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DISTRIBUTION EQUILIBRIA OF SOME IMPURITY ELEMENTS IN MOLTEN COPPER - Cu_2O BEARING SLAG SYSTEM

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Synopsis: Phase equilibria studies were conducted for Cu-Cu_2O slag system at 1473K where the distribution ratios (slag/copper) of Fe, Zn, Sn, Pb, Ni and Bi were obtained to explore the possibility of refining Cu under oxidation conditions. The activities of Cu_2O in slags with a few mass% of SiO_2, Al_2O_3 and B_2O_3 were found to be around 0.9 using a zirconia solid electrolyte. The distribution ratios of Fe was over 500, while those of Zn and Sn were in excess of 200. Thus these elements with high distribution ratio can be removed by the oxidation refining step. However, those of Pb and Ni were so low that the simple oxidation cannot be applied of their removal from copper.

Key Words: Distribution ratio, Copper refining, Oxidation refining, Cu_2O slag

1.Introduction

Pyrometallurgical refining processes, socalled fire refining, have not been used in copper refining, after the electrorefining process was developed. The fire refining of copper has been reevaluated recently not only for the removal of the group V elements[1][2] such as As and Sb but also for scrap copper treatment.

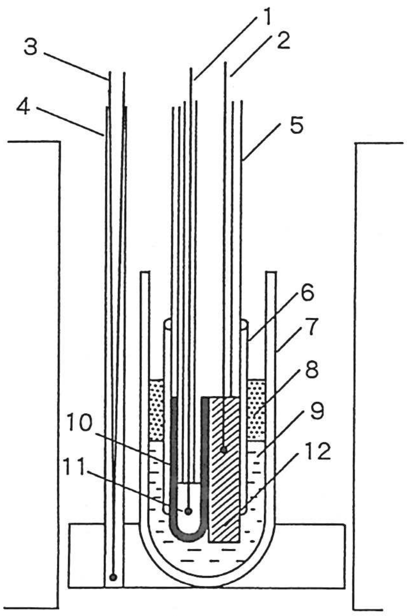
Fe, Zn, Sn, Pb and Ni are considered as the impurity elements in the scrap copper treatment. Since these elements are basic comparing Cu, an oxidizing refining is suitable to the refining process. Thermodynamic studies of a Cu_2O slag have been reported by several investigators[3][4]. However, sufficient thermodynamic data on the oxidizing refining of copper scrap can not be found. Thus distribution ratios of these elements in molten copper - Cu_2O bearing slag system were obtained with other thermodynamic properties in the present study.

2.Experimental

Slag compositions in the present study were mainly decided on the base of Cu_2O - SiO_2 phase diagram[5] to get the low melting point,under 1473K, and a high distribution ratio of Pb.

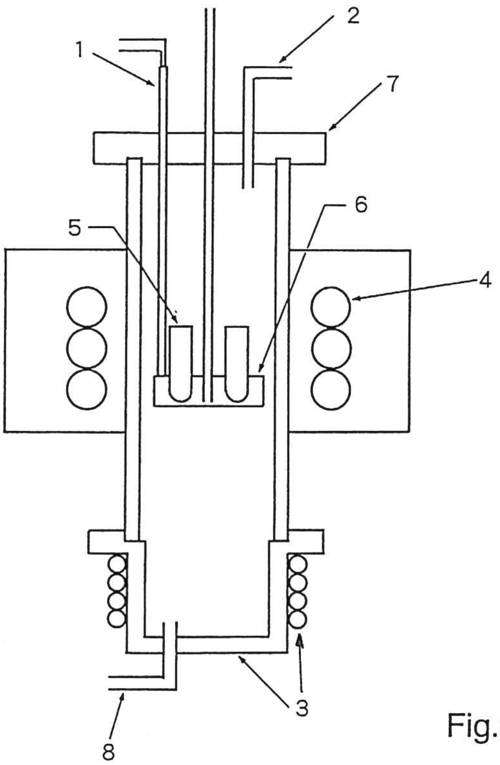
Equilibrium oxygen partial pressures in the system were measured by EMF technique with a zirconia sensor. A schematic cell arrangement of EMF measurements is shown in Fig.1. A mixture of FeO/Fe was used as a reference of the cell and a $LaCrO_3$ rod was applied for the electrode to molten copper.

