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Effects of oxygen potential and flux composition on dephosphorization and rephosphorization of molten steel

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Abstract: The dephosphorization experiments of low phosphorus containing steel by CaO-based and BaO-based fluxes were carried out. The effects of the oxygen potential in molten steel and the BaO content in the slag on dephosphorization and rephosphorization of molten steel were analyzed. The results showed that the dephosphorization ratio of more than 50% and the ultra-low phosphorus content of less than 0.005% in steel were obtained by the three kinds of dephosphorization fluxes as the oxygen potential of molten steel higher than 400×10^{-6}. Rephosphorization of molten steel was serious as the oxygen content of molten steel lower than 10×10^{-6}. BaO-based fluxes can improve the dephosphorization effect and reduce the phosphorus pick-up effectively under the condition of weak deoxidization of molten steel (the oxygen potential is about 100×10^{-6}), but can not prevent rephosphorization under the condition of deep deoxidization of molten steel (the oxygen potential less than 10×10^{-6}).

Key words: molten steel; dephosphorization; rephosphorization; oxygen potential; flux composition

1 Introduction

Phosphorus is a detrimental element for most steel grades. High-quality steel brings forward a higher demand for phosphorus content especially for the steel used at low temperature, marine steel and anti-hydrogen induced crack steel with the phosphorus content even lower than 0.01% or 0.005% generally. In order to produce low phosphorus steel and ultra-low phosphorus steel, deep dephosphorization treatment has been paying more and more attention. Deoxidizing and alloying operation after deep dephosphorization of molten steel in ladle may cause weak oxidization atmosphere even reductive atmosphere which makes the oxygen potential decrease. Rephosphorization will be easily caused under the unfavorable thermodynamic condition and the oxygen potential of molten steel has strong effect on rephosphorization of molten steel. BaO can effectively improve the basicity of the slag and prevent rephosphorization of molten steel [1-4]. Adding BaO to CaO-based fluxes can not only improve dephosphorization but also decrease rephosphorization. It is not very clear, however, under what conditions rephosphorization can be prevented by adding BaO to the flux. In this paper, the effect of oxygen potential on dephosphorization of molten steel and the effect of BaO on dephosphorization and rephosphorization of molten steel under different oxygen potential conditions were mainly discussed.

2 Experimental

The experiments were carried out in a 100 kg induction furnace with the temperature controlled 1600±10°C . Low carbon Al-killed steel was used in the experiment with the composition shown as **table 1.** The composition of fluxes is listed in **table 2.** Slags were prepared from analytical lime, barium oxide, fluorspar and ferric oxide.

The experimental procedure was briefly summarized as follows: 100 kg steel was charged into a induction furnace. After metal was melted and reached to 1600°C, the first steel sample was taken with a ϕ20 mm sampler. The composition of this sample was considered to be the initial composition of the steel. After this, 1 kg BOF slag as 1% slag carryover and 2 kg dephosphorization flux with a consumption of 20 kg per ton steel were charged onto the top of the molten steel and this moment was taken as the beginning time of the reaction. Steel samples were taken at 3, 6, 10 and 15 min, and the first slag sample was taken at 15 min. After the first slag sample was taken, steel was deoxidized by aluminum, ferrosilicon and ferromanganese to study rephosphorization. Steel samples were taken at 3, 6 and 15 min after adding deoxidizers. At the time of 25 min after adding deoxidizers, both the final steel and the slag sample were

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taken. The total time of the experiment was around 40 min.

Table 1 Composition of the molten steel wt%

C	Si	Mn	P	S
0.02-0.08	0.003-0.120	0.05-0.28	0.006-0.016	0.005-0.010

Table 2 Composition of fluxes wt%

Flux	BaO	CaO	CaF_2	FeO
A	—	75	15	10
B	10	65	15	10
C	20	55	15	10
D	30	55	15	—
E	60	20	20	—

In this paper oxygen activity was considered as oxygen potential. The oxygen activity of molten steel was measured by zirconia electrolyte probe. The composition of the steel was analyzed by spectrum analyser.

