ROLE OF SOLID CaO IN FeO-CaO-SiO_2-P_2O_5 MULTI PHASE FLUX AT HOT METAL DEPHOSPHORIZATION TEMPERATURE

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ABSTRACT

The demand for production of low phosphorus steel has been increasing. Dephosphorization is conducted during hot metal pretreatment process in Japan. Phosphorus is oxidized and removed from pig iron by injecting CaO and FeO, and blowing oxygen from the top of the melt. However, the produced FeO-CaO-SiO_2-P_2O_5 slag contains considerable amount of solid CaO and thus the utilization efficiency for CaO is not high. Moreover, solid CaO remaining in the generated slag makes the slag recycling difficult. It is required to increase the utilization efficiency of solid CaO to reduce the amount of slag from the viewpoint of environmental issues. In the present work, the dissolution mechanism of solid CaO into the liquid slag and the formation behavior of P_2O_5 containing phase during CaO dissolution are studied. The goal is not only to enhance the CaO dissolution but also to understand the role of solid CaO in the multi phase flux for the development of better hot metal dephosphorization process. It was clarified that the key factors for enhancement of solid CaO utilization during hot metal dephosphorization are i) the dissolution of CaO to bulk slag via CaO-FeO layer formed between solid CaO and liquid slag, ii) precipitation of $2CaO \cdot SiO_2$ from dissolved CaO and SiO_2 originally contained in the slag, iii) formation of $2CaO \cdot SiO_2$- $3CaO \cdot P_2O_5$ phase and iv) P_2O_5 concentration in the liquid slag phase.

INTRODUCTION

The hot metal dephosphorization process has been developed to meet the increasing demand for low phosphorus steel production in Japan. In hot metal dephosphorization process, usually the CaO-based fluxes are used to form basic slag with high phosphate capacity and phosphorus in the melt is removed as P_2O_5. However, the produced $FeO_x(FeO+Fe_2O_3)$-CaO-SiO_2-P_2O_5 slag contains considerable amount of solid CaO since hot metal dephosphorization is carried out at low temperatures around 1573 K, which causes problems such as lowering the utilization efficiency of CaO, increase of slag volume and difficulty of slag recycling. Though CaF_2 had been used as a flux to enhance CaO dissolution into liquid slag, it causes the environmental pollution and thus the utilization of CaF_2 is strictly restricted at present.

Recently, it is further required to reduce the steelmaking slag emissions from the viewpoint of environmental issues. Therefore, one of the most important subjects in steelmaking processes is the effective use of CaO based fluxes for the decrease of slag generation and the resource saving with high refining efficiency. The reaction mechanism between solid CaO and liquid slag must be clarified, especially regarding the role of solid CaO on the dephosphorization to utilize CaO more efficiently.

In the present study:

- Solid CaO piece was reacted with FeO_x-CaO-SiO_2-P_2O_5 slag at 1573 and 1673 K. The interface between molten slag and the solid oxide was observed and analyzed by SEM with EDS. The microscopic behaviors of CaO dissolution into molten slag and P_2O_5 contained in the molten slag were investigated.
- Furthermore, solid 2CaO·SiO_2 piece was reacted with FeOx- CaO-SiO_2-P_2O_5 slag at 1673 K to clarify the effect of 2CaO·SiO_2 formation on the condensation behavior of P_2O_5 from slag to form solid 2CaO·SiO_2-3CaO·P_2O_5 solid solution.

EXPERIMENTAL

The slag sample was produced by mixing wüstite synthesized by sintering an equimolar mixture of reagent Fe_3O_4 and Fe powders in Fe crucible at 1473 K with CO-CO_2 atmosphere (CO/CO_2 = 1) for 24 h, CaO prepared by calcination of reagent $CaCO_3$ at 1173 K for 24 h, reagent grade SiO_2 and $Ca_3(PO_4)_2$. A CaO piece of about 3 g was cut from a chunk of CaO (purity: 99.9%, density: 3.3×103 kg/m^3) and used as solid CaO specimen. A 2CaO·SiO_2 piece was manufactured by pressing and heating a mixture of calcined CaO and reagent grade SiO_2 on molar ratio of 2:1, together with about 1 mass% $Ca_3(PO_4)_2$ to prevent the dusting of 2CaO·SiO_2.

