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THE INFLUENCE OF CUPRIC IONS ON SHAPE OF POTENTIODYNAMIC CURVES OBTAINED ON 18 K GOLD

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Abstract

The shape of potentiodynamic curves depends mainly on the composition of investigated alloys, but also on the electrolyte used in experiments. In this work investigation were performed for pure gold, and pure silver and copper as alloying metals, then for binary alloys Au-Ag and Au-Cu containing gold as in 18 k gold (i.e. 75 % Au) and Ag-Cu with mass ratio 1:1 and, finally, for three component 18 k gold. It was established a catalytic effect of cupric ions present in electrolyte on oxidation of gold and 18 k gold alloys.

Keywords: 18k Gold, Alloy, Potentiodynamic method, Cupric ions

1. Introduction

Anodic linear sweep voltammetry (ALSV) method can be used for identification of phase structure of alloys that can be dissolved during anodic polarization [1]. The attempt to apply this method for characterization of gold alloys showed that the shape of obtained ALSV curves depends on the kind and content of alloying metals [2].

Beside alloy itself, electrolyte used in experiments may influence on the characteristics of obtained voltammograms. In this paper, the influence of cupric ions in nitrate solutions on the shape of potentiodynamic curves, peak potentials and peak currents will be shown. Results obtained on pure gold are compared with literature data [3,4].

Possible electrochemical reactions in the investigated system are:

$$2\,Au + 3\,H_20 \Leftrightarrow Au_2O_3 + 6\,H^+ + 6\,e^- \quad (1)$$

$$Ag \Leftrightarrow Ag^+ + e^- \quad (2)$$

$$Cu \Leftrightarrow Cu^{2+} + 2\,e^{2-} \quad (3)$$

The anodic polarization of gold electrodes in acid solution leads to the formation of an oxide on the electrode. This oxide has been well characterized as the Au_2O_3 or its hydrated species. The onset of this oxide formation occurs at 1.35 V vs. SHE (Standard Hydrogen Electrode) [3]. Standard potential for reaction (2) is $E^0 = 0.779$ V vs. SHE, and for reaction (3) $E^0 = 0.3$ V vs. SHE.

For the reduction of Au_2O_3 it was proposed [4,5] the following mechanism:

$$AuOOH + H^+ + e^- \overset{\text{fast}}{\Leftrightarrow} AuO + H_2O$$

$$AuO + H^+ + e^- \overset{\text{slow}}{\rightarrow} AuOH$$

$$AuOH + H^+ + e^- \overset{\text{fast}}{\rightarrow} Au + H_2O$$

Au-Ag and Au-Cu alloys belong to the alloys of solid solution type, because these metal pairs are mixing in all ratios in liquid state as well as in solid state. Ag-Cu system creates alloys of eutectic type, where these metals are completely soluble in liquid state and their restricted mutual solubility exists in solid state.

Triple Au-Ag-Cu system is characterized by solid solution single-phase areas and eutecticum. Alloys with gold content higher than 44% contain no eutecticum, so the same is for 18 k gold containing 75% of Au.

2. Experimental

Investigated alloys were obtained by smelting powders of pure metals mixed in corresponding ratio, casting and cooling in air. To achieve required mechanical properties, alloys had to be three times heat-treated. Then they were shaped to wire

form by rolling and drawing. Central part of wires was isolated by lacquer, one end with surface area of 0,1 cm^2 served as working part of electrode, and the other as an electric contact. Prior each experiment working electrode was mechanically polished first at abrasive paper 0000, and then by using felt soaked in alumina suspension, Al_2O_3 . After polishing had been completed, surface was washed by distilled water jet.

Experimental system consisted of:

- electrochemical cell with three electrodes: working, reference and counter
- galvanostat-potentiostat (AMEL, mod. 551)
- function generator (AMEL, mod. 556)
- interface
- AD-converter (RTI-800, Analog Devices)
- personal computer
- printer and display.