The experiments for distribution ratio measurements were carried out using the apparatus as shown in Fig.2. Three crucibles containing about 3g of slag and 10g of copper controlled the impurity amount can be kept in the gas tight alumina tube. The furnace was heated to the desirable temperature after the crucibles were set up in the alumina tube and Ar gas flashing. After 5 hours which was already checked for enough time to get an equilibrium in the system, the position of the crucibles was put down to the bottom of the alumina tube where it was cooled by a water jacket. After the equilibrium experiments the slag and copper samples were carefully separated from the crucibles. Impurity elements in the samples were analyzed by AAS and ICAP method.



1 Pt lead wire
2 Pt lead wire
3 Pt・Pt-Rh thermocouple
4 Alumina tube
5 Alumina tube
6 Alumina tube-cement
7 Al_2O_3/MgO crucible
8 Oxide melt
9 Liquid copper
10 ZrO_2 solid electrode
11 Fe-FeO ref. electrode
12 $LaCrO_3$ electrode

Fig.1 Schematic cell arrangement of EMF mesurements



1 Pt・Pt-Rh thermocouple
2 Gas outlet
3 Water jacket
4 SiC heater
5 Alumina tube
6 Support
7 Water jacket
8 Gas inlet

Fig.2 Experimental apparatus

3. Results and Discussions

Slag compositions after the experiments are shown in Table 1. Since alumina and magnesia crucibles were taken in the present experiments, both crucible materials were dissolved into the slag after the experiments. Magnesia was found to be suitable for a refractory. Slag D containing B_2O_3 was chosen to check the effect of acidic oxide on the removal of Pb.

Fig.3 shows relationship between Po_2 calculated by EMF and 1/T in the slag A and C. A linear relationship was obtained in the temperature range of the experiments. Activities of $CuO_{0.5}$ in slag A and C at 1473K were calculated from the data in Fig.3 using equation(1) by the same method of Takeda[4].

$$Cu(l) + \frac{1}{4} O_2 = CuO_{0.5} \qquad K(1) = \frac{aCuO_{0.5}}{aCu\ (Po_2)^{1/4}} \qquad (1)$$

0.98 for slag A and 0.96 for slag C were obtained as the activities of $CuO_{0.5}$. The activity of $CuO_{0.5}$ showed a positive deviation at the composition in the system. This was in good agreement with Takeda's results[4]. It may come from a relatively strong covalent bonding of Cu - O, although Cu_2O is considered to be a basic oxide.

Table 1 Slag compositions after experiments

	Mass %				
	Cu_2O	SiO_2	Al_2O_3	MgO	B_2O_3
slag A	79.6	9.8	10.3	–	–
slag B	82.0	3.3	4.5	–	–
slag C	85.8	3.2	–	1.3	–
slag D	84.2	–	15.7	–	1.0

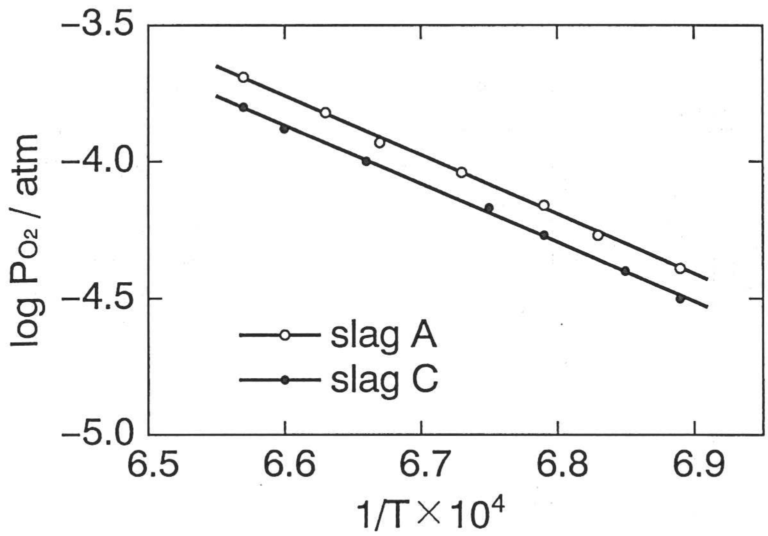


Fig.3 Relation between log Po_2 and 1/T

Table 2 Distribution ratios of impurities between copper and Cu_2O slag

	Distribution ratios					
	Fe	Zn	Sn	Pb	Ni	Bi
slag A	>500	450	143	21	4.6	2.1
slag B	>500	244	90	15	3.4	1.6
slag D	>500	238	52	22	2.6	1.9

Distribution ratios of Fe, Zn, Sn, Pb, Ni and Bi between Cu_2O slag and molten copper, $L_X^{s/Cu}$, are shown in Table 2. $L_X^{s/Cu}$ is defined in equation(2).

