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Kinetic study on deep dephosphorization treatment of liquid steel by BaO-based fluxes

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Abstract: Laboratory study was carried out on deep dephosphorization of liquid steel by BaO-based fluxes at 1600°C to achieve ultra low phosphorus level in the steel. A dynamic model of dephosphorization of liquid steel by BaO-based fluxes was established. According to the model, the controlling step of dephosphorization by BaO-based fluxes was the mass-transfer of phosphorus in steel phase under the condition of low phosphorus liquid steel. It is estimated that the apparent rate constant of dephosphorization by BaO-based fluxes was 0.4×10^{-3}-8.2×10^{-3} g/(cm^2·s) and the mass-transfer coefficient of phosphorus in bulk steel was 0.025-0.04 cm/s.

Key words: BaO-based fluxes treatment; deep dephosphorization; dynamic model; limiting step

1 Intruduction

In order to obtain ultra-low phosphorus steel, we needs dephosphorization in the secondary refining process besides the dephosphorization of hot metal and dephosphorization during the process of steelmaking. At present, CaO-based fluxes are studied widely for dephosphorization [1, 2]. Comparing with CaO-CaF_2 flux, BaO-CaF_2 flux has a higher phosphate capacity and a lower $PO_{2.5}$ activity coefficient. At 1400°C, the phosphate capacity of BaO-CaF_2 flux ranges from 10^{24} to 10^{27} while that of CaO-CaF_2 flux ranges from 10^{23} to 10^{24}. BaO is a strong basic oxide which can increase the basicity of the fulx and prevent rephosphorization in molten metal. Adding BaO to CaO-based fluxes can increase the phosphate capacity and lower the $PO_{2.5}$ activity coefficient of the fluxes [3, 4]. BaO-based fluxes are mainly used to the dephosphorization of stainless steel, ferrochrome and ferromanganese. The deep dephosphorization of low carbon steel was carried out in laboratory with BaO-based fluxes.

The dephosphorization reaction of molten steel (or hot metal) is a complicated slag-metal reaction. However the degree of dephosphorization depends on the dynamic condition of the reaction. Although a large number of fundamental and process researches of dephosphorization dynamics were carried out to improve the reaction rate, at present the researches on dephosphorization dynamics of liquid steel is still poorish especially for the dynamics of low phosphorus and ultra-low phosphorus steel. Combined with the experiment results of deep dephosphorization of steel by BaO-CaO-CaF_2-FeO flux, the dephosphorization dynamics of ultra-low phosphorus steel is discussed in this paper. Based on the dephosphorization dynamics, a mathematical model is established to describe the mechanism of dephosphorization and analyse the factors affecting the dephosphorization.

2 Experiment method

The experiments were carried out in a high temperature carbon tube furnace. The metal was prepared from industrial pure iron and ferrophosphorus. The slag was made up of chemical reagents.

1 kg metal and certain amount of ferrophosphorus were put into a magnesia crucible. The metal was heated under nitrogen atmosphere. After the metal melting and reaching to 1600°C, the initial sample was taken and the oxygen activity of the liquid steel was measured by using zirconia electrolyte probe. 0.09 kg slag was put onto the molten steel and this time was taken as the beginning time of the reaction. Samples were taken in specified intervals. The final slag sample and metal sample were taken when the crucible was cooled.

The initial phosphorus content in the liquid steel varied from 0.004% to 0.011%. The measured composition of the liquid steel were C, 0.046%-0.12%; Si, 0.086%-0.21%; Mn, 0.16%-0.28%; P, 0.0043%-0.0097%; and S<0.015%. The measured oxygen ac-

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tivity of the liquid steel ranged from 0.0043% to 0.0155%. The composition of the used BaO-based fluxes in the experiment are listed in **table 1**.

Table 1 Composition of fluxes used on this experiment

wt%

Flux	BaO	CaO	CaF_2	FeO
A	10	65	15	10
B	20	55	15	10
C	30	55	15	—
D	40	45	15	—
E	60	20	20	—

3 Experiment results

Figure 1 shows that phosphorus in molten steel changes with time at 1570 and 1600°C using flux A. It indicates that the lower phosphorus content of molten steel is obtained at a lower temperature. Low temperature is benefitial for dephosphorization.

