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Electrodeposition of silver from nitrate-tartrate solutions

Katodowe osadzanie srebra z roztworów azotanowo-winianowych

Abstract

The electrodeposition of silver from $AgNO_3$ solutions with the addition of L-tartaric acid was investigated. The cathodic reaction was accompanied by low electrode polarization and run under activation control for $AgNO_3$ concentrations of above 70 mM. Tartaric acid only slightly shifted the polarization curves towards more electronegative potentials (by approx. 50 mV), but it did not change the rate-determining step. The activation control of the process resulted in the formation of rough and coherent deposits, while the mixed or diffusion control of the process promoted the formation of dendritic-like structures and spongy deposits.

Keywords: electrolysis, morphology, nitrate, silver, tartrate

Streszczenie

Przeprowadzono badania katodowego osadzania srebra z roztworów $AgNO_3$ zawierających L-kwas winowy. Reakcji katodowej towarzyszy mała polaryzacja elektrody, a redukcja biegnie w zakresie kontroli aktywacyjnej dla stężeń $AgNO_3$ powyżej 70 mM. Dodatek kwasu winowego w niewielkim stopniu przesuwa krzywe polaryzacyjne w kierunku bardziej ujemnych potencjałów (o ok. 50 mV), nie zmieniając jednak etapu powolnego reakcji katodowej. W zakresie kontroli aktywacyjnej tworzą się szorstkie i zwarte warstwy srebra, natomiast zakres kontroli mieszanej lub stężeniowej sprzyja tworzeniu się struktur dendrytopodobnych lub gąbczastych.

Słowa kluczowe: elektroliza, morfologia, azotan, srebro, winian

1. Introduction

Electrodeposited metals are characterized with a variety of morphologies originating from the size, shape, and orientation of the grains as well as the porosity and adherence of the deposits. Based on microscopic observations, Hellmuth Fischer [1] proposed four types of growth of the electrodeposits; these were (i) field-oriented isolated crystals (whiskers, dendrites, and crystalline metal powders), (ii) a structure reproducing

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substrate (usually compact deposits), (iii) a field-oriented texture (compact layer), and (iv) very fine un-oriented crystals (coherent deposits). All types of the polycrystalline deposits are governed by both the inhibition intensity of the cathodic process and ratio of the current density to the concentration of the electroactive species *i/c* [2]. Winand et al. [2, 3] proposed a diagram showing the qualitative relationships among the different growth types, inhibiting, and electrolysis parameters. It was concluded that the external shape of the metallic crystals in cathodic deposits is affected by their growth rates in the directions parallel and perpendicular to the substrate. At a constant inhibition intensity, the rate of crystal growth in the horizontal direction (parallel to the substrate) decreases with increasing current density. Under such conditions, separate crystals and even dendrites are formed. On the other hand, an increase in the intensity of the process inhibition at a constant current density leads to an increase in the rate of crystal growth in the horizontal direction and the formation of compact layers. At a very low inhibition of the cathodic process and very low values of *i/c*, nucleation of the crystals may not occur at all. Therefore, the Type (i) crystals are observed at low inhibition of the electrodeposition, Type (ii) are developed at intermediate inhibition and/or medium current density, Type (iii) are characteristic for high inhibition and/or high current density, while Type (iv) are observed at very high inhibition and/or very high current density. Inhibition of the deposition is usually controlled by the presence of specifically adsorbed ions or molecules on the cathode surface. Adsorbed species influence the intermediate stages of the cathodic reduction and, thus, determine the form and number of the metallic nuclei.

Modification of the morphology of the cathodic deposits is especially important for the electrodeposition of metals characterized with high exchange currents. In such cases, dendrites can form even at very low overpotentials. This attribute is not typical for silver deposition from nitrate solutions regardless of the high exchange current density [4], and independent crystals and incoherent deposits are produced at low overpotentials [5–8]. Long-lasting experiments conducted below the limiting current density showed that silver deposits were smooth only at the beginning of the electrolysis, but the surface roughness seriously increased with time [9]. Silver electrodeposited at various overpotentials shows different disperse morphologies, such as granules, needle-like forms, and spongy-dendritic forms [5, 6, 8]. Analysis of the early stages of silver deposition showed that the two-dimensional nucleation is responsible for this abnormal behavior of silver in nitrate baths [4, 10, 11].

