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Structure of silver electrodeposits plated from different complex electrolytes

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The structure of silver deposits plated from different complex electrolytes is investigated. It is shown that from all electrolytes based on cyano-argentate complexes, electrodeposits with a basic orientation along the ⟨1 1 1⟩ axis are plated. If other complex-forming agents are used, textures along different crystallographic axes can be obtained. At high current densities the deposits display a random orientation. No evidence for a direct relationship between the type of texture and the deposition overvoltage of silver in the electrolytes studied has been established. Silver deposits with structural characteristics and properties similar to those of coatings deposited from cyanide baths can be obtained from ferrocyanide–thiocyanate electrolytes.

1. Introduction

The investigations of the structure of silver electrodeposits plated from cyanide electrolytes [1, 2] have revealed that in the absence of brighteners and at low current densities (CD) a preferential orientation of the crystallites along the ⟨1 1 1⟩ axis is present. As the current density is increased, a mixed texture along the ⟨1 1 1⟩ and ⟨5 1 1⟩ axes are observed, while at higher CD a transition to random orientation commences. Alteration of plating conditions (CD, temperature, silver content in the electrolyte, etc.) does not lead to the formation of deposits oriented along other crystallographic axes.

Numerous attempts have been reported in the literature to replace the toxic cyanide system by electrolytes based on other complex silver compounds, but there are few instances of practical implementation. The main difficulties are related to the instability of the electrolyte on the one hand and the quality of the plates on the other.

Literature data concerning the structure of coatings deposited from different electrolytes are quite scarce. Data concerning the structure of deposits plated from cyanide baths have been discussed in [1]. The results from thiosulphate electrolyte studies [3] with organic additives show that the deposits do not have a preferential orientation of the crystallites, but the lattice parameter, microhardness and electric resistance attain high values. In the case of ferrocyanide baths [4] at low current densities the ⟨0 1 1⟩ and ⟨0 1 2⟩ orientations have been obtained, while at high current densities the ⟨1 1 1⟩ orientation is obtained. In sulphamate formulations [5] highly imperfect ⟨1 1 0⟩ orientations have been observed. To the best of our knowledge, no data are available concerning the structures and textures of deposits plated from other types of complex silver electrolytes.

The present paper is aimed at the investigation of the structure of silver deposits plated from different electrolytes and the selection of a bath composition which will serve as a basis for the deposition of silver alloys with other metals.

2. Experimental details

All electrolytes used for plating silver contained approximately equal concentrations of silver ions and were prepared according to the formulations in Table 1. All chemicals used in this study were of analytical grade. Bidistilled water was used in preparing the electrolytes. The dicyano-argentate complex in the ferrocyanide–thiocyanate formulation (electrolyte 2) is obtained by mixing silver nitrate and potassium cyanide solutions in the appropriate stoichiometric ratio, while the potassium

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Table 1. Composition of electrolytes (concentrations in $g\,l^{-1}$)

Reagent	Electrolyte							
	1	2	3	4	5	6	7	8
$AgNO_3$	25	30	30	25	–	25	25	–
AgCl	–	–	–	–	20	–	–	–
Ag_2SO_4	–	–	–	–	–	–	–	25
$K_4Fe(CN)_6 \cdot 3H_2O$	70	57	–	–	–	–	–	–
K_2CO_3	30	–	–	8	–	–	–	–
KCN	–	23	23	45	–	–	–	–
KSCN	150	150	150	–	–	–	–	–
$KNaC_4H_4O_6 \cdot 4H_2O$	60	60	60	–	–	–	–	–
$Na_2SO_3 \cdot 5H_2O$	–	–	–	–	70	–	–	–
$NaHSO_3$	–	–	–	–	10	–	–	–
Na_2SO_4	–	–	–	–	20	–	–	–
EDTA sodium salt	–	–	–	–	–	200	–	–
NH_4NO_3	–	–	–	–	–	40	–	–
NH_4OH	–	–	–	–	–	(pH 10)	–	–
NH_4SCN	–	–	–	–	–	–	250	–
H_3BO_3	–	–	–	–	–	–	20	–
KI	–	–	–	–	–	–	–	250

ferrocyanide concentration corresponds to the surplus amount used for the preparation of electrolyte 1.

