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Minimization of steelmaking slag consumption by simultaneous desulfurization and dephosphorization

（同時脱硫·脱りんによる製鋼スラグ使用量最小化に関する研究）

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Thesis outline

Steelmaking slag is generated in the steelmaking processes during the separation of the molten steel from impurities. One of the most important roles which the slag plays in the steelmaking processes is to remove the impurity elements mainly including phosphorus and sulfur, from steel. In the traditional desulfurization and dephosphorization processes, CaO is widely utilized because it is cheap and has high phosphorous and sulfur absorbing ability; CaF_2 is added to the CaO based slags to decrease the melting point and increase the fluidity of slag, and then maximize the reaction efficiency of CaO.

In recent years, a growing attention has been paid to the waste emission and consumption of natural resources for desulfurization and dephosphorization of molten steel under the restriction of CaF_2 utilization due to the environmental concern. Regarding the problem, the ideas of replacing CaF_2 by $CaCl_2$ to increase the reaction efficiency of CaO and utilization of high-MnO slags generated as by-product in the molten steel for desulfurization and dephosphorization have been proposed. It is known that simultaneous desulfurization and dephosphorization may be carried out within a range of oxygen potential, which can simplify the steelmaking processes and significantly decrease the consumption of slag. Accordingly, the possibility of simultaneous desulfurization and dephosphorization in hot metal pretreatment by using CaO-$CaCl_2$ based slags and in secondary refining by using MnO-SiO_2 based deoxidation slags has been researched.

The thesis includes six chapters, and the content of each chapter is introduced briefly as follows.

Chapter 1 "General introduction": The background and significance of this work have been introduced; the objectives have been given.

Chapter 2 "**Measurement and calculation methods for phosphate and sulfide capacitites**"**:** The sulfide capacity and phosphate capacity are an important parameters used to evaluate the sulfur and phosphorous absorbing abilities of molten slag. The definitions and traditional measurement methods for sulfide and phosphate capacities have been introduced in this chapter.

To precisely measure the sulfide capacity of slags containing some volatile components, a new experimental method has been designed. For this method, a gas-slag-metal equilibration technique is employed in a closed system to determine the sulfide capacity of slags. The corresponding metallic oxide of reference metal is added into the slag as the source of oxygen and its final content should be controlled as low as possible. After the whole closed system reaching equilibrium at target temperature, by measuring the sulfur and oxygen contents in the metal and sulfur content in the slag and using the standard dissolution Gibbs energies of sulfur and oxygen into the reference metal, the sulfide capacity can be finally derived.

The correlation between sulfide and phosphate capacities has also been introduced and discussed, which makes the mutual calculations between sulfide and phosphate capacities for some slags possible.

Chapter 3 "Desulfurizing ability of the $CaO_{satd.}$-$CaCl_2$-CaF_2 Slags": To elucidate the effect of $CaCl_2$ as the substitute of CaF_2, the CaO solubility and sulfide capacity of CaO-$CaCl_2$-CaF_2 slag were determined at temperatures from 1573 K to 1673 K by equilibrating molten slag and molten copper in a CaO crucible which was sealed in a nickel holder. The CaO solubility increases by 4.5~5.5 mol pct and the sulfide capacity decreases by the factor of 1.5~1.8 times with an increase in $CaCl_2$ content from about 25 to 75 mol pct. The activity coefficient of CaS increases with a decrease in temperature and with the replacement of CaF_2 by $CaCl_2$, which indicates that CaF_2 has stronger interaction with CaS than $CaCl_2$. A consideration by ionic theory of molten slag has been made to explain the change in CaO solubility and sulfide capacity with the replacement of CaF_2 by $CaCl_2$.

Chapter 4 "Dephosphorizing ability of MnO-SiO_2 based slag": To make full utilization of the high-MnO slags generated as by-product in the molten steel, the effect of BaO and Na_2O addition and Al_2O_3 substitution for SiO_2 on the phosphate capacity of MnO-$MgO_{stad.}$-Fe_tO-SiO_2 deoxidation slags at 1843 and 1873 K was investigated by equilibrating the molten slag and iron in a MgO crucible.

