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—BaF$_2$—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 $P_0$, in the system and P activity in the alloy. The control limits of $P_0$, 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 $P_0$, 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 $P_0$, 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 $P_0$. For ferrochromium and some other alloys, $P_0$, 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 $P_0$, on oxidizing dephosphorization firstly, and then $P_0$, 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%)—BaF$_2$(30%)—MnO$_2$(20%) slag system was mixed with BaO, BaF$_2$, and MnO$_2$ 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 $M_{Mn}$ with C content was measured and shown in Fig. 1 and Fig. 2.

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 $[C]_i$ and $[C]_{eq}$ are around 3.20% and 4.20% respectively. When $[C]<[C]_i$, $L_P$ will increase with $[C]$ and reach the maximum value until $[C]=[C]_i$. When $[C]>[C]_i$, $L_P$ decreases with $[C]$. It is also shown in Fig. 1 that average carbon loss during ferromanganese dephosphorization is about 1%. The relation of $M_{Mn}$ with $[C]$ is not as evident as that of $L_P$, but similar change law can still be seen. $L_{Mn}$ will decrease with the increase of $[C]$ and reach minimum value until $[C]=[C]_i$. Further increase of $[C]$ has almost no effect on $L_{Mn}$. In addition, $[C]_i$ 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 $M_{Mn}$ 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:

$$\text{Mn}(l) + \frac{1}{2}O_2(g) = (\text{MnO}) \quad \Delta G^f = -392,400 + 88.51T \; J$$

(1)

$$C(s) + \frac{1}{2}O_2(g) = CO(g) \quad \Delta G^f = -112,000 + 87.80 \; T \; J$$

(2)

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

$$\text{Mn}(l) + CO(g) = C(s) + (\text{MnO}) \quad \Delta G^f = -280400 + 176.31T \; J$$

(3)

When Eq. (3) reaches equilibrium, $\Delta G^f = 0$, namely $P_{O_2}$ controlled by C is equal to that by Mn, Then the follow is obtained
\[ \ln K_s = \ln \frac{a_{\text{MnO}} \cdot a_C}{a_{\text{Mn}} \cdot a_P} = -1.406 \quad (4) \]

Where \( \ln K_s \) is derived from \( \Delta G^\circ \) based on \( T=1673K \)
and \( P_{O_2}=1\text{atm} \).

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

\[ \ln r_c = -1.635 + 10.889 X_C + 1.467 X_{\text{P}} \]  \[ (5) \]

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

When \( [C]<[C]^* \), \( P_{O_2} \) of the whole system is
controlled by \( \text{Mn-O} \) equilibrium. The change of \( C \) content has
minor effect on \( \text{Mn} \) activity because \( \text{Mn} \) 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. \( e^C \)
and \( e^P \) 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 \( [C] \). When \( [C]>[C]^* \), \( P_{O_2} \)
of the system is controlled by \( \text{C-O} \) equilibrium and
decreases with the increase of \( [C] \). \( P_{O_2} \) has larger effect
on \( L_P \) than phosphorus activity and \( L_P \) decreases
with \( [C] \). On the whole, the relation of \( L_P \) with \( [C] \), i.e.
\( P_{O_2} \), is in agreement with that shown in Fig. 1. The
change of \( L_{\text{Mn}} \) with \( [C] \) is due to the same reason and the
difference only lies in that \( C \) has smaller effect on
\( \text{Mn} \) activity and \( e^P \) is negative [1] (Fig. 2).

