

In Chapter 2, the experimental principle, the experimental procedure and the analytical method were introduced in detail. The chemical equilibration method was applied. The oxygen partial pressure was controlled by the mixture of CO and CO₂ gases. The electrolytic iron was used, in which concentration of P was less than 0.0003 mass%. The tablet was made by sintering the mixture with various ratios of reagent grade MgO, SiO₂, CaHPO₄·2H₂O and CaO obtained by the calcination of reagent grade CaCO₃. The mixture was held in air at 1873 K in a Pt crucible for 24 hours, quenched by Ar stream and then ground into fine powder. These steps were repeated twice and powder was pressed to form the tablet. The formation of target phases was confirmed by XRD. About 10 g electrolytic iron was equilibrated with the tablet in an MgO crucible at 1823 or 1873 K in an alumina tube (outer diameter: 60 mm, inner diameter: 50 mm, length: 1000 mm). The equilibrium duration was 24 hours which was confirmed by preliminary experiments. The oxygen partial pressure was 5.22×10^{-12} atm at 1823 K or 1.41×10^{-11} atm or 4.25×10^{-10} atm at 1873 K. After the equilibrium was established, the sample was quenched by Ar stream. Chemical composition of the tablet after reaction was analyzed by chemical analysis. The formation of phases after reaction was also confirmed by XRD.

In Chapter 3, the initial compositions of tablets were the 2CaO·SiO₂-3CaO·P₂O₅ solid solution. The tablet was contaminated more or less with MgO crucible particles and metallic iron particles, when the tablet was separated from the surface of solidified iron in the MgO crucible after equilibrium. For most samples, the contents of FeO and MgO were smaller than 1 mass%. The CaO, SiO₂ and P₂O₅ phases after reaction were undetected. At a certain temperature and oxygen partial pressure, the activity coefficient of FeO was almost constant. The equilibrium concentration of P in Fe increased with the increase of the 3CaO·P₂O₅ content in the solid solution. For a constant composition of the solid solution, the equilibrium concentration of P in molten iron with the oxygen partial pressure of 1.41×10^{-11} atm at 1873 K was larger than that with the oxygen partial pressure of 5.22×10^{-12} atm at 1823 K. As the oxygen partial pressure changed from 1.41×10^{-11} atm to 4.25×10^{-10} atm at 1873 K, the equilibrium concentration of P in Fe decreased. The phosphorus partition ratio between tablet and molten iron (mass%P)/[mass%P] decreased with the increase of the 3CaO·P₂O₅ content in the solid solution at both temperatures. When the oxygen partial pressure changed from 1.41×10^{-11} atm to 4.25×10^{-10} atm at 1873 K, the phosphorus partition ratio increased. The activity and activity coefficient of P₂O₅ increased with the increase of the 3CaO·P₂O₅ content in the solid solution at 1823 and 1873 K. The activity and activity coefficient of P₂O₅ at 1873 K were larger than those at 1823 K.

Since the excess lime is added into slag for better efficiency in practical dephosphorization process, it is necessary to study the thermodynamic properties of the 2CaO·SiO₂-3CaO·P₂O₅ solid solution saturated with CaO. In Chapter 4, the initial compositions of tablets were the 2CaO·SiO₂-3CaO·P₂O₅ solid solution containing 8 and 24 mass% CaO. The contents of FeO and MgO were smaller than 1 mass% and the activity coefficient of FeO was almost constant with the

change of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. The concentration of P in molten iron increased and the phosphorus partition ratio decreased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. The activity and activity coefficient of P_2O_5 increased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. For a constant composition of solid solution, the activity and activity coefficient of P_2O_5 were independent of the temperature. For the compositions in which the CaO phase was detected, the activity and activity coefficient of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ were calculated, which increased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. For a constant composition of the solid solution, the activity and activity coefficient of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ did not change with the temperature. The activity of $2\text{CaO}\cdot\text{SiO}_2$ in the solid solution was calculated from the activity of $3\text{CaO}\cdot\text{P}_2\text{O}_5$ by using the Gibbs-Duhem equation. The activity of $2\text{CaO}\cdot\text{SiO}_2$ in the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution decreased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution and the temperature dependency of the activity of $2\text{CaO}\cdot\text{SiO}_2$ was not clear within the experimental error range.

Since there is more or less MgO in metallurgical slag, it is necessary to study the thermodynamic properties of $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution containing a certain amount of MgO. In Chapter 5, the initial compositions of tablets were the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution containing 8 and 24 mass% MgO. For each sample, the MgO phase was detected after reaction. The content of FeO in the tablet after reaction was smaller than 1 mass% for most samples and the MgO content in the tablet after reaction was almost the same as the initial content. The activity coefficient of FeO was almost the same as that containing CaO. The concentration of P in molten iron increased and the phosphorus partition ratio decreased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. The activity and activity coefficient of P_2O_5 increased with the increase of the $3\text{CaO}\cdot\text{P}_2\text{O}_5$ content in the solid solution. For a constant composition of the solid solution, the activity and activity coefficient of P_2O_5 were independent of the temperature. The activity of P_2O_5 in the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution containing 8 and 24 mass% MgO was larger than that in the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution containing 8 and 24 mass% CaO.

In Chapter 6, the thermodynamic properties of calcium phosphate-based solid solution determined in the chapters 3, 4 and 5 were summarized. The effects of compositions on the thermodynamics of calcium phosphate-based solid solution were discussed. The extra CaO and MgO could decrease the activity of P_2O_5 in the calcium phosphate-based solid solution. The activity of P_2O_5 in the mixture of the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and MgO was larger than that in the mixture of the $2\text{CaO}\cdot\text{SiO}_2$ - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution and CaO. Moreover the innovative dephosphorization process was proposed based on the current and previous researches. The liquid slag is continuously used and only the solid phase is replaced in the process of dephosphorization at BOF. The solid phase from BOF is used for dephosphorization at the process of pretreatment, and finally the solid phase is utilized as the phosphate fertilizer.

In the end, the conclusions were presented as Chapter 7 by summarizing the previous chapters.