Figure 1 shows the schematic drawing of experimental apparatus. Ten grams of mixed slag sample was charged in an alumina crucible (I.D.: 34 mm, O.D.: 38 mm, Height: 45 mm), and the crucible was put inside a mullite reaction tube heated at experimental temperature. The slag was held for one hour to ensure the thermal equilibrium at CO-CO_2 atmosphere, or Ar atmosphere with a solid electrolytic iron piece submerged in the slag. The solid CaO or 2CaO·SiO_2 piece attached to the tip of the ceramic tube was firstly inserted in the reaction tube and held near the slag to preheat the piece for 120 s, and then dipped into the liquid slag to react. The count of reaction time started when the solid piece was dipped, and after the prescribed reaction time the solid sample was quickly taken out from the furnace and quenched in flushing argon gas or by immersing in liquid nitrogen. Quenched sample was embedded in the polyester resin and the cross section of the interface between solid piece and slag was exposed by polishing the embedded sample. The interface was observed and the chemical composition was analyzed by SEM with EDS.

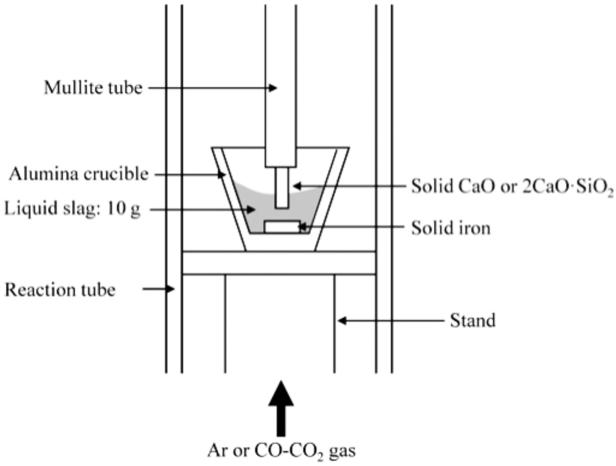

Figure 1: Schematic drawing of experimental apparatus

RESULTS AND DISCUSSION

Reaction between Solid CaO and Slag [1, 2]

Figures 2(a) to (d) show the SEM images around the interface between solid CaO and 25.3 mass%FeO_x- 30.8%CaO-33.1% SiO_2-10.8% P_2O_5 slag at 1573 K reacted for 2 to 30 s. Numbers in sample name represent reaction time in seconds. The numbered positions in figures were analyzed by EDS to obtain the chemistry. The CaO-FeO_x phase was observed adjacent to solid CaO, and the CaO-SiO_2 or CaO-SiO_2-P_2O_5 phase surrounded by liquid FeO_x-CaO-SiO_2 with high FeO_x content was formed next to the CaO-FeO_x layer. SiO_2 content in the CaO-FeO_x phase was less than 5 mass% and the ratio of CaO/FeO_x was approximately unity. CaO-SiO_2 surrounded by liquid slag was identified as 2CaO·SiO_2. CaO-SiO_2-P_2O_5 particles coexisting with FeO_x-CaO-SiO_2 slag contained from 1 to 10 mass% of P_2O_5, and CaO-SiO_2-P_2O_5 composition was a binary mixture of 2CaO·SiO_2 and 3CaO·P_2O_5. 2CaO·SiO_2 and 3CaO·P_2O_5 make wide solid solution region [3]. Therefore, it is considered that P_2O_5 was taken in 2CaO·SiO_2 as 3CaO·P_2O_5.

The compositions obtained by EDS analysis are plotted on the FeO_x-CaO-(SiO_2+P_2O_5) pseudo ternary diagram as shown in Figure 3. The solid curves represent the liquidus for the FeO_x-CaO-SiO_2 system equilibrated with iron at 1573 K [4]. The phases were classified into solid CaO, CaO-FeO_x, 2CaO·SiO_2, FeO_x-CaO-SiO_2 liquid with high FeO_x, and 2CaO·SiO_2 saturated phases. The compositions of FeO_x-CaO-SiO_2 liquid phase with high FeO_x content, coexisting with 2CaO·SiO_2 were close to the liquidus composition of 2CaO·SiO_2 saturation. Therefore, it is considered CaO content in liquid slag around solid CaO increased by CaO dissolution and local slag composition reached to the liquidus of 2CaO·SiO_2 saturation. Dissolved CaO and SiO_2 in the liquid were consumed to precipitate 2CaO·SiO_2 and the liquid phase composition changed along the liquidus resulting increase of FeO_x content.

