

# Oxidation Rate of Impurities in Liquid Copper by Gas and Slags

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## ABSTRACT

To develop an efficient refining method of copper scrap, kinetic behaviors of oxidation of some impurities in liquid copper have been investigated by blowing air or using  $B_2O_3-Cu_2O$  slags. Zn and Sn were removed down to less than 0.2%, however Pb was hard to be removed by blowing air on to liquid copper containing 1% of each impurity elements. On the other hand, Pb content in liquid copper was down to 0.01% by using  $B_2O_3-Cu_2O$  slags. The reaction model based on the two-film theory could simulate the kinetic behavior of removal of impurities from liquid copper.

## 1. INTRODUCTION

The recycling of valuable resources has currently become a worldwide subject in the industries from the viewpoint of saving energy and environmental protection. In the case of recycling of copper scrap, it is very important to develop the technology for the removal of impurities such as Fe, Zn, Sn, Pb and Ni from copper scrap. These impurities have higher affinity to oxygen than copper does; therefore their removal from liquid copper has been studied by an oxidation method<sup>1-3</sup>. The distribution ratio of impurities, such as Fe, Zn and Sn, between  $Cu_2O$ -based slags and liquid copper has been measured by Fujisawa *et al.*<sup>4</sup>. Oosumi<sup>5</sup> also measured the distribution ratio of impurities between  $Cu_2O$ -based slags and liquid copper, and the oxidizing rate of impurities in liquid copper by  $Cu_2O$ -based slags. However the oxidizing mechanism and, especially, kinetic behavior of removal of impurities in liquid copper have not been well understood.

In the present study, the kinetic behavior of removal of some impurities (Zn, Sn and Pb) from liquid copper has been investigated by blowing air or using  $B_2O_3-Cu_2O$  slags. The experimental results were simulated by a kinetic model developed on the basis of

the two-film theory.

## 2. EXPERIMENTAL PROCEDURES

A vertical electric resistance furnace<sup>6</sup> was employed for each experiment. About 200 g of electrolytic copper was first raised to the fixed temperature and melted in an alumina crucible (36mm ID) under argon atmosphere.

In experiments of air blowing, after the desired amounts of Zn, Sn and Pb were added into liquid copper, the first metal sample was taken by silica tube. Air through an alumina tube (4mm ID) was blown onto the liquid copper surface at the flow rate of 300 to 1000 cm<sup>3</sup>/min, and the distance of the tip of the tube from the liquid copper surface was kept 55mm. And then metal samples were taken at proper time intervals.

In experiments with B<sub>2</sub>O<sub>5</sub>-Cu<sub>2</sub>O slags, after 0.1mass% Pb were added into liquid copper, the first metal sample was taken by silica tube. At this moment, 20~40 g of liquid slag was brought into contact with the liquid copper, which was taken as the starting time of the slag-metal reaction. During the reaction, several metal samples were taken at predetermined time interval.

After a certain reaction time period for each experiment, the alumina crucible was withdrawn from the furnace and quenched rapidly in water. The reacted slag sample was collected from the crucible. The compositions of these metal and slag samples were determined by chemical analysis to follow the progress of reactions.

## 3. EXPERIMENTAL RESULTS

### 3.1 Air Blowing

Experimental conditions, final slag weights, and initial and final compositions of metals are shown in Table 1. Only a thin layer of slag was formed on a metal surface by 300cm<sup>3</sup>/min air blowing, so that the slag could not be separated from the metal after experiments.

The effect of flowing rate of air on the variation of the metal compositions, containing about 0.5~1.0 mass% Zn, Sn and Pb initially, with time is shown in Fig. 1. The oxidation of only Zn and Sn proceeded at the early stage of experiment. As Zn and Sn contents decrease, the oxygen content in copper increased and then the oxidation of Pb started after the oxygen content reached some critical value depending on flowing rate of air. The oxidation rate of these elements increased with increasing air flowing rate as shown in Fig.1.

Figure 2 shows the effect of air flowing rate on the oxidation behavior of the metal, containing about 1.0 mass% Pb only initially with time. The oxidation rate of Pb

increased with increasing flowing rate of air. However the oxidation rate of Pb in Cu-Pb-O metal was somewhat smaller than that in Cu-Zn-Sn-Pb-O metal. These results suggested that the activity coefficients of PbO decrease by the coexistence of ZnO and SnO<sub>2</sub> in Cu<sub>2</sub>O-based slag. The amount of formed slag increased with increasing flowing rate of air as shown in Table 1. And the results of chemical analysis of formed slag indicated that the content of Cu<sub>2</sub>O in the slag was about 80mass%. These results indicate that the oxidation rate of impurities and also the loss of Cu into the slag increased with increasing flowing rate of air.

