Effect of Lime Dissolution Rate in Slag on Hot Metal Dephosphorization

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In order to clarify the effect of the lime (CaO) dissolution rate in slag on hot metal dephosphorization, a 150 kg scale hot metal dephosphorization experiment was carried out. The rate of decrease of free CaO and the dephosphorization rate were measured while varying the ratio of CaO and SiO₂, which was defined as basicity.

The dephosphorization rate showed its maximum value at basicity of around 1.0. At basicity higher than 1.0, the dephosphorization rate decreased due to poor dissolution of CaO in the flux.

A thermodynamic calculation revealed that crystallization of 2CaO·SiO₂-(3CaO·P₂O₅) in the liquid slag deteriorated CaO dissolution when basicity was higher than 1.5.

The mass transfer coefficient of CaO in slag was calculated assuming that the interface between the CaO and liquid slag is saturated with CaO. High basicity showed a low mass transfer coefficient.

The apparent slag viscosity was calculated in terms of the solid phase and showed a correlation with the CaO diffusion rate. The CaO diffusion rate in slag decreased with higher values of not only the liquid slag viscosity, but also the solid-liquid coexistent slag viscosity. These results suggest the existence of an optimum basicity for effective CaO dissolution.

KEY WORDS: hot metal treatment; CaO dissolution rate; basicity; viscosity.

1. Introduction

In recent years, demand for lower phosphorus steel products has increased, while iron ore quality has deteriorated (trend toward higher phosphorus ore), increasing the importance of high efficiency hot metal dephosphorization. CaO efficiency for dephosphorization is important from the viewpoints of reducing both steelmaking slag generation and production costs. Many studies on increasing dephosphorization efficiency have been reported.^{1–7)} Ogasawara *et al.* reported that CaO dissolution was enhanced by increasing FeO generation in the early stage of dephosphorization.¹⁾ Tamura *et al.* reported that CaO dissolution was enhanced by blasting CaO powder from the top lance at the hot spot.²⁾ Other reports have also examined issues such as utilization of a lower melting point agent^{3,4)} and hot recycling of converter slag.⁵⁾ However, basic knowledge concerning the dissolution behavior of CaO into slag is still insufficient. Matsushima *et al.*⁶⁾ evaluated the CaO dissolution rate into slag by rotating CaO processed in a cylindrical shape at 200 to 400 rpm in FeO–CaO–SiO₂ slag at 1 673 K, and evaluated the CaO dissolution rate by measuring the rate of decrease in the diameter of the cylindrical CaO. However,

the slag composition was limited to the lower slag basicity ((%CaO)/(%SiO₂)) region between 0.6 and 1.0, which does not represent a practical condition in hot metal dephosphorization treatment. Kitamura *et al.*⁷⁾ reported the effect of precipitation and dissolution of the solid phase in slag on the dephosphorization rate by an analysis using a coupled reaction model. However, because they assumed the CaO dissolution rate under the condition of higher slag basicity based on the relationship between the solid phase ratio and the viscosity of the slag, an accurate evaluation of the effect of slag basicity was not possible.

In the present work, 60 kg-scale hot metal dephosphorization experiments were carried out in order to evaluate the effect of the CaO dissolution rate into slag on hot metal dephosphorization. In these experiments, the melting behavior of the undissolved CaO in the dephosphorization agent was investigated, and the relationship with the hot metal dephosphorization rate was evaluated. The factors which affect the dissolution behavior of the dephosphorization agent are the chemical composition, size, and amount of the dephosphorization agent, the hot metal temperature, and the stirring condition of the hot metal. However, it was difficult to evaluate the effect of the agent size, as a small-scale melting furnace was used in these experiments. Therefore, a well-ground agent was evaluated at a constant size in this work. Moreover, top-blowing oxygen should be supplied to

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the hot metal to simulate the hot metal dephosphorization process, but in this work, the oxygen was supplied by adding iron oxide powder at fixed intervals to avoid splashing of the hot metal and slag, which cannot be assumed as a constant condition. The effect of the slag composition (basicity) on the CaO dissolution rate was evaluated under the conditions of a constant hot metal temperature and bottom-blowing gas flow rate. The solubility of CaO was calculated by Factsage,^{9,10)} and the CaO dissolution rate was analyzed. In addition, the obtained mass transfer rate constant was compared with those in the other reports.

