Development of Hot Metal Dephosphorization with CaO Powder Top Blowing

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Abstract

Phosphorus in steel is detrimental to mechanical properties, and dephosphorization of hot metal is essential for manufacturing high-grade steel. Dephosphorization tests were conducted using a 2-t test converter, adding ladle slag, blowing CaO powder from above, and without using CaF₂, the use of which is restricted by environmental regulations, as a slagging accelerator. The following findings were obtained: (1) the phosphorus content in hot metal was decreased to 0.01 mass% when CaO/SiO₂ was 2, and to 0.001 mass% when it was 3; (2) the phosphorus distribution between top slag and hot metal at the end of blowing was much higher than that thermodynamically predicted; and (3) the molten FeO-CaO forming at the hot spot would likely decrease the phosphorus content in hot metal to an extremely low level even at considerably high temperature.

1. Introduction

Since phosphorus in steel adversely affects the mechanical properties of steel, hot metal dephosphorization is indispensable for producing high-grade steel. Many researchers have studied dephosphorization using flux of CaO-SiO₂-FeO¹⁻⁵⁾, and reported that CaF₂ was an excellent slagging accelerator and played a very important role in hot metal dephosphorization. Its use, however, has been restricted recently by environmental regulations. Since high phosphorus distribution ratios could not be obtained using low basicity slag, Banya et al. studied the use of Al₂O₂ as an alternative to CaF₂ and found that flux of CaO-Al₂O₂-FeO had good dephosphorizing ability.⁶⁾ One author conducted an experiment of hot metal dephosphorization in a 2-kg furnace and a 2-t converter (unless otherwise specified, all the units herein are metric) using CaO-SiO₂-FeO-Al₂O₂ flux, and obtained a high dephosphorization rate when (CaO)/(SiO₂) of the slag was 1.6 to 2.0, and (Al_2O_2) was 5 to 10 mass%.^{7,8)} However, increasing demand for low-phosphorus, high-grade steel and stricter environmental regulations require a new method that can improve dephosphorizing efficiency and avoid the increase in slag generation.

In consideration of the above, we focused attention on the method of blowing O_2 gas and CaO powder from above a hot metal bath during decarburization in the converter.^{9, 10)} By this method, dephosphorization reactions actually accelerated, and the phosphorus concentration at the initial stage of blowing decreased to 0.02 mass% or less. This means that the CaO powder easily melts at the high temperature at the hot spot, and accelerates the dephosphorization reactions. By this method, CaO powder is supplied all through the converter blowing, and as a consequence, the slag basicity in the initial stage of blowing is relatively low. In consideration of this, we thought that, if ladle slag was used as a source of Al_2O_3 , and the CaO powder was blown during all the hot metal treatment, it would be possible to raise the slag basicity and lower the phosphorus content yet further. The CaO powder top-blowing, however, had not been applied to hot metal pretreatment, and its effect was unknown.

In this situation, we conducted a series of tests using a 2-t top/ bottom blowing laboratory converter, and based on the results, studied the effects of applying CaO powder top blowing to hot metal pretreatment.

2. Experiment

2.1 Method

2.1.1 Normal hot metal dephosphorization experiment by converter blowing

Table 1 summarizes the experimental conditions. Two tons of hot metal were charged into the test converter, then iron ore and/or ladle slag were charged, oxygen gas and CaO powder, 0.15 mm or

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Table 1 Experimental conditions (low blowing rate)

Heat	Ladle slag	CaO powder	Initial [Si]	Charged
	(k/t)	(k/t)	(mass%)	basicity (-)
А	_	13.5	0.3	2.0
В	17.3	8.0	0.3	2.0
С	_	10.0	0.05	4.7



