

Theoretical Questions of Definition of Timepoint of a Cut-Off of Air at an Oxidizing Stage of Fire Refinement of Copper

Yuriy N. Chesnokov
UrFU

Yekaterinburg, Russia
ch_jur@mail.ru

Sergey I. Holod
UrFU

Yekaterinburg, Russia
Technical university of UMMC,
Verkhnyaya Pyshma, Russia
hsi503@yandex.ru

Vladimir G. Lisienko
UrFU

Yekaterinburg, Russia
lisienko@mail.ru

Anna V. Lapteva
UrFU

Yekaterinburg, Russia
annalapteva@mail.ru

Vladimir P. Gukov
UrFU

Yekaterinburg, Russia
zhukov.v.p@mail.ru

Oleg Yu. Voinov
UrFU

Yekaterinburg, Russia
delaoldi@mail.ru

Abstract

Fire refinement of copper is intended for purification of draft copper of the impurity having the increased affinity to oxygen. At the same time a part of impurity passes into slag, and a part in a gas phase. However full removal of impurity doesn't manage to be reached. Therefore the air volume demanded for the maximum removal of impurity at an oxidation stage needs to be controlled, using the combined methods. Especially it is relevant in the conditions of increased requirements to resource-, to energy saving.

1 General provisions of fire refinement of copper

Fire refinement of copper is a closing stage of pyrometallurgical purification of draft copper of the impurity having the increased affinity to oxygen. This method is directed to the maximum removal of sulfur, oxygen, iron, nickel, zinc, lead, arsenic, antimony and the gases dissolved in fusion. At the same time a part of impurity passes into slag, and a part – into a gas phase. Further cleaning is carried out by electrolytic refinement.

From practice of fire refinement of copper it is known that process of removal of impurity takes place at an oxidation stage due to creation of necessary concentration of the oxygen given as a part of air to furnace charge fusion.

At a temperature of fusion of 1 100 °C the content of oxygen can be brought to 0,34% depending on the chemical composition of furnace charge. At the same time change of structure of primary slag phase is defined by the content of oxides in the emerging oxidation products during process (table 1).

Table 1: Structure of products of oxidation, mass %

Structure of products of oxidation, %	PbO	FeO	SnO	SiO ₂	Al ₂ O ₃	NiO	ZnO	CuO
Beginning of oxidation	20,1	2,5	16,3	18,5	28,9	2,3	8,2	3,2
Middle of oxidation	31,7	4,8	39,9	1,2	2,7	4	9	6,7
End of oxidation	31,8	4,9	35,4	0	0	4,3	6,5	17,1

Refinement of copper by a melt purge air has the thermodynamic restrictions expressing that residual concentration of impurity in a melt depends not only on concentration of oxygen in a melt, but also on activity of oxide of impurity in slag. The activity of oxide of impurity in slag is less, the refinement due to shift of equilibrium of response of oxidation of impurity towards interaction products is deeper.

Process of refinement is complicated by the fact that on the enterprise blister copper of the variable chemical composition arrives. It leads to scope change of air at an oxidation stage from melting to melting [1–5].

Cleaning of copper from impurity is carried out for the purpose of execution enough increased requirements to its characteristics, such as conductance, the plasticity, corrosion resistance, etc., low values of these indices demonstrate that copper is unsuitable for use in production.

As pure copper is generally widely applied in the radio engineering industry, the main attention in case of its receiving is paid to electrical indices, in particular unit electrical resistance ρ which makes $0,0175 \Omega \cdot \text{mm}^2/\text{m}$ at 20°C . Quite often in practice use the size of specific electric conductivity $\sigma = 1/\rho$, ($\text{m}/(\Omega \cdot \text{mm}^2)$).

The physical and chemical analysis of various samples of copper shows direct dependence of specific electric conductivity by nature of substance (concentration of impurity) and temperatures (figure 1). Apparently from the figure 1, increase in concentration of impurity in copper leads to reduction of its specific electric conductivity and reduces quality electric indicators [6–9].

