Behavior of Phosphorous Transfer from CaO–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5}(–SiO\textsubscript{2}) Slag to CaO Particles

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Lime particles (0.5 to 1 mm) were added by dropping to CaO–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slag at 1400°C, followed by stirring and the reaction products near a CaO particle/slag interface were determined by a microprobe analysis (EPMA-EDX). The 3CaO·P\textsubscript{2}O\textsubscript{5} and 4CaO·P\textsubscript{2}O\textsubscript{5} phases were crystallized depending on the amount of added CaO particles which are rapidly dissolved after the contact with a molten slag. The phosphorous distribution ratios between calcium phosphates and CaO–Fe\textsubscript{t}O slag obtained at temperatures between 1400 and 1570°C are higher than those between 2CaO·SiO\textsubscript{2}–3CaO·P\textsubscript{2}O\textsubscript{5} solid solution and CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O slag. Lime particles (0.3 to 0.5 mm) are added to CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slag at 1400°C and the reaction products near a CaO particle/slag interface are determined by EPMA-EDX. The 2CaO·SiO\textsubscript{2}–3CaO·P\textsubscript{2}O\textsubscript{5} solid solution layer is formed on the surface of a CaO particle and thereafter the CaO–Fe\textsubscript{t}O slag layer is formed between a CaO particle and 2CaO·SiO\textsubscript{2}–3CaO·P\textsubscript{2}O\textsubscript{5} solid solution layer which is surrounded by CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slag. It is also experimentally confirmed that the meso-phase slag refining is superior to conventional slag refining and the discrepancy between the theoretical and experimental results obtained by the meso-phase slag refining is discussed.

KEY WORDS: phosphorous distribution ratio; lime; calcium phosphate; dicalcium silicate.

1. Introduction

In previous study\textsuperscript{1)} the phosphorous distribution ratios between a 2CaO·SiO\textsubscript{2} particle and liquid CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slags have been measured by dispersing mesoscopic scale (30 to 50 μm) 2CaO·SiO\textsubscript{2} particles dispersed uniformly in slag. Phosphorous transfer from slag to a 2CaO·SiO\textsubscript{2} particle has been studied as a function of holding time and temperature. It has been established that when a CaO particle contacts with CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slag, liquid CaO–Fe\textsubscript{t}O slag layer is formed between a CaO particle and 2CaO·SiO\textsubscript{2}–3CaO·P\textsubscript{2}O\textsubscript{5} solid solution.\textsuperscript{2,4) However, there is no reports dealing with the reaction mechanism immediately after the contact of CaO particles with a molten slag. On the basis of the present and previous\textsuperscript{1)} results for the phosphorous distribution ratio between calcium phosphate and CaO–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} or calcium silicate and CaO–SiO\textsubscript{2}–Fe\textsubscript{t}O–P\textsubscript{2}O\textsubscript{5} slag coupled with the phosphorous distribution ratios between slag and metal,\textsuperscript{7)} the characteristics of dephosphorization by using the mesoscopic scale particles dispersed uniformly in liquid slag have been discussed and the results obtained from the dephosphorization experiments by using CaO or 2CaO·SiO\textsubscript{2} particles dispersed in slag are compared with those from the theoretical analysis.

2. Experimental

2.1. Sample Preparation

CaO: Reagent grade CaCO\textsubscript{3} was decomposed at 950°C and mixed with reagent grade CaCl\textsubscript{2} (1 mass%). The mixture was pressed and heated at 950°C for 6 h, followed by heating at 1400°C for 24 h. The dense CaO particles were ground, followed by sieving and they are stored in desiccator containing P\textsubscript{2}O\textsubscript{5} drying agent before use.

3CaO·P\textsubscript{2}O\textsubscript{5}: Reagent grade 3CaO·P\textsubscript{2}O\textsubscript{5} powder was pressed in cylindrical shape and after heating at 1500°C for 24 h, a tablet was ground, followed by sieving.

4CaO·P\textsubscript{2}O\textsubscript{5}: Reagent grade 4CaO·P\textsubscript{2}O\textsubscript{5} powder was mixed with reagent grade CaCO\textsubscript{3} and the mixture was pressed, followed by heating at 950°C for 6 h and then at 1500°C for 24 h. After grinding, the powder was pressed
again and heated at 1600°C for 24 h, followed by He quenching.