Experiments were performed at room temperature in three various electrolyte solutions:

- 1 M $NaNO_3$ (solution R4)
- 0.05 M HNO_3 (solution R3)
- 0.05 M HNO_3 + 0.01 M $Cu(NO_3)_2$ + 0.05 M $NaNO_3$ (solution R2)

Before each experiment, electrochemical cell was washed by pure water and afterwards by distilled water, and finally by working solution. New quantity of fresh solution was poured in for each experiment. Before usage counter electrode was chemically treated in HNO_3 (1:1) solution, and after that it was washed by distilled water and electrolyte solution, while reference electrode was washed by distilled water and working solution.

Polarization started at reversible potential and was led till gaseous oxygen evolution.

Results at sweep rate of 100 mV/s will be shown, although researches were performed in wide range from 20 to 500 mV/s.

3. Results

Figures 1-7 show research results of nitrate solution composition impact on electrochemical behaviour of 18 k gold, appropriate binary Au-Ag, Au-Cu and Ag-Cu alloys as well as pure gold, silver and copper.

Figure 1 shows voltammograms obtained on pure gold in R2, R3 and R4 solutions. In solutions that contain no copper ions (i.e. 0.05M HNO_3 and 1M $NaNO_3$) current peak at the beginning of voltammograms anode part is very wide and low. In compare

to literature data [5,6], this current peak should match the first OH or gold oxide monolayer formation. Current peaks, corresponding to multi valence gold oxide forming, appear at more positive potentials (above 0,8V vs. SCE - Saturated Calomel Electrode). Active gaseous oxygen evolution is starting at about 1,5 V vs. SCE. A well-defined current peak appears at cathodic part of voltammogram.

Voltammograms recorded at the pure silver and the pure copper for more adequate result explanation obtained at alloys, are presented in Fig 2 and Fig 3, respectively. The data were obtained under identical conditions as voltammograms for pure gold (Fig. 1).

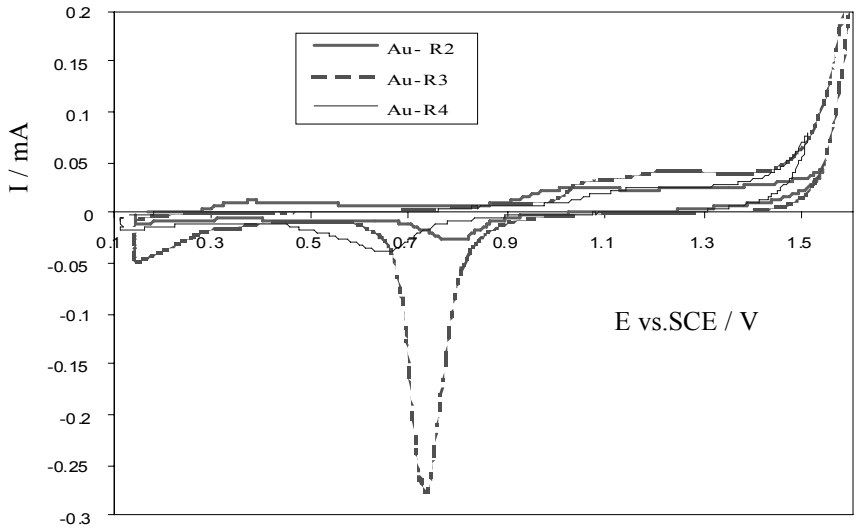

Fig.1. Voltammograms obtained on pure gold electrode by sweep rate 100 mV/s

From Fig. 2 it can be seen that in anode area the active silver dissolution begins starting from 0.37 V vs. SCE, and solution change has no influence on the potential of the bulk metal dissolution. During the potential change, current is increasing fastest in R4 solution (1M $NaNO_3$), then in R2 solution (0.05 M HNO_3 + 0.01 M $Cu(NO_3)_2$ + 0.05 M $NaNO_3$), and most slowly in R3 solution (0.05 M NHO_3). In cathode area, only silver deposition current peaks are appearing with various current maximal values at potential of about 0,37 V vs. SCE. The largest peak area is at voltammogram obtained in R4 solution, which is logical considering that the largest quantity of anode current had flown here and so the solution contained the largest quantity of silver ions. Cathode peak obtained in R3 solution has the smallest surface area from the same reason.

