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Silver electrodeposition from $AgNO_3$ solutions containing organic additives: Electrodeposition from binary water–methanol solvent systems in the presence of tartaric acid

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Abstract

The electrodeposition of silver at 25 °C from $AgNO_3$/tartaric acid solutions in binary water–methanol solvent systems was investigated. This study shows that it is possible to obtain compact and coherent silver deposits from $AgNO_3$ solutions only in the presence of tartaric acid (H_2A). The relevant chemical entity controlling growth inhibition is a neutral associate Ag(HA) formed in the solution between Ag^+ and tartaric monoanions HA^-. Most of the structural features of Ag deposits such as grain size, surface roughness and degree of the preferred orientation $\langle 1\ 1\ 0 \rangle$, depend on the concentration of this associate. These properties of the deposits can easily be controlled by: (a) modifying the concentration of $AgNO_3$ or H_2A, (b) adjusting the pH of the bulk solution by addition of HNO_3 and (c) modifying the composition of the mixed solvent system.

1. Introduction

The production of compact, smooth and coherent silver deposits is an important technological goal. For industrial application silver coatings are usually electrodeposited from cyanide solutions [1], which produce smooth and compact deposits free of dendritic growths. However, these solutions cause environmental damages and require delicate manipulation in the use and disposal of cyanides. For this reason many cyanide-free bath formulations have been previously proposed [1, 2]. Unfortunately, none of these baths has been accepted by industry in preference to the common cyanide solutions. In this respect, the production of smooth silver deposits of uniform thickness and physical properties from cyanide-free baths is of important environmental and economic interest.

To develop alternative silver plating solutions, which under certain conditions could replace cyanide baths, we have studied in [3–5] the possibility of plating from nitrate solutions using tartaric acid (abbreviated here as H_2A) as additive. It is noted that silver electrodeposits prepared from nitrate solutions, free of any organic or inorganic additive, are not smooth or compact regardless of the plating conditions used. They consist of grains growing independently of each other and under given plating conditions may degenerate as dendrites [3, 6–14]. Many substances, mainly organic, have been used as additives in plating solutions to prevent dendritic growth or to modify certain physical properties of the silver electrodeposits. Tartaric acid or tartrate salts, whose levelling effect has long been known [15], are among the most effective growth inhibitors [3–5, 10–12, 15–17].

We have shown [4] that, for silver coatings prepared from aqueous $AgNO_3/H_2A$ solutions, the relevant chemical entity controlling growth inhibition is a neutral associate Ag(HA) formed in the solution between Ag^+ and tartaric monoanions HA^-. Most of the structural features of Ag deposits such as grain size, surface roughness and degree of the preferred orientation $\langle 1\ 1\ 0 \rangle$, depend on the concentration of this associate. Subsequent work [5] on silver electrodeposition from $AgNO_3/H_2A$ solutions in binary water–dioxane solvent mixtures revealed that the above structural properties of the coatings also depend on the dioxane content of the mixtures. This behaviour was attributed to changes in the bulk concentration of Ag(HA) imposed by the addition of the organic cosolvent.

Assuming that this behaviour also occurs in other binary solvent systems, it was decided to extent this investigation to mixed water–methanol solvent systems.

The binary water–methanol solvent mixtures are well known as popular media for electrochemical studies.

The presence of water allows dissolution of various ionic solutes. Moreover, these solvent systems preserve, to a considerable degree, the excellent solvent properties of methanol for many organic compounds. Among the organic solvents methanol is the closest to water in structure and properties. However, this solvent can dissolve a wide majority of organic acids more effectively than water [18].

In addition to dioxane, the use of methanol as cosolvent in binary with water solvent systems extends the solubility range for various organic compounds. Consequently, the prospect of preparing smooth, compact and coherent silver deposits from such solvent media, which offer the possibility of using water-insoluble organic substances, is an interesting perspective for future studies.

2. Experimental details

Bi-distilled water was used throughout. Absolute methanol (Merck p.a.) was further purified according to a method described in the literature [19]. Tartaric acid (L(+) Carlo Erba RP-ACS), $AgNO_3$ (Merck p.a.) and 1 M HNO_3 solution were used for the preparation of the solutions. The pH, adjusted by adding HNO_3, was determined as described previously [5]. All plating experiments were carried out at 25 °C. The cathode was a rotating disc electrode (dia. 17.3 mm). The constant angular speed of this electrode (1000 rpm) ensured the reproducibility of hydrodynamic conditions. The anode was a broad flat disc (dia. 60 mm). Both cathode and anode were made of high purity silver (99.999% Matthey Chemicals). The current density was galvanostatically controlled at $0.02\ A\ cm^{-2}$ over a period of 47 min producing deposits of constant thickness ($\sim$60 μm). The electrolytic cell, the experimental conditions and procedure used for the preparation of the deposits were described previously [4, 20]. The apparatus used for the examination of the surface morphology, the roughness and the X-ray diffraction diagrams were described in [5].

