GOLD-REDUCING CATHODE REACTIONS KINETICS
IN ACID THIOUREA ELECTROLYTES

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Abstract. The kinetics of cathode reactions occurring on a gold electrode in acidic thiourea-citrate electrolytes has been studied. Using classical electrochemical methods (potentiometry, chronovoltammetry, electrogravimetry) and graphic-analytical calculations, the following were established: the instability constant of gold complexes, the type of kinetics, the nature of the delayed stage, and the main kinetic characteristics of the electrochemical reaction during gold deposition.

Keywords: gold (I) complex, thiourea, citric acid, cathode polarization, electrolytic deposition.

1. Introduction

Electrolytic gold deposition is a known and well-mastered technological process. It is widely used not only by the jewelry business but also by the industry. Gold coatings and alloys are widely used in electrical technology and electronics. They possess high-quality decorative properties and resist oxidation when exposed to high temperatures. The thickness of decorative coatings is 0.5 µm and it attains 30 µm when used in electrical technology and electronics. However, a minimum gold thickness is usually preferred due to its high cost.

Gold provides a high electrical conductivity and is important for the interconnection in advanced technological processes used to create integrated circuits. High thermal resistance and the deformation ability provide high reliability of such compounds in many technologies including a high-density packaging technology. A low contact resistance is in demand for the creation of high-quality low-current and electric power connectors and their excellent corrosion resistance extents considerably their service life.¹–³ The optical properties of gold provide an opportunity for the manufacturing of durable mirrors efficiently operating in the infrared range and special protective coatings for the aerospace industry.⁴

The biological inertness and high compatibility of this metal with human tissues are of high value for medicine. Gold enhances the bactericidal effect of silver. It has an antiseptic effect on viruses and bacteria. Gold compounds also have an antifungal and antimicrobial effect on many gram-positive and gram-negative microorganisms. Due to these facts, gold coatings are widely used in medicine, in particular in orthopedic dentistry.⁵⁻⁸

The items are usually coated with pure gold or alloys of different metals using the method of deposition.⁹ As a rule, the KAu(CN)₂-based complex electrolytes are used for the electrolytic gold deposition.³⁻⁴ The acidic cyanic electrolytes operating in the presence of the buffer (pH = 4–6) at slightly increased temperature found a wide application. The alkaline cyanic gold-plating electrolytes (pH = 11–11.5) are operated with soluble anodes and provide coatings of high purity. Neutral cyanic electrolytes (pH = 6.5–7.5) and acidic electrolytes work with insoluble anodes and provide denser and pore-free coatings in comparison to alkaline electrolytes.

All these prepared electrolytes contain no CN⁻ ions; however, these latter are formed on the cathode during the electrolysis due to the reducing reaction of gold out of complex ions. Cyanogen ions are partially turned into a highly toxic hydrocyanic acid HCN that is carried away to the atmosphere. However, a noticeable portion of CN⁻ is left in the electrolytic bath which is rather undesirable for the processes of gold application onto the blanks of printed boards and integrated circuits. These ions can interact with positive photoresists disintegrating the protecting relief and resulting in defects.¹⁻³

Complex electrolytes based on the sulfite or thiosulfite Au (I) also find a wide application.¹¹ The advantages of sulfite electrolytes include a high dissipating ability and the possibility of obtaining brilliant coatings of high elasticity. The main drawback of such compositions is the low stability of these complexes. As a result, we can observe the disproportioning reaction behavior with the formation of the Au (III) and metal gold ions:

\[ 3\text{Au}^{+} = 2\text{Au} + \text{Au}^{3+}. \] (1)
In practice, this phenomenon results in a spontaneous bath decomposition that can be retarded by the addition of patented stabilizing additives. During the electrolyte storage, sulfite is gradually oxidized by the air oxygen forming sulfate. In addition, sulfite ions are reduced on the cathode to $\text{SO}_4^{2-}$ which reduces gold ions to metal. Fine metal gold particles are removed from the electrolyte volume by filtration.

The $\text{HAuCl}_4$-based electrolytes are also known. Such compositions are mainly used for electrochemical gold refining. However, the coatings formed using such electrolytes have large-size crystals and the electrolytes are rather aggressive with regard to the item substrate material, therefore it is unreasonable to use them for the electroplating technology.

