Copper Distribution between FeS–Alkaline or –Alkaline Earth Metal Sulfide Fluxes and Carbon Saturated Iron Melt

Chao WANG,¹⁾ Tetsuya NAGASAKA, Mitsutaka HINO and Shiro BAN-YA

Faculty of Engineering, Tohoku University, Aza Aoba, Aramaki, Aoba-ku, Sendai, Miyagi-ken, 980 Japan.

1) Research Student, Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken, 980 Japan.

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Measurements have been made to study the effect of the addition of alkaline or alkaline earth metal sulfide such as Li_2S , K_2S , MgS , CaS , SrS or BaS to FeS on the copper distribution ratio between FeS flux and carbon saturated liquid iron at 1673 K. Since each solubility of MgS and CaS in liquid FeS was limited, no apparent effect of MgS or CaS on the copper distribution ratio was observed. Similar to the effect of Na_2S studied in our previous work, the addition of Li_2S , K_2S , SrS or BaS to FeS increased the copper distribution ratio, $L_{\text{Cu}} = (\text{mass}\% \text{Cu})_{\text{flux}} / [\text{mass}\% \text{Cu}]_{\text{Fe}}$, and L_{Cu} reached maximum value at certain content of these additives in each flux. The maximum values of L_{Cu} measured in each flux were 30, 20, 22 and 19 in FeS– $\text{LiS}_{0.5}$, – $\text{KS}_{0.5}$, – SrS and – BaS fluxes, respectively. The sulfur content in liquid iron also decreased by the addition of these sulfides to FeS.

KEY WORDS: tramp element; recycling of steel scrap; alkaline metal sulfide; alkaline earth metal sulfide; copper removal; physical chemistry; steelmaking.

1. Introduction

The removal of copper from iron melt is necessary if recycled steel scrap is to be reutilized.^{1,2)} The present study focused on the process of copper removal by sulfide fluxes.^{3–10)} It was hoped to reveal the thermodynamic relations existing in the process and the amount of copper it was possible to remove by this method.

As the first step, phase equilibria and thermodynamic properties of Fe–S–C ternary melt was determined as the basic system.¹¹⁾ The distribution ratio of copper between FeS and Fe– C_{sat} melts, the effect of $\text{NaS}_{0.5}$ on the distribution ratio and the sulfur content in iron melt was then investigated at 1673 K.¹²⁾ The copper distribution ratio between sulfide flux and liquid iron, L_{Cu} , was defined by Eq. (1).

$$L_{\text{Cu}} = (\text{mass}\% \text{Cu})_{\text{flux}} / [\text{mass}\% \text{Cu}]_{\text{Fe}} \dots\dots\dots (1)$$

It was observed that copper distribution ratio L_{Cu} was about 9 between FeS and Fe– C_{sat} melts and increased to 24 with the addition of $\text{NaS}_{0.5}$. The sulfur content in Fe– C_{sat} melt could be lowered to about 0.04 mass% at $X_{\text{NaS}_{0.5}} = 0.8$. The main reason for the increase of L_{Cu} is the decrease of the activity coefficient of $\text{CuS}_{0.5}$ by $\text{NaS}_{0.5}$ in the flux.

The alkaline metal sulfides K_2S and Li_2S are known to have physicochemical properties similar to those of Na_2S . It is thus expected that usage of these alkaline metal sulfides may enhance the capacity of sulfide flux for copper removal, in spite of a lack of knowledge of

the physicochemical properties of FeS– K_2S and – Li_2S binaries. The effect of K_2S and Li_2S on copper distribution was therefore investigated in the present work.

The chemical properties of alkaline earth metals are similar to those of alkaline metals, so the study was also extended to their sulfides. The alkaline earth metal sulfides investigated here were MgS , CaS , SrS and BaS , collectively referred to as MS for convenience; alkaline metal sulfides are called $\text{MS}_{0.5}$.