Figure 3 shows the effect of temperature on the oxidation behaviors of Zn, Sn and Pb with time. Although the oxygen content in liquid copper increased more rapidly at higher temperature, the oxidation rate of Zn and Sn decreased with increasing temperature, because oxidation of these elements is exothermic reaction. No effect of temperature on the oxidation of Pb was observed as shown in Fig.3.

It is found from this experiments that Zn and Sn could be removed down to about 0.08mass% and to about 0.03 mass% as shown in Table 1 (Run No. Cu-9). However, it is hard to remove Pb down to 0.1 mass% by blowing air onto liquid copper.

### 3.2 B<sub>2</sub>O<sub>3</sub>-Cu<sub>2</sub>O Slag

Initial compositions of the slag and the metal used in this study are shown in Table 2. All experiments were conducted at 1200°C. Table 3 shows final compositions of the slag and the metal. A sound slag for chemical analysis could not obtained for Run No. A-1 and A-2 in Table 3. The contents of Al<sub>2</sub>O<sub>3</sub> originated from the crucibles used in this study.

Figure 4 shows the change of Pb and O contents in liquid copper during the reaction with Cu<sub>2</sub>O-based slag containing about 5~6 mass% SiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub>. Pb content in copper decreased with time, and then finally reached 0.003 mass% for B<sub>2</sub>O<sub>3</sub> containing slag. On the other hand, in spite of the oxygen content is higher, the oxidation rate of Pb and the final Pb content in copper by using SiO<sub>2</sub> containing slag are slower and larger, respectively, than those by using B<sub>2</sub>O<sub>3</sub> containing slag.

Figure 5 shows the effect of B<sub>2</sub>O<sub>3</sub> content in Cu<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> slag on the oxidation behavior of Pb in liquid copper. The content of oxygen in copper increased with increasing Cu<sub>2</sub>O content of slag, and the removal of Pb from liquid copper was promoted as shown in Fig.5. In the case of 100 mass% B<sub>2</sub>O<sub>3</sub> slag, the amount of oxygen available for oxidation of Pb is so smaller that the oxidation rate of Pb and the final Pb content are much slower and larger than those of the other slag systems.

It is found from Figs. 4 and 5 that the addition of SiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub> is effective for the removal of Pb from liquid copper, and Pb content in liquid copper was down to

0.003mass% by using B<sub>2</sub>O<sub>3</sub>-Cu<sub>2</sub>O slags as shown in Table 3 (Run No. B-4) .

#### 4. DISCUSSION

##### 4.1 Distribution Ratios and Activity Coefficient

The following reactions are considered to occur simultaneously at the slag-metal interface. And the equilibrium constant,  $K$ , for each reaction is given as function of temperature<sup>6</sup>.



$$\log K_{Zn} = \log \frac{a_{ZnO}}{a_{Zn}a_O} = \frac{12755}{T} - 6.62$$



$$\log K_{Sn} = \log \frac{a_{SnO_2}}{a_{Sn}a_O^2} = \frac{19648}{T} - 11.4$$



$$\log K_{Pb} = \log \frac{a_{PbO}}{a_{Pb}a_O} = \frac{7617}{T} - 6.15$$



$$\log K_{Cu} = \log \frac{a_{CuO_{0.5}}}{a_{Cu}a_O^{0.5}} = \frac{842}{T} - 0.54$$



$$\log K_{O_2} = \log \frac{a_o^2}{P_{O_2}} = \frac{8916}{T} - 1.94$$

Here  $a_M$  and  $a_O$  are the activities of elements in liquid copper referred to the infinite dilute solution, and  $a_{MO}$  is the Raoultian activity of oxide in slag.  $P_{O_2}$  is oxygen partial pressure in atm. There are few available values of  $\gamma_{Zn}$ ,  $\gamma_{Sn}$  and  $\gamma_{Pb}$  in slags containing B<sub>2</sub>O<sub>3</sub> as used in this study. Therefore we estimated the value of  $\gamma_{Pb}$  based on the experimental results by using Cu<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> slag. The distribution ratio of Pb,  $L_{Pb}$ , can be expressed as follow in accordance with Eq. (3) .

$$L_{Pb} = \frac{(\% \text{Pb})}{[\% \text{Pb}]} = K_{Pb} \frac{(n_T) \gamma_{Pb}}{[n_T] \gamma_{PbO}} P_{O_2}^{1/2} \quad \text{.....(6)}$$

Where,  $(n_T)$  and  $[n_T]$  are the sum of moles of each element included in 100 g of slag and of metal, and  $\gamma$  is the Raoultian activity coefficient. Since the activity of oxygen could be defined as  $a_O = P_{O_2}^{1/2}$ ,  $P_{O_2}^{1/2}$  can be expressed of activity coefficient of

oxygen,  $\gamma_o$  and the oxygen content,  $X_o$  .