3. Results and discussion

3.1. *Main features of the deposits*

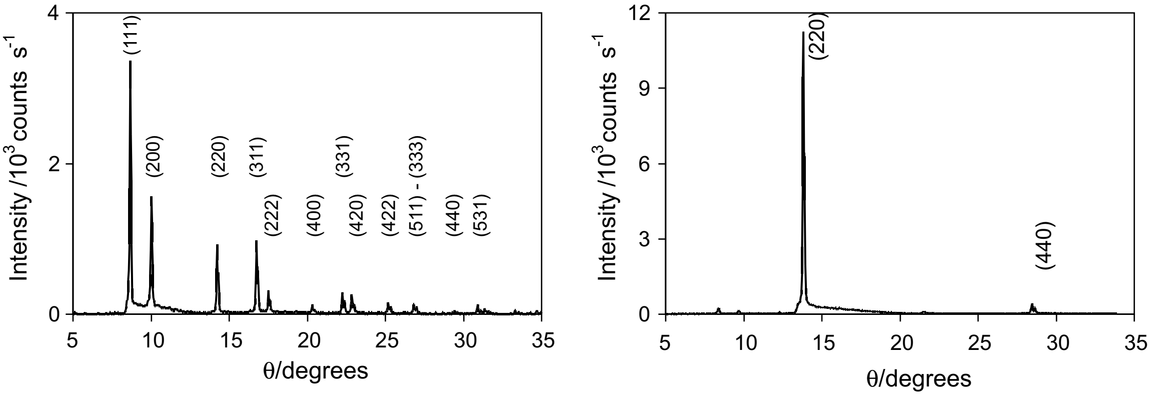
Six series of electrodeposits were studied. Each series corresponded to a definite $AgNO_3$ concentration and methanol content. The concentration of tartaric acid was 0.015 M in all cases. The solution pH was adjusted by modifying the HNO_3 concentration. The main composition parameters of the solutions for every case are listed in Table 1. The activities α_{HA^-} of HA^- were calculated by adapting a general method for polyprotic acids [21, 22] to diprotic ones. The values of the dissociation constants K_1 and K_2 of tartaric acid in water–methanol solvent systems were determined previously [23].

In the present work, the silver electrodeposition shows a similar behaviour to that observed previously in solutions of $AgNO_3/H_2A$ in water [4] or in binary water–dioxane solvent systems [5].

First, the analysis of X-ray diffraction (XRD) diagrams of the deposits showed that all the plates presented preferred orientation with a $\langle 1\ 1\ 0 \rangle$ texture axis. This effect was more pronounced for the more smooth, coherent deposits. The determination of the texture axis results from the comparison of the XRD diagrams of the deposits with that of randomly oriented silver powder [24, 25]. The preferred orientation $\langle 1\ 1\ 0 \rangle$ is readily detected from the increase in the intensities of (2 2 0) and (4 4 0) reflections comparatively to the

Table 1. Composition of $AgNO_3$/tartaric acid (H_2A) solutions in binary water–methanol solvent mixtures that give compact silver electrodeposits. $[H_2A]$ = 0.015 M

(a) 0.2 M $AgNO_3$, 10% (v/v) methanol				(b) 0.2 M $AgNO_3$, 20% (v/v) methanol				(c) 0.2 M $AgNO_3$, 30% (v/v) methanol			
Deposit	*$[HNO_3]$*	*pH*	$\alpha_{HA^-} \times 10^5$	*Deposit*	*$[HNO_3]$*	*pH*	$\alpha_{HA^-} \times 10^5$	*Deposit*	*$[HNO_3]$*	*pH*	$\alpha_{HA^-} \times 10^5$
A1	0.02	1.788	57.5	B1	0.02	1.822	45.6	C1	0.02	1.880	37.1
A2	0.03	1.642	41.7	B2	0.03	1.678	33.1	C2	0.03	1.732	26.7
A3	0.04	1.536	33.0	B3	0.04	1.569	26.0	C3	0.04	1.621	20.8
A4	0.05	1.457	27.6	B4	0.05	1.486	21.5	C4	0.05	1.537	17.2
A5	0.06	1.395	24.0	B5	0.06	1.419	18.5	C5	0.06	1.469	14.8
A6	0.08	1.294	19.2	B6	0.08	1.314	14.6	C6	0.08	1.363	11.6
A7	0.10	1.214	16.0	B7	0.10	1.235	12.2	C7	0.10	1.285	9.69
(d) 0.1 M $AgNO_3$, 10% (v/v) methanol				(e) 0.1 M $AgNO_3$, 20% (v/v) methanol				(f) 0.1 M $AgNO_3$, 30% (v/v) methanol			
D1	0.02	1.833	63.7	E1	0.02	1.871	50.8	F1	0.02	1.908	39.6
D2	0.03	1.675	45.0	E2	0.03	1.719	36.3	F2	0.03	1.756	28.2
D3	0.04	1.563	35.1	E3	0.04	1.611	28.6	F3	0.04	1.649	22.2
D4	0.05	1.481	29.2	E4	0.05	1.532	23.9	F4	0.05	1.569	18.5
D5	0.06	1.416	25.2	E5	0.06	1.468	20.7	F5	0.06	1.504	16.0
D6	0.08	1.308	19.8	E6	0.08	1.361	16.3	F6	0.08	1.395	12.5
D7	0.10	1.229	16.5	E7	0.10	1.274	13.3	F7	0.10	1.312	10.3



(a) (b)

Fig. 1. Comparison of XRD diagrams of a randomly oriented Ag powder and an Ag deposit prepared from a solution of Table 1. (a) Randomly oriented silver powder and (b) deposit D1 (0.1 M $AgNO_3$, 0.015 M H_2A, 0.02 M HNO_3 in water–methanol mixture containing 10% methanol).

respective intensities of the silver powder. Figure 1 shows as an example the XRD diagram of a deposit (D1) with strong preferred orientation in comparison to the XRD diagram of silver powder free from any preferred orientation. It should be noted that the ⟨1 1 0⟩ texture can quantitatively be expressed by a parameter, Q_{110}, known as the 'degree of preferred orientation', which can experimentally be determined from XRD diagrams [24, 25]. This parameter is defined by the relation:

$$Q_{110} = m_{110}\left(\frac{I_{220}}{I_{\mathrm{R}}}\right) \qquad (1)$$

m_{110} being the multiplicity of {1 1 0} planes, while I_{220} and I_{R}, the integrated intensities of (2 2 0) reflections corresponding to the deposit and to the randomly oriented silver powder, respectively. So, for metals with face centred cubic lattice (f.c.c.) the parameter Q_{110} can be measured from the intensities of (2 2 0) reflections of the corresponding XRD diagrams. Evidently, in the study of a single ⟨*hkl*⟩ texture axis, the use of the ratio I_{hkl}/I_{R} instead of Q_{hkl} leads to identical conclusions. However, here we used Equation 1, which permits the comparison of two or more texture axes with different multiplicities [24].

