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学位論文題目	Thermodynamic Study on the Removal of Copper in Steel Scrap by Sulfide Fluxes （硫化物系フラックスによる屑鉄中銅の除去に関する熱力学研究）
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論文内容要旨

ABSTRACT

Recycled steel scrap has been becoming an important source of iron in steelmaking. The present situation and prediction of ferrous scrap indicate that the accumulation of impurities like copper, tin, antimony etc., called as tramp elements, will cause serious problem for utilization of the scrap. Therefore, economical processes to remove these tramp elements have to be developed for solving this problem.

This thesis is to investigate the thermodynamics of the removal of copper in remelted steel scrap by sulfide fluxes. Experiments were carried out to measure the distribution of copper between various sulfide fluxes and carbon saturated iron melt. The evaluation of the thermodynamic parameters relative to the process was established at 1673 K. And the discussions are focused on these parameters to reveal the behavior of copper between fluxes and iron melt. The following gives a description to the thesis in the order of chapters.

I Introduction

Chapter I describes the background of copper removal from iron melt by sulfide fluxes. A survey is made for the present situation and trend of the supply and demand of steel scrap, and a conclusion is reached that economical processes have to be developed to remove the tramp elements from the scrap melt.

A review is made on the previous efforts to remove impurities, with the stress on removing copper by sulfide fluxes, from iron or steel melts. Principle of the removal of copper in iron melt by sulfide fluxes is introduced briefly.

II Phase Equilibria of Fe-S-C Ternary Melt

Fe-S-C ternary melt is the basic system in the process of copper removal by sulfide flux because the reations in this process are basically sulfurization reactions, and carbon is indispe nsable to enlarge the miscibility gap between FeS and iron melts and to increase activities of copper and sulfur.

Phase equilibria in Fe-S-C ternary melt are experimentally clarified in the temperature range from 1473 to 1873 K. The solubility of graphite in Fe-S melt and miscibility gap between molten iron sulfide and Fe-S-C melt observed in this work agree well with the results by previous investigators.

The interstitial solution model is applied to evaluate the thermodynamic quantities of this ternary melt. The interaction parameters of the model are derived for this ternary melt as

$$\theta_s^s = -270/T - 7.709$$

$$\theta_c^s = \theta_s^c = 6.0$$

$$\theta_c^c = 7830/T + 1.658$$

$$\pi_s^{ss} = -7500/T + 9.98$$

The phase diagram and activities of the constituents in Fe-S-C ternary melt are evaluated based on the interstitial solution model. The evaluated results are in agreement with the experimental one and literature data. Thus the evaluation of activities of Fe, S and FeS in Fe-S-C melt is established.

III Activity of Copper in Fe-$C_{sat.}$-S-Cu Melt at 1673 K

The activity of copper in Fe-$C_{sat.}$-S-Cu melt is one of the most important parameters for a thermodynamic study on the process of copper removal. It is determined experimentally at 1673 K by the distribution of copper between liquid silver and Fe-$C_{sat.}$ melt.

The activity of copper in carbon saturated iron shows strong positive deviation from Raoultian behavior. The activity coefficient of copper is about 35.5 in Fe-$C_{sat.}$ melt at 1673 K. An empirical relation to estimate γ_{Cu} in Fe-$C_{sat.}$-S-Cu melt is derived as a function of sulfur and copper contents

$$\log \gamma_{Cu} = 1.55 - 8.60\,X_{Cu} - 0.429\,X_S + 4.536\,X_S^2 - 3328\,X_S^3$$
$$X_{Cu} < 0.013 \text{ in Fe-C}_{sat.}\text{-S-Cu melt, 1673 K}$$

Ⅳ Distribution of Copper between Iron Sulfide and Carbon Saturated Iron Melt

Iron sulfide is the basic constituent of sulfide fluxes for copper removal from iron melt. So the distribution of copper between iron sulfide and Fe-$C_{sat.}$ melt is investigated in the temperature range from 1573 to 1773 K. The distribution ratio of copper, defined as $L_{Cu} = (\%Cu)_{in\ flux} / [\%Cu]_{in\ metal}$, is between 7 to 11 on the experimental condition and becomes larger at the higher temperature. The content of copper seems to affect little on the distribution ratio of copper in the investigated compostion range. The equilibrium sulfur content in Fe-$C_{sat.}$ melt is close to 2 mass pct. Therefore, improvements are required because of the high equilibrium sulfur content in iron melt and relatively low copper distribution ratio.

Activity coefficients of FeS and $CuS_{0.5}$ in sulfide phase are evaluated. The distribution behavior of copper can be described by means of the variation of these parameters.

Ⅴ Effect of Alkaline Metal Sulfide in Flux on the Distribution of Copper

The effect of alkaline metal sulfides $NaS_{0.5}$, $KS_{0.5}$ and $LiS_{0.5}$, noted as $MS_{0.5}$ for short, on copper distribution and equilibrium sulfur content is investigated at 1673 K in this chapter.