The formation of incoherent deposits is disadvantageous for electroplating and electrorefining applications [12]. To obtain smooth and compact silver deposits, the addition of organic additives acting as inhibitors of metal electrocrystallization is required [13]. A lot of additives were investigated, like gelatin [14], nitrate ions [7, 9], phosphate ions [15], thiourea [9, 12], and tartaric acid [12, 16, 17]. Tartaric acid seems to be the most often examined as perspective additive, but the detailed data is still limited. Therefore, the aim of this research was to determine the influence of current density and silver ions to tartaric acid concentration ratios on the electrochemical behavior and morphology of silver electrodeposited from an acidic nitrate solution.

2. Experimental

The electrodeposition of silver was realized from solutions containing silver nitrate at various concentrations (0.07–1.07 M) in the presence of L(+)-tartaric acid (3.5–15 mM). The pH level of the solutions was 2. All galvanostatic measurements were carried out at room temperature. A cylindrical vessel containing 300 cm^3 of the electrolyte (unstirred), a silver cathode substrate, and an anode (8.8 cm^2) were used. Both electrodes were hung vertically at distance of 6 cm. The cathode potential was determined by using an Ag/AgCl electrode as a reference. The electrodeposition of silver was carried out for 10 min at a constant tartaric acid concentration (15 mM) and various current densities corresponding to *i/c* ratios from a range of 5–20 A·dm/mol. The cathodic deposits were then observed by means of a scanning electron microscope (Hitachi).

3. Results and discussion

L-tartaric acid is a weak α-hydroxy-carboxylic acid $HCOO{-}[CH(OH)]_2{-}COOH$ (H_2A). This diprotic acid can dissociate by releasing two hydrogen cations from carboxylic groups (dissociation constants for 25°C) [18]:

$$H_2A \leftrightarrow H^+ + HA^- \qquad pK_{a1} = 3.036 \tag{1}$$

$$HA^- \leftrightarrow H^+ + HA^- \qquad pK_{a2} = 4.366 \tag{2}$$

L(+)-tartaric acid is an isomer of tartaric acid. It is industrially produced in the largest amounts and characterizes with much higher solubility in water (1.38 kg/kg at 20°C) than the DL racemic form (0.21 kg/kg at 20°C).

L-tartaric acid can generate a neutral complex with silver ions Ag(HA) with a stability constant $\log K_1 < 2.0$ [17]. Papanastasiou et al. [16] suggested that such species can be transported towards the cathode by convective diffusion. Due to its heavy incorporation into the metal lattice, it is strongly adsorbed to the electrode surface, affecting the silver's grain size and superficial roughness. An analysis of the equilibrium distribution of the soluble species in a nitrate-tartrate solution (Fig. 1) shows that, at the pH 2 level used in the current study, the Ag(HA) complex represents only 6% of the total concentration of silver ions, while for an increased amount of $AgNO_3$ in the solution at a constant concentration of the organic additive (15 mM), the percentage content of the Ag(HA) complex further decreases. Therefore, it seems that Ag(HA) cannot be the main electroactive species during silver deposition.

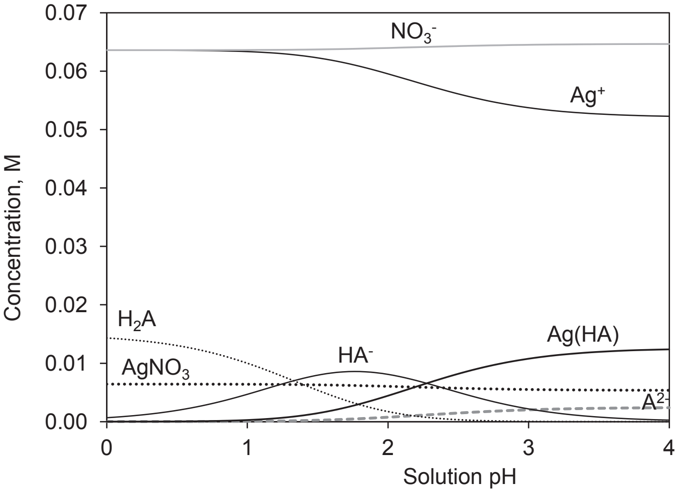

Fig. 1. pH-dependent speciation of baths containing 0.07 M $AgNO_3$ and 15 mM L-tartaric acid (H_2A)

