

論文の内容の要旨

論文題目: **Phase Relationship of Multi Phase Flux for Dephosphorization of Steelmaking Process**

(鉄鋼精錬の脱りんプロセスにおけるマルチフ
ェーズフラックスの相関係)

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Phosphorus is an associated element with iron ore, which always dissolves in molten iron after iron making. The existence of phosphorus in steel significantly decreases the toughness of the final product. Consequently, phosphorus has been normally considered as an impurity and its content in steel product must be controlled below certain level.

Following this requirement, dephosphorization process for ferrous metallurgy has been developed. Thermodynamically, proper low temperature, high basicity and high oxygen partial pressure benefit the removal of phosphorus from hot metal. Therefore, lime-silicate-wustite slag has been widely used for achieving high phosphate capacity due to the consideration of producing cost.

After the addition of lime into the molten slag, it is expected that the slag composition is controlled within the dicalcium silicate primary region. However, due to the slow dissolution speed of lime at low refining temperature, proportion of solid phase increases and the kinetic condition for dephosphorization becomes worse, which leads to low dephosphorization efficiency. Normally, fluorite acts as an effective melting agent to accelerating the dissolution of lime, but the utilization of it has been

restricted because of its harmfulness on the environment. Although larger FeO content provide better melting conditions, the FeO content in the slag cannot be increased too much, for the sake of preventing slag foaming and protecting the refractories. As a result, in order to achieve high basicity of the slag, the remained option is to add excessive amount of lime, which brings serious issues such as huge slag amount and low utilization efficiency of lime.

With the principle of effective utilization of the solid phase, an innovative development of refining process by using multiphase flux for dephosphorization has been investigated.

The research on the reaction behavior and mechanism of CaO with molten slag, mass transfer of phosphorus from liquid phase to solid solution, reaction behavior of phosphorus, phosphorus partition ratio between solid solution and liquid slag for various slag systems and the series of kinetic studies have been proceeded in last few decades.

However, on pursuing the reaction mechanism of phosphorus between solid solution and liquid slag, proper phase diagrams are still unavailable. Therefore, current research is aimed to focus on the equilibrium phase relationship for the multiphase flux system.

By using chemical equilibration technique the equilibrium phase relationship for the CaO-SiO₂-FeO-P₂O₅(-Al₂O₃) system with oxygen partial pressure of 10⁻¹⁰ atm or 10⁻⁸ atm at 1673K and 1623K have been investigated.

In the case of the CaO-SiO₂-FeO-P₂O₅ quaternary system with oxygen partial pressure of 10⁻¹⁰ atm at 1673K, liquidus has been proposed for the projection on the CaO-SiO₂-FeO ternary section after the discussion of phase relationship. Comparing with the isothermal for the CaO-SiO₂-FeO_x ternary system equilibrated with iron at the same temperature, the liquid phase area remains similar at moderate SiO₂ region, and shrinks towards the FeO apex with increasing T.Fe content. As equilibrated with liquid phase, the composition of solid solution locates along the tie line between 2CaO·SiO₂ and 3CaO·P₂O₅.

For the same slag system equilibrated with oxygen partial pressure of 10⁻⁸ atm at 1673K and 1623K, the phase relationship has also been clarified. Since higher oxygen partial pressure has been used, the liquidus at 1673K shifts against the CaO apex due to the increase of Fe³⁺/Fe²⁺ ratio. Also, the liquid phase shrinks with decreasing temperature. By comparing with the liquidus for CaO-SiO₂-FeO ternary system with oxygen partial pressure of 10⁻⁸ atm at 1573K, the liquid phase area with same temperature at 1623K even shrinks. This is because the condensation of 2CaO·SiO₂-3CaO·P₂O₅ solid solution consumes more CaO than 2CaO·SiO₂ or 2CaO·SiO₂.

Since Al_2O_3 normally exists in the slag system, the phase relationship for the $\text{CaO-SiO}_2\text{-FeO-P}_2\text{O}_5\text{-Al}_2\text{O}_3$ system has been observed with oxygen partial pressure of 10^{-10} atm at 1673K. It has been found that the liquidus shifts towards the CaO apex which means the liquid area enlarges, comparing with both the liquidus for the $\text{CaO-SiO}_2\text{-FeO}_x$ ternary system equilibrated with metallic iron and the liquidus for the $\text{CaO-SiO}_2\text{-FeO}$ ternary system with oxygen partial pressure of 10^{-10} atm at 1573K. The effect of Al_2O_3 addition on the enlargement of the liquid area is significant.

Besides, the solid solution equilibrated with the liquid phase in all slag systems investigated by current research, which has been confirmed to be $2\text{CaO}\cdot\text{SiO}_2\text{-3CaO}\cdot\text{P}_2\text{O}_5$ with different ratio between both, is homogeneous and other possible solid solutions such as $3\text{CaO}\cdot\text{SiO}_2$ have not been observed.

By comparison of the phase relationship for various slag systems in current study, comprehensive discussions on the liquid phase, solid solution and the combination of both have been conducted. The the conclusions for the liquid phase have been drawn as above. While for the solid solution, it has been found that the effect of oxygen partial pressure, temperature and the Al_2O_3 addition on the solid solution is negligible. After discussion on each of the liquid phase and solid solution, the combination between both by using phosphorus partition has also been studied. It has been found that the phosphorus partition ratio between solid solution and liquid phase increases linearly with increasing T.Fe content in liquid phase and decrease with increasing CaO content in liquid phase.

For further investigating the effect of slag composition on the phosphorus partition ratio, regular solution model has been adopted for calculating the activity coefficients of components in liquid phase. The calculated activity coefficients and activities of P_2O_5 are very low which indicates a high phosphate capacity for multiphase flux when reacts with carbon saturated iron. Then the relationship between the calculated thermodynamic properties and the slag compositions such as T.Fe and CaO content in liquid phase has been discussed.

In order to evaluate the utilization of multiphase flux for the dephosphorization process, simulation for the application of current observed phase relationships on the practical dephosphorization process with the perspective of mass balance has been conducted. The total slag amount and the CaO consumption of dephosphorization process by using multiphase flux have been obtained. Both values are much lower comparing with the condition of practical refining, which indicates the advantage of using multiphase flux for dephosphorization.