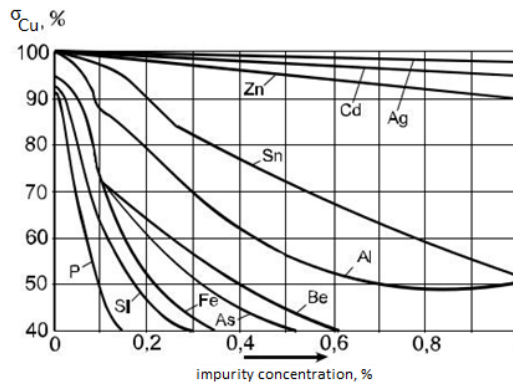


Figure 1: Dependence of specific electric conductivity of Cu on concentration of impurity, %

The dependence of the specific resistance (conductivity) of two component systems on the chemical composition of substance is described by the known rules, their application is defined by specific conditions in which there is a studied sample. In the theory of assessment of conductivity several rules use.

According to the rule Nordgeyma the specific resistance of alloy has to be approximately proportional to the work of mole fractions of two components [10].

According to the rule Linda the speed of increase in resistance with increase in concentration in the diluted alloys has to be proportional to a square of a difference of valency of components [10]. By the rule to Linda additional electric resistance $\Delta\rho$, caused by the content of impurity of 1%, in proportion to a square of a difference of valency of pure metal and Δz impurity:

$$\Delta\rho = a + b \cdot (\Delta z)^2, \quad (1)$$

where a, b – the sizes defining properties of metal-solvent.

Many fusions don't submit to this rule.

For assessment of influence of impurity at their rather low concentration use linear dependence of a gain of specific electric resistance $\Delta\rho$ from concentration of C_{imp} impurity

$$\rho = \rho_0 + \Delta\rho \cdot C_{\text{imp}}, \quad (2)$$

where ρ_0 – the specific electric resistance of the main component (solvent) depending on temperature;

$\Delta\rho$ – the residual electric resistance which isn't depending on temperature, caused by availability of impurity atoms and proportional to concentration of impurity.

The equation (2) is called Matissena-Fleming's rule [11]. According to the rule Matissena, full specific resistance is equal to the sum of the specific resistance answering to each of mechanisms separately.

Matissen's theory also assumes increase in specific resistance of pure metals with growth of temperature (figure 2). Apparently from the figure 2, specific resistance sharply increases in a copper melting temperature point.

The temperature dependence of electric resistance of metals submits to the following law:

$$\rho(t) = \rho_0 \cdot (1 + \alpha \cdot \Delta t), \quad (3)$$

where ρ_0 – unit resistance at a normal temperature, for example, 20°C ;

α – coefficient of thermal resistance

Δt – the difference of temperatures, as it can be considered a difference between 20 °C and a melting temperature.

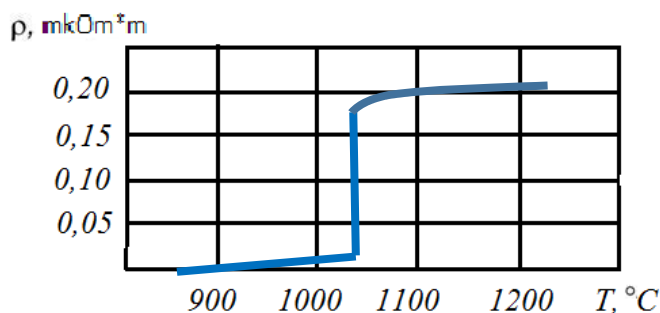


Figure 2: Dependence of specific resistance of Cu on temperature

Physical and chemical regularities of receiving electrotechnical copper are studied rather fully now. But despite it, in the conditions of increased requirements to resource-and energy saving, poor quality of raw materials and products with the variable chemical composition there is relevant a task of search of optimum conditions of refinement.