Second, the experimental weight of all deposits prepared in this work was significantly greater than the theoretical weight, *p*, required by Faraday's law. Mathers and Kuebler [15] first detected this effect for silver electrodeposits prepared from aqueous $AgNO_3$ solutions. However, Fuseya and Murata [11] showed for the first time that the excess weight Δp is due to the incorporation of tartaric acid molecules into the silver deposit.

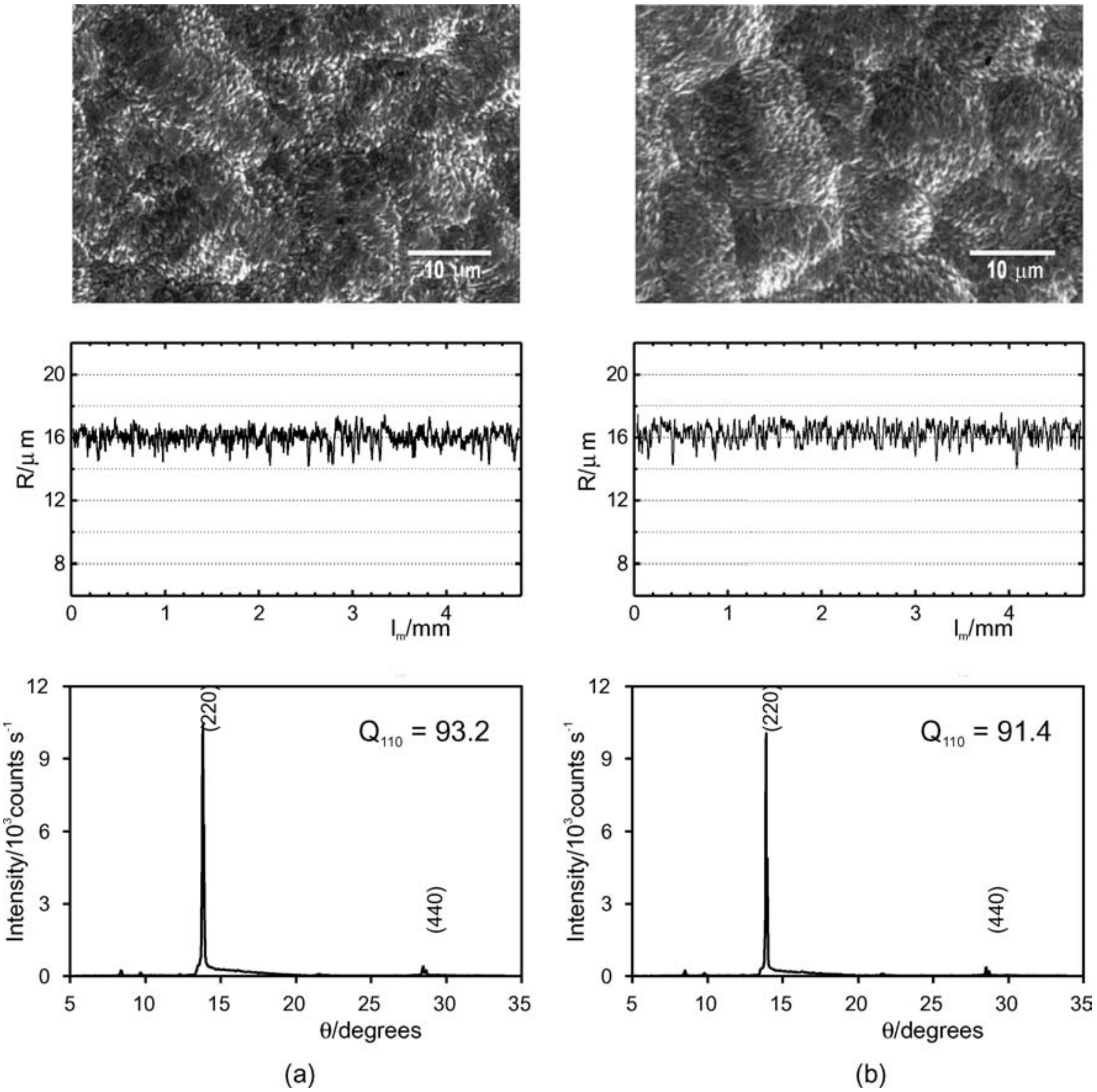
Some silver plates were prepared from $AgNO_3$ solutions without tartaric acid, in order to detect any inhibiting effect of methanol on the silver growth. The solutions contained 0.1 or 0.2 M $AgNO_3$, 10% or 20% (v/v) methanol and HNO_3 ranging from 0.05 to 0.6 M. It was found that only solutions with HNO_3 concentration greater than 0.5 M led to deposits with relatively good adherence to the substrate. However, these deposits showed high roughness. An analogous behaviour was observed in the case of silver deposits prepared from aqueous $AgNO_3$ solutions [26]. The experimental weight of these deposits obtained from solutions with HNO_3 concentration greater than 0.5 M was found to be equal to the weight required by Faraday's law ($\Delta p = 0$). Therefore, it was confirmed that, in the absence of tartaric acid, methanol does not participate in electrochemical reactions during the deposition process.

On the contrary, in the presence of tartaric acid, it was found that the ratio $\Delta p/p$ is closely related to structural parameters such as morphology, surface roughness and degree of preferred orientation ⟨1 1 0⟩. Greater values of $\Delta p/p$ mean smoother deposits with finer grain size and higher degree of preferred orientation. Deposits with quite similar surface morphology, roughness and degree of preferred orientation ⟨1 1 0⟩ exhibit nearly the same values of $\Delta p/p$. Indeed, in Figure 2 the comparison between the properties of two deposits (A2 and B3), obtained under different plating conditions but having almost equal values of $\Delta p/p$, illustrates that they exhibit a similar surface morphology, roughness and degree of preferred orientation ⟨1 1 0⟩. It thus appears that the quantitative parameter $\Delta p/p$ characterizes the global effect of growth inhibition.

