Mechanism of Dephosphorization with $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ Slags Containing Mesoscopic Scale $2\text{CaO} \cdot \text{SiO}_2$ Particles

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Dephosphorization of a liquid Fe–5mass%P alloy with a solid–liquid coexisting flux in which $2\text{CaO} \cdot \text{SiO}_2$ particles (20 to 50 μm) are uniformly dispersed in $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ slags has been studied at 1400°C. For the slag with high SiO_2 and low T.Fe contents, the change of slag composition is small and the fraction of $2\text{CaO} \cdot \text{SiO}_2$ particles to slag increases slightly during dephosphorization in which the $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$ values are low. For the slag with moderate SiO_2 and high T.Fe contents, the change of slag composition is considerable and the fraction of $2\text{CaO} \cdot \text{SiO}_2$ particles to slag increases considerably during dephosphorization in which the $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$ values are high at initial period, but these values decrease with time. For the slag with low SiO_2 and high T.Fe contents, the change of slag composition is small and the fraction of $2\text{CaO} \cdot \text{SiO}_2$ particles to slag decreases slightly during dephosphorization in which the $L_p^{\text{slag/metal}}$ and $L_p^{\text{solid/slag}}$ values are high, but $L_p^{\text{solid/slag}}$ value decreases considerably even with small change of slag composition.

KEY WORDS: dephosphorization; dicalcium silicate; phosphorous distribution ratio.

1. Introduction

New refining method by using a solid/liquid coexisting flux in which mesoscopic scale solid particles are uniformly dispersed in liquid slag has been developed. The phosphorous distribution ratios between a $2\text{CaO} \cdot \text{SiO}_2$ particle and liquid $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ slags have been measured as a function of slag composition and temperature.¹⁾ The measurement has been made by dispersing solid CaO particles in liquid slag in order to obtain the phosphorous distribution ratios between $4\text{CaO} \cdot \text{P}_2\text{O}_5$ or $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and liquid $\text{CaO-Fe}_7\text{O}(-\text{SiO}_2)$ slags.²⁾ Characteristics of the dephosphorization by using a solid/liquid coexisting flux have been estimated experimentally and theoretically based on the phosphorous distribution ratios among solid CaO or $2\text{CaO} \cdot \text{SiO}_2$ particles, liquid $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ slag and liquid Fe. It was found that dephosphorization becomes favorable with increasing the solid/liquid ratio in coexisting phases compared with the dephosphorization with liquid slag only under a given flux consumption.²⁾

In the present investigation the dephosphorization mechanism of a liquid Fe–5mass%P alloy by using $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ slags containing $2\text{CaO} \cdot \text{SiO}_2$ particles has been studied from the measurements of the composition change in solid particle and slag phases as a function of distance from meso-phase slag/metal interface. An Fe–5mass%P alloy whose phosphorous level is high compared with that of hot metal such as 0.1 mass% P is used in the present study because of the following two reasons; the composition change in slag phase near the meso-phase slag/metal interface should be significant in order to clearly study the

dephosphorization behavior, and melting point of metal sample should be close to the temperature of hot metal pretreatment in order to study the dephosphorization mechanism by meso-phase slag at this temperature. The dephosphorization mechanism of an Fe–0.1~0.5mass%P alloy by using meso-phase slag will be discussed in a future paper. The solid/liquid coexisting flux and solid particles denote the meso-phase slag and meso-phase, respectively, hereinafter.

2. Experimental

The methods for the preparation of $2\text{CaO} \cdot \text{SiO}_2$ particles (20 to 50 μm) and $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ slag powders (below 3 μm) are well mixed in an appropriate proportion and pressed in cylindrical shape. An Fe–5mass%P alloy (25 g) was melted at 1400 °C in a MgO crucible under Ar atmosphere ($200 \text{ cm}^3 \cdot \text{min}^{-1}$) and meso-phase slag tablet (3 g) was placed on a liquid alloy using SiO_2 tube. (% represents mass%, hereinafter) After a given time, a crucible containing a sample was quenched in water. Microprobe analysis was made for the polished cross section of meso-phase slag. More detailed description is given elsewhere.¹⁾

3. Results and Discussion

3.1. Meso-phase Slag A1 Containing High SiO_2 and low T.Fe Slag A

The composition of meso-phase slag A1 is given in the primary phase field of $2\text{CaO} \cdot \text{SiO}_2$ in $\text{CaO-SiO}_2\text{-Fe}_7\text{O}$ phase diagram shown in Fig. 1. This meso-phase slag was

