



## Effect of electrolysis conditions on the deposition of silver–bismuth alloys

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### Abstract

The electrochemical deposition and dissolution of silver, bismuth and silver–bismuth alloy from a cyanide–tartrate electrolyte were studied by means of cyclic voltammetry. The influence of the electrolyte composition on the electrochemical reactions is discussed. The deposition potentials of the two metals could be maintained close to each other by means of appropriate complex forming agents, leading to their codeposition. Silver deposition is the predominant reaction in the electrolyte studied and the bismuth content in the coating increases with increased current density. The dissolution potentials of the two metals are quite distinct; they differ by more than 0.5 V. In the presence of a free complex forming agent, both the deposition and the dissolution potentials of silver can be shifted in the negative direction. Depending on the type and amount of the complex forming agent, they can become more negative than the deposition and dissolution potentials of bismuth. Predominant deposition of bismuth is realized in this case and the codeposition of silver is enhanced at higher current densities. By varying the amount of the complex forming agent, silver–bismuth coatings of any desired composition can be obtained.

### 1. Introduction

Silver coatings find numerous applications since they impart useful properties to the coated surfaces, such as excellent thermal and electrical conductivity, chemical resistance, catalytic activity in some media and bactericidal activity. In order to overcome some drawbacks of silver, such as low hardness and wear resistance, tarnishing, etc., alloying with other metals is required [1, 2]. In this case, the inferior electrical properties may be compensated by the superior physico-mechanical parameters of the alloy obtained.

Silver–bismuth alloy finds application in electronics, radiotechnics, and in the production of coatings exposed to severe conditions, e.g., friction under high pressure [2, 3]. The deposition of this alloy is carried out mainly from cyanide electrolytes, hydroxyl and tartaric ions being used as complex forming agents for bismuth [4, 5]. A ferrocyanide–thiocyanate electrolyte for silver deposition can also be used by the introduction of bismuth as a pyrophosphate complex [6]. The study of the separate [7, 8] and combined [9] deposition of the two metals from an alkaline electrolyte based on  $\text{KAg}(\text{CN})_2$  containing  $\text{KSCN}$  as a free complex forming agent for silver revealed some disadvantages of this electrolyte, such as its time- and labour-consuming preparation due to the slow dissolution of the  $\text{Bi}(\text{V})$ -salt ( $\text{NaBiO}_3$ ) by boiling in a potassium hydroxide and potassium–sodium tartrate

solution. Furthermore, the electrolyte is not sufficiently stable and becomes turbid due to precipitate formation upon prolonged storage; due to its relatively low metal content, good quality coatings can be prepared only within a narrow range of current densities.

The present study is aimed at the modification of the above-described electrolyte in order to achieve deposition of alloys of good quality with high bismuth content within broader ranges of current density.

### 2. Experimental

The composition of the alkaline electrolyte studied is given in Table 1. Distilled water and *pro analysi* grade reagents were used for its preparation. The bismuth content ( $18 \text{ g dm}^{-3}$ ) is considerably higher than those used in previous investigations of the alloy deposition [9].

The labour-intensive procedure of electrolyte preparation [9] was avoided by the introduction of a trivalent bismuth salt ( $\text{BiNO}_3$ ). The latter was dissolved together with the hydroxide and potassium–sodium tartrate directly in water.  $\text{KAg}(\text{CN})_2$  solution was added to the clear solution obtained. The resulting electrolyte was colourless, clear and stable. Furthermore, unlike the electrolyte used in previous studies [9], it contained sodium hydroxide instead of potassium hydroxide as

Table 1. Electrolyte composition

Components	Concentration /g dm <sup>-3</sup>	Concentration /mol dm <sup>-3</sup>
Ag as KAg(CN) <sub>2</sub>	8–32	0.075–0.3
Bi as BiNO <sub>3</sub>	6–18	0.03–0.09
NaOH	26	0.64
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	60	0.213
KSCN	0–120	0–1.24
KCN	0–120	0–1.85

well as nitrate ions (0.09 M), which have a favourable effect on the cathodic process during silver deposition [10].