$$a_o = \gamma_o \cdot X_o = P_{O_2}^{1/2} \dots\dots\dots(7)$$

The values of distribution ratio,  $L_{Pb}$  , and  $P_{O_2}^{1/2}$  , obtained in this study are shown in Table 3. In the calculation, activity coefficient of oxygen ( $\ln \gamma_o^0 = 4.734 - 9462/T$ )<sup>7</sup>, interaction parameter ( $\epsilon_o^o = 11.5 - 27660/T$ )<sup>2</sup> and oxygen content determined in the present results were used. The relationship between  $L_{Pb}$  and  $P_{O_2}^{1/2}$  is shown in Fig. 6. The literature values for FeO-CaO-SiO<sub>2</sub> slag by Hino *et al.*<sup>8</sup> and Takeda *et al.*<sup>7</sup>, and for Cu<sub>2</sub>O-SiO<sub>2</sub> slag by R. P. Das *et al.*<sup>1</sup> are also shown in Fig.6. The obtained values of  $L_{Pb}$  in this study are larger than the literature values. The estimated values of  $\gamma_{Hb}$  from the present results are also shown in Table 3. In the calculation, the values of  $[n_T] = 100/M_{Cu} = 1.57$  and  $\gamma_{Hb} = 5.5$  were used. The values of 0.07 to 0.84 for  $\gamma_{Hb}$  were estimated. These values are smaller than those reported for slags without B<sub>2</sub>O<sub>3</sub><sup>1,7,8</sup>, but they show a tendency to increase with increasing the content of B<sub>2</sub>O<sub>3</sub> in slag. The reason for such an increase in  $\gamma_{Hb}$  does not clear now. B<sub>2</sub>O<sub>3</sub>-based slags generally have a large immiscibility gap at low temperature. Such a nature tends to induce the increase in activity coefficient of a solute, so that it was estimated that the value of  $\gamma_{Hb}$  increased in spite of the addition of much B<sub>2</sub>O<sub>3</sub>. The obtained value of  $\gamma_{Hb} = 0.07$  is smaller than the literature values of  $\gamma_{Hb} = 3.2$  for CaO-Fe<sub>2</sub>O<sub>3</sub> and 0.4 for CaO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> by Takeda *et al.*<sup>7</sup>, of  $\gamma_{Hb} = 0.15 \sim 0.6$  for Cu<sub>2</sub>O-CaO-FeO-SiO<sub>2</sub> slag by Hino *et al.*<sup>8</sup> and of  $\gamma_{Hb} = 0.08 \sim 0.9$  for Cu<sub>2</sub>O-SiO<sub>2</sub> slag by R. P. Das *et al.*<sup>1</sup> It is speculated from these results that Cu<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> slag is useful to the oxidation of Pb in liquid copper.

## 4.2 Kinetic Model

In the development of simultaneous reaction model for the present work, it was assumed that chemical reactions at the metal surface proceed so fast that they are in equilibrium with gas or slag during reactions. A kinetic reaction model for oxidizing behavior of impurities in liquid copper has been developed on the basis of the two-films theory<sup>6</sup> and has been compared to the experimental results. In this model, O<sub>2</sub> gas is assumed to react directly with metal through slag phase.

Then the flux of oxygen,  $\dot{n}_{O_2}$  , can be expressed by the following equation.

$$\dot{n}_{O_2} = Ak_g'(P_{O_2} - L_o^* a_o^*) \dots\dots\dots(8)$$

Where,  $k_g'$  is apparent mass transport coefficient of oxygen in gas phase (mol/cm<sup>2</sup> · atm · s).  $A$  and  $P_{O_2}$  are interfacial area (cm<sup>2</sup>) and oxygen partial pressure (atm) of the gas, and  $L_o^*$  is the distribution ratio of oxygen between gas and metal. The change of

each element in the metal with reaction time can be given by the following equations:

$$-\frac{d[\%Zn]}{dt} = \frac{Ak_{Zn}}{W_m} \{L_{Zn}^* [\%Zn] - (\%Zn)\} \quad \dots\dots\dots(9)$$

$$\frac{1}{k_{Zn}} = \frac{L_{Zn}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \quad \dots\dots\dots(10)$$

$$-\frac{d[\%Sn]}{dt} = \frac{Ak_{Sn}}{W_m} \{L_{Sn}^* [\%Sn] - (\%Sn)\} \quad \dots\dots\dots(11)$$

$$\frac{1}{k_{Sn}} = \frac{L_{Sn}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \quad \dots\dots\dots(12)$$

$$-\frac{d[\%Pb]}{dt} = \frac{Ak_{Pb}}{W_m} \{L_{Pb}^* [\%Pb] - (\%Pb)\} \quad \dots\dots\dots(13)$$

$$\frac{1}{k_{Pb}} = \frac{L_{Pb}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \quad \dots\dots\dots(14)$$

$$-\frac{d[\%O]}{dt} = \frac{Ak_m \rho_m}{W_m} \left\{ [\%O] - \frac{a_o^*}{f_o} \right\} \quad \dots\dots\dots(15)$$

$$-\frac{d(\%CuO_{0.5})}{dt} = \frac{Ak_s \rho_s}{W_s} \left\{ (\%CuO_{0.5}) - L_{CuO_{0.5}}^* a_o^{*0.5} \right\} \quad \dots\dots\dots(16)$$

