Equilibrium of $CaO-SiO_2-FeO-P_2O_5$ multi phase flux at 1673K with low oxygen partial pressure for dephosphorization

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Abstract: Dephosphorization process by using multi phase flux could significantly decrease the consumption of CaO and prevent environmental harmful fluorite addition. However, the equilibrium phase relationship remains unclear, which is important for understanding the reaction mechanism of solid phase in the multi phase flux. Therefore, it is necessary to clarify the phase diagrams for better utilization of multi phase flux on dephosphorization process. In this study, the $CaO-SiO_2-FeO-P_2O_5$ slag system is chosen since it represents the main slag composition during dephosphorization reaction, and the phase relationship of this slag system has been measured by using chemical equilibration technique. The results show that the condensed solid solution is mainly composed of $2CaO·SiO_2$ and $3CaO·P_2O_5$, but sometimes contains certain amount of $3CaO·SiO_2$ or $CaO·SiO_2$ according to the CaO/SiO_2 ratio in molten slag. The liquidus equilibrated with P_2O_5-containing solid solution shrinks to the FeO apex with the oxygen partial pressure of 10^{-10} atm comparing with the well-known isothermal phase diagram for the $CaO-SiO_2-FeO$ system equilibrated with metallic iron, and it shifts further towards the FeO apex with higher oxygen partial pressure of 10^{-8} atm. On the other hand, a stable CaO-FeO phase appears despite of oxygen partial pressures, which has been observed previously when solid CaO reacted with molten slag in previous works. The phosphorus partition ratio between solid solution and liquid slag obtained in this research agrees well with previous works, which is that the phosphorus partition ratio increases linearly with T.Fe content but decreases with CaO content in liquid phase.

Key words: Steelmaking, Multi phase flux, Phase relationship, Equilibrium, Dephosphorization

1. Introduction

In steelmaking process, dephosphorization process is often operated at the slag composition area of high CaO/SiO_2 ratio. Consequently insoluble CaO, condensed $2CaO·SiO_2$ and $3CaO·SiO_2$ could coexist with molten slag by excessive CaO addition, which leads to low dephosphorization efficiency because of bad kinetic situation and causes some environmental issues such as large amount of slag generation, difficulty of slag recycling, and phosphorus recovery and so on. On the other side, due to the restriction of the utilization of harmful melting agent such as fluorite and the economic reason for using other melting agent, the utilization of such solid and liquid phase coexisting slag (multi phase flux) must be seriously reconsidered.

Fix *et al.* [1] found out the $2CaO·SiO_2-3CaO·P_2O_5$ exists over a wide composition and temperature range, so this solid solution forms easily during dephosphorization process. Ito *et al.* [2] figured out that the phosphorus partition ratio between solid solution and molten slag increases with T.Fe content in the molten slag, which means most phosphorus is fixed as $2CaO·SiO_2-3CaO·P_2O_5$ solid solution and then the molten slag with low phosphorus but high T.Fe content remains. Subsequently, using the solid phase in multi phase flux as phosphorus fixture rather than promoting the melting status is of great benefit because less CaO consumption becomes possible leading to less slag generation and fluorite is no longer needed.

Many researches have been done during the past few decades towards the dephosphorization process by using multi phase flux. Inoue and Suito [3-5] studied the transfer behavior and the partition of phosphorus between solid solution and molten slag. They explained the reaction mechanism of phosphorus in the $CaO-SiO_2-Fe_tO$ system containing mesoscopic scale dicalcium silicate particles. Kitamura *et al.* [6] clarified the mass transfer of phosphorus between $2CaO·SiO_2-3CaO·P_2O_5$ solid solution and $2CaO·SiO_2-3CaO·P_2O_5$ saturated $CaO-SiO_2-Fe_2O_3-P_2O_5$ slag at 1673K. At the same temperature Shimauchi *et al.* [7] studied the phosphorus partition for the $CaO-SiO_2-Fe_2O_3-P_2O_5$ (6-18mass%) systems sometimes containing MgO or MnO, and the effects of MgO, MnO, and Al_2O_3 on phosphorus partition in various slag systems with FeO or Fe_2O_3 as iron oxides were also discussed. [8]