2. Experimental Procedure

Hot metal dephosphorization experiments were carried out with a 150 kg-scale induction furnace ($\phi 260 \times 500$ mmH). A schematic drawing and the experimental conditions are shown in **Fig. 1** and **Table 1**, respectively. First, 60 kg of pure iron was melted in a MgO crucible and adjusted to the predetermined chemistry (3.5 wt%C-0.1 wt%P) and temperature (1623 ± 20 K) with a carbon material (“CarboNet”, LNS, Asahi Industry Corporation) and Fe-P alloy. Burned CaO (Ube Material Industries, -0.1 mm) and SiO₂ (Kishida Chemical) were mixed and used as the dephosphorization agent. The aimed slag basicity, C/S_{aimed} , was set by changing proportions of the burned CaO powder and SiO₂. 18.7 kg/t of the dephosphorization agent was added from the top at the beginning of the experiment. Iron ore powder (Fe₂O₃: 95 wt%, SiO₂: 3 wt%, total amount: 50 kg/t) was added from the top between the beginning and

Fig. 1. Schematic illustration of experimental setup.

Table 1. Experimental conditions.

Furnace	150 kg induction Furnace	
Crucible	MgO, $\phi 0.25$ m	
Weight	60 (kg)	
Metal	Composition	[%C]=3.5, [%P]=0.1
	Temperature	1623 (K)
Flux	CaO + SiO ₂	18.7 (kg/t) (added at beginning of experiment)
	CaO/SiO ₂	0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5
	Fe ₂ O ₃	6.25 (kg/t) $\times$ 8 (added at 5 min intervals)

35 min at 5 min intervals (8 times). During the experiments, 25–30 NL/min of Ar gas was supplied from a porous plug at the bottom of the MgO crucible. Iron ore was not added between 35 and 60 min. Metal and slag samples were taken during the experiment at 5 min intervals. The metal samples were ground and supplied for wet analysis. The slag samples were cooled in the air, ground, and supplied for wet luminescence analysis. Free CaO in the slag was sampled by extraction separation with ethylene glycol and analyzed by atomic absorption.

3. Experimental Results

3.1. Dephosphorization Behavior

Figure 2 shows an example of the change of the phosphorus content (wt%) in the hot metal, [%P], with time. The dephosphorization reaction proceeded by addition of iron ore, which is an oxygen source. The dephosphorization rate was fast in the order C/S_{aimed} 1.0, 0.5, 3.5 and 2.0, which does not agree with the thermodynamic order. The change of [%P] during 0 to 20 min was regarded as a roughly first-order reaction. Under higher basicity conditions of more than 2.0, the dephosphorization reaction did not proceed after 25 min, even with iron ore addition.

The relationship between the dephosphorization rate between 0 and 20 min and C/S_{aimed} is shown in **Fig. 3**. The dephosphorization rate was defined by Eq. (1), and was also calculated for other conditions not shown in **Fig. 2**.

$$\frac{d[\%P]}{dt} = \frac{[\%P]_{20\text{min}} - [\%P]_{\text{initial}}}{20} \quad \text{..... (1)}$$

Here, [%P]_{20min} is the weight percent of the phosphorus content in the hot metal at 20 min, [%P]_{initial} is the weight percent of the phosphorus content in the hot metal at the beginning of the experiment, and t is time (min).

As shown in **Fig. 3**, the dephosphorization rate increased with increasing C/S_{aimed} in the range of C/S_{aimed} between 0.5 and 1.0. The maximum dephosphorization rate was obtained when C/S_{aimed} was 1.0, and the dephosphorization rate decreased at higher C/S_{aimed} of more than 1.5. It is considered that the dephosphorization rates at the lower C/S_{aimed} of 0.5 and 0.75 were low due to a shortage of CaO. On the

Fig. 2. Changes in [%P] with time.