3.2. *Effect of Ag(HA) on the growth inhibition*

In each series of deposits, the study of the properties of the plates revealed that smoothness, degree of preferred orientation and $\Delta p/p$ increased with increasing values of α_{HA^-}. Figure 3 illustrates such a tendency for two deposits of series (e). Both deposits were prepared from a 0.1 M $AgNO_3$ solution in 20% (v/v) methanol but E2 corresponds to a value of α_{HA^-}, which is 2.7 times greater than in the E7 case. The values of $\Delta p/p$ for both deposits of Figure 3 were 5.0% for E2 and 3.0% for E7.

It was also found that [$AgNO_3$] affects the properties of the deposits. Indeed, in all cases of deposits prepared



(a) (b)

Fig. 2. Surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of two deposits exhibiting equal values of $\Delta p/p$ but prepared from quite different solutions. (a) Deposit A2 ($[AgNO_3] = 0.2$ M, $\alpha_{HA^-} = 41.7 \times 10^{-5}$ M, methanol content = 10% v/v, $\Delta p/p = 5.50\%$) and (b) deposit B3 ($[AgNO_3] = 0.2$ M, $\alpha_{HA^-} = 26.0 \times 10^{-5}$ M, methanol content 20% v/v, $\Delta p/p = 5.43\%$).

from solution with the same α_{HA^-} and methanol content, the structural properties of the plates improved as $[AgNO_3]$ increased. Figure 4 illustrates this behaviour. Concerning the dependency of $\Delta p/p$ on the silver nitrate concentration, this study showed that $\Delta p/p$ was an increasing function of $[AgNO_3]$. For example, the values of $\Delta p/p$ for the deposits of Figure 4 were 4.0% for A6 and 3.0% for D6.

Taking into account that $\Delta p/p$ is closely related to the properties of the deposits, it results that the influence of α_{HA^-}, $[AgNO_3]$ and methanol content on the silver growth can be expressed by the graphs of Figure 5. These graphs show that, at a given methanol content, $\Delta p/p$ is an increasing function of α_{HA^-} and $[AgNO_3]$.

As previously [4, 5], this behaviour may be explained under the assumption that the parameter controlling the growth inhibition is the bulk activity α_c of an associate, which is formed in the solution between Ag^+ and HA^-.

In this respect, it was found that the graphs of Figure 5 can be fitted by a least squares technique to a simple logarithmic relation of the form ($R^2 > 0.993$):

$$\frac{\Delta p}{p} = a + b \log \alpha_{HA^-} \tag{2}$$

By assuming that an associate formed between Ag^+ and HA^- is the active component in the solution controlling growth inhibition, Equation 2 may be assumed to be a particular case of a more general empirical relation of the form:

$$\frac{\Delta p}{p} = A + B \log \alpha_c \tag{3}$$

where α_c is the activity of the component responsible for growth inhibition. Such a component might be an