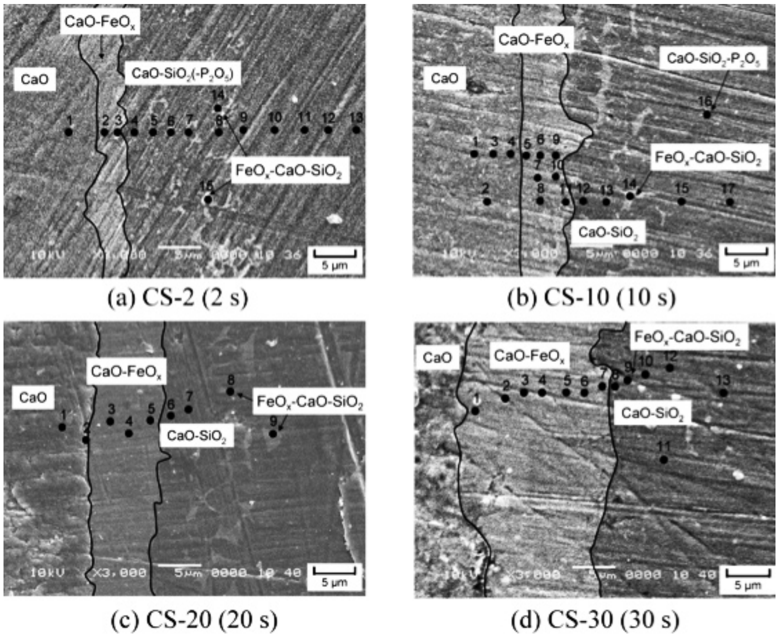

Figure 2: SEM images around the interface between solid CaO and molten slag at 1573 K

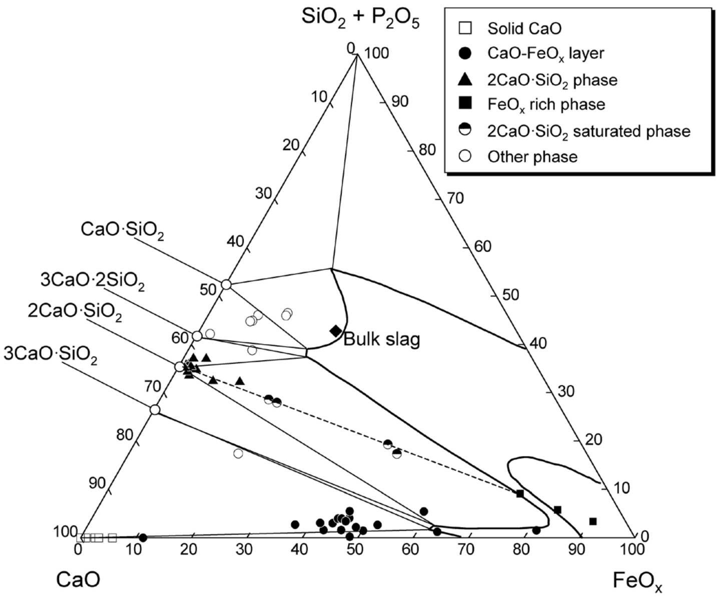

Figure 3: Chemical compositions analyzed by EDS for the FeO_x-CaO-(SiO_2+P_2O_5) system at 1573 K

The activities of FeO and CaO in each phase were estimated to clarify the reaction mechanisms between solid CaO and slag. The activities for the CaO-FeO system at 1573 K were investigated by Takeda and Yazawa [5]. Since CaO-FeO_x phase was equilibrated with solid CaO, the activities of FeO and CaO are equivalent to those of a liquidus composition of 28 mass%CaO-72%FeO at 1573 K, and the activities at that composition are reported to be

0.48 and 0.84 for FeO and CaO, respectively. Activities of FeO and CaO for the $2CaO{\cdot}SiO_2$ saturated liquid phase and bulk slag were calculated by the regular solution model [6].

The activity of FeO in the $2CaO{\cdot}SiO_2$ saturated liquid phase is higher than that in CaO-FeOx phase and bulk slag. Therefore, Fe^{2+} ion diffuses from $2CaO{\cdot}SiO_2$ saturated liquid phase to both the CaO- FeO_x phase and bulk slag. On the other hand, the activity of CaO in the CaO-FeO_x phase is much higher than that in other phases. Therefore, Ca^{2+} ion diffuses from solid CaO toward bulk slag through the CaO-FeO_x and $2CaO{\cdot}SiO_2$ saturated liquid phases.

