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OXIDIC AND SULFIDIC DISSOLUTION OF COPPER IN MATTE SMELTING SLAG

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Synopsis: Two kind of equilibrium experiments were carried out in iron crucibles at 1573K. The first experiments were equilibrium between FeO_x-SiO_2-CaO slag and metallic copper to calculate the activity coefficient of $CuO_{0.5}$ in the slag. The other experiments were equilibrium among the slag, matte and metallic copper. Dissolved copper in the slag is to be oxidic and sulfidic for the latter experiment. The concentrations of oxidic and sulfidic dissolution of copper were evaluated. The activity coefficients of $CuS_{0.5}$ in the slag were derived from the experimental data and presented as a function of sulfur content in slag.

Key words: sulfidic dissolution of copper, oxidic dissolution of copper, copper solubility in slag, sulfur solubility in slag, matte smelting, activity coefficient of $CuO_{0.5}$, activity coefficient of $CuS_{0.5}$.

1. Introduction

In practical copper smelting, copper losses in slag due to suspension and dissolution. Sehnalek and Imris pointed out that dissolved copper in sulfur-containing slag is as oxidic and sulfidic[1]. Nagamori assessed oxidic and sulfidic dissolution losses of copper by thermodynamic analysis assuming that the sulfidic dissolution loss of copper was proportional to sulfur content in slag[2].

In order to obtain basic information about oxidic and sulfidic dissolution of copper in FeO_x-SiO_2-CaO slag, equilibrium experiments carried out at 1573K in iron crucibles. In this experimental condition, essential activity such as oxygen, sulfur, copper or iron to calculation of activities of $CuO_{0.5}$ and $CuS_{0.5}$ was measured or evaluated. The oxygen or sulfur partial pressure was considerably lower and the activity of copper was higher than those in practical matte smelting.

2. Experimental

After slag and copper were brought into equilibrium in an iron crucible under argon gas stream for two hours at 1573K, an oxygen sensor was immersed in the metal to measure the oxygen partial pressure and the both phases were sampled quickly. Oxidic dissolution loss of copper and activity coefficient of $CuO_{0.5}$ were derived from this experimental data.

To determine the copper loss in sulfur-containing slag, the three melts of slag, matte and copper were equilibrated in an iron crucible and the oxygen partial pressure was measured also in the system.

3. Results and Discussion

Oxidic dissolution loss of copper was determined by the equilibrium experiment between slag and copper metal at 1573K. The slag composition was varied within homogeneous liquid region of FeO_x-SiO_2-CaO system, and the iron content in metal was around 7.9 mass% for every slag composition. Activity of copper, $a_{Cu(l)}$, and iron, $a_{Fe(s)}$, are 0.94 and 0.88 respectively[3]. Activity coefficient of $CuO_{0.5}$, $\gamma_{CuO0.5}$, is calculated by using the standard free energy of $CuO_{0.5}(l)$ formation, $\Delta G°$, [4] as follows:

$$Cu(l) + 1/4\ O_2(g) = CuO_{0.5}(l),$$

$$\Delta G°/J = -60670 + 21.46T \qquad (1)$$

and

$$(\gamma_{CuO\ 0.5}) = 497 a_{Cu} p_{O2}^{1/4} (n_T)/(\%Cu_O), \qquad (2)$$

where (n_T) is total mole of slag constituent and p_{O2} is oxygen partial pressure defined by $P_{O2}/P°_{O2}$, and P_{O2}(Pa) is measured oxygen pressure and $P°_{O2}$ is the standard oxygen pressure of 101325Pa. $(\%Cu_O)$ is oxidic dissolution loss of copper which is total dissolution of copper in the sulfur-free slag of this equilibrium experiment. The activity coefficient of $CuO_{0.5}$ is shown as Fig. 1. That is 3 to 4 for the

