Mechanisms of Oxidation and Vaporization of Antimony from Liquid Copper with CuCl–CaO Fluxes

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In order to clarify the reaction mechanisms of oxidation and vaporization of Sb in liquid copper by using CuCl–CaO fluxes, the vaporization behavior from CuCl–Sb₂O₃ and CuCl–CaO–Sb₂O₃ fluxes and the reaction behavior of Cu₂O between CuCl–Cu₂O flux and liquid copper were observed at 1 423 K with argon gas.

For the vaporization from CuCl–Sb₂O₃ and CuCl–CaO–Sb₂O₃ fluxes, SbCl₃ and SbOCl in flux were observed in the fluxes, and these chloride and oxychloride vaporized to gas phase.

In the reaction between CuCl–Cu₂O and liquid copper, the decomposition of Cu₂O in the flux was confirmed, and the copper weight and oxygen content of copper increased.

The mechanisms of oxidation and vaporization of antimony in liquid copper by using CuCl–CaO fluxes were discussed based on the observed results. The Cu₂O existing in CuCl–CaO flux is dissolved in copper melt, and the oxygen content of copper increases. The antimony in liquid copper is oxidized and removed to slag phase as Sb³⁺. The formed Sb³⁺ in flux vaporizes from flux as SbCl₃ and SbOCl.

KEY WORDS: oxidation and vaporization mechanisms; antimony; copper scrap; chloride; oxychloride.

1. Introduction

Recently, the recycling of metal scrap becomes more and more important from the viewpoints of the efficient use of resources, environmental issues and energy saving. In Japan, about 600 000 tons of copper scrap and about 30 million tons of steel scrap are recycled every year.^{1,2)} Copper next to steel and aluminum is massively produced to meet the social demand. Because copper ore has a short mining life of about 31 years,³⁾ the production of copper has to depend on the recycling of copper scrap in the future. In the recycling process of copper scrap, an important process is the removal of impurities such as Sb and Pb because these impurities affect not only the properties of copper such as the electric conductivity but also the environment. On the other hand, some removed impurities such as Sb used as the semiconductor and electrode materials should be recycled as resources.

The chlorination reaction with chlorine gas or chloride is utilized for the recycling of wastes such as aluminum scrap and steelmaking dust.^{4,5)} For the recycling of copper scrap, Tsukihashi and Hatta,⁶⁾ and Iwasaki and Tsukihashi⁷⁾ reported that the partition ratios of Fe and Pb between CuCl-based flux and liquid copper increased with increasing the content of Na₂CO₃, CaO or BaO in CuCl flux at 1 473 K, and a part of removed Fe and Pb vaporized to gas phase. Mochida and Mikuni⁸⁾ also reported that the concentration of Fe, Pb, Zn or Sn in copper largely decreased with time

by using Ar–10%Cl₂ mixture at 1 473 K. Therefore, the chlorination reaction is effective for the removal of impurities from liquid copper.

In the previous study,^{9,10)} the present authors measured the removal rate of Sb from liquid copper by using CuCl–CaO fluxes at 1 423 K with argon gas. The removal of Sb from liquid copper was difficult by using only CuCl flux as shown in Eqs. (1) and (2). Equation (2) was obtained by the linear regression of calculated free energy change of reaction (1) from 1 273 to 1 673 K by FactSage.¹¹⁾

$$\Delta G_1^\circ = 18\,380 + 35.1T \text{ J/mol}^{(11)} (1\,273\text{--}1\,673 \text{ K}) \dots\dots(2)$$

However, the addition of CaO to CuCl flux was effective for the removal of Sb. The concentration of Sb in liquid copper largely decreased with time and with increasing CaO content. About 99.9% of antimony was removed from liquid copper at 15 min by using CuCl–25mass%CaO flux. Moreover, it was also confirmed that a part of antimony vaporized from flux to gas phase according to the mass balance. Compared with the reported Na₂CO₃ and Cu₂O-based fluxes,^{12,13)} the CuCl–CaO fluxes have a high removal efficiency for Sb from liquid copper. For the CuCl–CaO fluxes, the oxidation reaction of Sb in liquid copper may proceed the removal of antimony from liquid copper because the chlorination reaction of antimony by CuCl is difficult at 1 423 K. The source of oxygen for the oxidation reaction of

Sb may be Cu_2O existing in flux according to the measured weight change of metal and oxygen content of copper. Both of metal weight and oxygen content of metal increased with time and with increasing CaO content. The detailed mechanisms of oxidation and vaporization of Sb in liquid copper with CuCl-CaO fluxes should be investigated.