From the above considerations, the reaction mechanisms between solid CaO and molten FeO_x-CaO- SiO_2-P_2O_5 slag are considered to be as follows:

- Dissolution of CaO into the slag resulting the increase of CaO content in the melt (Figure 4(a))
- Formation of $2CaO{\cdot}SiO_2$ from liquid slag, decrease of CaO and SiO_2 contents in the liquid, and relatively increase of FeO_x content (Figure 4(b))
- Diffusion of Fe^{2+} ion from FeO_x rich phase to both solid CaO and bulk slag (Figure 4(c))
- Formation of CaO-FeO_x phase adjacent to solid CaO (Figure 4(d))
- Diffusion of Ca^{2+} to bulk slag through formed CaO-FeO_x layer (Figure 4(e)).

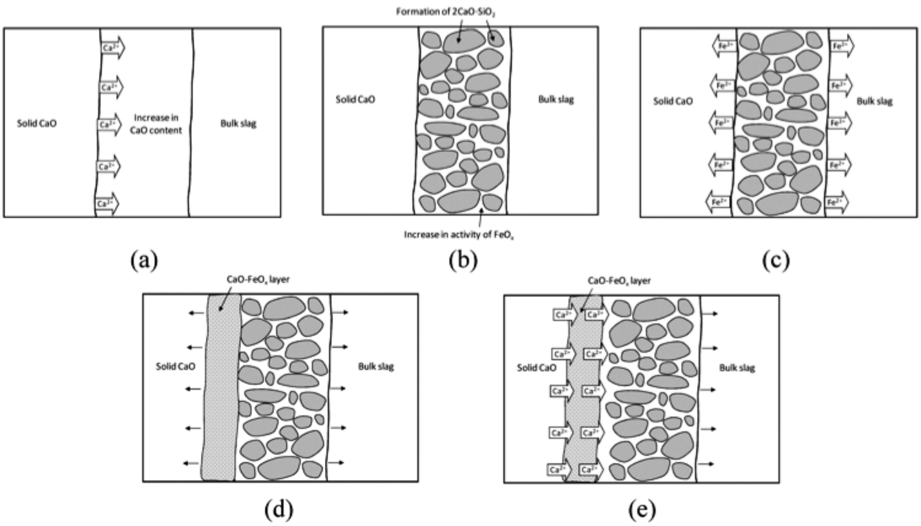

Figure 4: Schematics of reaction mechanisms

Figure 5 shows the relationship between P_2O_5 content in the $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase and the distance from CaO-slag interface to the $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase after dipping CaO in 25.0mass%FeO_x-35.6%CaO-29.4%SiO_2-10.0%P_2O_5 slag at 1673 K for 2, 5 and 10 s. P_2O_5 content increased from the CaO-slag boundary toward the bulk slag. After longer reaction time, P_2O_5 content in the $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase became higher. From this result, the formation of the $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase is considered to proceed through two steps; firstly, P2O5 in the slag is condensed as $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ solid solution precipitated from the molten slag. Afterward, P_2O_5 is absorbed as $3CaO{\cdot}P_2O_5$ in the existing $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase. The gradient of P_2O_5 content in the condensed phase is diminished after longer time reaction, indicating the formation of more homogeneous $2CaO{\cdot}SiO_2$-$3CaO{\cdot}P_2O_5$ phase.

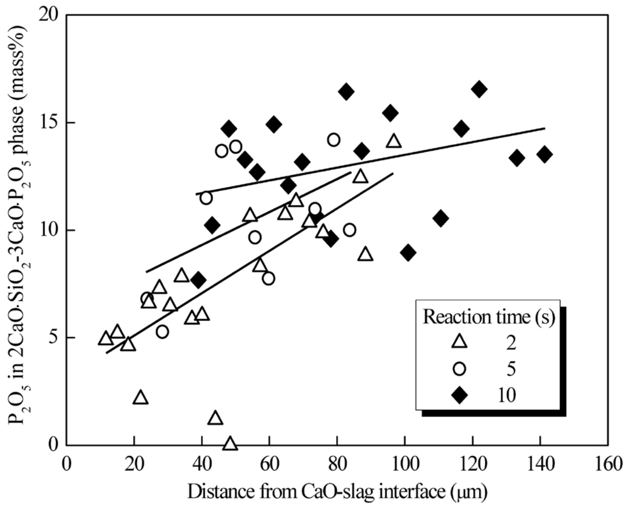

Figure 5: Relationship between P_2O_5 content in $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ phase and the distance from CaO-slag interface to $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ phase at 1673 K

