

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 "Uralektromed" JSC. Two types of oxide inclusions are defined:

– Cu_2O and $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$;

– selenide-tellurides in the form of Cu_xSeTeS 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 $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$ oxides, and from 3 to 1 mm for selenides. Lead is a basic component in $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$. 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 Cu_2O and $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$. 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 "Uralektromed" 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%, 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 copper (M00k), noble metals concentrating slime and electrolyte-refining cake are obtained on electrolysis stage.

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 with following formation of copper oxide. Oxygen, dissolved in copper, interacts with impurities with formation of PbO , Sb_2O_5 , As_2O_5 , NiO , FeO , SnO_2 and 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 Cu_2O . In this case, the formed oxides can be dissolved in excessive Cu_2O with formation of oxide melt. The silica

sand is used for the slagging of impurities. Slag of fining production stage of "Uralektromed" JSC contains the following substances: 49.0% (wt.) of Cu_2O ; 19.5% (wt.) of SiO_2 ; 14.0% (wt.) of FeO ; 3.0% (wt.) of Al_2O_3 ; 3.0% (wt.) of MgO ; 1.8% (wt.) of CaO ; 3.2% (wt.) of PbO ; 1.9% (wt.) of ZnO ; 1.6% (wt.) of Sb_2O_5 ; 1.1% (wt.) of SnO_2 ; 1.8% (wt.) of NiO and 0.2% (wt.) of As_2O_5 .

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

Me	Pb	Zn	Sb	Sn	Ni	As	Fe
$K_{Me} = (Me)/[Me]$	26	323	17	112	15	3	6,400

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

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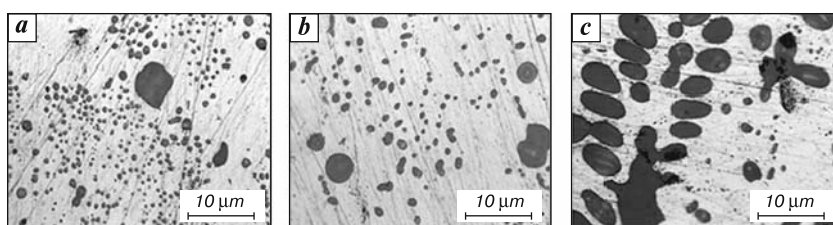


Fig. 1. Structure of copper samples:
a – sample 1; b – sample 2; c – sample 3

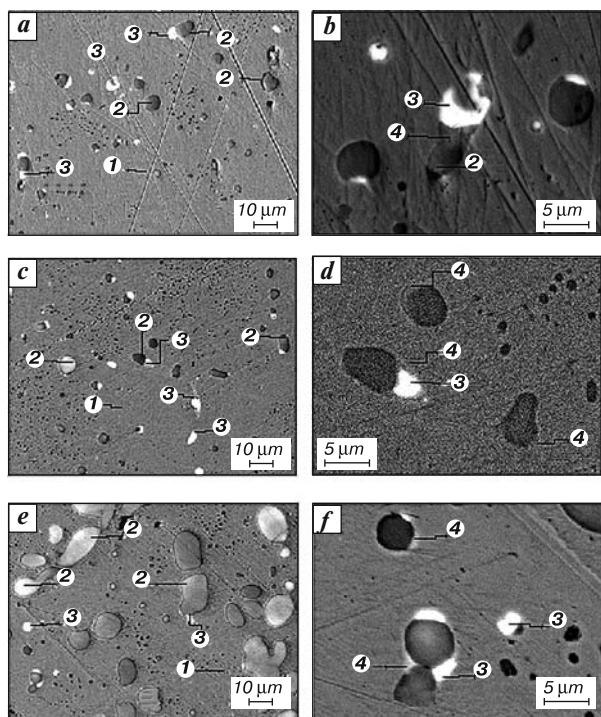


Fig. 2. Electron image of the samples' structure:
a, b – sample 1; c, d – sample 2; e, f – sample 3;
1 – Cu; 2 – Cu_2O ; 3 – $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$; 4 – Cu_xSeTeS

data processing, according to the SIAMS program and by X-ray spectrum microanalysis (JSM-59000LV and Oxford INCA Energy 200).

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 Cu_2O 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 Cu_2O , copper contains non-metallic inclusions with the size of 1–5 mm, which composition complies with the system of $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$ with low content of Ni, S, Se and 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: $\text{Cu}_{3.4}\text{Se}_{0.5}\text{Te}_{0.14}\text{S}_{0.9}$, $\text{Cu}_{3.8}\text{Se}_{0.5}\text{Te}_{0.15}\text{S}_{0.5}$ 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 $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$ and from 3 to 1 mm for selenides. A large quantity of these inclusions is found on the surface of Cu_2O 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 Cu_2O . 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 $\text{PbO} - \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5$ 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 (ρ_{oxide}):

Oxide density values are taken from the references [7–9], and the oxide share in inclusions is shown in the

$$\rho_{\text{oxide}} = \frac{\rho_{\text{Cu}_2\text{O}} \cdot \gamma_{\text{Cu}_2\text{O}} + \rho_{\text{PbO}} \cdot \gamma_{\text{PbO}} + \gamma_{\text{Sb}_2\text{O}_5} \cdot \rho_{\text{Sb}_2\text{O}_5} + \rho_{\text{As}_2\text{O}_5} \cdot \gamma_{\text{As}_2\text{O}_5}}{\gamma_{\text{Cu}_2\text{O}} + \gamma_{\text{PbO}} + \gamma_{\text{Sb}_2\text{O}_5} + \gamma_{\text{As}_2\text{O}_5}} \quad (1)$$

Table 1
Compositions of phases according to the data of X-ray spectrum microanalysis (sounding locations according to the Fig. 2)