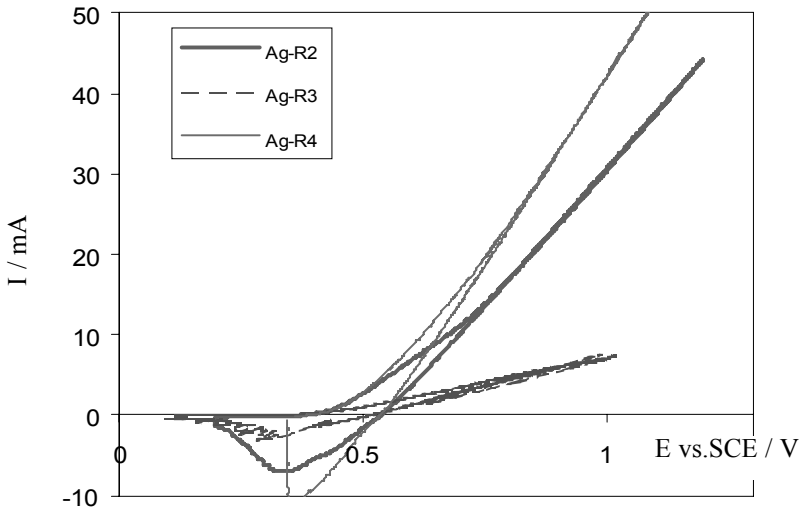

Fig.2 . Voltammograms obtained on pure silver electrode using sweep rate 100 mV/s

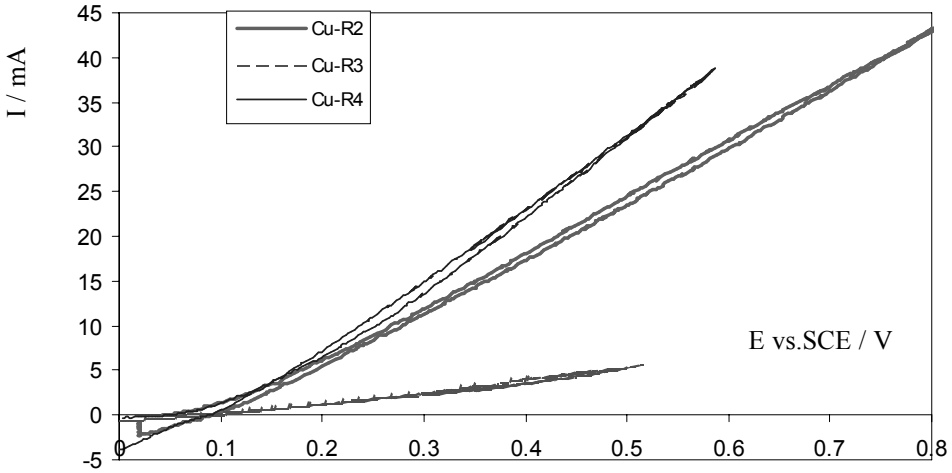

Fig.3. Voltammograms obtained on pure copper electrode by sweep rate 100 mV/s

Copper behaves similar to silver, apart from its active dissolution starts already at about 0.03 to 0.04 V vs. SCE (Fig. 3). At the same potential the highest current densities have been obtained in R4 solution, and the lowest have been obtained in R2 solution. For both metals, silver and copper, this behaviour can be explained by the fact that R4 solution has for two order of magnitude higher concentration related to other two solutions, while current densities obtained in R2 solution closer to those in rather more concentrated R4 solution than in R3 solution with more similar concentration, can be explained by additional catalytic effect of cupric ions.