Figure 2 shows the influence of tartaric acid on the course of the galvanostatic polarization curves registered at various Ag^+ concentrations. For comparative purposes, curves for the pure $AgNO_3$ solutions are also presented. It was found that the presence of an organic additive does not change the nature of the polarization curves but shifts them by about 50 mV towards the more electronegative potentials.

An analysis of the polarization curves was performed in terms of a rate-determining step. Table 1 shows the ranges of charge transfer control and mixed (i.e., charge transfer and diffusion steps have comparable rates) control for the $AgNO_3$ solutions of different concentrations and constant tartaric acid content. The reduction of silver ions was under activation control up to the current density of approx. 6 A/dm^2 for 1.07M Ag^+. Similar to pure nitrate solutions (no additive) [8], the range of activation polarization was gradually reduced to lower current densities with a decreased concentration of Ag^+ ions in the electrolyte resulting in the limiting current (0.6 A/dm^2) for 0.07M $AgNO_3$. It was seen that the transition from charge transfer to mixed control was slightly dependent on the i_t/c ratios, which were within a range of 4–6 A·dm/mol. However, the organic additive reduced the range of the activation control as compared to the pure $AgNO_3$ solutions, for which the i_t/c transition values were within a range of 8–10 A·dm/mol [8].

Figure 3 presents the polarization curves in a $\eta = f(\log i)$ coordinate system for various concentrations of the additive at a high content of Ag^+. It was observed that the silver deposited under activation control independent of the amount of tartaric acid. However, the organic agent seriously changed the slopes of the straight lines (almost fourfold). This can show that the molecules of the acid can adsorb on the cathode surface, inhibiting the reduction of the silver ions.

