

Anomalous electrodeposition of gold-indium alloys

B.-K. Choi¹, F. Sauer¹, G. Beck^{1,2}, R. Stauber³, Ts. Dobrovolska^{4*}

¹Fraunhofer Applied Research Center for Resource Efficiency, Alzenau, Germany

²Aschaffenburg University of Applied Sciences, Aschaffenburg, Germany

³Fraunhofer Project Group Materials Recycling and Resource Strategies, Alzenau, Germany

⁴Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received July 24, 2017; Accepted September 12, 2017

The process of anomalous deposition of gold–indium alloys from different electrolytes on the basis of ammonium sulphate (with addition of oxalic, malonic and lactic acid, and glycine) was investigated. The oscillations, observed at some current densities from the first three mentioned electrolytes were investigated in galvanostatic regime. By linear sweep voltammetry technique, besides the methods of cyclic voltammetry and conventional X-ray analysis the phase composition of the deposited alloys from glycine electrolytes were determined.

Keywords: glycine electrolytes, gold-indium alloys, oscillations, spatio-temporal structures

INTRODUCTION

In our previous investigations, the electrodeposition of gold-indium alloys was studied from several electrolytes - cyanide, citrate, acetate and glycine and some brief literature review on the deposition and properties of the alloy were presented elsewhere [1]. The morphology and the phase composition of the coatings from the mentioned electrolytes were determined, with particular attention being paid to the cathodic processes during electrodeposition of the alloy coatings from glycine electrolyte. Instabilities and oscillations of the potential during electrodeposition from the above mentioned electrolytes, namely the presence of oscillations at almost the same current densities (respectively reaching a similar coating composition) were observed. This behaviour of different indium electrolytes and the modes for the passivation/re-passivation are well-known [2], but the information about deposition of indium alloys in the literature is scarce [3]. The present study aims to show the processes of deposition of gold-indium alloys in more details.

It was also recognized that the process of electrodeposition of gold-indium alloy from glycine electrolytes is a very promising one because of the possibility to obtain a variety of spatio-temporal structures on the surface of the electrode which would allow comparison with other known indium alloy systems with similar nature [4-6]. The content of indium in alloys deposited from glycine electrolytes even at low current densities is more than 40 wt. %. This leads to the suggestion that the electrodeposition of the alloy is of anomalous type,

where the more noble metal does not deposit preferentially [7]. The second aim of our study was to apply anodic linear sweep voltammetry technique [8], besides the methods of cyclic voltammetry and conventional X-ray analysis [8] in order to determine the phase composition of the deposited alloys from glycine electrolytes.

EXPERIMENTAL

The Au-In alloy coatings were deposited from the electrolytes with the compositions presented in table 1.

Table 1: Chemical compositions of the electrolytes

Compounds, gdm ⁻³	Electrolytes			
	A	B	C	D
Au as KAu(CN) ₂	1	1	1	1
In as InCl ₃	6	6	6	6
Ammonium sulphate	40	40	40	40
Oxalic acid	40			
Malonic acid		40		
Lactic acid			40	
Glycine				40
pH	3.2	3.3	3.4	3.0

All solutions were made with *p. a.* purity chemicals and distilled water.

* To whom all correspondence should be sent.
E-mail: tsvetina@ipc.ipc.bas.bg

The experiments were performed in a 100 cm³ tri-electrode glass cell at room temperature. The vertical working electrode (area 2 cm²) and the two counter electrodes were made from gold. An Ag|AgCl reference electrode ($E_{\text{Ag|AgCl}} = 0.197$ V vs. SHE) was used.

The experiments were carried out at room temperature by means of a computerized PAR 273 A potentiostat/galvanostat using the software Power Suite.

The Au, In and alloy coatings were dissolved in the tri-electrode cell for anodic linear sweep voltammetry (ALS) experiments with platinum counter electrode and the Ag|AgCl reference electrode in a solution containing 12 M LiCl. Before each experiment the gold electrode was cleaned by cyclic CV curves in the 0.1 N solution of sulfuric acid to remove traces of undissolved hydroxides and chlorides. The In or Au distribution on the surface of the coatings was examined by energy-dispersive analysis (EDAX).

Additionally, the galvanostatic deposition was performed onto brass substrates (2x1 cm) in order to investigate elemental composition of the obtained alloy coatings. The In percentage in the coatings depending on the electrolysis conditions was determined in experiments by X-ray fluorescence analysis (Fischerscope X-RAY XDAL).