Voltammograms obtained at 18 k Au-Ag alloy (75% Au) in R2, R3 and R4 solutions are given in Fig. 4. Voltammograms obtained in R3 and R4 solutions are mutually similar in form as voltammograms obtained at pure gold. Anode peaks are very low until the multi-valence oxides start forming. In cathode area at both these voltammograms there is a well defined current peak of formed oxide layer reduction, while the small cathode peak at about 1.4 V vs. SCE is attributed to adsorbed gaseous oxygen reduction. This conclusion is also confirmed by the fact that this peak maximum and area are as large as oxygen evolution current is. Anode processes of multi valence gold oxide forming as well as oxygen evolution are faster in R4 solution and are performing at more negative potentials for about 100 mV than in R3 solution.

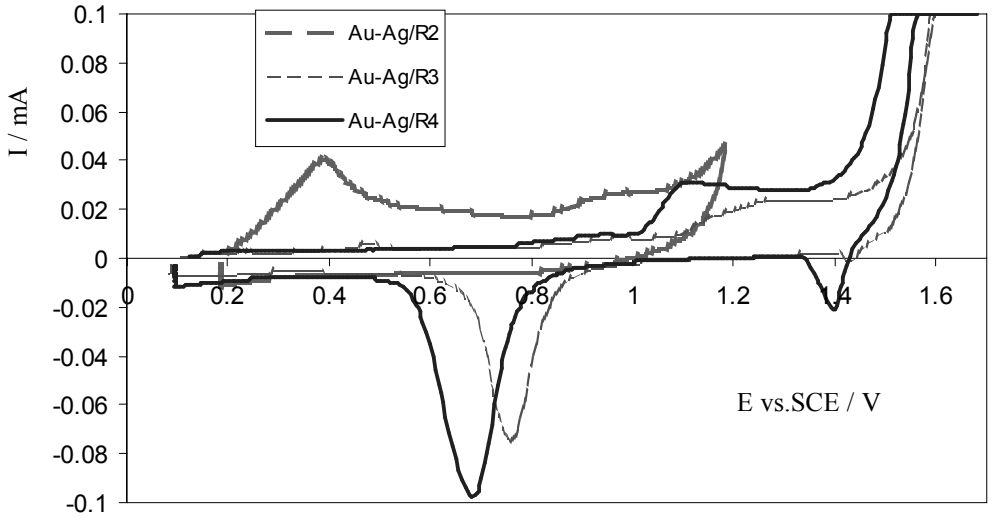

Fig.4. Voltammograms obtained on 18 k Au-Ag alloy using sweep rate 100 mV/s

Voltammogram obtained at this alloy at R2 solution is essentially different in relation to previous two solutions. In this case, already at potential 0,38 V vs. SCE, a high current peak, denoted to silver dissolution out of alloy, is appearing. Following current peak can be connected with oxide forming, but also with the alloy itself dissolution, which is, according to phase diagram, solid solution of silver and gold. Abrupt current increasing begins already at 1.1 V vs. SCE, so the polarization in R2 solution is led only to 1.2 V vs. SCE. At voltammogram cathode part in researched potential area, there is no current peaks at all, but there is an approximately constant cathode current.