As a series study, Hamano *et al.* [9] firstly clarified the dissolution and reaction mechanisms of solid CaO with molten slag, and based on that the reaction behavior of phosphorus in both homogeneous and heterogeneous slag systems was explained by Yang *et al.* [10-11]

However, the phase relationship between solid solution and molten slag could not be well explained because of lack of the related phase diagrams. Therefore, the liquidus of $CaO-SiO_2-FeO-P_2O_5$, which represents the main components of dephosphorization slag system, was measured experimentally at 1673K with oxygen partial pressures of 10^{-10} and 10^{-8} atm. The phase relationship between solid solution and liquid phase was discussed.

2. Experimental

The chemical equilibration technique was employed in this study, which had been well used for determining the phase equilibria. [12-16]

2.1 Sample preparation

The $CaO-SiO_2-FeO-P_2O_5$ slag was made by mixing reagent grade of SiO_2 and $Ca_3(PO_4)_2$, synthesized FeO and CaO. As considering the slag components in the steelmaking plant, P_2O_5 content was set to be 5mass% constantly during all the experiments. The above oxides were well mixed by an agate mortar and rotating blending machine for certain time. Then this mixture was dried to remove moisture. The compositions of original slag were chosen according to the $CaO-SiO_2-FeO_x$ ternary phase diagram equilibrated with metallic iron [17], and the special attention was paid to the slag with large CaO/SiO_2 ratio in this study.

2.2 Measurement

A platinum crucible (diameter:5mm; height: 5mm) loaded with 0.1 g of $CaO-SiO_2-FeO-P_2O_5$ oxide mixture was firstly hanged at the top area of a vertical recrystallized aluminum reaction tube as pre-heating and then quickly put into the hot zone at 1923K with argon atmosphere. For achieving liquid phase before equilibration, pre-melting temperature of 1923K was chosen. Slag was pre-melted for 3hours. After pre-melting, temperature of the furnace was slowly decreased to 1673 K by 10 K/min and during this period the atmosphere was switched from argon to CO/CO_2 gas. The volume ratios of CO to CO_2 gases for controlling the oxygen partial pressure of $9.24×10^{-11}$ atm and $1.06×10^{-8}$ atm were

5 and 0.5, respectively, according to equation (1).

$$\mathrm{CO(g)} + 1/2\mathrm{O_2(g)} = \mathrm{CO_2(g)} \quad (1)$$

$$\Delta G^{o} = -281000 + 85.23T \quad \text{J/mol}$$ [18]

Also based on preliminary experiments, the preservation time at 1673 K for achieving equilibrium was set to be 5 to 12 hours depending on the original slag compositions. After equilibration, the crucible was quickly taken out and immersed in liquid nitrogen for rapid quenching. Then the crucible containing slag was embedded in resin and polished for phase observation. By using SEM/EDS, the morphology of slag was observed and the composition of each phase was determined. Since the accuracy of EDS is limited, large scale of mapping analysis and repetition analyses were adopted. Also the continuous analysis was used for some phase with tiny surface area.

3. Results and discussion

3.1 Liquidus of CaO-SiO_2-FeO-P_2O_5 system equilibrated at 1673K with oxygen partial pressures of 10^{-10}atm and 10^{-8}atm

The equilibrium results of each phase of the CaO-SiO_2-FeO-P_2O_5 system equilibrated at 1673K with oxygen partial pressures of 10^{-10} and 10^{-8} atm were shown in Figure 1 by projecting on the CaO-SiO_2-FeO ternary section, comparing with the liquidus of the CaO-SiO_2-FeO_x ternary system equilibrated with metallic iron at 1673 K. [17]

