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COPPER DISTRIBUTION BETWEEN FeS-BASED SULFIDE FLUX
AND CARBON SATURATED IRON MELT

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Synopsis: Chemical equilibrium of copper distribution between FeS flux and carbon saturated liquid iron has been studied to establish the thermodynamic data concerning the copper removal from steel scrap by sulfide flux. Effect of the addition of alkaline metal sulfide $MS_{0.5}$ ($MS_{0.5}$: $LiS_{0.5}$, $NaS_{0.5}$, $KS_{0.5}$) or alkaline earth metal sulfide MS (MS: MgS, CaS, SrS, BaS) to FeS on copper distribution are also studied at 1673K.

The copper distribution ratio defined as L_{Cu}=(mass%Cu)$_{flux}$/[mass%Cu]$_{metal}$ was only about 9, and sulfur content in molten iron showed quite high value of about 1.9 mass% when pure FeS was used as the flux. However, the addition of $MS_{0.5}$, SrS or BaS to FeS increased L_{Cu} and lowered the sulfur content in liquid iron markedly. The maximum values of L_{Cu} of about 20 to 30 were obtained in each flux. On the other hand, no apparent effect of MgS or CaS on L_{Cu} was observed due to their limited solubility in liquid FeS.

Key words: tramp element, recycling of steel scrap, alkaline metal sulfide, alkaline earth metal sulfide, copper removal, physical chemistry, distribution, equilibrium

1. Introduction

A widely concerned problem in the recycling of steel scrap is the accumulation of tramp elements, mainly copper, in the scrap. A practical process for copper removal thus is to be developed as soon as possible. A number of suggestions have been proposed for copper removal process [1]. Among them, sulfide flux treatment [2]-[4] is considered to be most possibly acceptable for the industrial purpose. However, the equilibrium studies on this process by means of FeS-$NaS_{0.5}$ flux have recently been reported only by Imai and Sano [5], and Jimbo et al. [6]. Therefore, the present study focused on the chemical equilibrium of copper distribution between FeS-based flux and carbon saturated iron melt.

Present work consists of following four parts; 1) copper distribution between FeS and Fe-$C_{sat.}$ melts, 2) effect of alkaline metal sulfide, $MS_{0.5}$, such as K_2S, Na_2S or Li_2S, and 3) that of alkaline earth metal sulfide, MS, such as MgS, CaS, SrS or BaS on the copper distribution, and 4) distribution of Sn, Sb, Ni, Cr, Mn and Mo between FeS-Na_2S flux and iron melt. Most of the measurements were conducted at 1673K.

2. Thermodynamic background on the copper removal by sulfide flux

Copper removal by sulfide flux is based on the facts that the affinity of Cu for S is stronger than that of iron, and liquid FeS is immiscible with iron melt in Fe-S-C ternary system. Reaction of copper removal from iron melt by sulfide fluxes is given by Eq.(1).

$$\underline{Cu} + 1/2\ \underline{S} = CuS_{0.5}(1) \qquad \Delta G_1^\circ = 6{,}966 - 6.74\ T\ [7],\ [8] \quad (J/mol) \tag{1}$$

$$K_1 = a_{CuS_{0.5}}/(a_{Cu}a_S^{1/2}) = \gamma_{CuS_{0.5}}X_{CuS_{0.5}}/(\gamma_{Cu}\ X_{Cu}\ a_S^{1/2}) \tag{2}$$

Where a_{Cu} and $a_{CuS_{0.5}}$ refer to Raoult's law, and a_S refers to Henry's law. The sulfides in the flux is expressed as the monocationic species. Rearrangement of Eq.(2) gives the copper distribution ratio between flux and carbon saturated liquid iron as Eq.(3).

$$L_{Cu} = (\text{mass\%Cu})_{flux}/[\text{mass\%Cu}]_{iron} = C\ K_1\ a_S^{1/2}\ (\gamma_{Cu}/\gamma_{CuS_{0.5}}) \qquad (3)$$

Where C is the term to convert the concentration. Since a_{Fe} is almost constant in the present work [10], a_S is proportional to a_{FeS}. Accordingly, L_{Cu} can be written as Eq.(6).