Combined with the results using Na_2S flux,¹²⁾ a systematic analysis was done for the effects of various sulfides in FeS-based flux on copper distribution to determine the maximum copper removal possible with this process.

2. Experimental

The apparatus and operations were the same as described.¹²⁾ The following is a brief description of the experimental conditions.

2.1. Materials

Master fluxes consisted of K_2S and Li_2S of chemical reagent grade (assay: minimum 99.9%), and MgS , CaS , SrS and BaS of guaranteed reagent grade (assay: minimum 99%). These sulfides were respectively well mixed with an appropriate amount of iron sulfide powder to make up a predetermined composition. The mixture of FeS– $\text{MS}_{0.5}$ was premelted in an iron crucible, and that of FeS–MS was pressed into tablets of 10 mm diameter and 4 to 5 g in weight. The preparation of master

Fe-C alloy and FeS was the same as that given in Ref. 11).

2.2. Procedure

The charge consisted of about 8 to 10 g of each of master Fe-C alloy and sulfide flux. Melting was done in a high frequency induction furnace. Based on the preliminary experiments, the holding time to attain equilibrium was determined as from 30 min to 2 h for the run with FeS-MS_{0.5} flux and as 4 or 5 h for the run with FeS-MS flux. Following these periods, the power was turned off and the sample was quenched with a He jet.

2.3. Chemical Analysis

The analysis of contents of C, S in metal and Cu in both metal and sulfide has been described.^{11,12)} K and Li in sulfides were determined by atomic absorption spectroscopy. The contents of alkaline earth metals, *i.e.* Mg, Ca, Sr and Ba, in sulfides were analyzed by Inductively Coupled Plasma spectroscopy (ICP).

3. Results

Experimental results are shown in Table 1. Similar to the findings in Ref. 12), sulfide contents are defined by cationic fraction.

3.1. Effect of Alkaline Metal Sulfides on Copper Distribution

The increase of L_{Cu} by NaS_{0.5} was found to be hindered if the content of CuS_{0.5} was high in the flux.¹²⁾ Thus this investigation was carried out on two content levels of $X_{CuS_{0.5}}$, one of which was below 0.01 and the other from 0.01 to 0.05.

3.1.1. Effect of Flux Composition on L_{Cu}

Effects of contents of KS_{0.5} and LiS_{0.5} in the flux on copper distribution ratio between FeS-MS_{0.5} flux and carbon saturated iron melt are presented in Figs. 1(a) and 2(a), respectively. The investigated content range of KS_{0.5} was within $X_{KS_{0.5}}=0.55$ because of its high vapor pressure at 1 673 K.

Figures 1(a) and 2(a) show that copper distribution ratio increases with increasing content of either KS_{0.5} or LiS_{0.5} in flux and reaches a maximum of 20 at about $X_{KS_{0.5}}=0.3$ for FeS-KS_{0.5} flux and 30 at $X_{LiS_{0.5}}=0.6$ for FeS-LiS_{0.5} flux. That is, the addition of KS_{0.5} and LiS_{0.5} into FeS has the similar effect on L_{Cu} with that of NaS_{0.5} which increases copper distribution ratio. Also, further increase in MS_{0.5} content tends to lower L_{Cu} slightly after the maximum of L_{Cu} . The data of Imai and Sano^{9,13)} at 1 473 K are also given in Fig. 1, and appear in agreement with the present work.

The effect of CuS_{0.5} content in FeS-LiS_{0.5} flux on L_{Cu} shows the same tendency as that in FeS-NaS_{0.5} flux. That is, a high content of CuS_{0.5} in flux tends to lower copper distribution ratio in the high content range of LiS_{0.5}. On the other hand, no measurable effect of CuS_{0.5} in FeS-KS_{0.5} flux on L_{Cu} is seen in Fig. 1(a), which may be due to the limited composition range in both KS_{0.5} and CuS_{0.5}.

