# Anodic Processing of Non-Ferrous and Precious Metal Alloys in The Chloride Solution

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**Abstract.** The rate of anodic dissolution and dependence of current of partial components of the current density $D_a$ for alloys with different Au, Ag and Cu contents have been studied. At high $D_a$ both components of alloy etched with equal rate, whereas at low $D_a$ region of selective dissolution of electronegative components (Ag, Cu) has been observed, a top boundary of which rises with the increasing of Cu contents in the alloy.

**Introduction.** Copper clinker of zinc production, lead scrap in battery production, scrap of refining jewelry factories and alloys for dentures, special solders, etc. are a potential source of additional capacity building for the production of non–ferrous and precious (noble) metals in the metallurgy of the Republic of Uzbekistan. The development of technology for electrochemical refining of similar non-ferrous and other valuable metals from secondary raw materials is an urgent problem.

The most common gold jewelry alloys are triple alloys of gold with silver and copper (for example, 583rd and 375th samples), which together with silver alloys leads to the fact that the waste of jewelry alloys entering refining usually contains 30-60% Au, 8-25% Ad and 30-50% Cu. These alloys are a system of solid solutions containing both film-forming components. Therefore, their anodic behavior simultaneously manifests both the features of gold-silver and the features of gold-copper binary alloys.

This article is devoted to the development of recommendations on the technology of refining of real low-grade waste of secondary precious metals.

**Methodology.** The alloys were dissolved in a two-chamber electrolysis cell. The electrolysis cell, consisting of two compartments, is filled with a solution of hydrochloric acid. The anode (alloy) is lowered into one compartment, the cathode (copper plate) is lowered into the second. The study of anodic dissolution of alloys was carried out depending on the dissolution potential of the current density. Solutions in the composition of 1-3M HCl in the presence of 0.3 M NaCl were prepared for the experiments. The potential of the working electrode was measured relative to the saturated calomel electrode.

**Results And Their Discussion**

In [1], a method is proposed for processing secondary raw materials with a lower gold content, i.e. its alloys with silver, copper and other metals (Fig.1). The essence of our proposed method is the use of increased current densities (the specific value depends on the composition of the alloy), providing at the anode, along with the dissolution of the alloy components, periodic release of chlorine in small quantities, as well as by returning the de-gilded electrolyte to the cathode space for the release of impurities (for example, copper), followed by its reinforcement with hydrochloric acid and circulating using.
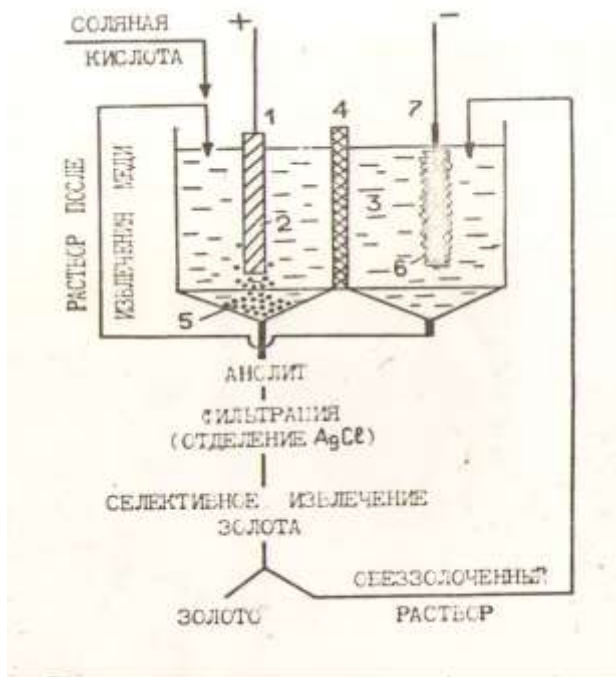
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Fig. 1. Technological scheme of processing alloys with low gold content.