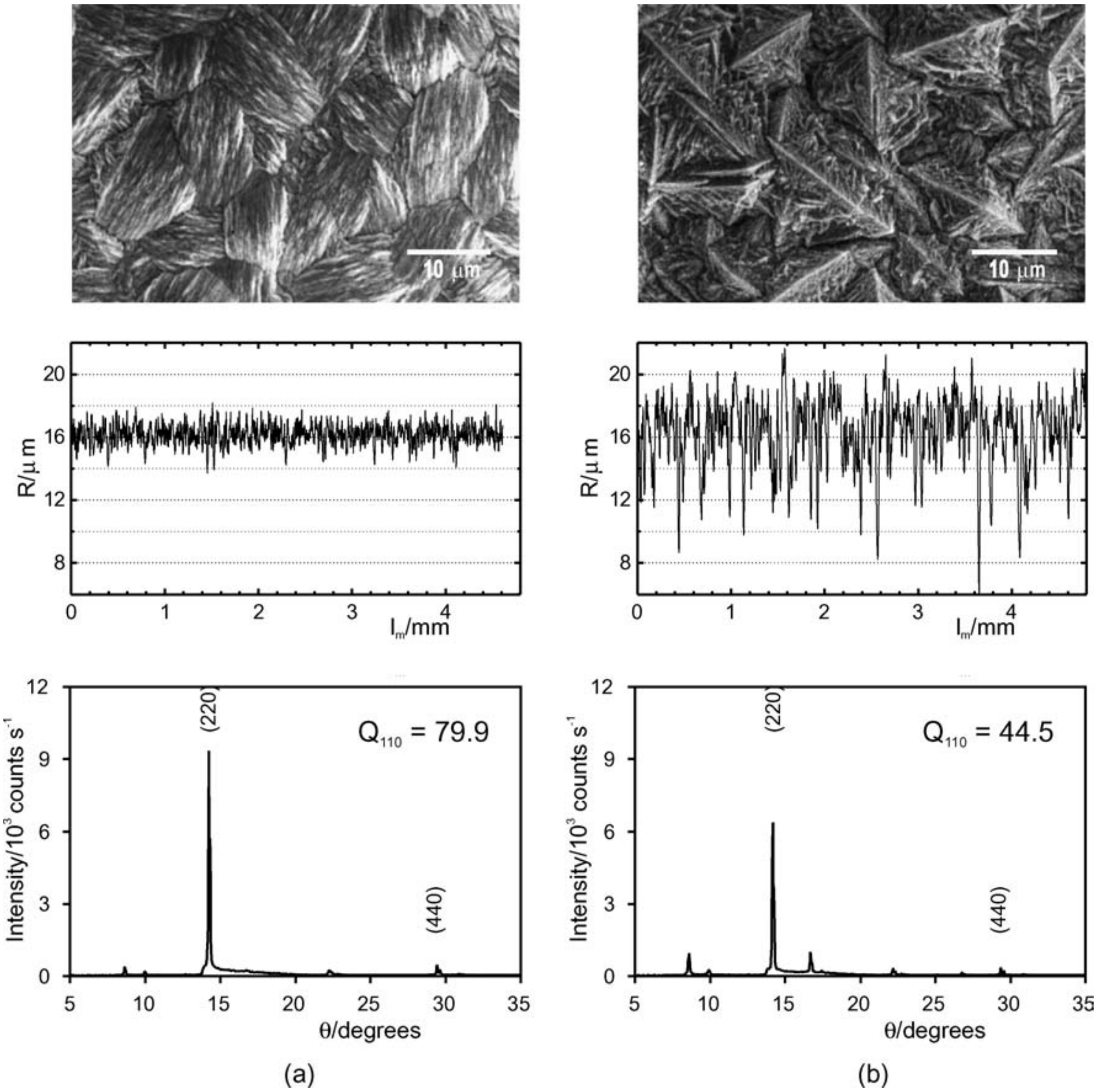


Fig. 3. Influence of monoanion activity on surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of two deposits. $[AgNO_3] = 0.1$ M in water – methanol mixture (20% methanol). (a) Deposit E2 ($\alpha_{HA^-} = 36.3 \times 10^{-5}$ M) and (b) deposit E7 ($\alpha_{HA^-} = 13.3 \times 10^{-5}$ M).

associate between one Ag^+ and n monoanions HA^-, according to the following equilibrium:

$$Ag^+ + nHA^- \Leftrightarrow \left[Ag(HA)_n\right]^{(n-1)-} \tag{4}$$

It follows then that:

$$\alpha_c = K_F\left(\alpha_{Ag^+}\right)\left(\alpha^n_{HA^-}\right) \tag{5}$$

The formation constant K_F of the associate depending on the dielectric constant D of the solution may remain invariable, provided that the solvent composition is constant. On the contrary, an increment in the methanol content lowers D [21] and increases the ionic attraction of various ionic species of opposite charge. Therefore, K_F also increases with increasing methanol content.

The combination of Equations 3 and 5 gives:

$$\frac{\Delta p}{p} = A_0 + B_1 \log\left(\alpha_{Ag^+}\right) + B_2 \log\left(\alpha_{HA^-}\right) \tag{6}$$

where $A_0 = A + B \log K_F$, $B_1 = B$ and $B_2 = nB$.

It is obvious that, in each series of deposits where α_{Ag^+} and methanol content remain constant (K_F = constant), Equation 6 reduces to Equation 2. However, in the general case, when α_{Ag^+} changes while the solvent composition remains constant, Equation 6 expresses the dependence of $\Delta p/p$ against α_{HA^-} and α_{Ag^+}.

Equation 6, having the form:

$$\frac{\Delta p}{p} = A_0 + B_1X_1 + B_2X_2 \tag{7}$$

predicts a linear dependence of $\Delta p/p$ against X_1 and X_2. Alternatively, the experimental confirmation of such a correlation supports the assumption that the active