The cathode process kinetics during gold-plating in cyanide electrolytes was studied in detail by Kubra et al. and Ozcelik et al. At the potentials varying in the range of 0.3 to 0.7 V the reduction process has a staged pattern and it adheres to the following mechanism:

\[
\begin{align*}
\text{Au(CN)}_2^- & \rightarrow \text{Au(CN)}_{\text{ads}} + \text{CN}^-; \\
\text{Au(CN)}_{\text{ads}} + e & \rightarrow \text{Au(CN)}_{\text{ads}}; \\
\text{Au(CN)}_{\text{ads}} + \text{H}^+ & \rightarrow \text{Au} + \text{HCN}. 
\end{align*}
\]

At more negative cathode potentials, a direct reduction of the complex ion to the metal is possible:

\[
\text{Au(CN)}_2^- + e + 2\text{H}^+ \rightarrow \text{Au} + 2\text{HCN}. 
\]

A kinetic of the gold deposition from non-cyanide electrolytes has been studied insufficiently so far. However, the studies of kinetic mechanisms of the cathode process during the gold-plating are of great practical interest for scientific developments and industrial use of new non-toxic electrolytes and the optimization of the operation of galvanic baths.

The purpose of the research is to study the kinetics of the cathode reactions during the electrolytic gold deposition out of thiourea solutions. In this case, the kinetics of cathode reactions can be interpreted as transformation mechanisms of the substance or reaction-active particles in the electrochemical system under the action of electric current generated by the external source. It gives us an opportunity to optimize the electrolyte composition and the golden coating deposition mode.

To attain this goal the following problems were solved:

- studying the effect of the electrolyte composition on the stability of gold and thiourea complexes;
- establishing the nature of the limiting stage of the cathode reaction and the mechanism of the electrolytic gold reduction;
- defining the process factors (component concentration, solution temperature, and electrolyte mixing) that affect the reaction rate.

2. Experimental

The solutions were prepared using chemically pure reagents in distilled water. The electrolyte composition includes such organic substances as thiourea $\text{CS(NH}_2\text{)}_2$ and citric acid $\text{C}_6\text{H}_8\text{O}_7$. The gold salt $\text{AuCl}_3$ was used as the original material for the preparation of the gold-plating electrolytes.

The experiment was carried out in the thermostatic electrochemical cell YaSE-2 with an electrolyte volume of 100 mL in the temperature range of 298 to 328 K. Gold (Au 999.9) with a surface area of 0.5 cm$^2$ was used as the working electrode and platinum (Pt 99.9) with a surface area of 2 cm$^2$ was used as an additional electrode. The electrode potentials were measured relatively chloride-silver reference electrode of an EVL-1M1 type. The pH value was measured using the pH-673M device.

The kinetics of cathode reactions was studied using the pulsed potentiostat PI-50-1.1 and programmer Pr-8. The changes in the current (voltage) were recorded by the self-recording device LKD-4. In this case, the registered current was correlated with the geometric surface of the studied specimen. The mechanism of cathode reactions was studied by analyzing the geometric surface of the studied specimen. The main kinetic characteristics of the reaction behavior at the phase interface (metal-electrolyte solution) were defined using the graphic-analytical method and special computer program “KINET”.

3. Results and Discussion

As it is known, gold is considered to be the most precious metal. It is resistant to diluted and concentrated acids. However, in the solutions containing inorganic and organic ligands, gold is dissolved due to the formation of complex compounds. For example, these can be thiourea solutions. Some thiourea complexes with monovalent gold are also available. It is explained by the fact that the trivalent gold is reduced to the metal by the ligands which redox potential is lower than 0.6 V and for the thiourea the redox potential Au (III) is lower than 0.42 V.

