1. Introduction

In the hot-metal dephosphorization process, rapid and complete dissolution of solid lime (CaO) into molten slag is required to maintain a high efficiency of CaO utilization, which reduces the dephosphorization slag evolved in the process. Although calcium fluoride (CaF₂) is known to be an effective flux which accelerates the dissolution of CaO, considerations have promoted discussion about reducing the amount added. Therefore, an alternative flux or a new slag system which does not contain calcium fluoride should be sought. Measurement of the dissolution rate of CaO will provide valuable information on this problem. However, in many previous studies experimental conditions of slag composition and experimental temperatures have been relatively limited.1–9

In the present work, CaCl₂, Al₂O₃ and B₂O₃ were chosen as the effective additives because they increase the CaO solubility and reduce the slag viscosity. The dissolution rate of CaO into FeO–CaO–SiO₂–X (X; CaF₂, CaCl₂, Al₂O₃, and B₂O₃) melts at hot-metal temperatures was measured, and the enhancement factor of the additives on CaO dissolution rate was estimated based on the experimental results.

2. Experimental

The experimental apparatus is schematically shown in Fig. 1. The slag samples were prepared by mixing the synthesized FeO and reagent grade CaO, SiO₂, CaF₂, CaCl₂, Al₂O₃ and B₂O₃. The slag composition was calculated from the weighed values of reagents because it was confirmed in the preliminary experiment that the slag composition was marginally changed after the melting. A polycrystalline CaO rod (purity: 99.9%, diameter: 10 mm, height: 30 mm, apparent density: 3.08 g/cm³) was prepared, which was attached to a stainless rod and rotated by a speed variable motor.

A slag sample of about 20 g charged in an iron crucible was heated and melted in a SiC electric resistance furnace under Ar atmosphere. After confirming the complete melting and homogenization of the slag sample, the CaO rod was carefully lowered to a position just above the slag and was kept there for at least 5 min to allow its temperature to become equal to that of the slag. The revolution speed of the CaO rod was set to a selected value and the rod was submerged in the slag; the submerged depth was fixed at 10 mm for each run. After the dissolution the rod was removed from the system and was quenched by flushing Ar. The un...
melted core radius of the rod was measured using a digital microscope and the dissolution rate of CaO calculated by decrease in the radius of the rod. As compared with the effect of the dissolution from the wall of the CaO rod, that from the bottom was less than 5% during the experiment, which was considered to be negligible. Therefore, only the dissolution from the wall of a sample was taken into account in calculating the dissolution rate of CaO.

3. Results and Discussion

Figure 2 shows the relationship between the decrease in CaO radius and the reaction time for 40 mol% FeO–30% CaO–30% SiO2 slag at 1 573 K, where the revolution speed of the CaO sample was 300 rpm. The decrease in CaO radius increased linearly with the reaction time within 6 min.

For a cylinder with radius \( r \) and height \( h \), the volume \( V \) and the surface area of the wall \( S \) are represented by Eqs. (1) and (2):

\[
V = \pi r^2 h \quad \text{........................(1)}
\]

\[
S = 2\pi rh \quad \text{..........................(2)}
\]

The dissolution rate of CaO, \( v_r \) (m/s) is defined as the dissolved volume per unit area in a unit of time:

\[
v_r = \frac{1}{S} \frac{dV}{dt} = \frac{dr}{dt} \quad \text{..........................(3)}
\]

The relationship between \( v_r \) and the revolution speed at 1 573 K for the 40% FeO–30% CaO–30% SiO2 system is shown in Fig. 3. Since the dissolution rate of CaO increased with the revolution, the dissolution of CaO was believed to be governed by the mass transfer of CaO in a liquid phase in the present work.

Figure 4 shows the effect of FeO concentration on the dissolution rate of CaO at 1 573 K, where (%CaO)/(%SiO2) of the melt was unity and the revolution speed was 300 rpm. The dissolution rate of CaO increased with FeO concentration. The same tendency was reported by Matsushima et al. The results of constitution, \( X \), added to the FeO–CaO–SiO2 melt are also plotted. For 10% addition of CaF2, CaCl2 accelerated the CaO dissolution; the effect of these additives to the slag will be discussed later.

Figure 5 shows the effect of basicity, (%CaO)/(%SiO2) of the melt on the dissolution rate of CaO at 1 573 K, for 40 mol% FeO, 300 rpm: the dissolution rate of CaO decreased with basicity. Consequently, from Figs. 4 and 5, the slag for high FeO content and low basicity accelerated CaO dissolution.

The liquid phase mass transfer coefficient, \( k \) (m/s) was calculated based on the results obtained using Eq. (4) which was derived by Matsushima et al.:

\[
-\frac{dr}{dt} = k \frac{\rho_{FeO} \times \Delta (\text{mol}\%\text{CaO})}{100} \quad \text{..........(4)}
\]

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where $\rho_s$ and $\rho_{CaO}$ are the density of the slag and CaO (kg/m$^3$), $\Delta$(mol%CaO) is the difference of the CaO concentration between the initial value and the saturation, where the saturated composition was determined by reading the liquidus on the Fe$_2$O–CaO–SiO$_2$ ternary phase diagram.

The relationship between the liquid phase mass transfer coefficient and Reynolds number at 1 573 K is plotted in Fig. 6. For the 40%Fe$_2$O–30%CaO–30%SiO$_2$ (full circle), Eq. (5) was obtained from the plots of the mass transfer coefficient, \(k\), against the Reynolds number.

\[
\log k = 0.70 \log Re - 5.87 \quad \text{..................................(5)}
\]

Therefore, the relationship between \(k\) and \(Re\) is expressed as Eq. (6),

\[
k = Re^{0.70} \quad \text{......................................(6)}
\]

The same relationship was obtained from the data reported by Matsushima et al.\(^6\) The power of \(Re\) was calculated as 0.66 for ironmaking slags at 1 773 K and as 0.69 for steelmaking slags at 1 673 K.