$$Fe(l) + \underline{S} = FeS(l) \qquad \Delta G_4^\circ = 9665 - 24.06\ T\ [8],\ [9]\ (J/mol) \qquad (4)$$

$$K_4 = a_{FeS}/(a_{Fe}\ a_S) \qquad (5)$$

$$L_{Cu} = C'\ a_{FeS}^{1/2}\ (\gamma_{Cu}/\gamma_{CuS_{0.5}}) \qquad (6)$$

Since γ_{Cu} in Fe-$C_{sat.}$ melt does not vary much in this work [11], L_{Cu} mainly depends on the terms of a_{FeS} and $\gamma_{CuS_{0.5}}$. A higher a_{FeS} and smaller $\gamma_{CuS_{0.5}}$ would result in the larger L_{Cu}. However, it is not practical to have a large a_{FeS} anyway. Thus the decrease of $\gamma_{CuS_{0.5}}$ in the flux becomes the key point for this process.

3. Experimental

About 10 g of master alloy and 6 to 10 g of synthetic flux are charged in a graphite crucible (35mm o.d., 20mm i.d and 40mm in depth), and a graphite lid was attached to the crucible to minimize the evaporation of alkaline metal from flux. Then the sample is heated and melted in the induction furnace under purified argon flow. The temperature was manually controlled within ±10 K to the aimed with a Pt-Pt13%Rh thermocouple. The holding time to attain equilibrium was preliminary determined by distributing copper from iron to flux and *vice versa*. After the attainment of the equilibrium, the sample quenched with a helium gas flow and each component in both phases is chemically analyzed.

4. Results and Discussion

4-1. Distribution of copper between molten FeS and Fe-$C_{sat.}$ melt

Figure 1 shows the variation of L_{Cu} between pure FeS flux and Fe-$C_{sat.}$ melt with $X_{CuS_{0.5}}$ in the flux at 1573, 1673 and 1773K. It is seen that the effect of $CuS_{0.5}$ content on L_{Cu} is very small so that L_{Cu} is almost constant value at a given temperature. At 1673 K, L_{Cu} is about 9. The higher temperature seems to favor the increase of L_{Cu}.

The sulfur pick-up in iron melt might be a problem in this process of copper removal. It is shown later in Figs. 3 and 5 that the sulfur content in Fe-$C_{sat.}$ melts is a high value of about 1.9 mass%.

According to above-mentioned results, FeS is capable of removing copper from iron melt. However, the L_{Cu} is not more than 10 in spite of the high sulfur potential of the system. Therefore, the effort to increase L_{Cu} has to be focused on the decrease of $\gamma_{CuS_{0.5}}$.

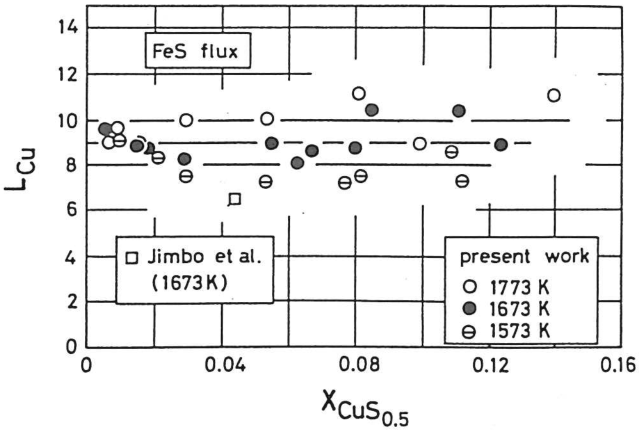

Fig. 1. Effect of $CuS_{0.5}$ on L_{Cu} between FeS flux and carbon saturated liquid iron.

4-2. Effect of alkaline metal sulfides on copper distribution

The effect of additives on $\gamma_{CuS_{0.5}}$ is examined in the low content range of $CuS_{0.5}$, e.g. $X_{CuS_{0.5}}<0.02$ herein after in the view of the practical situation.