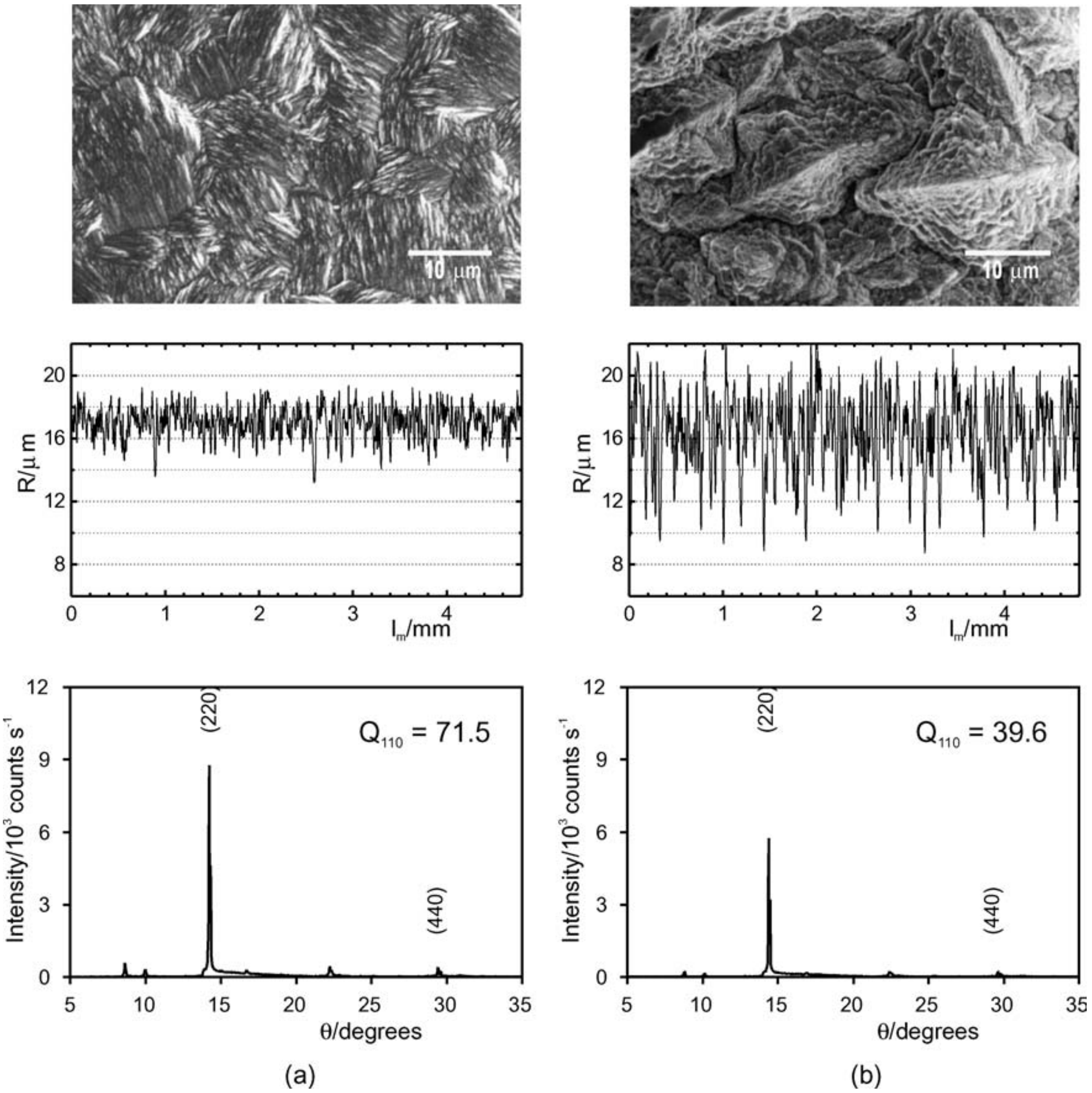


Fig. 4. Influence of $AgNO_3$ concentration on surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation $\langle 1\ 1\ 0\rangle$ (XRD diagrams) of two deposits prepared from solutions in water–methanol mixture (10% methanol). (a) Deposit A6 ($[AgNO_3] = 0.2$ M, $\alpha_{HA^-} = 19.2 \times 10^{-5}$ M), (b) deposit D6 ($[AgNO_3] = 0.1$ M, $\alpha_{HA^-} = 19.8 \times 10^{-5}$ M).

component in the solution controlling growth inhibition is an associate of the form $[Ag(HA)_n]^{(n-1)-}$. In such a case, the coordination number n can be determined from the ratio of the coefficients B_1 and B_2. Indeed, at each solvent composition studied, it was found that Equation 6 fits the experimental data ($R^2 \geqslant 0.9964$) very successfully. The coefficients A_0, B_1 and B_2 determined by a multiple linear regression method are listed in Table 2 along with the corresponding values of R^2. It is noted that in all these calculations the activities a_i of the various ionic species were calculated as described in [5]. The values of the dielectric constant D of the corresponding solvent media, necessary for these calculations, were taken from literature [21].

The values of Table 2 show that the coordination number n is nearly equal to unity for all solvent compositions. Thus, the active component, in the bulk solution, on the growth inhibition is a 1:1 associate formed between Ag^+ and HA^-.

Given that $n = 1$, Equation 6 can be written as:

Table 2. Coefficients of Equation 5, coordination number n and R^2 corresponding to various water–methanol solvent mixtures

% (v/v) methanol	A_0	B_1	B_2	n	R^2
10	0.2311(31)	0.0424(11)	0.0409(8)	0.96	0.9972
20	0.2398(36)	0.0429(13)	0.0408(9)	0.95	0.9964
30	0.2480(31)	0.0431(11)	0.0408(8)	0.95	0.9975

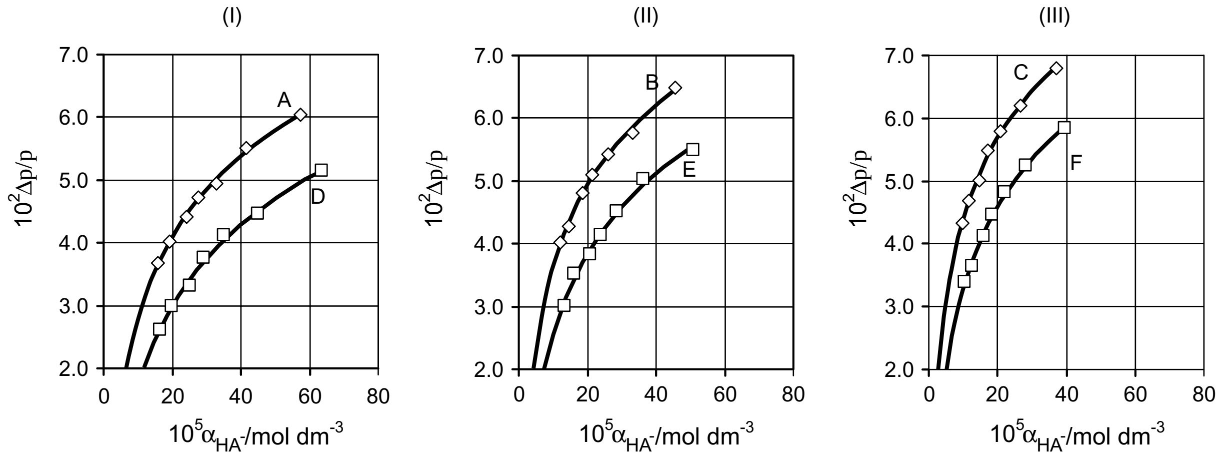


Fig. 5. Variation of $\Delta p/p$ with α_{HA^-} for all deposits of Table 1. Each curve corresponds to a definite AgNO$_3$ concentration and methanol content. (I) 10% methanol: (A) 0.2 M AgNO$_3$, (D) 0.1 M AgNO$_3$; (II) 20% methanol: (B) 0.2 M AgNO$_3$, (E) 0.1 M AgNO$_3$ and (III) 30% methanol: (C) 0.2 M AgNO$_3$, (F) 0.1 M AgNO$_3$.

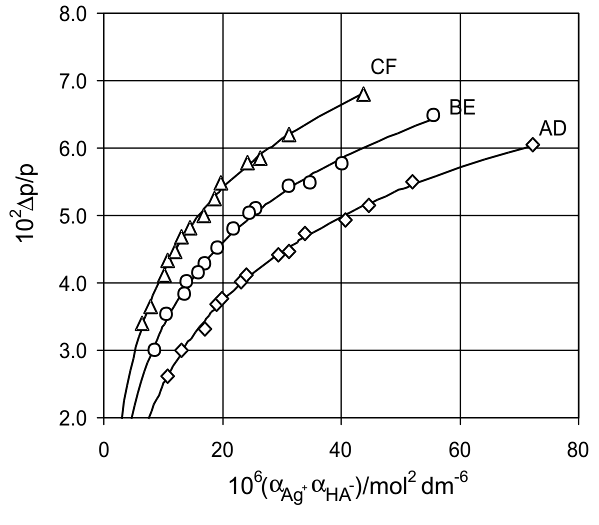


Fig. 6. Variation of $\Delta p/p$ with $\alpha_{Ag^+}\,\alpha_{HA^-}$. Each curve corresponds to a definite methanol content. (AD) 10% methanol (series (a) and (d)); (BE) 20% methanol (series (b) and (e)); (CF) 30% methanol (series (c) and (f)).

$$\frac{\Delta p}{p} = A_0 + B\log\left(\alpha_{Ag^+}\,\alpha_{HA^-}\right) \qquad (8)$$

Thus, from Equation 8, at each solvent composition, the dependence of $\Delta p/p$ on $\alpha_{Ag^+}\,\alpha_{HA^-}$ must be expressed by a unique curve for the two series of deposits. This is clearly shown by Figure 6.