Where,  $k_i$  ( $i = Zn, Sn, Pb$ ),  $W$ ,  $\rho$ ,  $L$ ,  $k$ , and  $f$  are overall mass transfer coefficient (cm/s), weight (g), density (g/cm), distribution ratio, mass transport coefficient (cm/s) and Henrian activity coefficient in metal. The symbols of m and s indicate metal and slag, and \* shows interface. For the case of mass transport controlled reaction, the interfacial distribution ratio,  $L_i^*$ , of each element can be expressed as a function of the interfacial oxygen activity,  $a_o^*$ , and the apparent equilibrium constant, B, as follow:

$$L_{Zn}^* = \frac{(\%Zn)^*}{[\%Zn]^*} = B_{Zn} a_o^* \quad \dots\dots\dots(17)$$

$$L_{Sn}^* = \frac{(\%Sn)^*}{[\%Sn]^*} = B_{Sn} a_o^{*2} \quad \dots\dots\dots(18)$$

$$L_{Pb}^* = \frac{(\%Pb)^*}{[\%Pb]^*} = B_{Pb} a_o^* \quad \dots\dots\dots(19)$$

$$L_{CuO_{0.5}}^* = \frac{(\%CuO_{0.5})^*}{a_o^{*0.5}} \quad \dots\dots\dots(20)$$

$$L_o^* = \frac{P_{O_2}^*}{a_o} \quad \dots\dots\dots(21)$$

On the assumption that no accumulation of oxygen at the slag-metal interface occurs, the following mass balance equation of oxygen can be obtained.

For experiments of air blowing:

$$\begin{aligned} & \frac{W_m}{100M_{Zn}} \frac{d[\%Zn]}{dt} + \frac{2W_m}{100M_{Sn}} \frac{d[\%Sn]}{dt} + \frac{W_m}{100M_{Pb}} \frac{d[\%Pb]}{dt} + 2\dot{n}_{O_2} \\ &= \frac{W_m}{100M_O} \frac{d[\%O]}{dt} + \frac{0.5W_m}{100M_{CuO_{0.5}}} \frac{d(\%CuO_{0.5})}{dt} \quad \dots\dots\dots(22) \end{aligned}$$

For experiments with  $Cu_2O-B_2O_3$  slag:

$$\frac{W_m}{100M_{Pb}} \frac{d[\%Pb]}{dt} = \frac{W_m}{100M_O} \frac{d[\%O]}{dt} + \frac{0.5W_m}{100M_{CuO_{0.5}}} \frac{d(\%CuO_{0.5})}{dt} \quad \dots\dots\dots(23)$$

Under the known values of  $k_p$ ,  $k_s$ ,  $k_g'$ ,  $B_{Zn}$ ,  $B_{Sn}$ ,  $B_{Pb}$ ,  $L_{CuO_{0.5}}^*$  and  $L_o^*$ , a value of  $a_o^*$  depending on slag and metal composition can be determined from Eqs. (22) and (23). By using the obtained values of oxygen activity, concentration change of each element in metal with reaction time can be calculated from Eqs. (7)~(14).

In the case of air blowing experiments, the estimated values of  $0.1 \text{ g/cm}^2$  for  $k_p$  and  $0.01 \text{ g/cm}^2 \cdot \text{s}$  for  $k_s$  were used<sup>9-11</sup>. The calculated value of  $L_o^*$  by Eq. (28) mentioned later was also used. The parameters were determined by comparing the simulation results with experimental results for each experiment. For simplification, it was assumed that the values of the parameters were constant during the entire period of the reactions.

## 4.2 Parameters

The parameters determined by modeling calculation are shown in Table 4 for the experiments of air blowing and in Table 5 for the experiments with  $Cu_2O-B_2O_3$  slag. An example of a simulation result for the experiments of air blowing is shown in Figure 8. The solid lines in Figs. 4 and 5 also show the simulation results for the experiments with  $Cu_2O-B_2O_3$  slag. The simulation results agree well with the experimental results in the both experiments.