3 Results

3.1 Influence of oxygen potential on dephosphorization and rephosphorization of molten steel

The dephosphorization treatment of the molten steel was carried out first under different oxygen potentials a_O by fluxes A. The results are shown in figure 1.

The dephosphorization ratio η_P can be written as

$$\eta_P=([P]_i-[P]_f)/[P]_i,$$

where $[P]_i$, $[P]_f$ represent the initial and final phosphorus contents in molten steel respectively. $\eta_P>0$ means the state of dephosphorization, $\eta_P<0$ means the state of rephosphorization and $\eta_P=0$ means the critical state of transition from dephosphorization to rephosphorization.

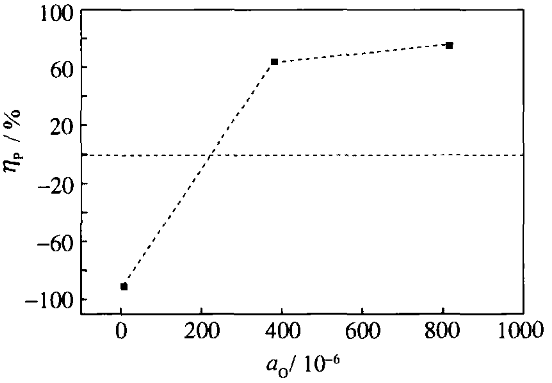

Figure 1 Effect of oxygen potential on dephosphorization of molten steel by the CaO-CaF₂-FeO system.

Figure 1 shows that dephosphorization ratio decreases with the oxygen potential decreasing. When the oxygen potential is less than 400×10^{-6}, the dephosphorization ratio increases sharply with the oxygen potential increasing. When the oxygen potential is higher than 400×10^{-6}, the change of dephosphorization ratio is not obvious with oxygen potential. Over 60% phosphorus was removed and a phosphorus content less than 0.004% was obtained by this kind of flux when the oxygen potential is higher than 400×10^{-6}. Due to the restriction of experimental conditions, it is difficult to determine the critical oxygen potential dephosphorized by this kind of flux for lack of experiment data near the critical oxygen potential. The figure indicates that great extent rephosphorization occurs after deep deoxidization of molten steel. The phosphorus both in the carryover slag during tapping and in the alloys nearly entirely turned back to the molten steel.

The dephosphorization treatment of the molten steel was also carried out under different oxygen potentials by $BaO-CaO-CaF_2FeO$ fluxes (flux B, C). The results are shown in figure 2.

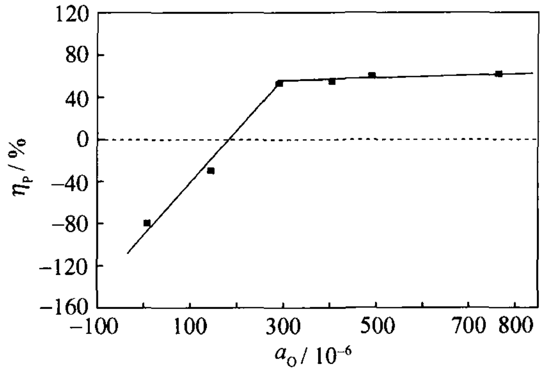

Figure 2 Effect of oxygen potential on dephosphorization of molten steel by the BaO-CaO-CaF₂-FeO system.

Figure 2 shows the dephosphorization ratio increases with the oxygen potential of molten steel increasing. When the oxygen potential is higher than 300×10^{-6}, oxygen potential has little effect on the dephosphorization efficiency by the given fluxes. With the decreasing of oxygen potential, the molten steel transits from dephosphorization state to rephosphorization state. The critical oxygen potential of molten steel from dephosphorization state to rephosphorization state is 176×10^{-6} with the BaO-CaO-CaF_2-FeO slag system. The results show that for deep deoxidation steel, the flux can not depress rephosphorization and the rephosphorization degree is also great.

The dephosphorization treatment of the molten steel was carried out under different oxygen potentials by BaO-CaO-CaF_2 fluxes (flux D, E). The results are shown in **figure** 3.