Fig. 3. Dephosphorization rate calculated at each aimed basicity.

other hand, solidified slag was observed under high C/S_{aimed} conditions between 1.5 and 3.5. Under those conditions, the dephosphorization rates were low because the added CaO did not melt, and thus did not function as a dephosphorization agent.

3.2. CaO Melting Behavior

The change in the slag chemistry corresponding to CaO dissolution is important for evaluating the effect of slag basicity on hot metal dephosphorization behavior. In this work, the transition of undissolved CaO, *i.e.*, free CaO (hereinafter, f-CaO), is the focus of study for evaluating the CaO dissolution at each slag basicity. The solid ratio of CaO is defined as shown in Eq. (2).

$$\text{CaO solid ratio} = \frac{(\%f - \text{CaO})}{(\% \text{CaO})} \times 100 \quad \text{..... (2)}$$

Here, (%CaO) is the total CaO content (wt%) including f-CaO, and (%f-CaO) is the free CaO content (wt%) in the slag. The change of the solid CaO ratio is shown in Fig. 4. The solid CaO ratio decreased under all conditions of aimed slag basicity. Substantially 100% of the added CaO dissolved at lower aimed slag basicities smaller than 1.0, and the remaining f-CaO increased as the aimed slag basicity increased.

Figure 5 shows the relationship between the aimed and observed slag basicity. Here, the observed slag basicity was calculated from the dissolved CaO content by subtracting (%f-CaO) from (%CaO) and (%SiO₂), as shown in Eq. (3).

$$\text{Basicity}_{\text{obs.}} = \frac{(\% \text{CaO}) - (\%f - \text{CaO})}{(\% \text{SiO}_2)} \quad \text{..... (3)}$$

As shown in Fig. 5, the observed slag basicities approached the aimed value with time, but the difference between the observed and aimed slag basicities expanded as the aimed slag basicity increased. Especially at the aimed slag basicity of 3.5, 50% of the added CaO did not contribute to the dephosphorization reaction at 10 min. Therefore, the added CaO did not contribute to dephosphorization at 1623 K due to the lower CaO dissolution rate.

3.3. Reduction Behaviour of Iron Oxide

Figure 6 shows an example of the change of the iron

Fig. 4. Influence of aimed basicity on decrease of f-CaO.

Fig. 5. Comparison between aimed and observed basicity.

 Fig. 6. Changes in (%FeO) + (%Fe₂O₃) with time.

oxide content (wt%FeO + wt%Fe₂O₃) in the slag at each level of C/S_{aimed} . The iron oxide content tends to be lower at higher slag basicities. Therefore, the reduction rate of the added iron oxide is considered to be higher at higher slag basicity, since the addition rate of iron oxide is the same

under all conditions. (The iron oxide mainly reacts with the carbon in the hot metal as an oxygen source). Although it is conceivable that slag foaming or other second-order effects caused by decarburization might affect CaO dissolution, this point is not considered here due to the complexity of the phenomena. Hence, the CaO dissolution rate was analyzed by using the obtained iron oxide content in the slag.

4. Discussion

4.1. Procedure for Calculation of CaO Dissolution Rate

The relationship between the slag basicity and CaO dissolution rate was evaluated based on the decreasing rate of the obtained f-CaO and the saturated CaO content calculated by Factsage.^{9,10} Figure 7 shows a conceptional diagram of CaO dissolution in slag. Solid CaO exists in the liquid bulk slag. At higher slag basicities, the liquid bulk slag coexists with the dicalcium silicate phase (2CS, or with tricalcium phosphate 2CS(-3CP)). The interface between the solid CaO and the liquid bulk slag can be regarded as CaO saturation during CaO dissolution.

