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 B2O3-CuO 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 B2O3-CuO 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 1). The distribution ratio of impurities, such as Fe, Zn and Sn, between Cu2O-based slags and liquid copper has been measured by Fujisawa et al.2). Osumi3) also measured the distribution ratio of impurities between Cu2O-based slags and liquid copper, and the oxidizing rate of impurities in liquid copper by Cu2O-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 B2O3-CuO 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 was employed for each experiment. About 200 g of electrolytic copper was first raised to the fixed temperature and melted in an alumina crucible (30 mm 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 (4 mm ID) was blown onto the liquid copper surface at the flow rate of 300 to 1000 cm³/min, and the distance of the tip of the tube from the liquid copper surface was kept 55 mm. And then metal samples were taken at proper time intervals.

In experiments with B₂O₃-CuO slags, after 0.1 mass% 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 300 cm³/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 flow rate of air. However, the oxidation rate of \( \text{Hb} \) in \( \text{Cu-Hb-O} \) metal was somewhat smaller than that in \( \text{Cu-Zn-Sr-Hb-O} \) metal. These results suggested that the activity coefficients of \( \text{HbO} \) decrease by the coexistence of \( \text{ZnO} \) and \( \text{SnO}_2 \) in \( \text{CuO} \)-based slag. The amount of formed slag increased with increasing flow rate of air as shown in Table 1. And the results of chemical analysis of formed slag indicated that the content of \( \text{CuO}_{0.5} \) in the slag was about \( 80 \) mass\%. These results indicate that the oxidation rate of impurities and also the loss of \( \text{Cu} \) into the slag increased with increasing flow rate of air.

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

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

3.2 \( \text{B}_2\text{O}_3\)-\( \text{CuO} \) 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 \( \text{Al}_2\text{O}_3 \) originated from the crucibles used in this study.

Figure 4 shows the change of \( \text{Hb} \) and \( \text{O} \) contents in liquid copper during the reaction with \( \text{CuO} \)-based slag containing about \( 5-6 \) mass\% \( \text{SiO}_2 \) or \( \text{B}_2\text{O}_3 \). \( \text{Hb} \) content in copper decreased with time, and then finally reached \( 0.003 \) mass\% for \( \text{B}_2\text{O}_3 \) containing slag. On the other hand, in spite of the oxygen content is higher, the oxidation rate of \( \text{Hb} \) and the final \( \text{Hb} \) content in copper by using \( \text{SiO}_2 \) containing slag are slower and larger, respectively, than those by using \( \text{B}_2\text{O}_3 \) containing slag.

Figure 5 shows the effect of \( \text{B}_2\text{O}_3 \) content in \( \text{CuO-B}_2\text{O}_3 \) slag on the oxidation behavior of \( \text{Hb} \) in liquid copper. The content of oxygen in copper increased with increasing \( \text{CuO} \) content of slag, and the removal of \( \text{Hb} \) from liquid copper was promoted as shown in Fig.5. In the case of \( 100 \) mass\% \( \text{B}_2\text{O}_3 \) slag, the amount of oxygen available for oxidation of \( \text{Hb} \) is so smaller that the oxidation rate of \( \text{Hb} \) and the final \( \text{Hb} \) 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 \( \text{SiO}_2 \) or \( \text{B}_2\text{O}_3 \) is effective for the removal of \( \text{Hb} \) from liquid copper, and \( \text{Hb} \) content in liquid copper was down to
0.003 mass\% by using B₂O₃–CuO slags as shown in Table 3 (Run No. D-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:

\[
\begin{align*}
\text{Zn} + \text{O} &= \text{(ZnO)} \\
\log K_{\text{Zn}} &= \log \frac{a_{\text{Zn}}}{{a_{\text{Zn}}a_{\text{O}}}} = \frac{12755}{T} - 6.62 \\
\text{Sn} + 2\text{O} &= \text{(SnO₂)} \\
\log K_{\text{Sn}} &= \log \frac{a_{\text{Sn}a_{\text{O}}}}{a_m a_{\text{O}}} = \frac{19648}{T} - 11.4 \\
\text{Pb} + \text{O} &= \text{(PbO)} \\
\log K_{\text{Pb}} &= \log \frac{a_{\text{Pb}a_{\text{O}}}}{a_m a_{\text{O}}} = \frac{7617}{T} - 6.15 \\
\text{Cu} + \frac{1}{2}\text{O} &= \text{(CuO₀.5)} \\
\log K_{\text{Cu}} &= \log \frac{a_{\text{Cu}a_{\text{O}_{0.5}}}}{a_m a_{\text{O}}} = \frac{842}{T} - 0.54 \\
\text{O₂(}g\text{)} &= 2\text{O} \\
\log K_{\text{O₂}} &= \log \frac{a_{\text{O}}}{{a_{\text{O}}a_{\text{O}}}²} = \frac{8916}{T} - 1.94
\end{align*}
\]