The purpose of the present study is to clarify the mechanisms of oxidation and vaporization of Sb in liquid copper with CuCl-CaO fluxes. The vaporization experiments of $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes without liquid copper were carried out to investigate the vaporization behavior of Sb in flux, and the reaction behavior of Cu_2O in $\text{CuCl-Cu}_2\text{O}$ flux with liquid copper was observed to confirm the source of oxygen for the oxidation reaction of Sb in copper.

2. Experimental

For the vaporization experiments of $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes at 1423 K, about 1 g of flux prepared by mixing the reagent grade CuCl , Sb_2O_3 and CaO calcined from CaCO_3 at 1273 K was used. About 5 g of flux (Exp. Nos. 16, 17, 24 and 25) was vaporized for 30 or 60 min to collect the enough amount of dusts for the X-ray diffraction (XRD) analysis. The flux specimen was charged in an alumina crucible (outer diameter 21, inner diameter 17 and height 100 mm). The crucible with flux was set in a porous magnesia protection crucible which was located in the hot zone of the mullite tube in an electric furnace. All experiments were carried out at 1423 K with the flow of dehydrated high purity argon (purity 99.999%) of 250 cm^3/min . After the predetermined reaction time, the crucible was quickly taken out from the furnace and then quenched with flushing argon gas.

To observe the reaction behavior of Cu_2O in $\text{CuCl-Cu}_2\text{O}$ flux coexisting with liquid copper, the $\text{CuCl-Cu}_2\text{O}$ flux was prepared by mixing the reagent grade CuCl and Cu_2O . Five grams of the flux and five grams of the high purity copper

(purity 99.99%) were charged in an alumina crucible. The used crucible, temperature, atmosphere and experimental procedure were the same as those of the vaporization experiments of $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes.

Inductively Coupled Argon Plasma Atomic Emission Spectroscopy was used to analyze the compositions of Cu, Sb and Al. The Mohr method was applied for chlorine analysis. For the experiments on the reaction behavior of Cu_2O , the LECO combustion analyzer was used to determine the content of oxygen in copper. For the vaporization experiments of $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes, some residues of fluxes and collected dusts were subjected to the XRD analysis. The basic data of JCPDS card (No. 6-0344, 5-0354, 11-689, 5-0667, 9-117, 1-0248, 21-52, 11-38, 49-1092, 28-775, 1-1104, 26-1053, 20-209 and 29-292) were used as reference.

3. Results and Discussion

3.1. Vaporization Behavior of Sb from $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ Fluxes at 1423 K

The vaporization experiments for $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes were carried out to investigate the vaporization behavior of Sb in flux. The experimental conditions and results are shown in **Table 1**.

The weight of the system before and after the experiments was measured, and the weight loss was calculated. **Figure 1** shows the change in weight loss of $\text{CuCl-Sb}_2\text{O}_3$ fluxes with time at 1423 K. The weight loss increases with time, and slightly decreases with increasing the content of Sb_2O_3 in flux. The CuCl and Sb_2O_3 easily vaporize as CuCl , Cu_3Cl_3 and Sb_4O_6 at high temperature. The calculated vapor pressures of CuCl , Cu_3Cl_3 and Sb_4O_6 are 0.0128, 0.803 and 0.0130 atm for the pure CuCl and Sb_2O_3 at 1423 K, respectively.¹¹⁾ Therefore, the weight loss of the system is mainly due to the simultaneous vaporization of CuCl and Sb_2O_3 . Moreover, it is also possible that the anti-mony compounds such as SbCl_3 vaporizes into gas phase.

Table 1. Experimental conditions and results for the vaporization experiments of flux.