The experiments were performed in a glass cell of 100 cm<sup>3</sup> volume at room temperature without stirring of the electrolyte. The working electrode (1 cm<sup>2</sup>) and the two counter electrodes were made of platinum. A reference electrode Ag/AgCl with  $E_{\text{Ag}/\text{AgCl}} = -0.197$  V vs the hydrogen electrode was used. During the experiments, the reference electrode was placed in a separate cell filled with 3 M KCl solution. It was connected to the electrolysis cell by a Haber–Luggin capillary through a salt bridge containing KCl solution of the same concentration. All potentials are given against this reference.

The cyclic voltammetric investigations were performed by means of a computerised potentiostat/galvanostat PAR 263A (Princeton Applied Research) using the SoftCorr II software for electrochemical corrosion studies.

The sweep rate was varied in the range of 0.005–1.000 V s<sup>-1</sup>. The thickness of the deposited alloy coatings was ca. 10 μm. The silver content in the coatings as well as their thickness were determined using a Fischer-scope XRAY XDVM-W apparatus for X-ray fluorescence.

### 3. Results and discussion

Figure 1 shows the dependence of the cyclic voltammetric curves on the silver concentration in the absence of bismuth in the electrolyte. Two cathodic reactions are observed at ca. -550 and -750 mV, probably corresponding to the deposition of silver from different cyanide complexes. The first anodic reaction (-445 mV) reflects the formation of an insoluble silver cyanide film on the electrode surface [7, 11], while the second (+60 mV) corresponds to the dissolution of this layer, as well as of silver itself, which is incomplete due to passivation of the electrode in the highly alkaline medium. The increase in silver concentration obviously leads to an increased cathodic reaction rate. The changes in the rate of the second anodic reaction are not proportional to the respective cathodic processes due to passivation. The current of the first anodic reaction increases with increase in silver concentration, which is possibly related to the increased alkalinity of

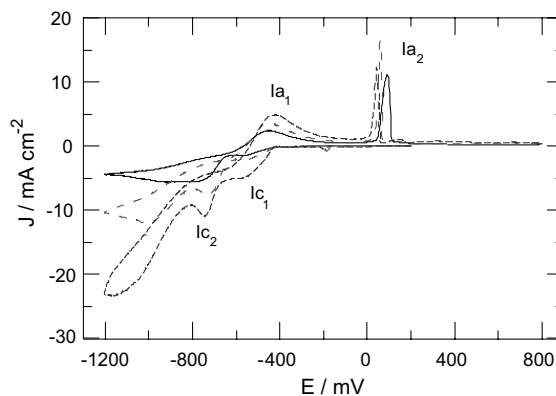


Fig. 1. Influence of  $C_{\text{Ag}}$  on the electrode processes in the absence of Bi in the electrolyte: (—) 8 g dm<sup>-3</sup>; (---) 16 g dm<sup>-3</sup>; (- - -) 32 g dm<sup>-3</sup>;  $\nu = 25$  mV s<sup>-1</sup>.

the electrolyte as compared to that in previous studies [7, 11]. The coatings obtained were light, dull, and homogeneous.

Upon investigation of bismuth deposition from the same electrolyte in the absence of silver, the occurrence of two cathodic reactions was established (Figure 2). The first is just noticeable and takes place at potentials of about -820 mV, while the second more clearly defined reaction takes place at a more negative potential of about -930 mV. Both potentials of bismuth deposition are more negative than those of silver deposition (see Figure 1).

Basically, the anodic process takes place at potentials of about -550 mV. The respective maximum is accompanied by a more or less clearly expressed smaller peak on the positive side, which also reflects oxidation of bismuth. In these oxidation processes, the electrode surface is passivated and a yellowish coating of bismuth oxides is observed.