Matsushima *et al.*⁶ reported that the CaO dissolution rate is proportional to the difference between the liquid CaO content ($(\%CaO)_{liquid}$) and the saturated CaO content at the interface of solid CaO ($(\%CaO)_{sat.}$). In their paper, $(\%CaO)_{sat.}$ was obtained by using the CaO–SiO₂–FeO phase diagram shown in Fig. 8. In Fig. 8, $(\%CaO)_{sat.}$ can be obtained by finding the intersection between the lines. In Fig. 8, one line is produced by joining the bulk slag composition (Fig. 8①) and the vertex of CaO, and the other line is the CaO saturated liquidus line (Fig. 8②). In their study, the precipitated solid phase can be ignored since the aimed slag basicities are 0.6 and 1.0. However, in actual hot metal dephosphorization, the solid phase cannot be ignored as the slag basicity is higher than those in their study. Hence, the change of $(\%CaO)_{liquid}$ is evaluated by expanding their approach as shown in Eq. (4). Here, the driving force of CaO dissolution ($\Delta(\%CaO)$) and $(\%CaO)_{liquid}$ are defined by Eqs. (5) and (6), respectively.

$$\frac{d(\%CaO)_{liquid}}{dt} = K_{CaO} \{ \Delta(\%CaO) \} \dots \dots \dots (4)$$

$$\Delta(\%CaO) = (\%CaO)_{sat.} - (\%CaO)_{liquid} \dots \dots \dots (5)$$

Fig. 7. Schematic illustration of CaO dissolution.

$$(\%CaO)_{liquid} = (\%CaO) - (\%f-CaO) - (\%CaO)_{2CS-3CP} \dots (6)$$

Here, K_{CaO} is the overall reaction rate constant (1/min) and $(\%CaO)_{2CS-3CP}$ is the precipitated CaO content (wt%) as 2CS-3CP. $(\%CaO)_{sat.}$ and $(\%CaO)_{2CS-3CP}$ are calculated by using the ternary phase diagrams shown in Figs. 8 and 9 based on the procedure in Fig. 10. First, the bulk slag composition is obtained by subtracting f-CaO from the slag composition obtained by a chemical analysis, and an equilibrium calculation using the obtained slag composition (① in Figs. 8 and 9). Here, the bulk liquid CaO content is assumed to be the bulk slag content in the case without precipitation of the 2CS(-3CP) phase (① Fig. 8). On the other hand, in the case with precipitation of the 2CS(-3CP) phase, the bulk slag composition is assumed to be the slag composition coexisting with 2CS-3CP. Next, an equilibrium calculation based on the obtained liquid slag composition is conducted by increasing the CaO content while keeping the same weight ratio of the other components except for CaO. The calculation is repeated until CaO precipitation occurs, and the obtained slag composition is assumed as $(\%CaO)_{sat.}$ (② in Figs. 8 and 9).

4.2. Calculation Results of $(\%CaO)_{sat.}$

The relationship between the observed slag basicity and $(\%CaO)_{sat.}$ is shown in Fig. 11. $(\%CaO)_{sat.}$ is obtained by an equilibrium calculation in a CaO–SiO₂–FeO–Fe₂O₃–Al₂O₃–P₂O₅–MgO–MnO system considering 2CS(-3CP)

Fig. 8. Calculation of $(\%CaO)_{sat.}$ without 2CS crystallization.

Fig. 9. Calculation of $(\%CaO)_{sat.}$ with 2CS crystallization.

Fig. 10. Procedure for calculation of liquid and CaO saturated slag composition.

