STABILITY OF GOLD COMPLEX BASED ON MERCAPTOTRIAZOLE WITH GOLD CONCENTRATION LOWER THAN OPTIMAL

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Abstract

The aim of this work was to investigate the stability of the gold complex based on mercaptotriazole at optimum pH value of nine in the electrolyte with gold concentration of 1.5 g/dm³. Investigations were performed by visual monitoring and electrochemical characterization of electrolytes in the period of four months. The first visible signs of the decomposition of the complex were appeared one month after synthesis. Electrochemical characterization of gold complex based on mercaptotriazole performed by the open circuit potential measurement, cycling voltammetry method and recording the polarization curves, with pH of the electrolyte measurement before and after each electrochemical experiment, showed that all the recorded characteristics remained almost unchanged for a period of four months.

Keywords: gold complex, mercaptotriazole. stability. visual monitoring. electrochemical characterization

1. INTRODUCTION

Electrodeposition of gold from aqueous solutions is always performed from gold complexes [1]. Gold compounds exist almost exclusively in the Au(I) and the Au(III) oxidation states, although complexes of Au(IV) are known, and several Au(II) complexes have been identified in solutions [2]. Gold compounds usually exist as complexes formed by covalent bonding between a central Au^+ and Au^{3+} cation and a number of ligands, which may either be ions such as Cl^-, Br^-, I^-, OH^-, CN^-, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, or neutral molecules such as NH_3, H_2O, $(NH_2)_2CS$, etc. [3].

The stability constants of Au(I) and Au(III) complexes are important properties when electrodeposition of gold from these complexes is considered, since they determine the distribution of various forms of gold ions, such as free metal and complexed ions, which become available for discharge at the cathode [3]. The traditional baths from which to plate soft gold as well as hard gold contain the cyanide complex, $[Au(CN)_2]^-$. Those compounds are very toxic, and formation and maintenance of cyanide baths is expensive and risky for technical personnel and also attacks photoresists used to delineate circuit patterns and bonding pads. Due to this reason, and especially in modern time, there is an environmentally caused trend of using the non-cyanide plating solutions [4,5,6,7].

At the Institute of Mining and Metallurgy Bor a completely new electrolytic bath based on a gold complex with mercaptotrizole was developed and tested. Contrary to the previous complexes [8], it retained a sufficient stability in a period of at least three months [9,10,11,12]. Detailed investigations carried out in order to determine the optimum conditions for obtaining quality decorative gold coatings from this electrolyte showed that the quality of decorative gold plating, obtained from a gold complex based on mercaptotriazole, satisfies all requirements of decorative gold plating. The most important advantage of this electrolyte is ecological, as the gold could be regenerated by simply settling with hydrogen peroxide in which the sulfur is precipitated [8,9].

Results published earlier pointed out that optimal gold concentration in this electrolyte is 2.5 g/dm^3, but enough good results can be obtained with lower concentrations. It is important because the engaged quantities of gold in gilding operations should be minimal.

2. EXPERIMENTAL

The aim of this work was to investigate the stability of gold complex based on mercaptotriazole with concentration of gold 1.5 g/dm^3 at optimum pH = 9. In the present investigation, we performed: the open circuit potential measurement, cycling voltammetry method, recording of the polarization curves and measurement of pH value. The electrolytes pH was measured before and after each electrochemical measurement for a period of four months and visual monitoring performed in paralel. The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control (National Instruments card. NI-6251) and data acquisition software (Lab VIEW 8.2 platform and applications specifically developed for electrochemical measurements). The system is fully developed by Technical Faculty in Bor [13]. The pH values were measured with a WTW pH 3110 instrument.

3. RESULTS AND DISSCUSION

3.1 Visual monitoring of electrolyte

Fresh synthesized electrolyte [8] with gold concentration of 1.5 g/dm^3 and pH = 9 is pale yellow (almost colorless). The first visual changes in the electrolyte were observed after one month due to the appearance of a small amount of brown precipitate which was dissolved by heating the electrolyte up to 25 ° C (temperature at which all electrochemical experiments were performed). After two months from the moment of synthesis there was no precipitate in electrolyte. After three months in the electrolyte was observed a small amount of precipitate which was also dissolved by heating the electrolyte to the working temperature. After four months the solution was almost colorless with a significant amount of dark brown residue which remained insoluble after heating up to the working temperature and for this reason the further electrochemical tests of electrolyte were stopped.