Reaction between Solid $2CaO{\cdot}SiO_2$ and Slag [7, 8]

Figure 6 shows the SEM image around the interface between $2CaO{\cdot}SiO_2$ and 20.0 mass%FeO_x-38.4%CaO-31.6%SiO_2-10.0%P_2O_5 slag after the reaction for 60 s at 1673 K. The left side is the original solid $2CaO{\cdot}SiO_2$ and the right side is the bulk slag, though the interface is not seen clearly because the fabricated $2CaO{\cdot}SiO_2$ piece was porous and the slag penetrated easily inside the $2CaO{\cdot}SiO_2$ piece. Chemical compositions at positions represented in Figure 6 were analyzed by EDS and plotted on the pseudo ternary diagram for the FeO_x-CaO-(SiO_2+P_2O_5) as shown in Figure 7 to examine the phase distribution and relationship at the interface. In this figure, solid lines indicate the liquidus for the FeO_x-CaO-SiO_2 system equilibrated with solid iron at 1673 K [4]. All phases appeared along the joint line between $2CaO{\cdot}SiO_2$ and the original bulk slag shown as dashed line in Figure 7. Observed phases are categorized to solid $2CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$ saturated liquid slag, and the solid-liquid coexisting phase.

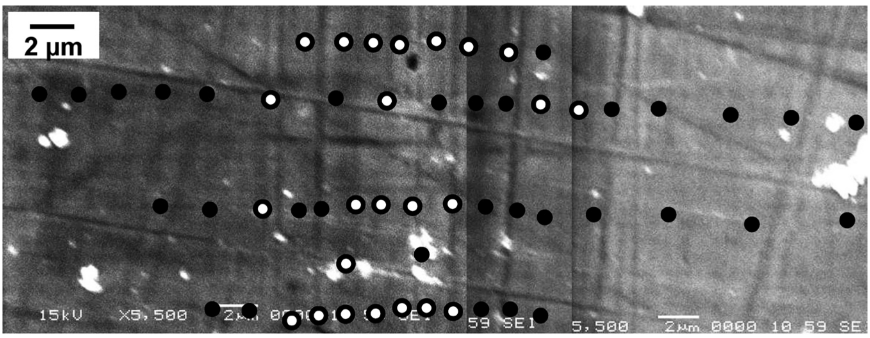

Figure 6: SEM image around the interface between solid $2CaO \cdot SiO_2$ and FeO_x-CaO-SiO_2-P_2O_5 slag at 1673 K

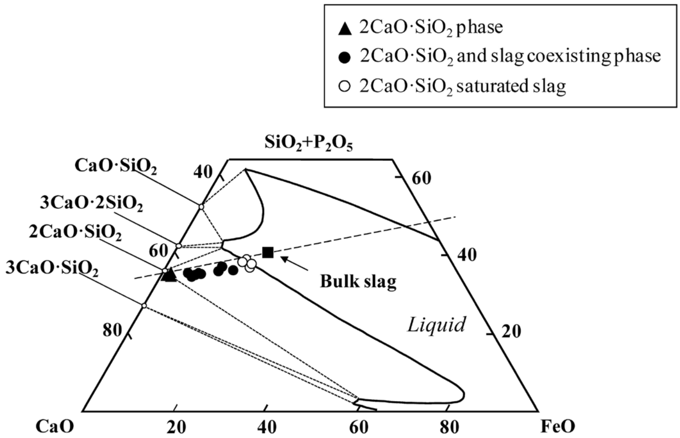

Figure 7: Phase distribution around the interface between solid $2CaO \cdot SiO_2$ and the bulk slag at 1673 K

The composition of each oxide was shown in Figure 8 as a function of position. The left side of the SEM image in Figure 6 corresponds to x=0 in Figure 8. CaO content decreased from $2CaO \cdot SiO_2$(left) toward bulk slag(right), while FeO content increased. SiO_2 content was almost constant. Positions in solid-liquid coexisting region in Figure 7 with high P_2O_5 content were represented as open symbols in Figure 8. P_2O_5 condensed phase was observed at the region where a gradient for CaO and FeO contents was seen. Since $2CaO \cdot SiO_2$ and $3CaO \cdot P_2O_5$ form solid solution in a wide composition range at 1673 K [3], it is considered the observed P_2O_5 condensed phase is a mixture of $2CaO \cdot SiO_2$- $3CaO \cdot P_2O_5$ and liquid FeO_x-CaO-SiO_2.

