Dissolution Behavior of Solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ in $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ Slag

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In order to clarify the dissolution behavior of solid P_2O_5 rich phase in slag, the solid phosphate compound silicocarnotite $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ being the representative of P_2O_5 rich phase was dipped into the molten $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag at 1573 and 1673 K. Since the initial slag was free of P_2O_5 , the increase of P_2O_5 content in the slag is the indication of the dissolution behavior of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$. Therefore, the concentration profile of P_2O_5 across the interface between solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag was analyzed to evaluate the dissolution behavior.

The results show that the dissolution of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ into slag can be divided into the following stages: interaction of solid phase with slag, disintegration of solid phase, reaction between disintegrated solid phase and surrounding slag, and diffusion of CaO and P_2O_5 from solid sample to slag. The diffusivity of P_2O_5 in the liquid slag was calculated. It was found that higher temperature is favored for the diffusion in some cases, whereas larger CaO/SiO_2 ratio of the slag restrains the diffusion. [doi:10.2320/matertrans.M-M2010810]

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1. Introduction

The hot metal dephosphorization process has been uniquely developed to meet the increasing demand for low phosphorus steel production in Japan. The dephosphorizing reagent is usually composed of lime, iron ore and some other additives. The generated $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x\text{-}\text{P}_2\text{O}_5$ based slag after dephosphorization contains considerable amount of solid CaO , which causes problems such as increase of slag volume and difficulty of slag recycling. Though fluorspar (CaF_2) had been used as an additive to enhance CaO dissolution into liquid slag and improve fluidity, the use of CaF_2 is strictly restricted at present owing to its toxic property to human society. Consequently, the hot metal dephosphorization slag is a multi phase flux with solid and liquid phases coexisting. Reduction of the CaO consumption and the slag emission is the existing problem that the steelmakers confront. Since the slag contains both liquid and solid phases, it is considered that the problem can be solved by means of improving the transfer of phosphorus from liquid phase into solid phase in the slag to promote the utilization efficiency of solid CaO .

A lot of researches¹⁻¹¹⁾ had been devoted to clarify the microscopic reaction mechanisms in the CaO based multi phase flux as the fundamental study to develop new refining technology. Since many researchers⁵⁻¹²⁾ had confirmed the existence of P_2O_5 in $2\text{CaO}\cdot\text{SiO}_2$ phase as $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution or compound in steelmaking slag, it is considered by the researchers that the precipitation of $2\text{CaO}\cdot\text{SiO}_2$ phase in the CaO based multi phase flux is the necessary condition for the formation of solid P_2O_5 rich phase. Following this idea, the present authors investigated the reaction behavior of P_2O_5 at the interface between solid $2\text{CaO}\cdot\text{SiO}_2$ and $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x\text{-}\text{P}_2\text{O}_5$ slag.^{13,14)} It was observed that the P_2O_5 condensed phases are formed at the $2\text{CaO}\cdot\text{SiO}_2$ /slag interface in less than 1 s. Moreover, it was

also aware that the solid P_2O_5 condensed phase is possible to re-dissolve into the slag after its formation, dependent on the slag composition and reaction temperature. Therefore, promotion of the formation at the same time restraint in the dissolution of the solid P_2O_5 rich phase in the multi phase flux should be the guiding idea to innovate the present refining technologies. However, it is firstly needed to understand the dissolution behavior of the solid P_2O_5 rich phase in the slag.

Inoue *et al.*¹⁵⁾ studied the equilibrium between $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and molten $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag to measure the partition ratio of phosphorus. Utagawa *et al.*¹⁶⁾ dipped the rod of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution into the $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{Fe}_2\text{O}_3$ slag and observed that the transfer of P_2O_5 from solid solution to liquid slag was not fast. These studies proved the occurrence of dissolution of solid P_2O_5 rich phase in slag. However, the detailed understanding about the dissolution process and mechanism is still unavailable.

The present study has been conducted to extend the understanding of the microscopic reaction mechanism in the multi phase flux by focusing on the dissolution behavior of the solid P_2O_5 rich phases in liquid slag. Silicocarnotite, $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$, which has the largest P_2O_5 concentration among the P_2O_5 rich phases and is stable at hot metal dephosphorization temperatures, was employed as the representative in the present work for the sake of an easier evaluation on the transfer behaviors of P_2O_5 in liquid slag. $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ was dipped into $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag and the interface between solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and liquid slag was observed. The concentration profile of P_2O_5 across the interface was analyzed to evaluate the dissolution behavior. The influence of reaction temperature and slag composition on the dissolution behavior was also discussed.

