Phosphorous Partition between 2Ca0 · SiO₂ Particles and CaO–SiO₂–Fe_tO Slags

Ryo INOUE and Hideaki SUITO

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1-1, 2-chome, Katahira, Aoba-ku, Sendai 980-8577 Japan.

(Received on July 27, 2005; accepted on November 30, 2005)

The behavior of phosphorous transfer from P_2O_5 -containing CaO-SiO₂-Fe_rO slags to 2CaO ·SiO₂ particles homogeneously dispersed in slag has been studied by using a microprobe analysis. The maximum phosphorus distribution ratio between 2CaO ·SiO₂ particle and slag is obtained at the nose composition of 2CaO ·SiO₂ primary phase region in CaO-SiO₂-Fe_rO 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 μ m 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 μ m) of a particle changes to the composition of 2CaO ·SiO₂-3CaO ·P₂O₅ solid solution within 5 s.

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

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 $2CaO \cdot SiO_2$ phase as $3CaO \cdot P_2O_5^{(1)}$ and is present in BOF slag as $2CaO \cdot SiO_2$ - $3CaO \cdot P_2O_5$ solid solution.²⁾ The phosphorous distribution ratio between $2CaO \cdot SiO_2$ and CaO-SiO₂-Fe₁O slag has been reported at 1350 and 1400°C.³⁾

In this study the phosphorous distribution ratios between $2\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} - \text{SiO}_2 - \text{Fe}_i\text{O}$ slags have been measured at 1 300 and 1 560°C by equilibrating the $2\text{CaO} \cdot \text{SiO}_2$ particles (20 to 50 μ m) with slags (particle/slag mass ratio=1/1 to 1/10). Furthermore, phenomenological study on phosphorous transfer from slag to a $2\text{CaO} \cdot \text{SiO}_2$ particle is carried out by using a microprobe analysis.

2. Experimental

2.1. Sample Preparation

 $2\text{CaO} \cdot \text{SiO}_2$: 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_2O_3 (% represents mass%, hereinafter) and heated at 900°C for 24 h in order to prevent the vaporization of B_2O_3 , followed by heating at 1400°C for 24 h. By the B_2O_3 addition, the dusting of 2CaO \cdot 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.

 $2\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution: In stead of adding B₂O₃ mentioned above, reagent grade $3\text{CaO}\cdot\text{P}_2\text{O}_5$ was added and the mixture was pressed to cylindrical shape and heated at $1\,400^{\circ}\text{C}$ for 48 h, and then was ground. This procedure was repeated twice and the ground sample was sieved.

CaO–SiO₂–Fe₁O and CaO–SiO₂–Fe₂O–P₂O₅ slags: Reagent grade CaCO₃ was heated at 950°C to obtain CaO. The mixture of CaO, SiO₂ and Fe₁O was melted at 1 420°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–Fe₁O phase diagram. The mixture of CaO, SiO₂ and Fe₁O was melted at 1 600°C in a MgO crucible and then rapidly quenched onto the water-cooled Cu plate. The CaO–SiO₂–Fe₁O–P₂O₅ slags were prepared by adding reagent grade 3CaO · P₂O₅ to CaO–SiO₂–Fe₁O slags and the



Fig. 1. Phosphorous distribution ratio between 2CaO · SiO₂ particle and CaO–SiO₂–Fe₇O slag.

slag samples were ground to below $3 \,\mu m$ 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 $2\text{CaO} \cdot \text{SiO}_2$ (or $2\text{CaO} \cdot \text{SiO}_2-3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution) and $\text{CaO}-\text{SiO}_2-\text{Fe}_t\text{O}-\text{P}_2\text{O}_5$ (CaO $-\text{SiO}_2-\text{Fe}_t\text{O}$) slags, the following five methods were used. All experiments were made under Ar flowing atmosphere ($200 \text{ cm}^3 \cdot \text{min}^{-1}$). 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: $2\text{CaO} \cdot \text{SiO}_2$ 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 $2\text{CaO} \cdot \text{SiO}_2$ 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 $2\text{CaO} \cdot \text{SiO}_2$ 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 1400°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 $2\text{CaO} \cdot \text{SiO}_2$ particles and slag were determined by using X-ray microprobe analyzer (EPMA). The $2\text{CaO} \cdot \text{SiO}_2$ -3CaO $\cdot \text{P}_2\text{O}_5$ 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.





