

## Effect of the electrolyte composition on In and Ag–In alloy electrodeposition from cyanide electrolytes

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### Abstract

A procedure for preparation of clear and stable indium cyanide electrolytes, containing indium salt, D(+)-Glucose and KCN is proposed. NMR investigations revealed that the formation of a complicated indium complex in which the products of the disintegration of D(+)-Glucose in the KCN-solution are closely situated to the indium ion ensures the clearness of the electrolyte. The effect of nitrate, chloride and sulphate ions on the electrochemical processes of indium and silver–indium alloy electrodeposition is studied by cyclic voltammetry. During alloy electrodeposition under galvanostatic conditions unique spatio-temporal structures are observed on the cathodic surface.

### 1. Introduction

The best electrolytes for electrodeposition of silver, indium and silver–indium alloy are still the cyanide electrolytes. The first empirically formulated cyanide electrolyte for the electrodeposition of indium and silver–indium alloys was proposed by Gray [1]. The difficulties in the preparation of this type of alkaline (cyanide and/or hydroxide containing) electrolyte are connected with the precipitation of indium hydroxide [1, 2]. The main components of the electrolyte, except indium salts, are KCN and dextrose (D(+)-Glucose). D(+)-Glucose is an important factor in the prevention of indium precipitation in alkaline cyanide and hydroxide solutions [1], but there are no literature data on the formation of indium complexes with D(+)-Glucose or its disintegration products in alkaline solutions, as well as on the existence of indium–cyanide complexes.

A procedure for a simple preparation of clear and stable strong alkaline cyanide–hydroxide indium electrolytes with high cathodic current yield was proposed in previous work [3], but the concentration ranges of the components necessary for obtaining clear and stable cyanide electrolytes in the absence of KOH were not determined. The influence of various anions on the cathodic reduction, as well as on the anodic ionisation, of indium has been studied on both an amalgam and a solid indium electrode in different acid electrolytes (sulphate, chloride, etc.) [4–6]. However, the possible effect of the type of indium salts (nitrate, sulphate and

chloride) on the properties of the alkaline indium electrolytes was also not investigated.

Stable cyanide electrolytes with high cathodic current efficiency are of practical interest for the electrodeposition of indium and silver–indium alloys. The electrodeposition of the silver–indium alloy from cyanide electrolytes is also of great scientific interest due to the observed self-organization phenomena and formation of periodic spatio-temporal structures on the cathode during electrodeposition [2, 7].

The elemental composition, the structure and the phase composition of the electrodeposited silver–indium alloy coatings from the investigated electrolytes are discussed in a previous paper [7].

The aim of the present investigation is to identify the conditions for obtaining clear and stable cyanide electrolytes in the absence of KOH and to study the effect of different anions on the electrodeposition of *In* and *Ag–In* alloys.

### 2. Methods and materials

Experiments for establishing the procedure for obtaining clear electrolytes were carried out in a volume of 25 cm<sup>3</sup> using indium chloride salt. The steady state cathodic potential of the indium cathode (area 1 cm<sup>2</sup>) was measured against a Ag/AgCl reference electrode and a platinum sheet (4 cm<sup>2</sup>) was used as a counter electrode.

Nuclear magnetic resonance investigations, *NMR*, were carried out in solutions of the electrolyte components in deuterium oxide with concentrations shown in Table 1, using a spectrometer Bruker DRX-250 (250 MHz).

The cyclic voltammetric experiments were performed in a 100 cm<sup>3</sup> tri-electrode glass cell at room temperature with a sweep rate of 0.025 V s<sup>-1</sup>. The electrolyte compositions are shown in Table 2. A platinum sheet (1 × 0.5 × 0.03 cm) was used as a cathode. Two platinum anodes of area 4 cm<sup>2</sup> each were placed symmetrically on both sides of the cathode. A Ag/AgCl reference electrode with  $E_{\text{Ag}/\text{AgCl}} = 0.197$  V vs. NHE was used. The electrode was placed in a separate cell filled with 3 M KCl solution. It was connected to the electrolyte cell by a Haber-Luggin capillary through an electrolyte bridge containing 3 M KCl solution. The experiments were carried out by means of a computerized potentiostat/galvanostat PAR 263 A (Software SoftCorr II). Prior to each experiment, the surface of the electrode was anodised in a 20% solution of HCl using a glassy carbon counter electrode.

The electrolyte composition for the galvanostatic electrodeposition of the silver–indium alloy using nitrate or chloride salt of indium is presented in Table 3. The coatings were deposited onto copper substrates with an area of 2 × 1 cm. Prior to deposition, the copper substrates were electrochemically degreased and pickled according to a standard procedure. In order to prevent contact deposition of silver the cathode was dipped into the electrolyte under current.

