ARCHIVES OF METALLURGY AND MATERIALS
Volume 56 2011 Issue 3
DOI: 10.2478/v10172-011-0070-4

T.S. DOBROVOLSKA*, I. KRASTEV*, P. ŻABIŃSKI**, R. KOWALIK**, A. ZIELONKA***

OSCILLATIONS AND SELF-ORGANIZATION PHENOMENA DURING ELECTRODEPOSITION OF SILVER-INDIUM ALLOYS. EXPERIMENTAL STUDY

OSCYLACJE I ZJAWISKA SAMOORGANIZACJI W CZASIE KATODOWEGO OSADZANIA STOPÓW SREBROWO-INDOWYCH. BADANIA DOŚWIADCZALNE

The relationship between galvanostatic oscillations and formation of spatio-temporal structures on the electrode surface during electrodeposition of silver–indium alloy coatings were established. The influence of the natural and forced convection onto the structure formation were investigated. A relationship between Ag to In metal ratio in the electrolyte and the current density has been established in slow-stirred electrolyte, which allows the reproducible formation and observation of the self–organization periodic structures also in stirred electrolytes. The diffusion coefficients of the reacting silver and indium species are experimentally determined. It was shown, that the formation of the spatio-temporal structures in Ag-In alloy electrodeposits follows a very complicated reaction mechanism, typical for non-linear dynamic processes.

Keywords: electrodeposition, oscillations, self-organization, silver–indium alloys

Określono związek pomiędzy galwanostatycznymi oscylacjami a powstawaniem struktur przestrzenno-czasowych na powierzchni elektrody w trakcie katodowego osadzania stopów srebrowo-indowych. Badano wpływ naturalnej i wymuszonej konwekcji na tworzenie się struktur. Określono związek pomiędzy stosunkiem zawartości w elektrolicie Ag do In oraz gęstością prądową w mieszanym powoli elektrolicie, który pozwalał na powtarzalne uzyskiwanie i obserwowanie samoorganizujących się periodycznych struktur. Współczynniki dyfuzji reagujących związków srebra i indu wyznaczono doświadczalnie. Wykazano, że pojawianie się czasowo-przestrzennych struktur w osadach katodowych stopu Ag-In przebiega według skomplikowanego mechanizmu, typowego dla zjawisk dynamiki nieliniowej.

1. Introduction

Many excellent review papers are devoted to the universal regularities, which describe different physical, chemical, biological and social excitable media [1-7]. Al. Mikhailov and K. Showalter [8] pointed out the importance of the Belousov–Zhabotinsky (BZ) reaction and the oxidation reaction of CO on Pt single crystals and emphasized that the respective chemical systems became paradigmatic for studies of spatio-temporal dynamics. Both of these reactions have been extensively investigated, their mechanisms are well explained and satisfactory theoretical models of their kinetics are available.

The silver-indium electrodeposition system as an example of excitable media with excellent reproducibility of the easy observed periodical spatio-temporal structures [9-14]. The formed patterns are constituted of different metal phases. They are stable in time within years, which allows their investigation not only during the electrodeposition process but also later (Figure 1).

The formation of spatio-temporal structures on the cathode surface is quite often accompanied by potential oscillations when electrodeposition is carried out under galvanostatic conditions [10].

The review articles of J. Wojtowicz [15] and L.I. Kadaner [16] summarized the early investigations of temporal oscillations. During the last 15 years, several excellent papers have been devoted to the creation of models for different types of oscillators and to the relation between oscillations and formation of spatio-temporal structures [17-20]. In these papers, the instabilities are investigated on the basis of the known activator–inhibitor mechanism and the developed models can be confirmed in relatively simple experiments.

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* INSTITUTE OF PHYSICAL CHEMISTRY, BAS, 1113 SOFIA, BULGARIA

** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, DEPARTMENT OF METALLURGY AND PHYSIOCHEMISTRY OF NON-FERROUS METALS, FACULTY OF NON-FERROUS METALS, 30-059 KRAKOW, 30 MICKIEWICZA AV., POLAND

*** FORSCHUNGSINSTITUT FÜR EDELMETALLE UND METALLCHEMIE, 73525 SCHWÄBISCH GMÜND, GERMANY

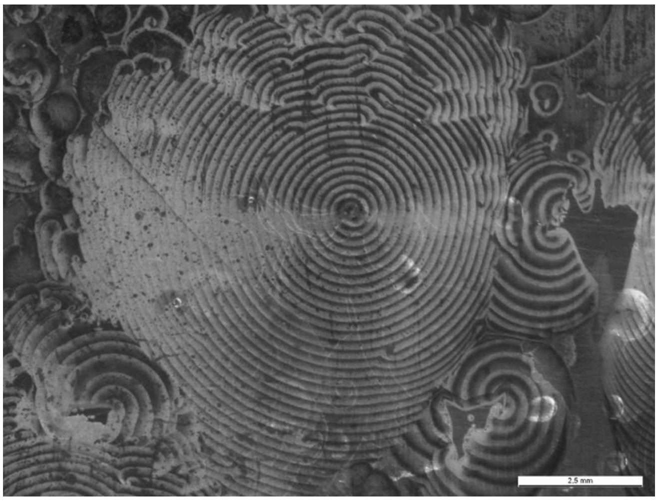


Fig. 1. Optical image of Ag-In alloy electrodeposit, kept under air condition more than 6 months after electrodeposition

The experimental strategy for the mechanistic classification of electrochemical oscillators was presented by P. Strasser *et al.* [21].

The silver-antimony system is similar to the silver-indium one and the phenomena of spatio-temporal structure formation during electrodeposition have been previously observed also in this system [22-27]. Several reasons allow the assumption that the spatio-temporal structure formation in the electrodeposited Ag-Sb and Ag-In alloys proceeds over similar, but in some extent unknown mechanisms.

In the studies of I. Krastev and M.T.M. Koper [24] the conclusions have been made that for the development of the pattern on the surface of electrodeposited silver-antimony alloy coatings, the hydrodynamic conditions close to the electrode appear to be of prime importance. The wave characteristics are discussed in relation with the studies on pattern formation in heterogeneous catalysis and on convection-induced chemical instabilities.

S. Nakabayashi *et al.* [25] made the conclusion that the spatial pattern observed during silver-antimony alloy electrodeposition can be considered as a macroscopic self-organized pattern formed by the concentration fluctuations of the antimony and silver ions on the electrode surface, and this fluctuation is spontaneously amplified by the coupling between the auto-catalytic nature of antimony electrodeposition and the flow of the electrolyte solution. The phenomenon was named “flow-induced electrochemical instability”.

M. Saitou *et al.* [26] investigated the transient changes during formation of the stripe pattern in electrodeposited Ag-Sb thin alloy films. They came to the conclusion that the experimental conditions for the onset of pattern formation are connected with the necessary conditions for the appearance of Turing instabilities in reaction-diffusion systems.

The bifurcation behaviour in the system Ag-Sb in the different stages of the wave’s formation has been studied by Y. Nagamine *et. al.* [27]. The authors reach to the conclusion that the calculated velocities of uniaxially propagating stripe pattern are nearly the same. Finally two bifurcated pattern at the initial stage are unified into one pattern with a longer wavelength in time, independently of their velocities. Y. Nagamine *et al.* [28] suggested also that some “labyrinthine structure” of Ag and Sb could be formed by the spinodal decomposition of the alloy.

