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Oscillations and spatio-temporal structures during electrodeposition of AgCd alloys

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ABSTRACT

During electrodeposition of cadmium both potentiostatic and galvanostatic oscillations are registered. Experiments under different hydrodynamic conditions show the possibility of formation/destruction of passive layers on the electrode surface, which besides the hydrogen evolution under limiting current density conditions could be an additional promoter of the oscillation behavior of the system. The duration of the observed galvanostatic potential oscillations decreases with increased current density, due to massive hydrogen evolution. XPS investigations confirm the existence of passive films at potentials corresponding to the onset of oscillations. Potential oscillations are observed again during electrodeposition Ag–Cd alloys at high current densities. They appear when the cadmium content in the deposits is more than 45 wt.% and they have possibly the same origin as the oscillations during cadmium electrodeposition. The period and regularity of the oscillations depend on the current density, respectively on the cadmium content.

At high cadmium content during alloy deposition, the formation of periodical structures consisting of different phases of the alloy is registered. The cadmium content of the different morphological areas of the patterns is almost identical. The XRD spectra of the obtained structured coatings suggest the existence of two textured phases, with a very strong preferred orientations of the crystallites in the direction $\langle 1\,0\,1\rangle$ for the pure cadmium phase.

1. Introduction

It was recently reported that during electrodeposition of silver–cadmium alloys instabilities were observed, resulting in periodical changes in the potential or current with time and formation of periodical spatio-temporal structures onto the electrode surface [1].

The interest in the investigation of this alloy system is based also on the wide variety of phases observed in the electrodeposited alloy coatings [2–6]. Recently the difficulties in determination of the phase content of the different zones in electrodeposited heterogeneous silver–cadmium alloy coatings were overcame by comparative investigations by X-ray diffraction and anodic linear sweep voltammetry (ALSV) [7].

Polukarov and Gorbunova supposed changes of the cathodic potential corresponding to the changes of the phase composition of the deposited silver–cadmium alloy [8]. They expected possible potential oscillations during electrodeposition of the alloy, but they were not able to register them (in this case the periodical potential changes should be a result of a layer-by-layer deposition of both metals – silver and cadmium). The results from the systematical investigations of some silver alloys [9–13], as well as literature data [14–16] allow the conclusion, that potential or current oscillations have not been registered in the pure silver cyanide electrolyte under investigated electrolysis conditions.

Otherwise, during cadmium electrodeposition from cyanide electrolytes intensive potential changes with an amplitude of more than 400–500 mV were observed by Vishomirskis [17] as well as by Kaneko et al. [18].

Vishomirskis stated that in the case of cadmium deposition from cyanide electrolytes the hydrogen evolution does not play the main role originating the potential oscillations in time. The reason is the formation/destruction of some passive film on the surface of the electrode [17]. According this concept, during electrodeposition of some metals from cyanide electrolytes, the passivation is a result of the formation of a compound with general formula $Me_x(CN)_y(OH)_z$ on the cathode.

Kaneko et al. [18] established that the potential oscillations result from the decrease in the surface concentration of cadmium ions during galvanostatic deposition almost nearly to zero, and as a result the potential shifts rapidly to higher negative values reaching the deposition potential of hydrogen. The evolved hydrogen

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bubbles from the cathode surface provoke some agitation of the electrolyte, facilitating in this way the mass transport process. As a result, the surface concentration of cadmium ions increases and the potential decreases again.

Current oscillations under potentiostatic conditions were observed neither by Vishomirskis, nor by Kaneko et al.

Thus, the process of oscillatory behavior of Cd is discussed from two different points of view in the galvanostatic case. Current oscillations could be observed under potentiostatic conditions. Obviously the oscillatory process is more complex and needs additional investigations.

The oscillations of potential and/or current, together with spatio-temporal structure formation are observed in some other silver alloy systems like Ag–Sb [19] and Ag–In [20]. Previous experiments show that the oscillations, registered during electrodeposition of silver–cadmium alloys and the observed pattern onto the electrode are richer in variety of types, amplitudes and periods [1].

The aim of this work is to answer the questions:

1. What is the nature of the oscillations, observed during electrodeposition of cadmium from cyanide electrolyte?
2. What is the connection between the oscillations during alloy electrodeposition and the phase composition of the silver–cadmium coatings with periodical spatio-temporal structures?