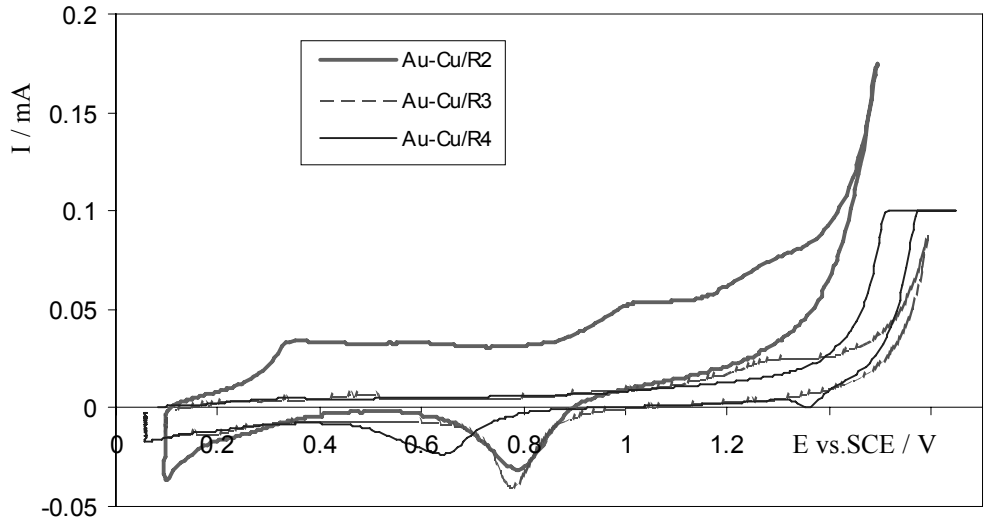

Fig.5. Voltammograms obtained on 18 k Au-Cu alloy by sweep rate 100 mV/s

Au-Cu 18 k alloy shows similar behaviour in R3 and R4 solution as Au-Ag alloy (Fig. 5). But, voltammogram obtained in R2 solution presents significant differences. In cupric ions presence, anode peaks potentials are significantly shifted toward more negative values, and current densities are multiple higher. High anode current peak appears at the beginning of voltammogram (0,36 V vs. SCE) corresponding to some present phase dissolution. Cathode peak corresponding to formed oxide reduction is shifted toward more positive values, that is also the result of cupric ion catalytic effect. This voltammogram on its more negative area, at its very end, presents current peak start fitting the settling phase dissolved at anode beginning part. This peak has a shoulder in researched potential area, indicating multi step reaction.

Figure 6 shows voltammograms for Ag-Cu alloy (50% mass.% Ag) in R2, R3 and R4 solution. It is obvious that in 05 M HNO_3 (R3) solution, at anode polarization immediately enters in field of alloy active bulk dissolution. In solution 1 M $NaNO_3$ (R4), distinctively separated copper dissolution peaks are appearing (at about 0,18 V vs. SCE) as well as silver dissolution peaks (at about 0,4 V vs. SCE), while the sudden current jump is appearing at potentials more positive than 0,5 V vs. SCE. Silver reduction current peak is reversible, while copper reduction is performing in several levels at rather more negative potentials. Height of these current peaks confirms the existence of significant quantities of copper dissolved in oxidation period. The voltammogram of this alloy obtained in R2 solution lacks the copper dissolution peak, but current peak at silver dissolution potential connected with beginning of alloy bulk dissolving can be noticed.

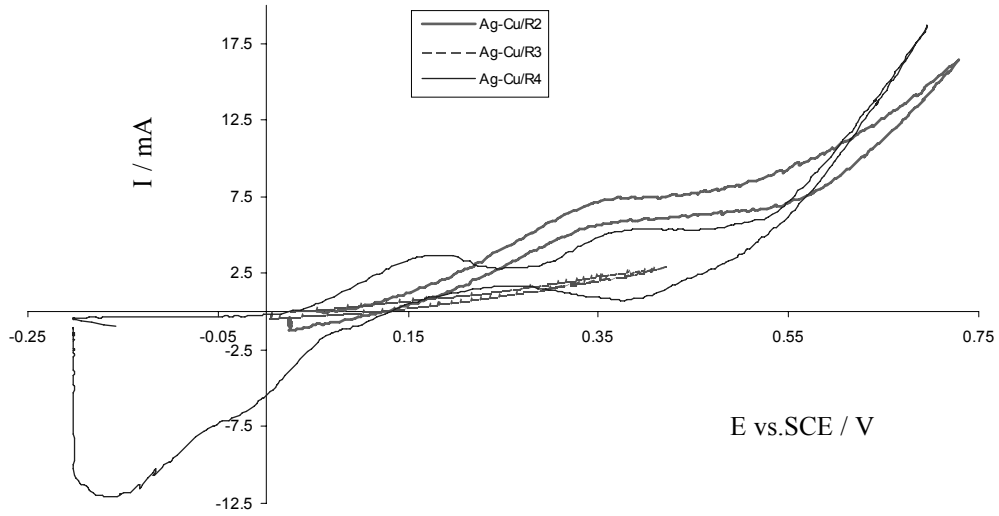

Fig. 6 Voltammograms obtained on Ag-Cu alloy (50 mass.% Ag)