Fig. 11. Variation of $(\%CaO)_{sat.}$ with observed basicity. Fig. 12. Variation of $\Delta(\%CaO)$ with observed basicity.

precipitation. The observed slag basicity is calculated by Eq. (3). In Fig. 11, the observed slag basicity changes from lower to higher slag basicity as CaO dissolution progresses with time. The 2CS(-3CP) phase precipitates under the condition that the observed slag basicity is higher than 1.2. The obtained $(\%CaO)_{sat.}$ is in the range between 40 and 60%. $(\%CaO)_{sat.}$ of the liquid slag tends to be lower with higher observed slag basicity. Moreover, the values of $(\%CaO)_{sat.}$ at lower aimed slag basicities between 0.5 and 1.0 are higher than those at higher aimed slag basicities of 2.0 to 3.5. This is caused by the change in the liquid slag composition as the reduction rate of the added iron ore changes. The relationship between the observed slag basicity and $\Delta(\%CaO)$ is shown in Fig. 12. Here, $\Delta(\%CaO)$ is calculated by Eq. (5). $\Delta(\%CaO)$ tends to decrease as the observed slag basicity increases, but stagnates due to 2CS(-3CP) precipitation. This is caused by the difference between the liquidus lines at the higher and the lower CaO side of the 2CS saturation region, as shown in Fig. 9.

4.3. Calculation of Overall Reaction Rate Constant (K_{CaO})

Equation (7) is obtained by integrating both sides of Eq. (4).

$$\ln \frac{(\%CaO)_{sat.}}{(\%CaO)_{sat.} - (\%CaO)_{liquid}} = K_{CaO} \times t \quad \text{..... (7)}$$

The CaO dissolution rate is organized by the calculated CaO saturation solubility. The result is shown in Fig. 13. In Fig. 13, the plots at 5 min are higher than the other plots after 5 min. It is thought that the added CaO at 5 min is easily dissolved in $SiO_2-Fe_2O_3$ slag, which is a dilute CaO solution. Hence, the analysis was carried out on the assumption that the CaO dissolution rate can be organized by the first-order reaction from 0 to 20 min if the data at 5 min are excluded. The lines in Fig. 13 are obtained by approximation by the least-squares method for the case in which the y-intercept is 0. The slope of the lines is equivalent to the overall reaction rate constant (K_{CaO}). K_{CaO} for the other conditions was

Fig. 13. Relationship between time and value of left side of Eq. (7).

also organized and calculated in the same way as in Fig. 13.

The mass transfer rate of CaO is discussed in order to understand the physical meaning of K_{CaO} . The relationship between K_{CaO} and the mass transfer rate is defined as show in Eq. (8). Here, V_{bulk_slag} (m^3) is the total slag volume combining the solid and liquid volumes, and A_{f-CaO} (m^2) is the sum of the surface area of f-CaO. The mass transfer rate of CaO in the liquid slag, k_{CaO} (cm/s), can be obtained by Eq. (9), which is obtained by deforming Eq. (8).

$$K_{CaO} \times \frac{1}{60} = -\frac{A_{f-CaO}}{V_{bulk_slag}} \times \frac{1}{100} \times k_{CaO} \quad (8)$$

$$k_{CaO} = K_{CaO} \times \frac{100}{60} \times \frac{V_{bulk_slag}}{A_{f-CaO}} \quad (9)$$

Here, the undissolved CaO is defined as a sphere of uniform size, and the slag volume, V_{bulk_slag} (m^3), and the sum of the surface area of f-CaO, A_{f-CaO} (m^2), are calculated by Eqs. (10) and (15), respectively.

$$V_{bulk_slag} = \frac{W_s}{\rho_s} \quad (10)$$

$$W_s = CaO(kg/kg) \times W_m \times \frac{100}{(\%CaO)} \quad (11)$$

$$V_{f-CaO} = \frac{W_{f-CaO}}{\rho_{f-CaO}} \quad (12)$$

$$W_{f-CaO} = W_s \times \frac{(\%f-CaO)}{100} \quad (13)$$

$$V_{f-CaO} = \frac{4\pi}{3} \times r^3 \times n \quad (14)$$

$$A_{f-CaO} = 4\pi \times r^2 \times n = \frac{3V_{f-CaO}}{r} \quad (15)$$

Here, W_s is the total weight of the slag (kg), W_m is the weight of the hot metal (60 kg), ρ_s is the density of the liquid slag (3 460 kg/m^3),¹⁴ V_{f-CaO} is the volume of f-CaO (m^3), W_{f-CaO} is the weight of f-CaO (kg), ρ_{f-CaO} is the density of f-CaO (3 346 kg/m^3),^{12,13} r is the radius of f-CaO (m),

Fig. 14. Photograph of f-CaO observed in slag.