The phase analysis was performed by means of a Bruker D8 Advance diffractometer at 2 θ -angles from 15 to 90° with Cu-K α irradiation and Sol X detector.

RESULTS AND DISCUSSIONS

Figure 1 (a-d) shows the chronopotentiometric curves obtained during electroplating of gold-indium alloys from electrolytes A, B, C and D (see Table 1). To the basic electrolyte containing ammonium sulphate four different organic ligands were added using oxalic, malonic and lactic acids and glycine. Thus, the galvanostatic curves obtained in the first three (A, B, C) investigated solutions show features associated with the occurrence of oscillations at the current density of 0.6 A dm⁻². In the glycine electrolyte single oscillations but at all investigated current densities were observed.

Oscillations with amplitude close to and above 300 mV are clearly visible (Figure 1A-C, insets). There is no trend in the behaviour with regard to the quantity of carbon atoms (in the order of oxalic, malonic and lactic ligands).

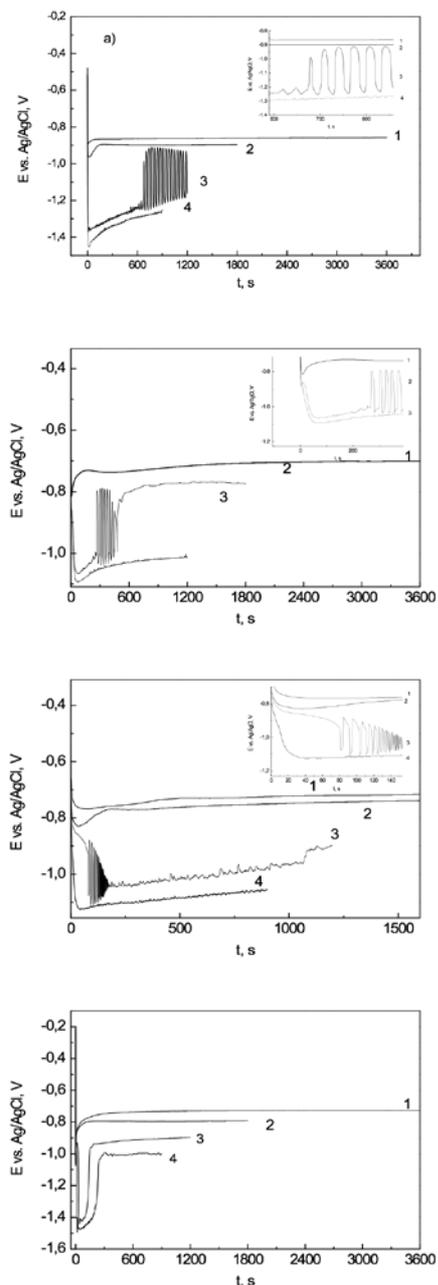


Fig. 1. Chronopotentiometric curves, obtained at different current densities: Curve 1 -0.2 A dm⁻²; curve 2 - 0.4 A dm⁻²; curve 3 -0.6 A dm⁻²; curve 4 -0.8 A dm⁻² in the electrolytes (see Table 1): a) A; b) B; c) D

Certainly, it can be supposed that the beginning of the oscillations is performed after process of nucleation, i.e. when the thickness of the coatings is more than 0.3 μm (in the electrolyte with an oxalic acid the oscillations start after the 600th second (Figure 1, inset 1a) after the beginning of the process, while with the malonic acid (Figure 1, inset 1b) they start markedly earlier - after the 80th second and in the case of using lactic acid - after about 180 seconds from the beginning of the reduction process (Figure 1, inset 1c).

Additionally, in all four investigated electrolytes the composition of the obtained coatings is similar and practically the same between 50 and 60 wt. %. The dependence of the composition on the current density is shown in Figure 2.

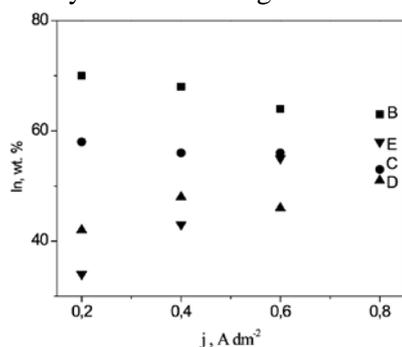


Fig. 2. Content of indium in dependence of the current density in the alloys deposited in the electrolytes A-D onto brass substrates.