Figure 3 gives a comparison among the effects of

Table 1. Experimental results of copper distribution between FeS-MS_x (M: K, Li, Mg, Ca, Sr, Ba) flux and carbon saturated liquid iron at 1 673 K.

Run No.	Iron phase			Flux phase			L _{Cu}
	[%Cu]	[%S]	[%C]	(%Cu)	(%Fe)	(%M)	
FeS-K ₂ S							
K- 6	0.058	0.53	4.71	1.07	41.66	24.34	18.45
K- 7	0.048	0.93	4.58	0.93	50.66	17.02	19.38
K- 8	0.054	1.13	4.51	0.96	59.15	10.10	17.78
K- 9	0.057	1.45	4.41	0.84	67.64	3.58	14.74
K-11	0.050	0.60	4.69	0.99	45.92	20.48	19.80
K-12	0.053	0.73	4.64	1.01	50.50	16.00	19.06
K-13	0.052	0.82	4.61	1.05	48.83	18.39	20.19
K-15	0.046	0.35	4.77	0.83	35.67	30.33	18.04
K-16	0.19	0.88	4.58	3.89	46.56	15.70	20.47
K-17	0.25	1.12	4.50	4.84	49.33	13.91	19.36
K-18	0.31	1.25	4.45	5.54	51.59	10.50	17.87
K-19	0.25	1.23	4.46	4.39	55.91	7.23	17.56
K-20	0.37	1.38	4.40	5.58	60.53	3.12	15.08
K-22	0.24	0.63	4.66	4.56	40.55	23.34	19.00
K-23	0.25	0.65	4.65	4.98	40.85	19.27	19.92
K-24	0.25	0.37	4.75	4.27	35.10	25.96	17.08
K-25	0.35	0.83	4.58	6.93	43.62	14.50	19.80
K-26	0.22	1.02	4.53	4.48	49.16	11.77	20.36
K-27	0.26	1.19	4.47	4.66	53.19	8.84	17.92
FeS-Li ₂ S							
Li- 7	0.026	1.55	4.38	0.35	57.21	3.42	13.46
Li- 8	0.034	1.86	4.27	0.39	61.32	2.29	11.56
Li- 9	0.028	1.84	4.28	0.29	64.76	1.33	10.39
Li-10	0.033	0.15	4.84	0.95	34.98	13.98	28.70
Li-11	0.027	0.28	4.80	0.86	46.14	9.64	31.85
Li-12	0.030	0.26	4.80	0.89	45.26	9.79	29.67
Li-13	0.079	1.63	4.34	0.98	61.41	3.19	12.41
Li-14	0.096	1.97	4.23	0.95	64.64	1.92	9.90
Li-15	0.081	2.05	4.21	0.92	69.90	1.04	11.36
Li-16	0.029	0.44	4.74	0.88	48.30	7.09	30.35
Li-17	0.028	0.60	4.69	0.78	50.14	6.08	27.86
Li-18	0.058	1.19	4.49	0.85	55.83	4.72	14.66
Li-19	0.277	0.11	4.83	6.02	27.74	15.11	21.74
Li-20	0.224	0.21	4.80	5.59	33.27	11.86	24.94
Li-21	0.210	0.34	4.76	5.43	39.42	9.03	25.88
Li-22	0.206	0.50	4.71	5.81	42.18	7.78	28.20
Li-23	0.321	1.07	4.51	5.22	45.20	5.22	16.26
Li-24	0.469	1.88	4.23	5.35	53.70	3.23	11.40
Li-26	0.207	0.62	4.67	5.35	44.98	6.11	25.86
Li-27	0.338	1.30	4.43	5.49	48.98	4.74	16.25
Li-28	0.556	1.49	4.35	5.59	54.68	2.79	10.06
FeS-MgS							
Mg- 2	0.136	1.52	4.38	1.15	64.21	2.90	8.46
Mg- 3	0.098	1.65	4.34	0.94	67.72	1.13	9.57
Mg- 5	0.071	1.27	4.46	0.59	62.40	3.76	8.27
Mg-10	0.038	1.42	4.42	0.38	63.33	3.25	9.90
FeS-CaS							
Ca- 4	0.088	1.14	4.51	0.77	58.33	7.82	8.75
Ca- 6	0.033	1.66	4.35	0.30	63.75	4.15	8.94
Ca- 7	0.072	1.46	4.41	0.67	62.04	4.45	9.31
Ca- 9	0.035	1.22	4.48	0.36	58.34	6.50	10.17
FeS-SrS							
Sr- 1	0.070	1.52	4.38	0.83	56.66	10.47	11.86
Sr- 2	0.069	1.39	4.43	0.74	61.63	6.39	10.73
Sr- 3	0.067	1.78	4.30	0.70	66.39	3.03	10.45
Sr- 4	0.042	1.24	4.48	0.63	48.37	18.83	15.00
Sr- 7	0.027	0.75	4.65	0.60	42.00	24.53	22.22
FeS-BaS							
Ba- 1	0.044	1.64	4.34	0.49	66.82	3.22	11.14
Ba- 2	0.012	1.73	4.32	0.11	63.91	7.08	9.50
Ba- 3	0.009	1.65	4.34	0.10	58.92	10.97	10.67
Ba- 4	0.029	1.08	4.53	0.49	43.47	25.74	16.79
Ba- 6	0.026	0.67	4.67	0.54	36.56	33.71	20.65
Ba- 9	0.065	0.49	4.72	1.16	30.41	39.99	17.85
Ba-10	0.052	0.45	4.74	0.97	29.60	41.13	18.65
Ba-12	0.087	0.56	4.74	1.57	32.13	37.96	18.05
Ba-13	0.084	0.61	4.68	1.64	34.89	34.23	19.52
Ba-14	0.097	0.87	4.59	1.66	41.83	27.76	17.11