Chemical substances of *pro analysi* purity and distilled water were used.

### 3. Results and discussion

#### 3.1. Preparation of clear and stable indium electrolytes

The procedure for preparation of clear and stable indium cyanide electrolytes containing KOH is described in a previous paper [3], where high concentrations of KCN and KOH were kept constant. The experiments in this study were carried out in the absence of KOH in the electrolyte, but at different molar ratios of KCN to In. They show that clear indium cyanide electrolytes could be obtained in the absence of KOH when:

- The necessary amount of D(+)-Glucose according to Gray [1] (0.5 g D(+)-Glucose for each gram indium) is added to the water solution of the indium salt and short electrolysis (CVA measurement) is carried out.

Table 1. Compounds investigated by NMR

Component	Concentration/mol dm <sup>-3</sup>
In as InCl <sub>3</sub> /Alfa Aesar/	0.2
D(+)-Glucose /Merck/	0.1
KCN /Merck/	1

Table 2. Electrolyte composition for galvanostatic deposition of indium

Component	Concentration/mol dm <sup>-3</sup>		
	A	B	C
In as In(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O/Aldrich/	0.2	0	0
In as In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · xH <sub>2</sub> O /Merck/	0	51.78 g dm <sup>-3</sup>	0
In as InCl <sub>3</sub> /Alfa Aesar/	0	0	0.2
D(+)-Glucose/Merck/	(0) 0.1	(0) 0.1	(0) 0.1
KCN/Merck/	(0) 1	(0) 1	(0) 1

Table 3. Electrolyte composition for Ag–In alloy electrodeposition

Components	Concentration/mol dm <sup>-3</sup>
In(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O/Aldrich/	0.1–0.2
InCl <sub>3</sub> /Alfa Aesar/	0.1–0.2
KAg(CN) <sub>2</sub> /Degussa/	0.04–0.08
KCN/Merck/	0.5–1.0
D(+)-Glucose/Merck/	0.1

The next step is the addition of KCN to the electrolyte. In absence of D(+)-Glucose, the addition of KCN to the solution leads to a precipitation within the next 1 h.

- The minimum molar cyanide to indium ratio in the electrolyte is at least 5:1 and all the KCN is added to the electrolyte at once, as a dry substance and under stirring. If this molar ratio is smaller or the necessary quantity of KCN is added in portions, the formed solutions are opaque and opalescent. The addition of KCN to the clear electrolyte in any molar ratio to indium does not influence its clearness. Conversely, the addition of any further amount of KCN to an opaque cyanide solution does not produce clearness. According to Mohler [8], it is most likely that the soluble compounds in the cyanide-hydroxide electrolyte (containing KCN and KOH) are KIn(CN)<sub>4</sub> and KIn(OH)<sub>4</sub> and the insoluble ones are In(CN)<sub>3</sub> and In(OH)<sub>3</sub>. This suggestion is simplistic because the influence of D(+)-Glucose on the complex formation in the electrolyte was not considered.

According to Goggin et al. [9] indium tri-cyanide is very soluble in water but the solution loses HCN and the indium slowly precipitates as hydroxide.

Normally, the clearness of an electrolyte is connected with the formation of metal complexes. One of the methods for establishing the presence of complex compounds in the electrolyte is the determination of the electrode potential, depending on the concentration of the supposed complex-forming agent. Our investigation with this method did not yield any positive results, because the measured potential of the indium electrode in the investigated cyanide electrolytes was not stable with time.

The composition and the structure of the complex compounds could be determined with nuclear magnetic resonance. The presence of an organic compound (in this case D(+)-Glucose in high concentration) allows

the registration of its spectrum changes when adding other components. Figure 1a shows the D(+)-Glucose spectrum in D<sub>2</sub>O, which reveals its nature as a low molecular mono-saccharide compound. In KCN solution (Figure 1b), the D(+)-Glucose spectrum is changed and shows the presence of compounds with lower molecular weight (products of disintegration). In the solution containing D(+)-Glucose, KCN, and indium salts (Figure 1c) (molar cyanide to indium ratio of 5:1 in order to ensure a clear solution), a broadening of the spectrum was observed due to the formation of a complex, in which disintegration products of D(+)-Glucose are located closest to the indium ions. We consider that in the cyanide solution a complicated indium complex with disintegration products of D(+)-Glucose and cyanide ions is formed, which ensures clearness of the electrolyte.