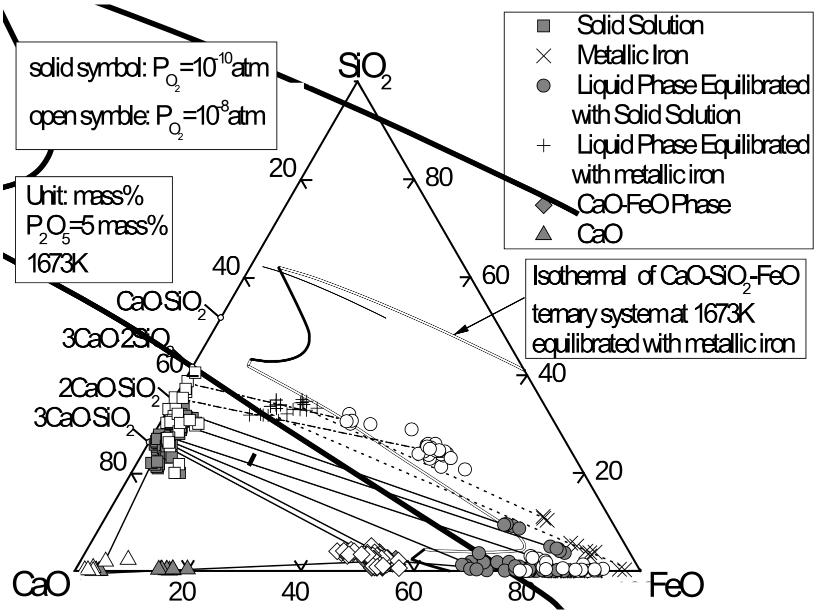


Fig. 1 Projections of observed phases equilibrated at 1673K with oxygen partial pressures of 10^{-10} and 10^{-8}atm on the CaO-SiO_2-FeO ternary system

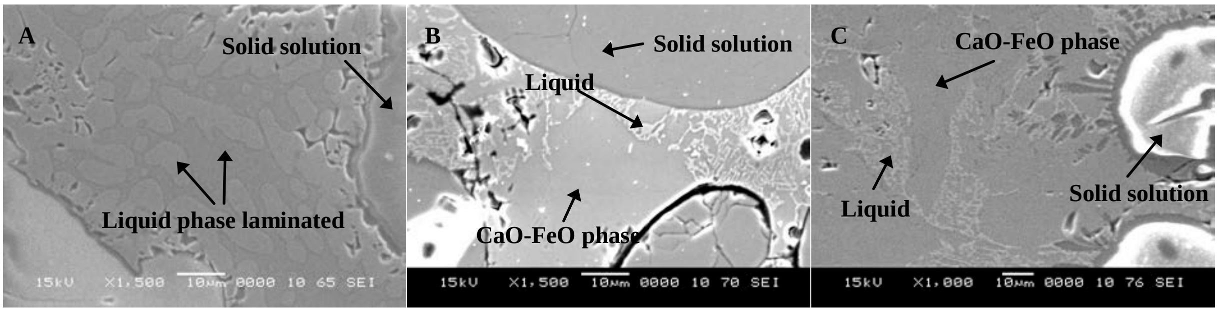
Liquid phase observed with the oxygen partial pressures of both 10^{-10} and 10^{-8} atm, shown as the circle symbols in Figure 1, moves towards the FeO apex by comparing with the liquidus of CaO-SiO_2-FeO_x ternary system equilibrated with metallic iron at 1673 K. This is because of the condensation of solid solution, which consumes much CaO and SiO_2 from the molten slag and consequently the molten slag with high FeO content remains. In Figure 1, the open circle representing the liquid phase observed with the oxygen partial pressure of 10^{-8} atm locates closer to the FeO apex comparing to the solid circle observed with oxygen partial pressure of 10^{-10}atm, which suggests that the liquid area is enlarged by lowering the oxygen partial pressure. This enlargement of liquid area at the iron oxides region with lower oxygen partial pressure agrees with the work by Kimura *et al.* [12] who measured the liquidus of the CaO-SiO_2-FeO_x ternary system at 1573K with various oxygen partial pressures.

Besides, another liquid phase (cross symbol) is found equilibrated with metallic iron only with the oxygen partial pressure of 10^{-10}atm, which has constant FeO activity according to the equilibrium between FeO and metallic iron. The appearance of FeO reduction blocks the liquidus extending to larger SiO_2 composition region but pins it at low SiO_2 and large FeO composition region, as noticed in Figure 1 that no solid circles appear at larger SiO_2 composition area.