Fig. 1. Phosphorous distribution ratio between 2CaO·SiO₂-3CaO·P₂O₅ particle and slag, and that between slag and metal calculated by Eq. (1).³⁾

prepared by mixing the slag with A composition and 2CaO·SiO₂ particles in the proportion of 1:1 on weight basis. The phosphorous distribution ratio between 2CaO·SiO₂-3CaO·P₂O₅ particles and slag, L_p ($=\frac{(\%P)_{\text{in } 2\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{P}_2\text{O}_5}{(\%P)_{\text{in slag}}}$) is also given in Fig. 1, along with that between slag and metal, L'_p ($=\frac{(\%P)_{\text{in slag}}}{[\%P]_{\text{in metal}}}$) which is calculated by the following empirical relation obtained by the present authors.³⁾

$$\log L'_p = 0.072\{(\%CaO) + 0.3(\%MgO)\} + 2.5\log(\%T.Fe) + 11570/T - 10.52 \dots \dots \dots (1)$$

After the reaction of this meso-phase slag with an Fe-5%P alloy for 1 and 5 min, the P₂O₅ contents at the rim and core of a 2CaO·SiO₂ particle were measured as a function of the distance from the meso-phase slag/metal interface. The results are shown in Fig. 2, indicating that the contents at the core are slightly lower than those at the rim. It was found that the rate of solid solution of P₂O₅ into a 2CaO·SiO₂ particle (20 to 50 μm) as 3CaO·P₂O₅ is significantly fast.

The P₂O₅ and T.Fe contents in slag phase of the meso-phase slag layer are plotted against the distance from the meso-phase-slag/metal interface in the upper and middle diagrams of Fig. 3, respectively. It can be seen that the change of P₂O₅ content with time for a given distance shows an opposite trend to the change of T·Fe content due to the fact that the T·Fe content decreases by the dephosphorization reaction: $2P + 5(Fe_2O_3) \rightarrow (P_2O_5) + 5Fe$. The phosphorous distribution ratios between a 2CaO·SiO₂ particle at the rim and slag are shown in the lower diagram. The L_p values near the meso-phase slag/metal interface are in good agreement with that obtained in previous equilibrium experiments¹⁾ which is indicated by an arrow. The L_p values observed at 5 min are slightly higher than the equilibrium value in the range between 200 and 1000 μm due to the change of slag composition.

The composition changes of slag, meso-phase slag and 2CaO·SiO₂ particles which are obtained near the meso-phase slag (mps)/metal interface and the meso-phase slag far from the interface (top) at 1 min are plotted in CaO-SiO₂-Fe₂O and CaO-SiO₂-P₂O₅ phase diagrams by the triangles, squares and circles, respectively, in Fig. 4. The change of slag composition from the interface to top

Fig. 2. P₂O₅ content at rim and core of a 2CaO·SiO₂-3CaO·P₂O₅ particle after reaction of meso-slag A1 with Fe-5%P alloy at 1 673 K for 1 and 5 min.

Fig. 3. Contents of P₂O₅ and T.Fe in slag and phosphorous distribution ratio between a 2CaO·SiO₂-3CaO·P₂O₅ particle (rim) and slag after reaction of meso-slag A1 with Fe-5%P alloy at 1 673 K for 1 and 5 min.

Fig. 4. Composition of slag (triangles) and that of a 2CaO·SiO₂-3CaO·P₂O₅ particle (circles) after reaction of meso-phase slag (mps) A1 with Fe-5%P alloy at 1 673 K for 1 min.

Fig. 5. P_2O_5 content at rim and core of a $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ particle after reaction of mesoslag C1 with Fe-5%P alloy at 1673 K for 0.5 and 1 min obtained by line scanning (lines 1 and 2).

Fig. 6. P_2O_5 content at rim and core of a $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ particle after reaction of meso-slag C1 with Fe-5%P alloy at 1673 K for 2 and 5 min obtained by line scanning (lines 1 and 2).

along the liquidus line corresponds to the results shown in the middle diagram of Fig. 3, in which T.Fe content increases from interface to top due to the dephosphorization reaction. The P_2O_5 content in a $2CaO \cdot SiO_2$ particle increases from top to interface about 10% due to the lower phosphorous distribution ratio between a $2CaO \cdot SiO_2$ particle and slag, as shown in the lower diagram of Fig. 3.

