1. Introduction

For the purpose of minimizing the refractory erosion, a steelmaking slag is generally used in solid–liquid coexisting state, which means that slag is saturated with refractory materials. However, such a heterogeneous slag has a drawback to fine control of refining elements and thus excess refining is usually forced to be made by using a large amount of heterogeneous slag. This should be reconsidered by all means in view of saving resources, energy and environmental protection. In the practical operation by using a heterogeneous slag, the refining is carried out based on the empirical knowledge due to the lack of the data on partition ratios between heterogeneous slag and steel, and parameters of reaction kinetics for various elements.

It has been known that phosphorous dissolves to 2CaO·SiO2 phase as 3CaO·P2O5\(^1\)) and is present in BOF slag as 2CaO·SiO2–3CaO·P2O5 solid solution.\(^2\)) The phosphorous distribution ratio between 2CaO·SiO2 and CaO–SiO2–Fe\(_t\)O slags has been reported at 1350 and 1400°C.\(^3\)

In this study the phosphorous distribution ratios between 2CaO·SiO2 particle and slag is obtained at the nose composition of 2CaO·SiO2 primary phase region in CaO–SiO2–Fe\(_t\)O phase diagram and the temperature dependence of this distribution ratio is small. The phosphorous transfer rate from slag to a 2CaO·SiO2 particle with 20 to 50 μm is considerably fast and a 2CaO·SiO2 particle changes to the particle with the composition of 2CaO·SiO2–3CaO·P2O5 solid solution within 5 s. In the case of particles present in cluster, only the rim part (5 μm) of a particle changes to the composition of 2CaO·SiO2–3CaO·P2O5 solid solution within 5 s, but small size particles with 3 to 8 μm completely change to the particles with the composition of 2CaO·SiO2–3CaO·P2O5 solid solution within 5 s.

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

2. Experimental

2.1. Sample Preparation

2CaO·SiO2: The mixture of reagent grade CaCO\(_3\) and SiO\(_2\) on molar ratio of 1:2.05 was pressed, followed by heating at 950°C. The sample was ground, pressed to cylindrical shape and heated again at 1400°C for 24 h. The ground sample was mixed with 1 mass% B\(_2\)O\(_3\) (% represents mass%, hereinafter) and heated at 900°C for 24 h in order to prevent the vaporization of B\(_2\)O\(_3\), followed by heating at 1400°C for 24 h. By the B\(_2\)O\(_3\) addition, the dusting of 2CaO·SiO2 was prevented. The ground sample was again pressed to cylindrical shape and heated at 1400°C for 24 h, and then was ground and sieved.

2CaO·SiO2–3CaO·P2O5 solid solution: In stead of adding B\(_2\)O\(_3\) mentioned above, reagent grade 3CaO·P2O5 was added and the mixture was pressed to cylindrical shape and heated at 1400°C for 48 h, and then was ground. This procedure was repeated twice and the ground sample was sieved.

CaO–SiO2–Fe\(_t\)O and CaO–SiO2–Fe\(_t\)O–P2O5 slags: Reagent grade CaCO\(_3\) was heated at 950°C to obtain CaO. The mixture of CaO, SiO\(_2\) and Fe\(_t\)O was melted at 1420°C in a pure Fe crucible under Ar atmosphere and quenched by water-cooled sandwich type Cu plates. The slag compositions (A to J) used in this study are shown in Fig. 1 for the CaO–SiO2–Fe\(_t\)O phase diagram. The mixture of CaO, SiO\(_2\), and Fe\(_t\)O was melted at 1600°C in a MgO crucible and then rapidly quenched onto the water-cooled Cu plate. The CaO–SiO2–Fe\(_t\)O–P2O5 slags were prepared by adding reagent grade 3CaO·P2O5 to CaO–SiO2–Fe\(_t\)O slags and the

Phosphorous Partition between 2CaO·SiO2 Particles and CaO–SiO2–Fe\(_t\)O Slags

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slag samples were ground to below 3 μm by using a stainless steel ball mill. All samples were stored in desiccator before use.