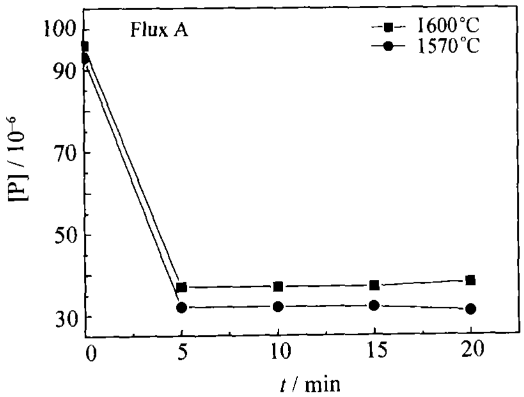

Figure 1 Effect of temperature on dephosphorization.

Using flux B at 1600°C the phosphorus content of molten steel changing with time for different initial phosphorus contents (0.004%-0.005% and 0.009%-0.010%) is shown in **figure 2**. The dephosphorization rate at initial stage increases with increasing the initial phosphorus content, but the final phosphorus content of molten steel is approximately at the same level.

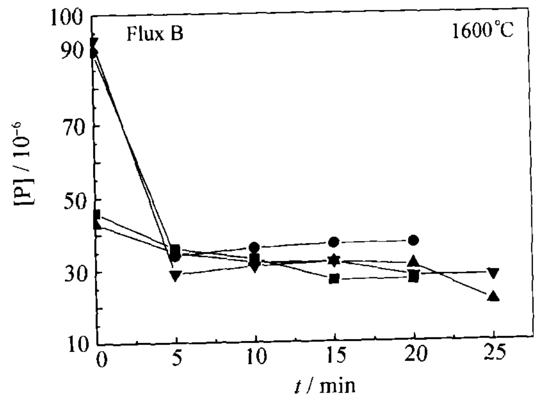

Figure 2 Effect of initial phosphorus content on dephosphorization rate.

Figure 3 shows the variations of phosphorus content of molten steel with time for the initial phosphorus content of 0.0073%-0.0093% at 1600°C by different kind of fluxes. For different kinds of fluxes, the higher the initial phosphorus content in molten steel, the bigger the dephosphorization rate at initial stage. The effects of composition of the fluxes, such as the content of basic oxide or oxidizability, on the dephosphorization rate are not remarkable. It is different from Kyoji Kunisada's work [5].

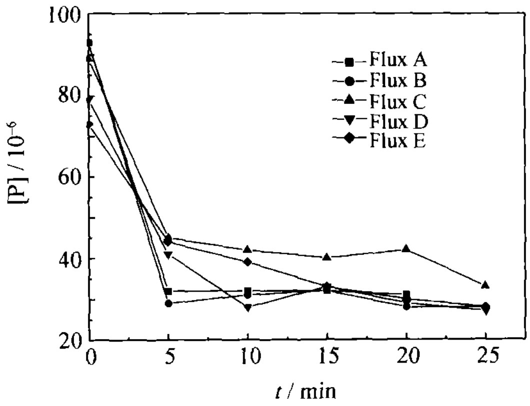

Figure 3 Variations of [P] with time for different fluxes.

4 Mathematical model

4.1 Description of the dephosphoration dynamic model

The basic equation of the oxidizing dephosphorization of steel (BaO as example) is:

$$2[P] + 5(FeO) + 4(BaO) = (4BaO \cdot P_2O_5) + 5Fe.$$

The dephosphoration steps are as follows.

- [P] transfers from the metal phase to the slag-metal interface.
- Fe^{2+} and O^{2-} transfer from the slag phase to the slag-metal interface.
- The chemical reaction at the slag-metal interface.
- P_2O_5 transfers from the slag-metal interface to the slag phase.
- Fe transfers from the slag-metal interface to the metal phase.

In the model, it is assumed that the chemical reactions at the slag-metal interface are rapid and equilibrated at any time. The reaction rate is determined by mass-transfer in both the metal and slag phases. **Figure 4** gives the distribution of phosphorus schemetically at the two sides of slag-metal interface based on the double film theory.

$$L_P' = (P)^* / [P]^*.$$

The metal side transfer equation is

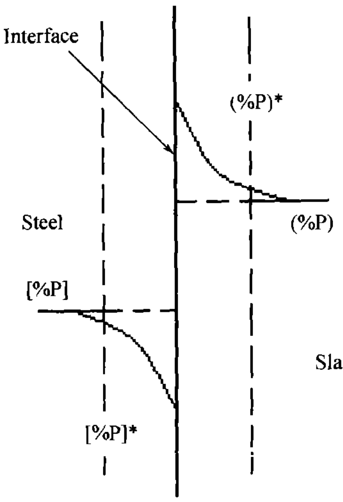

Figure 4 Distribution of phosphorus concentration.

$J_{[P]} = k_m\{[P]-[P]^*\}$.