From the above material it becomes obvious that the private task of optimization is search necessary and enough oxygen as a part of air at a stage of oxidation [6].

2 Integrated approach to definition of concentration of oxygen in the course of anode melting

In this operation the theoretical questions of determination of timepoint of a cut-off of air at an oxidation stage based on application of integrated approach are provided, using mathematical and instrumental methods.

Application of integrated approach is caused by the fact that only the experimental determination of concentration of oxygen in the course of anode melting is a difficult task, especially in the conditions of high temperatures and complex multicomponent raw materials of the variable chemical composition.

The decision of this task can be broken into several parts conditionally:

1. calculation of theoretically necessary amount of air for a melt purge;
2. wiring design of monitoring of unit resistance of a melt;
3. creation of an algorithm of automatic control of the system of air supply for oxidation of impurity.

In the first part, using stoichiometric dependences, calculated:

1. on mass of impurity as a part of furnace charge mass of oxide of Cu_2O copper (I);
2. on Cu_2O mass necessary value of theoretical mass and % (on mass) oxygen;
3. amount of the air in tons and m^3 given to a melt.

This information comes to the microcontroller.

The second part provides the wiring design of monitoring of unit resistance of a melt based on strain measurement by the compensation and difference method (figure 3). Two couples of electrodes 1,1' and 2,2' are for this purpose applied. One couple is dipped in a reference melt (a melt of electrotechnical copper) with unit resistance ρ_r , the second couple in a melt of blister copper with unit resistance ρ_{in} . The stabilized voltage sources of E_1 and E_2 are opposite connected to each couple of electrodes. On the one hand two electrodes of different couples are connected among themselves. The load resistances of identical value of R_{l1} and R_{l2} are provided in a circuit.

Between the free ends of electrodes 1 and 2 the digital microvoltmeter from which signal comes to the microcontroller is switched on. Through each couple of electrodes currents of I_1 and I_2 proceed. Currents cause falling of tension on reference ρ_r and initial ρ_{in} resistance.

For improving of the quantitative indices of measurement in a circuit use of the amplifier is allowed.

In a figure 4 the theoretical nature of change of voltage drop between electrodes is shown (points 1 and 2) in case of course of currents of I_1 and I_2 in the counter direction in the conditions of change ρ_{in} due to operation of oxidation of impurity.