In spite of the intensive studies on the silver-indum alloy electrodeposition in the last 5 years, the mechanism of spatio-temporal structure formation in this system is still not clear and requires additional knowledge about the influence of the different reaction parameters.

So, the aims of this work are to establish:

– The relationship between galvanostatic oscillations and formation of spatio-temporal structures on the electrode surface during electrodeposition of silver–indium alloy coatings;

– the influence of the natural and forced convection onto the structure formation;

– the diffusivities of reacting species.

2. Experimental

The composition of the electrolyte for deposition of Ag-In alloy coatings is given in Table 1.

TABLE 1

Electrolyte composition	Concentration	
	g dm^{-3}	mol dm^{-3}
In as $InCl_3$	5.6 - 22.4	0.05 - 0.2
In as $In(NO_3)_3$	5.6 - 22.4	0.15
Ag as $KAg(CN)_2$	4-8	0.04 - 0.08
D(+)-Glucose	20	0.1
KCN	16 - 65	0.25 - 1

The electrolytes were prepared using chemicals of *pro analisi* purity and distilled water by following procedure: The necessary quantities of D(+)-Glucose were added to the water solution of indium chloride. The electrolyte was pre-electrolyzed for a short time while recording a cyclic voltammetric curve, or during galvanostatic deposition within 2-3 minutes with a current density of about 0.2-0.5 Adm^{-2} in order to achieve some disintegration of the D(+)-Glucose [10] and after that the total amount of KCN according to the molar proportion of KCN to indium of 5:1 was added in one step to the electrolyte under stirring. After dissolution the silver salt was added.

The alloy coatings with thickness between 1 and 10 μm were deposited in the cell for cyclic voltammetric experiments under galvanostatic conditions. Copper cathodes mostly with an area of 2×1 cm were used. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing followed by pickling in a 20% solution of sulphuric acid. In order to avoid the contact deposition of silver, the cathode was immersed into the electrolyte under current.

Two platinum counter electrodes (about 4 cm^2 each) were used. As a reference electrode an Ag|AgCl electrode ($E_{Ag|AgCl}$= 0.198 V vs. SHE) was used. The reference electrode was placed in a separate cell filled with 3M KCl solution (Merck), connected to the electrolyte cell by a Haber-Luggin capillary through an electrolyte bridge containing also 3M KCl solution. The experiments were performed at room temperature by means of a computerized potentiostat/galvanostat (GAMRY Reference 600) using PHE 200 (version 5.5) software (Gamry Instruments).

The elemental composition of the coating surface was measured by EDAX and the surface morphology was studied by SEM and optical microscopy.

The measuring of the diffusion coefficients has been performed using a platinum Rotating Disc Electrode (Metrohm 628-10), with an area of 0.071 cm^2. The diffusion limited current densities have been determined at 1000, 2000 and 3000 rpm for indium (0.1M), silver (0.037M) and indium-silver electrolytes with the same concentration of the components. The diffusion coefficients have been calculated for every speed of rotation and after that were presented as average results. The used equation for the determination of the diffusion coefficients is [29]:

$i_d = 0,62.z.F.D^{2/3}.C_{Me^+}.\nu^{-1/6}.\omega^{1/2}$, where

i_d– diffusion-limited current density, A cm^{-2}; z – number of electrons participating in the overall deposition reaction (for silver reduction – $1e^-$, in case of indium reduction – $3e^-$), C^+_{Me} – concentration of the respective metal ions, M cm^{-3},$\omega = 2\pi f$ – angle velocity of rotation, (f – rev sec^{-1}) and ν – kinematic viscosity, 10^{-2} cm^2/sec, and F – Faraday constant.

3. Results and discussion

3.1. Relationship between oscillations and formation of spatio-temporal structures

Figure 2 shows the galvanostatic curves, registered in the alloy electrolyte at 0.5 Adm^{-2} (sample A) – (Figure 2 inset) and 0.7 A dm^{-2}(sample B). The electrode processes of the silver and indium electrodeposition separately and together are investigated and described elsewhere [10-12]. Briefly, the electrodeposition of the silver–indium alloy is of regular type – after reaching the limiting current density of silver (which is more positive metal in this system) the indium starts to co-deposit.

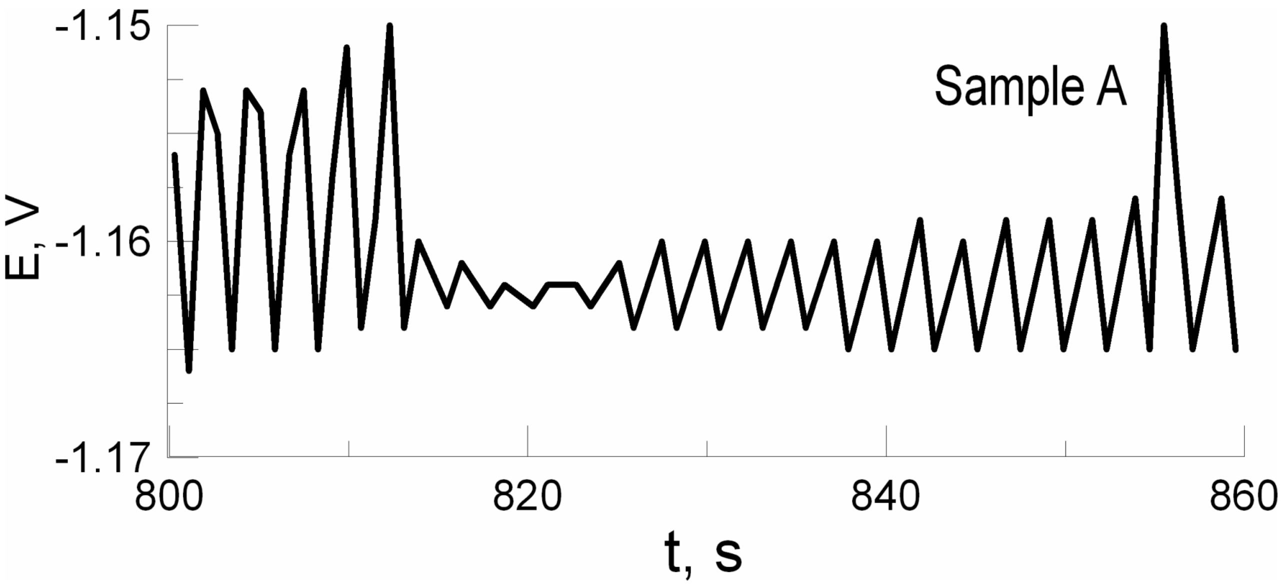


Fig. 2. Potential oscillations during deposition of Sample A in different axis limit

Optical image of sample A, obtained at 0.5 A dm^{-2} is shown in Figure 3a. The heterogeneity of the surface is optically well visible. The formation of structures could be detected, but the patterns are broken most probably because of the fast potential changes during deposition.

The SEM image of a coating's part of sample A from Figure 3a is shown in Figure 3b. The differences in the surface morphology of the dark and light areas are not substantial [11], but the surface is not very smooth. The heterogeneity in the depth of the coating is visible in the cross-section of the broken in liquid nitrogen sample A (Fig. 3c).