Fig. 15. Mass transfer coefficient of CaO calculated at each aimed basicity.

and n is the number of free-CaO particles.

An example of a slag sample obtained during the experiment is shown in Fig. 14. The observed f-CaO particles in the slag are larger than 0.1 mm, which is the size of the added CaO. This is attributed to aggregation of CaO particles during the experiments. The size of the aggregated CaO in the slag is not constant. Therefore, the maximum diameter of the added CaO, 0.1 mm is defined as the CaO size, and the radius of CaO, $r=5 \times 10^{-5}$ (m) is used in the calculations.

The relationship between the aimed slag basicity and k_{CaO} is shown in Fig. 15. The data reported by Matsushima *et al.*⁶ and Hamano *et al.*¹⁵ are also shown in Fig. 15. The k_{CaO} values obtained in this work are smaller than those in their reports.^{6,15} In the report by Matsushima *et al.*⁶ k_{CaO} was obtained by the rate of decrease of the radius of a CaO cylinder submerged and rotated in liquid slag, and the rate of decrease, dR/dt (cm/s) was evaluated by Eq. (16).

$$\frac{dR}{dt} = \frac{k_{CaO} \rho_s}{100 \rho_{f-CaO}} \{ \Delta(\%CaO) \} \quad (16)$$

Here, R is radius of the CaO cylinder (cm). In the present work, the slag is located on hot metal stirred by bottom-blowing gas, so the stirring condition of the slag is weak compared to that in Matsushima *et al.*⁶ The obtained k_{CaO}

values when the slag basicity is around 1.0 are nearly the same as those reported by Matsushima *et al.*⁶⁾ In this case, CaO dissolution proceeded to around 100%. Therefore, the obtained data are relatively consistent with the values in the previous reports, even when the added CaO is completely dissolved. In the case of higher slag basicities of more than 1.5, k_{CaO} tends to decrease with increasing slag basicity, and k_{CaO} was one order smaller than those in the lower slag basicity region smaller than 1.0.

Since differences in the properties of slag corresponding to slag basicity are considered to affect k_{CaO} , the following discussion focuses on the viscosity of slag.

4.4. Effect of Slag Viscosity on k_{CaO}

As indicated in 4.1, an equilibrium calculation was conducted based on the obtained slag composition excluding the f-CaO and precipitated solid phases at 1 623 K. The relationship between the slag viscosity, η_0 (Pa·s) at 1 623 K calculated by Factsage and k_{CaO} categorized by the volume fraction of the solid phase is shown in Fig. 16. The volume fraction of the solid phase, ϕ (-), is defined as shown in Eq. (17).

$$\phi = \frac{(\%f\text{-CaO})/\rho_{f\text{-CaO}} + (\%2\text{CS})/\rho_{2\text{CS}} + (\%2\text{CS-3CP})/\rho_{2\text{CS-3CP}}}{(\%f\text{-CaO})/\rho_{f\text{-CaO}} + (\%2\text{CS})/\rho_{2\text{CS}} + (\%2\text{CS-3CP})/\rho_{2\text{CS-3CP}} + (\%\text{slag}_{\text{liquid}})/\rho_s} \quad (17)$$

Here, the contents in Eq. (17) are all weight percent, $\rho_{2\text{CS}}$ is the density of 2CS (3 300 kg/m³),^{12,13)} and $\rho_{2\text{CS-3CP}}$ is the density of 2CS-3CP (3 195 kg/m³).^{12,13)} As shown in Fig. 16, k_{CaO} decreased slightly with increasing slag viscosity at the same volume fraction. This is attributed to a decreasing diffusion rate of CaO in slag with increasing slag viscosity. On the other hand, k_{CaO} is small under the condition of a high volume fraction of solid phase, even when the viscosity of the liquid slag is the same. Therefore, the effect of the solid phase in slag on the slag viscosity will be discussed as follows.