In fact, it could be assumed that the potential oscillations are not related to the phase formation but more likely they could be associated with an alkalization in the vicinity of the electrode and formation/destruction of passive layers. There is no evidence in the literature about the formation of indium complexes with the indicated organic acids (oxalic, lactic, malonic and glycine), but with ammonia ions and hydroxyl ions its complexes are strong enough (the instability constant of the complex of indium with two ligands of ammonium is about 10^{-9} and that with the hydroxide group, with four ligands reaches the value of 10^{-28} [9]). However, it should be noted that oscillations in the process of indium deposition in absence of gold (as well as of gold in absence of indium) are not observed.

It is known that at pH values higher than 3.4 some passive indium-hydroxide and indium-cyanide layers are formed [10]. Most probably the conditions to form these layers are favoured at 0.6 A dm^{-2} . The glycine electrolyte is more acid than the others and that could be the reason that the oscillations cannot appear. This phenomenon of formation/destruction of the oscillations is not new and has been observed and described by de Levie [2], developed and modelled by M. T. M. Koper et al. [11-15] in case of the reduction of In^{3+} to In^0 in the thiocyanate electrolyte. It could be a reason to state that the appeared oscillations are a result from the chemical formation/destruction of some passive layer of indium oxide/hydroxide layer formed due to the increased alkalinity around vicinity of the electrode/electrolyte interface and may be a further option or could play a role for detecting pH changes in the vicinity of the electrode.

As previously mentioned, the composition of the alloy coatings from the different electrolytes

obtained in the region of indicated current densities is similar and it could be stated that the alloy deposition is anomalous, i.e. even at the lowest current density some indium-containing alloy phase starts to form. The study of this phenomenon continued with the work of glycine electrolyte, where structure formation is observed.

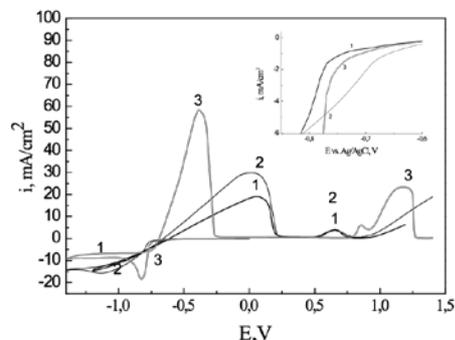


Fig. 3. Cyclic voltammetry curves, registered at $v = 20 \text{ mV s}^{-1}$ in the water solution of: 1) InCl_3 (curve 1); 2) $\text{InCl}_3 + \text{glycine}$ (curve 2); 3) $\text{InCl}_3 + \text{glycine} + (\text{NH}_4)_2\text{SO}_4$ (curve 3), Inset: Part of the same curves, in the potential region -0.6 to -0.7 V .

Figure 3 presents cyclic voltammetry curves, obtained in the alloy electrolyte, without gold ions. The addition of the glycine depolarized the cathodic process and addition of the ammonium sulphate polarized the process of reduction of indium (with a presence of glycine) which starts at -0.8 V . (Figure 3, inset).

The anodic part of the CV curves seems to be more interesting. The dissolution of indium deposited from aqueous solution of indium chloride as well as in the presence of glycine goes through two peaks – one wide, with a maximum at 0 V and a second, small one with a maximum at 0.7 V (Figure 3, curves 1 and 2). These two peaks are divided by region of passivity about 250 mV . Most probably, the first peak belongs to the dissolution of indium and the second one to the dissolution of the passive layer, formed at the beginning of the deposition process, where some oxide – hydroxide layer is formed [10]. Also, it cannot be excluded, that the second anodic peak could also be a result of dissolution at a more positive potential of similar layers formed by the dissolution of indium at the first anodic maximum. The addition of ammonium sulphate (curve 3), which does not affect markedly the cathodic process or accelerates the first anodic process and a big anodic peak with a maximum around -0.5 V could be registered. The second peak with a maximum around 1.25 V most probably is connected with the dissolution of the passive layer formed at the beginning of the indium reduction process.