### 3.2. Effect of different anions on the electrode processes in the indium electrolytes

Three different indium salts (In(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · xH<sub>2</sub>O and InCl<sub>3</sub>) were used in order to establish the effect of different anions on the electrodeposition of indium. The concentrations are given in Table 2. Regardless of the salt type used, the prepared solutions were clear and colourless.

The deposition of indium from the solution of In(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O starts at potentials more negative than -750 mV (Figure 2, curve 1). During potential back scanning in the positive direction, a hysteresis is observed in the cathodic branch of the curve due to the increased roughness of the cathode and small

oscillations were registered. The anodic dissolution is indicated by the anodic maximum at about 1000 mV.

The cathodic reaction in the solution of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · H<sub>2</sub>O is slower (Figure 2, curve 2) and anodic dissolution is registered as an unsymmetrical peak at 280 mV.

The cathodic reaction is faster in the water solution of InCl<sub>3</sub> (Figure 2, curve 3), and a well-defined cathodic peak is observed at -1050 mV. The hysteresis in the curve may be due to the roughness of the indium coating. A very large anodic maximum is registered at a potential of about 410 mV. The observed oscillations in the cathodic branch of the curve are more intensive than these in the nitrate electrolyte (see curve 1).

According to Losev and Molodov [10], in the absence of other complex formation indium exists in the solution in the form of an aqua-complex In(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, which is characterized by a very low rate of water molecule dissociation from its hydration shell. The kinetics of the processes of discharge and ionisation of indium depends on the pH of the solution, as well as on the type of anions in the electrolyte and is connected with their catalytic action [10]. The catalytic effect of the anions could possibly be related to the labialisation of the solvation shell around the indium ion, thereby facilitating its desolvation and is due to their ability to act as electron bridges between the indium ions and the electrode [11].

The catalytic effect of the anions on the kinetics of indium reduction increases in the order F<sup>-</sup> < ClO<sub>4</sub><sup>-</sup> < SO<sub>4</sub><sup>2-</sup> < Cl<sup>-</sup> on the mercury surface [6] and in the order -J<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> < NO<sub>3</sub><sup>-</sup> < SO<sub>2</sub>NH<sub>2</sub><sup>-</sup> < ClO<sub>4</sub><sup>-</sup> < SO<sub>4</sub><sup>2-</sup> on the solid indium electrode [6]. According to Munoz et al.