Here \( a_m \) and \( a_{\text{O}} \) are the activities of elements in liquid copper referred to the infinite dilute solution, and \( a_{\text{MO}} \) is the Raoultian activity of oxide in slag. \( P_{\text{O₂}} \) is oxygen partial pressure in atm. There are few available values of \( \gamma_{\text{O₂}} \), \( \gamma_{\text{Pb}} \) and \( \gamma_{\text{Cu}} \) in slags containing B₂O₃ as used in this study. Therefore we estimated the value of \( \gamma_{\text{O₂}} \) based on the experimental results by using Cu₂O–B₂O₃ slag. The distribution ratio of \( \text{O}_2 \), \( L_{\text{Pb}} \), can be expressed as follow in accordance with Eq. (3):

\[
L_{\text{Pb}} = \frac{\%\text{Pb}}{\%\text{Pb}} = K_{\text{Pb}} \frac{(n_{\text{Pb}})(\gamma'_{\text{Pb}})}{(n_1)(\gamma'_{\text{Pb}})} P_{\text{O₂}}^{\%\text{Pb}}
\]

Where, \( (n_1) \) and \( [n_2] \) 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 \( a_{\text{O}} = P_{\text{O₂}}^{\%\text{O₂}} \), \( P_{\text{O₂}}^{\%\text{O₂}} \) can be expressed of activity coefficient of
oxygen, $\gamma_o$ and the oxygen content, $X_o$.

$$a_o = \gamma_o \cdot X_o = P_o^{1/2}$$  \hspace{1cm} \text{..............(7)}

The values of distribution ratio, $L_{pb}$, and $P_o^{1/2}$, obtained in this study are shown in Table 3. In the calculation, activity coefficient of oxygen ($\ln \gamma_o = 4.734 - 9462/T$) \(^7\), interaction parameter (\(c_o^I = 11.5 - 27660/T\)) \(^2\) and oxygen content determined in the present results were used. The relationship between $L_{pb}$ and $P_o^{1/2}$ is shown in Fig. 6. The literature values for FeCr-CaO-SiO$_2$ slag by Hino et al.\(^8\) and Takeda et al.\(^7\) and for CuO-SiO$_2$ slag by R. P. Das et al.\(^1\) 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 $\gamma_{o0}$ from the present results are also shown in Table 3. In the calculation, the values of [$n_0$] = 100/$M_{o0}$ = 1.57 and $\gamma_o = 5.5$ were used. The values of 0.07 to 0.84 for $\gamma_{o0}$ were estimated. These values are smaller than those reported for slags without B$_2$O$_3$ \(^1\), but they show a tendency to increase with increasing the content of B$_2$O$_3$ in slag. The reason for such an increase in $\gamma_{o0}$ does not clear now. B$_2$O$_3$-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 $\gamma_{o0}$ increased in spite of the addition of much B$_2$O$_3$. The obtained value of $\gamma_{o0} = 0.07$ is smaller than the literature values of $\gamma_{o0} = 3.2$ for CaO-FeO and 0.4 for CaO-FeO-SiO$_2$ by Takeda et al.\(^7\), of $\gamma_{o0} = 0.15$-0.6 for CuO-CaO-FeCr-SiO$_2$ slag by Hino et al.\(^8\) and of $\gamma_{o0} = 0.08$-0.9 for CuO-SiO$_2$ slag by R. P. Das et al.\(^1\) It is speculated from these results that CuO-B$_2$O$_3$ 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-film theory\(^6\) and has been compared to the experimental results. In this model, O$_2$ gas is assumed to react directly with metal through slag phase. Then the flux of oxygen, $\dot{n}_{o2}$, can be expressed by the following equation.

$$\dot{n}_{o2} = A k'_{g} (P_o - L_{o2} a_o)$$  \hspace{1cm} \text{..............(8)}