Concentrations are in mass%.

Fig. 1. Variations of (a) L_{Cu} and (b) sulfur content in carbon saturated liquid iron with K_{2S} content in FeS- K_{2S} flux.

Fig. 2. Variations of (a) L_{Cu} and (b) sulfur content in carbon saturated liquid iron with Li_{2S} content in FeS- Li_{2S} flux.

K_{2S} , Na_{2S} and Li_{2S} on L_{Cu} . The data of $x_{CuS_{0.5}} < 0.02$ are shown here in order to approach the practical condition. Accordingly, the increasing magnitude of L_{Cu} is larger in the order of Li_{2S} , Na_{2S} and K_{2S} in the composition range below that corresponding to the maximum of L_{Cu} ; at a given low content of $MS_{0.5}$, the larger the atomic number of the cationic species is, the greater the increasing magnitude of L_{Cu} is. On the other side, the maximum of L_{Cu} is larger in a sequence of K_{2S} , Na_{2S} and Li_{2S} with values of about 20, 24

Fig. 3. Effect of alkaline metal sulfide, $MS_{0.5}$, on L_{Cu} in FeS- $MS_{0.5}$ fluxes.

Fig. 4. Effect of $MS_{0.5}$ on sulfur content in carbon saturated liquid iron in FeS- $MS_{0.5}$ fluxes.

and 30, respectively. That is, the maximum of L_{Cu} is larger at a smaller atomic number of M , the cationic species. Consequently, the content of $MS_{0.5}$ corresponding to the maximum of L_{Cu} is higher in a sequence of K_{2S} , Na_{2S} and Li_{2S} .