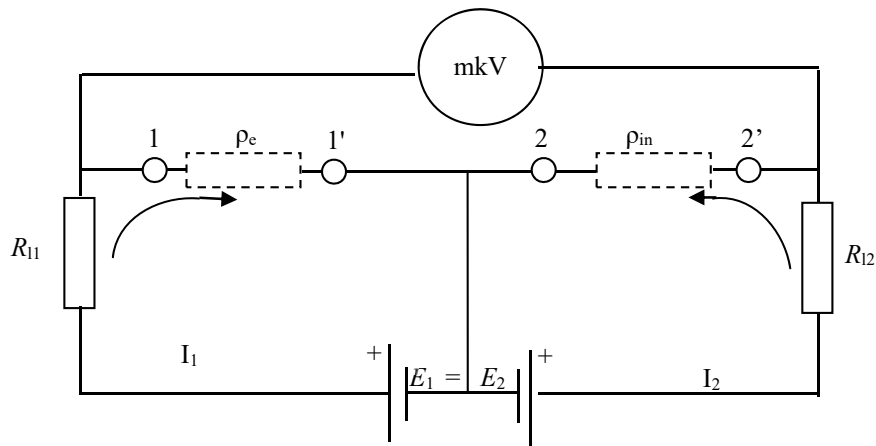


Figure 3: Compensation and differential scheme of voltage measurement

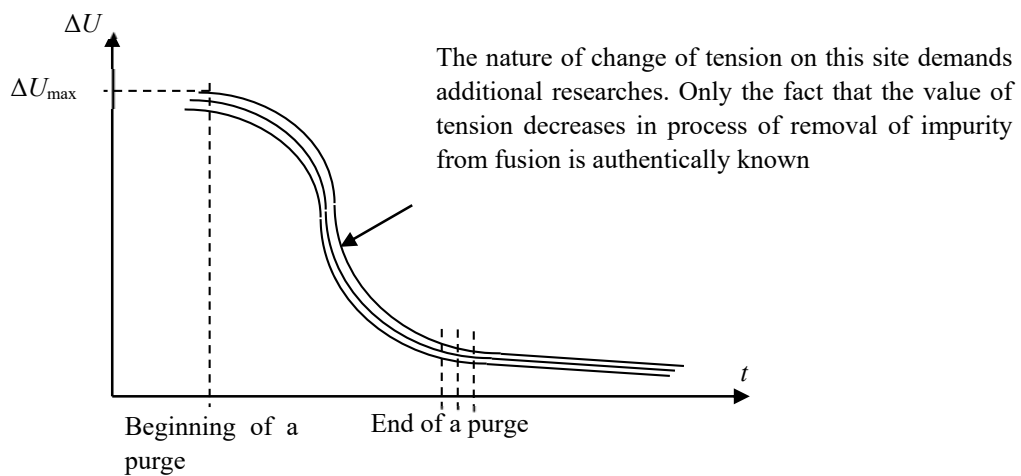


Figure 4: The nature of change of differential tension between electrodes

On a graphics several curves, initial values ΔU_{\max} which are various are shown and are defined by variable composition of the initial furnace charge.

At a final stage of value ΔU also differ from melting to melting. It is caused by thermodynamic restrictions as a result of which a part of impurity remains in anode copper. The instability of temperature of a melt and sources of current can also exert impact on value ΔU . All these restrictions exclude a possibility of a cut-off of air at an oxidation stage directly on the measured values ΔU .

In this regard it is safer to define the moment of a cut-off of air it is possible on change speed ΔU as the content of impurity as a part of a melt by the end of a purge has the small speed of change. When using microcontroller technique the decision of such task becomes simpler.

For an exception of instability of starting value ΔU_{\max} the microcontroller leads the law of change ΔU from time to a normal look:

$$\Delta U_n = \Delta U_i / \Delta U_{\max i}, \quad (4)$$

It is necessary to understand the current values as the index i .

Interesting challenge is selection of material and construction of electrodes.

The key parameter defining material is the melting temperature. Niobium, molybdenum, tantalum, tungsten and rhenium belong to the base refractory metals. Titanium, vanadium, chrome, zirconium, hafnium, ruthenium and osmium

have a melting temperature below, than the base refractory metals, but also can be considered as electrodes under certain conditions.

For lowering of temperature of an electrode it is possible to provide cooling with system water from two coaxial steel pipes. Cold water which passes into an external pipe comes to the central pipe, cooling it. To prevent influence of the slags floating on a surface electrodes it is necessary to cover on top with heat resisting and electrical insulation. The alternating current of industrial frequency is applied to preventing of sticking of ions to one electrode.

The metal choice problem also consists in that, as in the atmosphere, and in a copper melt in case of a purge there is an oxygen which at the given temperatures oxidizes metal. So, the tungsten as the most high-melting of metals (more high temperature of melt only carbon has) at a temperature of a red kaleniye slowly is oxidized in oxide of the tungsten (VI) WO_3 , losing the functions. A molybdenum begins to be oxidized at a temperature of 400 °C. In case of achievement of temperature over 600 °C a molybdenum quickly is oxidized to oxide of molybdenum (VI) MoO_3 . Titanium in case of heating up to temperature of 1 200 °C lights up a bright white flame with formation of oxide-coated phases of variable composition TiO_x . Inert platinum in case of heating up reacts with oxygen with formation of volatile oxides.