It was reported elsewhere [5], that the dark regions of the spatio-temporal structures in the optical images are formed by the phase Ag_3In (up to 22 wt.% In) and the white zones – by the solid solution of indium in silver (α-phase – up to 19 wt. % In).

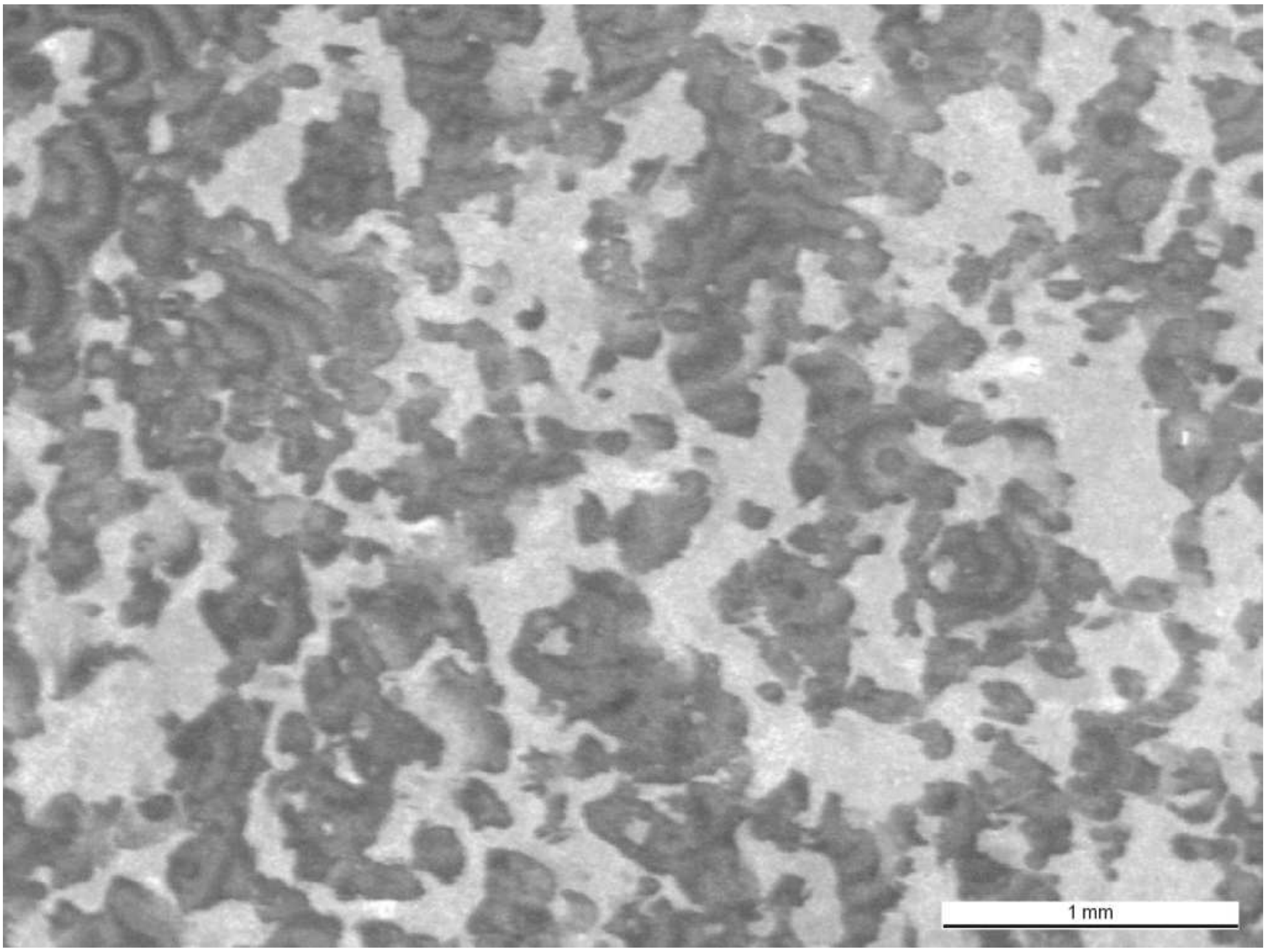


Fig. 3a. Optical image of a Ag-In coating; 0.5 A dm^{-2}, 20 min

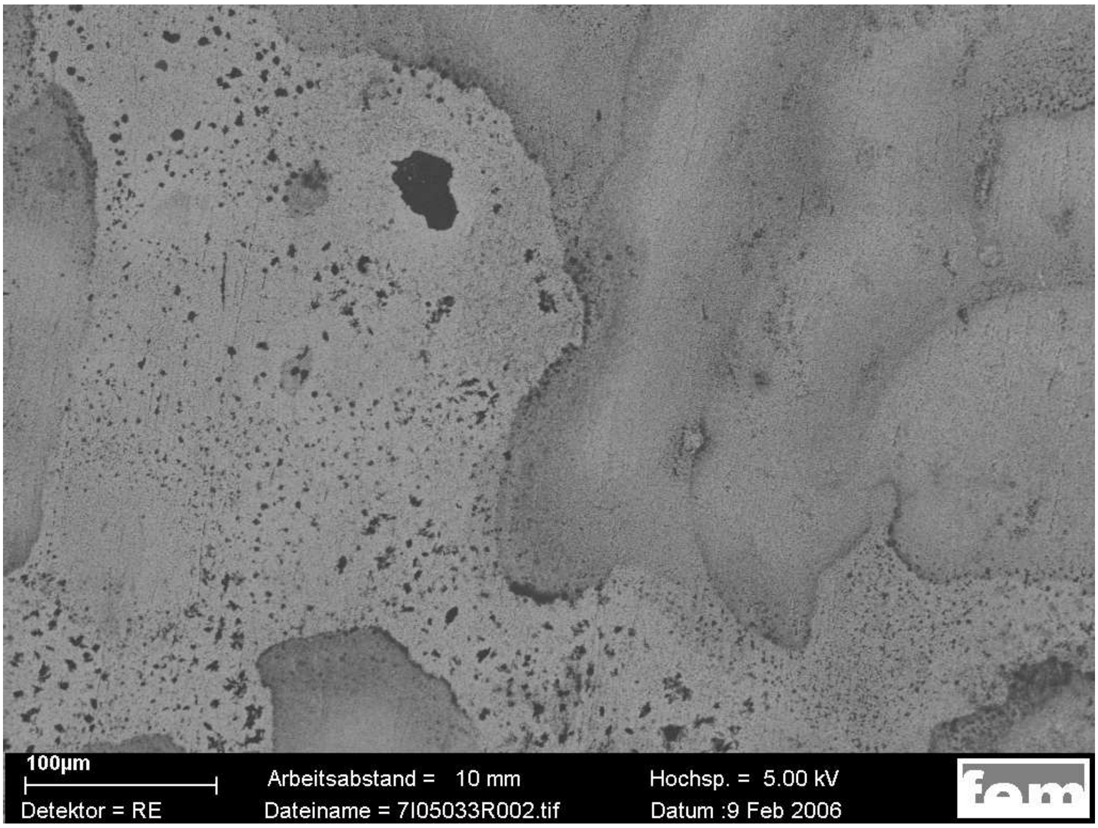


Fig. 3b. SEM image of a small area of the coating from Figure 3a

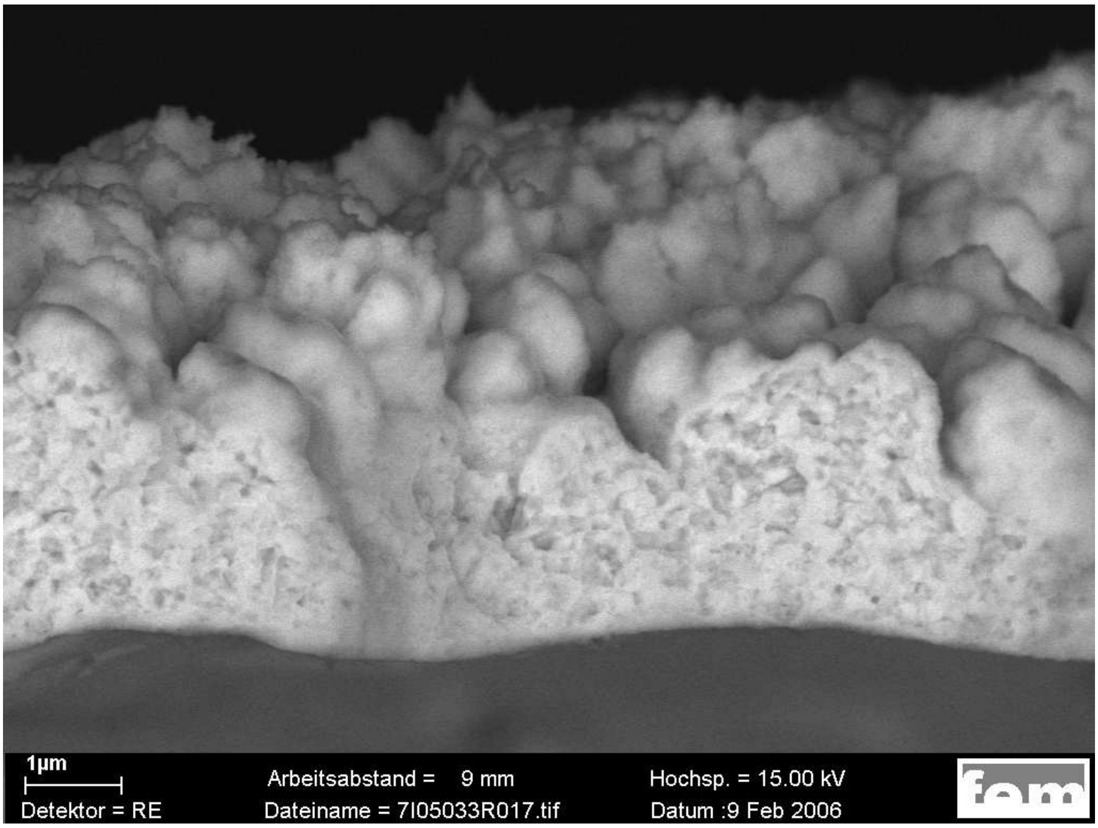


Fig. 3c. SEM image of the cross-section of sample A

The potential oscillations during deposition of sample A have a period of about 2.5-3 sec and an amplitude of about 16-18 mV. The theoretical calculations (100% cathodic current efficiency) show that the deposition of 10 nm of pure silver under the reported conditions requires a time of 1.9 s, and that of 10 nm pure indium – about 3.7 s in the case, if the metals are deposited separately. It could be supposed that for the time of one oscillation layers with different indium content could be deposited resulting in a layered structure formed by different alloy phases. Unfortunately, fine layered structure of such dimensions was not registered, probably because the oscillations are not connected with a uniform change in the composition of the alloy over all surface of the electrode.

Figure 4a shows the optical image of a coating of sample B from Figure 2. The convective flow in the case B should be stronger due to the higher current density and faster exhausting of the electrolyte in the cathode vicinity. The potential oscillations should have the same origin like the oscillations during deposition of sample A, they become smaller, with a lower amplitude (1-2 mV) and a shorter period of 7-8 oscillations per 10 sec. The spatio-temporal structures on the cathode surface become better organized and fully developed.

The SEM images are pale (Fig. 4b) due to the nearly same composition in the dark and light areas (19-22 wt.% In) and the similarity in their surface morphology and size of the crystallites [10-13; 30]. The heterogeneity in the depth of the coating can not be recognized at the same conditions (Fig. 4c).

The origin of the oscillations could be the formation of different phases with different indium content in the front of the Haber-Luggin capillary and their changes during deposition, leading to local changes in the measured potential. In this case the period and the amplitude of the oscillations should depend on the scale of the formed structures and the position of the capillary in the front of the cathode.