Fig. 2. SEM image of $2\text{CaO} \cdot \text{SiO}_2$ particles dispersed in liquid slag.



Fig. 3. Phosphorous distribution ratio between $2CaO \cdot SiO_2$ particle and $CaO-SiO_2$ -Fe_tO slag plotted against (% SiO₂)+ (% P₂O₅).

3. Results and Discussion

3.1. Dispersion of 2CaO·SiO₂ Particles in Slag

The slag A indicated in Fig. 1 was mixed with $2\text{CaO} \cdot \text{SiO}_2(\text{C}_2\text{S})$ particles (20 to 50 μ m) 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 1400°C for 30 min is shown in **Fig. 2**(a), in which $2\text{CaO} \cdot \text{SiO}_2$ particles are uniformly dispersed in liquid slag. Such uniform particle dispersion was observed in other methods except for the dipping method. In the case of the dipping method where stirring operation cannot be made, there is the region in which $2\text{CaO} \cdot \text{SiO}_2$ particles are present in cluster, as shown in Fig. 2(b).

3.2. Phosphorous Distribution Ratio between 2CaO· SiO₂ Particle and CaO-SiO₂-Fe₄O Slag

The phosphorous distribution ratios between $2\text{CaO} \cdot \text{SiO}_2$ particle and CaO–SiO₂–Fe₁O slag were measured at 1 400 and 1 560°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-

ISIJ International, Vol. 46 (2006), No. 2

Slag	Temp. / K	Slag					C ₂ S particle	
		(% CaO)	(% SiO ₂)	(% Fe,O)	(% MgO)	(% P ₂ O ₅)	(% P ₂ O ₅)	Lp
		EDX	EDX	EDX	EDX	WDX	WDX	
А	1573	39.4	38.4	20.7		$2.63 \!\pm\! 0.90$	5.0 ± 1.9	1.9 ± 0.6
	1623	41.5	38.1	19.3		2.94 ± 0.97	5.3 ± 1.7	1.8 ± 0.4
	1673	43.5	37.3	18.4		2.79 ± 0.81	5.3 ± 1.1	1.9±0.4
	1723	44.4	36.6	15.4	1.3	3.05 ± 0.54	5.8±1.3	1.9 ± 0.3
	1833	48.0	35.5	11.7	2.8	3.11 ± 0.72	5.9 ± 1.9	1.9 ± 0.6
В	1673	30.5	23.2	45.7	_	1.20 ± 0.22	7.1 ± 1.4	5.9±1.8
С	1673	20.7	9.8	69.2	_	0.42 ± 0.13	15.2 ± 5.1	36±8
	1833	29.9	15.9	51.0	1.9	1.31 ± 0.32	18.3 ± 7.1	14±6
F	1673	19.6	6.3	76.1	_	$0.32 {\pm} 0.11$	14.4±5.5	45±10
G	1673	29.6	3.0	65.8	_	$0.27\!\pm\!0.10$	17.0±7.1	63 ± 20
	1723	32.5	5.0	62.5	0.5	0.30 ± 0.11	18.1 ± 6.2	61 ± 19
	1833	34.4	6.4	61.9	1.5	0.31 ± 0.15	18.1 ± 6.6	58±23
Н	1673	21.3	15.1	62.0		0.97 ± 0.14	11.6 ± 1.4	12±3
J	1673	38.1	3.3	56.6		0.82±0.20	15.6 ± 6.3	19 ± 4

Table 1. Chemical composition of slag and 2CaO · SiO₂ particle analyzed by EPMA method.