The slag side transfer equation is

$J_{(P)} = k_s\{(P)^* - (P)\}$.

At the steady state,

$J = J_{[P]} = J_{(P)}$.

Then

$$J_{[P]}\left\{\frac{1}{k_m}+\frac{1}{k_s L_P'}\right\} = [P]-\frac{(P)}{L_P'},$$

$$J_{[P]} = \frac{L_P'[P]-(P)}{L_P'/k_m + 1/k_s}.$$

Modifying the upper equation to mass fraction, the following dephosphorization rate equation of steel is obtained:

$$-\frac{d[\%P]}{dt} = \frac{A}{W_m}\frac{L_P[\%P]-(\%P)}{L_P/\rho_m k_m + 1/\rho_s k_s} = \frac{A}{W_m}k_P\{L_P[\%P]-(\%P)\} \qquad (1)$$

here,

$$k_P = \frac{1}{\dfrac{L_P}{\rho_m k_m}+\dfrac{1}{\rho_s k_s}} \qquad (2)$$

When dephosphorization is controlled by the mass-transfer of phosphorus in both metal and slag phases,

$$-\frac{d[\%P]}{dt} = \frac{A}{W_m}k_P\{L_P[\%P]-(\%P)\}.$$

According to the principle of mass conservation, at any time t,

$W_m[\%P] = W_m[\%P]_i - W_s(\%P)$.

Put the upper equation to dephosphorization rate equation (1) and through integration the dynamic model of phosphorus content of liquid steel can be obtained.

$$\frac{[\%P]}{[\%P]_i} = \frac{1}{L_P+\dfrac{W_m}{W_s}}\left\{L_P e^{-\frac{A}{W_m}k_P\left(L_P+\frac{W_m}{W_s}\right)t} + \frac{W_m}{W_s}\right\} \qquad (3)$$

According to the dephosphorization dynamic model, if the controlling step of deep dephosphorization in liquid steel is the mass-transfer of phosphorus in both metal and slag phases, then in the process of dephosphorization reaction the change of phosphorus content will follow the dynamic model described in equation (3).

4.2 Model calculation

In the course of calculation, the following equation is adopted:

$$y = y_0 + A_1 e^{-t/B_1} \qquad (4)$$

where y is $[\%P]/[\%P]_i$, t the reaction time, y_0, A_1, B_1 are the coefficients of each item and the exact expressions of each coefficient can be represented by the following relations:

$$y_0 = \frac{\dfrac{W_m}{W_s}}{L_P+\dfrac{W_m}{W_s}},$$

$$A_1 = \frac{L_P}{L_P+\dfrac{W_m}{W_s}},$$

$$B_1 = \left[\frac{A}{W_m}k_P\left(L_P+\frac{W_m}{W_s}\right)\right]^{-1}.$$

Figure 5 shows the experiment values and the calculated values. The dots represent the measured values in the experiment and the curve is the calculated result.

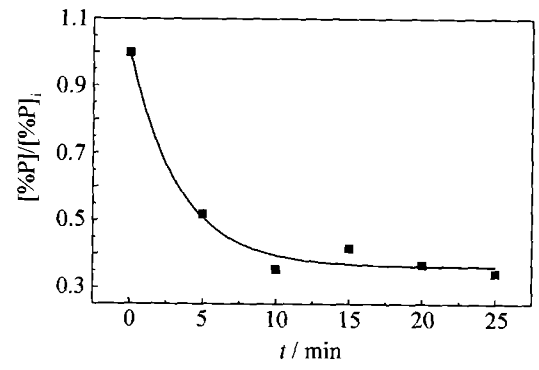

Figure 5 Experimental values and the calculated result during the dephosphorization process.

It's confirmed that the calculated result agrees with the experimental values well. It indicates that under the test condition the dephosphorization process can be described by the mathematical model. It's also approved that under the condition of the existing deep dephosphorization process of liquid steel the limiting step of the dephosphorization reaction is the mass-transfer of phosphorus in both metal and slag phases.

From the calculated results the coefficients y_0, A_1 and B_1 in the calculated equation can be obtained. According to these values the dephosphorization rate constant k_P can be estimited. The value of L_P at the end-point of the experiment was adopted during the course of estimation, for the phosphorus content hardly changing with time after 5-10 min, the reaction reached the quasi-equlibrium. The measured L_P rangs from 50 to 110. The k_P values are listed in **table 2**.