3.2. Meso-phase Slag C1 Containing Moderate SiO_2 and High T.Fe Slag C

The slag C whose composition is shown in Fig. 1 and $2CaO \cdot SiO_2$ particles were mixed in the proportion of 1 : 1 on weight basis and a pressed tablet with the composition of meso-phase slag C1 shown in Fig. 1 was reacted with an Fe-5%P alloy at 1400°C. The P_2O_5 contents in a $2CaO \cdot SiO_2$ particle obtained at 0.5 and 1 min are plotted against the distance from the mps/metal interface in Fig. 5 and those obtained at 2 and 5 min are shown in Fig. 6. The P_2O_5 contents at the rim of a particle are slightly higher than those at the core and this difference tends to increase

Fig. 7. Contents of P_2O_5 and T.Fe in slag and phosphorus distribution ratio between a $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ particle (rim) and slag after reaction of meso-slag C1 with Fe-5%P alloy at 1673 K for 0.5 and 1 min.

Fig. 8. Contents of P_2O_5 and T.Fe in slag and phosphorus distribution ratio between a $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ particle (rim) and slag after reaction of meso-slag C1 with Fe-5%P alloy at 1673 K for 2 and 5 min.

with the distance from the mps/metal interface. The P_2O_5 contents near the interface increase with time and are highest at 1 min. They decrease and tend to be independent of the distance from the mps/metal interface at 5 min.

The P_2O_5 and T.Fe contents in slag and the phosphorous distribution ratio between a $2CaO \cdot SiO_2$ particle at the rim

Fig. 9. Composition of slag (triangles) and that of a $2\text{CaO} \cdot \text{SiO}_2 - 3\text{CaO} \cdot \text{P}_2\text{O}_5$ particle (circles) after reaction of meso-phase slag (mps) C1 with Fe-5%P alloy at 1 673 K for 0.5 to 5 min.

and slag are shown in **Figs. 7 and 8** for 0.5 and 1 min and for 2 and 5 min, respectively. As shown in the upper diagram of Fig. 7, the P_2O_5 contents observed near the interface are highest at 1 min and then decrease with time. The diffusion distance of P_2O_5 from the interface increases continuously with time. The T.Fe contents in slag near the interface are lowest at 1 min, which corresponds to the P_2O_5 contents in slag near the interface. The range with the lowest content of T.Fe increases with time in proportion to the diffusion distance of P_2O_5 in slag. The phosphorous distribution ratios between a $2\text{CaO} \cdot \text{SiO}_2$ particle at the rim and slag obtained near the interface are lower than those observed far from the interface which are in good agreement with the value observed in the previous equilibrium experiments¹⁾ represented by an arrow.

The composition changes of slag, meso-phase slag and $2\text{CaO} \cdot \text{SiO}_2$ particle with time are shown in CaO-SiO₂-Fe₂O₃ and CaO-SiO₂-P₂O₅ phase diagrams in **Fig. 9** by the triangles, squares and circles, respectively. The slag composition near the mps/metal interface moves along the liquidus line from slag C (top) to the composition with low T.Fe with time. Consequently, the phosphorous distri-

bution ratios between a $2\text{CaO} \cdot \text{SiO}_2$ particle and slag near the interface decrease with time, as is clear in Fig. 1. The P_2O_5 content in a $2\text{CaO} \cdot \text{SiO}_2$ particle near the interface at 1 min (middle diagram) is higher than that at 0.5 min. This is contrary to the result in which the phosphorous distribution ratio near the interface at 0.5 min is higher than that at 1 min, as shown in Fig. 1. This can be explained by the kinetic effect; that is, the phosphorous transfer rate from slag to a $2\text{CaO} \cdot \text{SiO}_2$ particle is reduced. The finding that the solid/liquid ratio in meso-phase slag does not change significantly with time suggests that the dephosphorization is favorable. This is because the increase in the solid/liquid ratio favors the dephosphorization degree provided that the kinetic effect is disregarded.²⁾