The profile of FeO content showed a clear trend, and thus the region in Figure 8 was separated by dashed line; low FeO content(left), FeO increasing region (center) and high constant FeO content (right). The line was also drawn at the end of the region where P_2O_5 condensed phase was observed. The low FeO content region on the left side represents solid $2CaO \cdot SiO_2$ region, and the FeO content increasing region corresponds to the slag penetration layer. Therefore, it is considered there is an interface between solid $2CaO \cdot SiO_2$ and liquid slag around the right side of the slag penetration layer. The P_2O_5 condensed phase, i.e., $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ phase, seems to be formed by the reaction between solid $2CaO \cdot SiO_2$ and P_2O_5 contained in liquid slag, because P_2O_5 condensed phase was only observed at the solid-liquid interface. Some P_2O_5 condensed positions were also observed inside the slag penetration layer, and P_2O_5 content in these positions were lower than that in P_2O_5 condensed phase at liquid slag (high FeO content) region, because P_2O_5 content in the slag penetrating inside solid $2CaO \cdot SiO_2$ was lower than that in the bulk slag.

The formation reaction of $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ phase is considered to be fast since P_2O_5 condensed phase was observed even after 1 s reaction. On the other hand, the amount of P_2O_5 condensed phase was not large compared to that in the case of CaO dipping experiments, neither was P_2O_5 content. Since the effect of reaction time on the amount and P_2O_5 content of P_2O_5 condensed phase was not clearly observed, the reaction mechanisms between solid $2CaO \cdot SiO_2$ and P_2O_5 contained in the liquid slag are not completely clarified yet. The further investigations should be conducted to clarify the reaction mechanisms for the formation of P_2O_5 condensed phase.

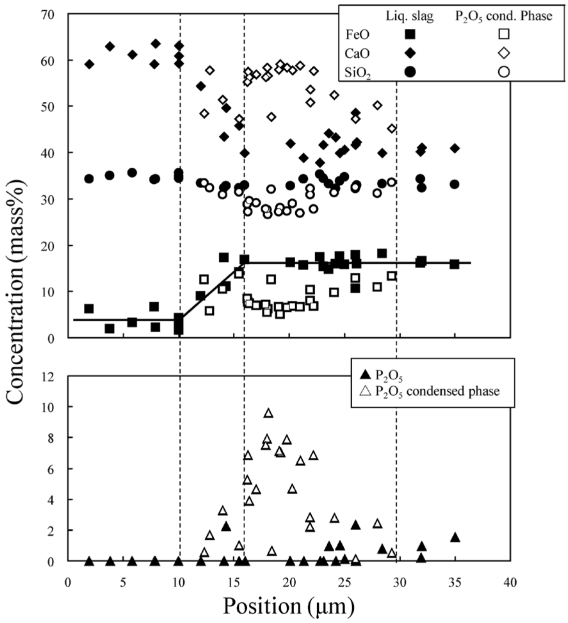

Figure 8: Concentration of oxides around the interface as a function of position after 60 s reaction at 1673 K

CONCLUSIONS

The FeO_x-CaO-SiO_2-P_2O_5 slag was reacted with solid CaO or 2CaO·SiO_2 at 1573 and 1673 K. In the case of the reaction between solid CaO and molten slag, the CaO-FeO_x and the 2CaO·SiO_2 and liquid slag coexisting phase were observed at the interface from solid CaO toward bulk slag side. P_2O_5 was condensed in 2CaO·SiO_2 as 2CaO·SiO_2-3CaO·P_2O_5 solid solution. P_2O_5 content in the condensed phase increased from CaO-FeO_x side to bulk slag side, and the gradient decreased with reaction time.

In the case of the reaction between solid 2CaO·SiO_2 and molten slag, P_2O_5 was condensed in some of 2CaO·SiO_2 phases located around the interface, though the liquid slag penetrated into the 2CaO·SiO_2 and the interface was not clearly observed. The interface was identified from the gradient of FeO content and P_2O_5 condensed phase was observed at slag penetration layer and near the solid-liquid interface. It is considered that P_2O_5 condensed phase was formed by the reaction between solid 2CaO·SiO_2 and P_2O_5 contained in liquid slag. The amount of P_2O_5 condensed phase was not large compared to that in the case of CaO dipping experiments, neither was P_2O_5 content.

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