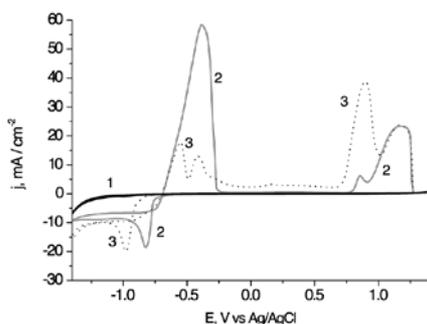


Fig. 4. Cyclic voltammetry curves, registered at $v = 20 \text{ mV s}^{-1}$ in aqueous solution of: a) $\text{KAu}(\text{CN})_2 + \text{Glycine} + (\text{NH}_4)_2\text{SO}_4$ (curve 1), b) $\text{InCl}_3 + \text{glycine} + (\text{NH}_4)_2\text{SO}_4$ (curve 2), c) $\text{KAu}(\text{CN})_2 + \text{Glycine} + (\text{NH}_4)_2\text{SO}_4 + \text{InCl}_3$ (curve 3)

Figure 4 shows cyclic voltammetry curves in the alloy electrolyte with the metals present separately and together. At this scale there are no visible peaks onto the CV curve (curve 1), obtained in the alloy electrolyte containing gold ions (in absence of indium). Curve 2, registered in the presence only of indium in the alloy electrolyte shows the already commented (in Figure 3) two well defined peaks with maximums around -0.4 V and 1.2 V (the last one is accompanied with a small bump at 0.85 V). The alloy electrolyte (curve 3) shows polarization of the cathodic reaction of about 200 mV , which is connected with a fact that indium reduction process proceed at the more negative potential onto already formed gold-indium alloy layer.

To clarify the nature of the peaks and the correspondence between cathodic and anodic processes, CVA curves reaching different vertex potentials in the cathodic period were recorded (Figure 5).

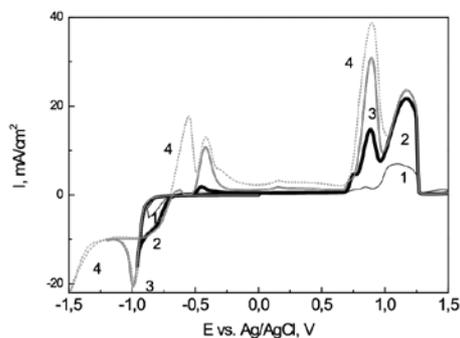


Fig. 5. Effect of the scan reversal potential on the anodic part at the CV curves, obtained in the electrolyte D (with glycine) registered at a scan rate of 20 mV s^{-1} , 1) -0.8 V ; 2) -0.95 V ; 3) -1.2 V ; 4) -1.5 V

The different vertex potentials are chosen as follows: Firstly – just after beginning of some visible reduction process (curve 1), at the middle of the

process of reduction (curve 2), at the end of first peak (curve 3) and up to the appearance of a hydrogen evolution reaction (curve 4).

It could be seen, that the beginning of the deposition process corresponds to the appearance of the anodic peak with a maximum about 1.2 V (curve 1), connected with the dissolution of the passive hydroxide indium layer, formed at the beginning of the cathodic process (i.e. only indium products are the players in the beginning of the process). Next run shows that during the first cathodic well-visible process the gold-containing phase appears (peak with a maximum around 0.87 V) together with increased peak. Small peak also appears at the potentials about -0.4 V , which belongs to the indium-rich phase dissolution. Running the curve until vertex potential after the end of the cathodic peak at about -1 V (curve 3) leads to the growing of all anodic peaks, which were registered in the previous run. With a vertex potential, where the hydrogen evolution reaction takes place the appearance of the most negative anodic peak (left part of the split peak) appears, which should be assigned to the dissolution of the pure indium.

The phase analysis of the deposited coatings at different current densities, with different metal content shows almost similar diffractograms with peaks of AuIn_2 - and In -phases.

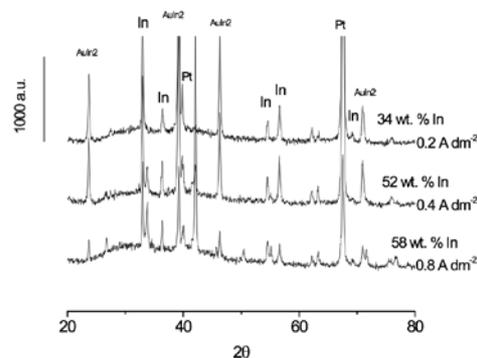


Fig. 6. XRD pattern of the coatings, obtained at 0.2 A dm^{-2} , 0.4 A dm^{-2} and 0.8 A dm^{-2} from the electrolyte D

From the performed experiments it is not possible to clarify the phenomena of anomalous deposition of the gold-indium alloy. The anodic linear sweep voltammetry technique is an appropriate tool to investigate the phase composition. The technique is described in [8] and the most important requirement is that during dissolution in the different electrolytes the re-precipitation is avoided which simplifies the “anodic” picture. So, the complicated nature of the anodic peaks directed the experiments to the anodic linear sweep experiments, performed on coatings

deposited at the 3 current densities parallel to the XRD experiments.