Fig. 1 Time chart of top blowing of oxygen gas and lime powder (low blowing rate)

less in particle size, were blown onto the surface of the hot metal bath through the top blowing lance, and then the bath and slag were rinsed, that is, stirred and mixed by bottom blowing. The chemical composition of the hot metal was set as follows: [C] = 4.0 to 4.3 mass%, [Si] = 0.05 to 0.3 mass%, [Mn] = 0.3 mass%, and [P] = 0.10 mass%; and that of the ladle slag: $(CaO)/(SiO_2) = 5.0$, total Fe (hereinafter [T.Fe]) = 8 mass%, and (Al_2O_3) = 19 mass%. The amount of iron ore addition was set at 10 kg/t, and when ladle slag was used, at 17.3 kg/t. When hot metal [Si] was 0.3 mass%, the blowing amount of CaO powder was set at 8 to 13.5 kg/t so that the blow-end slag basicity calculated from burden composition would be 2.0, and when the hot metal [Si] was 0.05 mass%, the blowing amount of CaO powder was set at 10 kg/t so that the calculated blow-end slag basicity would be 4.7. The oxygen top blowing rate Q_{T} and bottom blowing rate Q_p were set at 1.4 and 0.5 Nm³·min⁻¹·t⁻¹, respectively. Figure 1 shows the top blowing pattern. The hot metal temperature rose to the target figure of 1613 K (1340°C) at the end of blowing. The hot metal temperature was measured during the blowing with a thermocouple mounted on the sub-lance.

2.1.2 High-speed hot metal dephosphorization experiment by converter blowing

Table 2 summarizes the experimental conditions. Two tons of hot metal were charged into the test converter, then iron ore and/or ladle slag were charged, and oxygen gas and CaO powder, 0.15 mm or less in particle size, were blown onto the hot metal bath surface through the top blowing lance, and then the bath and slag were rinsed. The chemical composition of the hot metal was set as follows: [C] = 4.0 to 4.3 mass%, [Si] = 0.29 mass%, [Mn] = 0.3 mass%, and [P] = 0.10 mass%; and that of the ladle slag: (CaO)/ $(SiO_2) = 5.0$, T.Fe = 8 mass%, and $(Al_2O_2) = 19$ mass%. The charging/blowing amounts of iron ore, ladle slag, and CaO powder were set at 10, 17.3, and 17.0 kg/t, respectively. The amount of CaO powder was defined so that the calculated blow-end slag basicity would be 3.0. The blowing rate of CaO powder was determined so that FeO-CaO formed at the hot spot remained in the molten state. In Heat D, the top blowing rate of CaO powder was lowered because the flow rate of the top blowing oxygen was low and consequently

Table 2 Experimental conditions (high blowing rate)

Heat	$\begin{array}{c} Q_{B} \\ (Nm^{3} \cdot min^{-1} \cdot t^{-1}) \end{array}$	$\begin{array}{c} Q_{T} \\ (Nm^{3} \cdot min^{-1} \cdot t^{-1}) \end{array}$	$\begin{array}{c} Q_{p} \\ (kg \cdot min^{-1} \cdot t^{-1}) \end{array}$	t _{blowing} (min)
D	0.5	1.7	2.1	12.0
Е	0.5	3.3	2.8	8.0
F	1.0	3.3	2.8	6.5
G	1.6	3.3	2.8	6.5

Q_B: Argon bottom blowing rate

Q_T: Oxygen top blowing rate

Q_p: Lime powder top feeding rate



Fig. 2 Time chart of top blowing of oxygen gas and lime powder (high blowing rate)

the rate of FeO formation at the hot spot was low. The top blowing rate Q_T and the bottom blowing rate Q_B of oxygen were set at 1.7 to 3.3 and 0.5 to 1.6 Nm³·min⁻¹·t⁻¹, respectively. Figure 2 shows the top blowing pattern. The hot metal temperature rose to the target figure of 1673 K (1400°C) at the end of blowing.

2.2 Results

2.2.1 Hot metal dephosphorization by normal blowing

(1) Changes in hot metal temperature and composition during blowing

Figure 3 shows the change in hot metal temperature. The temperature at the end of blowing was roughly 1613 K in any of the Heats. **Figure 4** shows the change of [P] in hot metal during the blowing. The [P] of Heats A, B, and C after the blowing was 0.03, 0.01, and 0.04 mass%, respectively.

