Oxide inclusions in copper during its fire refining

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There is estimated the composition of non-metallic inclusions in blister copper during its air oxidation in the conditions of "Uralelektromed" JSC. Two types of oxide inclusions are defined:

- $\text{Cu}_2\text{O}$ and $\text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3$
- selenide-tellurides in the form of $\text{Cu}_2\text{SeTeS}$ particles, suspended in copper.

During the increasing of oxidation level of copper, the content and sizes of inclusions are decreased from 1–5 to 1–3 mm for the $\text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3$ oxides, and from 3 to 1 mm for selenides. Lead is a basic component in $\text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3$. The content of lead is not changed in oxidation process and makes up 55.3% (limiting values), while the content of Sb is increased from 24.8 to 35.2%. The contents of selenium and tellurium are increased in selenides, while the contents of sulphur are decreased by oxidation. There are calculated the rates of floating of oxide particles of $\text{Cu}_2\text{O}$ and $\text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3$. In connection with low rates of floating of high density oxide particles, it is necessary to assume the additional measures for intensification of refining process (for example, mixing and filtration of melt).

Key words: blister copper, refining, oxidation, impurities, oxide inclusions, lead, antimony, arsenic, selenium, oxygen, nickel, sulfur.

Metal from several enterprises is supplied to the stage of fire refining of copper at “Uralelektromed” JSC. The composition of blister copper is within a wide range, and the content of impurities reaches the following rates: 0.05–0.30% (wt.) of Fe; 0.03–0.10% (wt.) of Se; 0.1–1.2% (wt.) of Pb; 0.08–0.25% (wt.) of Sb; 0.09–0.40% (wt.) of As; 0.05–0.10% (wt.) of Ni and 0.08–0.20% (wt.) of S. Blister copper also contains Co, Zn, Bi, Te, Au and Ag [1]. Refining is carried out in reverberatory furnace, where the charging stage takes 15–20% of entire cycle duration. At the same time, the stages of melting, oxidation, recovery and casting take 30–35%, 15%, and 8% and 25% of entire cycle duration, respectively. After the fire refining, copper has the following average composition: 99.40% (wt.) of Cu; 0.11% (wt.) of Pb; 0.069% (wt.) of Sb; 0.041% (wt.) of As; 0.093% (wt.) of Ni; 0.0077% (wt.) of Sn; 0.0017% (wt.) of Fe; 0.005% (wt.) of Zn; 0.082% (wt.) of O; 24 g/t of Au and 700 g/t of Ag. Subsequently, metal is casted into anodes and is sent to electrolysis. The grade of O; 24 g/t of Au and 700 g/t of Ag. Subsequently, metal is casted into anodes and is sent to electrolysis.

Removal of such impurities as lead, antimony, arsenic and nickel [2–6] into slag on the fire refining stage is very difficult. The basic idea of copper refining supposes the oxidation of impurities and slagging of formed oxides. During the oxidation of blister copper by air oxygen, melt is saturated with oxygen following formation of copper oxide. Oxygen, dissolved in copper, interacts with impurities with formation of PbO, $\text{Sb}_2\text{O}_3$, $\text{As}_2\text{O}_3$, $\text{NiO}$, $\text{FeO}$, $\text{SnO}_2$ and $\text{ZnO}$. Liquid and solid fine dispersed particles of these oxides should be aggregated and slagged. Another probable mechanism of impurities oxidation is their interaction with $\text{Cu}_2\text{O}$. In this case, the formed oxides can be dissolved in excessive $\text{Cu}_2\text{O}$ with formation of oxide melt. The silica sand is used for the slagging of impurities. Slag of fining production stage of “Uralelektromed” JSC contains the following substances: 49.0% (wt.) of $\text{Cu}_2\text{O}$; 19.5% (wt.) of $\text{SiO}_2$; 14.0% (wt.) of $\text{FeO}$; 3.0% (wt.) of $\text{Al}_2\text{O}_3$; 3.0% (wt.) of $\text{MgO}$; 1.8% (wt.) of $\text{CaO}$; 3.2% (wt.) of $\text{PbO}$; 1.9% (wt.) of $\text{ZnO}$; 1.6% (wt.) of $\text{Sb}_2\text{O}_3$; 1.1% (wt.) of $\text{SnO}_2$; 1.8% (wt.) of $\text{NiO}$ and 0.2% (wt.) of $\text{As}_2\text{O}_3$.