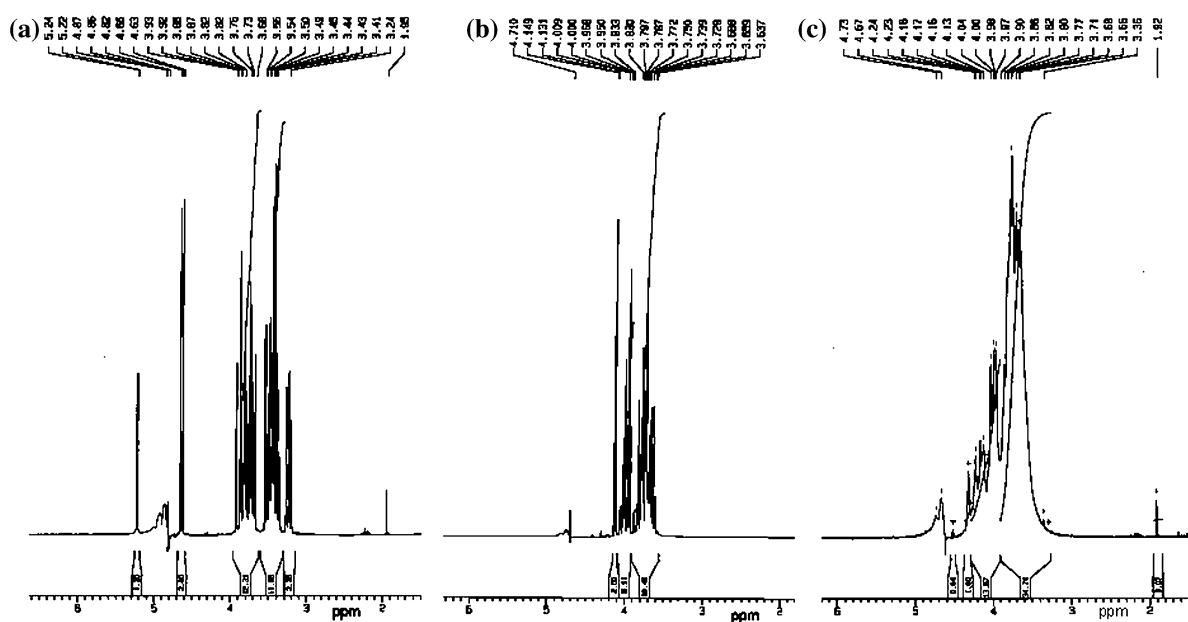


Fig. 1. (a) NMR spectrum of D(+)-Glucose in solution of D<sub>2</sub>O; C<sub>D(+)-Glucose</sub> = 0.1 mol dm<sup>-3</sup>. (b) NMR spectrum of D(+)-Glucose + KCN in solution of D<sub>2</sub>O; C<sub>D(+)-Glucose</sub> = 0.1 mol dm<sup>-3</sup>; C<sub>KCN</sub> = 1 mol dm<sup>-3</sup>. (c) NMR spectrum of D(+)-Glucose + KCN + InCl<sub>3</sub> in solution of D<sub>2</sub>O; C<sub>D(+)-Glucose</sub> = 0.1 mol dm<sup>-3</sup>; C<sub>KCN</sub> = 1 mol dm<sup>-3</sup>; C<sub>InCl<sub>3</sub></sub> = 0.2 mol dm<sup>-3</sup>.

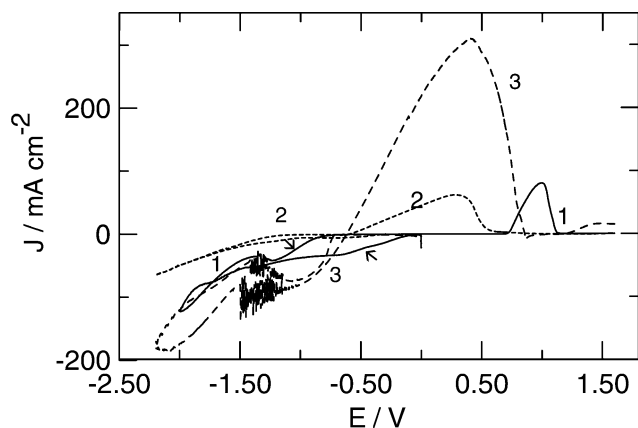


Fig. 2. CVA curves of indium electrolytes, prepared with different indium salts:  $\nu = 25 \text{ mV s}^{-1}$ ;  $C_{\text{In}} = 0.2 \text{ mol dm}^{-3}$ , curve 1,  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , pH = 2.02, curve 2,  $\text{In}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ , pH = 1.98, curve 3,  $\text{InCl}_3$ , pH = 3.14.

[12], the presence of  $\text{Cl}^-$  leads to the destabilization of the passive oxide layer on the indium electrode, forming soluble species  $\text{In}(\text{OH})_n\text{Cl}_m$  and leading to a higher anodic current. Our experiments also show significant acceleration of the electrode reaction on Pt electrode in the presence of  $\text{Cl}^-$  ions.

The addition of D(+)-Glucose to the indium salt solutions does not appreciably change the shape of the cyclic voltammetric curves, as well as the pH-value of the solutions. The aqueous solution of the D(+)-Glucose is not an electrolyte.

Figure 3 shows cyclic voltammetric curves of the different solutions after adding D(+)-Glucose and KCN. The whole amount of KCN was added at once, under stirring, in the molar ratio of cyanide to indium as 5:1.

The addition of KCN to the solution of  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and D(+)-Glucose (Figure 3, curve 1), leads to an increase in the pH-value to 8.7 and to polarisation of the cathodic process compared with those in the initial solution (Figure 2, curve 1). One

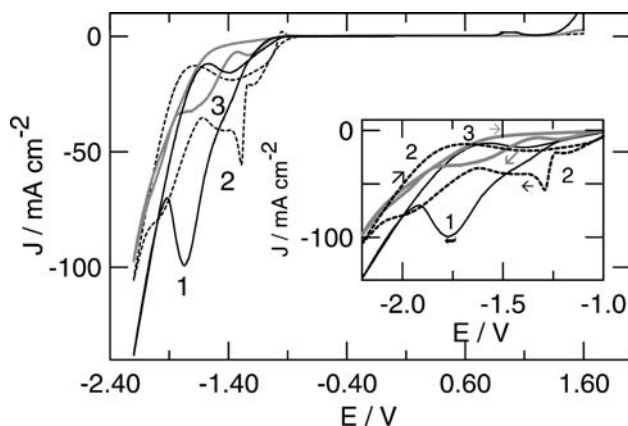


Fig. 3. CVA curves of cyanide indium electrolytes, prepared with different indium salts:  $\nu = 25 \text{ mV s}^{-1}$ ;  $C_{\text{In}} = 0.2 \text{ mol dm}^{-3}$ ;  $C_{\text{D}(+)\text{-Glucose}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{KCN}} = 1 \text{ mol dm}^{-3}$ , curve 1,  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; curve 2,  $\text{In}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ; curve 3,  $\text{InCl}_3$  inset: same CVA curves in the range  $E = -2.2$  to  $-1.00 \text{ V}$ .

large cathodic maximum is observed at a potential of about  $-1750 \text{ mV}$ . In the anodic region there is a small anodic maximum at  $+1000 \text{ mV}$ . The solution was coloured dark yellow. During the electrolysis (CVA measurement) a brown gas was evolved from the anode.