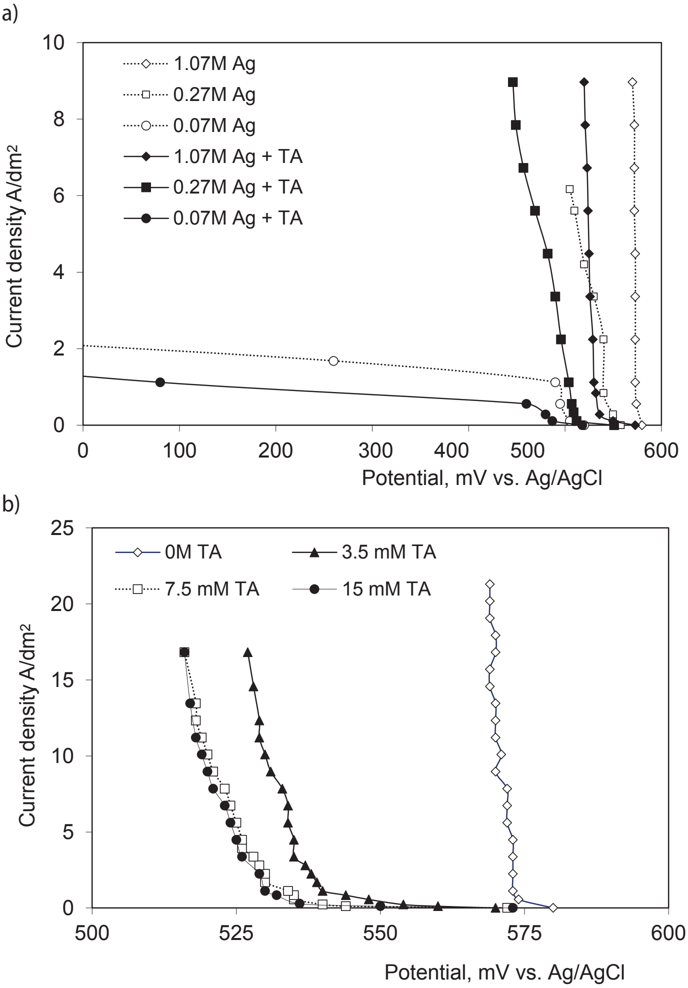

Fig. 2. Galvanostatic polarization curves registered: a) at constant concentration of tartaric acid (TA) 15 mM; b) at constant concentration of silver ions 1.07 M

Table 1. Influence of Ag^+ concentration at constant amount of tartaric acid (15 mM) on rate-determining step of cathodic reaction

Ag^+ concentration	**Charge transfer**		**Mixed / diffusion**		**i_t / c**
M	***i* [A/dm²]**	**η [mV]**	***i* [A/dm²]**	**η [mV]**	**[A·dm/mol]**
1.07	< 6.3	< 45	> 6.3	> 45	5.9
0.27	< 1.4	< 50	> 1.4	> 50	5.3
0.07	< 0.3	< 70	> 0.3 (i_l ~ 0.6)	> 70	4.1

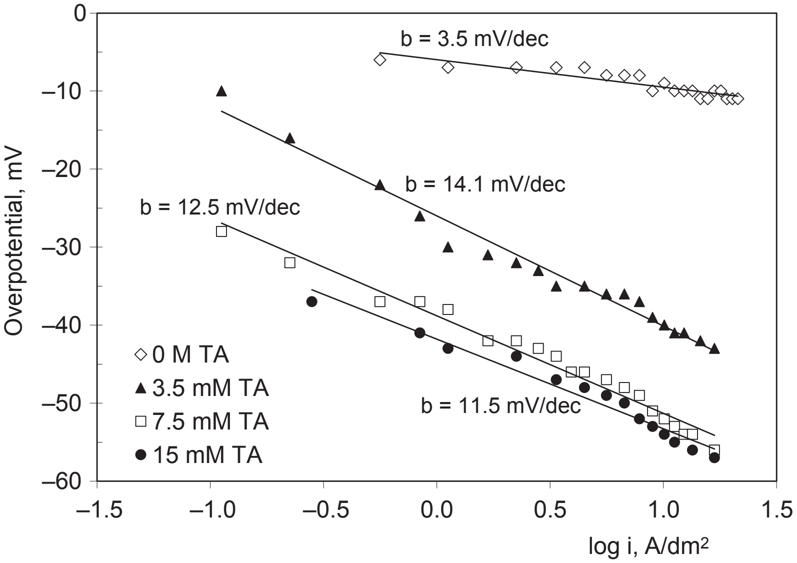

Fig. 3. Cathodic polarization curves plotted in "Tafel coordination system" for 1.07 M $AgNO_3$ and various concentrations of tartaric acid (TA)

The electrodeposition of silver from solutions containing tartaric acid leads to the formation of deposits with morphologies dependent on the concentration of the metal ions. The results of the macroscopic observations of the cathodic silver are summarized in Table 2, while Figure 4 shows micrographs of the deposits. It was found that both the coherent layers and dendrites can be produced in solutions with the highest concentration of Ag^+ ions. They are characterized by a rather rough surface with a characteristic superficial microstructure. The compact deposits showed a bright and smooth surface. In turn, the powdery deposits obtained from the electrolyte containing 0.27 M Ag^+ consisted of "dendrite-like" grains with rounded edges and a strongly rough surface. The electrodeposition of silver from the most diluted solutions produced extremely fine dendritic grains (about 4–5 μm in length), forming spongy products under a limiting current.

A comparison of the polarization measurements and microscopic observations shows that, in the presence of tartaric acid, compact silver deposits are formed only if the cathodic reduction is run under activation control. The additive changes the structure of the silver grains as compared to the pure $AgNO_3$ electrolyte (where isolated polyhedral grains were formed [8]). Concentration polarization (mixed control) promotes the formation of "dendrite-like" structures, but their appearance is also seriously modified as compared to the dendrites obtained from the bath without additives [8].