2.2. Procedure

In order to study the behavior of phosphorous partition between 2CaO·SiO₂ (or 2CaO·SiO₂–3CaO·P₂O₅ solid solution) and CaO–SiO₂–Fe₂O₃ (CaO–SiO₂–Fe₃O₅) slags, the following five methods were used. All experiments were made under Ar flowing atmosphere (200 cm³·min⁻¹). A pure Fe crucible was used in the experiments below 1 400°C and a MgO crucible containing Fe was used in the experiments above 1 460°C.

1. Pressing method: 2CaO·SiO₂ particles were uniformly mixed with slag powder in an appropriate proportion and a tablet obtained by pressing was heated in an Fe crucible, followed by rapid quenching in water.
2. Mixing method: A slag sample was melted at a given temperature and 2CaO·SiO₂ powder was added. A melt was stirred by an Fe rod and after a given time the sample was quenched by water-cooled sandwich type Cu plates.
3. Dipping method: A small MgO crucible with a hole at the crucible side in which 2CaO·SiO₂ particles are distributed was dipped into a slag melted in an Fe crucible or a MgO crucible. A small MgO crucible was withdrawn from the slag, followed by rapid quenching in water.
4. Isothermal crystallization method: A slag sample obtained by quenching from 1 600°C was melted in an Fe crucible for a given time at 1 400°C, followed by rapid quenching in water.
5. Temperature drop crystallization method: A slag sample was melted at 1 600°C in a MgO crucible containing Fe under Ar atmosphere. Then a melt was cooled to 1 400°C at 150°C·min⁻¹ and kept for a given time, followed by rapid quenching in water.

2.3. Analysis

The phosphorous contents of 2CaO·SiO₂ particles and slag were determined by using X-ray microprobe analyzer (EPMA). The 2CaO·SiO₂–3CaO·P₂O₅ solid solutions containing 0.5, 3, 5 and 19% P₂O₅, which were prepared at 1 400°C and chemically analyzed, were used for the phosphorous standard.

3. Results and Discussion

3.1. Dispersion of 2CaO·SiO₂ Particles in Slag

The slag A indicated in Fig. 1 was mixed with 2CaO·SiO₂(C₂S) particles (20 to 50 μm) in the proportion of 2:1 on weight pct basis and a tablet was made by the pressing method described in Sec. 2.2. The SEM image of the pressed mixture heated at 1 400°C for 30 min is shown in Fig. 2(a), in which 2CaO·SiO₂ particles are uniformly dispersed in liquid slag.

3.2. Phosphorous Distribution Ratio between 2CaO·SiO₂ Particle and CaO–SiO₂–Fe₂O₃ Slag

The phosphorous distribution ratios between 2CaO·SiO₂ particle and CaO–SiO₂–Fe₂O₃ slag were measured at 1 400°C by using the different methods described in Sec. 2.2 and the results are summarized in Table 1 and shown in Fig. 3. It is considered from the low con-
tent of MgO given in Table 1 that the effect of MgO on the phosphorous distribution ratio is negligibly small. The phosphorous distribution ratios are plotted against \((\% \text{SiO}_2) / \text{H}_{11001}(\% \text{P}_2\text{O}_5)\) in the slag composition saturated with 2CaO·SiO₂ phase in Fig. 1, along with the results by Ito et al. 3) Their values are slightly higher than the present ones. The reason for this difference is not certain. The values at 1560°C are higher than those at 1400°C for a given \((\% \text{SiO}_2) / \text{H}_{11001}(\% \text{P}_2\text{O}_5)\). This can be explained by the fact that the CaO content for a given \((\% \text{SiO}_2)/(\% \text{P}_2\text{O}_5)\) is higher at 1560°C in comparison with that at 1400°C.