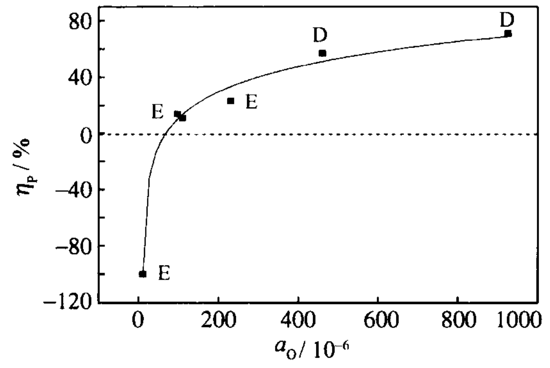

Figure 3 Effect of oxygen potential on dephosphorization of molten steel by the BaO-CaO-CaF_2 system.

Figure 3 shows that the dephosphorization ratio decreases sharply with the oxygen potential decreasing when the oxygen potential is less than 100×10^{-6} and, increases gradually with the oxygen potential increasing when the oxygen potential is higher than 100×10^{-6}. After regression treatment, the relation between oxygen potential and dephosphorization ratio is $\eta_P = -129.97+29.976\times\ln(a_O-8)$. According to the regressive equation, the critical oxygen potential is 84.4×10^{-6} in the BaO-CaO-CaF_2 slag system. The experimental results show that it is different from CaO-CaF_2-FeO and BaO-CaO-CaF_2-FeO fluxes. The BaO-CaO-CaF_2 flux has some dephosphorization ability at a lower oxygen potential ($a_O\approx100\times10^{-6}$). The rephosphorization ratio, however, reaches to 30% at $a_O=145\times10^{-6}$ by the BaO-CaO-CaF_2-FeO flux. The main reason for such difference is that the BaO-CaO-CaF_2 contains more BaO which results in a higher basicity than the other two fluxes and, at the same temperature the BaO-CaO-CaF_2 flux has a higher phosphate capacity than the other two fluxes [5]. Therefore the BaO-CaO-CaF_2 flux has a stronger dephosphorization ability than the other two at lower oxygen potential. It can not only depress rephosphorization of molten steel effectively but also obtain a little amount of dephosphorization. The experimental results indicate that similar to the other two kinds of fluxes, rephosphorization of molten steel is also serious by the BaO-CaO-CaF_2 flux under the condition of deep deoxidation.

3.2 Influence of BaO content in fluxes on dephosphorization and rephosphorization of molten steel

Deoxidation operation by ferromanganese, aluminum and ferrosilicon was carried out after deep dephosphorization of molten steel by different compositions of BaO-based and CaO-based fluxes without removing the dephosphorization slag. The rephosphorization of molten steel for different BaO contents in the slags and different oxygen potentials of molten steel were compared.

Figure 4 indicates that good dephosphorization results were obtained by different compositions of the fluxes. The phosphorus content in molten steel decrease from about 0.01% to 0.004% and the ultra-low phosphorus steel was achieved after the treatment. The phosphorus in dephosphorized steel ascends when deoxidation and alloying were carried out. When the oxygen potential in the range of 100×10^{-6} to 150×10^{-6}, the final phosphorus content, the amount of dephosphorization and rephosphorization are 0.008%, 0.001% and 0.004% respectively for the 60% BaO bearing fluxes, while the final phosphorus content, and the amount of rephosphorization are 0.013%, 0.009% respectively for the 20% BaO bearing fluxes. It is obvious that BaO-based fluxes can control rephosphrization of molten steel effectively as about 100×10^{-6} oxygen potential in molten steel and the rephosphorus amount decreases with the BaO content in the fluxes increasing. So the BaO-based fluxes can not only control rephosphorization but also can dephosphorize in some extent under the condition of weak deoxidization of molten steel. When the oxygen potential is less than 10×10^{-6}, the phosphorus pick-up is tremendous for different BaO bearing fluxes. After deep deoxidation, the phosphorus content in molten steel increased from initial 0.01% to final 0.02%. This indicates that not only the total phosphorus removed is back to the steel but also the phosphorus in BOF slag is reduced to the steel even with the phosphorus in alloy and so on.