In thiourea solutions, gold forms the $\text{Au\{SC(NH}_2\text{)}_2\}^{2-}$ complex whose instability constant ($K_i$) is $3.2 \times 10^{-26}$. As it was established earlier by Smirnova et al., the addition of citric acid to the water solutions of thiourea facilitates their stability ($\text{pH} = 1–3$) that is critically important for the preparation and operation of the gold-plating electrolytes. The standard potential of the gold electrode in thiourea solutions is equal to 0.38±0.01 V at 298 K. The value of the equilibrium potential of the gold electrode in acidic thiourea-citrate solutions is mainly influenced by the gold concentration and thiourea.
Fig. 1 shows potentiodynamic polarization curves for the gold electrode in the solutions with the same concentration of citric acid (0.1 mol/L) and different concentrations of thiourea (0.3–0.5 mol/L). According to the measurement data, the equilibrium potential of the gold electrode becomes more electronegative in these solutions with an increase in the thiourea concentration and it is recorded in the range of 0.385 V to 0.36 V. This fact is fully correlated with the Nernst equation according to which the lower the concentration of simple metal ions, which are not bound into a complex, the higher the electronegative equilibrium potential.

The cathode polarization of the gold electrode in the given solutions results in the appearance of the electric field and the formation of polarization dependences (curves 1–3) that show the sections of the electrolytic gold reduction from thiourea complexes (initial curve sections), maximum points (or ultimate current density), rather continuous plateaus and the sections of the joint gold and hydrogen release on the cathode. The obtained curves show that the higher the cathode polarization value the higher the ultimate current density with regard to gold.

A typical view of initial sections on curves 1 and 2 is indicative that not all gold ions are bound into the complex with thiourea and a certain portion of gold can be reduced in the solution out of simple ions Au$^{+}$.

A further increase in the thiourea concentration in electrolyte solutions results in a change of the pattern of the cathode deposition of gold and its kinetics (Fig. 2). The equilibrium potential of the gold electrode acquires more electronegative values and it is set in the range of 0.25 to 0.3 V. Working and ultimate cathode current densities actually decrease two times with an increase in the thiourea concentration. Such a change in kinetic dependences is evidently related to a higher stability of the thiourea complexes of gold and an increased surge of the gold release on the cathode.

The construction of the dependence of the ultimate current density on the thiourea concentration in logarithmic coordinates (Fig. 3) enables the computation of the order of chemical reaction $P$ that is equal to 1 for minimum ligand concentrations (0.3–0.5 mol/L) and to 2 for an increased ligand concentration (0.5–0.75 mol/L). Evidently, an insufficient amount of thiourea in the solution results in the fact that gold is present in the form of Au$^+$ and Au(SC(NH$_2$)$_2$)$_2$$^+$ ions, and an increased concentration of thiourea results in the formation of Au(SC(NH$_2$)$_2$)$_2$$_2$$^+$ ions. Hence, the concentration of thiourea 0.5 mol/L is critical for the gold concentration of 0.04 mol/L (in terms of metal). Therefore, the quantitative ligand-to-complexing agent ratio in the solution should be much higher than 10:1.

This research paper studies the effect of the temperature of electrolyte solution on the kinetics of the cathode reaction of the gold reduction (Fig. 4). For this purpose, the appropriate polarization dependences were taken in the optimal temperature range (298–328 K). A further increase in temperature has no sense because heavy heating of the solution results in the disintegration of thiourea complexes of gold and electrolyte destabi-
lization. The obtained curves show that a considerable increase in temperature results not only in increased working and ultimate current densities but also in the depolarization of the cathode reaction.

Fig. 5 shows the effect of the electrolyte mixing on the gold reduction kinetics. The type of polarization curves with no mixing and with different extents of mixing shows that the cathode reaction rate is actually independent of the convection mode. It is indicative that the diffusion stage of gold ions in the direction of the cathode surface is not limiting in this case.

Fig. 4. Cathode polarization dependences obtained for the gold electrode in acidic thiourea-citrate electrolyte, \( c(Au) = 0.04 \text{ M}, c(C_6H_8O_7) = 0.1 \text{ M}, c(CS(NH_2)_2) = 0.75 \text{ M}, \eta_s = 1 \times 10^{-2} \text{ V} \cdot \text{s}^{-1} \), at different temperatures \( T, \text{K}: 1 – 298; 2 – 313; 3 – 328 \)

Fig. 5. Cathode polarization dependences obtained for the gold electrode in acidic thiourea-citrate electrolyte, \( c(Au) = 0.04 \text{ M}, c(C_6H_8O_7) = 0.1 \text{ M}, c(CS(NH_2)_2) = 0.75 \text{ M}, \eta_s = 1 \times 10^{-2} \text{ V} \cdot \text{s}^{-1} \), at different mixing conditions: 1 – with no mixing; 2 – slight mixing (250 rpm); 3 – intensive mixing (500 rpm)

The effect of the potential scanning rate on the type of polarization curves and the cathode process rate is shown in Fig. 6. The diagrams show that an increase in the potential scanning rate and, as a consequence, in the curve-taking rate results in a noticeable increase in the reaction rate and in the value of the cathode polarization of the gold electrode.