The temperature dependence of phosphorous distribution ratio is demonstrated in Fig. 4 for slags A and G. These results for slags A and G are obtained in the 2CaO·SiO₂ particle/slag mass% ratio = 1/1 to 1/3 and 1/1 to 1/2, respectively. The phosphorous distribution ratio does not change with temperature for slag A, but it tends to slightly increase with a decrease in temperature for slag G. This indicates that a slag composition saturated with 2CaO·SiO₂ phase change with temperature, which influences the phosphorous distribution.

3.3. Phosphorous Transfer from CaO–SiO₂–FeO–P₂O₅ Slag to 2CaO·SiO₂ Particles

The variation of phosphorous distribution ratio with time was studied at 1400°C for the 2CaO·SiO₂ particles dispersed in slag. The results obtained by the pressing, mixing and dipping methods and the isothermal and temperature drop methods described in Section 2.2 are shown in Figs. 5 and 6, respectively. It can be seen that the phosphorous transfer from slag to 2CaO·SiO₂ particles is considerably fast. In the dipping method, 3CaO·P₂O₅ particles were dispersed in slag; that is, phosphorous equilibrium approaches from particle to slag. In this case the time for equilibrium was found to be longer, as shown in the top diagram of Fig. 5 by the half-filled triangles.

The 2CaO·SiO₂ particles with 20 to 50 μm were reacted with liquid slag C containing 5% P₂O₅ at 1400°C by using the dipping method and after 5 s, the sample was rapidly quenched in water. The line analysis of P-Kα in a 2CaO·SiO₂ grain was made in a polished cross section and the results are shown for the isolated and clustered particles zones on the left- and right-hand sides of Fig. 7, respectively. It can be seen from Fig. 7(a) that phosphorous content is constant through a 2CaO·SiO₂ grain in the case of isolated particle zone within 5 s. However, phosphorous dissolves to the rim layer of 5 mm from the grain/slag interface in the case of clustered particle zone, as shown in Fig. 7(b).

The length of phosphorous penetration from the P₂O₅-containing slag/a 2CaO·SiO₂ particle (20 to 50 μm) interface has been measured by a microprobe analysis. The
phosphorous diffuses into $2\text{CaO} \cdot \text{SiO}_2$ phase by the formation of $2\text{CaO} \cdot \text{SiO}_2 - 3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution. The depth of phosphorous penetration into a $2\text{CaO} \cdot \text{SiO}_2$ grain is plotted against time in Fig. 8 for the isolated and clustered particles zones. The phosphorous penetration into a whole grain occurs very rapidly for the isolated particles dispersed uniformly, regardless of slag composition and initial $\text{P}_2\text{O}_5$ content. On the other hand, the depth of phosphorous penetration for the clustered particles is very short and almost independent of time. This is due to the fact that the $\text{P}_2\text{O}_5$ content in slag around the clustered $2\text{CaO} \cdot \text{SiO}_2$ particles decrease quickly, thus resulting in the decrease of driving force for phosphorous penetration.

The depth of phosphorous penetration was measured as a function of temperature in the experiments where the isolat-
ed or clustered 2CaO·SiO₂ particles with 20 to 50 μm are in contact with the 5% P₂O₅ containing slags A and G for 5 s. The results are shown in Fig. 9. It is seen from the upper diagram that the length of phosphorous penetration in an isolated particle zone is independent of temperature. As shown in the lower diagram for the clustered particles the length of phosphorous penetration becomes longer with an increase in temperature and it is greater at higher phosphorous distribution ratio (slag G) for a given temperature.

3.4. Crystallization of 2CaO·SiO₂–3CaO·P₂O₅ Solid Solution Particles during Temperature Drop

Ten grams of slag G’ (m.p. 1 540°C) containing 5% P₂O₅ whose composition is shown in Fig. 1 was melted at 1 570°C in a MgO crucible along with pure Fe (3 g) in order to control the oxygen potential determined by the Fe/Fe₂O₃ equilibrium. After holding at 1 570°C for 30 min, a melt was rapidly quenched by water-cooled sandwich type Cu plates. Small particles of crystallized 2CaO·SiO₂–3CaO·P₂O₅ solid solution with 3 to 5 μm are shown on the left-hand side of Fig. 10(a), together with the line analysis of P-Kα for the particles shown on the right-hand side of Fig. 10(a).