The viscosity of a suspension of a solid and liquid mixture has been widely studied in the field of chemical engineering.^{16,17)} The slag in this work can be assumed as a suspension of a solid and liquid mixture. In the case of

dilute suspension (solid ratio <2%), the effect of the solid phase on viscosity can be evaluated by Einstein's equation, shown here as Eq. (18).

$$\eta_r = \frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (18)$$

Here, η_r (-) is relative viscosity, and η (Pa·s) is the viscosity of the suspension.

In this work, the solid fraction is larger than 2%, and in this case, the slag viscosity can be estimated by the Mori and Ototake¹⁷⁾ Eq. (19), which was expanded to the higher solid fraction.

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \frac{d - S_r}{2} \times \frac{1}{1/\phi - 1/\phi_{\text{vc}}} \quad (19)$$

Here, d (m) is the average diameter of the suspended particles, S_r (m²) is the specific surface area of the particles in a unit volume, and ϕ_{vc} (-) is the limit volume concentration. If the particle shape is assumed to be spherical, $d \cdot S_r/2 = 3$ regardless of the size distribution of the particles. Hence, the relative viscosity is a function only of the solid volume fraction. Moreover, if the cube filling rate of spherical particles of the same size can be defined as the limit volume concentration, ϕ_{vc} (-) = 0.52. This is the limit concentration in case shearing deformation of the spherical particle layer occurs continuously and steadily. In this work, the viscosity is calculated assuming that the solid particles are all spherical.

$$\eta = \eta_r \times \eta_0 = \eta_0 \times \left(1 + \frac{3}{1/\phi - 1/0.52} \right) \quad (20)$$

The calculated viscosity becomes infinitely large when the solid volume fraction is 0.52, and viscosity is calculated as a minus value when the solid volume fraction is larger than 0.52. That is, at solid fractions larger than 52%, it is assumed that the shearing deformation of the spherical particle layer is not realized due to contact between the solid particles, and for this reason, Eq. (20) cannot be applied.

Accordingly, in this work, the viscosity of the solid and liquid phase mixture was evaluated for solid fractions smaller than 52%. The calculation results are shown in Fig. 17. Equation (18) is used in case ϕ is smaller than 2%, and Eq. (20) is used in case ϕ is between 2 and 52%. The

Fig. 16. Influence of slag viscosity (liquid) on mass transfer coefficient of CaO.

Fig. 17. Influence of slag viscosity (solid-liquid coexistent) on mass transfer coefficient of CaO.

horizontal axis of Fig. 17 is the mass transfer rate of CaO in slag calculated by Eq. (9). k_{CaO} decreased with increasing slag viscosity considering the effect of the solid fraction. k_{CaO} decreased remarkably under the condition that the slag viscosity was in the range between 0.05 and 0.25 Pa·s, and shifted to the order of 10^{-5} cm/s at slag viscosities higher than 0.25 Pa·s.

In this work, the CaO dissolution rate is high, but the hot metal dephosphorization rate is low when the slag basicity is smaller than 1.0. On the other hand, the hot metal dephosphorization rate decreased with increasing CaO addition at higher slag basicities larger than 1.0. In this case, in addition to a smaller driving force of CaO dissolution into the liquid slag, $\Delta(\% \text{CaO})$, the slag viscosity also becomes higher overall due to the presence of solid phases such as f-CaO and 2CS(-3CP), and this higher viscosity prevents both mass transfer of CaO in the liquid slag and CaO dissolution. Therefore, under a condition of higher slag basicity, it is important to control the slag composition to the lower SiO_2 and higher FeO region before CaO addition, and strong stirring is effective for CaO dissolution. Moreover, the existence of an optimum slag basicity for obtaining higher CaO efficiency for dephosphorization and increasing the dephosphorization rate was also suggested. Further investigation is needed, including clarification of the oxygen supply by oxygen gas, the change in the melting point by iron oxide addition, and stirring by the decarburization reaction. Furthermore, an investigation of the effect of the size of CaO on its dissolution rate through larger scale experiments is also necessary.