The distribution ratio of copper increases with increasing the content of any of these alkaline metal sulfides in FeS-$MS_{0.5}$ fluxes; but the further increase in $MS_{0.5}$ contents turns to decrease L_{Cu} slightly in the high $MS_{0.5}$ concentration range.

The maximum of L_{Cu} are about 20, 23 and 30 for the fluxes of FeS-$KS_{0.5}$, -$NaS_{0.5}$ and -$LiS_{0.5}$, respectively. The increase in $CuS_{0.5}$ content in the flux tends to decrease L_{Cu}, especially at the high concentration of $MS_{0.5}$.

The equilibrium sulfur content in Fe-$C_{sat.}$ melt is reduced significantly by the addition of $MS_{0.5}$ into the fluxes. The difference in the sulfur content becomes insignificant among the three FeS-$MS_{0.5}$ fluxes as the content of $MS_{0.5}$ is high, e.g. $X_{MS_{0.5}} > 0.5$.

Accordingly, alkaline metal sulfides are the effective constituents of fluxes in increasing copper distribution ratio and suppressing the sulfur content in iron melt. FeS-$LiS_{0.5}$ seems to be the best among the three fluxes.

The activity coefficient of copper in Fe-$C_{sat.}$ melt does not change so much relative to the variation of copper distribution ratio. So the variation of L_{Cu} mainly depends on the behavior of parameters $\gamma_{CuS_{0.5}}$ and a_{FeS}.

The activity coefficient of copper sulfide decreases considerably with the addition of $MS_{0.5}$ into the fluxes, which is mainly responsible for the increase in the distribution ratio of copper. On the other hand, the decrease in the activity of sulfur or iron sulfide does not benefit the increment of L_{Cu}. As a result of the competition between the decrease rates of $\gamma_{CuS_{0.5}}$ and $a_{FeS}^{1/2}$, copper distribution ratio increases with increasing $MS_{0.5}$ contents in the fluxes, and exhibits the maximum value at a certain composition of fluxes.

Ⅵ Effect of Alkaline Earth Metal Sulfide in Flux on the Copper Distribution

This part of work is to investigate the distribution of copper between FeS-alkaline earth metal sulfide fluxes and Fe-$C_{sat.}$ melt. The alkaline earth metal sulfides investigated consist of MgS, CaS, SrS and BaS and are noted as MS for short.

The distribution ratio of copper are measured in the homogeneous liquid region of FeS-MS fluxes which, i.e. the solubility of MS in molten iron sulfide, is estimated based on the relation between sulfur content in Fe-$C_{sat.}$ melt and the content of MS in the fluxes. It is found that the usage of SrS and BaS increases copper distribution ratio obviously, and the result of the increase in L_{Cu} are close to that with alkaline metal sulfides. But the effect of MgS and CaS could not be well clarified because of their limited homogenous liquid range.

The equilibrium sulfur content in Fe-$C_{sat.}$ melt is decreased by the addition of MS into the fluxes up to MS saturation.

The activity coefficient of $CuS_{0.5}$ is lowered effectively by SrS and BaS so that a comparatively high copper distribution ratio is observed. The effects of the four alkaline earth metal sulfides on the activity of FeS or sulfur content in iron melt are almost the same.

A comparison in the copper distribution ratio is made among the seven kinds of fluxes investigated in the present work. It is found that FeS-$LiS_{0.5}$ is the most suitable flux for copper removal in the present work. However, the copper distribution ratio is not high enough to have practical significance.

Ⅶ Behavior of Tin, Antimony and Some Alloying Elements during Copper Removal Process Using Sulfide Flux

The distribution of tin, antimony and the alloying elements such as Cr, Ni, Mn and Mo between FeS-based flux and Fe-$C_{sat.}$ melt is determined at 1673 K to know their behavior during c opper removal by sulfide fluxes.

The distribution ratios of Sn and Sb between FeS and Fe-$C_{sat.}$ melts are about 1.1 and 1.6, respectively. The addition of sodium sulfide into iron sulfide lowers the values of L_{Sn} and L_{Sb} considerably.

The activity coefficients of tin and antimony in Fe-$C_{sat.}$ are experimentally determined at 1673K. The activity of tin in Fe-$C_{sat.}$ exhibits large positive deviation from Raoultian behavior. The activity coefficient of tin is expressed by the relation

$\gamma_{Sn} = 11.68$ in $Fe\text{-}C_{sat.}$, 1673 K

and

$$\ln \gamma_{Sn} = 2.447 - 60.84 X_{Sn} - 7.29 X_S - 139.65 X_S^{2}$$

in $Fe\text{-}C_{sat.}-S-Sn$, 1673 K

The activity of Sb in $Fe\text{-}C_{sat.}$ melt shows negative deviation from Raoultian behavior and

$\gamma_{Sb} = 0.52$ in $Fe\text{-}C_{sat.}$, 1673 K

$$\ln \gamma_{Sb} = -0.6505 - 42.23 X_{Sb} - 4.392 X_S$$

in $Fe\text{-}C_{sat.}-S-Sb$, 1673 K

A thermodynamic analysis demonstrates that Sb, as well as part of Sn, is more likely to dissolve in the sulfide phase in metallic state on the present experimental condition.