The determined values of  $k_p = 0.08 \sim 0.15 \text{ g/cm}^2 \cdot \text{s}$  for the experiments with  $Cu_2O-B_2O_3$  slag agree well with the estimated value of  $k_p = 0.1 \text{ g/cm}^2 \cdot \text{s}$  for the experiments of air blowing. The determined values of  $k_s = 0.005 \sim 0.01 \text{ g/cm}^2 \cdot \text{s}$  for the experiments with  $Cu_2O-B_2O_3$  slag were slightly smaller than the estimated value of  $k_s = 0.01 \text{ g/cm}^2 \cdot \text{s}$  for

the experiments of air blowing. This difference is attributed to the difference of the slag system, especially to the difference of the viscosity. The values of  $L_{CuO_{0.5}}^*$  obtained for the experiments of air blowing were in good agreement with those for experiments with  $Cu_2O$ -rich slags as shown in Tables 4 and 5.

The values of  $B_{Zn}$ ,  $B_{Sn}$  and  $B_{Pb}$  can be theoretically calculated from the thermodynamic data indicated by Eqs. (1)~(5). The theoretical values of these are given as follows:

$$B_{Zn} = \frac{K_{Zn} f_{Zn} M_{Zn} \sum \frac{(\%M)}{M_M}}{\gamma_{ZnO}} \dots\dots\dots(24)$$

$$B_{Sn} = \frac{K_{Sn} f_{Sn} M_{Sn} \sum \frac{(\%M)}{M_M}}{\gamma_{SnO}} \dots\dots\dots(25)$$

$$B_{Pb} = \frac{K_{Pb} f_{Pb} M_{Pb} \sum \frac{(\%M)}{M_M}}{\gamma_{PbO}} \dots\dots\dots(26)$$

$$L_{CuO_{0.5}}^* = \frac{K_{Cu} a_{Cu} M_{Cu} \sum \frac{(\%M)}{M_M}}{\gamma_{CuO_{0.5}}} \dots\dots\dots(27)$$

$$L_O^* = \frac{1}{K_{O_2}} \dots\dots\dots(28)$$

There are no available data of  $\gamma_{ZnO}$ ,  $\gamma_{SnO}$  and  $\gamma_{PbO}$  for  $Cu_2O$ - $ZnO$ - $SnO_2$ - $PbO$  slag system obtained by blowing air in this study. While Takeda *et al.*<sup>7</sup> investigated the distribution ratio of Zn, Sn and Pb between  $FeO \cdot 25\text{mass}\%CaO$  slag and molten copper at 1250°C, and reported the values of  $\gamma_{ZnO}=3\sim6$ ,  $\gamma_{SnO_2}=2.4$  and  $\gamma_{PbO}=3.2$ . Oosumi<sup>5</sup> investigated the distribution ratio of Zn, Sn and Pb between  $CuO_{0.5}$ - $1.57\text{mass}\%Al_2O_3$ - $1\text{mass}\%B_2O_3$  slag and molten copper at 1200°C, and reported the values of  $\gamma_{ZnO}=21$ ,  $\gamma_{SnO_2}=61$  and  $\gamma_{PbO}=0.7$ . These data were used in the estimation of values of B.

Figure 9 shows the comparison of the values obtained from the present study of blowing air, B(para.), with the theoretical values calculated from Eqs. (24) ~ (26) using the final composition of slag and metal, reported values of activity coefficient and other thermodynamic data, B(theo.). The values of  $L_{CuO_{0.5}}^*$  are also shown in Fig.9. In the calculation, as the content of each impurity in metal is less than 1mass% and as the content of  $CuO_{0.5}$  in the obtained slag is about 80mass%, the values of  $f_{Zn}$ ,  $f_{Sn}$ ,  $f_{Pb}$  and  $\gamma_{CuO_{0.5}}$  are considered unity. In the case of B(theo.) calculated from activity coefficient by Takeda *et al.*<sup>7</sup>, the value of  $B_{Pb}$  determined in the present work is slightly higher than the value from Eq. (26), while  $B_{Zn}$  and  $B_{Sn}$  are in agreement with



the values from Eqs. (24) and (25). In the case of B(theo.) calculated from activity coefficient by Oosumi<sup>5</sup> the value of  $B_{Pb}$  determined in the present work agree with the value from Eq. (26), while  $B_{Zn}$  is slightly higher than the value from Eq. (24), and  $B_{Sn}$  is deviate significantly from the calculated value by from Eq. (25). The theoretical and the calculated values of  $L_{CuO_{0.5}}^*$  agree well with each other as seen in Fig.9.

Further studies will be required to determine the thermodynamic data, activity coefficient etc., of slag-molten copper system for kinetic and thermodynamic analysis of the removal of impurities from molten copper.