3.1.2. Effect of Flux Composition on Sulfur Content in Fe- C_{sat} Melt

A higher sulfur potential in the system is expected to enhance the copper removal because of the greater sulfurization reaction. On the other hand, as a detrimental impurity in steel sulfur content should normally be lowered as much as possible. Figures 1(b) and 2(b) show, respectively, the relations between the equilibrium sulfur content in Fe- C_{sat} melt and the content of K_{2S} or Li_{2S} in flux at different levels of $CuS_{0.5}$. It is seen that the sulfur content in Fe- C_{sat} melt decreases markedly with increasing $MS_{0.5}$ content in FeS-based flux. For example, [mass% S] decreases from about 1.9 at $x_{MS_{0.5}} = 0$ to about 0.1 at $x_{Li_{2S}} = 0.75$.

The influence of $CuS_{0.5}$ in the flux on the sulfur content in Fe- C_{sat} melt does not seem to be clear for the fluxes of FeS- K_{2S} and - Li_{2S} under the present experimental conditions.

Figure 4 shows the relation between sulfur content and the content of $MS_{0.5}$ in FeS- $MS_{0.5}$ fluxes, including the data with Na_{2S} reported in Ref. 12). The concentration of $CuS_{0.5}$ in Fig. 4 is less than 0.02 mole fraction. Accordingly, at a given content of $MS_{0.5}$, the sulfur

content is the lowest by $\text{KS}_{0.5}$, followed by $\text{NaS}_{0.5}$ and $\text{LiS}_{0.5}$ in this order. However, the difference in sulfur content with these three fluxes tends to be negligible with increasing content of $\text{MS}_{0.5}$.

Based on the above results and those with $\text{FeS-NaS}_{0.5}$ flux,¹²⁾ it is concluded that the alkaline metal sulfides are effective in both increasing copper distribution ratio and reducing the sulfur content in Fe-C_{sat} melt. As presented in Fig. 3, though L_{Cu} tends to decrease slightly with greater $\text{MS}_{0.5}$ content after the maximum of L_{Cu} , this decrease is essentially insignificant. In contrast, Fig. 4 shows the sulfur content in Fe-C_{sat} decreases monotonously with increasing $\text{MS}_{0.5}$ content. Therefore, it is better to select a flux of high $\text{MS}_{0.5}$ content, e.g. $X_{\text{MS}_{0.5}} = 0.7$ to 0.8 , so that it is possible to obtain a L_{Cu} between 20 and 30 with $[\text{mass}\% \text{S}]$ in iron below 0.1.

3.2. Effect of Alkaline Earth Metal Sulfides on Copper Distribution

The content of $\text{CuS}_{0.5}$ was adjusted to below 0.03 mole fraction for this part of the experiments in view of practical usage.

3.2.1. Effect of Flux Composition on L_{Cu}

MS generally has high melting points above 2300 K,¹⁴⁾ thus, its solubility in molten FeS at 1673 K must be limited. However, there is little information on the phase diagram of FeS-MS binaries or the solubility of MS in molten FeS around 1673 K. The solubilities of MgS , CaS , SrS and BaS were therefore estimated experimentally in the present work, as shown in the Appendix.

Figure 5 shows the relation between L_{Cu} and X_{MS} in FeS-MS fluxes. The addition of MgS and CaS to molten FeS seems to have little effect on L_{Cu} , but it is difficult to fully define the effect of these sulfides on L_{Cu} from the available data because of the very limited homogeneous liquid range.

L_{Cu} does, however, obviously increase with increasing SrS or BaS content in molten FeS, its maximum value being about 22 with near saturation of SrS . The variation of L_{Cu} against X_{BaS} in the flux appears very close to that with FeS- $\text{MS}_{0.5}$ fluxes. L_{Cu} increases with increasing X_{BaS} when BaS content is low and becomes maximum of about 19 around $X_{\text{BaS}} = 0.25$ until BaS saturation. These data indicate that the maximums of L_{Cu} with FeS- SrS and - BaS fluxes are nearly equivalent to those

Fig. 5. Effect of alkaline earth metal sulfide, MS, on L_{Cu} in FeS-MS fluxes.

with FeS- $\text{MS}_{0.5}$ fluxes.