Fig. 4. Temperature dependence of phosphorous distribution ratio between 2CaO·SiO₂ particle and CaO–SiO₂–Fe₂O slag.

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 $(\%SiO_2)+(\%P_2O_5)$ in the slag composition saturated with $2CaO \cdot SiO_2$ 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 $1560^{\circ}C$ are higher than those at $1400^{\circ}C$ for a given $(\%SiO_2)+(\%P_2O_5)$. This can be explained by the fact that the CaO content for a given $(\%SiO_2)+(\%P_2O_5)$ is higher at $1560^{\circ}C$ in comparison with that at $1400^{\circ}C$.

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 $2\text{CaO} \cdot \text{SiO}_2$ par-

ticle/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 $2\text{CaO} \cdot \text{SiO}_2$ phase change with temperature, which influences the phosphorous distribution.

3.3. Phosphorous Transfer from CaO-SiO₂-Fe_tO-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, $3CaO \cdot P_2O_5$ 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 \cdot SiO₂ particles with 20 to 50 μ m were reacted with liquid slag C containing 5% P₂O₅ at 1 400°C by using the dipping method and after 5 s, the sample was rapidly quenched in water. The line analysis of P-K α in a 2CaO \cdot 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 \cdot 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 P_2O_5 containing slag/a 2CaO·SiO₂ particle (20 to 50 μ m) 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 P_2O_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 P_2O_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-



Fig. 5. Variation of phosphorous distribution ratio between 2CaO·SiO₂ particle and CaO–SiO₂–Fe_tO slag with time.



iig. 6. Variation of phosphorous distribution ratio between 2CaO · SiO₂ particle and CaO–SiO₂–Fe_iO slag with time.



Fig. 8. Variation of length of phosphorous penetration into a 2CaO · SiO₂ grain with time obtained by dipping method.



Fig. 7. Line analysis of P-Kα of 2CaO·SiO₂ grain in (a) isolated particle zone and (b) clustered particle zone after dipping method (2CaO·SiO₂/slag C (5% P₂O₅) mass ratio =1/10, 1 673 K, 5 s).



Fig. 9. Temperature dependence of length of phosphorous penetration into a $2CaO \cdot SiO_2$ grain after immersion for 5 s obtained by dipping method.

ed or clustered $2\text{CaO} \cdot \text{SiO}_2$ particles with 20 to 50 μ m 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. 1540°C) containing 5% P_2O_5 whose composition is shown in Fig. 1 was melted at 1570°C in a MgO crucible along with pure Fe (3 g) in order to control the oxygen potential determined by the Fe/Fe_iO equilibrium. After holding at 1570°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 μ m are shown on the lefthand side of **Fig. 10**(a), together with the line analysis of P-K α for the particles shown on the right-hand side of Fig. 10(a).

After holding slag G' with 5% P_2O_5 at 1570°C for 30 min, a melt was cooled to 1400°C at 50°C·h⁻¹, followed by rapid quenching in water. The crystallized 2CaO·SiO₂-3CaO·P₂O₅ solid solution particles with 7 to 130 μ m are shown on the left-hand side of Fig. 10(b), together with line analysis of P-K α 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 (L_p =63) shown in Fig. 1. This result indicates that the crystallized particles have the equilibrium composition with slag during the present cooling rate.



Fig. 10. Line analysis of P-K α of crystallized 2CaO·SiO₂ in slag G quenched at (a) 1843 K and (b) 1673 K after cooling from 1843 K and (b) 1673 K after cooling from 1843 K at T=150 K·h⁻¹.