There are three types of equilibrium status with the occurrence of liquid phase. One is that liquid phase and solid solution coexist, but sometimes the liquid phase is laminated by two phases with about 15mass% difference of FeO content at oxygen partial pressure of 10^{-10} atm as shown in Figure 2A. The reason of this lamination remains unclear.

Another is that liquid phase, solid solution and CaO-FeO phase coexist with both oxygen partial pressures used in current experiment. The mentioned CaO-FeO phase is assumed to be an individual stable phase based on the morphology of phases as shown in Figures 2B and 2C. The existence and the component of CaO-FeO phase shown as the diamond symbol in Figure 1 are independent of oxygen partial pressures. Some researchers reported the formation of this CaO-SiO_2 phase [4, 19, 20] as a solid solution when solid CaO reacted with P_2O_5-containing molten slag. However, because SiO_2 and P_2O_5 contents inside this phase could not be ignored and also proper phase diagram is unavailable, the existence form of the CaO-FeO phase remains uncertain.

The other type of equilibrium with the existence of liquid phase is that liquid phase, solid solution, CaO-FeO phase and insoluble CaO coexist. Considering together with the previous two equilibrium status, the appearance of CaO-FeO phase depends on the CaO/SiO_2 ratio in the slag system.



A: lamination of liquid ($P_{O_2} = 10^{-10}$atm) B: CaO-FeO phase occurrence ($P_{O_2} = 10^{-10}$atm) C: $P_{O_2} = 10^{-8}$atm

Fig.2 Typical morphology of each phase

The solid solution marked as square symbols in Figure 1 locates close to the CaO-SiO_2 tie line. However, 1 to 6mass% of FeO penetration in it indicates that the solid solution has low solubility of FeO. The discussion regarding the solid solution will be discussed in the latter section.

3.2 Solid solution of CaO-SiO_2-FeO-P_2O_5 system equilibrated at 1673K with oxygen partial pressures of 10^{-10} and 10^{-8} atm

In Figure 3, solid solutions are plotted on the CaO-SiO_2-P_2O_5 section by projecting from the FeO apex. All points locate around the tie line between $3CaO \cdot P_2O_5$ and $2CaO \cdot SiO_2$ but sifts a little towards the CaO apex, thus $3CaO \cdot P_2O_5$-$2CaO \cdot SiO_2$ should be the main component of solid solution. It can be seen that the effect of oxygen partial pressure on the composition of solid solution is small since all points locate closely in the $3CaO \cdot P_2O_5$-$2CaO \cdot SiO_2$ solid solution stable region. Because the existence area of $3CaO \cdot SiO_2$ is quite narrow and no point locates inside that area, it is also difficult to judge the existence of $3CaO \cdot SiO_2$ solid solution at equilibrium.