The substrates were mechanically polished copper plates of area 4 cm^2, surrounded by a framework of copper wire designed to ensure a more homogeneous distribution of the layer with respect to its structural parameters.

The silver deposits, 20 μm thick, were plated at 20° C in a cylindrical cell of capacity 100 cm^3 and with no agitation of the electrolyte. The purity grade of the silver anodes was 99.9%. Cathodic CD varied within the range 0.1–1.0 A dm^{-2}. The texture of the deposits was studied using an X-ray goniometer, and hardness was monitored with a Leitz microhardness meter. The coatings were electrodeposited under galvanostatic conditions and the potential was measured against a silver reference electrode using a Luggin capillary. The reference electrode was prepared by plating silver onto a platinum wire at a CD of 0.5 A dm^{-2} for 30 min in the electrolyte to be used in the experiment.

3. Results and discussion

Fig. 1 shows the cathodic polarization curves traced galvanostatically in the above-mentioned electrolytes without agitation. It can be noted that silver is deposited in different electrolytes at various degrees of polarization, starting from the lowest values in iodide electrolytes and reaching the highest figures in ferrocyanide–thiocyanate baths. The curves in electrolytes 1–3 are rather similar, reflecting the similarity in the bath formulation. The addition of potassium ferrocyanide to electrolyte 3 decreases the overvoltage, which does not agree with results of

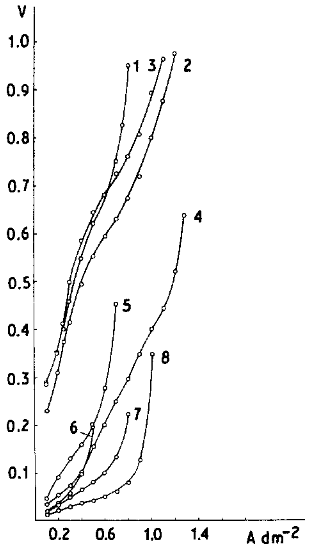

Fig. 1. Electrode potential versus cathodic CD. The number of the curve corresponds to the number of the electrolyte shown in Table 1.

other authors [6] who have investigated similar electrolytes but in the absence of KSCN and $KNaC_4H_4O_6 \cdot 4H_2O$.

The investigation of the preferential orientation of crystallites in the deposits by using X-ray techniques revealed the following picture. Deposits plated from electrolyte 1 (ferrocyanide–thiocyanate formulation) display textures oriented along the ⟨1 1 1⟩ and ⟨3 1 1⟩ axes together with twinning orientation ⟨5 1 1⟩. As CD increases, the number of ⟨3 1 1⟩-oriented crystallites decreases. At high CD (in the order of 1 A dm^{-2}) the deposits have random orientation. Electrolytes 2 and 3 display a similar ordering: ⟨1 1 1⟩ + ⟨5 1 1⟩ + ⟨3 1 1⟩ → ⟨1 1 1⟩ + ⟨5 1 1⟩ → random orientation.

These results show that in the case of complex silver plating electrolytes based on cyanoargentate complexes in the absence of organic additives the main orientation of the crystallites in the deposit is ⟨1 1 1⟩, regardless of the plating conditions or the formulation (pure cyanide, cyano-thiocyanate and ferrocyanide–thiocyanate). This basic orientation is also obtained regardless of the free cyanide of the cyano-argentate electrolytes within the entire range of CD.

If another complex-forming agent is used, an alteration of the preferential orientation of crystallites is observed in the silver deposit. Thus, when silver is plated from thiosulphate electrolyte 5 at low CD, the ⟨1 1 1⟩ orientation reappears together with the twinning orientation ⟨5 1 1⟩. Both orientations are very perfect and can be easily identified. At CDs of about 0.5 A dm^{-2} a ⟨1 1 0⟩ orientation is observed, a relatively rare phenomenon for silver deposits.