Table 2 Rate constant and related coefficients for different compositions of BaO-based fulxes

No.	k_P / (mg·cm^{-2}·s^{-1})	y_0	A_1	B_1 fitted	B_1 proved	L_P
1	2.50	0.436	2.518	0.563	0.564	81.0
2	8.10	0.392	1.278	0.608	0.608	54.0
3	8.20	0.363	1.543	0.637	0.638	54.0
4	0.59	0.608	7.431	0.385	0.392	82.5
5	5.90	0.414	1.431	0.586	0.586	63.7
6	0.40	0.610	8.000	0.383	0.389	110.0
7	8.02	0.329	1.074	0.670	0.671	71.7
8	2.15	0.362	3.378	0.639	0.637	81.0
9	1.64	0.493	3.587	0.504	0.507	80.0

According to this table, the estimated value of the apparent rate constant k_P of deep dephosphorization by BaO-based fluxes is about 0.4×10^{-3}-8.2×10^{-3} g/(cm^2·s).

4.3 Determination of the controlling step for deep dephosphorization

According to equation (2) if the mass-transfer in slag phase controls the dephosphorization reaction then the appareant rate constant of dephosphorization k_P would be independent of phosphorus distribution ratio L_P. **Figure 6** gives the relation between k_P and L_P. It indicates that the two values have a strong correlation, so the dephosphorization process of liquid steel by BaO-based fulxes is not only controlled by the mass-transfer of slag phase. On the other side, if the dephosphorization process is controlled by the mass-transfer in metal phase then, keeping the mass-transfer coefficient of phosphorus in metal phase as constant, k_P and L_P are of an inversely-proportional relation. Figure 6 shows this tendency apparently. In fact, even the dephosphorization process is only controlled by the mass-transfer in metal phase, because of the difference of the experimental conditions and the mass-transfer coefficient of phosphorus in steel phase, it is not merely the strict hyperbolic relation.

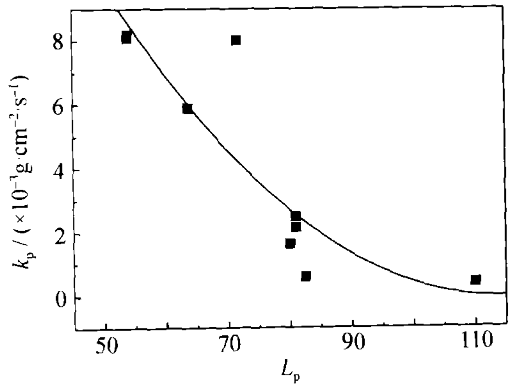

Figure 6 Relation between k_p and L_p.

The dephosphorization experiments were carried out for different initial phosphorus content steels. **Figure 7** shows the relation between the initial phosphorus content of liquid steel and the average dephosphorization rate in the first 5 min $\Delta[P]/5[P]_i$.

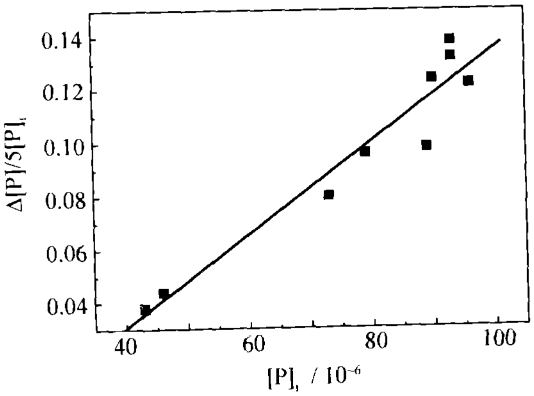

Figure 7 Relation between $[P]_i$ and $\Delta[P]/5[P]_i$.

Here, $\Delta[P]$ represents the mass fraction of phosphorus removal in the first 5 min and $[P]_i$ is the initial phosphorus content (mass fraction).

Figure 7 shows that the initial phosphorus content has a strong influence on the dephosphorization rate in the first 5 min. The dephosphorization rate increases with increasing the initial phosphorus content, and it appears a linear relation basically. All these indicate that under the existing condition, because the initial phosphorus content of liquid steel is very low, the dephosphorization of liquid steel is basically controlled by the mass-transfer of phosphorus in steel phase. In addition, according to figure 3 the compositions of the fluxes have no effect on the dephosphorization rate. When changing the compositions of the fluxes, the dephosphorization rate did not change. That is, mass-transfer in slag phase is not the limiting step of the whole reaction. When the phosphorus content of liquid steel below 0.01%, the dephosphorization of liquid steel by BaO-based fluxes is mainly controlled by the mass-transfer of phosphorus in steel phase.