(2) Change in slag composition during blowing

Figure 5 shows the change in the slag basicity $(CaO)/(SiO_2)$ during the blowing. In Heats A and B, the slag basicity increased during the blowing, and virtually reached the additive basicity of 2.0. In Heat C, slag data could not be obtained because the slag did not foam during the blowing, and it was impossible to collect a slag sample. Figure 6 shows the relationship between the estimated blow-end slag basicity and the basicity actually measured. The ladle slag melted in the early stage of the blowing, and the estimated basicity and the measured basicity agreed well with each other, which indicates that there was very little scattering loss of CaO powder blown through the top lance.

2.2.2 Hot metal dephosphorization by high-speed blowing

(1) Change in hot metal temperature during blowing

Figure 7 shows the change in the hot metal temperature during the blowing. The temperature at the end of the blowing was roughly 1673 K in all Heats. The blowing time was longer in Heat D than in the others because of the lower oxygen flow rate.

(2) Change in hot metal composition during blowing

Figure 8 shows the change in the hot metal [P] during the blow-

ing. In Heat D, in which $Q_{_T}$ and $Q_{_B}$ were 1.7 and 0.5 $Nm^3 \cdot min^{-1} \cdot t^{-1},$ respectively, dephosphorization continued until the end of the blowing, and [P] in the hot metal fell to 0.002 mass% or less. On the oth-



4.0 Heat-C: L indicates afte \bigcirc no data available top blowing Observed (CaO)/(SiO $_{\circ}$) 3.0 В 2.0 No Ladle CaO powder slag (k/t)(k/t) ΑO 13.5 1.0 17.3 ВΔ 8.0 $\wedge \wedge$ С□ 10.0 0.0 2.0 0.0 1.0 3.0 4.0 Charged $(CaO)/(SiO_2)$ (-)

Fig. 6 Relationship between calculated and observed slag basicity



Fig. 7 Time variation in temperature of hot iron



Fig. 8 Time variation in phosphorus content of hot iron

6

Time (min)

ВΔ

С□

8

17.3

8.0

10.0

12

10

0.5

0

0

Heat-C:

2

no data available

4

er hand, in Heats E and F, in which Q_T was twice that of Heat D, the dephosphorization rate increased remarkably, and [P] decreased to 0.001 mass% in 8 min. Even when Q_T was the same at 3.3 Nm³·min⁻¹·t⁻¹, the dephosphorization rate increased with the increase in Q_B . However, in Heat G, in which Q_B was the highest of all Heats, [P] decreased to 0.006 mass% in 6.5 min, and then rephosphorization took place. This suggests that, under the condition of high stirring power due to a high bottom blowing rate such as in Heat G, (FeO) in the slag decreased at the end of the blowing and rephosphorization occurred.

(3) Change in slag composition during blowing

Figure 9 shows the change in the slag basicity during the blowing. In Heat D, the slag basicity in the initial stage of blowing was low because the CaO powder supply rate was lower than those of the other Heats. In any of the Heats, the slag basicity at the end of the blowing was roughly 3.0, the estimated blow-end basicity.

Figure 10 shows the change in (T.Fe) of slag during the blowing. In Heat D, after (T.Fe) became 30 mass% or more in the early stage of the blowing, it decreased gradually, but it continued to be 15 mass% or more until the blow end. In Heat E with Q_T twice that of Heat D, the (T.Fe) after blowing for 7 min was more than 30 mass%. When Q_T was the same at 3.3 Nm³·min⁻¹·t⁻¹, (T.Fe) decreased as Q_B increased. In Heat G in particular, (T.Fe) fell to 10 mass% or less at the end of the blowing.

2.3 Discussion

2.3.1 Comparison of dephosphorization rates

The sites where dephosphorization reactions took place in the present experiments are the hot spot and the interface between the slag and the hot metal. The overall reaction rate covering both these reaction sites is expressed by Equation (1).

$$-\frac{[P]}{dt} = K_T([P] - [P]_{T,e}) + K_P([P] - [P]_{P,e})$$
(1)

where t is time (min), K is the dephosphorization rate constant (min⁻¹), [P] is the phosphorus concentration (mass%) in hot metal, and e is the equilibrium, and the subscripts T and P indicate hot spot and slag, respectively.