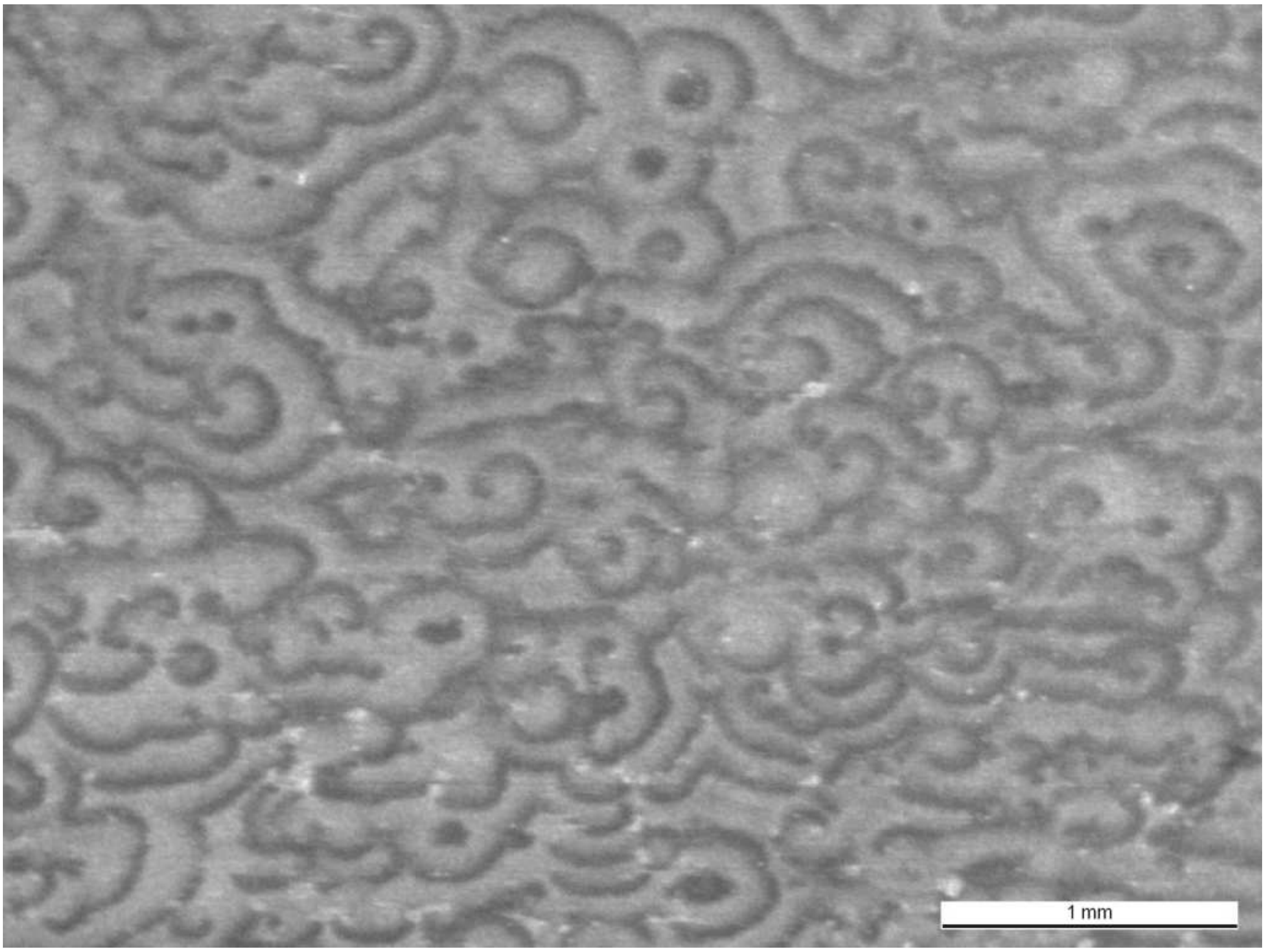


Fig. 4a. Optical image of a Ag-In coating; 0.7 A dm^{-2}, 22 min

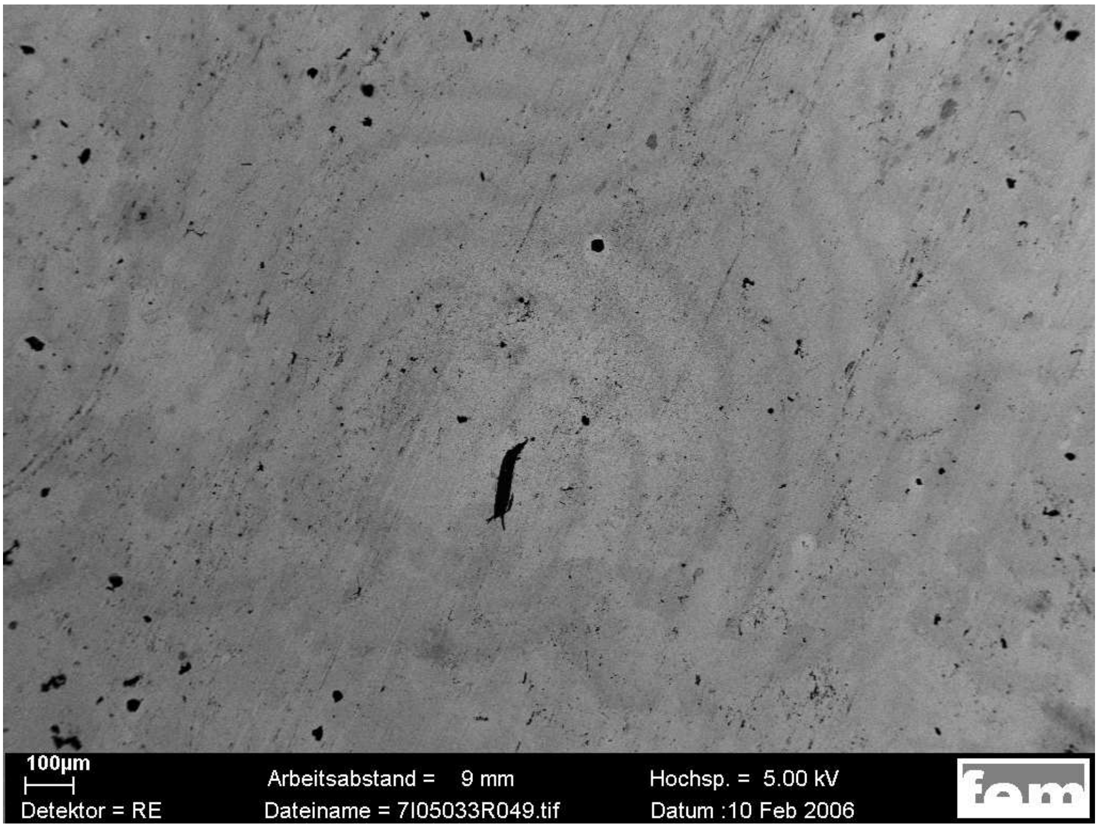


Fig. 4b. SEM image of a small area of the coating from Figure 4a

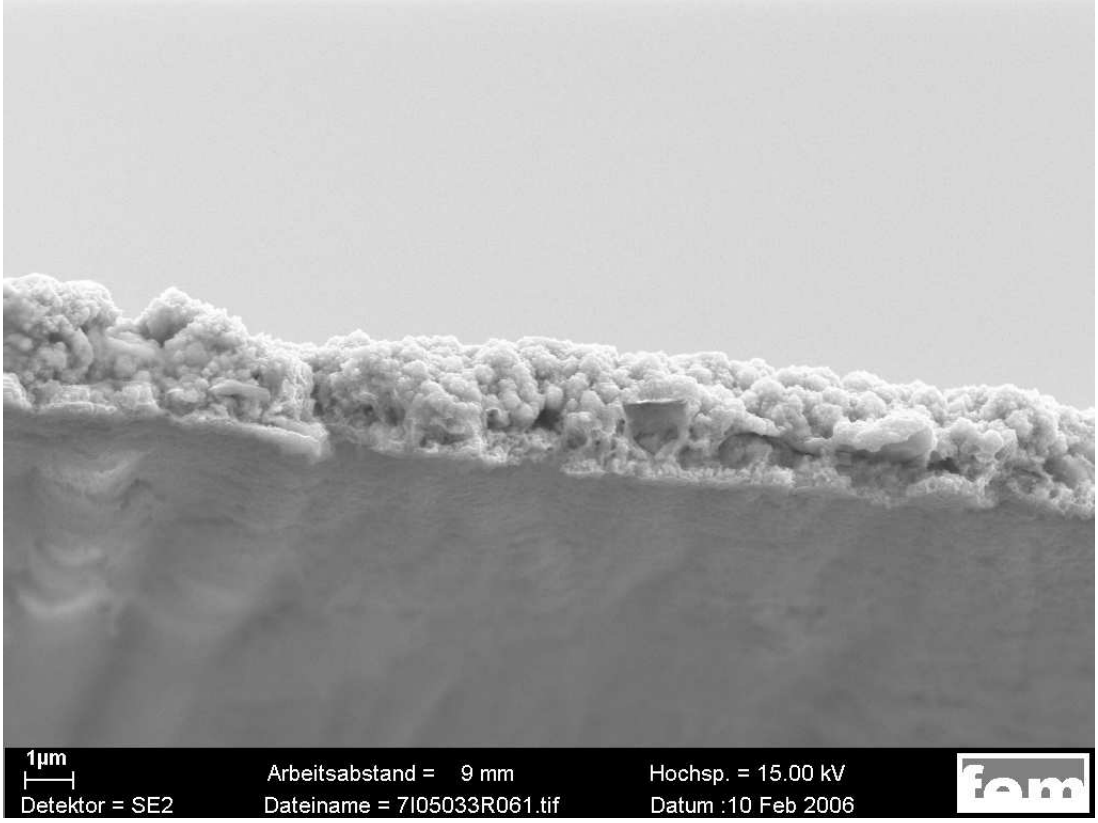


Fig. 4c. SEM image of the cross-section of sample B

3.2. The influence of the natural and forced convection

3.2.1. Natural convection

The investigations on the silver-indium electrodeposition were performed onto vertical electrodes and at appropriate conditions the spatio-temporal structures covered almost the whole surface of the electrode (Fig. 5).

