論文内容の要旨

Reaction Behavior of Phosphorus by Using Multi Phase Flux in Hot Metal Dephosphorization Process

(鉄鋼精錬におけるマルチフェーズフラックス中りんの反応機構)

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The hot metal dephosphorization has been uniquely developed to meet the increasing demand for low phosphorus steel production in Japan. The dephosphorizing reagent is usually composed of lime (CaO), iron ore (FeO_x) and some other additives. The generated $CaO-SiO_2-FeO_x-P_2O_5$ 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, the using of CaF_2 is 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. The reduction of CaO consumption and slag emission is the existing problem that the steel makers confront. Since the dephosphorizing slag contains both liquid and solid phases, it is considered that the problem can be solved by improving the transfer of phosphorus from liquid phase into solid phase in the slag. Therefore, the idea of developing an innovative refining process by using multi phase flux is proposed. In order to develop the new

technology, the fundamental information including thermodynamic data, mass transfer, microscopic reaction mechanism, physical properties of the multi phase flux etc are indispensable. As a part of the whole research project, the present thesis is devoted to clarify the reaction behavior of phosphorus in the multi phase flux and the influence factors.

The experimental investigation is composed of three parts: reaction between solid $2CaO\cdot SiO_2$ and homogeneous CaO-SiO_2-FeO_x-P_2O_5 slag at 1573 and 1673 K, reaction between $2CaO\cdot SiO_2$ and multi phase CaO-SiO_2-FeO_x-P_2O_5 slag at 1573 K and dissolution behavior of silicocarnotite ($5CaO\cdot SiO_2\cdot P_2O_5$) into the homogeneous CaO-SiO_2-FeO_x slag at 1573 and 1673 K.

Many researchers suggested that the precipitation of $2CaO\cdot SiO_2$ phase is the necessary condition for the formation of solid $2CaO\cdot SiO_2$-$3CaO\cdot P_2O_5$ phases in the multi phase flux. Following this idea, solid $2CaO\cdot SiO_2$ is firstly reacted with homogeneous CaO-SiO_2-FeO_x-P_2O_5 slag to examine the formation of solid P_2O_5 rich phases. The synthesized solid $2CaO\cdot SiO_2$ disc is dipped into liquid slag with various composition for different reaction time at 1573 and 1673 K. After the reaction, the interface between $2CaO\cdot SiO_2$ and slag is observed and analyzed by SEM/EDS. According to the analysis of the interfaces after reaction for different time, the reaction mechanism is clarified. It is understood that the P_2O_5 condensed phases are formed at the $2CaO\cdot SiO_2$/slag interface as fast as less than 1 s. However, the solid P_2O_5 rich particle is not big enough to be detected separately by the present analysis method. Thus the P_2O_5 condensed phase is identified as the mixture of $2CaO\cdot SiO_2$-$3CaO\cdot P_2O_5$ solid solution or compound and the surrounding liquid slag. The occurrence of dissolution of the solid P_2O_5 rich phase soon after its formation is observed, indicating that the transfer of phosphorus in the multi phase flux from liquid phase to solid phase is reversible. Reaction temperature and CaO/SiO_2 ratio of the initial slag influence the stability of solid P_2O_5 rich phases. Higher temperature induces the dissolution of P_2O_5 condensed phase while larger CaO/SiO_2 ratio of the bulk slag has the opposite effect.

Upon the finding that the solid P_2O_5 condensed phase re-dissolves into the liquid slag, solid $2CaO \cdot SiO_2$ is also reacted with the multi phase $CaO-SiO_2-FeO_x-P_2O_5$ slag. The liquid phase of the multi phase slag is saturated with solid $5CaO \cdot SiO_2 \cdot P_2O_5$ at 1573 K before the reaction. The P_2O_5 condensed phases with FeO content less than 16.0 mass%, CaO/SiO_2 ratio larger than 1.5 and P_2O_5 content over 1.0 mass% are observed at the interface. It is considered that the solid $2CaO \cdot SiO_2$ reacts with the liquid phase in the multi phase slag to form the P_2O_5 condensed phase. Compared with the results of reaction with homogeneous slag, the P_2O_5 condensed phases can be observed in much wider region. Such difference implies that the re-dissolution of the P_2O_5 condensed phases is restrained in the case that the bulk liquid phase is saturated with solid P_2O_5 rich phase.

Since it is observed that the transfer of phosphorus in the multi phase flux from liquid phase to solid phase is reversible, the dissolution behavior of the $2CaO \cdot SiO_2-3CaO \cdot P_2O_5$ solid solution or compound in liquid slag is studied. The synthesized $5CaO \cdot SiO_2 \cdot P_2O_5$ being the representative of solid P_2O_5 rich phase is dipped into the homogeneous $CaO-SiO_2-FeO_x$ slag at 1573 and 1673 K. Since the initial slag is free of P_2O_5, the increase of P_2O_5 content in the slag is the indication of the dissolution behavior of solid $5CaO \cdot SiO_2 \cdot P_2O_5$. The result shows that the dissolution of solid phosphate compound can be divided into the following stages: interaction, disintegration, reaction and diffusion. The diffusivity of P_2O_5 in the liquid slag is calculated according to the concentration profile of P_2O_5 across the interface. In accord with the results in the abovementioned study, higher temperature is favored for the dissolution in some cases, while larger CaO/SiO_2 ratio of the bulk slag has the opposite effect.

A synthetic consideration is made on the reaction behavior of P_2O_5 by comparing the present findings of phosphorus behavior at $2CaO \cdot SiO_2$/slag interface with the previously reported results of phosphorus behavior at CaO/slag interface. It is clarified that the $2CaO \cdot SiO_2-3CaO \cdot P_2O_5$ solid solution or compound formed at CaO/slag interface is not the product of the reaction between firstly formed $2CaO \cdot SiO_2$ phase, and CaO plus P_2O_5 in the slag as proposed by the previous researchers, but directly formed by the reaction between solid CaO, and SiO_2 plus P_2O_5 in the slag. In the phase diagram of the CaO-SiO_2-FeO_x-P_2O_5 quaternary system, the existence of primary phase regions of solid 5CaO·SiO_2·P_2O_5 and 2CaO·SiO_2-3CaO·P_2O_5 solid solution is assured according to the formation of 2CaO·SiO_2-3CaO·P_2O_5 phases both at CaO/slag and 2CaO·SiO_2/slag interfaces. The reaction behavior of P_2O_5 in the CaO-SiO_2-FeO_x-P_2O_5 multi phase flux can be well explained by considering the phase relationship in the CaO-SiO_2-FeO_x-P_2O_5 quaternary system.

According to the experimental findings and the synthetic consideration of the reaction mechanism, an innovative dephosphorization process is proposed to improve the refining efficiency while ease the environmental burden. In the new process, two types of lime with different function are added by different patterns. Lime powder with small particle size is mainly served as the reagent for slag formation and dephosphorization, while porous lime lump with large particle size is used for fixing the phosphorus from the liquid phase. The purpose of reducing the lime consumption and slag emission can be achieved. The innovative process also shows better recyclability than the present existing technology.

In brief, the reaction behavior of P_2O_5 in the multi phase flux is clarified in the present thesis. The mechanism, procedure and influence factors for the phosphorus transfer from liquid phase into solid phase are understood. This study has provided reliable fundamental information to develop the innovative refining technology in steel production.