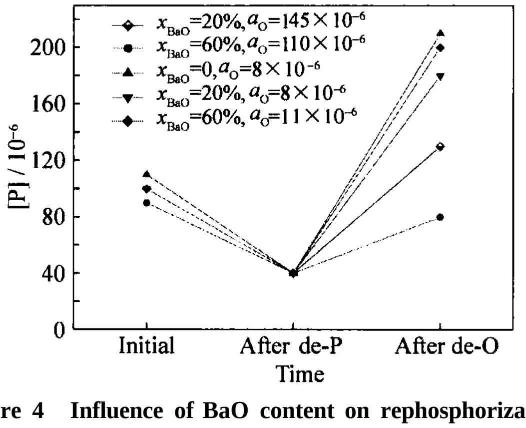

Figure 4 Influence of BaO content on rephosphorization of molten steel. The de-P presents dephosphorization, and the de-O presents deoxidation.

In the practice of producing killed steel, when the silicon-manganese deoxidation process is used, the content of silicon in molten steel is about 0.2%-0.3% and the oxygen potential ranges from 70×10^{-6} to 80×10^{-6}. According to the present regression, the critical oxygen potential for steel dephosphorization by the BaO-CaO-CaF$_2$ is 80×10^{-6}-90×10^{-6}. Therefore, in this case the BaO-based flux can not only assure the phosphorization content in molten steel less than 0.01%, but also depress rephosphorization of molten steel. When the aluminum deoxidation process is adopted, the oxygen potential in molten steel is very low, always less than 10×10^{-6}, which is less than the critical oxygen potential of steel dephosphorization greatly by the BaO-based flux. In this case, the BaO-based flux can not constrain rephosphorization of steel absolutely.

4 Discussion

4.1 Equilibrium between phosphorus and oxygen in molten steel

The basic reaction of oxidation dephosphorization is:

$$[\mathrm{P}]+\frac{5}{4}\mathrm{O}_2(\mathrm{g})=\frac{1}{2}(\mathrm{P}_2\mathrm{O}_5) \tag{1}$$

$\Delta G_1^\ominus = -666210+271.7T$, J/mol [6].

The equilibrium constant K_P is

$$\lg K_\mathrm{P}=\frac{34794}{T}-14.19\,,$$

$$K_\mathrm{P}=\frac{(a_{\mathrm{P_2O_5}})^{1/2}}{a_{[\mathrm{P}]}\cdot p_{\mathrm{O_2}}^{5/4}}=\frac{\gamma_{\mathrm{P_2O_5}}^{1/2}X_{\mathrm{P_2O_5}}^{1/2}}{[\%\mathrm{P}]\cdot f_\mathrm{P}\cdot p_{\mathrm{O_2}}^{5/4}}\,,$$

and

$$[\%\mathrm{P}]=\frac{\gamma_{\mathrm{P_2O_5}}^{1/2}X_{\mathrm{P_2O_5}}^{1/2}}{K_\mathrm{P}\cdot f_\mathrm{P}\cdot p_{\mathrm{O_2}}^{5/4}} \tag{2}$$

where $a_{\mathrm{P_2O_5}}$, $\gamma_{\mathrm{P_2O_5}}$ and $X_{\mathrm{P_2O_5}}$ are the activity, activity coefficient and mole fraction of P$_2$O$_5$ in the slag respectively; $a_{[\mathrm{P}]}$, f_P and [%P] are the activity, activity coefficient and mass fraction of phosphorus in the metal respectively; $p_{\mathrm{O_2}}$ is the partial pressure of oxygen gas of the system.

According to equation (2), for oxidation dephosphorization at a given composition of molten steel, dephosphorization flux and temperature, the dephosphorization reaction will take place so long as the oxygen potential of the system is a higher than the critical oxygen potential. Therefore, a higher oxygen potential is beneficial to dephosphorization and makes the equilibrium phosphorus content of molten steel decrease. So it is necessary to choose a proper oxygen potential to ensure phosphorus oxidized from molten steel to slag.

