P_{O_2} is controlled by $\text{Mn}-\text{O}$ equilibrium when $[\text{C}] < 3.3\%$ and by $\text{C}-\text{O}$ equilibrium when $[\text{C}] > 3.3\%$. It can be calculated by substituting the data at equilibrium when $[\text{C}] > 3.3\%$. It can be calculated by substituting the data at equilibrium into Eq. (1) or Eq. (2) that $P_{\text{O}_2} = 2 \times 10^{-15}\text{atm}$. The values of P_{O_2} at $\text{Mn}-\text{O}$ and $\text{C}-\text{O}$ equilibrium are obtained from Eq. (1) and (2) and their relations with C content are shown in Fig. 3.

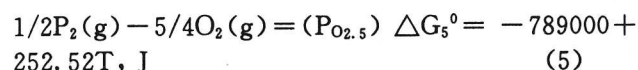
When $[\text{C}] < [\text{C}]^*$, P_{O_2} of the whole system is controlled by $\text{Mn}-\text{O}$ equilibrium. The change of C content has minor effect on Mn activity because Mn content is stable in the alloy. Meanwhile, the components of the slag are also stable and P_{O_2} is a constant as a whole. e_{P}^{C} obtained by previous research is 12.87^[2], that is, P activity increases with the increase of C content. It also shows that L_{P} increases with $[\text{C}]$. When $[\text{C}] > [\text{C}]^*$, P_{O_2} of the system is controlled by $\text{C}-\text{O}$ equilibrium and decreases with the increase of $[\text{C}]$. P_{O_2} has larger effect on L_{P} than phosphorus activity and L_{P} decreases with $[\text{C}]$. On the whole, the relation of L_{P} with $[\text{C}]$, i.e. P_{O_2} is in agreement with that shown in Fig. 1. The change of L_{Mn} with $[\text{C}]$ is due to the same reason and the difference only lies in that C has smaller effect on Mn activity and e_{Mn}^{C} is negative^[1] (Fig. 2).

According to the above research, proper C content might result in optimum dephosphorization effect in ferromanganese by using BaO —based slag. It is beneficial to both dephosphorization and Mn preservation

by adding 15%–20% MnO into the slag. The proper average C content at equilibrium is 3.3% and related initial C content should be controlled within 4.2%–4.5% under this condition.

3.2 Theoretical limit of ferromanganese dephosphorization

The basic reactions of oxidizing dephosphorization are as follows

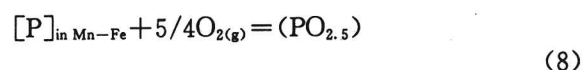


$$K_5 = \frac{a_{\text{P}_{\text{O}_{2.5}}}}{P_{\text{P}_2}^{1/2} \cdot P_{\text{O}_2}^{5/4}} = \frac{r_{\text{P}_{\text{O}_{2.5}}} \cdot X_{\text{P}_{\text{O}_{2.5}}}}{P_{\text{P}_2}^{1/2} \cdot P_{\text{O}_2}^{5/4}} \cdot b \quad (6)$$

where b is conversion coefficient of $\text{P}_{\text{O}_{2.5}}$ between mass percentage and molar fraction, and in this system $b = 0.0163$. If P capacity (C_{P}) is defined as $(\% \text{P}_{\text{O}_{2.5}}) / (P_{\text{P}_2}^{1/2} \cdot P_{\text{O}_2}^{5/4})$, it has already been measured by previous work that $C_{\text{P}} = 10^{25}$ ^[2] in $\text{BaO}-\text{BaF}_2-\text{MnO}$ system. It is calculated by introducing Eq. (6) that $r_{\text{P}_{\text{O}_{2.5}}} = 10^{-11.77}$ in this slag system. There still exists a reaction



Introducing Eq. (5) into (7), the dephosphorization reaction in ferromanganese is obtained as follows



$$K_3 = \frac{r_{\text{P}_{\text{O}_{2.5}}} \cdot b \cdot (\% \text{P}) \cdot M_{\text{P}_{\text{O}_{2.5}}} / M_{\text{P}}}{f_{\text{P}} \cdot [\% \text{P}] \cdot P_{\text{O}_2}^{5/4}} \quad (9)$$

$L_{\text{P}} = (\% \text{P}) / (\% \text{P})$ is adopted to describe dephosphorization limit. By substituting the data obtained into Eq. (9) and taking the logarithm, the following equation is obtained

$$\text{Lg} L_{\text{P}} = (\text{lg} K_3 + 5/4 \text{lg} P_{\text{O}_2} + 13.20) + 0.24[\% \text{C}] \quad (10)$$

Where $\text{lg} f_{\text{P}} = e_{\text{P}}^{\text{C}} [\% \text{C}]$, and $e_{\text{P}}^{\text{C}} = 0.24$ ^[3] in ferromanganese. When $[\text{C}] < [\text{C}]^*$, P_{O_2} is a constant controlled by $\text{Mn}-\text{O}$ equilibrium. Let the terms in

parenthesis be A, and substitute the data related to LgP_L and $[\%C]$ into Eq. (10). The following data are obtained from calculation: $A = -0.185$, $lgK_3 = 4.99$ and $\Delta G_3^0 = -159800J$ (at 1673K) [using Eq. (8)]. Then the solution free energy of P in ferromanganese is obtained: $\Delta G_3^0 = -206600J$ (at 1673K). When $[C] > [C]^*$, Po_2 is controlled by C-O equilibrium. The following is obtained from Eq. (1).

$$LgPo_2 = 2(-8.082 - lg r_C - lg X_C) \quad (11)$$

It is calculated by substituting $ln r_C$ introduced in Ref. [1] into Eq. (11) and converting X_C into $[\%C]$ that $lgPo_2 = -12.07 - 0.338[\%C] - 0.0066[\%Fe] - 2lg [\%C]$. The theoretical limits of dephosphorization in ferromanganese using BaO based slag system at 1673K is obtained by substituting $lgPo_2$ into Eq. (10)

$$LgP_L = \begin{cases} -0.185 + 0.24[\%C] & [C] < [C]^* \\ 3.10 - 0.18[\%C] - 0.0165[\%Fe] - 2.5lg [\%C] & [C] > [C]^* \end{cases} \quad (12)$$

The final P contents with various slag used might be worked out by applying Eq. (12) if initial P content in the alloys is known. It is indicated by comparing the solution free energy of P in ferromanganese and that in iron melt, $\Delta G^0 = -122200 - 19.25T J$, that property of metal phase is one of the key factors hindering ferromanganese dephosphorization. The analyses show that Po_2 is another key factor. As the metal phase properties of ferromanganese are stable,

proper choice of Po_2 is an effective measure to improve dephosphorization and preserve Mn.

4 Conclusions

(1) There exists in ferromanganese an optimum $[C]^*$ which corresponds to maximum L_P and minimum L_{Mn} . $[C]^*$ is around 3.3% with initial $[C]$ controlled between 4.2% - 4.5%. The existence of $[C]^*$ is due to P activity in the alloy and Po_2 in the system.

(2) When adopting BaO-BaF₂-MnO slag system, the theoretical limits of dephosphorization in ferromanganese are obtained as follows

$$LgP_L = \begin{cases} -0.185 + 0.24[\%C] & [C] < [C]^* \\ 3.10 - 0.18[\%C] - 0.0165[\%Fe] - 2.5lg [\%C] & [C] > [C]^* \end{cases}$$

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