3.2 Open Circuit Potential

Table 1 shows the measured values of open circuit potential (monitored over 60 s) and pH value of electrolyte before and after electrochemical measurements after 1 h. 1 month, 2 months, 3 months and 4 months from the time of synthesis. The most negative value of the open circuit potential of -0.205 V vs. SCE was measured after 1h of the electrolyte synthesis. After 24 h, the measured value of the open circuit potential was -0.169 V vs. SCE.

Table 1- Open circuit potential and pH value of electrolyte before and after electrochemical measurements for different standing time from the moment of synthesis; pH=9, C_{Au}=1.5 g/dm^3

Time	E vs. SCE (V)	pH (before)	pH (after)
1 h	-0.205	9.10	9.03
24 h	-0.169	9.05	9.01
7 days	-0.169	9.02	8.97
1 month	-0.167	8.99	8.96
2 month	-0.168	8.97	8.93
3 month	-0.169	8.95	8.90
4 month	-0.162	8.92	8.87

The changes in value of the open circuit potential over a period of for months were small (after four months it was -0.162 V vs. SCE). The small changes of value of the open circuit potential in

this period indicate that the stable structure is formed after 24 h from the moment of synthesis of electrolyte. The pH value of electrolyte decreased after all electrochemical experiments, which can be explained by oxygen evolution due to the oxidation of hydroxyl ions [8].

3.3 Cyclic Voltammetry

Figure 1 shows the cathodic part of cyclic voltammograms (CVs) for the electrolyte with pH = 9 and concentration of gold C_{Au} = 1.5 g/cm^3 after: 1 h, 24 h, 1 month, 2 months, 3 months and 4 months from the time of the electrolyte synthesis. CVs were recorded with a scan rate of 100 mV/s in the range: (-0.1 ÷ -1.6) V vs. SCE. On voltammogram recorded after 1 h a sharp current peak appears at the potential of -0.95 V vs. SCE and from the potential value of -1.30V vs. SCE starts a sharp increase in the cathodic current density. On the voltammograms recorded after 24 h and after seven days current peaks appear at similar values of potential: -0.93 V vs. SCE and - 0.91 V vs. SCE, respectively. The sharp increase in the cathodic current density starts from the potential of -1.10 V vs. SCE (on the voltammogram after 24 h) and -1.15 V vs. SCE (after 7 days). On voltammogram recorded after a month current peak appeared at the potential of -0.91 V vs. SCE. Also, on this voltammogram a fold appeared at -0.55 V vs. SCE. On the voltammograms recorder after one, two and three months current peaks appear at the same value of potential (-0.93 V vs. SCE). On the voltammogram recorded after three months the folds appear at the potential value of (-0.50 V vs. SCE). On all four voltammograms the sharp increase in the cathodic current density start approximately from the potential of -1.00 V vs. SCE.
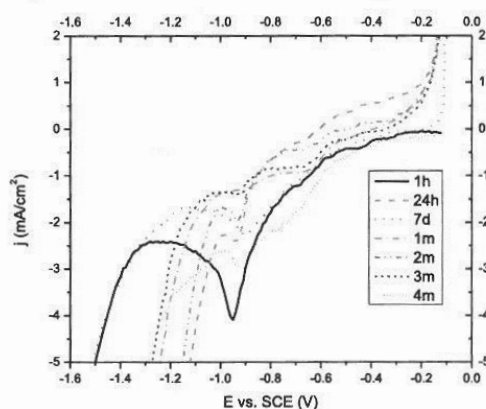

Figure 1 - Cyclic voltammograms (cathodic part) recorded for the gold complex based on mercaptotriazole at pH = 9 and CAu=1.5 g/cm3 for different elapsed time after the electrolyte synthesis: 1 h, 24 h, 1 month, 2 months, 3 months and 4 months