In this case, the dependence of \( j_{lim}/\sqrt{\eta_s} = f(\eta_s) \) represents a straight line parallel to the abscissa axis. It is indicative that the potential scanning rate \( \eta_s \) has no effect on \( j_{lim}/\sqrt{\eta_s} \). The same dependence in the \( j_{lim} = f(\eta_s) \) coordinates is absolutely linear and it goes out of the coordinate origin which can be a peculiar feature both for reversible and irreversible reactions.

Fig. 6. Cathode polarization dependences obtained for the gold electrode in the acidic thiourea-citrate electrolyte, \( c(Au) = 0.04 \text{ M}, c(C_6H_8O_7) = 0.1 \text{ M}, c(CS(NH_2)_2) = 0.75 \text{ M}, T = 298 \text{ K} \), at different potential scanning rates \( \eta_s, \text{ V} \cdot \text{s}^{-1}: 1 – 1 \times 10^{-3}; 2 – 5 \times 10^{-3}; 3 – 1 \times 10^{-2}; 4 – 5 \times 10^{-2} \)

The speed criterion or the Semerano criterion was also used for the definition of the limiting stage of the process. Fig. 7 shows the logarithmic dependence of the ultimate current density on the potential scanning rate. As it is seen from the Figure, such dependence is linear and it intersects the coordinate origin. The dependence pattern shows that the rate of the electrochemical stage is lower than that of the diffusion stage. The calculated value of the Semerano criterion is equal to 0.5. This criterion value is peculiar for the processes that are limited by the charge transfer rate, diffusion rate, and chemical reaction rate and exclude the catalytic and adsorption process. The potential of the peaks of appropriate potentiodynamic curves (Fig. 6) is shifted to the positive side with an increase in the potential scanning rate and it depends on \( \eta_s \) and it is indicative of the irreversible cathode reaction.

Fig. 7. Logarithmic dependence of the ultimate current density on the potential scanning rate in the solution of \( c(Au) = 0.04 \text{ M}, c(C_6H_8O_7) = 0.1 \text{ M}, c(CS(NH_2)_2) = 0.75 \text{ M}, T = 298 \text{ K} \)
Fig. 8 gives polarization curves for the electrolytes with the same concentration of citric acid and different concentrations of gold and thiourea. The ligand-to-complexing agent ratio is approximately equal to 20:1 for both electrolytes. The Figure shows that the higher the gold content in the electrolyte the higher the working and ultimate current densities for actually the same value of cathode polarization. In both cases (curve 1 and curve 2), we observe the formation of a rather extended area of the ultimate current.

The transformation of the initial sections (to the ultimate current density $j_{lim}$) of polarization curves (Fig. 8) in semi-logarithmic coordinates of electrochemical, diffusive, and mixed kinetics (Fig. 9) allows us to get an idea of the most retarded stage nature of the cathode reaction of the gold reduction.

As it is seen in Fig. 9, none of the coordinates shows an absolutely linear dependence of the reaction surge on the current density. It is indicative that all the stages (discharge, diffusion, and chemical reaction) have an effect on the cathode reaction rate and in this case, the chemical stage preceding the discharge and the discharge of gold ions makes a maximum contribution in comparison to that of the diffusion stage.

The calculated kinetic performances of the cathode reaction and the instability constants of the complex ions of gold are given in Table. The values of $K_i$ are indicative that the thiourea complex of gold is sufficiently stable and gold is released on the cathode with a high overvoltage which is an important premise for the formation of the compact and dense sediment.