The most pronounced variation of textures is established in deposits plated from electrolyte 6, based on EDTA sodium salt. At a CD of 0.1 A dm^{-2} the texture is along the ⟨3 1 1⟩ axis together with the twinning orientation ⟨7 5 5⟩; at a CD of 0.25 A dm^{-2} the ⟨1 0 0⟩ orientation is obtained; while at a CD of 0.5 A dm^{-2} the ⟨1 1 0⟩ orientation emerges. It must be noted here that the potentials at which the ⟨1 1 0⟩ orientation is obtained in electrolytes 5 and 6 are approximately similar, i.e. about 200 mV.

All silver deposits plated in the thiocyanate electrolyte 7, over the entire range of investigated CDs, show random orientation.

Table 2. Characteristics of deposits with varying CD

Electrolyte	*A dm^{-2}*	*Texture*
1	0.1–0.25	⟨1 1 1⟩ + ⟨5 1 1⟩ + ⟨3 1 1⟩
	0.5	⟨1 1 1⟩ + ⟨5 1 1⟩
	0.75–1.0	random orientation
2	0.1–0.75	⟨1 1 1⟩ + ⟨5 1 1⟩ + ⟨3 1 1⟩
	1.0	⟨1 1 1⟩ + ⟨5 1 1⟩
	1.5	random orientation
3	0.1–0.5	⟨1 1 1⟩ + ⟨5 1 1⟩ + ⟨3 1 1⟩
	0.75	⟨1 1 1⟩ + ⟨5 1 1⟩
	1.0	⟨1 1 1⟩ + ⟨5 1 1⟩ poor perfection
	1.5	random orientation
4	0.1–0.25	⟨1 1 1⟩ + ⟨5 1 1⟩ + ⟨3 1 1⟩
	0.5–0.75	⟨1 1 1⟩ + ⟨5 1 1⟩
	1.0–1.25	random orientation
5	0.1–0.25	⟨1 1 1⟩ + ⟨5 1 1⟩
	0.5	⟨1 1 0⟩
6	0.1	⟨3 1 1⟩ + ⟨7 5 5⟩
	0.25	⟨1 0 0⟩
	0.5	⟨1 1 0⟩
7	0.1–0.75	random orientation
8	0.1–0.5	⟨2 1 1⟩ + ⟨5 2 2⟩ + ⟨2 2 1 1⟩
	0.75–1.0	⟨1 0 0⟩ + ⟨2 2 1⟩

The potassium–iodide electrolyte 8 is characterized by silver deposits plated at low CDs (up to 0.5 A dm^{-2}), which are oriented along the ⟨2 1 1⟩ axis together with intensive twinning: not only first-order twinning, i.e. orientation ⟨5 2 2⟩, is registered, but also that of the second order ⟨2 2 1 1⟩ [7]. At elevated CDs (0.75–1 A dm^{-2}), textures along the ⟨1 0 0⟩ and ⟨2 2 1⟩ axes are obtained which in the case of the higher CD display some imperfection.

These experimental results (Table 2) lead to the conclusion that the use of different complex-forming agents for the preparation of silver-plating electrolytes can produce deposits with various textures, although a direct correlation between the axis of preferential orientation of the crystallites in the deposit and the plating overvoltage in the different electrolytes is still to be established. Obviously in this case the texture depends not only on the silver deposition overvoltage but also on the type of the complex ion from which the metal is discharged.

A difference was established in the appearance and quality of the deposits plated from different electrolytes. Thus, plates deposited from electrolytes 1–4, where silver is bonded in a cyanoargentate complex, are homogeneous, matt and fine-grained, which is related to the higher cathodic polarization during deposition. As already mentioned these electrolytes produce deposits with similar textures, and their microhardness values are also very similar – within the range 90–100 kg mm^{-2}. Similar silver lattice parameter values (4.08–4.09 Å) are also obtained.

