論文の内容の要旨
Abstract of Dissertation

Title of Dissertation:

THERMODYNAMICS ON HARMLESS TREATMENT OF COPPER IN STEEL USING SULFIDE

(鋼中銅の硫化物による無害化に関する熱力学)

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ABSTRACT

Steel scrap has been used long as one of main raw materials for steelmaking. However, it contains considerable amount of Cu, which is a harmful element in steel because of Cu-induced hot shortness during the heat treatment. Generally, it is difficult to remove Cu from steel by conventional oxidation refining process since the chemical affinity of Cu for oxygen is smaller than that of iron.

One of the possible methods to avoid the hot shortness induced by residual Cu in steel may be carried out by its removal from molten iron with sulfide fluxes followed by its stabilization as inclusions during the heat treatment, because Cu removal from molten iron by FeS-Na_2S fluxes is considered as a possible method for the industrial application and Cu in solid steel can form copper sulfides which always coexist with other sulfides, such as MnS and FeS, to form complex sulfide inclusions.

The purpose of this study is to investigate the fundamental thermodynamic properties needed for the formation of MnS-$CuS_{0.5}$ and FeS-MnS-$CuS_{0.5}$ inclusions in γ-Fe steel as well as the dissolution behaviors of MgO and Al_2O_3 into the FeS-Na_2S fluxes for finding the optimal ladle lining against the erosion induced by FeS-Na_2S fluxes.

In **chapter 2**, in order to control the formation of MnS-$CuS_{0.5}$ inclusion in γ-Fe, the thermodynamic properties of the MnS-$CuS_{0.5}$ binary system have been investigated. The phase diagram was determined using Confocal Scanning Laser Microscopy (CSLM) and chemical

equilibration technique, X-ray diffraction (XRD) and Electro Probe Micro Analysis (EPMA). It shows a simple eutectic type with mutual solid solubility of MnS and $CuS_{0.5}$.

The activity coefficient of Mn at its infinite dilute solution and its self-interaction parameter in Cu at 1473 K were determined as 0.197±0.006 and 3.25±0.06, respectively, by equilibrating the MnS saturated sulfide melt with a reference metal of Cu in a purified Ar atmosphere. Activities of both MnS and $CuS_{0.5}$ in the liquid sulfide melt were then determined at 1473 K by equilibrating the sulfide melt with a reference metal of Cu in a purified Ar atmosphere. Both of them show positive deviation from the ideality at 1473 K.

The stability diagram of MnS-$CuS_{0.5}$ phases in γ-Fe at 1473 K was calculated based on the determined thermodynamic data. The liquid MnS-$CuS_{0.5}$ inclusion was stable in the region of high Cu and extremely low Mn contents.

In **chapter 3**, based on the results obtained in chapter 2, the investigation was extended to the FeS-MnS-$CuS_{0.5}$ ternary system at 1473K as FeS is considered to be another probable component in the solid steel besides $CuS_{0.5}$ and MnS. In order to control the formation of FeS-MnS-$CuS_{0.5}$ inclusion in solid steel, the thermodynamic properties of the FeS-MnS-$CuS_{0.5}$ ternary system were investigated at 1473 K using chemical equilibration technique.

As Fe-$C_{sat.}$ alloy was considered as the optimal reference metal to determine the activities of components in the sulfide melt. The activity coefficient of Cu in the Fe-$C_{sat.}$-Cu-S alloy was thus investigated by distribution of Cu between the Fe-$C_{sat.}$-Cu-(S) and Ag-Cu-(S) alloys. The activity coefficient of Cu in the Fe-$C_{sat.}$-Cu-S alloy at 1473 K was determined as equation: $\ln\gamma_{Cu}=3.76-11.45\cdot X_{Cu}-4.74\cdot X_S$, ($0\le X_{Cu}\le 0.033$, $0\le X_S\le 0.018$).

The isothermal section of the FeS-MnS-$CuS_{0.5}$ ternary system was determined at 1473K by measuring the solubility of MnS in the FeS-MnS-$CuS_{0.5}$ melt and the solid solubility of $CuS_{0.5}$ in the FeS-$CuS_{0.5}$ solid solution. The activities of FeS and $CuS_{0.5}$ in the system were determined by equilibrating the sulfide melt with Fe-$C_{sat.}$-Cu-S-(Mn) and Cu-Fe-S-(Mn) alloys at 1473 K in an Ar atmosphere, and that of MnS was estimated from the determined activities of FeS by Gibbs-Duhem integration method proposed by Schuhmann. The non-stoichiometry of the sulfide melt equilibrated with Fe-$C_{sat.}$ based alloy was discussed and considered to be insignificant.

Based on the determined thermodynamic data, the Equilibrium relation between the solid steel and the sulfide inclusion at 1473K was estimated. To decrease the Cu content in γ-Fe to form the liquid FeS_{1-x}-MnS-$CuS_{0.5}$ inclusion, the composition of steel should be controlled in high S content and low Mn content.

In **chapter 4**, in order to find out the optimal ladle lining against the erosion induced by FeS-$NaS_{0.5}$ fluxes, the dissolution behaviors of MgO and Al_2O_3 into FeS-Na_2S fluxes were investigated by holding a chunk of solid MgO or Al_2O_3 in the FeS-Na_2S fluxes under different conditions.

Carbon saturation, lower partial pressure of CO, higher temperature and higher Na_2S content in the fluxes increased the dissolved Mg and Al contents of the final fluxes. As dissolution of MgO in the fluxes was more significant than that of Al_2O_3, Al_2O_3 based refractory materials are considered to be better than MgO based ones for Cu removal considering the erosion of the refractory materials induced by FeS-Na_2S fluxes. The dissolutions of MgO and Al_2O_3 into the FeS-Na_2S fluxes were estimated as following reactions: for dissolution of MgO: C (s) + MgO (s) + Na_2S (l) = CO (g) + 2Na (g) + MgS (s); for dissolution of Al_2O_3: 3C (s) + Al_2O_3 (s) + 3Na_2S (l) = 3CO (g) + 6Na (g) + Al_2S_3 (s).

In **chapter 5**, the formations of MnS-$CuS_{0.5}$ and FeS-MnS-$CuS_{0.5}$ inclusions in γ-Fe at 1473 K are mainly discussed with/without considering oxidation process in the heat treatment process.

Summarily in **Chapter 6**, in order to decrease the Cu content in γ-Fe to form the liquid MnS-$CuS_{0.5}$ or FeS_{1-x}-MnS-$CuS_{0.5}$ inclusion, the composition of steel should be controlled in high S content and low Mn content, and that Al_2O_3 based refractory materials are considered to be better than MgO based ones for Cu removal considering the erosion of the refractory materials induced by FeS-Na_2S fluxes.

Keywords: thermodynamic properties; phase diagram; activity; isothermal section; the MnS-$CuS_{0.5}$ binary system; the FeS-MnS-$CuS_{0.5}$ ternary system; dissolution behavior; FeS-Na_2S fluxes.