

**ELECTROCHEMICAL BEHAVIOR OF GOLD-SILVER ALLOYS IN HYDROCHLORIC ACID SOLUTIONS: EFFECT OF SILVER CONCENTRATION**

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академии наук, Новосибирск, Россия**Abstract**

The effect of silver (up to 20 % by weight) on the kinetics of anodic dissolution of gold-silver alloys in hydrochloric acid solutions was studied by the method of potentiostatic inclusion curves. It is shown that the dependence of current density on time can be consistently described by models of formation and thickening of a porous film of silver chloride.

Introduction: scrap from jewelry refineries, lead scrap, dentures, special solders, etc. is a potential source of additional increase in the production of non-ferrous and precious metals in the Republic of Uzbekistan. The development of a technology for purifying such non-ferrous and other valuable metals from secondary raw materials is an urgent problem.

Objects and methods of research. Gold-silver alloys (with a silver content of 4 to 20% by weight) in the form of cylinders with a diameter of about 1 mm were prepared from weights of pure (99.99%) gold and silver by melting under vacuum in a special graphite container and holding the melt for 3-5 hours. as well as anodic polarization curves were recorded using the RA-3 polarograph.

Results and discussion. On the anodic polarization curve of pure gold in chloride solutions (Fig. 1, curve 1) in the region of overvoltages $\eta = 300-600$ mV There is a stationary zone of active dissolution with a clearly defined limiting current. The value of this current is proportional to the chloride concentration [3] and the square root of the potential sweep velocity, i.e. it is the limiting diffusion current for Cl anion-. With further anodic polarization, the gold surface is passivated by a film of oxides, followed by the release of chlorine.

Objective: to study the effect of silver on the kinetics of anodic dissolution of gold-silver alloys in chloride solutions.

Keywords: alloys, electrochemical dissolution, anode, cathode, current density, potential.

Introduction

Electrochemical dissolution of blister gold in hydrochloric acid solutions is widely used in the technology of refining precious metals according to the Wolville method [1]. At the same time, one of the most tightly controlled impurities in anodes is silver (its content should not exceed 12% by



weight), since during dissolution it forms a film of insoluble silver chloride on the anode, which complicates the refining process. However, in recent years, the proportion of alloys (e.g. jewelry, dental and special alloys) with a higher silver content has been increasing in the raw materials to be processed. Their processing by adding to gold-rich raw materials is not always possible, so the study of the features of anodic dissolution of such alloys is an urgent task. Since low-grade gold alloys are multicomponent systems, it is advisable to start studying them with simpler binary gold-silver alloys.

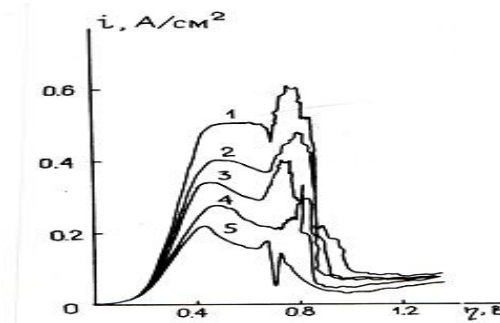


Fig.1. Anode polarization curves of dissolution of pure gold (1) and gold-silver alloys with silver content, wt% : 4 (2), (3), 16 (4), 20 (5). Solution composition: 0.5 M HCl + 1.5M NaCl, potential sweep speed 2 mV/s, temperature 250C.

In contrast to pure gold, during the anodic dissolution of gold-silver alloys (Fig. 1, curves 2-5), a stationary region of active dissolution is not observed: with all overvoltages, over time, a gradual passivation of the anode by the formed silver chloride film occurs. It can also be seen that the effects of passivation are more pronounced the higher the silver content in the alloy.

In the potentiostatic mode, the anode current decreases with time, and its initial value and rate of decay depend on the overvoltage (Fig. 2), the concentration of chloride ions in the solution and the silver content in the alloy (Fig. 3).

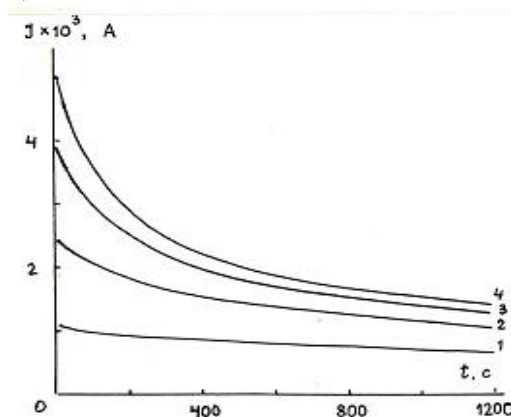


Fig.2. Potentiostatic Inclusion Curves of Anodic Dissolution of Alloy with 4% Silver at $\eta = 500 \text{ mB}$ in solutions with different total chloride concentrations (regulated by adding NaCl, mol/l): 1 -0.5; 2 - 1,0; 3 -2,0; 4 - 3,0.

With an increase in overvoltage, the initial current and the rate of decay increase, but starting from $\eta = 400 - 450 \text{ mB}$ i, t - transients at different η practically merge, apparently reflecting the dissolution of the predominant component of the alloy in the diffusion mode. Quantitative regularities of the growth of anode films on metals (including the shape of i, t curves) have been



considered in a number of works, but only for pure metals [4]. In the case we are studying, it is necessary to additionally take into account that although the anode current is spent on the dissolution of both components, the passivating layer of the insoluble compound forms only one of them.