Where, $k'_{g}$ is apparent mass transport coefficient of oxygen in gas phase (mol/cm$^2$ \cdot atm \cdot s). $A$ and $P_o$ are interfacial area (cm$^2$) and oxygen partial pressure (atm) of the gas, and $L_{o2}^*$ 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:

\[- \frac{d[\%\text{Zn}]}{dt} = \frac{Ak_{2n}}{W_m} \left\{ L_{2n}^*[\%\text{Zn}] - (\%\text{Zn}) \right\} \]

\[\frac{1}{k_{2n}} = \frac{L_{2n}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \]

\[- \frac{d[\%\text{Sn}]}{dt} = \frac{Ak_{2n}}{W_m} \left\{ L_{2n}^*[\%\text{Sn}] - (\%\text{Sn}) \right\} \]

\[\frac{1}{k_{2n}} = \frac{L_{2n}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \]

\[- \frac{d[\%\text{Pb}]}{dt} = \frac{Ak_{2n}}{W_m} \left\{ L_{2n}^*[\%\text{Pb}] - (\%\text{Pb}) \right\} \]

\[\frac{1}{k_{2n}} = \frac{L_{2n}^*}{k_m \rho_m} + \frac{1}{k_s \rho_s} \]

\[- \frac{d[\%\text{O}]}{dt} = \frac{Ak_{2n}}{W_m} \left\{ \left[\%\text{O}\right] - \frac{a_o^*}{f_o} \right\} \]

\[- \frac{d[\%\text{CuO}_{0.5}]}{dt} = \frac{Ak_{2n}}{W_s} \left\{ \left[\%\text{CuO}_{0.5}\right] - \frac{a_{o^*}}{a_o^*} \right\} \]

Where, \( k_i \ (i = \text{Zn, Sn, Pb}) \), \( W \), \( \beta \), \( L \), \( k \), and \( f \) are overall mass transfer coefficient \((\text{cm/s})\), weight \((\text{g})\), density \((\text{g/cm})\), distribution ratio, mass transport coefficient \((\text{cm/s})\) and Warnier 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, \( B_i \), as follow:

\[ L_{2n}^* = \frac{(\%\text{Zn})^*}{[\%\text{Zn}]} = B_{2n} a_o^* \]

\[ L_{2n}^* = \frac{(\%\text{Sn})^*}{[\%\text{Sn}]} = B_{2n} a_o^* \]

\[ L_{2n}^* = \frac{(\%\text{Pb})^*}{[\%\text{Pb}]} = B_{2n} a_o^* \]

\[ L_{\text{CaO}, *} = \frac{(\%\text{CuO}_{0.5})^*}{a_o^*} \]
\[ L_0^* = \frac{P_{O_2}}{a_0^*} \quad \text{(21)} \]

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:

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

For experiments with CuO-B₂O₃ slag:

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

Under the known values of \( k_{\rho_1} \), \( k_{\rho_2} \), \( k'_{\rho_1} \), \( R_{Zn} \), \( R_{Sn} \), \( R_{Pb} \), \( L_{\text{CuO}_{0.5}} \), and \( L_0^* \), a value of \( a_0^* \) 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 g/cm² for \( k_{\rho_1} \) and 0.01 g/cm²·s for \( k_{\rho_2} \) were used \(^{[20]}\). The calculated value of \( L_0^* \) 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 CuO-B₂O₃ 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 CuO-B₂O₃ slag. The simulation results agree well with the experimental results in the both experiments.

The determined values of \( k_{\rho_1} = 0.08 \text{ to } 0.15 \text{ g/cm}^2 \cdot \text{s} \) for the experiments with CuO-B₂O₃ slag agree well with the estimated value of \( k_{\rho_1} = 0.1 \text{ g/cm}^2 \cdot \text{s} \) for the experiments of air blowing. The determined values of \( k_{\rho_2} = 0.005 \text{ to } 0.01 \text{ g/cm}^2 \cdot \text{s} \) for the experiments with CuO-B₂O₃ slag were slightly smaller than the estimated value of \( k_{\rho_2} = 0.01 \text{ g/cm}^2 \cdot \text{s} \) 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 $L^*_{\text{CuO}_{1,5}}$ obtained for the experiments of air blowing were in good agreement with those for experiments with CuO-rich slags as shown in Tables 4 and 5.