Similarly to the already by ALSV technique investigated silver-indium electrodeposited alloys [8] the electrolyte for the dissolution of the alloy was chosen to be lithium chloride, which is appropriate for the investigated gold-indium system as well.

The dissolution curves of the at 0.2, 0.4 and 0.8 A dm⁻² deposited gold and indium layers are presented in Figure 7 a, b.

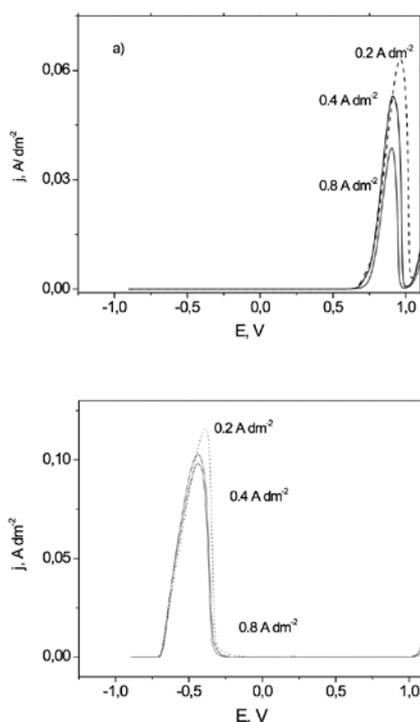


Fig. 7. ALSVs of gold and-indium coatings ($v = 1 \text{ mV s}^{-1}$) deposited with a constant charge of electricity $Q = 1.25 \text{ C cm}^{-2}$ at different current densities: Dashed line – 0.2 A dm^{-2} ; black solid line – 0.4 A dm^{-2} ; grey solid line – 0.8 A dm^{-2} , dissolution of gold coatings, dissolution of indium coatings

The dissolution of indium in the lithium chloride takes place at -0.5 V , and that of gold at $+1 \text{ V}$. The small difference in the area under peaks depends on the different cathodic efficiency during deposition of the coatings.

The dissolution of the alloy coatings was performed in the solution of LiCl and the obtained anodic linear sweep voltammetry curves are presented in Figure 8. For the coatings deposited at different current densities all peaks exists, but the content range of the elements is different. This fact corresponds to our previously obtained results [8].

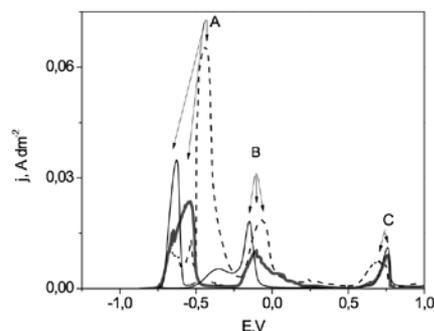


Fig. 8. ALSVs of gold-indium alloy coatings ($v = 1 \text{ mV s}^{-1}$) deposited with a constant charge of electricity $Q = 1.25 \text{ C cm}^{-2}$ with different current densities: Dashed line - 0.2 A dm^{-2} ; black solid line - 0.4 A dm^{-2} ; grey solid line - 0.8 A dm^{-2}

Considering the XRD pattern of the alloy system Au–In (Figure 6) it appears that each phase exists in a very broad range of percentages in the alloy. The potential range of each phase registered by ALSV technique depends on the weight percentage range of its appearance. Taking into account that the distribution of indium in the coating is non-homogeneous, the observed change of the position of some peaks on the ALSV is reasonable.

According to the ALSV curves shown in Figures 7 and 8 together with the results of the X-ray analysis presented in Figure 6 it could be stated that:

- the peak A corresponds to the pure In;
- the peak B corresponds to the phase AuIn₂;
- the peak C corresponds to the pure Au and/or to the alpha phase of the system.