The anode 1 from the alloy to be processed is placed in the anode space 2 of a two-chamber electrolyzer, separated from the cathode space 3 by a partition 4 impervious to AuCl-4 anions (a cation exchange membrane or an inert diaphragm with a small pore radius). The electrolyte is a solution containing 1-3M HCl in the presence of 0.3 M NaCl.

The anode current density required for the dissolution of this alloy depends on its composition (with an increase in the silver content in the alloy, it decreases), but in all cases it should be such that during anodic dissolution, periodic passivation of the anode and a potential shift to the chlorine release region occur, as well as periodic depassivation of the anode due to loosening of the AgCl film by releasing chlorine and reducing the anode potential below the oxidation boundary of Cl-ions. In addition to loosening the chloride film, the periodic release of chlorine leads to saturation of the anolyte with active chlorine and additional chemical dissolution of gold, for example, small gold particles from the anode sludge. As a result, the anode sludge contains only silver chloride. Falling off the anode, silver chloride (AgCl) $_5$ accumulates at the bottom of the electrolyte or in the anode basket. The other two components of the alloy (Au and Cu) pass into solution, with gold in the form of AuCl-$_4$ anion, and copper – Cu2$^+$ cation. Therefore, gold is not transferred through the cation exchange membrane and remains in the anolyte, while copper is partially transferred to the catholyte along with other cations – H$^+$ and Na$^+$.

After the accumulation of gold in the solution, the anolyte (or part of it) is periodically or continuously directed to the selective extraction of gold, for example, by electrolysis, extraction or chemical precipitation.As a result, a solution containing practically no gold is obtained (for example, when precipitated with bisulfite, the concentration of gold in the solution decreases by 10$^6$ times [2]). Copper chlorides are present in it along with HCl and NaCl. Next, the gold-plated copper-containing solution is sent to the catholyte, where copper is extracted from it due to the release of metallic copper 6 at the cathode 7. The cathodically treated solution (containing residual concentrations of hydrochloric acid, sodium and copper chlorides), after further strengthening by HCl, re-enters the anolyte, i.e. the reverse use of the chloride electrolyte is ensured.

Experimental data on the processing of jewelry alloy of the 583rd and 375th samples are presented in [3].

**Processing of alloy of the 583rd sample (58.3% Au, 8.7% Ag and 33% Cu).**
This alloy is a system (like a binary gold-silver alloy similar in silver content) up to a current density of 1200 A / m$^2$, the potential is in the zone of active dissolution of gold, strong passivation of the anode by chloride films and chlorine release is not observed. When the current increases to 1600 A / m$^2$, the anode

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potential increases to 1.6-2 V and begins to fluctuate periodically, indicating the beginning of parallel chlorine release and passivation of the anode. At the same time, like binary gold-copper alloys, when this triple alloy is anodically dissolved, selective dissolution of the electronegative component (copper) is observed at low current densities (up to 250 A/m$^2$). And only at a current density above 1000 A / m$^2$, uniform etching of all alloy components occurs, and at even higher current densities equal to 1500-3000 A / m$^2$, a wide range of stationary anode dissolution of the alloy with periodic fluctuations in the anode potential is achieved. It is this range of current densities that is optimal for the anodic dissolution of this alloy.

 Selective isolation of gold from an anolyte was carried out electrochemically in a potentiostatic mode on a rotating titanium rod at a cathode potential of 0.4 V (saturated hydrogen electrode), at which the discharge of copper ions does not occur yet. The initial gold content in the anolyte is 73 g/l, the final one is 1-3 mg/l. This decontaminated solution was poured into the cathode space of the first electrolyzer. The cathode was a titanium plate in a polypropylene mesh cover. During electrolysis, copper was released at the cathode. The sediment was dense in thin layers, but with increasing thickness it turned into spongy and was easily removed along with the mesh cover. The initial copper content is 42 g/l, the final one is about 1 g/l. The final concentration of hydrochloric acid in the catholyte is 0.7–1.1 M. After the HCl solution was strengthened to the initial concentration, the catholyte was used to dissolve the next batch of the alloy.