Effect of content of $KS_{0.5}$, $NaS_{0.5}$ or $LiS_{0.5}$ in the flux on L_{Cu} is presented in Fig. 2. Figure 2 shows that L_{Cu} increases with increasing any $X_{MS_{0.5}}$ in the flux and reaches a maximum at about $X_{KS_{0.5}}=0.3$, $X_{NaS_{0.5}}=0.4$ and $X_{LiS_{0.5}}=0.6$. This fact indicates that the addition of $MS_{0.5}$ to molten FeS is effective in promote copper removal. However, the further increase of $MS_{0.5}$ tends to decrease L_{Cu} slightly. The maximum of L_{Cu} is 20, 24 and 30 in FeS-$KS_{0.5}$, -$NaS_{0.5}$ and -$LiS_{0.5}$ flux, respectively.

Figure 3 shows the relation between the equilibrium sulfur content in Fe-$C_{sat.}$ melt and $X_{MS_{0.5}}$ in flux. It is seen that the sulfur content in Fe-$C_{sat.}$ melt decreases markedly with increasing $X_{MS_{0.5}}$ in FeS-based flux, e.g. [mass%S] decreases from about 1.9 at $X_{MS_{0.5}}$=0 to about 0.1 at $X_{LiS_{0.5}}$=0.75.

Based on the above results, it is concluded that the alkaline metal sulfides are effective in both increasing L_{Cu} and suppressing the sulfur content in Fe-$C_{sat.}$ melt. The main reason for this result is regarded as that $MS_{0.5}$ in the flux reduces the activity coefficient of $CuS_{0.5}$ largely. Though L_{Cu} tends to decrease slightly with greater $MS_{0.5}$ content after the maximum of L_{Cu}, this decrease is essentially insignificant. In contrast, Fig. 3 shows the sulfur content in Fe-$C_{sat.}$ decreases monotonously with increasing $X_{MS_{0.5}}$. Therefore, it is possible to obtain L_{Cu} of 20 to 30 with [mass% S] in iron below 0.1 if the flux composition is selected at high $X_{MS_{0.5}}$, e.g. $X_{MS_{0.5}}$ = 0.7 to 0.8.

4-3. Effect of alkaline earth metal sulfides on the copper distribution

Figure 4 shows the relation between L_{Cu} and X_{MS} in fluxes. No apparent effect of MgS and CaS on L_{Cu} was observed due to their limited solubility in liquid FeS. L_{Cu} does, however, obviously increase with increasing X_{SrS} or X_{BaS}, the maximum value being about 22 with near saturation of SrS. The variation of L_{Cu} against X_{BaS} appears very close to that with FeS-$MS_{0.5}$ fluxes. L_{Cu} increases with increasing X_{BaS} when BaS content is low and becomes maximum of about 19 around X_{BaS}=0.25 until BaS saturation. The maximums of L_{Cu} with FeS-SrS and FeS-BaS fluxes are nearly equivalent to those with FeS-$MS_{0.5}$ fluxes.

Figure 5 shows the relation between the sulfur content in Fe-$C_{sat.}$ melt and X_{MS}. The sulfur content decreases monotonously with increasing X_{MS} and becomes a certain value after MS saturation. The difference in [mass%S] is negligible at a given X_{MS} for four FeS-MS fluxes within the homogeneous liquid range of fluxes. This means that

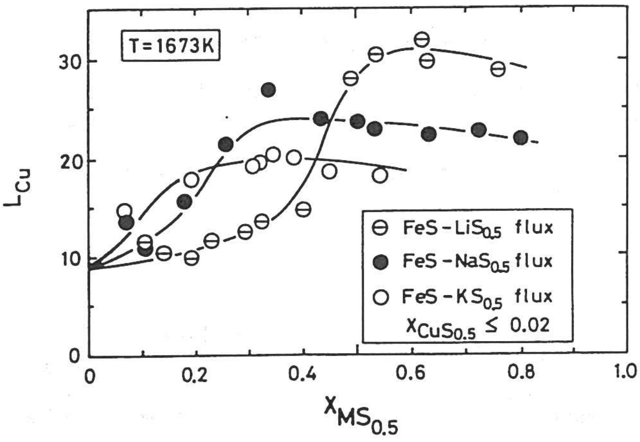

Fig. 2. Effect of alkaline metal sulfide, $MS_{0.5}$, on L_{Cu} in FeS–$MS_{0.5}$ fluxes.