CONCLUSIONS

The electrodeposition of gold–indium alloys from different electrolytes on the basis of ammonium sulphate (with addition of oxalic, malonic and lactic acid, and glycine) belongs to the anomalous electrodeposition due to the fact that the gold-indium phases deposit preferentially than the gold, as a more noble metal. The oscillations, observed at some current densities from the first three mentioned electrolytes depend on the pH value near to the electrode/electrolyte interface where the formation/destruction of passive layers takes place. The dissolution potentials of gold, indium and gold-indium alloys depend on the deposition current density, respectively on the percentage of the alloy.

Each ALSV peak is ascribed to a corresponding phase and there is a very good agreement between the alloy characterization by the ALSV technique and by the X-ray technique.

Acknowledgments: The authors are thankful to Prof. I. Krastev (Institute of Physical Chemistry, Bulgarian Academy of sciences), for critical remarks and helpful comments; also the authors gratefully acknowledge the financial support for the travel expenses provided by the KIC EIT RawMaterials via the International Doctoral School in Functional Materials and Innovation (IDS-FunMat-INNO) and are thankful to National Scientific fund for the financial support of project T 02/27 - 2014.

REFERENCES

1. Ts. Dobrovolska, M. Georgiev, I. Krastev, *Transactions of the IMF*, **93**, 321 (2015).
2. L. Pospisil, R. De Levie, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **25**, 245 (1970).
3. T. Dobrovolska, I. Krastev, M. Georgiev, in M. Aliofkhazraei (Ed.), *Comprehensive Guide for Nanocoatings Technology*, Volume 1: Deposition and Mechanism, M. Aliofkhazraei (eds), NOVA publisher, 2015, ch. 1 p. 269
4. N. Dimitrova, T. Dobrovolska, I. Krastev, *Arch. Metall. Mater.*, **58**, 255 (2013).
5. T. Dobrovolska, L. Veleva, I. Krastev, A. Zielonka, *J Electrochem Soc*, **152**, C137 (2005).
6. I. Krastev, T. Dobrovolska, U. La-Injevac, S. Nineva, *J. Solid State Electrochem.*, **16**, 3449 (2012).
7. A. Brenner, *Electrodeposition of alloys: principles and practice*, Academic Press, New York and London, 1963, p.41.
8. T. Dobrovolska, V. D. Jovic, B. M. Jovic, I. Krastev, *J Electroanal Chem.*, **611**, 232 (2007).
9. J. A. Dean, *Lange's handbook of chemistry*, University of Tennessee, Knoxville: McGrawHill, Inc, 1999.
10. T. Dobrovolska, I. Krastev, A. Zielonka, *Galvanotechnik*, **95**, 872 (2004).
11. M. T. M. Koper, J. H. Sluyters, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **303**, 65 (1991).
12. M. T. Koper, P. Gaspard, *The Journal of Physical Chemistry*, **95**, 4945 (1991).
13. M. T. Koper, P. Gaspard, J. H. Sluyters, *The Journal of Physical Chemistry*, **96**, 5674 (1992).
14. M. T. Koper, *Electrochim. Acta*, **37**, 1771 (1992).
15. M. T. M. Koper, J. H. Sluyters, *J. Electroanal. Chem.*, **347**, 31 (1993).

АНОМАЛНО ЕЛЕКТРООТЛАГАНЕ НА СПЛАВ ЗЛАТО –ИНДИЙ

Б.-К. Чой¹, Ф. Зауер¹, Г. Бек^{1,2}, Р. Щаубер³, Цв. Доброволска^{4*}

¹Фраунхофер център за приложни изследвания по ресурсна ефективност, Алценау, Германия

²Университет по приложни науки в Ашафенбург, Ашафенбург, Германия

³Фраунхофер проектна група по рециклиране на материали и ресурсни стратегии, Алценау, Германия

⁴Институт по физикохимия, Българска академия на науките, София, България

Постъпила на 24 юли, 2017 г.; приета на 12 септември, 2017 г.

(Резюме)

Изследван е процесът на аномално отлагане на сплав злато-индий от различни електролити на базата на амониев сулфат (с добавянето на оксалова, малонова и млечна киселини, както и глицин). При галваностатичен режим на работа с първите три горепосочени електролити се наблюдават осцилации на потенциала. При електроотлагане на сплавта от глицинов електролит се наблюдава структурообразуване на повърхността на електрода. Фазовият състав на хетерогенните покрития, получени от глицинов електролит, са изследвани с анодна линейна волтамперометрия и резултатите са сравнени с данните от конвенционалния рентгеноструктурен анализ.

Ключови думи: глицинов електролит, сплав злато-индий, осцилации, периодични пространствено-времеви структури