The metal distribution coefficients ($K_{Me}$) between slag (Me) and copper [Me] can be estimated on the basis of the foregoing data:

<table>
<thead>
<tr>
<th>Me</th>
<th>Pb</th>
<th>Zn</th>
<th>Sb</th>
<th>Sn</th>
<th>Ni</th>
<th>As</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{Me}=\frac{\text{[Me]}\text{/[Me]}}{28}$</td>
<td>323</td>
<td>17</td>
<td>112</td>
<td>15</td>
<td>3</td>
<td>6,400</td>
<td></td>
</tr>
</tbody>
</table>

On the basis of the given values of $K_{Me}$, oxidability of impurities is increased in the following sequence: $\text{As} < \text{Ni} < \text{Sb} < \text{Pb} < \text{Sn} < \text{Zn} < \text{Fe}$. This sequence is practically identical to the one, given in the reference [2]. It describes not the affinity of pure elements to oxygen, but a real oxidability and oxidation sequence, taking into account the mass fraction of impurities. It is naturally, that during the refining of blister copper with low content of nickel, a $K_{Ni}$ value will be significantly lower than this value for the high-nickel metal. That is why the shown sequence is significant only for a certain enterprise.

This research work estimates the forms of impurities location in the process of blister copper oxidation. Industrial samples of copper in the process of oxidation stage were taken for analysis. Copper oxidation degree was evaluated on the basis of oxygen content in it: 0.47% (wt.) in the beginning of oxidation (sample 1, Fig. 1, a); 0.60% (wt.) in an hour of oxidation (sample 2, Fig. 1, b) and 0.64% (wt.) in 3.5 hours of oxidation (sample 3, Fig. 1, c).

Microstructure and composition of samples’ phases was estimated by methods of optical microscopy (Olympus) with...
According to the optical microscopy data (Fig. 1), the size of non-metallic inclusions is changed during the oxidation of copper. Considering the sample, taken in the initial period of oxidation, it is shown that size of \( \text{Cu}_2\text{O} \) inclusions makes up 0.5–4.0 mm, and the size of single coagulated inclusions reaches 7–10 mm. Oxide inclusions in the sample 2 and sample 3 are consolidated and, at the last oxidation stage, are segregated in the form of dendrites, consisting of individual globules with the size of 10–40 mm.

On the basis of X-ray spectrum microanalysis (Fig. 2, Table 1), besides \( \text{Cu}_2\text{O} \), copper contains non-metallic inclusions with the size of 1–5 mm, which composition complies with the system of \( \text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3 \) with low content of \( \text{Ni}, \text{S}, \text{Se} \) and \( \text{Te} \). The content of lead, antimony and arsenic in non-metallic inclusions of the sample 1 reaches 54.3%, 24.8% and 8.0%, respectively, while the content of nickel, sulfur, selenium and tellurium does not exceed 0.5%, 4.1%, 0.8% and 1.0%, respectively. Limit contents of the considered elements in non-metallic inclusions (sample 2) practically do not differ from the foregoing ones. Limit contents of sulfur in the sample 3 (taken on a final oxidation stage) are lower in inclusions, while the limit contents of antimony, arsenic and nickel are higher than in the sample 1 and sample 2.

Copper contains the selenides with the following compositions: \( \text{Cu}_3\text{Se}_{0.5}\text{Te}_{0.14}\text{S}_{0.9}, \text{Cu}_3\text{Se}_{0.5}\text{Te}_{0.15}\text{S}_{0.85} \) and \( \text{Cu}_4\text{Se}_{0.65}\text{Te}_{0.25}\text{S}_{0.08} \) in the samples 1–3 respectively. The content of selenium and tellurium in these samples is increased, and the content of sulfur is decreased in the process of oxidation. As the copper oxidation level is increased, the contents and sizes of inclusions are decreased from 1–5 mm to 1–3 mm for \( \text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3 \) and from 3 to 1 mm for selenides. A large quantity of these inclusions is found on the surface of \( \text{Cu}_2\text{O} \) particles in the form of local areas (lead oxides – phase 3 and selenides – phase 4) (Fig. 2).

In that way, according to the research results, the metallic copper contains 0.5–0.8% of oxygen, and its content becomes slightly higher as oxidation duration is increased. Copper oxide phase contains up to 11.5% of oxygen, which corresponds to the composition of \( \text{Cu}_2\text{O} \). Content of accompanying metals in copper and its oxide does not exceed 0.1%, which is below their determination boundary according to the used method. The basic element in oxide component, complying with the \( \text{PbO} – \text{Sb}_2\text{O}_5 – \text{As}_2\text{O}_3 \) system, is lead, which content does not change in the process of oxidation and makes up 55.3% (limit value). Content of antimony and nickel in this phase is increased from 24.8 to 35.2%, and from 0.4 to 1%, respectively. At the same time, arsenic in this phase is distributed non-uniformly (2.7–9.3%), and the sulfur content is decreased from 4.1 to 1.1%. Complex selenide-telluride of copper contains the following substances (beginning and end of oxidation): 4.5–1.2% of Pb; 1.5–0.9% of Sb; 9.2–1.0% of S; 12.6–18.3% of Se and 5.6–11.1% of Te. Dependence of metals and sulfur content in non-metallic inclusions (by the limit values) on oxidation duration points out the change of their composition (Fig. 3).