After holding slag G’ with 5% P₂O₅ at 1 570°C for 30 min, a melt was cooled to 1 400°C at 50°C·h⁻¹ and subsequently quenched in water. The crystallized 2CaO·SiO₂–3CaO·P₂O₅ solid solution particles with 7 to 130 μm are shown on the left-hand side of Fig. 10(b), together with line analysis of P-Kα for the particles shown on the left-hand side of Fig. 10(b). Based on these results it was confirmed that the P content was constant through a large grain and the obtained phosphorous distribution ratio agrees with the equilibrium value (L₀=63) shown in Fig. 1. This result indicates that the crystallized particles have the equilibrium composition with slag during the present cooling rate.

3.5. Phosphorous Transfer from CaO–FeO–P₂O₅ Slag to 2CaO·SiO₂ Particles

The 2CaO·SiO₂ particles with 0.5 to 1 mm were added to slag D containing 5% P₂O₅ at 1 400°C and immediately stirred for 5 s, followed by holding for 30 s. The added 2CaO·SiO₂ particles and the line analysis of P-Kα on the surface of a particle are shown on the left- and right-hand sides of Fig. 11, respectively. Small grains of 2CaO·SiO₂–3CaO·P₂O₅ (33 to 37% 3CaO·P₂O₅) solid solution with 5 to 25 μm, which are peeled off from the surface of a 2CaO·SiO₂ particle, are observed at a 2CaO·SiO₂ particle/slag interface, as shown on the right-hand side of Fig. 11.

The 2CaO·SiO₂ particles (0.5 to 1 mm) were added to slag D containing 5% P₂O₅ at 1 300 or 1 400°C, followed by stirring for 5 s and the thickness of the peeled off layer was measured as a function of holding time. The results are demonstrated in Fig. 12, indicating that the thickness of peeled off layer remains almost constant after 30 s. These results suggest that P₂O₅ in slag in the neighborhood of a 2CaO·SiO₂ particle dissolves in this particle within 30 s.

The phosphorous penetration into the surface layer of a 2CaO·SiO₂ particle and the peeling off of 2CaO·SiO₂–3CaO·P₂O₅ solid solution layer are schematically illustrated in Fig. 13. The following three reaction steps are proposed.

Step I: The dissolution of CaO and SiO₂ from the surface of a 2CaO·SiO₂ particle occurs, thus resulting in the slag composition change from slag D to slag D’, as shown in the upper diagram.

Step II: The CaO and P₂O₅ in slag D’ dissolve into
2CaO·SiO2, leading to the formation of 2CaO·SiO2–3CaO·P2O5 solid solution. The slag composition changes from D/H to H1 as a result of decrease in CaO and P2O5 contents.

Step III: The 2CaO·SiO2–3CaO·P2O5 solid solution layer starts to peel off and the peeled grains separate from the surface. This phenomenon is only observed in the case that 2CaO·SiO2 particles are in contact with CaO–FeO–P2O5 slag and not observed in the case that 2CaO·SiO2 particles are in contact with CaO–SiO2–FeO–P2O5 slag. Further study is needed to clarify the reason that the peeling of 2CaO·SiO2 particles occurs for the slag with low SiO2 and high FeO contents.

4. Conclusion

The 2CaO·SiO2 particles are dispersed in CaO–SiO2–FeO slags containing P2O5 and the phosphorous transfer to a particle has been studied. The following conclusions are obtained:

(1) The maximum phosphorous distribution ratio between 2CaO·SiO2 particles and CaO–SiO2–FeO slags is obtained at the nose of 2CaO·SiO2 primary phase in CaO–SiO2–FeO phase diagram.

(2) The temperature dependence of phosphorous distribution ratio between 2CaO·SiO2 and slag is found to be very small.

REFERENCES