In the third part creation of an algorithm of automatic control of the system of air supply for oxidation of impurity on the basis of data of the first and second part is supposed [12–14]. The microcontroller normalizes indications on a formula (4) and compares to the previous indications. In a figure 5 process of a cut-off of air in time is shown. In case of the difference of these indications less preset value ΔU_n the microcontroller gives a command on an air cut-off (figure 6). The value ΔU_n depends on the frequency of inquiry of the microvoltmeter and the expenditure of air on a purge which is also controlled by the microcontroller.

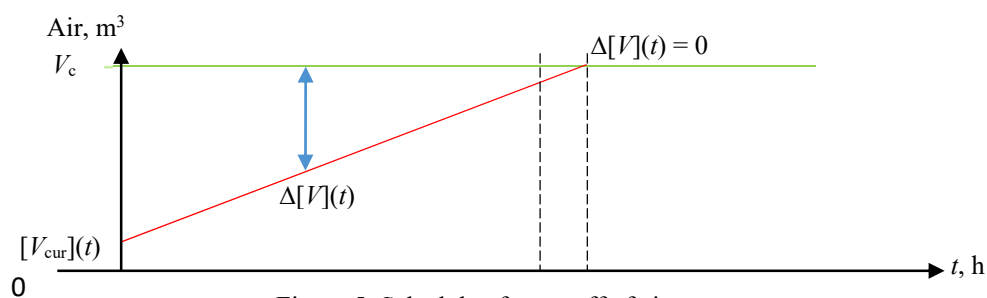


Figure 5: Schedule of a cut-off of air

Results of work will be coordinated with the general theory of fire refinement and can be of interest to practice of anode melting.

3 Conclusion

In this operation questions of methodology of integrated approach to determination of timepoint of a cut-off of air at an oxidizing stage of fire refinement of copper in the conditions of high temperatures and complex multicomponent raw materials of the variable chemical composition are considered.

Theoretical questions of preparation of the scheme of control of specific resistance of fusion are shown by a compensation and differential method.

The main restrictions imposed on use of materials as electrodes are considered. The possibility of creation of an algorithm of control and management of the air given to copper fusion at an oxidation stage is shown.

The offered methodology can be considered as the first development stage of the complex scheme of automation of process of fire refinement of draft copper.