Knowing the composition and sizes of non-metallic inclusions, their behavior in metallic copper melt can be estimated. According to the conditions of the properties’ additivity, there was estimated the density of non-metallic inclusions \( (\rho_{\text{oxide}}) \):

\[
\rho_{\text{oxide}} = \frac{\rho_{\text{Cu}_2\text{O}} \cdot \gamma_{\text{Cu}_2\text{O}} + \rho_{\text{PbO}} \cdot \gamma_{\text{PbO}} + \gamma_{\text{Sb}_2\text{O}_5} \cdot \rho_{\text{Sb}_2\text{O}_5} + \rho_{\text{As}_2\text{O}_3} \cdot \gamma_{\text{As}_2\text{O}_3} \cdot \gamma_{\text{Cu}_2\text{O}}}{\gamma_{\text{Cu}_2\text{O}} + \gamma_{\text{PbO}} + \gamma_{\text{Sb}_2\text{O}_5} + \gamma_{\text{As}_2\text{O}_3}}.
\]
HEAVY NON-FERROUS METALS

Table 1. According to the calculations, the oxide value makes up 7.4 g/cm\(^3\). Assuming that melted copper density makes up 8.3 g/cm\(^3\) at the temperature of 1,083 °С [1], it is possible to evaluate the floating rate (\(\nu\)) of oxide droplets, according to the Stokes equation for Cu\(_2\)O particles (2) and Rybchinsky-Adamar equation for PbO – Sb\(_2\)O\(_5\) – As\(_2\)O\(_5\):

\[
\nu_{\text{oxide}} = \frac{2(\rho_{\text{Cu}} - \rho_{\text{oxide}}) \cdot g \cdot r^2}{9 \eta_{\text{Cu}}},
\]

(2)

\[
\nu_{\text{oxide}} = \frac{2(\rho_{\text{Cu}} - \rho_{\text{oxide}}) \cdot g \cdot r^2 \times (\eta_{\text{Cu}} + \eta_{\text{oxide}})/(3\eta_{\text{Cu}} \cdot (2\eta_{\text{Cu}} + 3\eta_{\text{oxide}}))},
\]

(3)

where: \(\rho_{\text{oxide}}\) and \(\rho_{\text{Cu}}\) – the densities of oxide inclusions and copper, g/cm\(^3\); \(\eta_{\text{oxide}}\) and \(\eta_{\text{Cu}}\) – the viscosities of oxide inclusions and copper, Pa·s; \(r\) – the radius of particles; \(g\) – the free fall of acceleration.

The floating rates \(u\) of Cu\(_2\)O and PbO – Sb\(_2\)O\(_5\) – As\(_2\)O\(_5\) particles with the sizes from 1 to 40 mm, were determined, taking into account the following values and inserting them into equations (2) and (3):

- viscosity of melted copper is equal to 0.0036 Pa·s at the temperature of 1,100 °С [1];
- viscosity of oxide inclusions is close to viscosity of lead oxide, equal to 0.0145 Pa·s [10].

In order to bind the obtained data to real refining conditions, there was defined the duration of floating of inclusions (\(\tau\)) from copper melt with 0.5 m height (Table 2).

The change of the content of metals and sulfur in oxide inclusions of PbO – Sb\(_2\)O\(_5\) – As\(_2\)O\(_5\) in the process of oxidation:

\[
\begin{align*}
1 & \quad \text{Pb} \\
2 & \quad \text{Sb} \\
3 & \quad \text{As} \\
4 & \quad \text{S}
\end{align*}
\]

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\begin{align*}
1 & \quad \text{Pb} \\
2 & \quad \text{Sb} \\
3 & \quad \text{As} \\
4 & \quad \text{S}
\end{align*}
\]
Conclusions

The example of oxidation of blister copper impurities in anode furnaces at “Uralelektromed” JSC shows, that during the process, there are formed the high density oxide inclusions of the PbO – Sb₂O₅ – As₂O₅ system. In order to intensify the impurities oxidation during the refining of copper in anode furnaces, both additional mixing of melt (ensuring the coalescence of fine particles) and formation of low melting temperature slag are appropriate. Filtration of copper melt through porous ceramic filters for separation of fine oxide inclusions and selenides is interesting.

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References