3.5. Phosphorous Transfer from CaO-Fe₁O-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 1400°C and immediately stirred for 5 s, followed by holding for 30 s. The added 2CaO·SiO₂ particles and the line analysis of P-K α on the surface of a particle are shown on the left- and righthand sides of **Fig. 11**, respectively. Small grains of 2CaO·SiO₂-3CaO·P₂O₅ (33 to 37% 3CaO·P₂O₅) solid solution with 5 to 25 μ m, 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% P_2O_5 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 P_2O_5 in slag in the neighbor of a 2CaO·SiO₂ particle dissolves in this particle within 30 s.

The phosphorous penetration into the surface layer of a $2\text{CaO} \cdot \text{SiO}_2$ particle and the peeling off of $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution layer are schematically illustrated in **Fig. 13**. The following three reaction steps are proposed.

Step I: The dissolution of CaO and SiO_2 from the surface of a $2CaO \cdot SiO_2$ 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



Fig. 11. Line analysis of P-Kα on surface of 2CaO·SiO₂ particle dipped in CaO–65%Fe₁O–5%P₂O₅ slag at 1 673 K for 30 s: 2CaO·SiO₂ /slag mass ratio=1/3.



Fig. 12. Thickness of $2CaO \cdot SiO_2-3CaO \cdot P_2O_5$ layer peeled from $2CaO \cdot SiO_2$ particle in CaO-65%Fe₂O-5%P₂O₅ slag.

 $2\text{CaO} \cdot \text{SiO}_2$, leading to the formation of $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution. The slag composition changes from D' to D" as a result of decrease in CaO and P_2O_5 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– Fe₁O–P₂O₅ slag and not observed in the case that 2CaO· SiO₂ particles are in contact with CaO–SiO₂–Fe₁O–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 Fe₁O contents.

4. Conclusion

The $2\text{CaO} \cdot \text{SiO}_2$ particles are dispersed in CaO-SiO₂– Fe_tO 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 $2\text{CaO} \cdot \text{SiO}_2$ particles and $\text{CaO}-\text{SiO}_2-\text{Fe}_t\text{O}$ slags is obtained at the nose of $2\text{CaO} \cdot \text{SiO}_2$ primary phase in $\text{CaO}-\text{SiO}_2-\text{Fe}_t\text{O}$ phase diagram.

(2) The temperature dependence of phosphorous distribution ratio between $2\text{CaO} \cdot \text{SiO}_2$ and slag is found to be very small.



Step I : C₂S dissolution

Step II : CaO, P_2O_5 penetration $\rightarrow C_2S-C_3P$ formation $\rightarrow C_2S-C_3P$ growth Step III: C_2S-C_3P peeled off

Fig. 13. Schematic diagram of reaction sequence at $2CaO \cdot SiO_2$ particle/slag D interface.

(3) The isolated $2\text{CaO} \cdot \text{SiO}_2$ particles with 20 to 50 μ m in P₂O₅-containing slag completely change to uniform $2\text{CaO} \cdot \text{SiO}_2$ -3CaO \cdot P₂O₅ solid solution particles within 5 s.

(4) The rim layer of $5 \,\mu$ m from a $2\text{CaO} \cdot \text{SiO}_2$ particle (20 to $50 \,\mu$ m)/slag interface changes to $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution, when the particles are distributed in cluster in slag. The $2\text{CaO} \cdot \text{SiO}_2$ particles with 3 to $8 \,\mu$ m in the clustered zone become uniform $2\text{CaO} \cdot \text{SiO}_2$ - $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid solution within 5 s.

REFERENCES

- W. Fix, H. Heymann and R. Heinke: J. Am. Ceram. Soc., 52 (1969), 346.
- H. Suito, Y. Hayashida and Y. Takahashi: Tetsu-to-Hagané, 63 (1977), 1252.
- K. Ito, M. Yanagisawa and N. Sano: *Tetsu-to-Hagané*, 68 (1982), 342.
- W. Deer, R. Howie and J. Zussman: *Rock Form. Miner.*, 2A (1978), 546.
- 5) P. Roux: C. R. Seances Acad. Sci., C, 286 (1978), 549.