Carbon Reduction Rate of Phosphorus in Oxide Melt

Hideki ONO¹, Kenichi KOBATA² and Tateo USUI³

¹ Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
² Graduate School of Engineering, Osaka University, now Yodogawa Steel Works, Ltd.
³ Graduate School of Engineering, Osaka University, now Fukui University of Technology

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Abstract
The reduction rate of P₂O₃ in a 50mass%CaO-50mass%Al₂O₃ melt and a dephosphorization slag by carbon was investigated. The apparent rate constant of the reduction reaction of P₂O₃ in the 50mass%CaO-50mass%Al₂O₃ melt by carbon is determined. The activation energy for the reduction reaction of phosphorus in dephosphorization slag is calculated to be E=473 kJ/mol, and the chemical reaction is considered to be the rate-limiting step. Because the FeO content of the dephosphorization slag is much lower than that of the converter slag, the phosphorus is removed by the gasification, and it is expected that the separation and recovery of the phosphorus is possible.

Key words
Iron, Steelmaking, Phosphorus, Reduction, Oxide Melt

1. Introduction
Recently, the demands for the high cleanliness steel have been increased with the upgrading and the diversification of steel products. As refining technologies in steelmaking process, the pretreatment of hot metal, such as desiliconization, desulfurization, and dephosphorization, has been developed. The production rate of the slag is about 120kg/t-steel in the steel-making process, in general. But, it cannot be said that the effective utilization of the slag can be recycled in the iron- and steel-making processes. Moreover, it is desirable to recover the phosphorus from the dephosphorization slag is possible, and the slag sample weighing 20 g was put in a carbon crucible(O.D. 25mm, I.D. 20mm, and height 45mm) and was inserted in an electric resistance furnace. It was heated up to 1773 K in an argon for 120 min. After that, the sample was withdrawn from the furnace and was cooled rapidly. Then, the sample was quickly crushed, and the P₂O₃ content of slag was analyzed by the molybdophosphoric acid blue absorptiometry.

2.2 Reduction rate of phosphorus in dephosphorization slag
The composition of a dephosphorization slag used in this study is shown in Table 1. The slag sample weighing 10 g was put in a carbon crucible(O.D. 40mm, I.D. 30mm, and height 55mm) and was inserted in the electric resistance furnace. The sample was heated and was kept at 1723, 1773, or 1823 K in an argon. After the slag sample was melted, about 0.2 g of the sample was taken out. After that, the slag was sampled at 3 times at interval of about 20 min. After it was cooled rapidly, the phosphorus content was analyzed by the molybdophosphoric acid blue absorptiometry.

2.3 Reduction behavior of phosphorus in dephosphorization slag
The dephosphorization slag sample weighing 20 g was put in the carbon crucible and was inserted in the electric resistance furnace. The sample was heated and was kept at 1773 K in an argon for 120 min. After that, the sample was withdrawn from the furnace and was cooled rapidly. Then, the sample was quickly crushed, and the P⁵⁺ and P⁷⁺ contents of slag were separately analyzed in order to investigate the reduction behavior of phosphorus. The phosphorus content of the granular iron which was formed during the experiment was also analyzed.

3. Results and Discussion
3.1 Reduction rate of phosphorus in 50mass%CaO-50mass%Al₂O₃
Fig.1 shows the variation in P₂O₃ content of 50mass%CaO-50mass%Al₂O₃ melt with time at 1773K. As shown in Fig.1, the P₂O₃ in the 50mass%CaO-50mass%Al₂O₃ melt is reduced by carbon according to Eq.(1). The P₂O₃ in the 50mass%CaO-50mass%Al₂O₃ melt decreases with the passage of time at each oxygen partial pressure.

\[ \text{P}_2 \text{O}_3 \text{(in slag)} + 5 \text{C(s)} = \text{P}_2 \text{(g)} + 5 \text{CO(g)} \]  \hspace{1cm} (1)

For the reaction expressed by Eq.(1), the first order rate equation can be defined by Eq.(2).
where $V$, $A$ and $t$ denote the volume of slag ($m^3$), the reaction area ($m^2$) and time (s), respectively. The integration of Eq.(2) from $(\text{mass}\%P_2O_5)_0$ at $t=0$ to $(\text{mass}\%P_2O_5)$ at $t=t$ gives

$$\ln \left( \frac{\text{mass}\%P_2O_5}{(\text{mass}\%P_2O_5)_0} \right) = k_i \frac{A}{V} t$$  \hspace{1cm} (3)

