CONDITIONS OF RATIONAL ELECTROREFINING OF ANODES FROM COPPER-SILVER SCRAP

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ABSTRACT

The reasons of formation low quality cathode deposits and conditions of the anode passivation in electrorefining of copper silver alloys with increased (more then 5%) silver content in electrolyte, g/l: Cu 40; H_2SO_4 50; 150 and 250; T= $40\pm1°C$ have been investigated. As it is shown, increased acidity, anodic current density and silver content in anodes favor passivation. The assumption is made that the ingress of silver on cathode is the most probable reason of growing dendrites on cathode. We have determined that addition of ethylene carbonic acid to electrolyte in the amount of 3.5 – 10 ml/l suppresses the dendrite formation.

INTRODUCTION

The most effective scheme of processing secondary raw materials with any composition variation at maximum recovery of precious metals (PM) involves the combination of mechanical and thermal scrap preparation operations with its melting on copper collector and subsequent electrorefining of produced copper anodes. Contrary to the anodes from primary blister copper, which usually comprise 99.0 – 99.7 % Cu and up to 0.6 % of precious metals (PM) in total, the anodes melted from secondary raw materials are characterized by low content of Cu, S, Se, Te, As, Bi, increased total content of PM and such metals as Ni, Pb, Sn, Zn, Fe, up to 4 – 5 % and above.

Specialized firms, created in Ukraine for processing scrap, comprising PM, are faced with such situation when, as a result of melting some forms of conversion wastes, the copper alloys are formed in which the total content of precious metals exceeds significantly the ordinary composition. Such firms, using copper electrorefining process, have a good possibility to work with anodes, comprising increased content of precious metals, because it can improve the feasibility of their process.

However, as it is commonly known [1], the increased content of precious metals in copper anodes complicates the electrorefining process, because the quality of cathode deposit is deteriorated and the anodic current density of passivation is decreased. That is why the investigation of the possibility of rational copper refining process with increased content of precious metals is a high – priority task.

AIM AND METHOD OF INVESTIGATION

The main aim of the investigation is the following:

1. To determine the influence of main process variables on the anodic dissolution of copper – silver alloys.

2. To reveal the reason of formation of low quality copper cathode deposits and methods of prevention this phenomenon.

Model anodes with varying Ag content from 0 up to 100% (step in every 3-5% for anode composition from 0 to 30% Ag and 10% in the range of 30-100% Ag) were used as objects of investigation. Anodes were melted from pure (99.99) copper and silver in the induction furnace under covering flux. In order to simplify the real system the gold (and platinum group metals) was not introduced in model anodes, because gold being more electropositive in comparison to silver, was almost completely concentrated in anode sludge and could be recovered easily at the stage of silver affinage.

The experiment method was based on laboratory investigations, which due to peculiarities of the mass transfer at vertical fixed electrode could not be extrapolated to commercial scale but could assess the influence of some process factors on electrolysis. Volt – ampere measurements were also used in stationary and potentiodynamic conditions.

To simplify the experiment the tests were carried out simultaneously in three parallel connected electrolytic cells (V = 1L), each of which was serial connected with copper coulometer. The anode (S = 48 cm^2) was positioned between two diaphragms made of polypropylene cloth. Chlorine cloth could led to uncontrolled appearance of chlorine ions and copper ions diffusion was hindered through mipora. In low part of the anode space there was a collecting hopper for sludge, which was evacuated through special output hole. The cathodes made of polished stainless steel were positioned near both sides of anode, interelectrode space was 38 mm.

Potentiodynamic polarization curves were read by potentiostat П – 5848 with recording potentiometer КСП – 4 in thermostatting glass cell (V = 0.2 l) and by chlorosilver reference electrode. Teflon insulated anode surface was 7.1 cm^2. The potential scanning (E) at the rate 4 mV/c was started from stable stationary potential at T = 40 ± 1° C. The electrolyte composition, g/l: Cu^{2+} 40; H$_2$SO$_4$ 50, 150 and 250 corresponded to main variables of laboratory experiments. All values of potentials were cited in reference to normal hydrogen electrode (n.h.e.).

RESULTS

Laboratory Process Investigations and Volt – Ampere Measurements.