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

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

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

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

$$L^*_{\text{CuO}_{1,5}} = \frac{K_{\text{Cu}} a_{\text{Cu}} M_{\text{Cu}} \sum (\% M) / M_M}{\gamma_{\text{CuO}_{1,5}}}$$  

$$L^*_{\text{O}} = \frac{1}{K_{O_2}}$$

There are no available data of $\gamma_{\text{Zn}}$, $\gamma_{\text{Sn}}$, and $\gamma_{\text{Pb}}$ for CuO-ZnO-SnO-PbO slag system obtained by blowing air in this study. While Takeda et al. investigated the distribution ratio of Zn, Sn and Pb between FeO-25mass%CaO slag and molten copper at 1250°C, and reported the values of $\gamma_{\text{ZnO}} = 3.6$, $\gamma_{\text{SnO}} = 2.4$ and $\gamma_{\text{PbO}} = 3.2$. Osaumi investigated the distribution ratio of Zn, Sn and Pb between CuO-1.5mass%Al₂O₃-1mass%B₂O₃ slag and molten copper at 1200°C, and reported the values of $\gamma_{\text{ZnO}} = 21$, $\gamma_{\text{SnO}} = 61$ and $\gamma_{\text{PbO}} = 0.7$. 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 $L^*_{\text{CuO}_{1,5}}$ 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_{1,5} in the obtained slag is about 80mass%, the values of $f_{\text{Zn}}$, $f_{\text{Sn}}$, $f_{\text{Pb}}$ and $\gamma_{\text{CuO}_{1,5}}$ are considered unity. In the case of B(theo.) calculated from activity coefficient by Takeda et al., the value of $B_{\text{Pb}}$ determined in the present work is slightly higher than the value from Eq. (26), while $B_{\text{Zn}}$ and $B_{\text{Sn}}$ are in agreement with
the values from Eqs. (24) and (25). In the case of B (theo.) calculated from activity coefficient by Osumi 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 $L_{CuO}$, 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_{2}O_{3}-CuO 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_{2}O_{3}-CuO 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.

4. REFERENCES

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

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (°C)</th>
<th>Flow rate of air (cm³/min)</th>
<th>Reaction time (s)</th>
<th>Final slag weight (g)</th>
<th>Initial metal</th>
<th>Final metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>1200</td>
<td>300</td>
<td>7202</td>
<td>*</td>
<td>0.859 0.898 0.951 0.022</td>
<td>0.020 0.038 0.827 0.256</td>
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<tr>
<td>Cu-2</td>
<td>1200</td>
<td>600</td>
<td>5405</td>
<td>50.2</td>
<td>0.912 0.509 0.989 0.200</td>
<td>0.012 0.002 0.530 0.998</td>
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<tr>
<td>Cu-3</td>
<td>1200</td>
<td>1000</td>
<td>5087</td>
<td>67.0</td>
<td>0.837 0.612 0.929 0.011</td>
<td>0.014 0.041 0.149 1.620</td>
</tr>
<tr>
<td>Cu-4</td>
<td>1200</td>
<td>300</td>
<td>7198</td>
<td>*</td>
<td>- - 0.959 0.028</td>
<td>- - 0.910 0.432</td>
</tr>
<tr>
<td>Cu-5</td>
<td>1200</td>
<td>600</td>
<td>7194</td>
<td>44.5</td>
<td>- - 0.942 0.020</td>
<td>- - 0.782 0.850</td>
</tr>
<tr>
<td>Cu-6</td>
<td>1200</td>
<td>1000</td>
<td>7186</td>
<td>88.0</td>
<td>- - 0.750 0.032</td>
<td>- - 0.218 1.930</td>
</tr>
<tr>
<td>Cu-7</td>
<td>1300</td>
<td>300</td>
<td>7194</td>
<td>*</td>
<td>0.810 0.728 0.850 0.011</td>
<td>0.139 0.096 0.750 0.831</td>
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<tr>
<td>Cu-8</td>
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<td>300</td>
<td>7202</td>
<td>*</td>
<td>0.821 0.512 1.081 0.026</td>
<td>0.251 0.190 0.678 0.429</td>
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<tr>
<td>Cu-9</td>
<td>1200</td>
<td>300</td>
<td>7229</td>
<td>*</td>
<td>0.139 0.169 0.112 0.023</td>
<td>0.078 0.034 0.110 0.141</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial slag composition(mass%)</th>
<th>Weight(g)</th>
<th>Initial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu₂O  Fe₂O₃  B₂O₃  SiO₂  Al₂O₃</td>
<td>Slag</td>
<td>Metal</td>
</tr>
<tr>
<td>A-1</td>
<td>94.3    -      -      4.7     1.0</td>
<td>20</td>
<td>200.0</td>
</tr>
<tr>
<td>A-2</td>
<td>94.3    -      -      4.7     1.0</td>
<td>40</td>
<td>219.7</td>
</tr>
<tr>
<td>B-1</td>
<td>-       -      100     -      -</td>
<td>40</td>
<td>226.9</td>
</tr>
<tr>
<td>B-2</td>
<td>26.5    -      73.5    -      -</td>
<td>20</td>
<td>220.3</td>
</tr>
<tr>
<td>B-3</td>
<td>49.3    -      49.2    -      1.5</td>
<td>40</td>
<td>229.6</td>
</tr>
<tr>
<td>B-4</td>
<td>91.0    -      5.8     -      3.2</td>
<td>40</td>
<td>238.1</td>
</tr>
</tbody>
</table>

