ROLE OF SOLID CaO IN FeO-CaO-SiO$_2$-P$_2$O$_5$ MULTI PHASE FLUX AT HOT METAL DEPHOSPHORIZATION TEMPERATURE

Xiao Yang, Reita Saito, Tasuku Hamano, Hiroyuki Matsuura & Fumitaka Tsukihashi
The University of Tokyo, Japan

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$_2$O$_5$ 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$_2$O$_5$ 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·SiO$_2$ from dissolved CaO and SiO$_2$ originally contained in the slag, iii) formation of 2CaO·SiO$_2$·3CaO·P$_2$O$_5$ phase and iv) P$_2$O$_5$ 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$_2$O$_5$. However, the produced FeO$_x$(FeO+Fe$_2$O$_3$)-CaO-SiO$_2$-P$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ contained in the molten slag were investigated.

- Furthermore, solid 2CaO∙SiO$_2$ piece was reacted with FeO$_x$-CaO-SiO$_2$-P$_2$O$_5$ slag at 1673 K to clarify the effect of 2CaO∙SiO$_2$ formation on the condensation behavior of P$_2$O$_5$ from slag to form solid 2CaO∙SiO$_2$-3CaO∙P$_2$O$_5$ solid solution.

EXPERIMENTAL

The slag sample was produced by mixing wüstite synthesized by sintering an equimolar mixture of reagent Fe$_3$O$_4$ 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.
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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ particles coexisting with FeO$_x$-CaO-SiO$_2$ slag contained from 1 to 10 mass% of P$_2$O$_5$, and CaO-SiO$_2$-P$_2$O$_5$ composition was a binary mixture of 2CaO-SiO$_2$ and 3CaO-P$_2$O$_5$. 2CaO-SiO$_2$ and 3CaO-P$_2$O$_5$ make wide solid solution region [3]. Therefore, it is considered that P$_2$O$_5$ was taken in 2CaO-SiO$_2$ as 3CaO-P$_2$O$_5$.

The compositions obtained by EDS analysis are plotted on the FeO$_x$-CaO-(SiO$_2$+P$_2$O$_5$) 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.
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\textsubscript{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-SiO₂ saturated liquid phase and bulk slag were calculated by the regular solution model [6].

The activity of FeO in the 2CaO-SiO₂ saturated liquid phase is higher than that in CaO-FeOₓ phase and bulk slag. Therefore, Fe²⁺ ion diffuses from 2CaO-SiO₂ saturated liquid phase to both the CaO-FeOₓ phase and bulk slag. On the other hand, the activity of CaO in the CaO-FeOₓ phase is much higher than that in other phases. Therefore, Ca²⁺ ion diffuses from solid CaO toward bulk slag through the CaO-FeOₓ and 2CaO-SiO₂ saturated liquid phases.

From the above considerations, the reaction mechanisms between solid CaO and molten FeOₓ-CaO-SiO₂-P₂O₅ 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-SiO₂ from liquid slag, decrease of CaO and SiO₂ contents in the liquid, and relatively increase of FeOₓ content (Figure 4(b))
- Diffusion of Fe²⁺ ion from FeOₓ rich phase to both solid CaO and bulk slag (Figure 4(c))
- Formation of CaO-FeOₓ phase adjacent to solid CaO (Figure 4(d))
- Diffusion of Ca²⁺ to bulk slag through formed CaO-FeOₓ layer (Figure 4(e)).

Figure 5 shows the relationship between P₂O₅ content in the 2CaO-SiO₂-3CaO-P₂O₅ phase and the distance from CaO-slag interface to the 2CaO-SiO₂-3CaO-P₂O₅ phase after dipping CaO in 25.0mass%FeOₓ-35.6%CaO-29.4%SiO₂-10.0%P₂O₅ slag at 1673 K for 2, 5 and 10 s. P₂O₅ content increased from the CaO-slag boundary toward the bulk slag. After longer reaction time, P₂O₅ content in the 2CaO-SiO₂-3CaO-P₂O₅ phase became higher. From this result, the formation of the 2CaO-SiO₂-3CaO-P₂O₅ phase is considered to proceed through two steps; firstly, P₂O₅ in the slag is condensed as 2CaO-SiO₂-3CaO-P₂O₅ solid solution precipitated from the molten slag. Afterward, P₂O₅ is absorbed as 3CaO-P₂O₅ in the existing 2CaO-SiO₂-3CaO-P₂O₅ phase. The gradient of P₂O₅ content in the condensed phase is diminished after longer time reaction, indicating the formation of more homogeneous 2CaO-SiO₂-3CaO-P₂O₅ phase.
Figure 5: Relationship between P$_2$O$_5$ content in 2CaO·SiO$_2$-3CaO·P$_2$O$_5$ phase and the distance from CaO-slag interface to 2CaO·SiO$_2$-3CaO·P$_2$O$_5$ phase at 1673 K