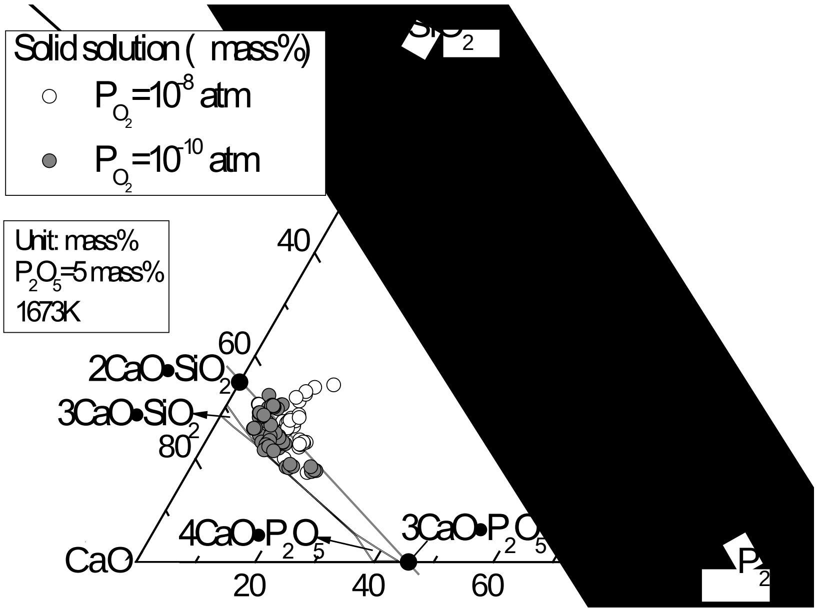


Fig. 3 Projection of solid solution observed with various oxygen partial pressures on the CaO-SiO_2-P_2O_5 ternary system

By converting the P_2O_5 content of solid solution to $3CaO \cdot P_2O_5$, which should be the only possible existing form for phosphate under current experimental conditions according to Figure 3, the relationship between $3CaO \cdot P_2O_5$ content and the remained CaO/SiO_2 mole ratio in solid solution is shown in Figure 4. The CaO/SiO_2 mole ratios after removal of $3CaO \cdot P_2O_5$ distribute in a range from 1.5-2.75 rather than constant value of 2, which explains the deviation from the tie line between $3CaO \cdot P_2O_5$ and $2CaO \cdot SiO_2$ shown in Figure 3. One of the explanations for this phenomenon is that the solid solution does not only contain $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ but also $CaO \cdot SiO_2$ or $3CaO \cdot SiO_2$.

On the other hand, the condensation amount of $3CaO \cdot P_2O_5$ increases with increasing CaO/SiO_2 mole ratio in solid solution, the trend is clearer for the results observed with oxygen partial pressure of 10^{-10} atm. This indicates the condensation of $3CaO \cdot P_2O_5$ is promoted by increasing CaO/SiO_2 ratio in slag system, which determines the equilibrium status as discussed before.

Besides, it can be seen that the CaO/SiO_2 ratios of those solid solutions observed with oxygen partial pressure of 10^{-8} atm are always lower or close to 2 while in the case of 10^{-10} atm mainly higher than 2, as shown in Figure 4. The indirect effect of oxygen partial pressure on the composition of solid solution is confirmed.

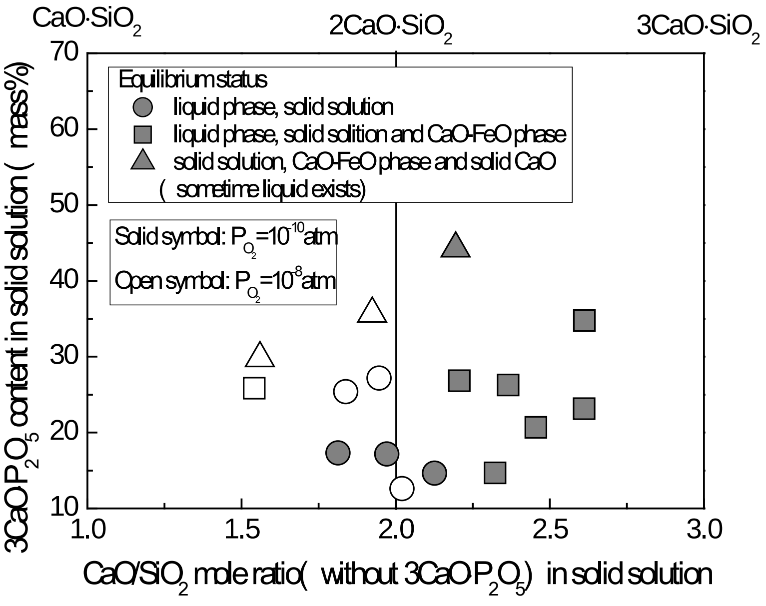


Fig. 4 Relationship between $3CaO·P_2O_5$ content and CaO/SiO_2 mole ratio after removal of $3CaO·P_2O_5$ in solid solution

3.3 Phosphorus partition ratio between solid solution and liquid phase

The relationship between the phosphorus partition ratio and the T.Fe content in liquid phase is shown in Figure 5 comparing with previous research by Ito *et al.* [2] The phosphorus partition ratio obtained at present experimental conditions agrees well with previous work, since the linear relationship between phosphorus partition ratio and T.Fe content in liquid remains steady in spite of valences of iron ion which means various oxygen partial pressures at equilibrium. The partition ratio reaches the highest value after the CaO-FeO phase forms, because the formation of CaO-FeO phase drives the liquidus moving to larger T.Fe content region as shown in Figure 1.