We have determined that unlike the anodic dissolution of pure copper when dense uniform pink deposits are formed on the cathode, even with building during several days, the main drawback of the copper electrorefining process with increased (from 1-3%) silver content is an active development of the cathode surface leading to deposit flaking off, short circuits between electrodes and silver contamination of cathode copper. The more is the Ag content in the anode and less is the H$_2$SO$_4$ concentration in electrolyte the earlier is the appearance of dendrites with heavily developed surface and more is the intensity of their development. In the conditions of anodes with composition 19.8 – 30.7 % Ag and acidity 50g/l the cathode dendrites are growing through the diaphragm and causing short circuit, and Ag content in the Cu cathode deposit is reaching–1.2 %.

Visual observations and sample analysis have shown that silver sludge is present on the anode surface, on the diaphragm near the cathode space, in the form of partly sedimentated suspension in both electrode spaces. Fig. 1A shows clearly that the sludge fraction (if we take the total quantity of separated sludge as 100%) is increasing in the cathode space, but decreasing in the anode space as Ag content is increasing in the anode alloy up to 20 %. Further changes are weak. With increase of H$_2$SO$_4$ concentration up to 250 g/l the sludge distribution could depend the anode composition in the range of 10 – 30% Ag. Sludge metallographic examination has shown that along side with fine Ag crystals, observed directly on the microsection of anode alloy there are large petalled dendrites which size is by an order of magnitude greater. To our opinion this can evidence the secondary crystallization of silver.
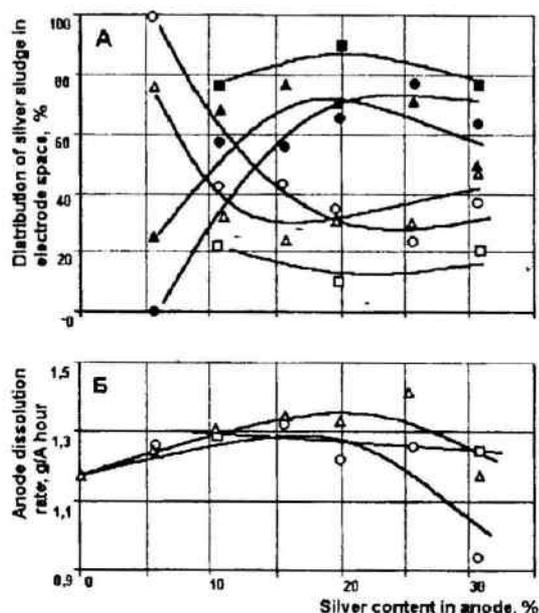

Fig. 1 The influence of silver content in copper - silver anode alloy on the distribution of silver sludge in anode and cathode spaces (A) and the anode dissolution rate (Б) in electrolyte, g/l : Cu - 40, H$_2$SO$_4$: o and ● - 60; Δ and ▲ - 160; □ and ■ - 250 (light symbol for anode space, black for cathode space) at T = 40° C and cathodic current density 160 A/m^2.

Measurement results of anode potentials (Fig 2) have shown that at the beginning of electrolysis and in the period of 5-7 hours for anodes, comprising up to 19.8 % Ag, they are practically the same, gradually increasing in 24-hour electrolysis. The alloy, comprising up to 30.7 % Ag, is characterized by passivation effect, which appears in 2 hours after the electrolysis start, and by depassivation (5-6 hours). When oxygen released on the anode blows away the passive film and the anode potential returns to initial values.

In the range of anode composition up to 15-17 % Ag the rate of the anode dissolution (Fig 1Б) depends slightly the acid concentration and is 1.2 – 1.3 g/Ah, rising steadily with the increase of Ag content in the anode. It is quite explained by greater value of Ag

electrochemical equivalent in comparison to Cu. In the process sense it is preferable to conduct the electrolysis at H_2SO_4 concentration near to 150 g/l, because for anodes rich in Ag this acidity provides the highest rate of the anode dissolution at relatively short period of their presence in passive condition.
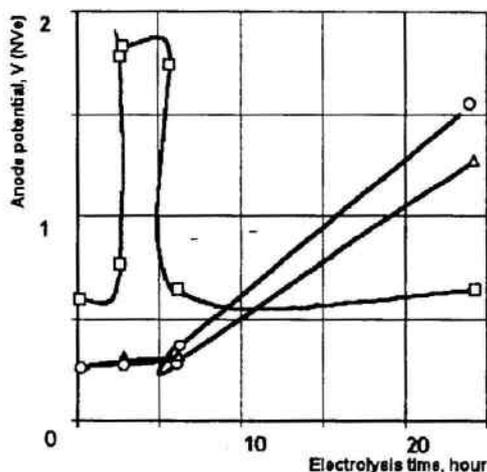

Fig. 2 The change of anode potentials with time in electrolysis of solution 30 g/l Cu^{2+} and 250 g/l H_2SO_4. Silver content in anode, %:

Δ - 10.7;
o - 19.8;
□ - 30.7.