**Processing of the Z75 alloy (37,5 % Au, 12,1 % Ag и 47,3 % Cu).**
Since this alloy differs from the previous one by a higher (approximately 1.5 times) content of Bp and Cu, the mode of uniform dissolution of all components of the alloy is achieved at higher anode current densities (about 1500 A / m$^2$, and the mode of periodic short–term chlorine release - at an anode current density of 2000-3000 A/ m$^2$. Therefore, the optimal current density range for processing this alloy is 2000-4000 A/m$^2$ (Fig.2).

**Processing of artificial triple alloy with the highest expected silver content (49,8 % Au, 24,5 % Ag and 25,7 % Cu).**
Due to the very high Ag content, passivation phenomena on this alloy are most pronounced. So the periodic release of chlorine begins already at an anode current density of about 250 A / m$^2$, the area of uniform dissolution of all components of the alloy is 300-600 A/ m$^2$. With a further increase in the anode current density, the amount of chlorine released increases. Therefore , the optimal range of current densities for this alloy is 300-500 A/m$^2$.
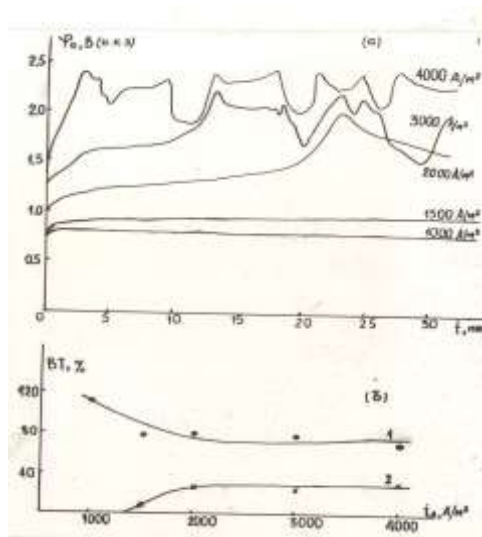


Fig. 2. The change in the anode polarization over time during the anodic dissolution of the alloy of the 375–th sample with different current densities (a) and the dependence of the current output on $Cu^{2+}$ (1) and $Au^{3+}$ (2) (b).

The choice of an effective mode of anodic dissolution solves only part of the problem of processing jewelry alloys. Another part of it is associated with the rapid accumulation of copper ions in the solution, which, during the process without separating the cathode and anode spaces, are released on the cathode together

with gold, preventing its purification. Therefore, additional measures are required to separate the flows of gold and copper. For this purpose, cation- and anion-exchange membranes (MK-40L and MA-40 L) are used. It was found that when the electrode spaces are separated by a cationic membrane, the gold remains completely in the anolyte. Copper is present in the anolyte mainly in cationic form and is therefore partially transferred to the cathode, although the number of copper ion transfer is small: the main current carriers through the membrane are $H^+$ and $Ka^+$.

Thus, using the example of the three alloys studied, which overlap the usual waste of jewelry production in terms of the content of film–forming components (Ad up to 25%, Cu - up to 50%), it can be concluded that for each type of alloy there are conditions that ensure its sufficiently effective dissolution in hydrochloric acid solution, and as a result of processing to obtain them in the form of individual components: Ad – in the form of AgCl, Au and Cu – in metallic form). At the same time, the efficiency of the process is significantly increased due to the rational use of cathode current for copper extraction, as well as the recycling of chloride solution. A common feature of these conditions is the beginning of the joint release of chlorine, accompanied, as a rule, by oscillations of the anode potential and providing periodic destruction of a continuous film of chlorides. An additional positive effect of this mode is the saturation of the anolyte with chlorine and chemical dissolution of the particles of the anode sludge (similar to hydrochlorination).

### References

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