Table 3  Chemical compositions of final metal and slag , and values of $P_{O₂}$, $L_{Pb}$ and $\gamma_{PbO}$ calculated from final condition.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Final metal</th>
<th>Final slag composition(mass%)</th>
<th>$P_{O₂}$</th>
<th>$L_{Pb}$</th>
<th>$\gamma_{PbO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[%Pb]</td>
<td>[%O]</td>
<td>Cu₂O  Fe₂O₃  B₂O₃  SiO₂  Al₂O₃  PbO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-1</td>
<td>0.014</td>
<td>0.971</td>
<td>-       -      -      -      -      -</td>
<td>0.4</td>
<td>0.23</td>
</tr>
<tr>
<td>A-2</td>
<td>0.007</td>
<td>1.132</td>
<td>-       -      -      -      -      -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-1</td>
<td>0.077</td>
<td>0.040</td>
<td>0.63     98.7    -      -      -      -</td>
<td>0.4</td>
<td>0.23</td>
</tr>
<tr>
<td>B-2</td>
<td>0.036</td>
<td>0.114</td>
<td>19.7     69.3    -      -      -      -</td>
<td>10.2</td>
<td>0.78</td>
</tr>
<tr>
<td>B-3</td>
<td>0.011</td>
<td>0.148</td>
<td>34.0     50.6    -      -      -      -</td>
<td>14.8</td>
<td>0.59</td>
</tr>
<tr>
<td>B-4</td>
<td>0.003</td>
<td>0.843</td>
<td>59.3     29.8    -      9.8    1.12</td>
<td>0.00541 372 0.07</td>
<td></td>
</tr>
</tbody>
</table>
Table 4  Calculated values of parameters for the experiments of air blowing.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$k_S \times 10^6$ (mol/cm$^2$·atm·s)</th>
<th>$B_{Zn}$</th>
<th>$B_{Sn}$</th>
<th>$B_{Pb}$</th>
<th>$L_{CuO,5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>3.5</td>
<td>1,000</td>
<td>3,000</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Cu-2</td>
<td>9.0</td>
<td>1,000</td>
<td>1,500</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Cu-3</td>
<td>30.0</td>
<td>1,000</td>
<td>1,500</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Cu-4</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Cu-5</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Cu-6</td>
<td>30.0</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>Cu-7</td>
<td>4.0</td>
<td>500</td>
<td>3,000</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Cu-8</td>
<td>3.5</td>
<td>150</td>
<td>1,000</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Cu-9</td>
<td>1.5</td>
<td>700</td>
<td>4,000</td>
<td>10</td>
<td>220</td>
</tr>
</tbody>
</table>

Table 5  Values of parameters used in the simulation for the experiments with $\text{B}_2\text{O}_3$-$\text{Cu}_2\text{O}$ slags.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$\kappa_m \rho_m$</th>
<th>$\kappa_p \rho_s$ (g/cm$^3$·s)</th>
<th>$B_{Pb}$</th>
<th>$L_{CuO,5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>0.08</td>
<td>0.005</td>
<td>450</td>
<td>90</td>
</tr>
<tr>
<td>A-2</td>
<td>0.08</td>
<td>0.005</td>
<td>150</td>
<td>90</td>
</tr>
<tr>
<td>B-1</td>
<td>0.08</td>
<td>0.0061</td>
<td>2500</td>
<td>10</td>
</tr>
<tr>
<td>B-2</td>
<td>0.08</td>
<td>0.009</td>
<td>800</td>
<td>300</td>
</tr>
<tr>
<td>B-3</td>
<td>0.11</td>
<td>0.0092</td>
<td>1200</td>
<td>280</td>
</tr>
<tr>
<td>B-4</td>
<td>0.08</td>
<td>0.0062</td>
<td>600</td>
<td>130</td>
</tr>
</tbody>
</table>
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 MxOy on the oxidation behavior of lead in liquid copper by Cu₂O-MₓOᵧ binary slags. (solid lines are the simulation results.)
Fig. 5  Effect of B$_2$O$_3$ content on the oxidation behavior of lead in liquid copper by Cu$_2$O-B$_2$O$_3$ binary slags.
(solid lines are the simulation results.)
Fig. 7  Calculated and experimental results of change in metal composition (No.Cu-1)