#### 4. CONCLUSION

The kinetic behaviors of oxidation of some impurities in liquid copper have been investigated by blowing air or using  $B_2O_3-Cu_2O$  slags. A kinetic model has been developed and verified by the observed reaction rate. The key conclusions are as follows:

- (1) Zn and Sn were removed down to less than 0.2%, however Pb was hard to be removed by blowing air onto liquid copper containing 1% of each impurity elements.
- (2) Pb content in liquid copper was down to 0.01% by using  $B_2O_3-Cu_2O$  slags.
- (3) A kinetic analysis developed on the basis of the two-film theory showed that the removal rate of impurities from liquid copper was controlled by the mass transport in metal and slag.

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Table 1 Experimental conditions, final slag weight and initial and final compositions of metals.

Run No.	Temp. (°C)	Flow rate of air (cm <sup>3</sup> /min)	Reaction time (s)	Final slag weight (g)	Initial metal				Final metal			
					[%Zn]	[%Sn]	[%Pb]	[%O]	[%Zn]	[%Sn]	[%Pb]	[%O]
Cu-1	1200	300	7202	*	0.859	0.898	0.951	0.022	0.020	0.038	0.827	0.256
Cu-2	1200	600	5405	50.2	0.912	0.509	0.989	0.020	0.012	0.002	0.530	0.998
Cu-3	1200	1000	5087	67.0	0.837	0.612	0.929	0.011	0.014	0.041	0.149	1.620
Cu-4	1200	300	7198	*	-	-	0.959	0.028	-	-	0.910	0.432
Cu-5	1200	600	7194	44.5	-	-	0.942	0.020	-	-	0.782	0.850
Cu-6	1200	1000	7186	88.0	-	-	0.750	0.032	-	-	0.218	1.930
Cu-7	1300	300	7194	*	0.810	0.728	0.850	0.011	0.139	0.096	0.750	0.831
Cu-8	1400	300	7202	*	0.821	0.512	1.081	0.026	0.251	0.190	0.678	0.429
Cu-9	1200	300	7229	*	0.139	0.169	0.112	0.023	0.078	0.034	0.110	0.141

\* The slag weight could not be determined owing to low slag formation.

Table 2 Initial experimental conditions of slag and metal.(at 1200 °C)

Run No.	Initial slag composition(mass%)					Weight(g)		Initial	
	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Slag	Metal	[%Pb]	[%O]
A-1	94.3	-	-	4.7	1.0	20	200.0	0.097	0.024
A-2	94.3	-	-	4.7	1.0	40	219.7	0.090	0.024
B-1	-	-	100	-	-	40	226.9	0.105	0.035
B-2	26.5	-	73.5	-	-	20	220.3	0.086	0.020
B-3	49.3	-	49.2	-	1.5	40	229.6	0.087	0.012
B-4	91.0	-	5.8	-	3.2	40	238.1	0.098	0.045

Table 3 Chemical compositions of final metal and slag, and values of  $P_{O_2}$ ,  $L_{Pb}$  and  $\gamma_{PbO}$  calculated from final condition.

Run No.	Final metal		Final slag composition(mass%)						$P_{O_2}^{1/2}$	$L_{Pb}$	$\gamma_{PbO}$
	[%Pb]	[%O]	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	PbO			
A-1	0.014	0.971	-	-	-	-	-	-	-	-	-
A-2	0.007	1.132	-	-	-	-	-	-	-	-	-
B-1	0.077	0.040	0.63	-	98.7	-	0.4	0.23	0.00034	2.9	0.84
B-2	0.036	0.114	19.7	-	69.3	-	10.2	0.78	0.00092	20.1	0.29
B-3	0.011	0.148	34.0	-	50.6	-	14.8	0.59	0.00119	50.0	0.14
B-4	0.003	0.843	59.3	-	29.8	-	9.8	1.12	0.00541	372	0.07

Table 4 Calculated values of parameters for the experiments of air blowing.

Run No.	$k_g' \times 10^6$ (mol/cm <sup>2</sup> .atm.s)	B <sub>Zn</sub>	B <sub>Sn</sub>	B <sub>Pb</sub>	$L_{CuO_{0.5}}^*$
Cu-1	3.5	1,000	3,000	10	100
Cu-2	9.0	1,000	1,500	10	100
Cu-3	30.0	1,000	1,500	10	80
Cu-4	2.5	-	-	10	100
Cu-5	3.5	-	-	20	100
Cu-6	30.0	-	-	10	90
Cu-7	4.0	500	3,000	10	60
Cu-8	3.5	150	1,000	40	100
Cu-9	1.5	700	4,000	10	220

Table 5 Values of parameters used in the simulation for the experiments with FeO<sub>3</sub>-Cu<sub>2</sub>O slags.