In the presence of the two metals in the electrolyte, the respective processes of deposition and dissolution of the individual metals are recorded in the cyclic voltammetric curves shown in Figure 3. The processes of dissolution

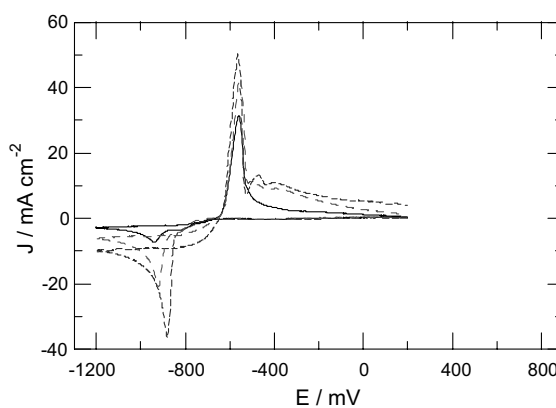


Fig. 2. Influence of  $C_{\text{Bi}}$  on the electrode processes in the absence of Ag in the electrolyte: (—) 6 g dm<sup>-3</sup>; (---) 12 g dm<sup>-3</sup>; (- - -) 18 g dm<sup>-3</sup>;  $\nu = 25$  mV s<sup>-1</sup>.

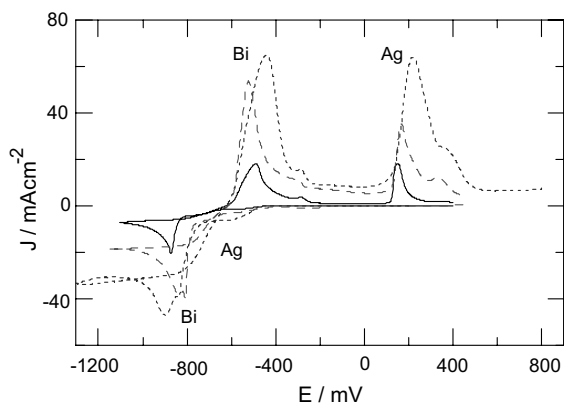


Fig. 3. Influence of  $C_{Bi}$  at different  $C_{Ag}$  in the electrolyte: (—)  $C_{Ag} = 8 \text{ g dm}^{-3}$ ,  $C_{Bi} = 6 \text{ g dm}^{-3}$ ; (---)  $C_{Ag} = 8 \text{ g dm}^{-3}$ ,  $C_{Bi} = 18 \text{ g dm}^{-3}$ ; (- · -)  $C_{Ag} = 32 \text{ g dm}^{-3}$ ,  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $\nu = 25 \text{ mV s}^{-1}$ .

of silver and bismuth are quite distinct. It should be noted that the dissolution of bismuth occurs in the same potential region where the formation of insoluble film of cyanide compounds on the silver surface is observed. Upon silver dissolution, additional maxima are observed at more positive potentials. These may correspond to dissolution of small amounts of the alloy phase if its dissolution potential is more positive than that of silver, or the silver remaining on the electrode surface after bismuth dissolution may probably possess a higher surface area rendering its passivation more difficult. Bismuth itself should dissolve more completely in the presence of silver, as is the case in the presence of copper [12]. The increase in bismuth concentration in the electrolyte at a constant silver concentration results in some depolarisation of the bismuth deposition and an increase in the cathodic current. Greater amounts of bismuth are dissolved in the anodic period and the increased anodic current for silver may be related to its higher surface area after dissolution of greater amounts of bismuth from the coating.

At higher silver concentrations in the electrolyte, a further increase in both the cathodic and the anodic currents is observed.

Figure 4 shows the effect of the complex forming agent for silver (KSCN in this case) on the electrode processes. The increase in KSCN concentration leads to a slight polarization and inhibition of the cathodic reactions since the silver ions are involved in the extremely stable cyanide complex and the possible additional increase in the number of ligands due to  $\text{SCN}^-$  should not be of great significance for the cathode polarization. Furthermore, bismuth is also bound in stable hydroxy-tartrate complexes and the thiocyanate ions should not affect their stability.