Similarly, the second order rate equations are represented as follows:

$$-\frac{V}{A} \frac{d(\text{mass}\%P_2O_5)}{dt} = k_i (\text{mass}\%P_2O_5)^2$$ \hspace{1cm} (4)

Fig.1 Variation in $P_2O_5$ content of 50mass%CaO-50mass%Al$_2$O$_3$ melt with time at 1773K

Fig.2 Relationship between $\log(\text{mass}\%P_2O_5)_i/(\text{mass}\%P_2O_5)$ and time at 1773 K when $P_{O_2} \leq 5.15 \times 10^{-18}$ (atm)

$$-\frac{V}{A} \frac{d(\text{mass}\%P_2O_5)}{dt} = k_i (\text{mass}\%P_2O_5)^2$$ \hspace{1cm} (4)

where $V$, $A$ and $t$ denote the volume of slag ($m^3$), the reaction area ($m^2$) and time (s), respectively. The integration of Eq.(2) from $(\text{mass}\%P_2O_5)_0$ at $t=0$ to $(\text{mass}\%P_2O_5)$ at $t=t$ gives

$$\ln \left( \frac{\text{mass}\%P_2O_5}{(\text{mass}\%P_2O_5)_0} \right) = k_i \frac{A}{V} t$$ \hspace{1cm} (3)

Similarly, the second order rate equations are represented as follows:

$$-\frac{V}{A} \frac{d(\text{mass}\%P_2O_5)}{dt} = k_i (\text{mass}\%P_2O_5)^2$$ \hspace{1cm} (4)

Fig.3 Relationship between $1/(\text{mass}\%P_2O_5)_i - 1/(\text{mass}\%P_2O_5)$ and time at 1773 K when $P_{O_2} \geq 7.44 \times 10^{-18}$ (atm)

Fig.4 Dependence of the apparent rate constant on the oxygen partial pressure at 1773 K when $P_{O_2} \leq 5.15 \times 10^{-18}$ (atm)

Fig.5 Dependence of the apparent rate constant on the oxygen partial pressure at 1773 K when $P_{O_2} \geq 7.44 \times 10^{-18}$ (atm)
According to Eq.(3), the value for \( \log(\text{mass}\%P_{2}O_{5})/\text{mass}\%P_{2}O_{5} \) is plotted against time in Fig.2 for the results at \( P_{O_2} \leq 5.15 \times 10^{-18} \) (atm). It is found from Fig.2 that a good linearity is found on the relationship between \( \log(\text{mass}\%P_{2}O_{5})/\text{mass}\%P_{2}O_{5} \) and time. Accordingly, the reaction expressed by Eq.(1) is considered to be the first order with respect to the \( P_{2}O_{5} \) content of the oxide melt at \( P_{O_2} \leq 5.15 \times 10^{-18} \) (atm). Similarly, from the results in Fig.1, the relationship between \( 1/(\text{mass}\%P_{2}O_{5}) - 1/(\text{mass}\%P_{2}O_{5})_i \) and time is also investigated according to Eq.(5). The relationship at \( P_{O_2} \geq 7.44 \times 10^{-18} \) (atm) is shown in Fig.3, from which a good linearity is found on the relationship between \( 1/(\text{mass}\%P_{2}O_{5}) - 1/(\text{mass}\%P_{2}O_{5})_i \) and time. Accordingly, when \( P_{O_2} \geq 7.44 \times 10^{-18} \) (atm), the reaction expressed by Eq.(1) is considered to be the second order with respect to the \( P_{2}O_{5} \) content of the oxide melt. That is to say, the reaction mechanism may change by the oxygen partial pressure. From the slope of the straight line in Figs.2 and 3, the apparent rate constants, \( k_1 \) (m/s) and \( k_2 \) (m/(s⋅mass\%)), can be derived. The dependence of \( k_1 \) and \( k_2 \) on the oxygen partial pressure is shown in Figs.4 and 5, respectively. Under the condition of \( P_{O_2} \leq 5.15 \times 10^{-18} \) (atm), the apparent rate constant, \( k_1 \), slightly increases with an increase of the oxygen partial pressure. Under the condition of \( 7.44 \times 10^{-18} \leq P_{O_2} \leq 2.09 \times 10^{-17} \) (atm), the apparent rate constant, \( k_2 \), is almost fixed to be \( 7.94 \times 10^{-9} \) (m/(s⋅mass\%)), regardless of the oxygen partial pressure.