CaO–FeO and CaO–FeO–P2O5 slags: The CaO powder produced by the aforementioned method, reagent grade FeO and 3CaO·P2O5 were well mixed and the mixture was melted at 1420°C under Ar flowing atmosphere in an Fe crucible, followed by stirring with an Fe rod. The melt was quenched by using a water-cooled sandwich type Cu plates. The present slag compositions D1 and D2 are plotted in the CaO–FeO–P2O5 phase diagram8,9 shown in Fig. 1. The slag samples were ground to below 3 μm by a stainless steel ball mill.

2.2. Procedure

The CaO–FeO–P2O5 or CaO–FeO slag was melted at 1400°C in an Fe crucible under Ar flowing atmosphere (200 cm³·min⁻¹) and then CaO (0.5 to 1 mm) or calcium phosphate (20 to 50 μm) particles were added by dropping into a molten slag, followed by stirring with an Fe rod. A melt was quenched by using a water-cooled sandwich type Cu plates. In the experiments carried out at temperatures above 1500°C, a MgO crucible containing Fe was used in stead of an Fe crucible. This procedure denotes the isothermal method.

In the experiments where calcium phosphate phase is crystallized during cooling, the CaO–FeO–5mass%P2O5 slag D3 (mp 1560°C) shown in Fig. 1 was melted at 1600°C under Ar flowing atmosphere in a MgO crucible containing Fe. The melt was cooled to 1570°C at 0.83°C·min⁻¹ and held for 30 min. Then, it was cooled at 2.5°C·min⁻¹ from 1570 to 1400°C, followed by quenching in water. For comparison a melt was cooled from 1600 to 1570°C at 0.83°C·min⁻¹ and quenched in water after holding for 30 min at 1570°C. This denotes the temperature drop method.

The dephosphorization of an Fe–0.5%P alloy (20 or 25 g) by using the solid-liquid coexisting flux, which means the 2CaO·SiO2 or CaO particles dispersed in CaO–SiO2–FeO or CaO–FeO slag (2 or 7 g), was carried at 1560°C in a MgO crucible for 30 or 120 min (% represents mass%, hereinafter.)

2.3. Analysis

The compositions of solid and slag phases in a polished cross section were determined by a X-ray microprobe analysis (EPMA-EDX). The 3CaO·P2O5 prepared at 1500°C was used as the phosphorous standard sample. In the experiments where an Fe–0.5%P alloy was dephosphorized by solid-liquid coexisting flux at 1560°C, the phosphorous content in metal was determined by the molybdenum-blue absorptiometry (JIS-G-1214) and that in solid-liquid coexisting flux was determined by EPMA-EDX method. The average value of phosphorous content in this flux for eight different areas (0.1 to 0.4 mm²×8) was in good agreement with that determined by the molybdenum-blue absorptiometry (JIS-M-8216).

3. Results and Discussion

3.1. Phosphorous Partition between CaO Particles and CaO–FeO–P2O5 Slag

Lime particles (0.5 to 1 mm) were added to slag D1 containing 5% P2O5 at 1400°C, followed by stirring. The SEM image of a CaO particle obtained immediately after the addition is shown in Fig. 2(a), indicating that an original CaO particle starts to split into small grains. This phenomenon arises from the slag penetration and subsequent dissolution.
In the case of a small amount of CaO addition (CaO/slag mass ratio 1/15), CaO particles dissolve completely after 30 s and 3CaO·P_2O_5 with 40 to 200 μm crystallizes, as shown in Fig. 2(b). In the case of a large amount of CaO addition (CaO/slag mass ratio 1/5), CaO particles become smaller after 5 s due to dissolution and then 4CaO·P_2O_5 with 20 to 40 μm crystallizes, as shown in Fig. 2(c). These 4CaO·P_2O_5 crystals grow during 300 s to the size of 70 to 130 μm. In both cases of the precipitation of 3CaO·P_2O_5 and 4CaO·P_2O_5, final slag composition was D2.

The phosphorous distribution ratio between 4CaO·P_2O_5 and slag D2 and that between 3CaO·P_2O_5 and slag D2, which are obtained at 1 400°C by the isothermal method described in Sec. 2.2 are shown in Fig. 3. It is clear from the results by the open circles that the distribution ratio approaches the equilibrium value in a very short time. When the phosphorous approaches from 4CaO·P_2O_5 or 3CaO·P_2O_5 to slag D2 shown in Fig. 1 which contains a small amount of P_2O_5, the rate of phosphorous transfer to the equilibrium by dissolving calcium phosphate particles is slow, as shown by the half-filled marks in Fig. 3.