In the anodic processes, the effect of the thiocyanate ions on bismuth dissolution is ambiguous. A separate peak is formed on the positive side of the basic maximum, i.e., the more the thiocyanate ions in the electrolyte, the faster the dissolution of the portion of the coating corresponding to this peak.

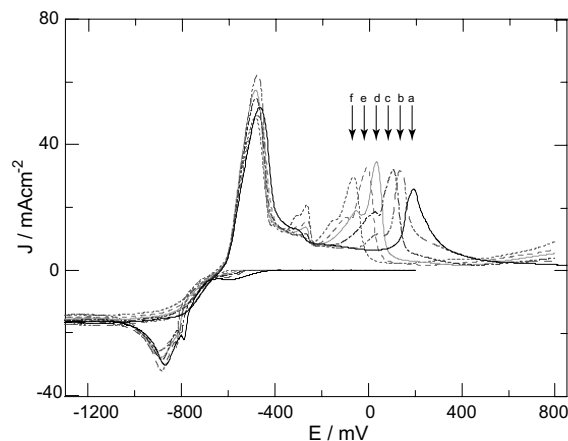


Fig. 4. Influence of  $C_{KSCN}$  in the electrolyte:  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $\nu = 25 \text{ mV s}^{-1}$ . (a)  $0 \text{ g dm}^{-3}$ ; (b)  $20 \text{ g dm}^{-3}$ ; (c)  $40 \text{ g dm}^{-3}$ ; (d)  $60 \text{ g dm}^{-3}$ ; (e)  $80 \text{ g dm}^{-3}$ ; (f)  $120 \text{ g dm}^{-3}$ .

In the absence of thiocyanate ions the electrode is passivated and darkens due to oxide formation. The addition of  $\text{SCN}^-$  leads to depassivation of the electrode and to a considerable depolarisation of the silver dissolution reaction – from  $+195 \text{ mV}$  at  $0 \text{ g dm}^{-3}$  to  $-65 \text{ mV}$  at  $120 \text{ g dm}^{-3}$  KSCN. A new peak appears on the negative side of the curve maximum, suggesting that not only silver, but also the possible alloy phase, dissolve more readily in the presence of thiocyanate ions. The ratio of the rates of these two reactions depends on the concentration of thiocyanate ions in the electrolyte.

The effect of the considerably stronger complex forming agent for silver, i.e., cyanide ions, is much more pronounced (Figure 5). In addition to the increase in cathode polarization with increase in cyanide ion concentration and the disappearance of the maxima for silver, which completely overlap those of bismuth, a substantial depolarization of the silver dissolution reaction is observed. The shift of the respective anodic maximum in the negative direction is of the order of  $1 \text{ V}$  at  $120 \text{ g dm}^{-3}$  KCN, thus rendering this anodic reaction more negative than that of bismuth dissolution. Under

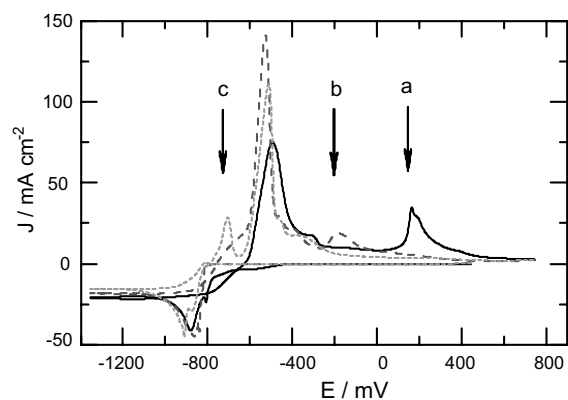


Fig. 5. Influence of the  $C_{KCN}$  in the electrolyte:  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $\nu = 25 \text{ mV s}^{-1}$ . (a) (—)  $0 \text{ g dm}^{-3}$ ; (b) (---)  $40 \text{ g dm}^{-3}$ ; (c) (···)  $120 \text{ g dm}^{-3}$ .