Alternatively, Equation 8 predicts a linear relation between $\Delta p/p$ and $\log(\alpha_{Ag^+}\,\alpha_{HA^-})$ at each solvent composition, where A_0 remains constant. As the methanol content increases, K_F and A_0 also increase and this fact may result in a displacement of the corresponding line toward higher $\Delta p/p$ values. Indeed, in all solvent mixtures used in the present work, the expected linear relationships between $\Delta p/p$ and $\log(\alpha_{Ag^+}\cdot\alpha_{HA^-})$ were observed (Figure 7).

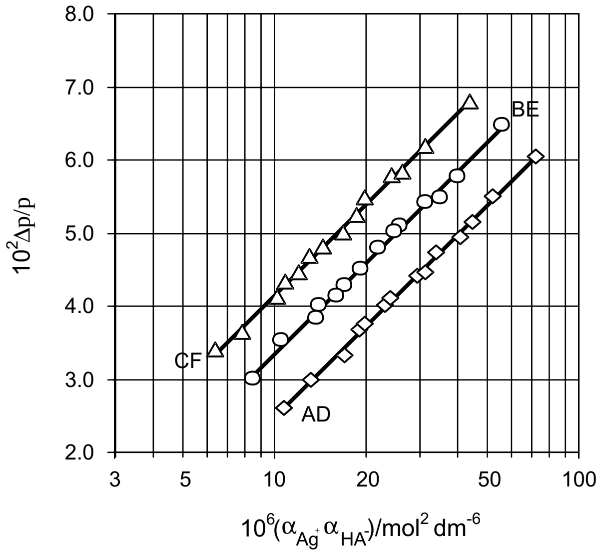


Fig. 7. Logarithmic plot of the curves of Figure 6.

The influence of methanol on silver electrodeposition is indicated in Figures 6 and 7. At constant values of $\alpha_{Ag^+}\alpha_{HA^-}$, as the methanol content rises, $\Delta p/p$ also increases and the corresponding plates must become smoother with higher Q_{110} values. This behaviour is clearly shown by the examples illustrated in Figure 8.

3.3. *Ag(HA) as the relevant parameter for the structural features of the deposits*

As previously [5], in order to establish a quantitative correlation between growth inhibition and the structural features of deposits, the values of a quantitative structural parameter such as Q_{110} were plotted against $\Delta p/p$ (Figure 9(a)). For all the series of deposits, a unique straight line with positive slope was obtained showing a clear correlation between growth inhibition, quantitatively expressed by $\Delta p/p$, and Q_{110}.