2. Experimental

The $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag was prepared by mixing synthesized CaO , FeO_x , and reagent grade SiO_2 . Powder of CaO was obtained by the calcination of reagent grade CaCO_3 for

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24 h at 1173 K in air. FeO_x was synthesized by sintering an equimolar mixture of reagent grade Fe_3O_4 and electrolytic Fe powders in iron crucible at 1473 K with $\text{CO}\text{-CO}_2$ atmosphere ($\text{CO}/\text{CO}_2 = 1$) for 24 h. The $\text{CaO}\text{-SiO}_2\text{-FeO}_x$ slags with two CaO/SiO_2 molar ratios and the same FeO_x content were used as listed in Table 1 where iron oxide is represented by FeO . The compositions are also plotted on the phase diagram for the $\text{CaO}\text{-SiO}_2\text{-FeO}_x$ ternary system in Fig. 1 in which the solid curves indicate the liquidus for the $\text{CaO}\text{-SiO}_2\text{-FeO}$ system equilibrated with iron at 1573 and 1673 K.

The solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ was prepared by the following procedure. Firstly, the mixture of CaO obtained by calcination of CaCO_3 and reagent grade SiO_2 on molar ratio of 2 : 1 was sintered in a platinum crucible at 1773 K for 24 h in air to synthesize $2\text{CaO}\cdot\text{SiO}_2$. Then, the $2\text{CaO}\cdot\text{SiO}_2$ powder was mixed with reagent grade $3\text{CaO}\cdot\text{P}_2\text{O}_5$ on molar ratio of 1 : 1 and pressed at 50 MPa into cylindrical shape (diameter 10 mm, thickness 1 mm), followed by heating at 1673 K for 200 h in air. The last step was the confirmation of the formation of $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ by X-ray diffraction analysis.

The experimental method is similar as that in the previous reports.^{13,14)} Ten grams of slag was charged in an alumina

Table 1 Slag compositions.

Slag	CaO/SiO_2 (molar ratio)	Composition, C/mass%		
		FeO	CaO	SiO_2
A	1.0	30.0	33.8	36.2
B	1.3	30.0	38.4	31.6

Fig. 1 Slag compositions corresponding to Table 1 on the $\text{CaO}\text{-SiO}_2\text{-FeO}_x$ ternary system. Fig. 2 SEM images and element mappings for P and Fe around interfaces between $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag A at 1573 K. (5CSP is short for $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$)

Fig. 3 Concentration profiles of components against the position at the interface between 5CaO·SiO₂·P₂O₅ and slag A at 1573 K.

crucible (I.D.: 34 mm, O.D.: 38 mm, Height: 45 mm) with the coexistence of electrolytic iron (about 3 g) to maintain the Fe³⁺/Fe²⁺ ratio in the slag constant. The crucible was set in the hot zone of the reaction tube (I.D.: 52 mm, O.D.: 60 mm, Length: 1000 mm) at 1573 or 1673 K. High purity Ar gas with a flow rate 700 cm³/min was introduced from the bottom of the reaction tube. After the slag had been maintained for 3600 s at experimental temperature, the solid 5CaO·SiO₂·P₂O₅ disc attached to the tip of the ceramic tube by platinum wire was inserted in the reaction tube, suspended slightly above the liquid slag for 120 s to ensure thermal equilibrium, and then dipped into the slag. After dipping for 1 to 600 s, the solid 5CaO·SiO₂·P₂O₅ with adhered liquid slag was rapidly withdrawn from the reaction tube and quenched by immersing in liquid nitrogen, followed by embedding in the polyester resin. The cross-section was polished and the interface between 5CaO·SiO₂·P₂O₅ and slag was observed and analyzed by SEM/EDS.

3. Results

Since the initial slag was free of P₂O₅, the increase of P₂O₅ content in the slag is the indication of the dissolution behavior of solid 5CaO·SiO₂·P₂O₅. Therefore, the interface between solid 5CaO·SiO₂·P₂O₅ and slag was analyzed with special concern given to the concentration profile of P₂O₅ across the interfaces to evaluate the dissolution behavior.

The SEM images of the interfaces between solid 5CaO·SiO₂·P₂O₅ and slag A after dipping the solid for 1, 10 and 60 s at 1573 K together with the element mapping for P are shown in Fig. 2. The left side of the figure is the original solid 5CaO·SiO₂·P₂O₅, while the bulk slag is on the right. As can be seen in these SEM images, the synthesized solid 5CaO·SiO₂·P₂O₅ pieces were much porous, though the porosity of solid pieces was not measured in the present study. Therefore, it is believed that the liquid slag penetrated into the solid phase after the solid piece was dipped in the

Fig. 4 Concentration profiles of components against the position at the interface between $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag A at 1673 K.

liquid slag. This phenomenon was also confirmed by the fact that the gradual change of color was observed at the cross section of dipped solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ pieces, while synthesized $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ pieces were purely white. The boundary between solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag can be identified according to the element mapping for phosphorus by EDS across the interface.