The relationship between the phosphorus partition ratio and the equilibrium status can be explained as follows: due to the increasing of CaO/SiO_2 ratio in liquid slag, firstly the CaO-FeO phase forms leading to high T.Fe content remaining in liquid phase. Subsequently, the phosphorus partition as well as the $3CaO·P_2O_5$ condensation is promoted. Then insoluble CaO coexists with CaO-FeO phase, and T.Fe content in liquid phase could not be increased further since the formation of CaO-FeO phase reaches the limitation. Therefore the phosphorus partition could neither be further promoted.

In addition, the straight line shown in Figure 5 ends at T.Fe content of about 60mass%, and the results in this study fit the extension up to T.Fe content of 70mass% in liquid phase.

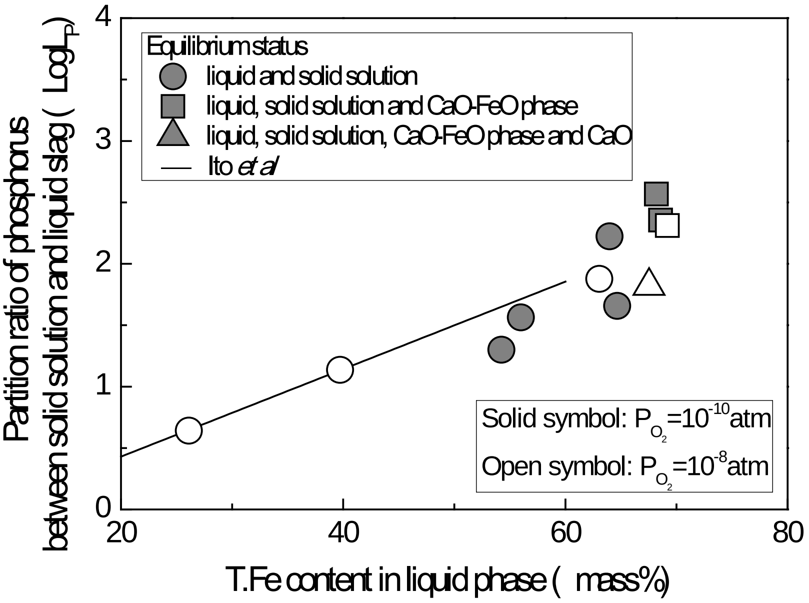


Fig.5 Relationship between phosphorus partition ratio and T.Fe content in liquid phase

4. Conclusions

By using the chemical equilibration technique, liqudus of the $CaO-SiO_2-FeO-5mass\%P_2O_5$ system was measured at 1673K with oxygen partial pressures of 10^{-10} and 10^{-8} atm. The conclusions are summarized as followed:

1) Liquid regions observed with oxygen partial pressures of both 10^{-10} and 10^{-8} atm shrink towards the FeO apex comparing with the liquidus of the $CaO-SiO_2-FeO_x$ ternary system at 1673K equilibrated with metallic iron. The liquid area is enlarged in the area around FeO apex with oxygen partial pressure of 10^{-10}atm rather than that with oxygen partial pressure of 10^{-8}atm.

2) The main component of solid solution at equilibrium is $3CaO{\cdot}P_2O_5-2CaO{\cdot}SiO_2$, but sometime the solid solution contains $CaO{\cdot}SiO_2$ or $3CaO{\cdot}SiO_2$. Oxygen partial pressure does not affect the composition of the solid solution.

3) The phosphorus partition ratio increases with increasing T.Fe content in liquid phase, and the reason of this relationship as well as the condensation of $3CaO{\cdot}P_2O_5$ has been discussed.

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