3.2 Reduction rate of phosphorus in dephosphorization slag

Figure 6 shows the variation in \( P_{2}O_{5} \) content of the dephosphorization slag with time. The \( P_{2}O_{5} \) in slag is reduced by carbon according to Eq.(1) at each temperature. The \( P_{2}O_{5} \) in the slag decreases with the passage of time. It is found from Fig.6 that the reaction rate increases by the addition of carbon powder weighing 3.0 g at 1773K. By rearranging the results in Fig.6, the relationship between \( \log(\text{mass}\%P_{2}O_{5})/\text{mass}\%P_{2}O_{5} \) and time is investigated according to Eq.(3). The relationship is shown in Fig.7, from which a good linearity is found on the relationship between \( \log(\text{mass}\%P_{2}O_{5})/\text{mass}\%P_{2}O_{5} \) and time. Accordingly, the reaction expressed by Eq.(1) is considered to be the first order with respect to the \( P_{2}O_{5} \) content of slag. The apparent reaction rate increased with an increase of temperature and with the addition of carbon powder. Figure 8 shows the dependence of the apparent rate constant on temperature. From the slope of the straight line in Fig.8, the activation energy is calculated to be \( E = 473 \) kJ/mol. This value is much larger than the activation energy of P diffusion in 39.4 mass\%CaO - 38.8 mass\%SiO\(_2\) - 21.2 mass\%Al\(_2\)O\(_3\) melt at 1773 K, \( E = 187 \) kJ/mol.
kJ/mol[1]. The single bonding energy of PO₄ is $E=351$ kJ/mol[2], and the chemical reaction is considered to be the rate-limiting step.

### 3.3 Reduction behavior of phosphorus in dephosphorization slag

Under the strong reducing condition, the phosphorus is reported to be dissolved in slag as P₃⁻, as expressed by Eq.(6) [3].

$$\frac{1}{2} P_2(g) + \frac{3}{2} O^-(\text{in slag}) = P^-(\text{in slag}) + \frac{3}{4} O_2(g) \quad (6)$$

The ratio of P⁵⁺ and P³⁻ in the slag and P in the granular iron after carbon reduction in an argon at 1573K against total P before the reduction is shown in Table 2. The rest (about 95%) of P is considered to be gasified. From the result, it is found that a part of P remains in the slag as P³⁻ after reduction. In case of a converter slag, which includes a lot of FeO component, Eq.(7) proceeds with Eq.(1), and most of the formed phosphorus gas moves to the reduced molten iron.

$$P_2(g) = 2P(\text{in Fe}) \quad (7)$$

Accordingly, in this case, it is difficult to separate and recover only the phosphorus. On the other hand, in this work, only 0.1 mass% of phosphorus dissolves into the granular iron which is formed by the reduction. Accordingly, because the FeO content of the dephosphorization slag is much lower than that of the converter slag, the phosphorus is removed by the gasification, and it is expected that the separation and recovery of the phosphorus is possible.

### 4. Conclusions

The carbon reduction rate of P₂O₅ in an oxide melt (50mass%CaO-50mass%Al₂O₃) and a dephosphorization slag was investigated. The conclusions are as follows:

1. The reduction reaction of P₂O₅ in the 50mass%CaO-50mass%Al₂O₃ melt is the first order with respect to the P₂O₅ content of the oxide melt at $P_{O_2} \leq 5.15 \times 10^{-18}$ (atm). On the other hand, at $P_{O_2} \geq 7.44 \times 10^{-18}$ (atm), the reaction becomes the second order with respect to the P₂O₅ content of the oxide melt. The reaction mechanism may change by the oxygen partial pressure.

2. Under the condition of $P_{O_2} \leq 5.15 \times 10^{-18}$ (atm), the apparent rate constant slightly increases with an increase of the oxygen partial pressure. Under the condition of $7.44 \times 10^{-18} \leq P_{O_2} \leq 2.09 \times 10^{-17}$ (atm), the apparent rate constant is almost fixed to be $7.94 \times 10^{-8}$ (m/(s · mass%)), regardless of the oxygen partial pressure.

3. The activation energy for the reduction reaction of phosphorus in dephosphorization slag is calculated to be $E=473$ kJ/mol, and the chemical reaction is considered to be the rate-limiting step.

4. Because the FeO content of the dephosphorization slag is much lower than that of the converter slag, the phosphorus is removed by the gasification, and it is expected that the separation and recovery of the phosphorus is possible.

### References