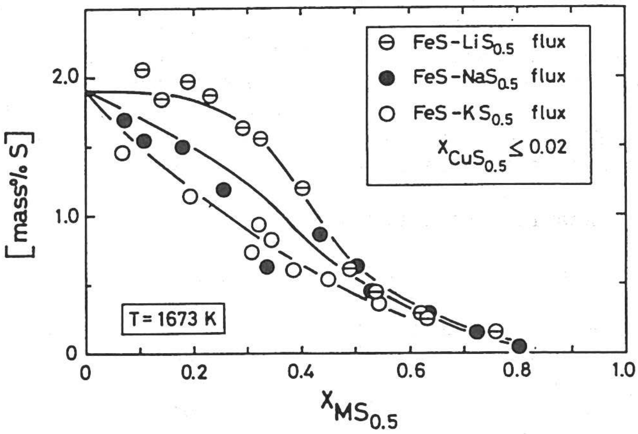

Fig. 3. Effect of $MS_{0.5}$ on sulfur content in carbon saturated liquid iron in FeS–$MS_{0.5}$ fluxes.

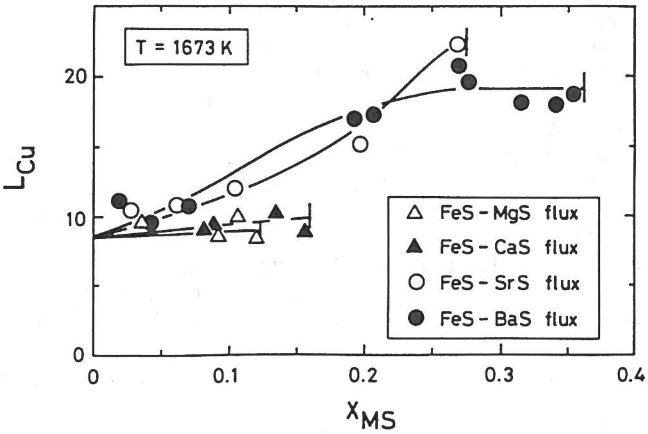

Fig. 4. Effect of alkaline earth metal sulfide, MS, on L_{Cu} in FeS–MS fluxes.

the effects of the four sulfides on a_{FeS} in the flux are the same.

4-4. Activity coefficient of $CuS_{0.5}$ and activity of FeS in flux

From Eq.(6), the distribution ratio of copper is mainly dominated by $\gamma_{CuS_{0.5}}$ and a_{FeS} which depend largely on flux composition. Therefore, the effect of the flux composition on L_{Cu} is described quantitatively from the behavior of these two factors.

The activity coefficient of $CuS_{0.5}$ and the activity of FeS in the flux are related to Eq.(7) from Eq.(2) and to Eq.(8) from Eq.(4), respectively.

$$\gamma_{CuS_{0.5}} = K_1\, a_{Cu}\, a_S^{1/2}/X_{CuS_{0.5}} \qquad (7)$$

$$a_{FeS} = K_4\, a_{Fe}\, a_S \qquad (8)$$

Since a_S, a_{Fe} and γ_{Cu} in liquid iron are known [10], [11], $\gamma_{CuS_{0.5}}$ and a_{FeS} in the flux can be calculated from the compositions of metal and flux.

Figure 6 shows the relation of $a_{FeS}^{1/2}$ to the contents of various $MS_{0.5}$ and MS in fluxes. Generally, $a_{FeS}^{1/2}$ decreases monotonously with increasing $X_{MS_{0.5}}$, i.e. $MS_{0.5}$ lowers activity of FeS so that it is able to suppress the pick-up of sulfur. $KS_{0.5}$ among $MS_{0.5}$ seems to be the most effective to decreasing $a_{FeS}^{1/2}$, and the effect is followed by $NaS_{0.5}$. However, no measurable difference is observed between $a_{FeS}^{1/2}$ and $X_{MS_{0.5}}$ among three kinds of fluxes when $X_{MS_{0.5}}$ exceeds 0.5. The effect of MS on $a_{FeS}^{1/2}$ is considered to be equivalent as shown also in Fig. 5.