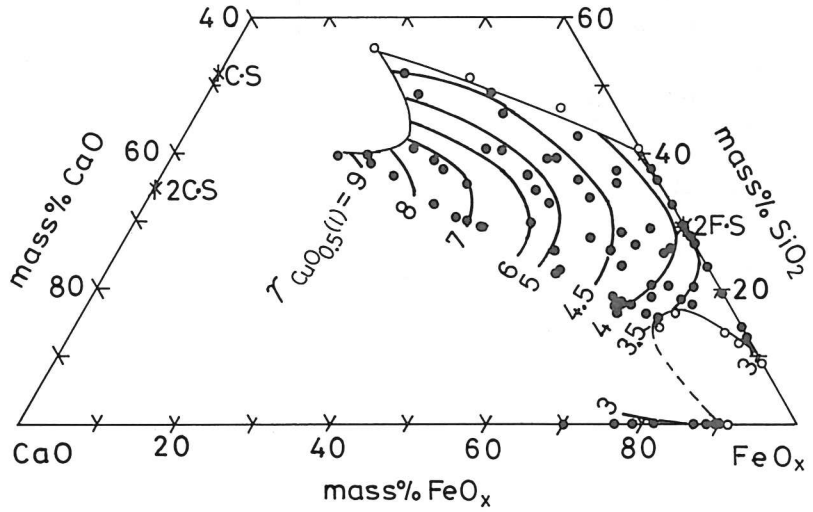

Fig. 1 Activity coefficient of $CuO_{0.5}(1)$ for FeO_x-SiO_2-CaO slag saturated with solid iron at 1573K.

pseudo-binary slag of FeO-SiO_2 or FeO-CaO. On the other hand, the activity coefficient of $CuO_{0.5}$ for the ternary slag of FeO-SiO_2-CaO is higher than that in the binary, and the maximum activity coefficient is observed in the ternary slag whose ratio of CaO to SiO_2 is 1. Formation of stable calcium-silicate solution by acid-base reaction causes that the activity coefficient of $CuO_{0.5}$ increases. Lower oxidic copper dissolution in slag leads to high activity coefficient of $CuO_{0.5}$ as shown by eq. (2).

Copper, sulfur, silica and iron contents in the slag of the slag-matte-copper equilibrium experiment are shown in Fig. 2 as a function of oxygen partial pressure. And copper content in matte is also shown in Fig. 3. Copper and sulfur content in slag increase and copper content in matte decreases as iron content in slag increases with increasing oxygen partial pressure. These composition changes in slag and matte with increasing oxygen partial pressure are mainly due to mutual dissolutions between slag and matte. Slag and matte make homogeneous oxysulfide melt blow the oxygen partial pressure of solid wustite separation. The copper in this sulfur containing slag is dissolved as