Assuming that the [P] at the equilibrium is negligibly small in both the sites, Equation (1) can be expressed as follows:

$$-\frac{d[P]}{dt} = -K_T \cdot [P] + K_P \cdot [P]$$
(2)

The ratio R_T (%) of the reaction rate at the hot spot to the overall reaction rate is expressed as follows:

$$R_T = 100 \cdot \frac{K_T}{(K_T + K_p)} \tag{3}$$

In Heat C, in which CaO powder was blown onto desiliconized hot metal, the reaction ratio R_T at the hot spot is presumed to be 100%. This is because the basicity of the slag that formed during the blowing was so high at 4.7 that it solidified except at the hot spot, and the share of the dephosphorization reactions by the slag was negligibly small. It is also presumed that the dephosphorization reactions in Heat C were controlled by the molten FeO-CaO forming at the hot spot. From **Fig. 11**, in which the change in [P] during the processing is plotted logarithmically, the apparent reaction rate constant K_T in Heat C was estimated at 0.163 (min⁻¹).

It is likely that in Heat B, in which CaO powder was blown onto hot metal without desiliconization pretreatment, the reaction rate constants K_T and K_p were combined in a certain ratio. This is because the estimated blow-end slag basicity was lower than 2.0, and the melting point of the slag was low, and for these reasons, dephosphorization by the slag could not be ignored. The value of R_T was



Fig. 9 Time variation in slag basicity, (CaO)/(SiO₂)



calculated using Equation (3) based on the $(K_T + K_p)$ obtained from the result of Heat B given in Fig. 11. As seen in **Fig. 12**, the calculated value of R_T was roughly 35%. The reason why there was no contribution of K_T in Heat B in an early stage is that CaO powder was not blown then.

2.3.2 Evaluation of experimental results using coupled reaction model

We evaluated the above experimental results using the coupled reaction model¹¹⁾ that Kitamura et al. proposed for hot metal dephosphorization. The model assumes as follows: (1) CaO powder quickly dissolves in slag; and (2) the dephosphorization reactions proceed at the interface between slag and hot metal. Figure 9 confirms that assumption (1) is correct. Assumption (2), however, has to



Fig. 11 Time variation in phosphorus content of hot iron



be verified by comparing the calculation results with the experimental results. This is because the effect of the powder is not considered in the model.

The coupled reaction model was unable to reproduce what happened at the end of the processing, that is, after 8 min of blowing in Heats D and E, and after 4.8 min in Heats F and G. This is because the coupled reaction model was constructed based on the dephosphorization reactions at the interface between slag and hot metal alone, and did not take into consideration the reactions caused by molten FeO-CaO at the hot spot.

As shown in Figs. 7 to 10, the calculated changes in temperature, [P], $(CaO)/(SiO_2)$, and (T.Fe) during the blowing are in good agreement with the experimental results. However, as seen in Fig. 8, the change in [P] in the low concentration range is not very clear. To make it clearer, the [P] concentration is plotted logarithmically in **Fig. 13**. Although the calculated [P] agrees well with the experimental results, the calculated values are higher than the experimental results at and below 0.02 mass%. This suggests that it is necessary to consider, in addition to the slag/hot metal reactions, the reactions at the hot spot where the top-blown CaO powder directly contacts the hot metal.