Phase	Phase composition	Content of elements, % (wt.)								
		Cu	Pb	Sb	As	Ni	S	Se	Te	O
Sample 1										
1	Cu	99.4–100.0	0	0	0	0	0	0	0	0.0–0.6
2	Cu ₂ O	88.6–89.0	0	0	0	0	0	0	0	10.8–11.5
3	PbO – Sb ₂ O ₅ – As ₂ O ₅	–	47.3–54.3	19.1–24.8	5.3–8.0	up to 0.5	2.4–4.1	up to 0.8	up to 1.0	12.6–17.8
4	Cu _{3,4} Se _{0,5} Te _{0,14} S _{0,9}	70.5–88.8	1.2–4.5	0.0–1.5	0	0	9.2–8.9	12.6–11.3	5.5–5.6	1.1–1.4
Sample 2										
1	Cu	99.5–100.0	0	0	0	0	0	0	0	up to 0.5
2	Cu ₂ O	87.9–90.8	0	0	0	0	0	0	0	9.2–11.9
3	PbO – Sb ₂ O ₅ – As ₂ O ₅	–	47.5–55.3	17.9–24.4	6.3–7.7	0.4	2.0–3.6	0	0	16.5–18.6
4	Cu _{3,8} Se _{0,5} Te _{0,15} S _{0,5}	74.3–74.9	0	1.5–0.6	2.1–1.0	0	4.4–5.0	12.5–12.2	5.2–6.3	0
Sample 3										
1	Cu	99.2–100.0	0	0	0	0	0	0	0	up to 0.8
2	Cu ₂ O	88.3–89.2	0	0	0	0	0	0	0	10.8–11.7
3	PbO – Sb ₂ O ₅ – As ₂ O ₅	–	44.3–53.6	19.4–35.2	2.7–9.3	up to 1.0	up to 1.1	0	0	15.7–16.5
4	Cu ₄ Se _{0,65} Te _{0,25} S _{0,08}	69.3–79.1	up to 1.2	up to 0.9	0	0	0.7–1.0	18.3–11.3	11.1–6.8	0

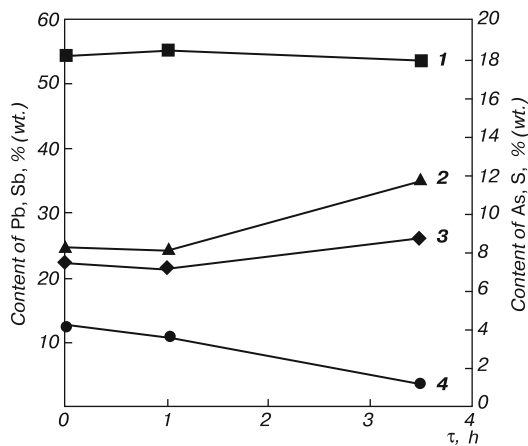


Fig. 3. Change of the content of metals and sulfur in oxide inclusions of PbO – Sb₂O₅ – As₂O₅ in the process of oxidation: 1 – Pb; 2 – Sb; 3 – As; 4 – S

Table 1. According to the calculations, the ρ_{oxide} value makes up 7.4 g/cm³. Assuming that melted copper density makes up 8.3 g/cm³ at the temperature of 1,083 °C [1], it is possible to evaluate the floating rate (v) of oxide droplets, according to the Stokes equation for Cu₂O particles (2) and Rybchinsky-Adamar equation for PbO – Sb₂O₅ – As₂O₅:

$$v_{\text{oxide}} = 2(\rho_{\text{Cu}} - \rho_{\text{oxide}}) \cdot g \cdot r^2 / 9\eta_{\text{Cu}}, \quad (2)$$

$$v_{\text{oxide}} = 2(\rho_{\text{Cu}} - \rho_{\text{oxide}}) \cdot g \cdot r^2 \times (\eta_{\text{Cu}} + \eta_{\text{oxide}}) / (3\eta_{\text{Cu}} \cdot (2\eta_{\text{Cu}} + 3\eta_{\text{oxide}})), \quad (3)$$

where: ρ_{oxide} and ρ_{Cu} – the densities of oxide inclusions and copper, g/cm³; η_{oxide} and η_{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 Cu₂O and PbO – Sb₂O₅ – As₂O₅ particles with the sizes from 1 to 40 mm, were determined,

Table 2
Rate and duration of floating of oxide particles of Cu₂O and PbO – Sb₂O₅ – As₂O₅ in copper melt

Particle radius, mm	$v_{\text{oxide}} \cdot 10^{-6}$, m/s		τ , h	
	Cu ₂ O	PbO – Sb ₂ O ₅ – As ₂ O ₅	Cu ₂ O	PbO – Sb ₂ O ₅ – As ₂ O ₅
0.5	0.35	0.2	390.00	920.0
1.0	1.40	0.6	100.00	230.0
2.0	5.60	2.4	25.00	59.0
5.0	34.00	14.0	3.90	9.4
10.0	139.00	59.0	1.00	2.3
20.0	550.00	230.0	0.25	0.6

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 °C [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 (τ) from copper melt with 0.5 m height (Table 2).

On the basis of the fact that in the process of oxidation, the melt is mixed with the rate of convection streams at the level of 0.1–0.5 m/s [11], the floating of fine oxide particles on the melt surface is practically impossible. That is why in the process of copper refining at “Uralektromed” JSC, coagulations of fine particles and their assimilation with large particles define the duration of refining.

Conclusions

The example of oxidation of blister copper impurities in anode furnaces at “Uralkhrommet” JSC shows, that during the process, there are formed the high density oxide inclusions of the $PbO - Sb_2O_5 - As_2O_5$ 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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