The phosphorous distribution ratio obtained in this study is compared with that between 2CaO·SiO_2–3CaO·P_2O_5 solid solution and CaO–SiO_2–FeO–P_2O_5 slag obtained in previous studies. The results are demonstrated in Fig. 4. The former distribution ratios indicated by the lines are plotted against (%SiO_2)/(%P_2O_5) which corresponds to the slag composition on the liquidus line of primary 2CaO·SiO_2 phase at 1 400°C. It is clear that the distribution ratio between 4CaO·P_2O_5 phase and slag D2 has been measured in the range between 1 400 and 1 560°C by the experiments where CaO particles were added to slag D1 (CaO/slag mass ratio 1/10 to 1/4). The results are shown in Fig. 5, indicating that the distribution ratio increases with a decrease in temperature, which is as expected for dephosphorization reaction. It is to be noted, however, that the distribution ratios obtained at different temperatures are not measured at constant slag composition.

3.2. Crystallization of 4CaO·P_2O_5 during Cooling

Ten grams of slag D3 (mp 1 560°C) containing 5% P_2O_5 shown in Fig. 1 was melted at 1 600°C in a MgO crucible together with 3 g of Fe in order to control the oxygen potential determined by the Fe/FeO equilibrium. Then, a melt was cooled to 1 570°C and held for 30 min, followed by rapid quenching in water. Figure 6(a) represents the SEM image of crystallized CaO (2 to 20 μm) and 4CaO·P_2O_5 (3 to 80 μm). A melt (slag D3) was cooled from 1 570 to 1 400°C at 2.5°C·min^{-1}, followed by rapid quenching. The SEM image is shown in Fig. 6(b), indicating that needle-like 4CaO·P_2O_5 crystals with the size of 1 to 3 μm in width and 2 to 40 μm in length are distributed uniformly together with well grown CaO crystals (40 to 70 μm).

The phosphorous distribution ratio at 1 400°C by this temperature drop method is shown in Fig. 3 by the reverse triangle, which is in agreement with the results obtained from the isothermal method by using CaO particles. As shown by the reverse triangle in Fig. 5, the distribution ratio...
obtained at 1 400°C fall well on the line obtained by the isothermal method at different temperatures.

3.3 Reaction of a CaO Particle with CaO–SiO₂–Fe₆O₅–P₂O₅ Slag

The CaO–SiO₂–Fe₆O₅–5%P₂O₅ slag whose composition is indicated by the point A in Fig. 7 was melted at 1 400°C and then CaO particles (0.3 to 0.5 mm) was added by dropping, followed by stirring. Since this slag is saturated with 2CaO·SiO₂ phase, the composition of the surface on dispersed CaO particles changes to 2CaO·SiO₂ due to the reaction with slag. The reaction products around a CaO particle has been observed by SEM and identified by EPMA as a function of holding time.

According to the SEM image and the schematic illustration of the reaction of a CaO particle with slag shown in Fig. 8(a), it is seen that 89%2CaO·SiO₂–11%3CaO·P₂O₅ solid solution layer is formed on a CaO particle after 30 s. After 5 min, however, a slag penetrates through the space between the 2CaO·SiO₂–3CaO·P₂O₅ grains and the CaO–Fe₆O molten slag layer is formed between a CaO particle and 2CaO·SiO₂–3CaO·P₂O₅ layer, as illustrated in Fig. 8(b).

The aforementioned observation can be explained from the path of slag composition after the contact of a CaO particle with slag A, which is shown in Fig. 7. The 2CaO·SiO₂ phase is formed on the surface of a CaO particle because slag A is saturated with 2CaO·SiO₂ phase. Because of the formation of 2CaO·SiO₂ on a CaO particle, the slag composition near the 2CaO·SiO₂ layer changes along the 2CaO·SiO₂ liquidus line to the point b together with the formation of the 2CaO·SiO₂–3CaO·P₂O₅ solid solution. Eventually the composition of slag in contact with a CaO particle becomes the composition between c and d. However, it was found that the CaO–Fe₆O slag layer without P₂O₅ was formed between the solid solution layer and a CaO particle after 5 min.

The thickness of the 2CaO·SiO₂–3CaO·P₂O₅ solid solution layer and the P₂O₅ contents in this layer observed in the reaction of a CaO particle with slag are plotted against holding time at 1 400°C in the upper and lower diagrams of Fig. 9. The thickness of 2CaO·SiO₂ layer becomes about 90 μm in a short time and does not vary with holding time. The constant P₂O₅ content (6%) in 2CaO·SiO₂–3CaO·P₂O₅ solid solution layer is obtained rapidly. These results suggest that the reaction of a CaO particle with slag A is very rapid and a CaO particle is in equilibrium with CaO–Fe₆O slag (d) and the outside of it is surrounded by the slag A.