$$L_X^{s/Cu} = \frac{(\%X)}{[\%X]} \qquad (2)$$

(%X): mass % of element X in slag
[%X]: mass % of element X in Cu

Distribution ratios of Fe and Zn were over 200 and those of Sn were about 100, while those of Pb, Ni and Bi were less than 20. It was suggested that Fe, Zn and Sn are easily removed from molten copper by oxidizing refining but removal of Pb, Ni and Bi is difficult, especially Ni and Bi. Yazawa et al[6] reported that Ni must be easily oxidized from molten copper than Pb in considering the activity coefficients of both elements in molten copper and free energy changes of oxide formation. The reverse result was found in the experiments. This indicates that the slag composition affect on the order of the distribution ratios.

The oxidation reaction as shown in equation(3) was discussed to clarify the effect of the slag composition on removal of impurities.

$$\underline{X} + \frac{\nu}{2} O_2 = (XO_\nu) \qquad (3)$$

$\underline{X}$: impurity element in copper
ν : valency of impurity oxide
(XO_ν): oxide form in slag

The distribution ratio was derived as follows from equation(3) by Yazawa et al[7].

$$L_X^{s/Cu} = \frac{(\%X)}{[\%X]} = K(3)\frac{(n_T)\cdot \gamma_X \cdot Po_2^{\nu/2}}{[n_T]\cdot \gamma(XO_\nu)} \qquad (4)$$

$L_X^{s/Cu}$: distribution ratio of impurity element X
K(3) : equilibrium constant of oxidation reaction
(n_T) : total molar number in 100g of slag
$[n_T]$: total molar number in 100g of molten copper
γ_X : activity coefficient of impurity element in copper
$\gamma(XO_\nu)$: activity coefficient of impurity oxide in slag
Po_2 : equilibrium oxygen partial pressure

Table 3 Activity coefficients of impurity elements in molten copper.(1473K)

	Fe	Zn	Sn	Pb	Ni	Bi
$\gamma_{\underline{X}}$	35.9	0.142	0.043	5.5	3.3	2.53

Table 4 Activity coefficients of oxides in Cu_2O slag systems.(1473K)

	$\gamma_{(XO_\nu)}$					
	Fe	Zn	Sn	Pb	Ni	Bi
slag A	<270	11	22	0.7	27	0.42
slag B	<270	20	36	1.0	37	0.6
slag D	<270	21	61	0.7	48	0.5

The distribution ratio is a function of K(3), Po_2, $\gamma_{\underline{X}}$ and $\gamma(XO_\nu)$. K(3) and $\gamma_{\underline{X}}$ are automatically fixed when impurity element is decided and Po_2 does not vary very much by the slag composition at equilibrium. Only $\gamma(XO_\nu)$ is influenced by the slag composition. The activity coefficients of the impurity elements in multi-component copper alloy used in the present study are necessary to calculate the values of $\gamma(XO_\nu)$ using equation(3). Those data were selected in Table 3 from a review of Oishi et al[8] and were compensated by only the influence of oxygen. The results are shown in Table 4. Although γ(FeO) was apparently very high comparing other oxides, it may cause from the limitation of Fe analysis in the copper alloy. Since Fe in copper was very easily removed, analytical values of Fe were always less than 1 ppm. Let notice the data of Pb and Ni. It is easily understood from the results in Table 4 that higher distribution ratio of Pb than Ni resulted from the lower γ(PbO) than γ(NiO) in the copper slag.

An activity coefficient of oxide in a multi-component slag are normally understood from the acid - base concept point of view. For instance, when alkaline earth oxides such as CaO which are typical basic oxides make silicate slags, the activity of these oxides show strongly negative deviation from ideal values. There has no consist tendency in the relationship between the values in Table 4 and basicity values of the oxides calculated by optical basicity[9]. It was suggested that the activity coefficient of transition metal oxides can not be arranged only from the concept of basicity.

4. Conclusions

Thermodynamical study was carried out in molten copper - Cu_2O bearing slag system. Over 0.96 for activity values of $CuO_{0.5}$ were obtained at the Cu_2O rich compositions in Cu_2O - SiO_2 slag. The activity of $CuO_{0.5}$ was found to deviate positively from the ideal solution.

Distribution ratios of some impurity elements were also measured in the system. It was clarified from the data that Fe, Zn and Sn are easily removed from molten copper scrap by oxidizing refining but removal of Pb, Ni and Bi is very difficult.

5. References

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