It is noticed from Fig. 5 that the increase of L_{Cu} by MS is larger in the order of MgS , CaS , SrS and BaS at a given content of MS in the low range, i.e. the larger the atomic number of M is, the greater the value of L_{Cu} is. However, the maximum of L_{Cu} becomes larger with FeS- SrS flux than with FeS- BaS , i.e. the smaller atomic number of M leads to a larger value for the maximum of L_{Cu} . This tendency is coincident with that observed in the fluxes of FeS- $\text{MS}_{0.5}$. It suggests that the effect of $\text{MS}_{0.5}$ and MS in the flux on L_{Cu} may chemically be the same, though the investigated composition range is limited for FeS-MS system.

3.2.2. Effect of the Composition of FeS-MS Flux on the Sulfur Content in Fe-C_{sat} Melt

Figure 6 shows the relation between the sulfur content in Fe-C_{sat} melt and the concentration of MS in the fluxes. The sulfur content decreases monotonously with increasing content of any MS in the flux and becomes a certain value after MS saturation. Also as shown, the difference in sulfur content is negligible at a given MS concentration for four FeS-MS fluxes within the homogeneous liquid range of fluxes. This means that the effects of the four sulfides on the activity of FeS in the flux are the same.

3.3. Copper Distribution Ratio in Mole Fraction

The molecular weights of $\text{MS}_{0.5}$ and MS ranged widely

Fig. 6. Effect of MS on sulfur content in carbon saturated liquid iron in FeS-MS fluxes.

Fig. 7. Effect of $\text{MS}_{0.5}$ or MS on the molar distribution ratio of copper, L'_{Cu} , in FeS- $\text{MS}_{0.5}$ and FeS-MS fluxes.

in the present work. For example, the molecular weight of $\text{LiS}_{0.5}$ was only 22.97 while that of BaS was about 6 times larger at 169.40. Thus the distribution ratio of copper is defined in mole fraction as Eq. (2), and this equation can also reevaluate the results presented in Figs. 3 and 5.

$$L'_{\text{Cu}} = (\text{mol}\% \text{Cu})_{\text{flux}} / [\text{mol}\% \text{Cu}]_{\text{Fe}} \quad \text{.....(2)}$$

Figure 7 shows the relation between L'_{Cu} and the content of $\text{MS}_{0.5}$ and MS in fluxes. Compared with Figs. 3 and 5, the distribution ratio of copper becomes relatively larger in L'_{Cu} for the flux containing a sulfide of large molecular weight such as SrS or BaS. On the contrary, L'_{Cu} for the flux containing $\text{LiS}_{0.5}$ which has the smallest molecular weight becomes relatively smaller. As a result, the maximum of L'_{Cu} with FeS–SrS or FeS–BaS flux becomes the largest, while the maximums with FeS– $\text{MS}_{0.5}$ fluxes are about the same and slightly lower than that with FeS–SrS or FeS–BaS flux.

4. Discussion

4.1. Effect of Alkaline and Alkaline Earth Metal Sulfides on the Activity of FeS in the Fluxes

The reaction of copper removal and that between iron and sulfur are given by Eqs. (3) and (5), respectively.

$$K_3 = a_{\text{CuS}_{0.5}} / (a_{\text{Cu}} a_{\text{S}}^{1/2}) \quad \text{.....(4)}$$

$$K_5 = a_{\text{FeS}} / (a_{\text{Fe}} a_{\text{S}}) \quad \text{.....(6)}$$

From Eqs. (1), (3) and (5), the distribution ratio of copper between flux and iron melt may be written as Eq. (7)¹²⁾ as

$$L_{\text{Cu}} = C' \gamma_{\text{Cu}} a_{\text{FeS}}^{1/2} / \gamma_{\text{CuS}_{0.5}} \quad \text{.....(7)}$$

where C' is about a constant. The value of γ_{Cu} , depending on the composition of Fe– C_{sat} melt, is about constant under the present condition.¹²⁾ Hence, L_{Cu} may be expressed as a function of a_{FeS} and $\gamma_{\text{CuS}_{0.5}}$ which depend on flux composition. That is, it is necessary to reveal the variation of these two thermodynamic quantities for full understanding of the effect of flux composition on copper

distribution.