3.4 Polarization Curves

Figure 2 shows the polarization curves for electrolyte at pH = 9 and concentration of gold C_{Au}=1.5 g/cm^3 after: 1 h, 24 h, 1 month, 2 months, 3 months and 4 months from the time of the electrolyte synthesis. Polarization curves were recorded with scan rate 5 mV/s in the range: (-0.1 ÷ -1.2) V vs. SCE. It can be seen from Figure 2 that on the curve recorded after 1 h two plateaus and one current peak appear, first narrow plateau at current density of 0.3 mA/cm^2 and second at 2.4 mA/cm^2. A sharp current peak appeared at potential of – 0.95 V vs. SCE. On the curve recorded after 24 h at 2.4 mA/cm^2 appears a narrow plateau. On the polarization curve recorded after seven days two plateaus can be observed, current density of of the first being 0.3 mA/cm^2 and of the second 1.68 mA/cm^2. On the polarization curves recorded after one month, two, three and four months two plateaus appear. On polarization curves recorded after one and two months plateaus appear at the same potential areas and almost the same current densities; the first current density was 0.84 mA/cm^2, and the other 1.34 mA/cm^2. On the curve recorded after three months,

the first plateau appears at the same value of current density as well as on the first plateau on the curve recorded after two months, while the second plateau appears at current density of 1.80 mA/cm^2. The first plateau on the polarization curve recorded after four months occurs at a current density of 0.83 mA/cm^2 while the other coincide with the other plateau of the polarization curve recorded for one month old electrolyte.
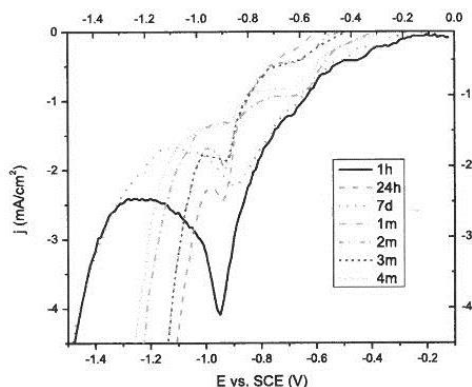

Figure 2 - Polarization curves recorded for the gold complex based on mercaptotriazole at pH = 9 and C_{Au}=1.5 g/cm^3 for different elapsed time after the electrolyte synthesis: 1 h, 24 h, 1 month, 2 months, 3 months and 4 months

4. CONCLUSION

Electrochemical characterization of gold complex based on mercaptotriazole performed by the visual monitoring, open circuit potential measurement, cycling voltammetry method and recording the polarization curves with pH of electrolyte measurement before and after each electrochemical experiment for a period of four moths did not show any significant difference of electrochemical characteristics in depending on time. This proved that no negative consequence of gold concentration in electrolyte lower than optimal appeared.

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REFERENCES

[1] X.Wang, N. Issaev, J. G. Osteryoung. J. Electrochem. Soc. 145 (1998) 974-981
[2] L. B. Hunt. Gold Bull. 6(1) (1973) 16-27
[3] C. Wan Ngah, Ph.D. Thesis, Universiti Sains Islam Malaysia (2004)
[4] Honma H.. Hagiwara K.. J. Electrochem. Soc. 142(1) (1995) 81-84
[5] Kato M.. Okinaka Y.. Gold Bulletin. 37(1-2). (2004) 37-44
[6] Gabe D.R.. Trans. Inst. Met. Finish. 75 (1997) 101-107
[7] S. Roy. ECS Transactions. 16(36) (2009) 667-672
[8] S. Dimitrijević. M. Rajčić-Vujasinović. S. Alagić. V. Grekulović. V. Trujić. Electrochim. Acta. 104 (2013) 330-336
[9] S. B. Dimitrijević, M. M. Rajčić-Vujasinović, R. M. Jančić-Hajneman, J. B. Bajat, V.K. Trujić, D. D. Trifunović. Intern. J. Mater. Resear. 105 (2014) 271-281
[10] S. B. Dimitrijević, M. M. Rajčić-Vujasinović, D. D. Trifunović, B. T. Trumić, Z. M. Stević, S. P. Dimitrijević, Intern. J. Mater. Resear. 107(7) (2016) 624-630
[11] S. Dimitrijević. V. Trujić. M. Rajčić-Vujasinović. Proceedings of 13th International Research/Expert Conference TMT 2009. Hammamet. Tunisia. (2009) p893.
[12] S. Dimitrijević, Z. Stević, M. Vujasinović, V. Grekulović, S. Dimitrijević, B. Trumić, S. Alagić, Metallurgical and Materials Engineering, Vol. 21 (4) (2015) p. 269.
[13] Z. Stević, M. Rajčić-Vujasinović, Hemijska industrija. 61(1) (2007) 1-6