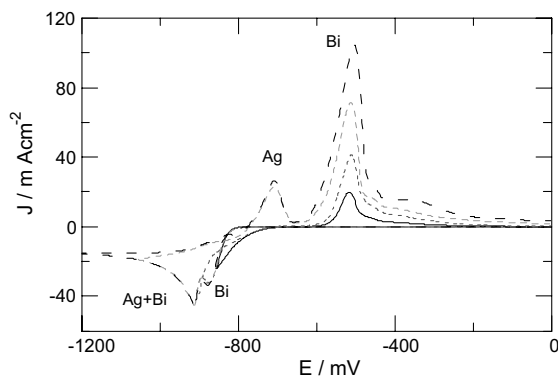


Fig. 6. Influence of the vertex potential:  $C_{\text{Ag}} = 8 \text{ g dm}^{-3}$ ;  $C_{\text{Bi}} = 18 \text{ g dm}^{-3}$ ;  $C_{\text{KCN}} = 120 \text{ g dm}^{-3}$ ;  $v = 25 \text{ mV s}^{-1}$ . (—)  $-850 \text{ mV}$ , (---)  $-900 \text{ mV}$ , (- - -)  $-1050 \text{ mV}$ , (- - -)  $-1200 \text{ mV}$ .

these conditions, bismuth becomes the more readily depositing element of the coating while silver becomes the more readily dissolving one.

These peculiarities of the process are shown in Figure 6 as a function of the potential of scan reversal. The first maximum corresponds to the deposition of pure bismuth while at the second codeposition of silver also takes place. This is suggested by the more negative anodic maximum corresponding to silver dissolution, which appears only when scan direction is changed after the current maximum corresponding to the second cathodic reaction. This means that the deposition of coatings with very high bismuth content is possible at relatively low cathode potentials (or current densities).

Figures 7 and 8 show the changes in the parameters of the electrochemical process as a function of sweep rate at various concentrations of the two metals in the electrolyte. The potentials of the cathodic maxima depend slightly on the silver and bismuth concentrations and shift somewhat in the negative direction with the increase in  $v$ . The potentials of the anodic maxima, i.e., the dissolutions of the two metals of the coating do not depend on  $C_{\text{Ag}}$  and  $C_{\text{Bi}}$ . They shift slightly in the positive direction with increase in scan rate, i.e., the potential difference between the cathodic and the anodic processes increases. The processes of dissolution of the two components of the coating are quite distinct; they differ by more than  $0.5 \text{ V}$  (Figure 7).

The cathodic currents depend on the concentrations of the two metals in the electrolyte. An increase in the concentration of silver or bismuth leads to an increase in the current of the corresponding cathodic reaction (Figure 8). The current function  $J/\sqrt{v}$  for bismuth deposition decreases with the increase in sweep rate while this function changes insignificantly for silver deposition, particularly at low bismuth concentrations. This means that silver deposition under these conditions is almost entirely diffusion-controlled [13–16]. The dissolution of the two metals depends strongly on their concentrations in the electrolyte. It is clear that, using the electrolyte as described above, the processes of deposition and dissolution of the coating are complex