The expression for a_{FeS} may be written as Eq. (8) from Eq. (6):

$$a_{\text{FeS}} = K_5 a_{\text{Fe}} a_{\text{S}} \quad \text{.....(8)}$$

As a_{Fe} , a_{S} and K_5 are available from Refs. 11) and 12), the activity of FeS can be evaluated using Eq. (8).

Figure 8 shows the relation of $a_{\text{FeS}}^{1/2}$ to the contents of various $\text{MS}_{0.5}$ and MS in fluxes. Generally, $a_{\text{FeS}}^{1/2}$ decreases monotonously with increasing $\text{MS}_{0.5}$ content. But comparatively, among alkaline metal sulfides, $\text{KS}_{0.5}$ seems to be the most effective in decreasing $a_{\text{FeS}}^{1/2}$, followed by $\text{NaS}_{0.5}$. However, no measurable difference is observed between $a_{\text{FeS}}^{1/2}$ and $X_{\text{MS}_{0.5}}$ for three kinds of fluxes when $X_{\text{MS}_{0.5}}$ exceeds 0.5. The effect of MS on $a_{\text{FeS}}^{1/2}$ is considered to be equivalent according to Fig. 8.

4.2. Effects of $\text{MS}_{0.5}$ and MS in Fluxes on $\gamma_{\text{CuS}_{0.5}}$

The activity coefficient of $\text{CuS}_{0.5}$ may be written as Eq. (9) from Eq. (4).

$$\gamma_{\text{CuS}_{0.5}} = K_3 a_{\text{Cu}} a_{\text{S}}^{1/2} / X_{\text{CuS}_{0.5}} \quad \text{.....(9)}$$

Accordingly, $\gamma_{\text{CuS}_{0.5}}$ may be evaluated from Eq. (9).¹²⁾

Figures 9 and 10 present the relations of $\gamma_{\text{CuS}_{0.5}}$ to the contents of $\text{MS}_{0.5}$ and MS in fluxes, respectively. At a given content of $X_{\text{MS}_{0.5}}$ in flux within $X_{\text{MS}_{0.5}} < 0.5$, $\text{KS}_{0.5}$ is relatively the most effective in decreasing $\gamma_{\text{CuS}_{0.5}}$ among the three kinds of additives. But at $X_{\text{MS}_{0.5}} > 0.5$, $\gamma_{\text{CuS}_{0.5}}$

Fig. 9. Variation of $\gamma_{\text{CuS}_{0.5}}$ with $\text{MS}_{0.5}$ content in FeS– $\text{MS}_{0.5}$ fluxes.

Fig. 8. Effect of $\text{MS}_{0.5}$ or MS on $a_{\text{FeS}}^{1/2}$ in FeS– $\text{MS}_{0.5}$ fluxes.

Fig. 10. Variation of $\gamma_{\text{CuS}_{0.5}}$ with MS content in FeS–MS fluxes.

Fig. 11. Relationship between L_{Cu} and sulfur content in carbon saturated liquid iron equilibrated with FeS- $MS_{0.5}$ and FeS-MS fluxes.

becomes nearly equivalent for three FeS- $MS_{0.5}$ fluxes and tends to a constant of about 0.5 with further increasing $X_{MS_{0.5}}$. Topkaya¹⁵⁾ 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 $\gamma_{CuS_{0.5}}^0$ 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 thus suggested that $\gamma_{CuS_{0.5}}$ might not be lowered further, i.e. much lower than 0.5, by the addition of $MS_{0.5}$ to molten FeS.