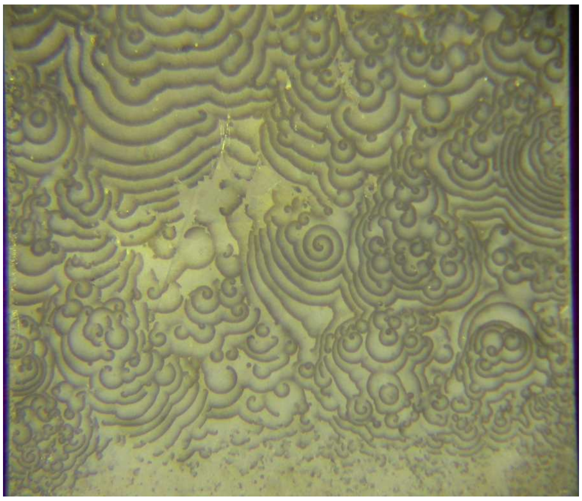


Fig. 5. Optical image of a Ag-In coating; 0.4 A dm^{-2}, 35 min, electrolyte composition: 0.15 M In, 0.06 M Ag, 0.5 M KCN and 0.1 M D(+)-Glucose. Width of the sample – 1 cm

Depending on the electrolyte composition, the electrolysis conditions and their influence on the natural convection flow sometimes non-homogeneity of the coatings along the height of the electrode is observed (Fig. 6). Pure silver in the lower part and waves which curl to spirals and "labyrinthine structures" in the middle part of the electrode are registered (Fig. 6, inset).

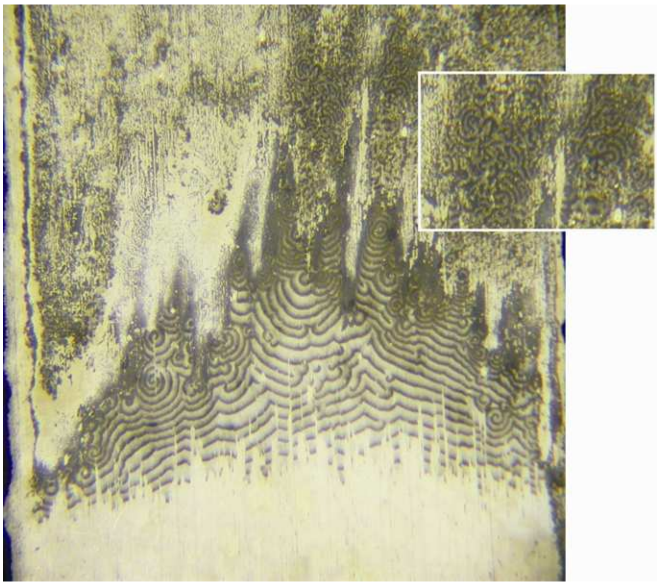


Fig. 6. Optical image of a Ag-In coating; 0.2 A dm^{-2}, 90 min, electrolyte composition: 0.1 M In, 0.04 M Ag, 0.5 M KCN and 0.1 M D(+)-Glucose, "labyrinthine structure". Width of the sample – 1 cm

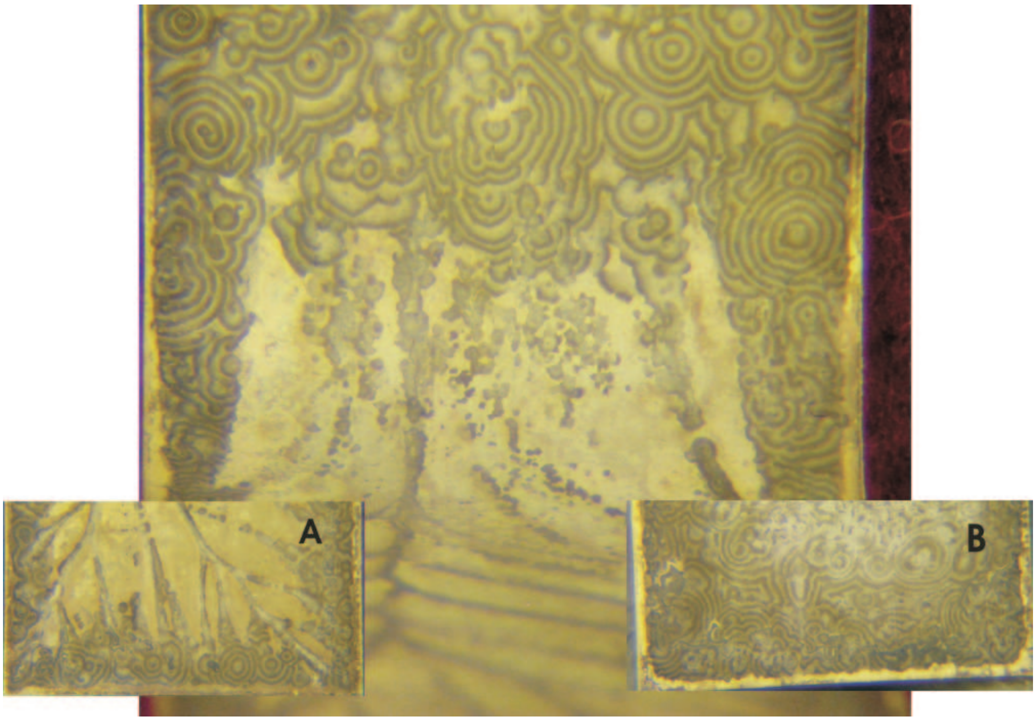


Fig. 7. Optical image of a L-shaped electrode with a Ag-In coating; 0.3 Adm^{-2}, 52 min, electrolyte composition: 0.1 M In, 0.04 M Ag, 0.5 M KCN and 0.1 M D(+)-Glucose; A – edge of the top of the horizontal part; B - bottom of the horizontal part. Width of the sample – 1 cm

To check the influence of the natural convection an L-shaped electrode has been used. Figure 7 shows a silver-indium alloy coating on this cathode. The structures appear everywhere, even on the top and on the bottom of the horizontal part of the L-shaped electrode. Most probably, the development of such structures does not depends so strongly on the convective flow along the electrode as in the case of silver-antimony alloy electrodeposition [24]. Definitely, the observed self-organization phenomena are closely connected to the electrolyte flow due to the natural convection along the electrode.

3.2.2. Forced convection

The establishment of the relation between the Ag to In metal ratio in the electrolyte and the applied current density in non-stirred electrolytes was an important step for the reproducible observation of the self-organization phenomenon without any preliminary treatment of the freshly prepared electrolyte [11].

The possibility to observe pattern formation in a stirred electrolyte was experimentally checked (Fig. 8). Because of stirring the diffusion limited current density of the metal deposition increases and the appearance of the structures could be observed at higher current densities in comparison with the non-stirred electrolyte. It was established, that the spatio-temporal structures still appeared at stirring intensity up to 50 rev min^{-1} in the investigated concentration range of electrolyte components. Higher rotation speeds lead to transition to more chaotic (disordered) pattern on the coatings surface. Possibly the formation of spatio-temporal structures could be observed at higher concentrations (or ratios of both metals) at much more higher current densities in the more intensive stirred electrolyte.