Figures 7 and 8 presents the relation of $\gamma_{CuS_{0.5}}$ to $X_{MS_{0.5}}$ and X_{MS} in fluxes, respectively. At a given $X_{MS_{0.5}}$ within $X_{MS_{0.5}}$ of 0.5, $KS_{0.5}$ is the most effective to decreasing $\gamma_{CuS_{0.5}}$ among the three kinds of $MS_{0.5}$. But at $X_{MS_{0.5}}$ of 0.5, $\gamma_{CuS_{0.5}}$ becomes nearly equivalent for three FeS-$MS_{0.5}$ fluxes and tends to a constant of about 0.5 with further increasing $X_{MS_{0.5}}$.

Topkaya [12] has measured the activities in $NaS_{0.5}$-$CuS_{0.5}$ binary. An extrapolation from his data leads to a value of about 0.6 for $\gamma^{o}_{CuS_{0.5}}$ in $NaS_{0.5}$ melt, which is very close to the result at high content of $MS_{0.5}$ in the present work. It is

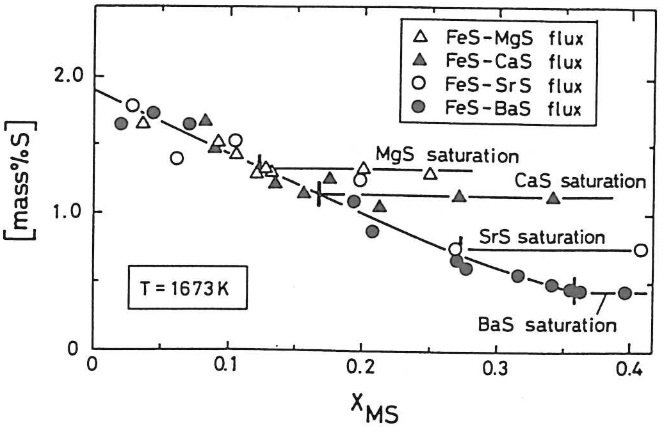

Fig. 5. Effect of MS on sulfur content in carbon saturated liquid iron in FeS–MS fluxes.

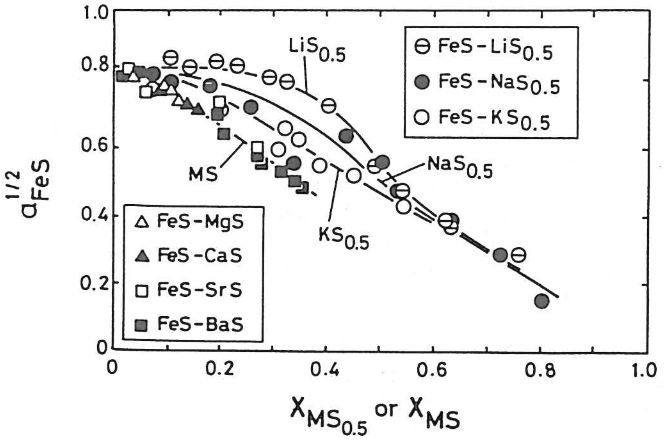

Fig. 6. Effect of $MS_{0.5}$ or MS on $a_{FeS}^{1/2}$ in FeS–$MS_{0.5}$ fluxes.

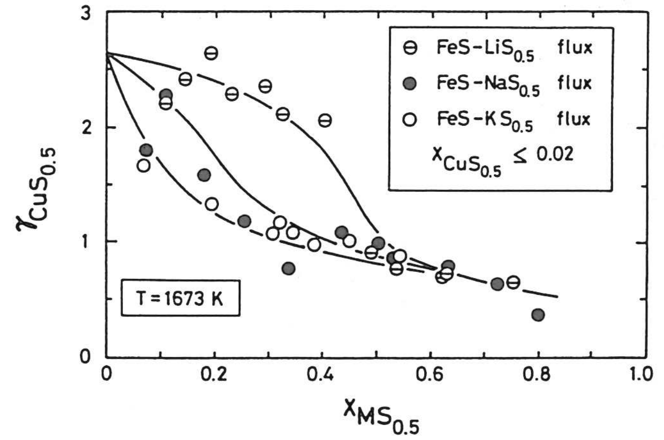

Fig. 7. Variation of $\gamma_{CuS_{0.5}}$ with $MS_{0.5}$ content in FeS–$MS_{0.5}$ fluxes.

thus suggested that $\gamma_{CuS_{0.5}}$ might not be lowered than 0.5 by the addition of $MS_{0.5}$ to molten FeS.