The slags containing SiO_2, normally with a basicity less than 5, were generally adopted for dephosphorization by former researchers [6, 7], and the common conclusion is that dephosphorization is controlled by the mass-transfer of phosphorus in slag phase or by the mixed mass-transfer of phosphorus in both slag and metal phases. In this paper high basic slag was used for dephosphorization of steel with low phosphorus and carbon content, and the dephosphorization was found to be controlled by the mass-transfer of phosphorus in steel phase.

4.4 Determination of mass-transfer coefficient

When the apparent rate constant k_P is known the relation between k_m and k_s can be determined by equation (2). Based on the results of No.8 in table 2, if the mass-transfer is absolutely controlled by phosphorus mass-transfer in the steel phase, then the mass-transfer coefficient of phosphorus in liquid steel is about 0.025 cm/s. In order to analyse the mass-transfer resistance, taking No.8 as an example, assuming the mass-transfer coefficient k_m of phosphorus in steel phase is 0.025, 0.030, 0.035, 0.045, and 0.050 cm/s, the values of k_s and the phosphorus mass-transfer resistance in slag phase and steel phase for various k_m were calculated. The calculated results are listed in **table 3**.

Table 3 Mass-transfer coefficient and mass transfer resistance of phosphorus (No.8)

K_m / (cm·s^{-1})	K_s / (mg·cm^{-2}·s^{-1})	Mass-transfer resistance of phosphorus in steel		Mass-transfer resistance of phosphorus in slag	
		Value	Ratio / %	Value	Ratio / %
0.025	—	465.1	100	0.0	0
0.030	3.59	385.7	83	79.4	17
0.035	2.14	330.6	71	134.5	29
0.040	1.58	289.3	62	175.8	38
0.045	1.37	257.1	55	208.0	45
0.050	1.22	231.4	50	233.7	50

According to the calculated results, if dephosphorization is mainly controlled by the mass transfer in steel phase, the mass-transfer coefficient of phosphorus in low carbon steel is about 0.025-0.040 cm/s. When analysing the dephosphorization rate of high carbon hot metal, Takashi Sato obtained that the mass-transfer coefficient of phosphorus in hot metal is about 0.035-0.040 cm/s [6].

The main factor that affects the mass-transfer coefficient of molten steel (or hot metal) is their viscosity. According to reference [7], at the same temperature the viscosity of molten steel (or hot metal) decreases with the increasing of P, Si, Mn, and C contents in metal. And the viscosity of the molten steel (or hot metal) gradually decreases with increasing the temperature. At 1350°C, [%C]=4.4, the viscosity of hot metal is 7×10^{-3} Pa·s and at 1600°C the viscosity of industry pure iron is 6.2×10^{-3} Pa·s. It is measured that at 1550°C the viscosity of liquid pure iron is 6.44×10^{-3} Pa·s [8]. Due to the many-sides effects of the composition of molten steel (or hot metal) and the temperature, the high carbon iron and low carbon steel have the similar viscosity, so the mass-transfer coefficient of phosphorus in low carbon steel and high carbon iron does not have remarkable difference.

5 Conclusions

(1) A dynamic mathematical model for dephosphorization of low carbon steel is established. And the model can describe the dephosphorization process of liquid steel well.

(2) It's estimated that the apparent rate constant of deep dephosphorization of liquid steel by BaO-based fluxes is 0.4×10^{-3}-8.2×10^{-3} g/(cm^2·s) and the mass-transfer coefficient of phosphorus in liquid steel is 0.025-0.040 cm/s.

(3) The dephosphorization of steel by BaO-based fluxes is mainly controlled by the mass-transfer of phosphorus in steel phase when the phosphorus content in liquid steel is below 0.01%.

Nomenclature

(P): The phosphorus content in slag phase, mol/cm^3;

[P]: The phosphorus content in metal phase, mol/cm^3;

*: Interface;

(%P): The phosphorus content in slag phase, wt%;

[%P]: The phosphorus content in metal phase, wt%;

$[\%P]_i$: The initial phosphorus content of metal, wt%;

L_P': The equilibrium phosphorus distribution ratio with concentration;

L_P: The equilibrium phosphorus distribution ratio with mass fraction;

k_m: The mass-transfer coefficient in metal phase, cm/s;

k_s: The mass-transfer coefficient in slag phase, cm/s;

J: The molar flux density, mol/(cm^2.s);

A : The interfacial area, cm^2;

W_m, W_s: The mass of metal or slag, g;

ρ_m, ρ_s: The density of metal or slag, g/cm^3;

k_P: The apparent dephosphorization rate constant, g/(cm^2·s);

t: The time, min.

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