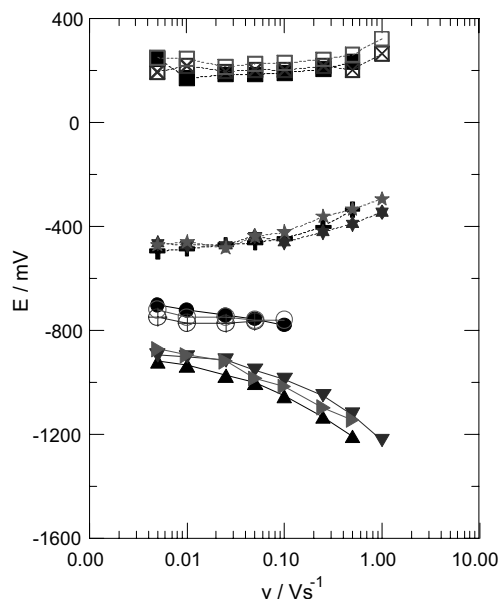


Fig. 7. Dependence of the potential of the electrode reaction on the sweep rate at constant  $C_{\text{Ag}}$ :  $C_{\text{Ag}} = 32 \text{ g dm}^{-3}$ ;  $C_{\text{Bi}} = 6, 12, \text{ and } 18 \text{ g dm}^{-3}$ .  $E_{c1}$ : (●)  $6 \text{ g dm}^{-3}$ ; (○)  $12 \text{ g dm}^{-3}$ ; (⊕)  $18 \text{ g dm}^{-3}$ .  $E_{c2}$ : (▲)  $6 \text{ g dm}^{-3}$ ; (▶)  $12 \text{ g dm}^{-3}$ ; (▼)  $18 \text{ g dm}^{-3}$ .  $E_{a1}$ : (⊕)  $6 \text{ g dm}^{-3}$ ; (★)  $12 \text{ g dm}^{-3}$ ; (☆)  $18 \text{ g dm}^{-3}$ .  $E_{a2}$ : (■)  $6 \text{ g dm}^{-3}$ ; (□)  $12 \text{ g dm}^{-3}$ ; (⊗)  $18 \text{ g dm}^{-3}$ .

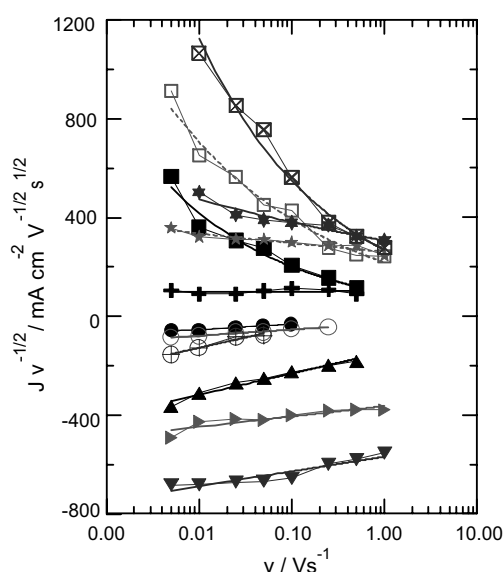


Fig. 8. Dependence of the current function  $I/\sqrt{v}$  on the sweep rate at constant  $C_{\text{Ag}}$ :  $C_{\text{Ag}} = 32 \text{ g dm}^{-3}$ ;  $C_{\text{Bi}} = 6, 12, \text{ and } 18 \text{ g dm}^{-3}$ .  $J_{c1}$ : (●)  $6 \text{ g dm}^{-3}$ ; (○)  $12 \text{ g dm}^{-3}$ ; (⊕)  $18 \text{ g dm}^{-3}$ .  $J_{c2}$ : (▲)  $6 \text{ g dm}^{-3}$ ; (▶)  $12 \text{ g dm}^{-3}$ ; (▼)  $18 \text{ g dm}^{-3}$ .  $J_{a1}$ : (⊕)  $6 \text{ g dm}^{-3}$ ; (★)  $12 \text{ g dm}^{-3}$ ; (☆)  $18 \text{ g dm}^{-3}$ .  $J_{a2}$ : (■)  $6 \text{ g dm}^{-3}$ ; (□)  $12 \text{ g dm}^{-3}$ ; (⊗)  $18 \text{ g dm}^{-3}$ .

and cannot be explained on the basis of the data obtained. In the present case, the possibility of depositing silver–bismuth coatings with broad ranges of metal contents is more interesting. Figure 9 shows the dependence of the silver content in the coatings on the current density. In the absence of KCN, the curves are situated between the curves of the two limiting cases – of