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**Fig. 8.** Cathode polarization dependences obtained for the gold electrode in acidic thiourea-citrate electrolytes, $\nu = 1 \times 10^{-2}$ V s$^{-1}$: 1 – $c$(Au) = 0.026 M, $c$(C$_6$H$_8$O$_7$) = 0.1 M, $c$(CS(NH$_2$)$_2$) = 0.5 M; 2 – $c$(Au) = 0.04 M, $c$(C$_6$H$_8$O$_7$) = 0.1 M, $c$(CS(NH$_2$)$_2$) = 0.75 M

**Fig. 9.** Interpretation of curves 1 and 2 (Fig. 8) in the coordinates of the electrochemical (a), diffusive (b), and mixed (c) kinetics.
Based on the obtained experimental data we can assume that the reaction behavior is observed on the cathode in acidic thiourea-citrate electrolytes with the quantitative thiourea-to-gold ratio (in terms of metal) starting from 20:1 and higher:
\[
\text{Au}[^{SC(NH}_2)_2]_2^+ \rightarrow \text{Au}[^{SC(NH}_2)_2]^+ + \text{CS(NH}_2)_2. \quad (6)
\]

We can also assume that the process of cathode reduction of gold out of thiourea complex at a slight electrode polarization relative to the equilibrium potential has a stage-like character and follows the following mechanism:
\[
\begin{align*}
\text{Au}[^{SC(NH}_2)_2]_2^+ \rightarrow \text{Au}[^{SC(NH}_2)_2]^+ + \text{CS(NH}_2)_2; \\
\text{Au}[^{SC(NH}_2)_2]^+ \rightarrow \text{Au}^0 + \text{CS(NH}_2)_2; \\
\text{Au}^0 + e \rightarrow \text{Au}^0. 
\end{align*}
\]

(7)

(8)

(9)

Based on the obtained experimental data we can draw a conclusion that the reaction kinetics of the cathode reduction of gold is characterized by an increased effect of the gold and thiourea concentration and the solution temperature. The electrolyte mixing has no noticeable effect on the gold deposition rate. A considerable role in the kinetics of the cathode reaction is played by the heterogeneous chemical reaction, in particular the dissociation of the thiourea complex and the subsequent discharge of gold (I) ions.

4. Conclusions

Hence, acidic thiourea-citrate solutions are suitable for the creation of safer gold-plating electrolytes on their basis. They are prepared using ordinary and available salt, i.e., gold (III) chloride. However, due to the reduction reaction and association of gold ions with the thiourea in the solution rather stable complex gold (I) compounds \(\text{Au}[^{SC(NH}_2)_2]_2^+\) and \(\text{Au}[^{SC(NH}_2)_2]^+\) are formed. In this case, citric acid serves as the buffer and contributes to the solution stability.

The gold reduction reaction behavior in these electrolytes is characterized by a mixed control in which the main role is played by the retarded electrochemical stage and the stage of chemical transformation on the cathode. The gold deposition rate can be increased due to an increase in the content of the metal salt in the electrolyte as a result of the solution heating up to 328 K. The electrolyte mixing has actually no effect on the process rate.

A mechanism of the cathode reduction of gold presupposes the discharge of \(\text{Au}^+\) ions and the previous heterogeneous chemical reaction prior to it, i.e., the dissociation of the thiourea complex of gold with the stage-like behavior at a slight electrode polarization. The charge of complex gold ions in the given solutions is equal to +1. Their reduction on the cathode occurs with a maximum electrochemical equivalent, making these electrolytes highly efficient. Therefore, acidic thiourea-citrate electrolytes can be a successful solution to the problem of the replacement of the toxic cyanide electrolytes of the gold-plating by less efficient but more ecologically friendly solutions.

References


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КІНЕТИКА КАТОДНИХ РЕАКЦІЙ ВІДНОВЛЕННЯ ЗОЛОТА В КИСЛИХ ТІОСЕЧОВИНИХ ЕЛЕКТРОЛІТАХ

Анотація. Досліджено кінетику катодних реакцій, що відбуваються на золотому електроді в кислих тіосечовино-цитратних електролітах. За допомогою класичних електрохімічних методів (потенціометрія, хроновольтамперометрія, електрогравіметрія) та графоаналітичних розрахунків встановлено константу нестійкості комплексів золота, вид кінетики, природу уповільненої стадії й основні кінетичні характеристики електрохімічної реакції під час осадження золота.

Ключові слова: комплекс золота (I), тіосечовина, цитратна кислота, катодна поляризація, електролітичне осадження.