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Potentiodynamic measurements have shown that the anode polarization curves for copper and its alloys comprising 5 – 25 % Ag have an identical form (Fig. 3, curve 1), and stationary potentials (E) are also practically identical and account for 0.321 – 0.326 V. Only for alloys with higher Ag concentration the stationary potentials start rising (75 % Ag E = 0.339 V, 100 % Ag E = 0.491 V). It is easily explained by the fact that Cu-Ag alloys form mechanical mix of these metals crystals, in which stationary electrode potential is defined by the potential of more negative component, i.e. by copper. For pure Ag (Fig. 3, curve 3) the polarization curve has typical form, including the region of active dissolution at E > 0.64 V, salt passivation at E = 0.8 V at the expense of formation low soluble film of Ag_2SO_4, and sharp current jump at E = 1.85 V which corresponds to the beginning of the oxygen release. 25 % Ag alloy (curve 2) shows clearly two peaks of active dissolution and two regions of passive condition. The second region of passivation is observed in the same E range as for pure Ag.
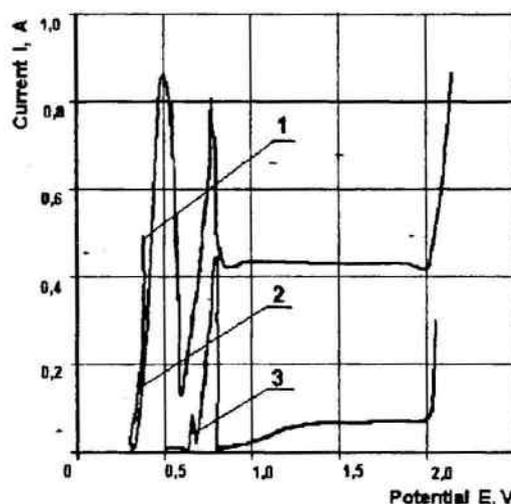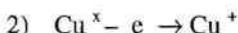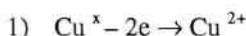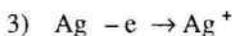

Fig. 3 Anodic potentiodynamic polarization curves of Cu - Ag alloys whith composition, % : 1 - 0.5, 15 and 25; 2 - 60; 3 - 100 Ag in the electrolyte, g/l : Cu - 40; H_2SO_4 - 150, T = 40°C

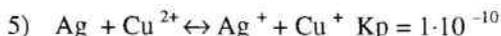## Discussion of Results. Reasons of Dendrite Formation

The above data concerning the values realized on the anode potentials (Fig. 2), which reach the magnitude of the silver equilibrium potential in sulphate solution $E_0 = 0.654$ V [2], as well as the appearance of silver in the cathode space and its crystals deposits on diaphragm near the cathode space allow to make an assumption that in investigated conditions of anode polarization of copper-silver alloys on the anode there is not only oxidation reaction of copper:
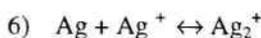
1) $Cu^x - 2e \rightarrow Cu^{2+}$

2) $Cu^x - e \rightarrow Cu^+$

but also of silver:

3) $Ag - e \rightarrow Ag^+$

In addition there are equilibria in electrolyte [2,3]:

4) $Cu^{2+} + Cu \leftrightarrow 2Cu^{2+}$ $Kp = 0.3 \cdot 10^6$

5) $Ag + Cu^{2+} \leftrightarrow Ag^+ + Cu^+$ $Kp = 1 \cdot 10^{-10}$

and probably:

6) $Ag + Ag^+ \leftrightarrow Ag_2^+$

as a result of which the silver is present in electrolyte either in the form of ions, or in the state of colloid suspension formed as a result of shift the equilibrium to the right (5), i.e. the reduction of silver ions by univalent copper ions. Due to this we can assume that

with the increase of silver content in anodes, the quantity of Cu^+ ions, formed primary in anodic dissolution, is not enough for complete reduction of Ag^+ ions, formed according to reaction (3). This is the cause of their penetration in the cathode space by diffusion and migration via diaphragm.