3.3. Meso-phase Slag G1 Containing Low SiO₂ and High T.Fe Slag G

The slag G whose composition is shown in Fig. 1 and $2\text{CaO} \cdot \text{SiO}_2$ particles were mixed in the proportion of 1 : 1 on weight basis and a pressed tablet was reacted with an Fe-5%P alloy at 1 400°C. The P_2O_5 contents at the rim of a $2\text{CaO} \cdot \text{SiO}_2$ particle are plotted against the distance from

the mps/metal interface in the top diagram of **Fig. 10**. Similar to the results for moderate SiO_2 and high T.Fe slag shown in Figs. 7 and 8, the P_2O_5 contents in a $2\text{CaO} \cdot \text{SiO}_2$ particle near the interface has the maximum and then decrease as a result of solid solution of P_2O_5 in $2\text{CaO} \cdot \text{SiO}_2$

Fig. 10. Contents of P_2O_5 at rim of a $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ particle, P_2O_5 and T.Fe in slag and phosphorus distribution ratio between a $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ particle and slag after reaction of meso-slag G1 with Fe-5%P alloy at 1673 K for 1 and 2 min.

particles located at the interior of the meso-phase slag.

From the P_2O_5 contents in slag shown in Fig. 10, it can be seen that the P_2O_5 content in slag near the interface has the maximum at 1 min and then the phosphorous diffuses into the interior of the meso-phase slag and dissolves in $2\text{CaO} \cdot \text{SiO}_2$ particles with time. The T.Fe content in slag near the interface decreases with time due to the dephosphorization. The phosphorous distribution ratio between a $2\text{CaO} \cdot \text{SiO}_2$ particle and slag shown in the bottom diagram obtained at 1 min is high due to the higher T.Fe in slag in the range between 50 and 300 μm . However, the phosphorous distribution ratios obtained at 2 min decreases due to the decrease in T.Fe content in slag in this range.

The composition change of slag, meso-phase slag and a $2\text{CaO} \cdot \text{SiO}_2$ particle from the mps/metal interface to the interior of meso-phase slag (top) are shown in **Fig. 11** by the triangles, squares and circles, respectively. Since the slag G in the meso-phase slag G1 is located on the liquidus line below the tie line between $2\text{CaO} \cdot \text{SiO}_2$ and the top of the $2\text{CaO} \cdot \text{SiO}_2$ nose, the slag composition moves to a triple-saturated point J shown in Fig. 1 after dephosphorization. Due to the decrease in T.Fe in slag, the phosphorous distribution ratio between a $2\text{CaO} \cdot \text{SiO}_2$ particle and slag decreases from 63 (G) to 19 (J). The P_2O_5 contents in a $2\text{CaO} \cdot \text{SiO}_2$ particle near the mps/metal interface are considerably high at 1 min. Even at 2 min the P_2O_5 contents in a $2\text{CaO} \cdot \text{SiO}_2$ particle near the interface are still high due to the fact that T.Fe content in slag is determined by a slag composition at a triple-saturated point (J) with relatively high distribution ratio between slag and a $2\text{CaO} \cdot \text{SiO}_2$ particle. The fact that the P_2O_5 contents in a $2\text{CaO} \cdot \text{SiO}_2$ particle at top is nearly zero indicates that phosphorous does not diffuse to the interior of the meso-phase slag layer. The thickness of the dif-

Fig. 11. Composition of slag (triangles) and that of a $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ particle (circles) after reaction of meso-phase slag (mps) G1 with Fe-5%P alloy at 1673 K for 1 and 2 min.

Fig. 12. Path of slag composition after reaction of slag A (upper diagram), slag C (middle diagram) and slag G (lower diagram) containing 2CaO·SiO₂ particles with Fe-5% P alloy.

fused layer by phosphorous is discussed in next section.

3.4. Dephosphorization Mechanism by Meso-phase Slag

Characteristics of the dephosphorization by using meso-phase slag are already discussed in previous article.²⁾ If the distribution ratio between a 2CaO·SiO₂ particle and slag in meso-phase slag is greater than unity, the dephosphorization becomes advantageous under a given flux consumption in comparison with a conventional dephosphorization by using a liquid slag only. In this section the characteristics of phosphorous transfer from slag to a 2CaO·SiO₂ particle are discussed by focusing on the change of the respective distribution ratios with slag composition and the solid/liquid ratio during dephosphorization.