By addition of KCN to the solution of indium sulphate and D(+)-Glucose (Figure 3, curve 2) at least three cathodic peaks – at about  $-1200 \text{ mV}$ ,  $-1500 \text{ mV}$  and  $-1970 \text{ mV}$  and one sharp cathodic peak at  $-1300 \text{ mV}$  are registered. The pH-value of the solution was 8.7. A small anodic peak is registered at a potential of about  $-950 \text{ mV}$ . No other anodic reactions were observed within the investigated potential range. The solution was yellowish and after addition of KCN a white precipitate appeared.

Investigation of the dried precipitate with IR-spectroscopy shows peaks (Figure 4) characteristic for  $\text{K}_2\text{SO}_4$  [13].

After adding KCN to the indium chloride solution containing D(+)-Glucose (Figure 3, curve 3) two cathodic maxima are registered at potentials  $-1250 \text{ mV}$  and  $-1780 \text{ mV}$  and the pH-value becomes 10.14.

The most probable reason for the differences in the cyclic voltammetric curves of the different electrolytes is the effect of the different anions on the strength of the indium complexes with the D(+)-Glucose disintegration products and the cyanide ions.

The preparation of the cyanide electrolyte with  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{In}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  and  $\text{InCl}_3$  is easy. The precipitate formed when using indium sulphate makes this electrolyte unusable.

### 3.3. Electrodeposition of Ag–In alloys

The experiments show that indium nitrate and chloride salts are suitable for the preparation of electrolytes for electrodeposition of indium. By addition of  $\text{KAg}(\text{CN})_2$  to them, an electrolyte for deposition of Ag–In alloys can be obtained. The silver salt addition to the indium electrolyte does not affect its clearness.

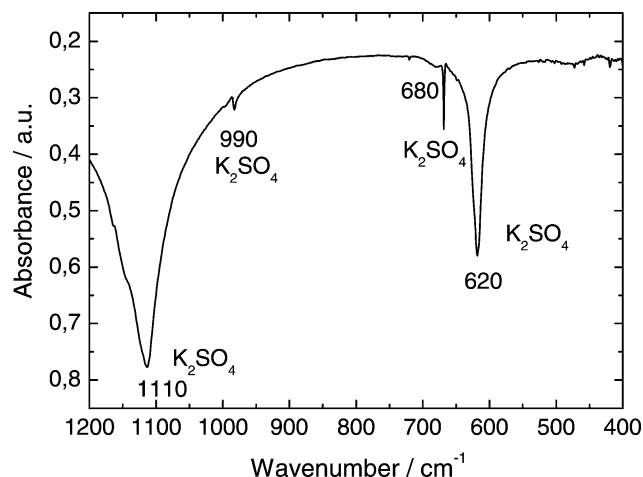


Fig. 4. IR – spectrum of the precipitate, from the cyanide indium electrolyte containing indium sulphate.

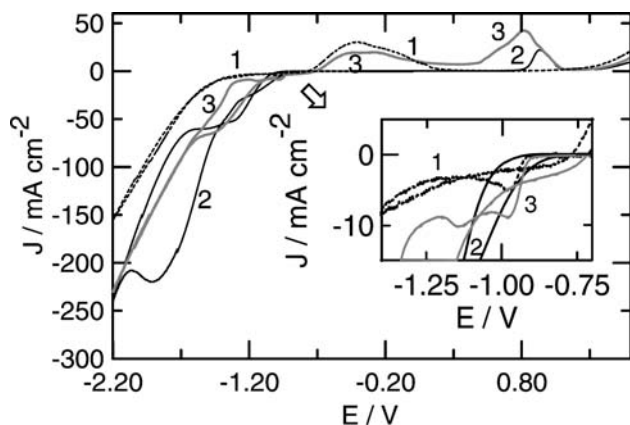


Fig. 5. CVA curves in the cyanide–nitrate electrolytes, in the presence of Ag and In separately and together:  $\nu = 25 \text{ mV s}^{-1}$ ;  $C_{\text{D}(+)\text{-Glucose}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{KCN}} = 0.75 \text{ mol dm}^{-3}$ ; curve 1,  $C = 0.08 \text{ mol dm}^{-3}$ ; curve 2,  $C = 0.15 \text{ mol dm}^{-3}$  as  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; curve 3,  $C_{\text{In}} = 0.15 \text{ mol dm}^{-3}$  as  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ;  $C_{\text{Ag}} = 0.08 \text{ mol dm}^{-3}$ ; inset: same CVA curves in the range  $E = -1.4$  to  $-0.7 \text{ V}$ .