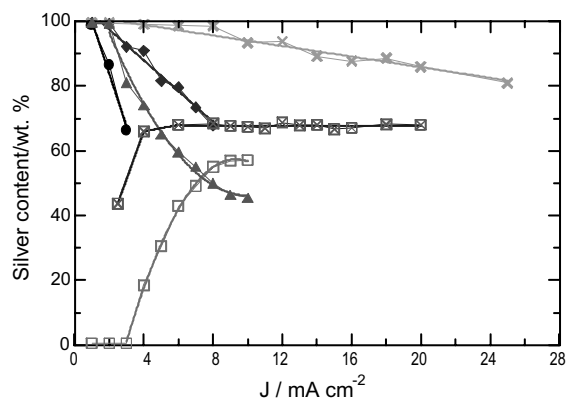


Fig. 9. Influence of the current density on the silver content in the alloy: (●)  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 6 \text{ g dm}^{-3}$ ; (▲)  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ; (×)  $C_{Ag} = 32 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ; (◆)  $C_{Ag} = 16 \text{ g dm}^{-3}$ ;  $C_{Bi} = 12 \text{ g dm}^{-3}$ ; (□)  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $C_{KCN} = 60 \text{ g dm}^{-3}$ ; (⊠)  $C_{Ag} = 32 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $C_{KCN} = 60 \text{ g dm}^{-3}$ .

the fastest (at the lowest electrolyte concentration) and of the slowest (at the highest concentration) increase in bismuth content in the coating. Under these conditions, in the absence of KCN, coatings with maximum bismuth content of about 50% are possible.

Taking into account the changes in the electrochemical processes in the presence of a free complex forming agent for the basic metal in the electrolyte (KCN in this case, see Figures 5 and 6) it is possible to obtain coatings containing mainly bismuth, this observation being in agreement with the reports of other authors [5]. Increase in cathodic current leads to an increase in silver content (Figure 9). Coatings with high bismuth content can be deposited from such an electrolyte, so that by varying the free cyanide concentration coatings containing from 0 to 100% bismuth are possible. When the concentrations of the two metals in the electrolyte are high, coatings of constant composition can be obtained within broad current density ranges, which may be of practical interest.

The surface of the coatings is grey, dull, and becomes dark grey to black at high bismuth contents. When the coating is deposited in the absence of KCN and has a high bismuth content, its surface is heterogeneous in colour and consists of dark and light regions, which may sometimes be ordered (Figure 10). In this case, self-organisation phenomena occur leading to spatio-temporal structures known from the studies of other silver alloys, such as silver–indium [17] and silver–antimony [18–20].

#### 4. Conclusions

In the electrolyte studied, the deposition potentials of silver and bismuth are close to each other, thus making the deposition of Ag–Bi coatings possible. The difference of about 0.5 V in the dissolution potentials of the components offers the possibility for the electrochemical

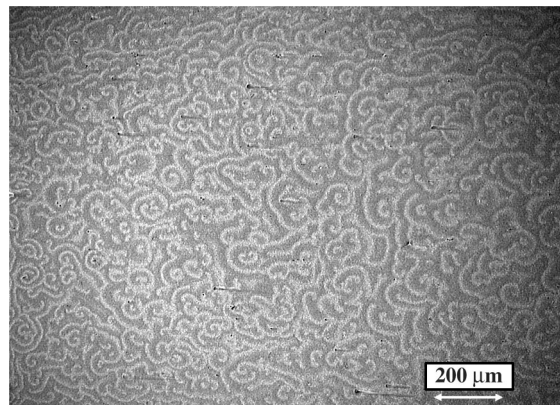


Fig. 10. Surface of a silver–bismuth alloy coating:  $C_{Ag} = 8 \text{ g dm}^{-3}$ ;  $C_{Bi} = 18 \text{ g dm}^{-3}$ ;  $J = 6 \text{ mA cm}^{-2}$ ; 47 wt.% Bi.

determination of their amounts in the electrodeposited layer.

By means of appropriate complex forming agents, the deposition potential of silver can be shifted in the negative direction, so that bismuth deposition becomes predominant. By changing the electrolyte composition and the conditions of electrolysis, coatings of any desired composition can be obtained.

By the proper choice of the concentrations of the electrolyte components, the deposition of coatings with constant composition is possible over a broad range of current densities.

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