It has been reported⁶) that when a CaO particle is in contact with CaO–SiO₂–Fe₆O–P₂O₅ slag, 2CaO·SiO₂, 3CaO·SiO₂ and (Ca,Fe)O solid solution phases are formed on a CaO particle. The formation of CaO–Fe₆O slag between CaO particles and 2CaO·SiO₂ layer has been already ob-
served in the reaction of a CaO particle with CaO–SiO₂–FeO slag for 10 min and that of a CaO particle with CaO–SiO₂–FeO–P₂O₅ slag for 5 to 40 min.

From the present results it can be concluded that when a CaO particle is in contact with CaO–SiO₂–FeO–P₂O₅ slag, the 2CaO·SiO₂–3CaO·P₂O₅ solid solution phase is formed on a CaO particle and this layer is partially broken, thus leading to the slag penetration into the interface between a CaO particle and 2CaO·SiO₂ layer. Since 2CaO·SiO₂ changes to 2CaO·SiO₂–3CaO·P₂O₅ solid solution, the composition of penetrated CaO–SiO₂–FeO–P₂O₅ slag changes to CaO–FeO slag containing a very small amount of P₂O₅ which is in equilibrium with 2CaO·SiO₂–3CaO·P₂O₅ solid solution.

3.4. Characteristics of Dephosphorization by Using Solid/Liquid Coexisting Flux

The phosphorous transfer to a 2CaO·SiO₂ particle has been previously studied by using the 2CaO·SiO₂ or CaO particles (30 to 50 μm) homogeneously dispersed in CaO–SiO₂–FeO–P₂O₅ slag. The characteristics of dephosphorization of hot metal or steel by using the mesoscopic scale particles dispersed in a slag are considered in this section. The solid particle and liquid slag phases denote the meso-phase (solid) and slag, respectively and the refining by using this solid–liquid coexisting flux (meso-phase slag or meso slag) denotes the meso-phase refining, hereinafter.

The phosphorous distribution ratio between meso-phase slag and metal, \( \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} \), can be given by

\[
L_p \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} = L_p (1 + L_p \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} A) (1 + A) \quad \ldots \ldots \ldots (1)
\]

where \( L_p \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} \) is the phosphorous distribution ratio between slag and metal, \( L_p \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} \) is the phosphorous distribution ratio between meso-phase (solid) and slag and \( A = \frac{W_{\text{meso}}}{W_{\text{slag}}} \) where \( W_{\text{meso}} \) and \( W_{\text{slag}} \) are the weight of meso-phase (solid) and that of slag in kg·ton⁻¹ of metal, respectively.

\( L_p \frac{W_{\text{meso/slag}}}{W_{\text{metal}}} \) is given by the following empirical relation obtained by the present authors:

\[
\log \{\frac{\% P}{\% P_f}\} = 0.072 \left\{\frac{\% CaO}{\% MgO}\right\} + 2.5 \log(\% T·Fe) + 11.570/T - 10.52 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTS

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184
crease of study into Eq. (3), the final phosphorous content, \( \%P_f \), is obtained as a function of SiO\(_2\) and Fe\(_2\)O\(_4\). Therefore, the \( W_{\text{meso-slag}} \) value is not below the points a and b for \( W_{\text{meso-slag}}/W_{\text{slag}} = 1/1 \) and 1/2, respectively, in the range of (%SiO\(_2\))<8, as shown in the lower diagram of Fig. 10.

By substituting \( [%P] = 0.1, L_{\text{slag/metal}} = 100 \) and \( L_{\text{meso-slag}} = 50 \) into Eq. (3), the final phosphorous contents are plotted against the meso-phase slag consumption, \( W_{\text{meso-slag}} (= W_{\text{meso}} + W_{\text{slag}}) \) as a function of \( W_{\text{meso}}/W_{\text{slag}} \) in Fig. 11. It is apparent that \( W_{\text{meso-slag}} \) decreases drastically with an increase of \( W_{\text{meso}}/W_{\text{slag}} \) ratio for a given \( [%P] \). In order to obtain the final phosphorous content of 0.02% under the aforementioned conditions, the slag consumption of 40 kg·ton\(^{-1}\) is necessary for slag refining, but with the meso-phase (solid) addition of 5% of total amount of meso-phase and slag, \( W_{\text{meso-slag}} \) decreases to one-fourth of \( W_{\text{meso-slag}} \) obtained by slag only. These calculated results show the merit of meso-phase slag refining for dephosphorization. However, in practice kinetic effects and change of respective distribution ratios due to the compositional change during dephosphorization must be taken into account in the case of low \( W_{\text{meso-slag}}/W_{\text{metal}} \) ratio.