Exp. No.	Time (min)	Initial composition (g)			Final composition (mass%)			Weight loss (g)		
		Sb_2O_3	CuCl	CaO	Cu	Sb	Al	System	Sb	CuCl
1	8	0.999	0.117	-	7.714	72.66	0.729	0.151	0.123	-0.001
2	15	0.998	0.116	-	8.629	70.84	0.909	0.288	0.238	0.003
3	20	0.999	0.116	-	9.321	69.35	1.07	0.374	0.310	0.006
4	8	0.888	0.223	-	13.42	65.66	0.465	0.122	0.086	0.015
5	15	0.889	0.222	-	13.93	64.79	0.669	0.252	0.179	0.033
6	20	0.889	0.224	-	14.13	63.59	0.798	0.314	0.226	0.045
7	8	0.367	0.747	-	45.00	25.36	0.051	0.181	0.070	0.092
8	15	0.366	0.746	-	45.11	26.05	0.043	0.322	0.100	0.190
9	20	0.366	0.746	-	45.15	26.88	0.153	0.409	0.116	0.250
10	8	0.550	0.550	-	34.28	42.18	0.091	0.171	0.067	0.053
11	15	0.550	0.550	-	34.74	44.96	0.298	0.310	0.103	0.120
12	20	0.550	0.550	-	34.00	45.45	0.378	0.352	0.117	0.151
13	8	0.221	0.880	-	56.61	14.14	0.081	0.141	0.048	0.032
14	15	0.220	0.880	-	57.62	14.61	0.061	0.315	0.069	0.174
15	20	0.221	0.879	-	60.49	14.42	0.070	0.408	0.085	0.226
16	60	4.003	0.998	-	-	-	-	1.11	-	-
17	60	0.999	4.002	-	-	-	-	1.35	-	-
18	8	0.350	0.712	0.038	-	-	-	0.115	-	-
19	15	0.350	0.714	0.038	-	-	-	0.200	-	-
20	20	0.349	0.714	0.038	-	-	-	0.248	-	-
21	8	0.324	0.660	0.117	-	-	-	0.056	-	-
22	15	0.324	0.660	0.117	-	-	-	0.102	-	-
23	20	0.324	0.661	0.117	-	-	-	0.128	-	-
24	30	1.589	3.239	0.169	-	-	-	0.482	-	-
25	30	1.470	3.001	0.527	-	-	-	0.235	-	-

Fig. 1. Change in weight loss of CuCl-Sb₂O₃ system with time.

Fig. 2. Change in weight loss of Sb for CuCl-Sb₂O₃ system with time.

The change in weight loss of Sb was also calculated according to the mass balance as shown in Eq. (3).

$$W_{\text{Sb}}^{\text{loss}} = W_{\text{Sb in flux}}^0 - W_{\text{flux}}^t \times \frac{(\text{mass}\% \text{Sb})}{100} \quad \text{.....(3)}$$

where $W_{\text{Sb in flux}}^0$, W_{flux}^t and (mass%Sb) indicate the initial weight of Sb, the final weight of flux and the final concentration of Sb in flux, respectively. **Figure 2** shows the change in weight loss of Sb from CuCl-Sb₂O₃ system with time at 1423 K. The weight loss of Sb increases with time or with increasing the Sb₂O₃ content of flux. The weight loss of Sb is due to the vaporization of Sb₂O₃ and other antimony compounds such as SbCl₃ and SbOCl according to the XRD analysis results in the following sections.

Figure 3 shows the change in weight loss of CuCl-CaO-Sb₂O₃ fluxes with time at 1423 K. The ratio of the initial content of CuCl to that of Sb₂O₃ was fixed at 2.04. The weight loss increases with time, and decreases with increasing the CaO content in flux. The decrease in the weight loss with the addition of CaO may be due to the decrease in the activity coefficient of Sb₂O₃ as acidic oxide because of the addition of CaO as basic oxide.¹³⁾ The weight loss of Sb from the CuCl-CaO-Sb₂O₃ system has not been estimated because of the difficulty of chemical analysis. The analysis results of collected dusts shown in **Table 2** can qualitatively confirm the vaporization of Sb from flux though the col-

Fig. 3. Change in weight loss of CuCl-CaO-Sb₂O₃ system with time.

Table 2. Analysis results of collected dusts.

Flux	Vaporization time (min)	mass%Sb
CuCl-10.6%CaO-29.4%Sb ₂ O ₃	30	5.51
CuCl-3.40%CaO-31.8%Sb ₂ O ₃	30	5.14

Fig. 4. XRD patterns of CuCl-Sb₂O₃ fluxes after the vaporization reaction.

lected dusts also absorb water from air.

Figure 4 shows the XRD patterns of the vaporization residues from CuCl-80mass%Sb₂O₃ (No. 16) and CuCl-20mass%Sb₂O₃ (No. 17) fluxes for 60 min. For CuCl-80mass%Sb₂O₃ flux, the XRD peaks for antimony oxychloride, SbOCl, and cuprous oxide, Cu₂O, were found. The XRD peaks for Cu₂O were also found for CuCl-20mass%Sb₂O₃ flux. It is considered that the observation of XRD peak corresponding to Cu₂O indicates the affinity between Cu⁺ and O²⁻ ions in liquid flux, though the XRD analysis of solidified flux may not represent the structure of liquid flux completely. Though the reactions expressed by Eqs. (4) and (5) were considered, Eq. (5) indicates that the reaction (4) is quite difficult to proceed. Nevertheless, the XRD peaks corresponding to SbCl₃ were observed for corrected dusts and the reason for this fact has not been clarified yet. The formation of SbOCl in flux expressed as reaction (6) was also taken into consideration. The SbCl₃ and SbOCl in flux may vaporize to gas as expressed by Eqs. (7)