For the dephosphorization by using the meso-phase slag A1 (b) consisting of slag A (a) and 2CaO·SiO₂ particle (c), the compositions of slag and meso-phase slag change from a→a' and b→b', as shown in the top diagram of Fig. 12. The phosphorous distribution ratio between meso-phase slag and slag, $L_p^{\text{solid/slag}} (= (\%P) \text{ in } 2\text{CaO} \cdot \text{SiO}_2 / (\%P) \text{ in slag})$ and that between slag and metal, $L_p^{\text{slag/metal}} (= (\%P) \text{ in slag} / (\%P) \text{ in metal})$ are both low during dephosphorization and the

Fig. 13. Relationships between thickness of meso-phase slag layer containing 2CaO·SiO₂-3CaO·P₂O₅ particles and that containing P₂O₅ in slag.

solid/liquid ratio in meso-phase slag increases slightly from ab/bc to a'b'/b'c, which results in a favorable effect.

For the dephosphorization by using the meso-phase slag C1 (b) consisting of slag C (a) and 2CaO·SiO₂ particle (c), the compositions of slag and meso-phase slag change from a→a' and b→b', as shown in the middle diagram. The values for $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$ decrease markedly and the solid/liquid ratio increases drastically. The increase in the solid/liquid ratio from ab/bc to a'b'/b'c theoretically increases the dephosphorization degree,²⁾ but it decreases due to the kinetic reason. This problem with respect to the meso-phase slag refining is experimentally confirmed and the results are reported in a separate publication.

For the dephosphorization by using only slag C, the consumption of Fe₂O₃ for dephosphorization leads to the formation of solid/liquid coexisting phase. For this reason, the degree of dephosphorization becomes unfavorable, as explained above. It follows that the continuous feeding of Fe₂O₃ to the meso-phase slag or slag is necessary in order to keep high degree of dephosphorization.

For the dephosphorization of liquid iron by using the meso-phase slag G (b) consisting of slag G (a) and 2CaO·SiO₂ particle (c), the compositions of slag and meso-phase slag change from a→a' and b→b', as shown in the lower diagram. The $L_p^{\text{solid/slag}}$ value decreases, whereas the $L_p^{\text{slag/metal}}$ value increases,¹⁾ as shown in Fig. 1. The solid/liquid ratio in meso-phase slag, which changes from ab/bc to a'b'/b'c, does not decrease considerably in the case of meso-phase slag refining by meso-slag G1. On the basis of the results shown in Fig. 12, it can be concluded that the dephosphorization by using the meso-phase slag whose slag composition is on the liquidus line below the tie line between the top of the nose and 2CaO·SiO₂ is recommended.

The thickness of meso-phase slag layer, $l_{\text{C}_2\text{S-C}_3\text{P}}$, in which 2CaO·SiO₂-3CaO·P₂O₅ particles are observed in the meso-phase slag A1, C1 and G1 is plotted against the thickness of slag layer, $l_{\text{P}_2\text{O}_5}$, in which phosphorous is observed in slag phase in Fig. 13 as a function of time. It can be seen that $l_{\text{C}_2\text{S-C}_3\text{P}}$ is nearly equal to $l_{\text{P}_2\text{O}_5}$ except for the meso-phase slag A1. This can be explained by the lower distribution ratio between slag and a 2CaO·SiO₂ particle for A1 as

compared with those for C1 and G1 since the phosphorous transfer rate from slag to a particle is dependent on the distribution ratio.

4. Conclusions

The dephosphorization of liquid iron by using the meso-phase slag consisting of $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ slag and $2\text{CaO}\cdot\text{SiO}_2$ particles (20 to 50 μm) which are dispersed uniformly has been studied at 1400°C. The conclusions are obtained as follows:

(1) For the meso-phase slag of high SiO_2 and low T.Fe, the composition change of slag is small and the solid/liquid ratio increases slightly during dephosphorization. As a result, dephosphorization proceeds by the meso-phase slag with low $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$ values.

(2) For the meso-phase slag of moderate SiO_2 and high T.Fe, the composition change of slag is considerable and the solid/liquid ratio increases drastically. As a result, dephosphorization proceeds initially by the meso-phase slag

with high values for $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$, but at later stage the dephosphorization near the mps/metal interface is reduced due to low values for $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$.

(3) For the meso-phase slag of low SiO_2 and high T.Fe, the composition change of slag is small and the solid/liquid ratio changes little during dephosphorization. As a result, dephosphorization occurs initially by the meso-phase slag with high values for $L_p^{\text{solid/slag}}$ and $L_p^{\text{slag/metal}}$, but later dephosphorization is reduced due to the decrease in $L_p^{\text{solid/slag}}$ value.

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