Figure 7 shows voltammograms obtained for three component Au-Ag-Cu alloy with the following content 75 mass.% Au, 12,5 mass.% Ag and 12,5 mass.% Cu, corresponding to basic composition of commercially used 18 k gold. Voltammograms are obtained in R2, R3 and R4 solutions. All of them at the beginning of anodic part contain current peaks of selective dissolution of copper or some phase rich with

copper. In R3 solution this peak appears at 0,24 V vs. SCE, while in R2 and R4 solutions it is at 0,34 V vs. SCE potential. At higher potentials, current peaks of gold oxide forming are appearing, and this wave in R3 solution is very complex and consists of one lower shoulder at the beginning followed by two higher curves. Abrupt current jump appears beyond these peaks as a result of beginning of gaseous oxygen evolution at the electrode. That is the cause of a little sharp peak at the beginning of voltammogram cathode part obtained for R4 solution, corresponding to reduction of absorbed gaseous oxygen delayed at electrode.

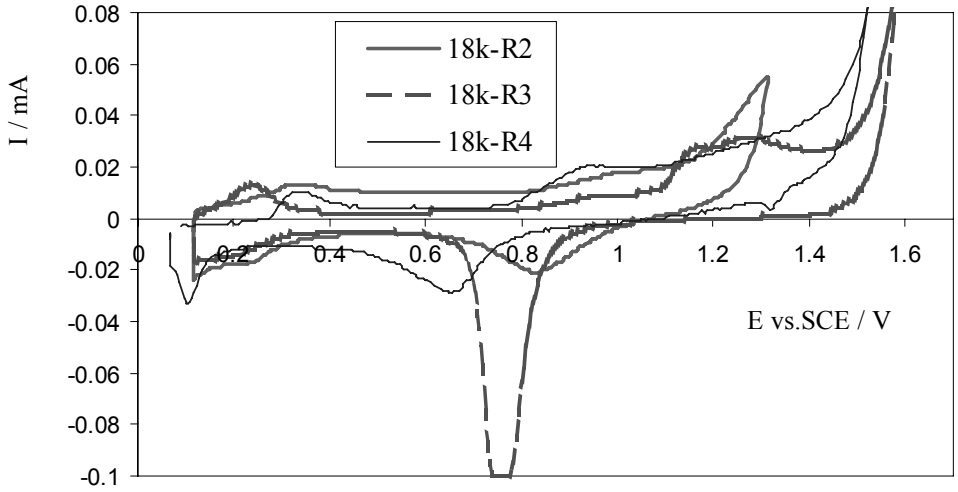

Fig.7. Voltammograms obtained on Au-Ag-Cu alloy (75 % Au, 12.5 % Ag, 12.5 % Cu) by sweep rate 100 mV/s

Abrupt increasing of current density in R2 solution occurs at more negative potential, already at about 1,1 V vs. SCE In the cathode area all three voltammograms contain well-defined current peak of formed oxide layer reduction located at the most positive potential value (0,18 V vs., SCE) for R2 electrolyte, and at the most negative potential for R4 electrolyte (0,63 V vs. SCE). First shoulder and the beginning of the second peak of two-step copper ion reduction from solution can be seen at the most negative cathode part.

4. Conclusion

At voltammograms obtained at pure gold, two-component Au-Ag and Au-Cu alloys and three component Au-Ag-Cu 18k alloy in nitrate solutions, in anodic area, current peaks corresponding to formation of the first OH mono-layer (this current peak is very low and can be covered by peak of selective dissolution of some alloying component) and multi valence gold oxides or their hydrate forms, are present. In cathode part, a well-defined current peak of formed oxides reduction is appearing.

Researching the various nitrate solutions, catalytic influence of cupric ions presence in electrolyte to electrochemical oxidation of gold and its 18 k alloys has been determined. Presence of this ion kind in electrolyte also has a catalytic effect on reduction reaction, shifting cathode peak position toward more positive potential values.

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