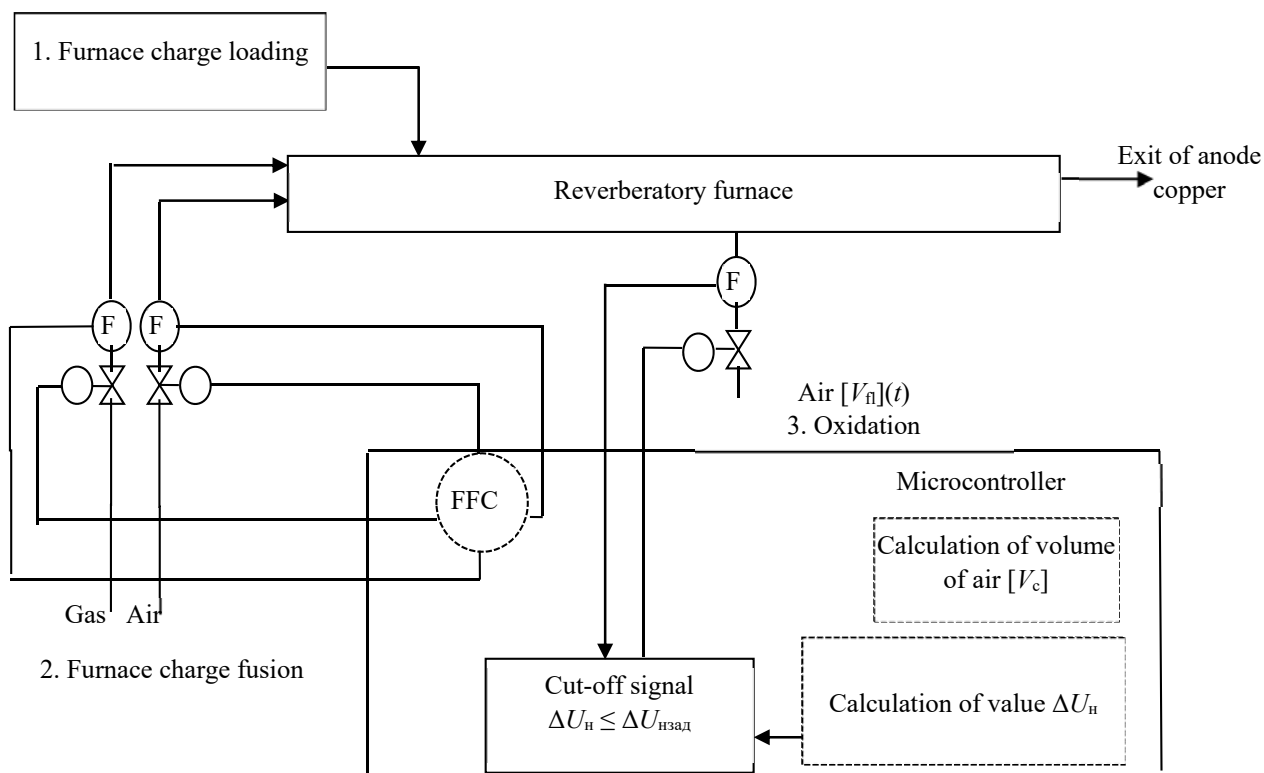


Figure 6: Function chart of an algorithm of a cut-off of air

References

1. Davenport W.G., King M., Schlesinger M., Biswas A.K. Extractive metallurgy of copper, fourth edition. – Oxford: Elsevier Sci. Ltd., 2002. – 481 p.
2. Biswas A.K., Davenport W.G. Extractive metallurgy of copper. – Oxford: Pergamon, 1996. – 290 p.
3. Gerlach J., and Herfort P. The Rate of Oxygen Uptake by Molten Copper // Metall. 1968. 22 (11). – P. 1068–1090.
4. Bugs of Accusative, Spitchenko V. S., Novokreshchenov S.A., S.I. Cold. Copper refinement. – Yekaterinburg: URFA, 2010. – 317 p.
5. Bugs of Accusative, Skopov G. V., S.I. Pirometallurgiya's Cold of copper. – Yekaterinburg: OURO RAHN, 2016. – 632 p.
6. Bogoroditsky N.P., Stepsons V. V., Tareev B.M. Electrotechnical materials. – L.: Energoatomizdat, 2000. – 304 p.
7. Wren V.T. Electrotechnical materials. – L., 1984. – 269 p.
8. Koritsky Yu.V., Stepsons V. V., Tareev B.M. Reference book on electrotechnical materials. – M.: Energoatomizdat, in 3 t., 1986–1988. – 368 p., 464 p., 728 p.,
9. Livshits B.G., Kraposhin V.S., Linetsky Ya.L. Physical properties of metals and alloys. – M.: Metallurgy, 1980. – 320 p.
10. Vilson D.R. Structure of liquid metals and the alloys / translation from English L.A. Koledov; under the editorship of the prof. V.M. Glazov. – M.: Metallurgy, 1972. – 247 p.
11. Okazaki K. Posobiye on electrotechnical materials / Kiyesi of Okazaki; edition of L.R. Zayonts. – The lane with яп. M.M. Bogachikhina, I.B. Reuta – M.: Energy, 1979. – 432 p.
12. Krupsky V.N. Theory of algorithms. – M.: Academy, 2009. – 208 p.
13. Akho A. V. Structures of data and algorithms / lanes from English and an edition of Minko A.A. / Akho A.V., Hopcroft D. E., Ullman D.D. – M.: Williams, 2001. – 382 p.
14. Kormen T.H., Leyzerson Ch.I., Rivest R.L., Stein K. Algorithms: construction and analysis. – M.: MTsMNO, 1999. – 960 p.