In the absence of In in the cyanide electrolyte a maximum in the cathodic region of the cyclic voltammetric curve at a potential of about  $-970 \text{ mV}$  (Figure 5, curve 1) is observed. The coating deposited during the cathodic period dissolves during the anodic period and a broad anodic maximum at  $-400 \text{ mV}$  is observed.

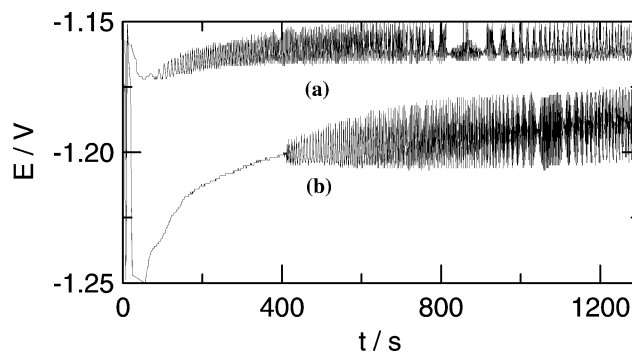


Fig. 6. Potential oscillations under galvanostatic conditions during Ag–In alloy electrodeposition;  $J = 0.5 \text{ A dm}^{-2}$ ;  $C_{\text{In}} = 0.15 \text{ mol dm}^{-3}$  as  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ;  $C_{\text{Ag}} = 0.08 \text{ mol dm}^{-3}$ ;  $C_{\text{D}(+)\text{-Glucose}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{KCN}} = 0.75 \text{ mol dm}^{-3}$ ; (a) first sample; (b) second sample.

In the absence of Ag in the cyanide solution of indium nitrate the indium deposition is observed at a potential of  $-1970 \text{ mV}$  (Figure 5, curve 2) and the potential of the corresponding anodic maximum is about  $950 \text{ mV}$ .

The first cathodic maximum in the alloy electrolyte (Figure 5, curve 3) corresponds to the electrodeposition of pure silver. The second cathodic maximum at  $-1170 \text{ mV}$  corresponds to the electrodeposition of Ag–In alloy. The two anodic maxima observed represent