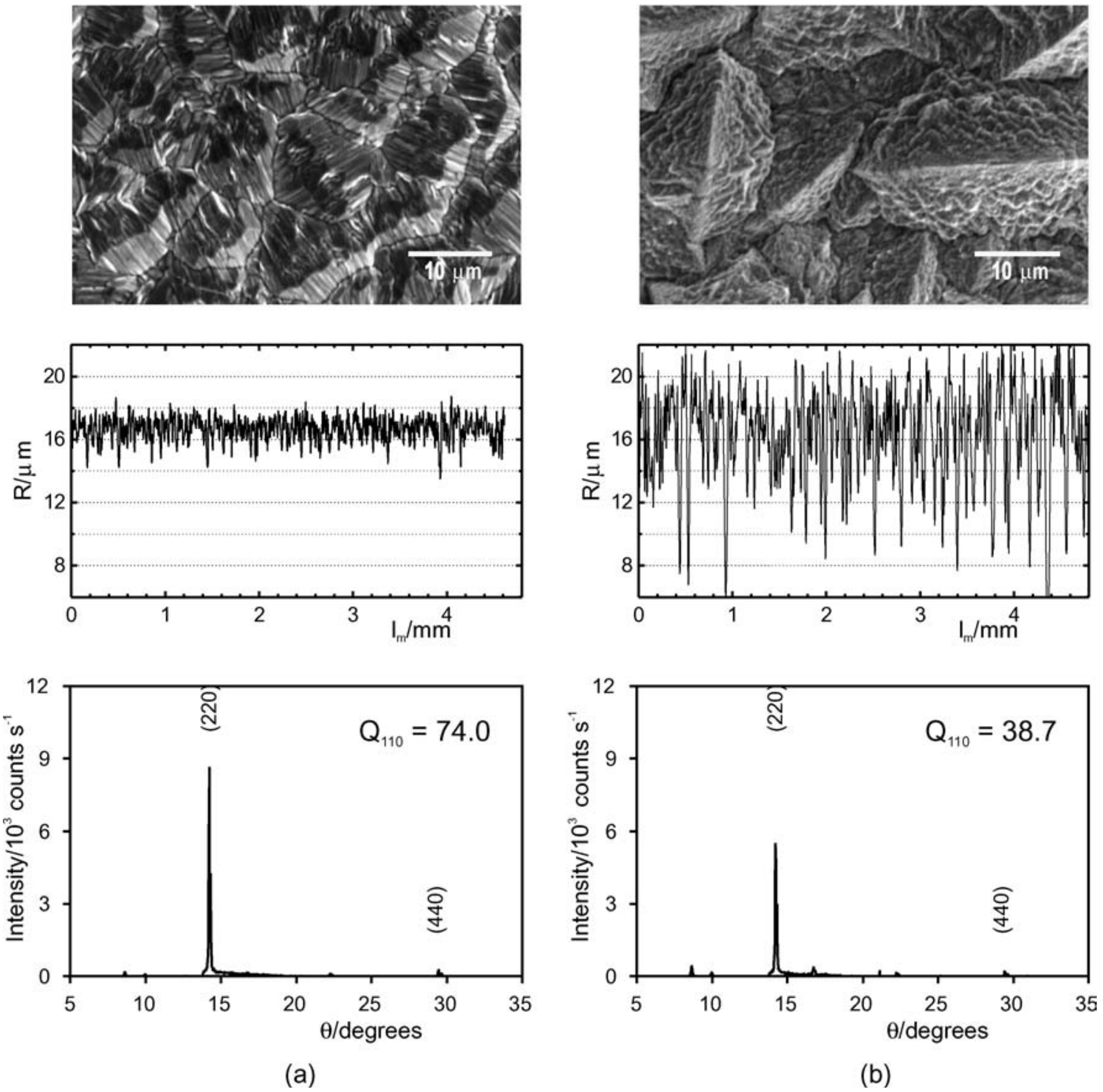


Fig. 8. Influence of methanol content on surface morphology (SEM micrographs), roughness (curves) and degree of preferred orientation ⟨1 1 0⟩ (XRD diagrams) of two deposits prepared from solutions with the same value of the product $\alpha_{Ag^+}\,\alpha_{HA^-}$ (1.08×10^{-5} M). (a) Deposit C7 (methanol content 30%) and (b) deposit D7 (methanol content 10%).

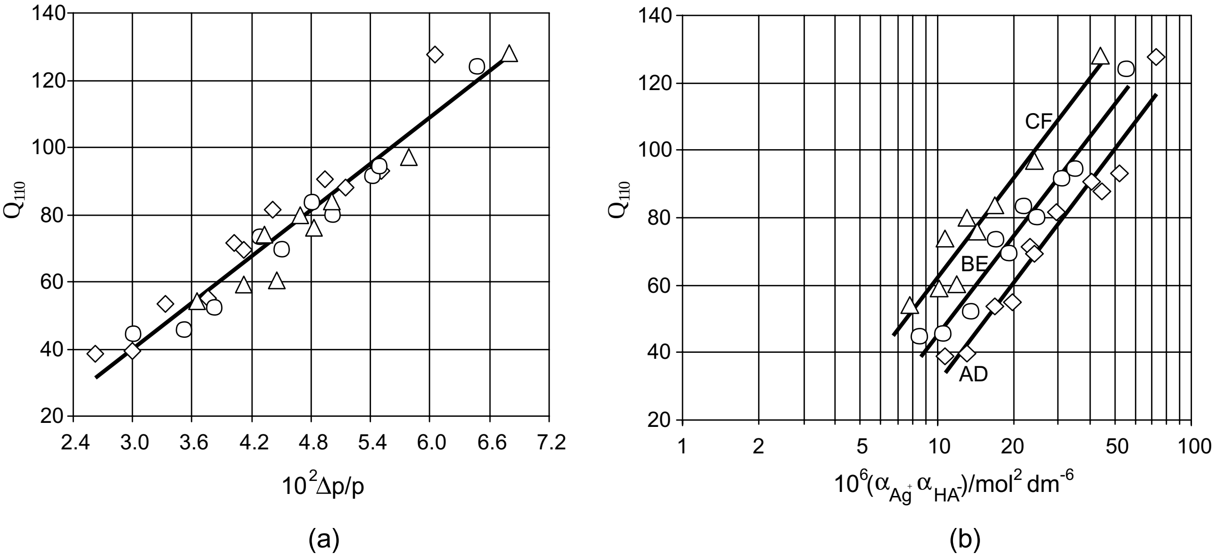
Furthermore, taking into account the linear relations between $\Delta p/p$ and $\log \alpha_c$ at each solvent composition, analogous dependencies between Q_{110} and $\log \alpha_c$ are expected, the product $\alpha_{Ag^+}\,\alpha_{HA^-}$ being a measure of α_c. Indeed, the graphs of Figure 9(b) prove such a correlation. The similarity between the graphs in Figures 9(b) and 7 provides further experimental evidence that Ag(HA) is the active component in the solution, which also controls the structural features of the deposits.

4. Conclusions

A systematic study of Ag electrodeposits obtained from $AgNO_3$ solutions in binary water – methanol solvent systems showed that it is possible to obtain compact and coherent silver deposits from such solvent media only in the presence of tartaric acid. In these media, a similar behaviour to that observed previously in solutions of $AgNO_3 - H_2A$ in water [4] or in binary water – dioxane solvent systems [5] was observed. Thus, it was found that an associate Ag(HA) formed in the bulk solution between Ag^+ and HA^- is the active component in the solution controlling the growth inhibition. Due to its electrical neutrality, Ag(HA) has to be transported towards the cathode by convection.

The structural features of the plates such as grain size, surface roughness and degree of preferred orientation ⟨1 1 0⟩ depend on the concentration of this associate.

Consequently, the structural features of the deposits can be modified by changing the concentration of Ag(HA) in the bulk solution. The Ag(HA) concentration can be easily controlled by: (a) modifying the concentrations of $AgNO_3$ or H_2A, (b) adjusting the pH of the bulk solution and (c) modifying the composition of the mixed solvent system.



(a)

(b)

Fig. 9. Variation of Q_{110} with $\Delta p/p$ (a) and $\alpha_{Ag^+}\ \alpha_{HA^-}$ (b). (AD) 10% methanol; (BE) 20% methanol and (CF) 30% methanol.

The prospect of preparing smooth, compact and coherent silver deposits from such solvent media, which offer the possibility of using as additives that are insoluble in water, is an interesting perspective for future studies.

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