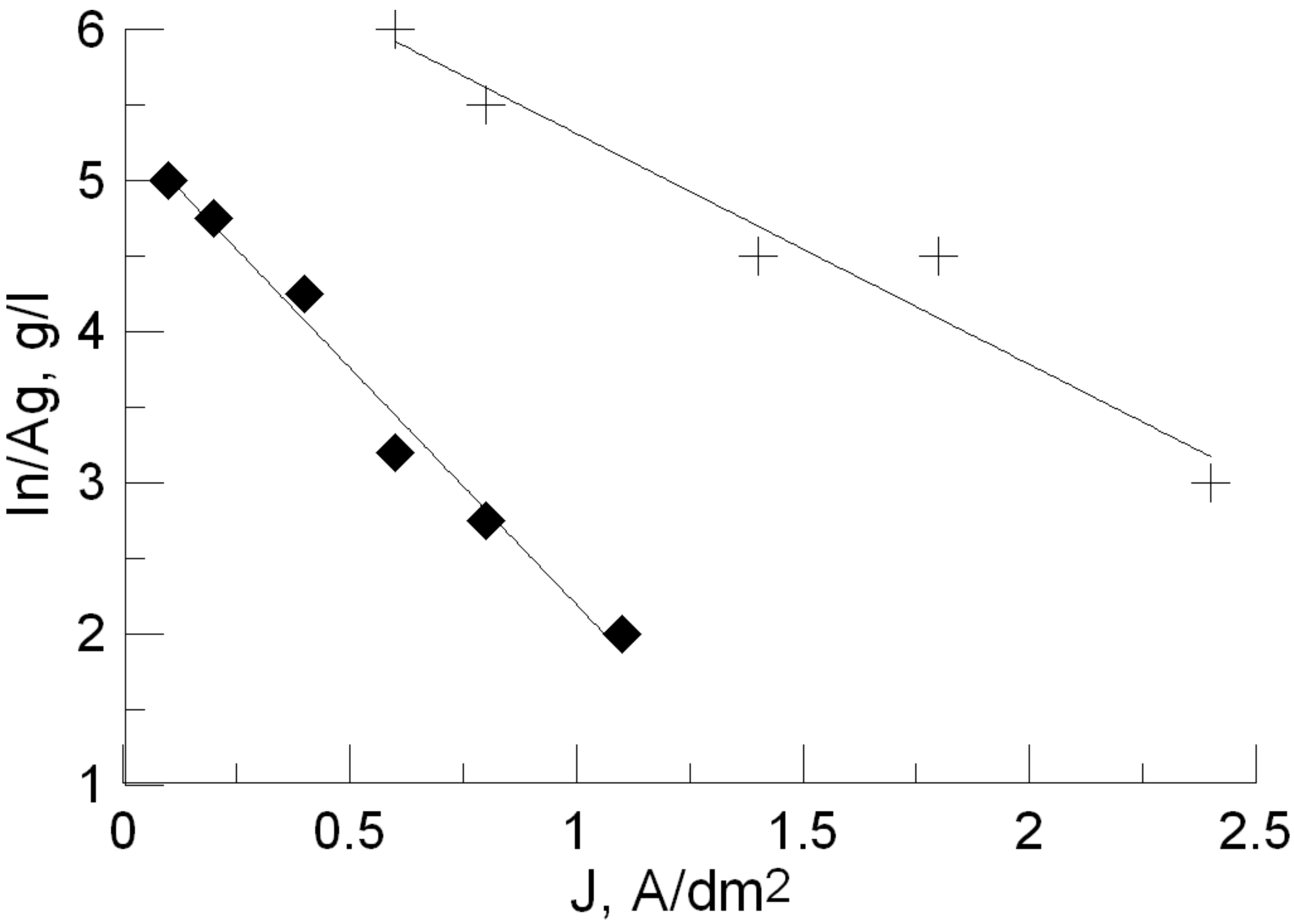


Fig. 8. Relationship between Ag to In metal ratio in the electrolyte and the current density for reproducible observation of spatio-temporal structures; + - stirred electrolyte, 50 rev^{-1} min; ■ – non – stirred electrolyte

3.3. Diffusivities of the reacting species

The formation of spatio-temporal structures during electrodeposition of silver-indium alloys proceeds over a kind of reaction-diffusion mechanism where the two reacting species diffuse to the surface and react with each other and co-deposit under applied electrochemical conditions, producing stable patterns of different silver-indium phases. As a result a variety of spots, stripes and spiral patterns, could be observed. The determination of the diffusivities of the species (silver and indium ions) is of significant importance for the understanding of the phenomenon.

In generally, it could be supposed that the deposition of the alloy starts with the silver discharge reaction from the dicyanoargentate complex:

$$Ag(CN)_2^- + e^- \leftrightarrow Ag + 2CN^- \qquad (1)$$

After reaching the limiting current density for the silver reduction the indium co-deposition starts:

$$In[(DPGl^n)CN_5]^{-2-n} + 3e^- \leftrightarrow In + n(DPGl) + 5CN^- \qquad (2)$$

Reaction 2 is most probably the only reaction in the single indium electrolyte, where the *DPGl* means a disintegration product of D(+)-Glucose, which forms according nuclear magnetic resonance experiments the closest ligands to the indium in the formed complicated indium cyanide complex [10].

Independently of the concentration of free cyanide ions in the solution the silver discharge proceeds from the dicyanoargentate ions [31]. They are produced on the cathode from the dominating complex $Ag(CN)_3^{2-}$in the electrolyte (formed due to the increase of the free cyanide ions released according to reactions 1 and 2) by a fast chemical reaction preceding the silver reduction:

$$Ag(CN)_3^{2-} \leftrightarrow Ag(CN)_2^- + CN^- \qquad (3)$$

The diffusion-limited current densities for silver and indium electrodeposition in the alloy electrolyte but with single metals have been determined using rotating disc electrode technique. The metal concentrations used were 0.1 M for indium or 0.037 M for silver in an electrolyte containing 0.1M D(+)-Glucose and 0.5M KCN. These concentrations of both metals in the alloy electrolyte ensure the appearance of spatio-temporal structures at current densities of about 0.1-0.15Adm^{-2}.

Following diffusion coefficients were established for the silver dicyanoargetate ion – 1.257x10^{-8}cm^{2}sec^{-1} and for the complex indium ion – 2.52x10^{-9} cm^2 sec^{-1}.

The obtained data about the different diffusivities of the complex ions are insufficient to conclude which ions are the inhibitor and the activator of the pattern formation process. Moreover the pattern is formed by different alloy phases and not by the separate metals.