The composition analysis by EDS at different positions across the interface was conducted to observe the concentration profiles of the main components in the system. An arbitrary reference location was chosen inside the solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ phase. The composition at each analyzed position was recorded as the function of its distance from the reference location as shown in Figs. 3 to 6 for slags A and B at 1573 and 1673 K. In the present study, the iron oxide was calculated as FeO. From solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ (left side) to bulk slag (right side), CaO and P_2O_5 contents are decreasing while SiO_2 and FeO are increasing. It is considered that firstly the solid compound dissolves and then CaO and P_2O_5 diffuse

into the bulk slag driving by the activity gradient. The penetration of slag into solid phase also occurs.

In order to clarify the diffusion behavior of P_2O_5 , in the present study the position where CaO and P_2O_5 content start to decrease while SiO_2 and FeO are sharply increasing is regarded as the boundary between solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag. According to the concentration profile of P_2O_5 , the thickness of the diffusion layer of P_2O_5 can be obtained by measuring the relative distance between the position where P_2O_5 content becomes zero and the boundary, as marked in the figures.

4. Discussion

4.1 Dissolution procedure of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ into slag

The dissolution procedure of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ into the slag can be divided into three stages as illustrated in Fig. 7. First is interaction, the solid contacts with the liquid

Fig. 5 Concentration profiles of components against the position at the interface between $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag B at 1573 K.

slag (Fig. 7(a)). Second is disintegration, the rim layer of the solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ disintegrates into isolated particles due to the penetration of liquid slag (Fig. 7(b)). Reaction and diffusion are the third stage (Fig. 7(c)). The reaction at the interface between solid particle and surrounding slag is assumed to be instantaneous making the adjacent liquid slag film be saturated with $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$, though the saturation of liquid slag cannot be confirmed since the liquidus compositions for the $\text{CaO}\cdot\text{SiO}_2\cdot\text{FeO}_x\cdot\text{P}_2\text{O}_5$ slag saturated with solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ have not been reported so far. Because of the activity gradient, CaO and P_2O_5 diffuse from the liquid slag film to the surrounding liquid slag. Correspondingly the CaO and P_2O_5 contents in the diffusion layer next to the solid phase increase. The white arrows in the figure show the multi directional local diffusion from the liquid slag film saturated with the solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ to the surrounding liquid slag in the slag penetration layer. The overall diffusion is regarded from the solid phase to the bulk slag.

In addition, the liquid slag composition rapidly reaches to the solid-liquid coexisting region saturated by $2\text{CaO}\cdot\text{SiO}_2$ because the initial liquid slag composition is very near from the liquidus saturated with $2\text{CaO}\cdot\text{SiO}_2$ as shown in Fig. 1. Therefore, the precipitation of $2\text{CaO}\cdot\text{SiO}_2$ (more exactly $2\text{CaO}\cdot\text{SiO}_2\cdot 3\text{CaO}\cdot\text{P}_2\text{O}_5$), or the selective dissolution of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ from solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ is expected. As a whole, dissolution of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ proceeds as an overall dissolution reaction.

The solid particles as depicted in Figs. 7(b) and (c) were not clearly observed from SEM/EDS observations as shown in Figs. 2 to 6. The precipitation of P_2O_5 rich phase at the interface between liquid $\text{CaO}\cdot\text{SiO}_2\cdot\text{FeO}_x\cdot\text{P}_2\text{O}_5$ slag and $2\text{CaO}\cdot\text{SiO}_2$ from EDS analysis was observed in the previous study.^{13,14} However, the measured compositions being not on the $2\text{CaO}\cdot\text{SiO}_2\cdot 3\text{CaO}\cdot\text{P}_2\text{O}_5$ tie line but at the region between liquid bulk slag composition and the tie line. Furthermore, the compositions of P_2O_5 rich phases moved toward the $2\text{CaO}\cdot\text{SiO}_2\cdot 3\text{CaO}\cdot\text{P}_2\text{O}_5$ tie line with increasing

Fig. 6 Concentration profiles of components against the position at the interface between $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag B at 1673 K.

reaction time. It is considered that these phenomena are observed because the initially precipitated $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ particle are smaller than the spot size of electron beam (approximately $2\text{ }\mu\text{m}$) and the average composition of solid and liquid phases under the beam spot is measured. The shift of average composition to the tie line is due to the growth of precipitated particle. From above discussion, it is concluded the dispersion of small particles around the solid-liquid interface, which were formed by disintegration of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ or precipitation of $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$, are reasonably possible.