By substituting \( [%P] = 0.1, W_{\text{meso-slag}} = 10 \) kg·ton\(^{-1}\), \( L_{\text{slag/metal}} \) from Eq. (2), and \( L_{\text{meso-slag}} \) obtained in previous study\(^1\) into Eq. (3), the final phosphorous content, \( [%P] \), is obtained as a function of SiO\(_2\) and FeO contents on the 2CaO·SiO\(_2\) liquidus line in CaO–Fe\(_2\)O–SiO\(_2\) system. The calculated \( [%P] \) values are plotted against (%SiO\(_2\)) and (%FeO) as a function of \( W_{\text{meso}}/W_{\text{slag}} = 0/1, 1/2 \) and 1/1 in the upper and lower diagrams of Fig. 12. It can be seen from the upper diagram that \( [%P] \) decreases with a decrease in (%SiO\(_2\)) for a given \( W_{\text{meso}}/W_{\text{slag}} \) ratio and the \( [%P] \) value decreases with an increase in \( W_{\text{meso}}/W_{\text{slag}} \) ratio for a given (%SiO\(_2\)). A small amount of meso-phase (solid) in slag is more effective to the \( [%P] \) value for a given (%SiO\(_2\)) content.

3.5. Experimental Confirmation of Merit of Meso-phase Slag Refining

An Fe–0.5%P alloy (25 g) was dephosphorized at 1560°C in a MgO crucible by using the following three fluxes (7 g); slag G (solid circles) whose composition is indicated in Fig. 13, meso-phase slag of G+2CaO·SiO\(_2\) (squares) and meso-phase slag of G+CaO (open circles). The melt was kept for 2 h without stirring, followed by rapid quenching in water. The reason that no stirring was made is to study how the protective layer formed in meso-phase slag near the meso-phase slag/metal interface affects the \( L_{\text{meso-slag/metal}} \) value, which is the major concern in the application of meso-phase slag to practical hot metal dephosphorization. The \( L_{\text{meso-slag/metal}} \) values are plotted in CaO–SiO\(_2\)–FeO phase diagram shown in the upper diagram of Fig. 13. The MgO contents in meso-phase slag are 1 to 3% and the P\(_2\)O\(_5\) contents for slag G+CaO and slagG+2CaO·SiO\(_2\) are 4 to 8 and 0.8 to 4%, respectively. The effect of MgO on \( L_{\text{meso-slag/metal}} \) is not clear in the present study because of the low MgO content in slag. Further research for clarify this effect is necessary. The \( L_{\text{meso-slag/metal}} \) values are also plotted in CaO–P\(_2\)O\(_5\)–FeO phase diagram shown in the lower diagram by the open circles, since the composition of SiO\(_2\) in the meso-phase slag of G+CaO is comparatively low. In the case of G+CaO meso-phase slag, 4CaO·P\(_2\)O\(_5\) and CaO solid phase were observed in meso-phase slag. The SiO\(_2\) content in 4CaO·P\(_2\)O\(_5\) phase was below the limit of quantitative analysis by EPMA.

An Fe–0.5%P alloy (20 g) was dephosphorized at 1560°C for 30 min in a MgO crucible by using the following fluxes; meso-phase slag of G+2CaO·SiO\(_2\) (squares with bar), meso-phase slag of G+CaO (circles with bar),
meso-phase slag of slag D + 2CaO·SiO₂ (inverse triangles with bar) and meso-phase slag of D + CaO (triangles with bar). These results are plotted in Fig. 13, indicating that these experimental results for the $L_{p_{\text{meso slag/metal}}}$ values are higher than the former ones indicated by open marks for a given meso-phase slag composition. The datum point by asterisk corresponds to the latter experimental results with stirring, which are significantly high.