As seen in Fig. 13, the logarithmic value of [P] decreases in proportion to the blowing time. Based on this, **Fig. 14** shows the rela-



Fig. 13 Time variation in phosphorus content of hot iron



Fig. 14 Relationship between rate constant of dephosphorization and stirring power

tionship between the dephosphorization rate constant K (min⁻¹) and the stirring power¹² when the [P] calculated from Fig. 13 is 0.02 mass% or less; the rate constant K is obtained by Equation (4). Here, $[P]_e$ is the equilibrium phosphorus concentration in hot metal, and it was assumed to be zero in the calculation.

$$-\frac{d[P]}{dt} = K([P] - [P]_e)$$
(4)

As seen in Fig. 14, the rate constant K is largest when the stirring power ε is 2800 W·t⁻¹. It is clear from the graph that when the stirring power is too large, the dephosphoriz Actually, in Heat E, K increased 2.5 times as much as that in Heat D, in which the topblown oxygen flow rate was only a half. However, in both the present experiments, ε was 1300 W·t⁻¹, lower than 4000 W·t⁻¹, which Mukawa et al. regarded as the critical value below which K would not change depending on the oxygen blowing rate.¹³⁾ The difference can be explained by the effect of CaO powder at the hot spot. This is because Mukawa et al. ation rate constant decreases. confirmed the critical condition without considering the top blowing of CaO pow-

der. The dephosphorization behavior of CaO at the hot spot will be described later.

2.3.3 Achievement level of dephosphorization equilibrium

Using the calculated phosphorus distribution $L_{p, cal.}$ obtainable through Equation (5) proposed by Ogawa et al.¹⁴), we investigated to what extent the dephosphorization equilibrium could be achieved. In Equation (5), concentration (%) or [%] is in mass%, and T is absolute temperature (K).

$$L_{Pcal.} = log \left\{ \frac{(\%P)}{[\%P]} \right\}$$

= 2.5 log (%T.Fe) + 0.0715 {(%CaO) + 0.25 (%MgO)}
+ $\frac{7710.2}{T} - 8.55 \left(\frac{105.1}{T} + 0.0723 \right) \cdot [%C]$ (5)

As shown in **Fig. 15**, the phosphorus distribution L_{P, obs.} obtained through the experiments was much higher than the calculated value L_{P, cal.}, especially in the final stage of blowing. This suggests that the dephosphorization reactions in the present experiments cannot be explained based only on the equilibrium between slag and hot metal. 2.3.4 Evaluation of composition of molten FeO-CaO forming at hot spot

As described above, the dephosphorization behavior at the end of blowing is determined by conditions that cannot be explained without referring to the dephosphorization reactions at the hot spot. For the purpose of this sub-section, the composition of the molten FeO-CaO forming at the hot spot at the end of blowing was calculated based on the following assumptions: (1) all the top-blown oxygen exceeding what is consumed for decarburization is used for the formation of FeO; and (2) the top-blown CaO powder forms molten FeO-CaO. Eventually, the FeO concentrations in the molten FeO-CaO forming at the hot spot in Heats D, E, F, and G were calculated to be 64, 80, 79, and 58 mass%, respectively. The low FeO concentration in Heat G is due to the increased decarburization rate owing to high stirring power.

In Fig. 16, in consideration of the hot spot temperature of 2273 to 2573 K (2000 to 2300°C)¹⁵⁾ and the hot metal temperature of 1673 K (1400°C), approximately, the FeO concentration in the molten FeO-CaO is plotted in the phase diagram of the CaO-FeO binary system.¹⁶⁾ The whole molten FeO-CaO is considered to be in the liquid phase at the hot spot. The liquidus temperature of Heat G is, however, higher than those of Heats D, E, and F. Since the difference between the hot spot temperature and the liquidus temperature is small, the melt is considered to solidify easily when it is away from the spot even by a small distance. On the other hand, the larger the temperature difference between the hot spot and the liquidus line, the greater the contribution of the hot spot is considered to be. Therefore, the method of dephosphorization using the top blowing of CaO powder will likely be improved by increasing the flow ratio of the oxygen to that of the CaO powder and maintaining the high FeO concentration at the hot spot by adequately controlling the top and bottom blowing conditions.

The reason why the rate constant K of Heat G is low as in Fig. 14 is that the FeO-CaO melt that formed at the hot spot solidified and hindered the dephosphorization reactions.