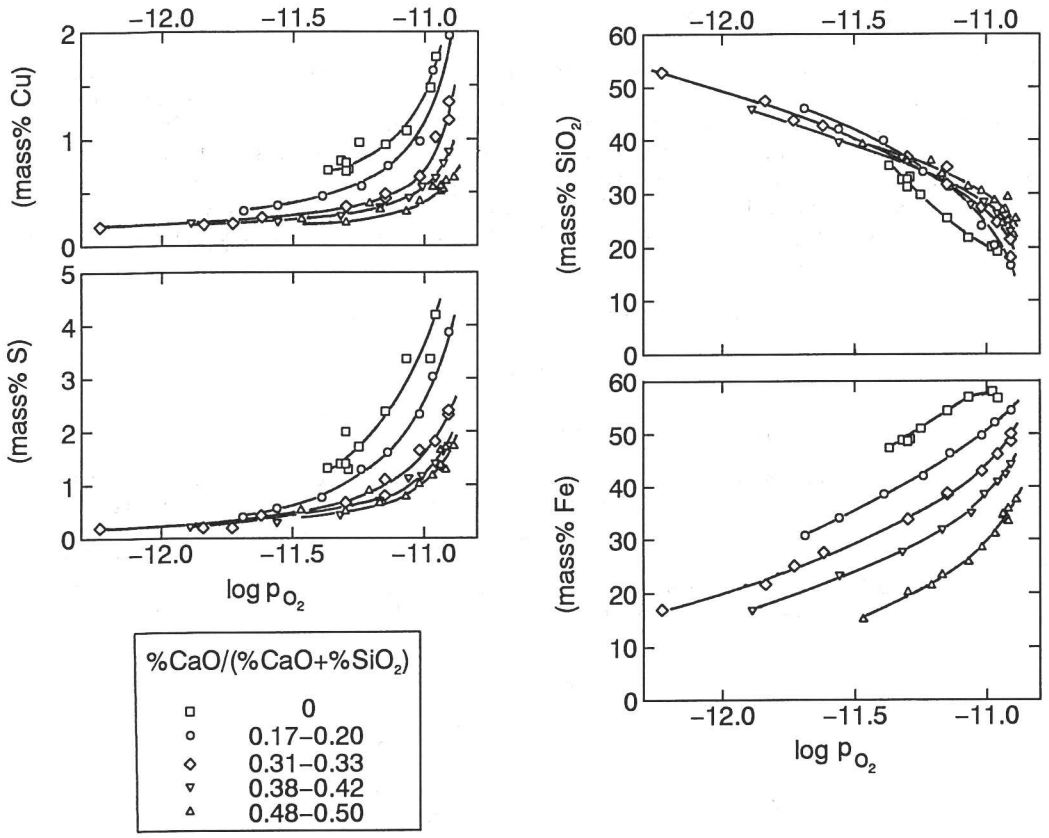

Fig. 2 Copper, sulfur, silica and iron content in the slag equilibrated with matte and copper at 1573K.

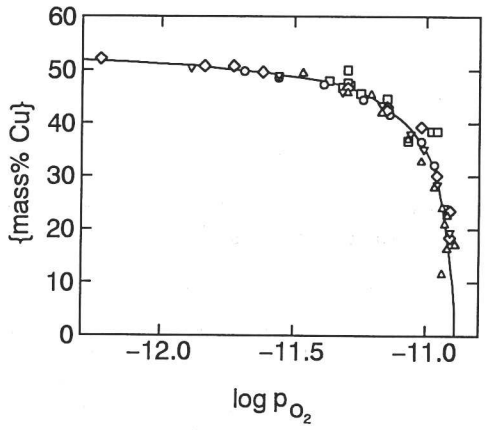

Fig. 3 Copper content in the matte equilibrated with slag and copper.

oxidic and sulfidic. Briefly sulfidic dissolution loss subtracts the oxidic dissolution loss calculated by using the activity coefficient of $CuO_{0.5}$ from total copper loss shown in Fig. 2.

The metal composition of the slag-matte-copper equilibrium experiment is shown as Fig. 4, and the metal consists of the ternary of copper, iron and sulfur. The metal marked by m is equilibrated with matte containing around 50% copper, and the metal marked by n is equilibrated with 10% matte containing around 10% copper. Linear relation between sulfur content and iron is observed. A closed circle

marked by f is phase boundary of Cu-Fe binary alloy which is the metal composition of the slag-copper equilibrium experiments, the other closed circle marked by s is phase boundary of Cu-S binary alloy coexisting with Cu_2S melt.

Sulfur partial pressure, p_{S2}, in Fig. 4(a) was estimated from the data measured by Alcock and Richardson[5]. The activity of Cu(l) in Fig. 4(b) was obtained by integrating the Gibbs-Duhem equation for Cu-Fe-S ternary alloy. Since we know the relations of the sulfur partial pressure and the activity of Cu to the metal composition, we can calculate activity of $CuS_{0.5}$ by standard free energy data Eq. (3)[6] of following reaction:

$$Cu(l) + 1/4\ S_2(g) = CuS_{0.5}(l),$$

$$\Delta G^\circ/J = -71648 + 19.70T. \qquad (3)$$

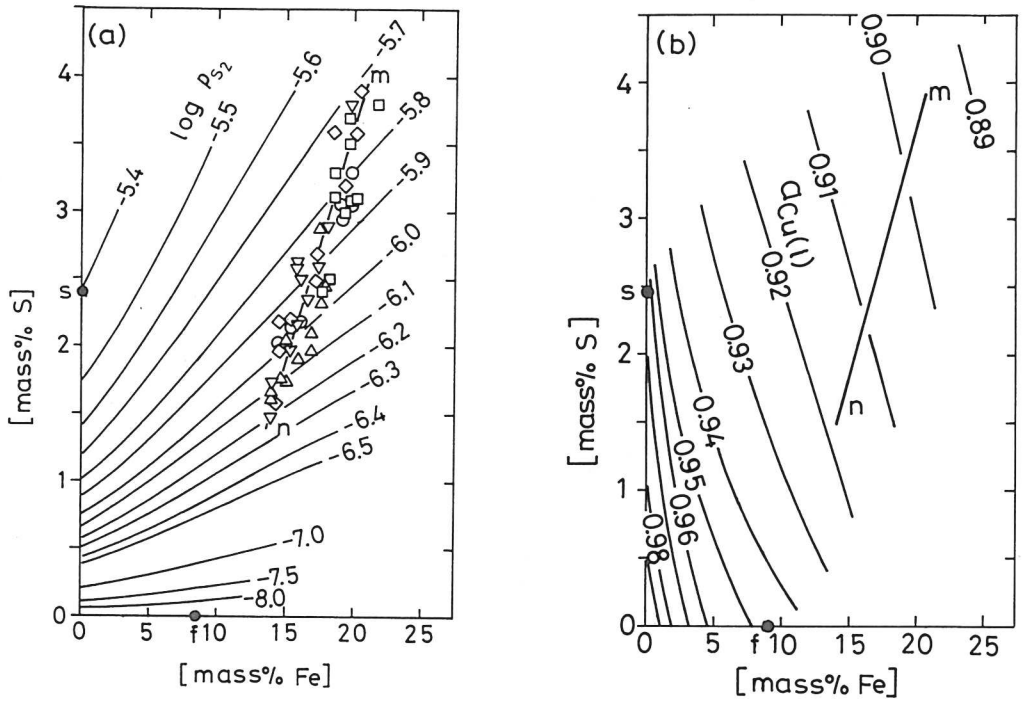

Fig. 4 Composition of the metall with partial pressure of sulfur (a) and activity of copper (b) at 1573K.

Total dissolved copper, $(\%Cu_T)$ in sulfur-containing slag as shown in Fig. 2 is the sum of sulfidic, $(\%Cu_S)$ and oxidic dissolution. Substituting the activity coefficient of $CuO_{0.5}$ in Fig. 1, the activity of Cu in Fig. 3 and the oxygen partial pressure for Eq. (2), we can evaluate oxidic dissolution loss in the sulfur-containing slag, and oxidic and sulfidic dissolutions of copper are shown in Fig. 5. In the figure, R is $\%CaO/(\%CaO+\%SiO_2)$ on a mass% base. Mutual dissolutions between slag and matte with increasing iron content in slag lead to high sulfidic dissolution loss of copper. Most sulfur are associated with iron ion as FeS, and it is assumed here that FeS has the same effect on the activity coefficient of $CuO_{0.5}$ as FeO has.

Since the activity of $CuS_{0.5}$ is estimated as mentioned earlier, activity coefficient of $CuS_{0.5}$, $(\gamma_{CuSO.5})$ is calculated by following equation,