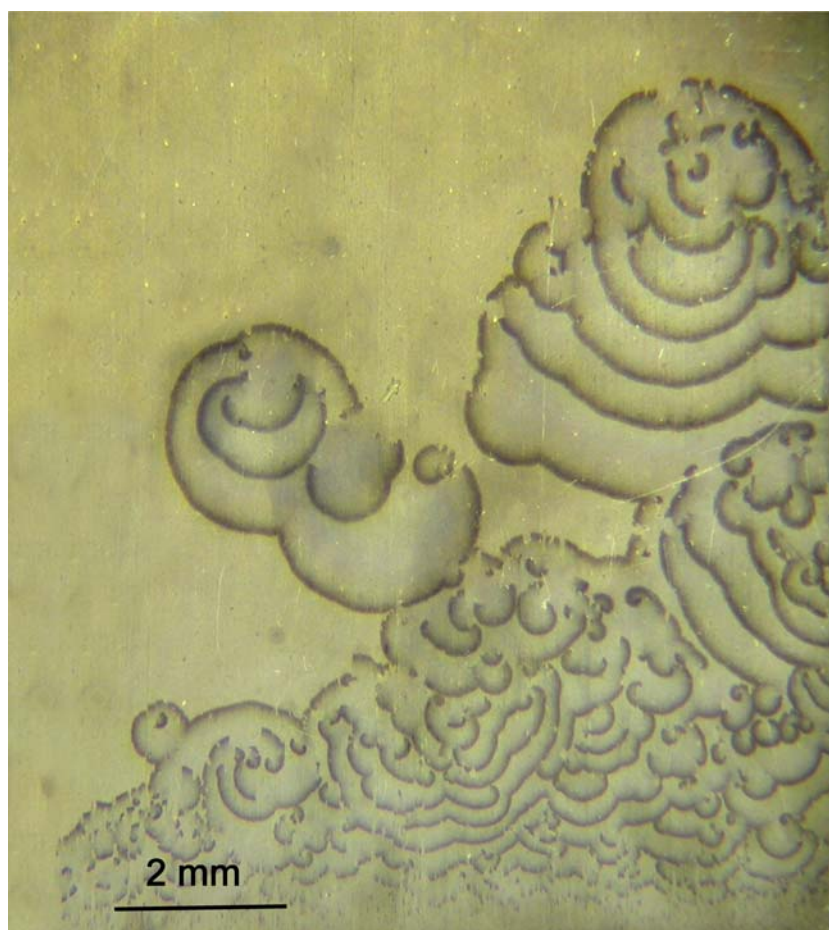


Fig. 7. Optical microscopic image on Ag–In coating electrodeposited from an exhausted electrolyte:  $C_{\text{D}(+)\text{-Glucose}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{KCN}} = 0.75 \text{ mol dm}^{-3}$ ;  $C_{\text{In}} = 0.15 \text{ mol dm}^{-3}$  ( $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ );  $C_{\text{Ag}} = 0.04 \text{ mol dm}^{-3}$ ;  $J = 0.4 \text{ A dm}^{-2}$ ;  $t = 2343 \text{ s}$ ; width of the image  $-1 \text{ cm}$ .



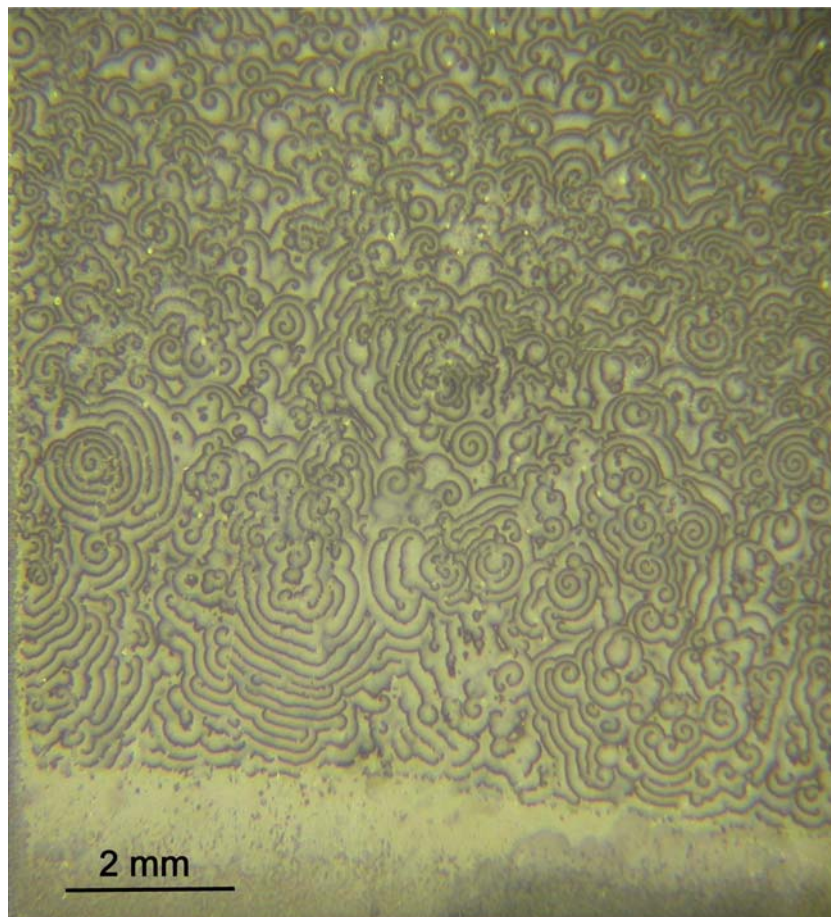


Fig. 8. Optical microscopic image on Ag–In coating electrodeposited from an exhausted electrolyte:  $C_{D(+)-Glucose} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{KCN} = 0.75 \text{ mol dm}^{-3}$ ;  $C_{In} = 0.15 \text{ mol dm}^{-3}$  ( $InCl_3$ );  $C_{Ag} = 0.04 \text{ mol dm}^{-3}$ ;  $J = 0.4 \text{ A dm}^{-2}$ ;  $t = 2343 \text{ s}$ ; width of the image – 1 cm.

the dissolution of the alloy phases formed in the cathodic period. The first large anodic maximum is observed at potentials between  $-500$  and  $-200$  mV and the second one is observed at about  $900$  mV. The indium rich alloy phase dissolves at more positive potentials (about  $900$ – $1000$  mV).