When phosphorus is oxidized, the condition of dephosphorization is $\Delta G_1<0$. The following expression can be derived from the chemical isothermal equation.

$$\lg a_{\mathrm{P_2O_5}}<\frac{69588}{T}-28.38+2\lg a_{[\mathrm{P}]}+\frac{5}{2}\lg p_{\mathrm{O_2}} \tag{3}$$

Activity interaction coefficients are adopted to calculate the activity coefficient of phosphorus f_P in the molten steel. It can be written as

$$\lg f_\mathrm{P}=e_\mathrm{P}^\mathrm{P}[\%\mathrm{P}]+e_\mathrm{P}^\mathrm{C}[\%\mathrm{C}]+e_\mathrm{P}^\mathrm{O}[\%\mathrm{O}]=$$
$$0.062[\%\mathrm{P}]+0.13[\%\mathrm{C}]+0.13[\%\mathrm{O}]\,,$$

where e_P^P, e_P^C, e_P^O are the activity interaction coefficients of P-P, P-C, P-O respectively in molten steel. At 1873 K, the activity coefficient of phosphorus in the molten steel listed in table 1 is 1.03, so the activity of phosphorus is 0.0103 when the phosphorus content is 0.01%. Then the relationship between the activity of P$_2$O$_5$ and the oxygen potential is

$$\lg a_{\mathrm{P_2O_5}}<4.8+\frac{5}{2}\lg p_{\mathrm{O_2}} \tag{4}$$

4.2 Estimation of critical oxygen potential for dephosphorization

The activity coefficient of P$_2$O$_5$ in the present slag system ranges from 10^{-18} to 10^{-20} and the mole fraction of P$_2$O$_5$ in slag is about 5×10^{-4}, therefore the activity of P$_2$O$_5$ in the present system varies from 5×10^{-24} to 5×10^{-22}. Based on equation (4) the relations between the calculated activity of P$_2$O$_5$ and the critical dephosphorization oxygen potential are listed in **table 3.**

Table 3 Relations of $a_{\mathrm{P_2O_5}}$ and $P_{\mathrm{O_2}}$ (at 1873 K)

a_{P2O5} / 10^{-24}	P_{O2} / 10^{-12} atm	a_O / 10^{-6}
500	36.1	167
50	14.4	105
5	5.72	66

The activity of oxygen a_O in molten steel were calculated according to the following equation and listed in table 3.

$$\frac{1}{2}\mathrm{O}_2=[\mathrm{O}] \tag{5}$$

$\Delta G_2^\ominus = -117110-3.39T$, J/mol [7].

The equilibrium constant is $K_2=\dfrac{a_\mathrm{O}}{p_{\mathrm{O_2}}^{1/2}}$. It is 2.775×10^3 at 1873 K.

According to table 3, to ensure 0.01% phosphorus content in molten steel, the oxygen potential must be higher than 66×10^{-6} for $a_{\mathrm{P_2O_5}}$=5×10^{-24} in the slag and 167×10^{-6} for $a_{\mathrm{P_2O_5}}$=5×10^{-22} in the slag. That is to say, the lower the activity of oxygen in molten steel or the lower the dephosphorization oxygen potential, the lower the activity of P$_2$O$_5$ is required in the slag to achieve the target value of dephosphorization. So if the oxygen potential of system is very low, the dephosphorization ability of the dephosphorization fluxes should be much stronger than that of the fluxes with high oxygen potential to achieve the same target value of dephosphorization.

The experiments show that the phosphorus capacity increases from CaO-CaF_2-FeO, BaO-CaO-CaF_2-FeO to BaO-CaO-CaF_2 at steelmaking temperature, and the dephosphorization ability is also in this sequence [8-9]. The activity coefficient of P_2O_5 ($\gamma_{P_2O_5}$) decreases in the sequence and the critical oxygen potential has the same changing tendency with $\gamma_{P_2O_5}$. In the present experiment system the critical oxygen potential of the fluxes is 84.4×10^{-6} for the BaO-CaO-CaF_2 system and 176×10^{-6} for the BaO-CaO-CaF_2-FeO system. The thermodynamic calculated value of the critical oxygen potential of steel dephosphorized by the present fluxes ranges from 66×10^{-6} to 167×10^{-6}. The values of critical oxygen potential by regression are very close to the theoretical calculations.