Ag^+ ions, penetrating into the cathode space, are partly discharged on the cathode and partly interact with Cu^+ ions, always present in it, reducing into metal and forming colloidal suspension, which also can be transferred on the cathode and occluded by the growing cathode deposit as well as sedimented in the form of sludge. This scheme explains clearly the formation of silver sludge on the diaphragm surface near the cathode space (point of meeting Cu^+ and Ag^+ ions) and in the volume of the cathode space. Moreover, a special experiment (15.6% Ag anode), in which near the cathode surface an additional diaphragm in the form of screen is set, has detected the preferential accumulation of sludge between the cathode and additional diaphragm, hindering the copper – ions transfer to the main diaphragm, on which surface the silver sludge is practically absent in this experiment. Thus, the received data allow to make the conclusion that the most probable reason of formation low quality dendritic cathode deposits in electrolysis of copper anodes with increased silver content is the ingress of silver on the cathode.

Prevention of Dendrite Formation

According to the above point of view we can assume that any stimulation of the Cu^+ ions formation in the anodic space (or suppression of the Ag^+ formation) will favor reduction of Ag^+ ions into metal silver and prevent, their ingress to the cathode, which in its turn decrease the growth of dendrites. At the same time it is known [4] that the concentration of Cu^+ ions in acidic solution of $CuSO_4$ may be increased by introduction of ethylene carbonic acid (ECA); the more is the acid concentration the larger is the ions concentration. In this connection we have conducted experiments to investigate the influence of ECA on the electrorefining process of Cu – Ag anodes.

We have determined that addition of ECA to the electrolyte causes the shift of cathode potentials to negative side (≈ 100 mV), and anode ones to positive side (≈ 200 mV). The addition of ECA in the amount of 3.5 ml/l (Table) is already enough to decrease sharply (by an order of two magnitude greater) the silver content in the cathode deposit.

The influence of ethylene carbonic acid (ECA) on silver content in cathode copper and sludge

distribution in electrode spaces. Electrolyte, g/l: Cu^{2+} 40, H_2SO_4 150, T = 40°C, cathodic current density 200 A/m^2; anode – 10.7% Ag, 89.3% Cu.

Table 1.

ECA concentration in electrolyte, ml/l	0	3.5	6.0	10.0
Sludge content in cathode space, %	50	39	8	1.7
Sludge content in anode space, %	50	60	92	98.7
Silver content in cathode copper, %	0.67	0.007	0.0019	0.0016

The dendrite formation is taken place but to a lesser extent than in pure electrolyte without ECA addition. With the increase of ECA from 3.5 up to 10 ml/l almost all (98.3%) sludge is concentrated in the anode space and the dendrite formation is completely suppressed.

CONCLUSIONS

Thus, the investigation of electrorefining process for copper – silver anodes in the electrolyte, g/l: Cu 40, H_2SO_4 50, 150 and 250, t= 40$\pm$ 1° C, has shown that the anodic process is rather stable. The higher is the anodic current density, acidity and silver content in anode the more rapid is the passivity of anodes. However, the passivity is not stable. Dissolution rate of anodes, comprising in average to 20% Ag, remains stable even in 7-10 days of electrolysis up to their complete consumption.

Main drawback of this process is inadequate quality of copper cathode deposit. The cathode is characterized by dendritic growth; deposit becomes friable, dark and is easily crumbling. The silver content may reach 1.5 % in it.

It is supposed that the main reason of the dendrite formation is the oxidation of silver on the anode and its ingress into the cathode space, where silver ions are reduced by the cathode discharge or by interaction with univalent copper ions disturbing the normal growth of the cathode deposit.

The information received about positive influence of ethylene carbonic acid, which addition to electrolyte in the amount of 3.5 ml/l and more suppresses the dendrite formation, is the evidence in favor of the above assumption and confirms the possibility of using copper anodes, comprising increased (to 30%) content of silver. It indicates also the

necessity of further investigation of electrorefining process for precious metals – rich anodes in presence of ethylene carbonic acid and other surface – active additives, because it can gain a significant applied importance.

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