2.3.5 Dephosphorization behavior at hot spot

We thermodynamically studied the dephosphorization behavior in the extremely low [P] concentration region at the hot spot through the following procedure:

(1) The composition of the FeO-CaO-P₂O₅ melt at the hot spot was determined from the composition of the molten FeO-CaO cal-



Fig. 15 Time variation in apparent extent of equilibrium achievement



Fig. 16 Calculated content of (FeO) at hot spot

culated in the previous sub-section and the P_2O_5 formation rate calculated from the change in [P] concentration in the molten steel.

(2) The value of [P] at the hot spot at 2273 to 2573 K (2000 to 2300°C) was evaluated using Healy's equation¹⁷ given below, where (%) or [%] is in mass%, and (% T.Fe), which is used in the above procedure (1), is converted from (% FeO).

$$log\left\{\frac{(\%P)}{[\%P]\cdot(\%T.Fe)^{2.5}}\right\} = 0.08\,(\%CaO) + \frac{22350}{T} - 16 \qquad (6)$$

Figure 17 shows the relationship between temperature and the calculated [P] concentration. At the average temperature of the hot spot of 2423 K (2150°C), calculated [P] is lower than that actually mea-



Temperature at hot spot (K)

Fig. 17 Relationship between calculated [P] and temperature at hot spot

sured. At the end of the blowing, phosphorus distribution much higher than that according to the slag/hot metal equilibrium was obtained, which suggests that the high oxygen potential of the molten FeO-CaO made up for the high temperature at the hot spot, a condition unfavorable for dephosphorization.

2.3.6 Relationship between (T.Fe) and top and bottom blowing condition

The control of (T.Fe) in slag during oxygen top blowing strongly affects slopping, and for this reason, it is essential in actual converter operation. Since (T.Fe) in slag is influenced by experimental conditions such as temperature, (CaO)/(SiO₂), and the ratio of top and bottom blowing, the control of (T.Fe) is not easy. Figure 18 shows that (CaO)/(SiO₂) has little effect on (T.Fe) under the conditions of $(CaO)/(SiO_{2}) = 1.8$ to 3.0 and temperature from 1580 to 1630 K. When the effect of the top and bottom blowing condition on (T.Fe) is strong, the effect can be estimated using the ICO value (index of metallurgical characteristics in BOF) proposed by Higuchi et al.¹⁸⁾ The ICO value is obtained from Equation (7).

$$ICO = 4.2 \times 10^3 \cdot \left(\frac{Q}{W}\right) \cdot \left(\frac{L}{L_0}\right)^{-0.4} \cdot \varepsilon^{-0.33} \cdot [C]^{-1}$$
(7)

Here, Q is the top blown oxygen flow rate $(Nm^3 \cdot s^{-1})$, W is the metal weight (kg), L is the depth of the metal surface depression formed by the top blown oxygen (mm)¹⁹, L_0 is the bath depth (mm), ε is the stirring power density $(W \cdot kg^{-1})^{12}$ and [C] is the carbon concentration (mass %) in hot metal.

From the relationship between (T.Fe) and the ICO value shown in Fig. 19, (T.Fe) increases with the increase in ICO, which suggests that (T.Fe) can be controlled by adequately controlling the top and bottom blowing condition.

3. Conclusions

Using a 2-t top/bottom-blowing test converter, test runs of hot metal dephosphorization were conducted under top blowing of CaO powder, and the following findings were obtained.

- (1) By adding ladle slag and blowing CaO powder from above together with oxygen, the phosphorus concentration in the hot metal could be reduced to 0.01 mass% when CaO/SiO, was 2, and to 0.001 mass% when CaO/SiO₂ was 3.
- (2) Through comparison of the experimental results obtained with and without ladle slag addition, the share of the top blowing of the CaO powder to the hot spot in the total dephosphorization



Fig. 18 Relationship between (T.Fe) and slag basicity, (CaO)/(SiO,)



Fig. 19 Relationship between (T.Fe) and ICO value

rate was estimated at roughly 35%.

- (3) The phosphorus distribution between the top slag and the hot metal at the end of the blowing was much higher than that thermodynamically predicted.
- (4) It is suggested that the molten FeO-CaO forming at the hot spot could reduce the phosphorus content in hot metal to an extremely low level even at considerably high temperature.

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