According to the above research, proper \( C \) content
might result in optimum dephosphorization effect in
ferromanganese by using \( \text{BaO} - \text{based} \) slag. It is
beneficial to both dephosphorization and \( \text{Mn} \) preservation
by adding 15%–20% \( \text{MnO} \) 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

\[ \frac{1}{2}P_i(g) - \frac{5}{2}O_2(g) = (P_{O_2})_s \quad \Delta G_s = -789000 + 
252.52 T, J \quad (5) \]

\[ K_s = \frac{P_{O_2} \cdot X_{P_{O_2}} \cdot b}{P_{P_2} \cdot P_{O_2}^4} \quad (6) \]

where \( b \) is conversion coefficient of \( P_{O_2} \) between mass
percentage and molar fraction, and in this system \( b = 
0.0163 \). If \( P \) capacity (\( C_P \)) is defined as \( (\%P_{O_2})/ 
(P_{P_2}^{1/2} \cdot P_{O_2}^{3/4}) \), it has already been measured by
previous work that \( C_P = 10^{6}[2] \) in \( \text{BaO-BaF}_2-\text{MnO} 
\) system . It is calculated by introducing Eq. (6) that
\( r_{P_{O_2}} = 10^{-11.77} \) in this slag system . There still exists a
reaction

\[ \frac{1}{2}P_i(g) - \frac{5}{2}O_2(g) = \frac{([P]_{\text{Mn-Fe}})_{slag}}{([P]_{\text{Mn-Fe}})_{slag}} \quad (7) \]

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

\[ [P]_{\text{Mn-Fe}} + \frac{5}{2}O_2(g) = (PO_{2.5})_s \quad (8) \]

\[ K_s = \frac{r_{P_{O_2}} \cdot b \cdot (\%P) \cdot M_{P_{O_2}}}{f_P \cdot [\%P] \cdot P_{O_2}^{3/4}} \quad (9) \]

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

\[ \log L_P = \log K_s + \log \frac{5}{2} + 13.20 + 0.24 [\%C] \quad (10) \]

Where \( \log _P = \epsilon_P [\%C] \) and \( \epsilon_P = 0.24 \) is
ferromanganese. When \( [C]<[C]^* \), \( P_{O_2} \) is a constant
controlled by \( \text{Mn-O} \) equilibrium. Let the terms in
parenthesis be A, and substitute the data related to \( \log L_p \) and \( [\%C] \) into Eq. (10). The following data are obtained from calculation: \( A = -0.185 \), \( \log K_s = 4.99 \) and \( \Delta G_0^* = -15800(J/\text{mol}) \) (at 1673K) [using Eq. (8)]. Then the solution free energy of P in ferromanganese is obtained, \( \Delta G_0^* = -206600(J/\text{mol}) \) (at 1673K). When \( [C]>[C]^* \), \( P_2 \) is controlled by \( C/O \) equilibrium. The following is obtained from Eq. (1).

\[ LGP_2 = 2(-8.082 - \log r_c - \log X_c) \]  

(11)

It is calculated by substituting \( \log r_c \) introduced in Ref. [1] into Eq. (11) and converting \( X_c \) into \( [\%C] \) that \( \log P_2 = -12.07 - 0.338[\%C] - 0.0066[\%Fe] - 2\log [\%C] \). The theoretical limits of dephosphorization in ferromanganese using BaO based slag system at 1673K is obtained by substituting \( \log P_2 \) into Eq. (10)

\[ LGP_L = -0.185 + 0.24 \times [\%C] \times [C]>[C]^* \]
\[ 3.10 - 0.18[\%C] - 0.0165[\%Fe] - 2.5\log [\%C] \times [C]>[C]^* \]

(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, \( \Delta G^* = -122200 - 19.25T \) J, that property of metal phase is one of the key factors hindering ferromanganese dephosphorization. The analyses show that \( P_2 \) is another key factor. As the metalphas properties of ferromanganese are stable, proper choice of \( P_2 \) 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 \( L_{Mn} \) \( [C]^*_m \) 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 \( P_2 \) in the system.

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

\[ LGP_L = -0.185 + 0.24 \times [\%C] \times [C]<[C]^* \]
\[ 3.10 - 0.18\times [\%C] - 0.0165\times [\%Fe] - 2.5\times [\%C] \times [C]>[C]^* \]

REFERENCES