Figure 8 shows that the effect of MgS and CaS on $\gamma_{CuS_{0.5}}$ does not seem to be significant, though $\gamma_{CuS_{0.5}}$ tends to decrease slightly. In the case of FeS-SrS and FeS-BaS fluxes which have a wider homogeneous liquid range, $\gamma_{CuS_{0.5}}$ decreases notably with increasing the content of SrS or BaS in the flux, so that L_{Cu} is increased. However, the decrease rate of $\gamma_{CuS_{0.5}}$ becomes lower with the increase of X_{SrS} and X_{BaS}, $\gamma_{CuS_{0.5}}$ tends to be an certain value at the composition close to SrS and BaS saturation similar to the case of FeS-$MS_{0.5}$ fluxes. This tendency of $\gamma_{CuS_{0.5}}$ variation suggests that the increase in the capacity of copper removal with FeS-based flux by the addition of $MS_{0.5}$ and MS is limited.

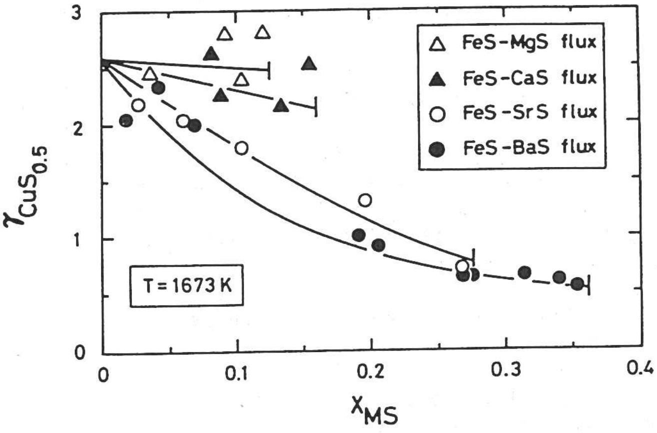

Fig. 8. Variation of $\gamma_{CuS_{0.5}}$ with MS content in FeS–MS fluxes.

4-5. Limitation of copper removal by FeS-based fluxes

The copper distribution ratio using various fluxes and the corresponding sulfur content in iron melt are summarized in Fig. 9. In view of practical application, it is desirable to obtain a larger L_{Cu} and a lower sulfur content in iron melt. Therefore, the preferable condition is shown in the upper-left corner of the figure. For this purpose, FeS-$LiS_{0.5}$ system is the most suitable flux among the fluxes investigated here. Imai and Sano [5] substituted $KS_{0.5}$, $LiS_{0.5}$, CaS and BaS for a part of $NaS_{0.5}$ in FeS-$NaS_{0.5}$ flux by to examine their effects on L_{Cu}. Their results indicated that L_{Cu} could not be raised by these substitutions. Jimbo et al. [6] reported that there was no beneficial effect on L_{Cu} by the addition of PbS, MnS and Al_2S_3 into FeS-$NaS_{0.5}$ flux.

Thus, it might be difficult to develop a sulfide which can drastically lower $\gamma_{CuS_{0.5}}$, though information on phase diagrams of sulfides has not been yet adequate. Therefore, the L_{Cu} by FeS-based fluxes might be limited to be about 30 which can be obtained with $LiS_{0.5}$.

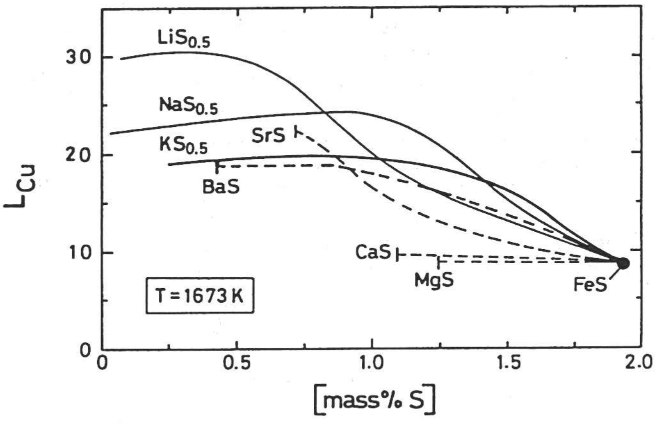

Fig. 9. Relationship between L_{Cu} and sulfur content in carbon saturated liquid iron equilibrated with FeS–$MS_{0.5}$ and FeS–MS fluxes.