The distribution ratio of Cr is about 3 between FeS and $Fe\text{-}C_{sat.}$ melts, which seems not to be affected obviously by increasing $NaS_{0.5}$ content. The values of L_{Ni} and L_{Mo} between FeS and $Fe\text{-}C_{sat.}$ phases are about 1.2 and 0.04 respectively, and decrease largely by the addition of $NaS_{0.5}$. The value of L_{Mn} reaches as high as hundreds and would increase with increasing the content of sodium sulfide in the flux.

It is concluded that the removal of tin and antimony is not effective during copper removal process by sulfide fluxes, and among the alloying elements the loss of Ni, Mo and Cr may be negligible but Mn will lose almost in all.

Ⅷ Summary

A summary is made for the chapters Ⅰ to Ⅶ.

Accordingly, the distribution ratio of copper may reach as high as 20 to 30 by using FeS-alkaline metal sulfide fluxes without a signficant sulfur pick-up. Thus this method might be applicable in a certain condition. However, such a distribution ratio of copper is normally too low for a practical application. Therefore, some more efforts have to be made to develop the optimal treatment condition or more effective flux constituents, or develop new techniques for copper removal from steel scrap.

審 査 結 果 の 要 旨

製鋼原料としての屑鉄供給量の増大に伴い，屑鉄と一緒に混入してくる不純物元素を，製鋼過程で除去することが大きい問題になっている。本研究は，これら混入不純物元素の中で最も除去が困難とされている銅を，硫化物の形で除去する方法の可能性について，化学平衡論的立場から研究した結果をまとめたもので，全編8章よりなる。

第1章は緒言である。

第2章ではFe-C-S 3元系融体の相平衡について測定し，溶融硫化物とFe-C合金の2相分離範囲を明らかにして熱力学的考察を行った。これらは溶鉄相から硫化物を折出する基礎的関係を明らかにしている。

第3章では溶融銀と炭素飽和Fe-C-S-Cu系合金間の銅の分配平衡を測定して，炭素飽和Fe-C-S-Cu合金中の銅の活量を銅および硫黄濃度の関数として求めた。これは溶鉄中銅を硫化銅の形で折出せしめる時の重要な基礎数値である。

第4章では溶融硫化鉄と炭素飽和溶鉄間の銅の分配平衡を，1573Kから1773Kの温度，溶鉄中銅濃度1.2 mass%以下の範囲で測定した結果を述べている。銅分配比 L_{Cu}（=（%Cu）$_{in\ flux}$／[%Cu]$_{in\ metal}$）は大略7～11程度であった。

第5章では銅分配比におよぼすアルカリ金属硫化物，Li_2S, Na_2S, K_2Sの影響を1673Kで広いアルカリ金属硫化物組成範囲につき測定した結果を述べている。銅分配比は硫化鉄中アルカリ金属硫化物濃度の上昇により向上し，その最大値は L_{Cu}≒30程度になり，溶鉄中硫黄濃度は0.2mass%まで低下する。

第6章では銅分配比におよぼすアルカリ土類金属硫化物MgS，CaS，SrSおよびBaSの影響を1673Kで測定した結果をまとめている。溶融硫化鉄へのMgSおよびCaSの溶解度は低く，銅分配比におよぼす影響は小さいが，SrSおよびBaSの添加により銅分配比は L_{Cu}≒20程度まで向上し，溶鉄中硫黄濃度は0.5mass%まで低下することを明らかにしている。

第7章では他の混入元素であるSn，Sb，Ni，Cr，MoおよびMnについて，炭素飽和溶鉄と硫化物間の分配比を1673Kで測定した。硫化物として硫化鉄のみを使用した時の分配比は，それぞれ L_{Sn}≒1.1，L_{Sb}≒1.6，L_{Ni}≒1.2，L_{Cr}≒3.0，L_{Mo}≒0.04および L_{Mn}≒400であった。

第8章は結論である。

以上要するに本論文は，屑鉄再溶解時に混入してくる銅を硫化物の形で除去する方法に関係する，相平衡，熱力学的基礎数値，平衡分配値などにつき詳細な研究を行ない，溶鉄中銅の硫化除去に関する可能性と限界を明らかにしたもので，金属工学の発展に寄与するところが少なくない。

よって，本論文は工学博士の学位論文として合格と認める。