Figure 10 shows that the effect of MgS and CaS on the activity coefficient of $CuS_{0.5}$ seems not to be significant within the investigated range, though $\gamma_{CuS_{0.5}}$ tends to decrease slightly. In the case of FeS-SrS and -BaS fluxes which have a wider homogeneous liquid range, $\gamma_{CuS_{0.5}}$ decreases notably with increasing contents of SrS or BaS 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} and, similar to that in FeS- $MS_{0.5}$ fluxes, $\gamma_{CuS_{0.5}}$ tends to be a certain value at the composition close to SrS and BaS saturation. This tendency for $\gamma_{CuS_{0.5}}$ to vary suggests that the increase in the capacity of copper removal of FeS-based flux by the addition of $MS_{0.5}$ and MS is limited.

4.3. 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. 11. 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. Accordingly, the system of FeS- $LiS_{0.5}$, among the fluxes investigated, is the most suitable flux for this purpose.

Imai and Sano^{9,13)} substituted part of $NaS_{0.5}$ in FeS- $NaS_{0.5}$ flux by $KS_{0.5}$, $LiS_{0.5}$, CaS, and BaS to examine their effect on L_{Cu} . Their results indicated that L_{Cu} could not be raised by these substitutions. Jimbo *et al.*¹⁰⁾ tested the addition of PbS, MnS and Al_2S_3 into FeS- $NaS_{0.5}$ flux, and reported that there was no beneficial effect on copper distribution.

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

5. Conclusions

Effects of alkaline and alkaline earth metal sulfides on copper distribution between sulfide flux and Fe- C_{sat} melt were investigated at 1673 K and the following conclusions were made:

(1) The addition of alkaline metal sulfides, such as K_2S , Na_2S and Li_2S , and alkaline earth metal sulfides, SrS and BaS, increase copper distribution ratio while markedly suppressing the sulfur content in iron melt. However, the increase in L_{Cu} is quite limited. The maximums of L_{Cu} are 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} is the significant decrease of $\gamma_{CuS_{0.5}}$ by the addition of these sulfides.

(2) Effects of alkaline and alkaline earth metal sulfides on the capacity of copper removal of flux are chemically the same.

(3) It is possible to remove copper by FeS- $MS_{0.5}$ or FeS-MS flux while controlling sulfur content below 0.1 mass%. The expected copper distribution ratio is about 20 to 30.

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Appendix. Solubilities of Alkaline Earth Metal Sulfides in Molten FeS

The activity of sulfur in iron melt is determined by the relation shown in Eq. (6), *i.e.* the equilibrium between sulfide and iron phases. a_{FeS} will remain constant if the flux is saturated with solid MS. It is known that a_{Fe} in the present work is almost constant,¹¹⁾ so a constant a_{FeS} would assure a constant a_{S} at MS saturation. Sulfur content in Fe–C_{Sat.} melt will therefore be constant at MS saturation.

Figure 6 shows that, as expected, the sulfur content tends to be constant beyond a certain concentration of MS in fluxes considered to be saturated with MS. It has been observed after the experiments that an unmelted phase existed in those samples considered to be MS saturation. Accordingly, the solubility of MS in molten

Table 2. Solubility of MgS, CaS, SrS or BaS in liquid FeS at 1 673 K.

	MgS	CaS	SrS	BaS
Solubility	0.125	0.16	0.275	0.36

Solubilities are in mole fraction.

FeS was estimated based on the result in Fig. 6, and these estimated solubility are given in **Table 2**. According to the phase diagram for FeS–CaS system suggested by Heumann,¹⁶⁾ the solubility of CaS in FeS approximates 0.23 mole fraction at 1 673 K, which is somewhat larger than that estimated in the present work. There are few data available on the solubilities of the other MS in molten FeS. It is seen from Table 2 that the solubility of MS in molten FeS is larger in the order of MgS, CaS, SrS and BaS. This order is coincident with that of solubilities of alkaline earth metal oxides, MO, in FeO.¹⁷⁾

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