In Figure 9 the snapshots from the growth process of a structure are presented. The surface diffusion coefficient of the activator could be determined according following equation [1, 24]:

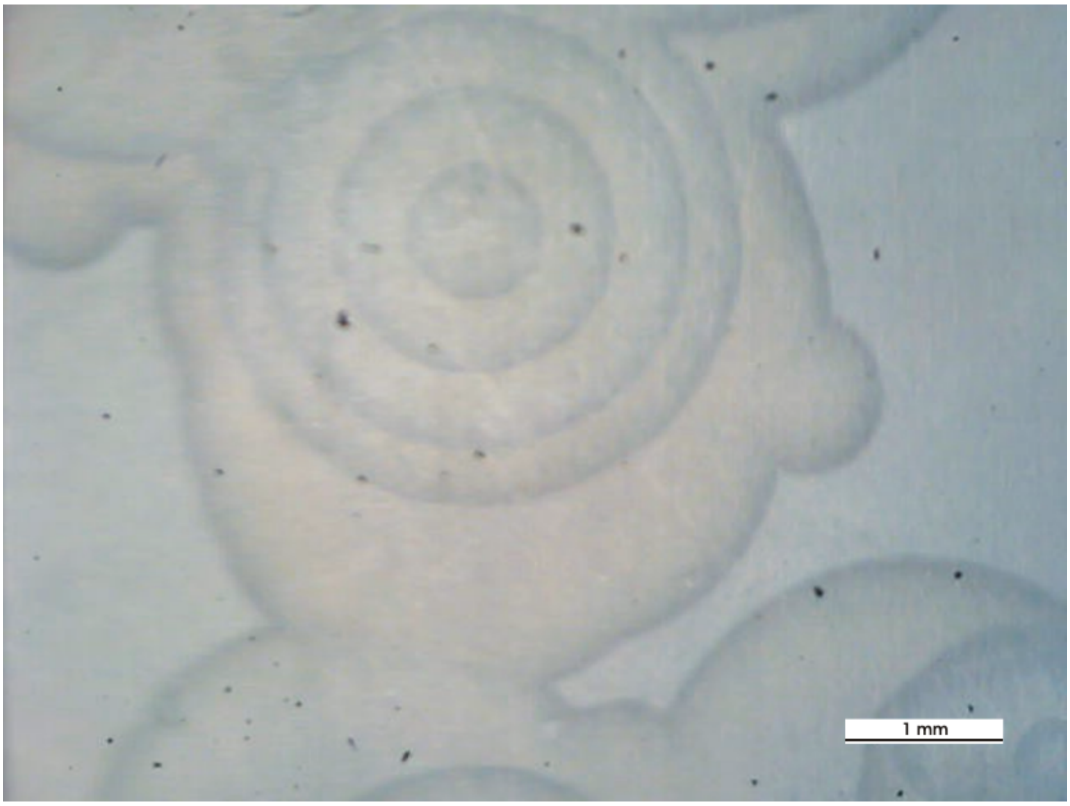
$$c^2 \cong 20D/T, \qquad (4)$$

where c is the wave speed, D – the surface diffusion coefficient and T – the rotating period of the spirals.

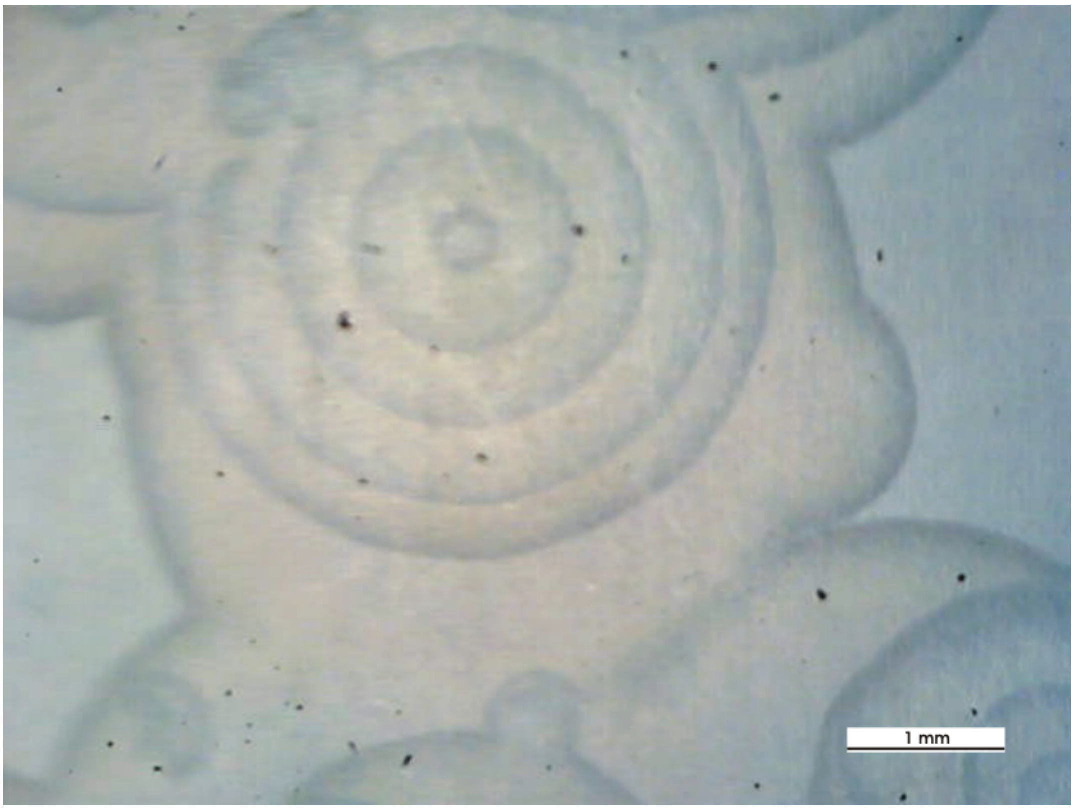
From Figure 9 the parameter c and T were determined as: c ≈ 9 .μm s^{-1} and T ≈120 s, and the resulting value for the surface diffusion coefficient D is between 2-5.10^{-6} cm^{2}s^{-1}.

This value differs from the diffusion coefficients of silver and indium complex ions obtained by the electrochemical rotating disk technique, and it is hardly to imagine to which species this diffusion coefficient corresponds. Moreover the big variety of the pattern sizes and the differences in the speed of their growth complicate the decision. In spite of the difficulties in discovering the mechanism of formation of the silver-indium structures, it includes the typical characteristics of the well known non-linear dynamic processes and the possibility to obtain spatio-temporal structures with a different shapes and size under well-controllable electrolysis conditions is a great advantage of this system.

a)



b)



c)

Fig. 9. Snapshots from a spatio-temporal structure on the surface of a Ag-In alloy coating during electrodeposition; electrolyte composition: 0.1 M In, 0.037 M Ag , 0.5 M KCN and 0.1 M D(+)-Glucose; 0.1 A dm^{-2} a) start of the observation; b) after 60 sec.; c) after 120 sec. – appearance of the next concentric circumference

4. Conclusions

Intensive potential oscillations can be observed during electrodeposition of Ag-In alloys under galvanostatic conditions and they influence the formation of the periodic structures in the obtained coatings.

A relationship between Ag to In metal ratio in the electrolyte and the current density has been established in slow-stirred electrolyte, which allows the reproducible formation and observation of the self–organization periodic structures also in stirred electrolytes.

The diffusion coefficients of the reacting silver and indium species are experimentally determined.

The formation of the spatio-temporal structures in Ag-In alloy electrodeposits follows a very complicated reaction mechanism, typical for non-linear dynamic processes, The wide variety of observed patterns under electrochemically well controllable conditions forms the basis for further investigations on the self-organization phenomena in electrodeposition of alloys.

Acknowledgements

The authors express their gratitude to the Mianowski Fund - Polish Science Fund and to the Deutsche Forschungsgemeinschaft (Project 436 BUL 113/97/0-4) for financial support of this work.

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Received: 10 February 2011.