Run No.	$k_m \rho_m$ (g/cms)	$k_s \rho_s$	B <sub>Pb</sub>	$L_{CuO_{0.5}}$
A-1	0.08	0.005	450	90
A-2	0.08	0.005	150	90
B-1	0.08	0.010	2500	10
B-2	0.08	0.008	800	300
B-3	0.11	0.009	1200	280
B-4	0.08	0.006	600	130

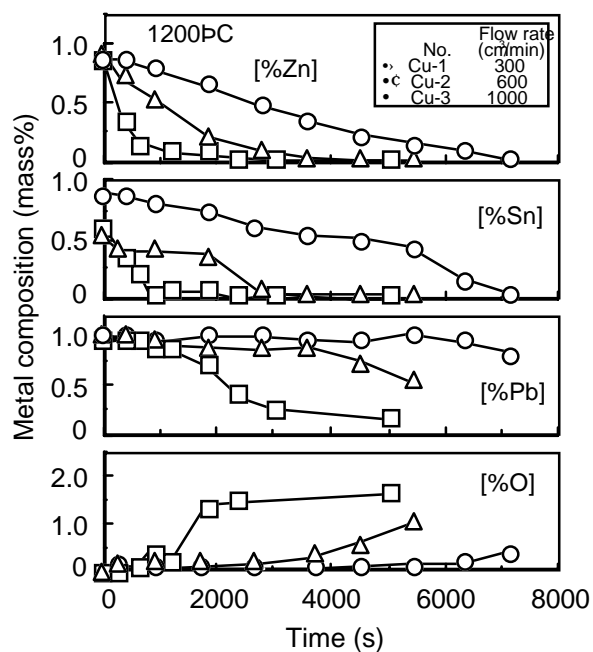


Fig. 1 Change in the composition of metal with time for various flow rate of air (Cu-Zn-Sn-Pb-O metal).

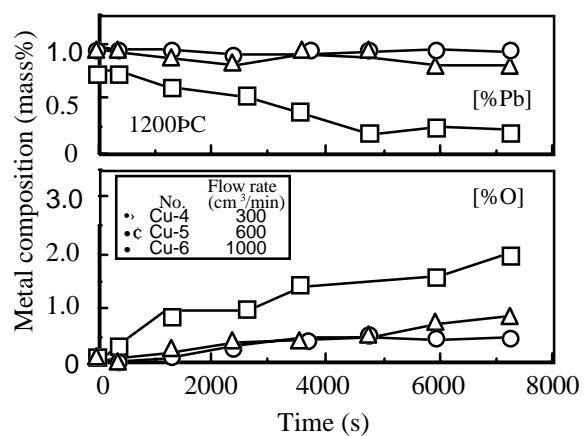


Fig. 2 Change in the composition of metal with time for various flow rate of air (Cu-Pb-O metal).

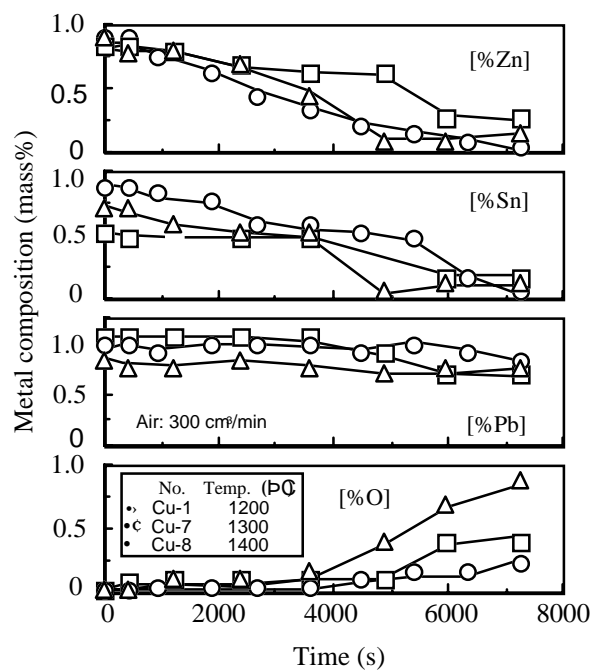


Fig. 3 Change in the composition of metal with time for various temperature.