For the dissolution of a rotating cylindrical specimen in a liquid, it has been reported that the boundary layer thickness is proportional to $Re^{-0.7}$ for benzoic acid to water,\(^10\) and to $Re^{-0.62}$ for steel to liquid aluminum or to liquid zinc.\(^11\) If we assume that the composition of the bulk liquid phase is constant, the diffusion coefficient would be constant. Therefore, the mass transfer coefficient should be inversely proportional to the boundary layer thickness. The results of the present work denote good agreement with the results using other kinds of materials.

The dimensionless numbers: Sherwood number \(Sh\), Reynolds number \(Re\) and Schmidt number \(Sc\) were calculated from the results obtained and from the literature.\(^12\)–\(^14\) For the solid–liquid mass transport phenomenon in some metallurgical processes, the relationship between these three dimensionless numbers could be expressed as

\[
Sh = CRe^{\alpha}Sc^{\beta} \quad \text{..................................(7)}
\]

In the present work the relationship between \(k\) and \(Re\) was found to be expressed using Eq. (5). Since \(Sh\) is proportional to \(k\), \(\alpha\) in Eq. (7) was determined to be 0.70. On the other hand, \(\beta\) in Eq. (7) was difficult to estimate because of the lack of physicochemical properties such as a diffusivity of calcium ion in the slag used in the present study. The value of \(\beta\) was assumed to be 1/3, which was reported for the solid–liquid mass transfer in the literature.\(^12\)–\(^14\) The relationship between \(Sh\) and \(Re^{0.70}Sc^{1/3}\) for 40%Fe$_2$O–30%CaO–30%SiO$_2$ slag at 1 573 K was derived as Eq. (8):

\[
Sh = 0.36Re^{0.70}Sc^{1/3} \quad \text{..................................(8)}
\]

Figure 7 shows the relationship between the mass transfer coefficient and the reciprocal temperature for the Fe$_2$O–CaO–SiO$_2$ system, when the revolution speed was 300 rpm. According to Arrhenius’ law, the slope of the solid line accords with $-E/R$, where \(E\) is activation energy (J/mol) and...
R is gas constant (J/mol · K). Equation (9) was obtained by the least squares method:

\[ \log k = -0.71 \times 10^4 \frac{T}{T} + 0.05 \] ..........................(9)

Calculation from the value of the slope yields the activation energy of 137 kJ/mol (32.6 kcal/mol) for the dissolution of CaO into the 40%FeO–30%CaO–30%SiO₂ melt.

The effect of additives, X: CaF₂, CaCl₂, Al₂O₃ and B₂O₃ to FeO–CaO–SiO₂ melt on the decrease in rod radius at 1573 K is shown in Fig. 8, when the revolution speed of sample was 300 rpm. The dissolution of CaO is accelerated by the addition of these composites; CaF₂, in particular, increases the dissolution significantly. The acceleration effect of CaF₂ on CaO dissolution has been confirmed in many reports, however, studies on the addition of CaCl₂, Al₂O₃ and B₂O₃ are quite limited. From the figure, CaCl₂ and B₂O₃ also enhance the dissolution rate but the effect of adding Al₂O₃ was minimal. Since the decrease in rod radius increases linearly with the reaction time within 2 min, the dissolution rate of CaO was calculated using slopes of each line in the figure.

Figure 9 shows the effect of the concentration of additives on the dissolution rate, and it can be found that \( v_e \) increases linearly with additive concentration up to 10 mol%. For convenience in practical operation, the concentration unit was converted from mol% to mass% in the figure. The effect of additives on \( v_e/v_0 \) can be estimated using Eq. (10),

\[ v_e = v_0 \times \{1.0 + E_{dis} \times (\text{mass}\%X)\} \] ..........................(10)

where \( v_0 \) (m/s) is the dissolution rate of CaO into 45mass%FeO–27%CaO–28%SiO₂ melt at 1573 K and \( E_{dis} \) (mass%⁻¹) is the enhancement factor defined in the present study.

Table 1 is a list of the enhancement factors.

### 4. Conclusions

The dissolution rate of solid CaO in FeO–CaO–SiO₂–X (X: CaF₂, CaCl₂, Al₂O₃ and B₂O₃) melts was measured at hot-metal temperatures, and the results can be summarized as follows;

1. At constant temperature and slag composition, the dissolution rate of CaO was governed by the mass transfer in the bulk liquid phase.
2. The dissolution rate of CaO increased with FeO concentration and decreases with basicity of the melt.
3. The relationship between the mass transfer coefficient and Reynolds number at 1573 K for the 40%FeO–30%CaO–30%SiO₂ melt was expressed as \( k = Re^{1.70} \).
4. The relationship among dimensionless numbers \( Sh \), \( Re \) and \( Sc \) was expressed as \( Sh = 0.36 Re^{0.70} Sc^{0.33} \) for the 40%FeO–30%CaO–30%SiO₂ melt at 1573 K.
5. The activation energy of 137 kJ/mol (32.6 kcal/mol) for the CaO dissolution in the 40%FeO–30%CaO–30%SiO₂ melt was calculated from the data obtained.
6. The effect of additives to FeO–CaO–SiO₂ melt on raising the dissolution rate of CaO was CaF₂ > CaCl₂ > B₂O₃ > Al₂O₃.
7. The enhancement factor, \( E_{dis} \) for each additive was evaluated from the data and tabulated.

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