The addition of BaO and Na_2O to the MnO-$MgO_{satd.}$-Fe_tO-SiO_2 system dramatically increases the activity coefficient of MnO and phosphate capacity and decreases the activity coefficient P_2O_5. The phosphate capacity increases nearly 85 times with an addition of 12 mass pct Na_2O, whose effect is significantly bigger than that of BaO. At 1843 K, the phosphate capacity of 9.5Na_2O-46.1MnO-7.7$MgO_{stad.}$-14.1Fe_tO-24.9SiO_2 slag is nearly same with that of 36.9CaO-11.6$MgO_{stad.}$-24.32Fe_tO-26.33SiO_2 slag, indicating the feasibility of MnO based slags with addition of Na_2O as a substitute for CaO based slag. By replacing SiO_2 by Al_2O_3, the basicity of slags increases, but in contrast the phosphate capacity decreases and activity coefficient P_2O_5 increases, which was researched to be caused by the increase of activity coefficient of phosphate ion.

Chapter 5 "Proposal for practical steel refining processes": From the sulfide capacity obtained, the phosphate capacity of $CaO-CaCl_2-CaF_2$ slag saturated with CaO was estimated at temperatures from 1573 K to 1673 K by using the correlation between sulfide and phosphate capacities. An increase in content of $CaCl_2$ from about 25 to 75 mol pct in the slag, causes a decrease in phosphate capacity just by 2.3~3.3 times, indicating the replacement of CaF_2 by $CaCl_2$ would not significantly influence the dephosphorizing ability of $CaO-CaCl_2-CaF_2$ slags saturated with CaO. The influence of temperature on phosphate capacity is pronounced; more specifically, the phosphate capacity multiplies 66.8~81.1 times with decreasing temperature from 1673 to 1573 K.

Based on the experimental results obtained, some proposals for the practical steel refining processes have been given in this chapter. Firstly, the feasibility of using $CaO-CaCl_2$ slags for simultaneous desulfurization and dephosphorization in the hot metal pretreatment has been discussed. With an increase of temperature from 1573 to 1673 K, the phosphorous distribution ratio (L_P) and sulfur distribution ratio (L_S) between $CaO-CaCl_2$ slags and carbon-saturated iron melts decreases by 38.8 times and increases by 4.1 times, respectively, indicating the influence of temperature change on L_P is much bigger than that on L_S. A successful simultaneous desulfurization and dephosphorization can be achieved within a big range of oxygen potential, about $10^{-14.3}$ to $10^{-12.5}$ atm at 1573 K and $10^{-12.9}$ to $10^{-11.1}$ atm at 1673 K, and the optimum condition for simultaneous desulfurization and dephosphorization corresponds to $P_{O_2} = 10^{-13.8}$ atm and $L_P = L_S \approx 500$ at 1573 K, and $P_{O_2} = 10^{-12.4}$ atm and $L_P = L_S \approx 500$ at 1673 K.

Secondly, in the secondary refining, when the oxygen content in the molten steel exceeds about 800 ppm, the L_P estimated by the obtained phosphate capacity for the $MnO-MgO_{stad.}-Fe_tO-SiO_2$ slag with an addition of 12 mass pct Na_2O is large enough for an effective dephosphorization of steel. If 20 kg of above composition of slag per ton steel is added into the steel tapped from a basic oxygen furnace having 0.010 mass pct phosphorous and 0.10 mass pct oxygen at 1843 K, the equilibrium phosphorous content would be 26 ppm.

Chapter 6 "Conclusions": Based on the experimental results and discussion, the proposals of conducting simultaneous desulfurization and dephosphorization in hot metal pretreatment by using $CaO-CaCl_2$ based slags and in secondary refining, conducting dephosphorization by using $MnO-Na_2O-SiO_2$ based slags before deoxidation process and desulfurization by using $MnO-SiO_2$ based deoxidation slags after deoxidation process have been given.