$$(\gamma_{CuSO.5}) = 63.54 a_{CuSO.5}(n_T)/(\%Cu_S). \qquad (4)$$

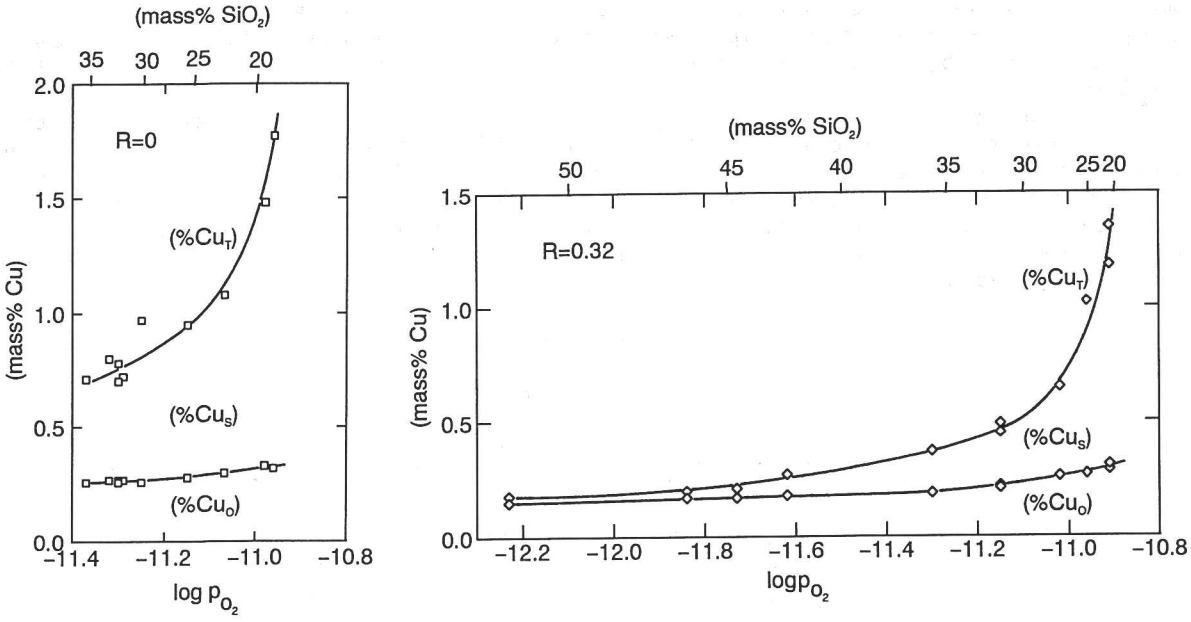

Fig. 5 Oxidic and sulfidic dissolution of copper in slag.

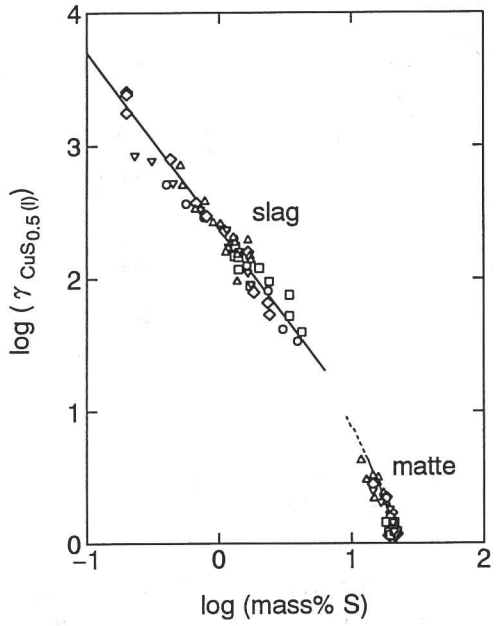

Fig. 6 Relation between activity coefficient of $CuS_{0.5}$ and sulfur content.

Then the logarithmic activity coefficients of $CuS_{0.5}$ for slag and matte are plotted against logarithmic sulfur content shown as Fig. 6.Connecting the plots for the slag has a linear relation and shown by following equation,

$$(\gamma_{CuSO.5}) = 234(\%S)^{-1.33}. \qquad (5)$$

If the relation of Eq. (5) is kept applicable to commercial slags condition, estimations of sulfidic and oxidic dissolution loss of copper in commercial slag are made easy.

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