Reaction between Solid 2CaO·SiO$_2$ and Slag [7, 8]

Figure 6 shows the SEM image around the interface between 2CaO·SiO$_2$ and 20.0 mass%FeO$_x$-38.4%CaO-31.6%SiO$_2$-10.0%P$_2$O$_5$ slag after the reaction for 60 s at 1673 K. The left side is the original solid 2CaO·SiO$_2$ and the right side is the bulk slag, though the interface is not seen clearly because the fabricated 2CaO·SiO$_2$ piece was porous and the slag penetrated easily inside the 2CaO·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$_2$O$_5$) 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·SiO$_2$ and the original bulk slag shown as dashed line in Figure 7. Observed phases are categorized to solid 2CaO·SiO$_2$, 2CaO·SiO$_2$ saturated liquid slag, and the solid-liquid coexisting phase.

Figure 6: SEM image around the interface between solid 2CaO·SiO$_2$ and FeO$_x$-CaO-SiO$_2$-P$_2$O$_5$ 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·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$_2$O$_5$ content were represented as open symbols in Figure 8. P$_2$O$_5$ condensed phase was observed at the region where a gradient for CaO and FeO contents was seen. Since 2CaO·SiO$_2$ and 3CaO·P$_2$O$_5$ form solid solution in a wide composition range at 1673 K [3], it is considered the observed P$_2$O$_5$ condensed phase is a mixture of 2CaO·SiO$_2$-3CaO·P$_2$O$_5$ 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$_2$O$_5$ condensed phase was observed. The low FeO content region on the left side represents solid 2CaO·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·SiO$_2$ and liquid slag around the right side of the slag penetration layer. The P$_2$O$_5$ condensed phase, i.e., 2CaO·SiO$_2$-3CaO·P$_2$O$_5$ phase, seems to be formed by the reaction between solid 2CaO·SiO$_2$ and P$_2$O$_5$ contained in liquid slag, because P$_2$O$_5$ condensed phase was only observed at the solid-liquid interface. Some P$_2$O$_5$ condensed positions were also observed inside the slag penetration layer, and P$_2$O$_5$ content in these positions were lower than that in P$_2$O$_5$ condensed phase at liquid slag (high FeO content) region, because P$_2$O$_5$ content in the slag penetrating inside solid 2CaO·SiO$_2$ was lower than that in the bulk slag.

The formation reaction of 2CaO·SiO$_2$·3CaO·P$_2$O$_5$ phase is considered to be fast since P$_2$O$_5$ condensed phase was observed even after 1 s reaction. On the other hand, the amount of P$_2$O$_5$ condensed phase was not large compared to that in the case of CaO dipping experiments, neither was P$_2$O$_5$ content. Since the effect of reaction time on the amount and P$_2$O$_5$ content of P$_2$O$_5$ condensed phase was not clearly observed, the reaction mechanisms between solid 2CaO·SiO$_2$ and P$_2$O$_5$ 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$_2$O$_5$ condensed phase.
CONCLUSIONS

The FeO$_x$-CaO-SiO$_2$-P$_2$O$_5$ 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$_2$O$_5$ was condensed in 2CaO·SiO$_2$ as 2CaO·SiO$_2$-3CaO·P$_2$O$_5$ solid solution. P$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ condensed phase was observed at slag penetration layer and near the solid-liquid interface. It is considered that P$_2$O$_5$ condensed phase was formed by the reaction between solid 2CaO·SiO$_2$ and P$_2$O$_5$ contained in liquid slag. The amount of P$_2$O$_5$ condensed phase was not large compared to that in the case of CaO dipping experiments, neither was P$_2$O$_5$ content.

REFERENCES