4-6. Distribution of the other elements between FeS-$NaS_{0.5}$ flux and Fe-$C_{sat.}$ melt

It is of significance to know the distribution behavior of the other tramp elements and some valuable alloying elements for treating iron melt with sulfide fluxes. Figure 10 shows distribution ratios of Sn, Sb, Cr, Ni, Mn and Mo between FeS-$NaS_{0.5}$ flux and Fe-$C_{sat.}$ melt against the content of $NaS_{0.5}$ in the flux.

The distribution ratios of Sn and Sb between FeS and Fe-$C_{sat.}$ melts are about 1.1 and 1.6, respectively. The increase of X_{NaS} in the flux tends to lower L_{Sn} and L_{Sb}, especially for L_{Sb}. It is known that the chemical affinity of Sn and Sb for sulfur is weaker than that of iron. Hence it may be concluded that, as expected, the removal of Sn and Sb with FeS-$NaS_{0.5}$ flux is not effective. Among the alloying elements, the distribution ratios of Cr, Ni and Mo are about 3, 1.2 and 0.04, respectively. L_{Cr} does not seem to change so much with increasing $X_{NaS_{0.5}}$ in the flux, while L_{Ni} and L_{Mo} decrease obviously.

Thus the loss of these elements is regarded to be insignificant in this process. In contrast, Mn which has strong affinity for sulfur reaches a distribution ratio as high as 400 which increases further with increasing $NaS_{0.5}$ in the flux. This means the loss of Mn during the treatment is inevitable.

5. Conclusions

Chemical equilibrium of copper distribution between FeS-based sulfide flux and Fe-$C_{sat.}$ melt were observed and the following conclusions were made:

(1) L_{Cu} was only 9 at 1673K when pure FeS is used alone despite the high sulfur content of about 1.9 mass% in iron melt.

(2) The addition of alkaline metal sulfides, such as K_2S, Na_2S and Li_2S, and alkaline earth metal sulfides, SrS and BaS, increased L_{Cu}, while [mass%S] was suppressed markedly. However, the increase in L_{Cu} was quite limited. The maximums of L_{Cu} were about 20, 24, 30, 22 and 19 for the fluxes of FeS-K_2S, -Na_2S, -Li_2S, -SrS and -BaS, respectively. The main reason for the increase of L_{Cu} was the significant decrease of $\gamma_{CuS_{0.5}}$ by the addition of these sulfides.

(3) An effective removal of Sn and Sb could not be expected during copper removal by sulfide fluxes. On the other hand, the loss of Cr, Ni and Mo was insignificant but Mn would be lost almost in all.

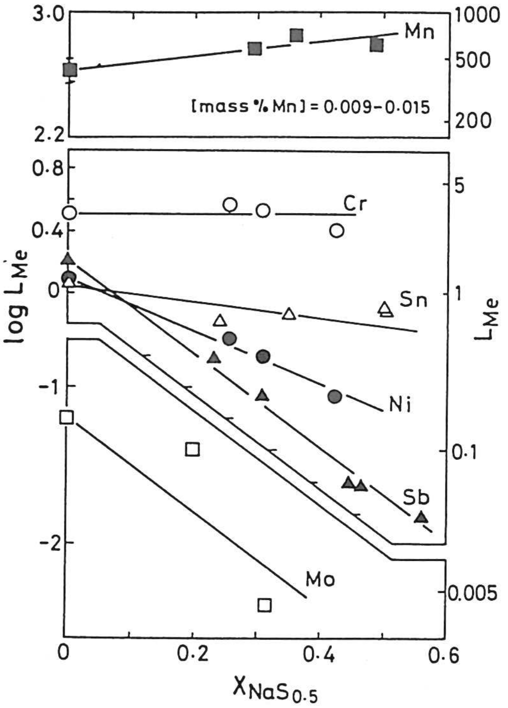

Fig. 10. Effect of $NaS_{0.5}$ content on the distribution ratio of Sn, Sb, Ni, Cr, Mn and Mo between FeS–$NaS_{0.5}$ flux and carbon saturated liquid iron at 1 673 K.

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