5. Conclusion

The effect of the CaO dissolution rate on hot metal dephosphorization was investigated in small-scale experiments. The conclusions are as follows,

(1) The dephosphorization rate at 1 623 K showed higher values at basicities of 0.5 to 1.0. At basicity higher than 1.0, the dephosphorization rate decreased due to poor CaO dissolution in the flux.

(2) The free CaO (f-CaO: undissolved CaO) content in the slag increased with increasing slag basicity. The saturated CaO content in slag, $(\% \text{CaO})_{\text{sat.}}$, obtained by a thermodynamic calculation for $2\text{CaO} \cdot \text{SiO}_2$ ($-3\text{CaO} \cdot \text{P}_2\text{O}_5$) precipitation decreased with increasing slag basicity.

(3) The total reaction rate constant of CaO dissolution and the mass transfer coefficient of CaO in slag was calculated from the f-CaO content and $(\% \text{CaO})_{\text{sat.}}$ obtained by a thermodynamic calculation. The obtained k_{CaO} was substantially the same as that in the previous reports at the aimed basicity of around 1.0, which is the condition of a higher liquid fraction.

(4) Higher k_{CaO} was obtained by a smaller liquid slag viscosity in the case of a lower solid fraction of slag. In the case of a higher solid fraction of slag, k_{CaO} decreased as the solid fraction increased, even at the same liquid slag viscosity. The stirring energy acting on slag is decreased by the solid fraction. These results suggest the existence of an optimum basicity for higher CaO efficiency and an increased

dephosphorization rate.

Symbols

- $A_{\text{f-CaO}}$: Sum of surface area of free-CaO (m^2)
- $(\% \text{CaO})$: Total CaO content in slag (wt%)
- $(\% \text{CaO})_{\text{liquid}}$: CaO content in liquid slag (wt%)
- $(\% \text{CaO})_{2\text{CS-3CP}}$: CaO content in 2CS-3CP (wt%)
- $(\% \text{CaO})_{\text{sat.}}$: Saturated CaO content in liquid slag (wt%)
- C/S_{aimed} : Aimed basicity (-)
- d : Average diameter of suspended particles (m)
- f-CaO: Free CaO (undissolved CaO in slag)
- $(\% \text{f-CaO})$: Free CaO content in slag (wt%)
- k_{CaO} : Mass transfer rate (cm/s)
- K_{CaO} : Total reaction rate constant (1/min)
- n : Number of free CaO particles (N)
- $[\% \text{P}]$: Phosphorus content in hot metal (wt%)
- R : Radius of CaO cylinder (cm)
- S_r : Specific surface area of particles in a unit volume (m^2)
- t : Time (min)
- $V_{\text{bulk slag}}$: Total slag volume (m^3)
- $V_{\text{f-CaO}}$: Free CaO volume (m^3)
- V_m : Hot metal volume (m^3)
- $W_{\text{f-CaO}}$: Free CaO weight (kg)
- W_m : Hot metal weight (kg)
- W_s : Slag weight (kg)
- η : Viscosity of suspension (Pa·s)
- η_0 : Viscosity of liquid slag (Pa·s)
- η_r : Relative viscosity (-)
- $\rho_{2\text{CS}}$: Density of 2CS phase (kg/m^3)
- $\rho_{2\text{CS-3CP}}$: Density of 2CS-3CP phase (kg/m^3)
- $\rho_{\text{f-CaO}}$: Density of CaO (kg/m^3)
- ρ_s : Density of liquid slag (kg/m^3)
- ϕ : Volume fraction of solid phase (-)
- ϕ_{vc} : Limit volume concentration (-)

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