In the former experiments in which the mass ratio of meso-phase slag and metal weight is 7/25, it was observed that meso-phase slag was covered over the metal during de-phosphorization experiment and phosphorous in slag far from the meso-phase slag/metal interface was not present. For this reason, the values for $L_{p_{\text{meso slag/metal}}}$ are underestimated. In the latter experiments, however, in which the mass ratio of meso-phase slag and metal weight is 1/10, meso-phase slag was located only around the crucible wall and phosphorous in slag was present in entire layer of meso-phase slag. More detailed description is given in a separate publication. It can be said from the data points on the tie line represented by the broken lines in Fig. 13 that $L_{p_{\text{meso slag/metal}}}$ values tend to increase with increasing the fraction of solid in meso-phase slag.

The $L_{p_{\text{meso slag/metal}}}$ values with respect to the tie line between 2CaO·SiO₂ and slag G and that between CaO and slag G shown in the upper diagram of Fig. 13 are plotted against the meso phase (solid)/slag mass ratio as a function of meso-phase slag/metal mass ratio = 1/10 and 7/25 in the upper and lower diagrams of Fig. 14, respectively. It can be seen that the $L_{p_{\text{meso slag/metal}}}$ values increases with an increase in the content of 2CaO·SiO₂ in meso-phase slag.

Furthermore, the $L_{p_{\text{meso slag/metal}}}$ values for a given $W_{\text{meso}}/W_{\text{slag}}$ ratio increases with an increase in the mass ratio of meso-phase slag and metal weight. However, these values are below the calculated line which are obtained from Eq. (1) by substituting the $L_{p_{\text{slag/metal}}}$ value from Eq. (2) and the $L_{p_{\text{meso slag}}}$ value obtained in previous study. The datum point indicated by asterisk shown in the upper diagram corresponds to the result obtained by stirring. This value is significantly higher than those without stirring, indicating the
importance of increasing the interfacial area for the present meso-phase slag refining. It was found that the protective layer between metal and meso-phase slag is formed in the experiment without stirring. More detailed observation is given in a separate publication.

The $L_{\text{p} \text{meso slag/metal}}$ values shown in the lower diagram of Fig. 13 are plotted against the mass ratio of meso phase (solid) and slag in meso-phase slag in Fig. 15, along with the calculated lines. It can be seen that the $L_{\text{p} \text{meso slag/metal}}$ values increase with an increase of CaO content in meso-phase slag, but they decrease in the range of $W_{\text{meso}} / W_{\text{slag}} > 0.4$. These data points are considerably smaller than the calculated line. The reason that the $L_{\text{p} \text{meso slag/metal}}$ values are lower than the $L_{\text{p} \text{slag/metal}}$ value is explained by the fact that the dephosphorization by the meso-phase slag is inhibited by the protective layer formed at the meso-phase slag/metal interface if stirring is not made. On the basis of the present results it can be concluded that agitation of meso-phase slag/metal interface in addition to an increase of mesophase slag/metal ratio is prerequisite in order to satisfy the characteristics of meso-phase slag refining shown in Figs. 10 to 12.

4. Conclusions

The CaO particles are added to CaO–Fe,O slags containing P,O, and the region near the interface between a CaO particle and slag has been observed by SEM and the reaction products are identified by EPMA-EDX. The following conclusions are obtained:

1. When a CaO particle is in contact with CaO–Fe,O slag, a CaO particle splits into small grains. 3CaO·P,O crystallize rapidly in the case of a small and a large amount of CaO addition, respectively.

2. The phosphorous distribution ratio between calcium phosphate and CaO–Fe,O slag is higher than that between 2CaO·SiO₂·3CaO·P,O solid solution and CaO–SiO₂–Fe,O slag. The temperature dependence of phosphorous distribution ratio between 4CaO·P,O and CaO–Fe,O slag is small.

3. When a CaO particle is in contact with CaO–SiO₂–Fe,O–P,O slag, the 2CaO·SiO₂·3CaO·P,O solid solution layer is formed rapidly on a CaO particle and then the CaO–Fe,O slag without P,O is formed between a CaO particle and 2CaO·SiO₂·3CaO·P,O solid solution.

4. The superiority of the meso-phase slag refining for dephosphorization is confirmed theoretically by using the phosphorous distribution ratios between 4CaO·P,O and slag and that between 2CaO·SiO₂·3CaO·P,O and slag.

5. It was experimentally confirmed that the phosphorous distribution ratios between meso-phase slag and an Fe–0.5%P alloy increase with an increase of the fraction of solid in meso-phase slag, indicating that the meso-phase slag refining is superior to conventional slag refining. The observed phosphorous distribution ratios are strongly dependent on the meso-phase slag/metal ratio and stirring condition.

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REFERENCES

4) K. Fujita and K. Ito: CAMP-ISIJ, 17 (2004), 646.