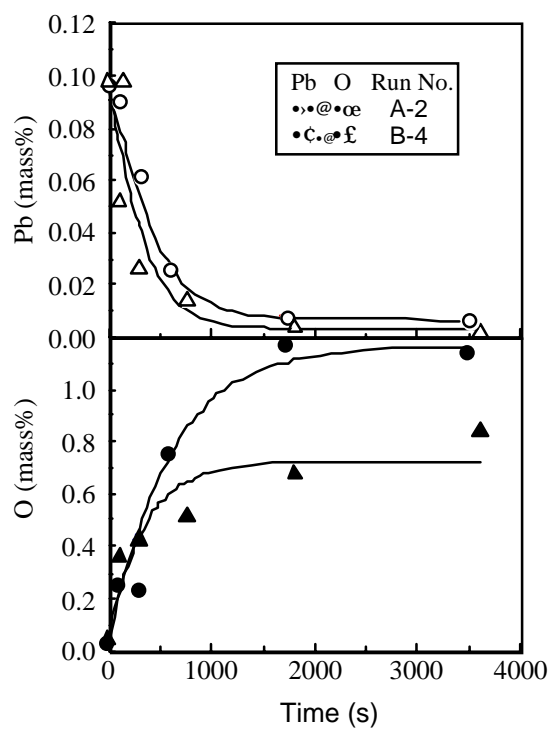


Fig. 4 Effect of  $M_xO_y$  on the oxidation behavior of lead in liquid copper by  $Cu_2O-M_xO_y$  binary slags. (solid lines are the simulation results.)

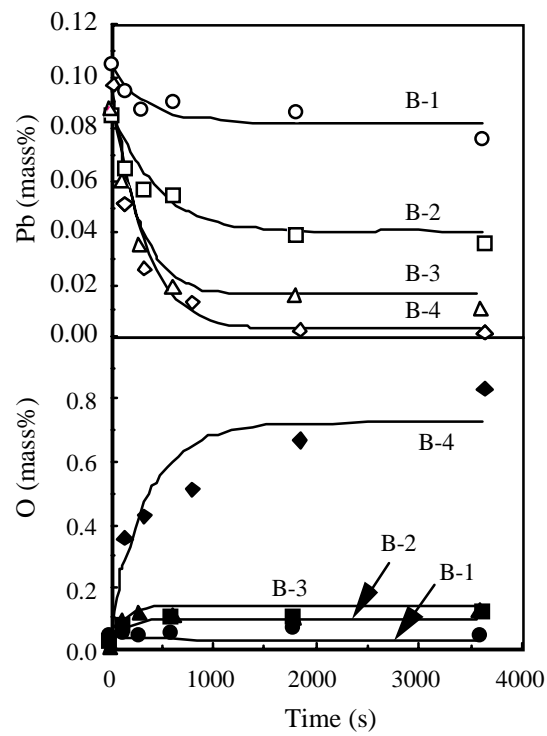
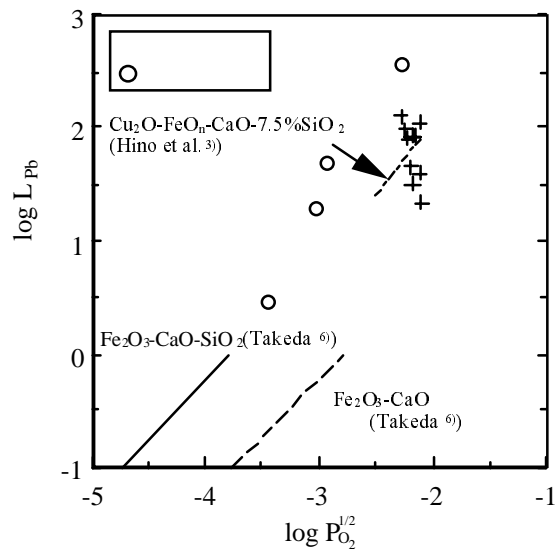


Fig.5 Effect of  $B_2O_3$  content on the oxidation behavior of lead in liquid copper by  $Cu_2O-B_2O_3$  binary slags. (solid lines are the simulation results.)



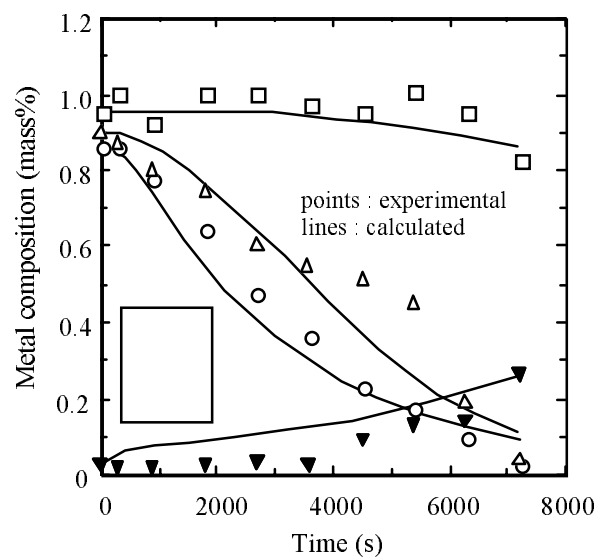


Fig. 7 Calculated and experimental results of change in metal composition. (No.Cu-1)