Fig. 5. XRD patterns of collected dusts from CuCl-Sb₂O₃ fluxes.

to (9), if these species are thermodynamically preferable. The similar XRD analysis results for all samples shown in Table 1 were obtained. Equations (5) and (8) were obtained by the linear regression of calculated free energy changes of reactions (4) and (7) from 1 273 to 1 673 K by FactSage.¹¹⁾

$$\Delta G_4^\circ = 312\,100 + 15.2T \text{ J/mol}^{(11)} \text{ (1 273–1 673 K) } \dots\dots(5)$$

$$\Delta G_7^\circ = 3\,470 - 43.1T \text{ J/mol}^{(11)} \text{ (1 273–1 673 K) } \dots\dots(8)$$

Figure 5 shows the XRD patterns of collected dusts vaporized from CuCl–80mass%Sb₂O₃ (No. 16) and CuCl–20mass%Sb₂O₃ (No. 17) fluxes for 60 min. The XRD peaks for CuCl, SbCl₃ and Sb₈O₁₁Cl₂ were observed. The coexistence of Sb³⁺ and Cl[–] ions in the fluxes results in the vaporization of antimony chlorides or oxychlorides to gas phase. Binnewies and Schnockel¹⁴⁾ reported that the oxychloride SbOCl was formed in gas phase at 1 300 K from the measurement by the mass spectroscopy combined with Knudsen cell according to the reaction (10). They also reported that the formed SbOCl was not stable in gas phase. Since SbOCl was confirmed in flux as shown in Fig. 4, the antimony may vaporize as SbOCl into gas phase as well as Sb₄O₆, and then SbOCl may react with Sb₄O₆ to form Sb₈O₁₁Cl₂ in the solid state.

Figure 6 shows the XRD patterns of the vaporization residues from CuCl–3.40mass%CaO–31.8mass%Sb₂O₃ (No. 24) and CuCl–10.6mass%CaO–29.4mass%Sb₂O₃ (No. 25) fluxes for 30 min. The XRD peaks for SbOCl and Cu₂O were observed. **Figure 7** shows the XRD patterns of collected dusts from the vaporization of these two fluxes. The XRD peaks for antimony chloride and antimony oxychlorides were observed, which suggests the vaporization of Sb

Fig. 6. XRD patterns of CuCl–CaO–Sb₂O₃ fluxes after the vaporization reaction.

Fig. 7. XRD patterns of collected dusts from CuCl–CaO–Sb₂O₃ fluxes.

from flux as chloride and oxychloride.

3.2. Reaction Behavior of Cu₂O between CuCl–Cu₂O Flux and Liquid Copper at 1 423 K

For the removal of Sb from liquid copper by using CuCl–CaO fluxes at 1 423 K, Sb is considered to be removed by the oxidation reaction. In order to clarify the source of oxygen for oxidation, the reaction behavior of Cu₂O between CuCl–Cu₂O flux and liquid copper was observed at 1 423 K. The initial contents of Cu₂O were 0, 3 and 6 mass%. The experimental conditions and results are shown in **Table 3**.

The solubility of oxygen in copper equilibrated with solid Cu₂O at 1 423 K is 1.06 mass% according to the phase diagram of Cu–O system.¹⁵⁾ From the thermodynamic viewpoint, it can be confirmed that the Cu₂O in flux decomposes into oxygen and copper at 1 423 K as shown in Eqs. (11) and (12). Therefore, in this study the source of oxygen to oxidize Sb in copper may come from the dissolution of Cu₂O existing in CuCl–CaO flux to molten copper.

Table 3. Experimental conditions and results for the reaction behavior of Cu₂O.

Exp. No.	Time (min)	Initial composition (g)			Final composition (mass%)			Weight change (g)		
		Cu	CuCl	Cu ₂ O	Cu _{in flux}	Cl _{in flux}	O _{in metal}	System	Flux	Metal
26	15	5.010	5.006	-	68.48	33.67	0.0829	0.371	0.351	-0.020
27	30	5.003	5.004	-	66.80	33.39	-	0.636	0.610	-0.026
28	45	5.008	5.004	-	64.61	32.52	-	0.858	0.844	-0.014
29	15	5.014	4.845	0.151	70.10	32.36	0.258	0.284	0.300	0.016
30	15	5.013	4.702	0.302	65.06	31.61	0.381	0.254	0.326	0.072

Fig. 8. Change in weight loss of CuCl–Cu₂O system with time.

$$\Delta G_{11}^{\circ} = 25\,840 - 18.0T \text{ J/mol}^{(11,16)} (1\,383\text{--}1\,693 \text{ K}) \dots(12)$$

Figure 8 shows the change in weight loss of CuCl–Cu₂O system with time at 1423 K. The weight loss increases with time, and slightly decreases with increasing the content of Cu₂O in flux. The weight loss of the system is mainly due to the vaporization of CuCl from the flux.