Table 2. Macroscopic description of silver deposited from $AgNO_3$ solutions with addition of 15 mM tartaric acid

i/c **[A·dm/mol]**	**Ag^+ concentration in bath**		
	1.07 M	**0.27 M**	**0.07 M**
5	compact deposit with golden gloss	–	–
10	compact deposit, semi-bright, gray-golden; dendrites at cathode edges	compact deposit, mat, dark-gray, loose powder at cathode edges	loose gray spongy deposit, not adherent to substrate
15	compact deposit, dull, dark gray, dendrites at cathode edges	loose dark-gray powder	loose dark-gray spongy deposit, not adherent to substrate
20	–	loose dark-gray powder	black spongy deposit, not adherent to substrate

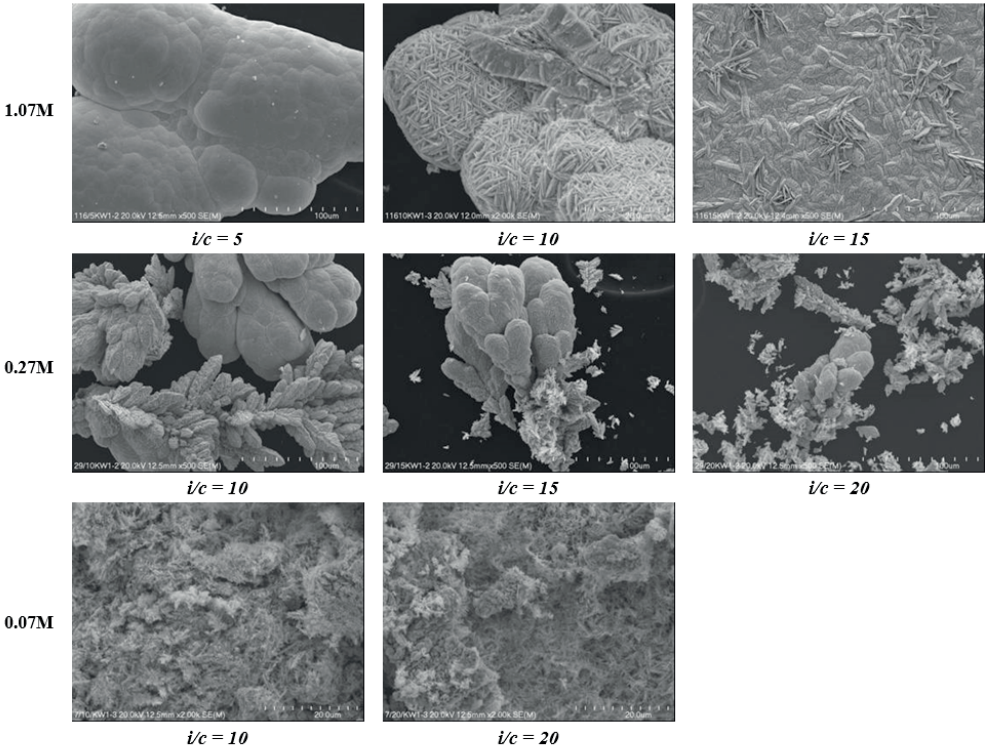

Fig. 4. Influence of i/c (in A·dm/mol) on morphology of silver deposited from $AgNO_3$ solutions containing 15 mM tartaric acid

4. Conclusions

From the performed experiments, the following conclusions can be made:

- The electrodeposition of silver from $AgNO_3$ solutions runs mainly under activation control.
- The presence of tartaric acid in the electrolyte slightly increases the polarization of the cathode and reduces the range of the activation control.
- The morphology of the cathodic deposits depends on the ratio of Ag^+ and tartaric acid concentrations in the electrolyte.
- Tartaric acid promotes the formation of smaller grains and more-compact deposits for a high-enough concentration of Ag^+.

Acknowledgements

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