Deposits plated from thiosulphate electrolytes are fine-grained and, at low CDs, bright or semibright; this is obviously a result of the sulphur content in the thiosulphate. Their hardness is enhanced within the range 170–180 kg mm^{-2} at a CD of 0.25 A dm^{-2}. These deposits are also characterized by substantial internal stresses which cause a cracking tendency. At a CD of 0.5 A dm^{-2} the silver deposits are matt. Silver coatings electrodeposited from electrolyte 6 with EDTA complex-forming agent are homogeneous, milky white and coarse-grained. We were unable to determine their microhardness. As expected, with increase of CD the deposits become more fine-grained but still far more coarse than coatings deposited in the first five electrolytes. The thiocyanate electrolyte 7 offers the possibility of obtaining matt and rough deposits with a slightly yellowish shade, the best quality being obtained at a CD of 0.5 A dm^{-2}. The microhardness of these coatings was also difficult to determine with the available equipment. The iodide electrolyte makes possible the electrodeposition of light-coloured homogeneous silver coatings, but they are coarse-grained. As the CD increases the deposits become more fine-grained but still much more rough than plates deposited from ferrocyanide or cyanide electrolytes.

These investigations lead to the conclusion that silver deposits with characteristics nearest to cyanide silver plates can be obtained from ferrocyanide–thiocyanate electrolytes. This electrolyte also offers the possibility for the codeposition of elements which increase the hardness and wear-resistance of the deposits, e.g. antimony.

4. Conclusions

1. Different silver-plating electrolytes have been used, based on various silver complexes, to investigate the metal deposition overpotential, the preferential orientation of the crystallites and the quality of the coatings.

2. It has been established that in all electrolytes where silver is deposited from a cyanoargentate complex and cathodic overvoltages are the highest, the textures obtained are similar, mainly along the $\langle 1\,1\,1 \rangle$ axis. Intensive twinning occurs in some cases with the appearance of a texture component $\langle 3\,1\,1 \rangle$.

3. It is shown that when different complex-forming agents are used it is possible to deposit coatings with other axes of preferential orientation of crystallites, e.g. $\langle 1\,0\,0 \rangle$, $\langle 1\,1\,0 \rangle$ and $\langle 2\,1\,1 \rangle$, but no direct relationship between the texture axis and deposition overvoltage has been established.

4. It is shown that, in the absence of brighteners, semi-bright or bright hard deposits can be plated only from thiosulphate baths, but the coatings are characterized by increased internal stresses. Deposits obtained from thiocyanate, iodide and EDTA complex containing electrolytes are coarse-grained but homogeneous.

5. Thiocyanate electrolytes produce random-oriented deposits over the entire CD range investigated.

6. Deposits having characteristics nearest to those of silver plates from cyanide electrolytes can be obtained from the ferrocyanide–thiocyanate electrolyte 1 since in this case textures are quite similar.

References

[1] I. Kristev and V. Velinov, *Surface Technol.* **5** (1971) 1.

[2] *Idem, ibid.* **5** (1977) 13.

[3] J. Culjkovic, R. Ludwig and W. Riedel, *Metall* (*W. Berlin*) **29** (7) (1975) 700.

[4] A. A. Hmil, V. V. Surkov and M. D. Tjavlovskii, 'Chimicheskie i electrochimicheskie metodi zashtiti metallov', Saratov (1977), 60 (in Russian).

[5] T. Novev, S. Ovtcharov and N. Jordanov, 32 ISE Meeting, Dubrovnik-Cavtat, Yugoslavia, Extended Abstracts, Vol. II (1981) p. 1060.

[6] N. P. Fedotjev and V. A. Iljin, *Zh. prikl. Khim.* **36** (1963) 1763 (in Russian).

[7] I. Tomov, *Commun. Dept. Chem. Bulgar. Acad. Sci.* **4** (1971) 213.