4.3 Effect of oxygen potential on dephosphorization and rephosphorization of steel

Based on equation (2) at a certain temperature, K_P is a constant and [%P] is correlated with the oxygen potential and activity coefficient of P_2O_5. According to equations (3) and (5), at 1873 K the relationship among the three parameters can be expressed as follows.

$$\lg(f_P[\%P]) > \frac{1}{2}\lg(X_{P_2O_5}\gamma_{P_2O_5}) + 4.22 - \frac{5}{2}\lg a_O \qquad (6)$$

Figure 5 shows the phosphorus content in molten steel changing with the oxygen potential for different $\gamma_{P_2O_5}$.

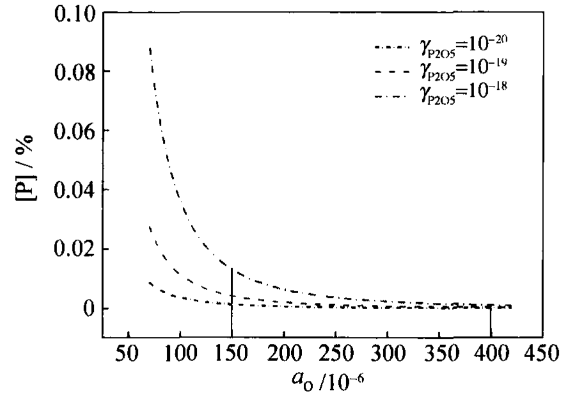

Figure 5 Effects of the oxygen potential and activity coefficient of P_2O_5 on phosphorus in molten steel.

Figure 5 indicates that when the oxygen potential of molten steel is higher than 400×10^{-6}, the phosphorus content in molten steel has very little change for different $\gamma_{P_2O_5}$ and it is very low, less than 0.002%. This indicates that [%P] is mainly correlated with a_O, and $\gamma_{P_2O_5}$ has little effect on [%P]. Therefore although the difference of $\gamma_{P_2O_5}$ results from different fluxes, the dephosphorization results are similar. So oxygen potential should be given more attention when the oxygen potential of molten steel higher than 400×10^{-6}. When the oxygen potential of molten steel is less than 150×10^{-6}, the phosphorus contents in molten steel have large gaps for different $\gamma_{P_2O_5}$. This indicates that the influence of a_O on [%P] is decreasing, however the influence of $\gamma_{P_2O_5}$ increasing. Therefore, $\gamma_{P_2O_5}$ has certain effect on dephosphorization efficiency. So in order to prevent rephosphorization of steel, the appropriate oxygen potential and dephosphorization flux should be considered.

5 Conclusions

(1) Oxygen potential has great influence on dephosphorization results. When the oxygen potential higher than 400×10^{-6}, good dephosphorization results could be obtained with phosphorus decreasing from initial 0.01% to an ultra-low phosphorus level of 0.004%. When oxygen potential less than 400×10^{-6}, with the oxygen potential of molten steel decreasing, the dephosphorization ratio decreases and the molten steel changes from the state of dephosphorization to rephosphorization. In order to reduce rephosphorization and obtain ultra-low phosphorus steel, dephosphorization should be executed before steel deoxidation and after dephosphorization the slag should be removed.

(2) The influence of BaO content in fluxes on dephosphorization and rephosphorization of molten steel is restricted by oxygen potential. When the oxygen potential is about 100×10^{-6}, BaO-based fluxes can control rephosphorization of molten steel effectively and even can dephosphorize to some extent, and the rephosphorus amount decreases with the BaO content in the fluxes increasing. At deep deoxidization of molten steel (the oxygen potential less than 10×10^{-6}) both CaO-based fluxes and BaO-based fluxes can not restrain rephosphorization of steel. However it is very difficult to prevent rephosphorization of molten steel by controlling the oxygen potential of molten steel in industrial production. Therefore, whichever kind of fluxes is used, dephosphorization slag must be removed before deoxidation and alloying to decrease rephosphorization as much as possible.

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