Electrochemical instabilities leading to oscillations of the cathodic potential can be observed during galvanostatic deposition of Ag–In alloys (Figure 6). Such instabilities are a characteristic phenomenon in some electrochemical systems and they need special attention. In some cases during electrodeposition of alloys the oscillating phenomena could lead to formation of spatio-temporal structures, like the structures in the Ag–Sb [14–17] and Ag–Bi [18, 19] systems.

Spatio-temporal structures can be also obtained during Ag–In alloy electrodeposition [2, 7]. Some optical microscopic images of the Ag–In alloy obtained under galvanostatic conditions from cyanide electrolytes are shown in Figures 7 and 8. The samples were deposited after an exhaustion of the electrolyte, corresponding to  $1.5 \text{ Ah dm}^{-3}$ . The difference between the samples is only in the type of the indium salts used. In both electrolytes periodical spatio-temporal structures appear and can be observed. The structures formed in the electrolyte on indium nitrate basis are larger and sparse (Figure 7) compared with those obtained under similar conditions

in an electrolyte prepared with indium chloride (Figure 8). Waves, target patterns and spiral structures can be observed on the cathode surface in both cases. The system allows *in situ* investigation of the self-organization process under electrochemically exactly controlled conditions, as well as the investigation of the phase composition, structure and properties of the deposited coatings.

The thickness of the coatings when using indium chloride is twice higher than that in the case of indium nitrate at equal electrolysis conditions, which means that the current efficiency of the electrolyte on the basis of indium chloride is much better.

#### 4. Conclusions

1. Clear and stable cyanide electrolytes in the absence of KOH can be obtained at molar cyanide to indium ratio of at least 5:1.
2. The electrolysis of the indium salt solution after addition of D(+)-Glucose helps to prevent the precipitation of insoluble indium compounds.
3. The clearness of the electrolyte is due to the formation of a complex in the cyanide solution, where the D(+)-Glucose disintegration products are the closest ligands to the indium ion.
4. Precipitation of  $K_2SO_4$  occurs when using sulphate salt in the alkaline medium. Clear and stable cy-

nide electrolytes can be prepared with indium nitrate and indium chloride salts.

5. Electrochemical instabilities are observed, leading to spatio-temporal structures on the cathode during electrodeposition of *Ag–In* alloy under galvanostatic conditions. The structures are larger when using indium nitrate and have a smaller period and more complicated forms in the chloride ions containing electrolyte.

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### References

1. D. Gray, *Trans. Electrochem. Soc.* **65** (1934) 377.
2. E. Raub and A. Schall, *Z. Metallkunde* **30** (1938) 149.
3. Ts. Dobrovolska, I. Krastev and A. Zielonka, *Galvanotechnik* **94**(5) (2004) 1134.
4. B. Lovrecek and V. Markovac, *J. Electrochem. Soc.* **109** (1962) 727.
5. R. Piercy and N.A. Hampson, *J. Appl. Electrochem.* **5** (1975) 1.
6. M.A. Loshkarev and A.A. Kazarov, *Elektrokhimiya* **1**(3) (1967) 39 (in Russian).
7. Ts. Dobrovolska, L. Veleva, I. Krastev and A. Zielonka, *J. Electrochem. Soc.* **152**(3) (2005) C137–C142.
8. J.B. Mohler, *Metal Finishing* **43**(2) (1945) 60–77.
9. P.L. Goggin, I.J. McColm and R. Shore, *J. Chem. Soc. A* **10** (1966) 1314.
10. V.V. Losev and A.I. Molodov, in Bard J. Allen (ed.) 'Encyclop. Electrochem. Elements', (Marcel Dekker, Inc. New York and Basel), 1973, chapter VI-I, 1–32.
11. R. de Levie, *J. Electrochem. Soc.* **8** (1971) 185.
12. A.G. Munoz and J.B. Bessone, *Electrochim. Acta* **43** (1998) 2033.
13. K. Nakamoto, *Infrakrasnie spektri neorganicheskikh i koordinatsionnih soedinenij*, Mir, Moskva, 1966, 153 (in Russian).
14. I. Krastev and M. Nikolova, *J. Appl. Electrochem.* **16** (1986) 875.
15. I. Krastev, M. Nikolova and I. Nakada, *Electrochim. Acta* **34** (1989) 1211.
16. I. Krastev and M.T.M. Koper, *Physica A* **213** (1995) 199.
17. I. Krastev, M.E. Baumgärtner and Ch.J. Raub, *Metalloberfläche* **46**(3) (1992) 115.
18. I. Krastev, T. Valkova and A. Zielonka, *J Appl Electrochem* **33** (2003) 1199.
19. I. Krastev, T. Valkova and A. Zielonka, *J. Appl. Electrochem.* **34** (2004) 79.