Figure 9 shows the weight change of copper with time at 1423 K. The measured oxygen contents of copper are also shown in this figure. The weight of copper coexisting with CuCl flux decreases with time and the molar ratio of Cu to Cl in flux is 1.12. For the CuCl–Cu₂O fluxes, both of copper weight and oxygen content of copper increase with increasing the Cu₂O content. It can be confirmed that the increase in copper weight and oxygen content of copper is due to the dissolution of Cu₂O existing in the CuCl–CaO flux to molten copper. Therefore, the source of oxygen for the removal reaction of Sb by using CuCl–CaO fluxes is Cu₂O in flux as shown in Eqs. (11) and (12).

3.3. Mechanisms of Oxidation and Vaporization of Sb by Using CuCl–CaO Fluxes at 1423 K

In the previous study,^{9,10)} it was reported that the removal of Sb from liquid copper was difficult by using only CuCl flux, while the addition of CaO to CuCl flux was effective for the removal of Sb at 1423 K with argon atmosphere. Moreover, a part of Sb vaporized from flux to gas phase. The oxidation reaction of Sb in liquid copper may proceed the antimony removal and the removed antimony vaporizes from flux as antimony chloride and oxychloride.

For the removal of Sb by using CuCl–CaO fluxes at 1423 K, Cu₂O is formed by the reaction expressed by Eqs. (13) and (14). Equation (14) was obtained by the linear re-

Fig. 9. Weight change of metal coexisting with CuCl–Cu₂O system with time.

gression of calculated free energy change of reaction (13) from 1273 to 1673 K by FactSage.¹¹⁾ As described in the previous section, oxygen is supplied by the dissolution of Cu₂O existing in the flux into liquid copper according to reaction (11), and oxidizes Sb in copper as shown in reaction (15). The overall oxidation reaction of Sb can be expressed by reaction (16). The addition of CaO increases CaO activity in the flux. Moreover, the oxygen content in copper also increases with increasing CaO content in the CuCl–CaO fluxes. Therefore, the oxidation reaction of Sb in liquid copper can be accelerated because of the increase in CaO activity in the flux and the oxygen content in copper with increasing CaO content.

$$\Delta G_{13}^{\circ} = -77\,260 + 26.4T \text{ J/mol}^{(11)} (1\,273\text{--}1\,673 \text{ K}) \dots(14)$$

The removed antimony in flux may vaporize from flux as forms of Sb₄O₆, SbCl₃ and SbOCl as expressed by reactions (4) to (9). In Sec. 3.1, the vaporization of SbCl₃ and SbOCl from CuCl–Sb₂O₃ and CuCl–CaO–Sb₂O₃ fluxes have been confirmed according to the XRD analysis results of collected dusts.

4. Conclusions

In order to clarify the mechanisms of oxidation and vaporization of Sb from liquid copper by using CuCl–CaO fluxes, the vaporization behavior of CuCl–Sb₂O₃ and CuCl–CaO–Sb₂O₃ fluxes and the reaction behavior of Cu₂O between CuCl–Cu₂O flux and liquid copper were observed

at 1423 K with argon atmosphere.

For the vaporization experiments of $\text{CuCl-Sb}_2\text{O}_3$ and $\text{CuCl-CaO-Sb}_2\text{O}_3$ fluxes, antimony vaporized from fluxes as forms of Sb_4O_6 , SbCl_3 and SbOCl .

For the reaction of Cu_2O between $\text{CuCl-Cu}_2\text{O}$ flux and liquid copper, the dissolution of Cu_2O existing in flux was confirmed, and the copper weight and oxygen content of copper increased.

Based on the experimental results, the mechanisms of oxidation and vaporization of Sb by using the CuCl-CaO fluxes were discussed. The Cu_2O existing in CuCl-CaO flux dissolved and resulted in an increase of oxygen content of copper. The antimony in liquid copper was oxidized and removed to flux. The antimony in flux vaporized as forms of Sb_4O_6 , SbCl_3 and SbOCl from flux.

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