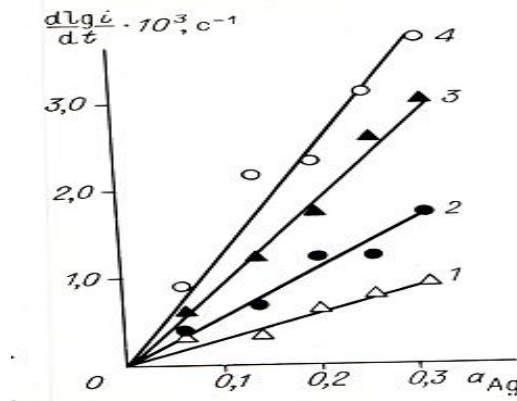


Fig.3. Dependence of the slope of the initial (semilogarithmic) section i, t – curve on the atomic fraction of silver in the alloy at different concentrations of chloride (mol/l): 1 -0.5; 2 - 1,0; 3 - 2; 4 - 3; Overvoltage $\eta = 500 \text{ mB}$.

The objective of the study was to consider the process of anodic dissolution of a binary alloy over time, one of the components of which forms a well-soluble, and the other is an insoluble compound with the electrolyte anion. Based on general physical concepts, at least two sections can be expected on the i, t -curve. The first of them reflects the dynamics of the formation of a continuous film of AgCl from individual islands at a constant layer thickness, and the second reflects the dynamics of thickening of an already formed layer.

Assuming that the anode current flows on unfilmed surface areas, let us express the relationship between the total current density i and the proportion of the surface occupied by the film $S(t)$,

$$i = i_0 (1-S(t)), \quad (1)$$

where i_0 is the current density on the film-free surface. The proliferation of the anode film can be determined by various reasons: for example, the localization of the process on the periphery of the growing film island or the rate of dissolution of the film-forming component. In the latter case,

$$\frac{dS}{dt} = \frac{M i_{Ag}}{FP\delta}, \quad (2)$$

where i_{Ag} is the partial density of the current on silver, M is the molecular weight of silver chloride, P is its density, δ - film thickness. Let us express the partial current in terms of the total current and current output for silver BT_{Ag} , and also take into account that with not very high silver content in the alloy

$$BT_{Ag} = \frac{z_1 a_{Ag}}{z_2} \quad (3)$$

Here, a_{Ag} is the fraction of silver atoms in the alloy, z_1, z_2 is the number of electrons required to dissolve silver and gold, respectively. After substituting (3) and (2) into (1) and integrating, we finally get



$$i = i_0 \exp(-t/T), \quad (4), \quad T = 3 F P \delta / M_{\text{Ag}}$$

It follows from equation (4) that, within the framework of the accepted assumptions i , t , the inclusion curve at the stage of formation of a continuous film AgCl is linearized in the coordinates $\lg i$, t , and the slope of this direct line is proportional to the fraction of silver atoms in the alloy.

Processing of the initial sections of the experimental inclusion curves showed that at times up to ≈ 100 s is indeed the exponential nature of the current roll-off. The slope of this section increases linearly depending on the silver content in the alloy (Fig. 3), and with a fixed alloy composition, it is proportional to the chloride concentration in the solution. The latter is due to the diffusion nature of the anodic dissolution current of gold at a given overvoltage and is taken into account in equation (4) by the value of i_0 . The dynamics of the growth of the formed porous anode film was first considered by Müller [4], who believed that only the thickness of the film increases over time, and its properties (number of pores, their diameter, etc.) do not change.

This leads to an increase in the proportion of ohmic losses in the pore liquid channels of the film in the total overvoltage over time and to a proportional decrease in current $1/\sqrt{t}$. Another approach to explaining such a dependence of current on time (due to the diffusion of anions through the film) was proposed by Fleischmann and Thirsky [5]. Taking into account the above-mentioned nature of the dependence of the anodic dissolution current of gold on the concentration of Cl ions⁻, it can be assumed that in our case it is the second option. The anode current density will then be determined by the flux of diffusion of chloride ions through the pores of the silver chloride, i.e.

$$i(t) = nFD \frac{C}{\delta(t)} \quad (5)$$

where C is the concentration of Cl⁻ ions in the solution, D is their effective diffusion coefficient through the AgCl layer, $\delta(t)$ is the thickness of this layer.

In accordance with Faraday's law, the latter value is expressed in terms of the partial current density of silver and takes into account its relationship with the total current and the fraction of silver atoms in the alloy:

$$\delta(t) = \frac{aM}{3FD} \int_0^t i(t) dt \quad (6)$$

Substituting (6) into (5) and solving the resulting equation with respect to $i(t)$, we finally get

$$i(t) = k \sqrt{c/a} \frac{1}{\sqrt{t}} \quad (7), \quad \text{where } k = \sqrt{\frac{3F^2 DP}{2M}}.$$



Thus, the model under consideration predicts linearization of i, t transients at the stage of film thickening in coordinates $i, 1/\sqrt{t}$, and the slope of these linear sections should be proportional to the square root of the concentration of chloride ions in the solution and inversely proportional to the square root of the concentration of silver in the alloy [6].

Conclusions

The kinetics of anodic dissolution of gold-silver alloys in chloride solutions can be satisfactorily described by existing models of the formation of a continuous film of silver chloride and its subsequent thickening, if these models take into account the partial current current on silver, as well as its dependence on the composition of the alloy, instead of the total current density.

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