4.2 Estimation of the diffusivity of P_2O_5 in slag

As above mentioned, the region where the change of P_2O_5 concentration was observed was regarded as a diffusion layer for P_2O_5 . The form of the concentration profile of P_2O_5 in liquid phase across the interface is influenced both by the slag penetration into solid phase and the P_2O_5 diffusion into bulk slag as illustrated in Fig. 8. Since the thickness of the

penetration layer is negligible in most cases in this study, the thickness of the diffusion layer is defined as the distance between the position where P_2O_5 content turns to zero and the instant solid/slag boundary.

According to the experimental results shown in Figs. 3–6, the thickness of the diffusion layer was plotted as the function of the square root of dipping time as shown in Fig. 9. Since only one profile for P_2O_5 concentration has been measured for each slag composition at each temperature, the obtained values of diffusion layer thickness have been scattered. Nevertheless, the increase of the thickness with the dipping time was observed. Therefore, it is considered that the dissolution of the solid phase is governed entirely by the diffusion in slag.

In order to calculate the diffusivity of P_2O_5 , the following assumptions are made.

- (1) Diffusion of P_2O_5 is single dimensional.
- (2) Diffusion time equals the dipping time.
- (3) The diffusion of other components such as CaO has

Fig. 7 Dissolution procedure of solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ into slag. (5CSP is short for $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$)

Fig. 8 Form of the concentration profile of P_2O_5 in liquid phase across the interface between solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ and slag. (5CSP is short for $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$)

Fig. 9 Relationship between thickness of the diffusion layer and dipping time.

little influence on the P_2O_5 diffusion.

(4) There are no wall effects.

(5) The concentration at the solid/liquid boundary is constant (P_2O_5 content in the liquid slag film saturated with solid $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$).

(6) There are no convection currents in the liquid slag.

The diffusivity (D) of P_2O_5 was calculated based on eq. (1) derived from above assumptions, where L and t denote the thickness of diffusion layer and diffusion time, respectively.

$$L = 4\sqrt{Dt} \quad (1)$$

Roughly estimated diffusivity of P_2O_5 in Slag A was 3×10^{-12} and $2 \times 10^{-12} \text{ m}^2/\text{s}$ at 1573 and 1673 K, and those in Slag B was 2×10^{-13} and $6 \times 10^{-13} \text{ m}^2/\text{s}$ at 1573 and 1673 K, respectively. The value of diffusivity of P_2O_5 in the $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag has not been found in published literature. However, the diffusivities of P_2O_5 in the 30 mass% CaO -45% SiO_2 -25% Fe_2O_3 slag at 1623, 1673 and 1723 K measured by Ukyo *et al.*¹⁷⁾ are in the range from 5.5×10^{-11} to $1.6 \times 10^{-10} \text{ m}^2/\text{s}$, respectively. These values are slightly larger than the diffusivities calculated in the present study. However, the dependence of diffusivity of P_2O_5 on the slag composition is not well clarified yet.

The influence of temperature and CaO/SiO_2 molar ratio on the diffusion of P_2O_5 in slag can be understood from estimated diffusivities. For slag A, since the difference of diffusivity at different temperature is in the range of experimental error, it is regarded that the temperature has little influence on the diffusion for slag A. However, for slag B, the diffusivity at 1673 K is about three times larger than that at 1573 K, indicating that the higher temperature promotes the dissolution and diffusion considerably. Comparing the results for slags A and B, the value is much larger in the case of slag with lower CaO/SiO_2 molar ratio, implying that the diffusion is restrained by increasing the CaO/SiO_2 molar ratio of the slag.

For further understanding of P_2O_5 behavior in the $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x\text{-}\text{P}_2\text{O}_5$ multi phase fluxes, the physicochemical properties of slags such as the phase diagram, or equilibrium phosphorus partition between solid and liquid phases must be clarified.

5. Conclusions

The dissolution behavior of solid phosphate compound $5\text{CaO}\cdot\text{SiO}_2\cdot\text{P}_2\text{O}_5$ in the molten $\text{CaO}\text{-}\text{SiO}_2\text{-}\text{FeO}_x$ slag at 1573 and 1673 K was investigated. The influence of temperature and CaO/SiO_2 ratio on the diffusion of P_2O_5 was discussed.

The dissolution of solid phosphate compound into liquid slag can be divided into the following stages: interaction of solid phase with slag, disintegration of solid phase, reaction between disintegrated solid phase and surrounding slag, and diffusion of CaO and P_2O_5 from solid phase to slag. The diffusivity of P_2O_5 in the liquid slag was calculated. Higher temperature is favored for the diffusion in some cases, whereas higher CaO/SiO_2 ratio of the slag restrains the diffusion.

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