2. Experimental

The cadmium, silver and alloy coatings were deposited from cyanide electrolytes. Pure cadmium was deposited from a solution containing mainly 0.15 M Cd as $CdSO_4{\cdot}8/3H_2O$ + 0.6 M KCN, pure Ag from a solution containing 0.06 M Ag as $KAg(CN)_2$ + 0.6 M KCN and Ag–Cd alloys – from a solution containing 0.06 M Ag as $KAg(CN)_2$ + 0.15 M Cd as $CdSO_4{\cdot}8/3H_2O$ + 0.6 MKCN. Chemical substances of *pro analisi* purity and distilled water were used.

The experiments were performed in a 100 cm^3 tri-electrode glass cell at room temperature. The vertical working electrode (area 2 cm^2), the rotating disc electrode (Metrohm 628-10) (area 0.07 cm^2) and the two counter electrodes were made from platinum. An Ag/AgCl reference electrode ($E_{Ag/AgCl} = -0.197$ V vs NHE) was used. The reference 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 also 3 M KCl solution.

The experiments were carried out at room temperature by means of a computerized potentiostat/galvanostat Reference 600 (Gamry Instruments Inc.) using the software PHE 200. The polarization curves are recorded at the sweep rate of 25 mV s^{-1}.

The coatings were deposited under potentiostatic, or galvanostatic conditions at room temperature.

For the XPS analysis (ESCALAB MkII (VG Scientific)) of the surface composition of the coatings, the cadmium electrodeposition was performed onto copper substrate 2 cm × 1 cm. Symmetrical Gaussian–Lorentzian curve fitting after Shirley-type subtraction of the background was performed [21].

The surface morphology of the coatings was studied by scanning electron microscopy (SEM).

For the investigation of the phase composition and texture of the coatings the deposition was performed onto copper substrate with an area of 3.2 cm^2. The cadmium or silver distribution on the surface of the coatings was determined by energy dispersive analysis (EDX). X-ray diffraction patterns for phase identification of the potentiostatically deposited cadmium and alloy coatings were recorded in the interval 20–120° (2Θ) with a Philips PW 1050 diffractometer, equipped with Cu-K_α tube and scintillation detector. The texture of the coatings was investigated with the computer controlled four circle X-ray texture goniometer Philips PW 1048.

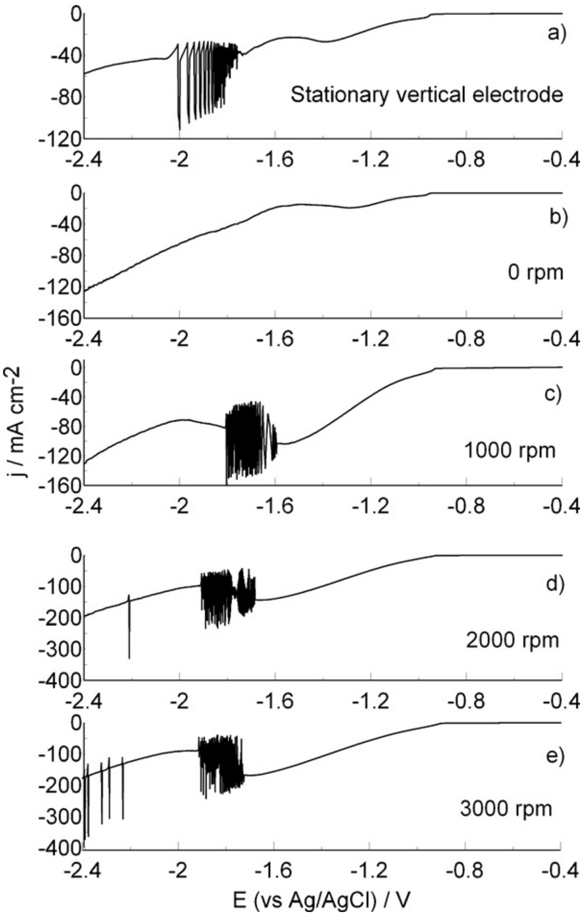

Fig. 1. Polarization curves recorded at the sweep rate of 25 mV s^{-1} for deposition of pure Cd: curve a – stationary vertical electrode; curves b–e – rotating disk electrode, with different rotation speeds.

3. Results and discussion

3.1. Electrodeposition of cadmium

Fig. 1 shows parts of the linear cathodic polarization curves, registered in the electrolyte for deposition of cadmium on two different types of electrodes – on a stationary vertical electrode under natural convection conditions and on the rotating disc electrode (RDE) under definite mass transport conditions corresponding to the different rotating speeds: 0, 1000, 2000 and 3000 rpm. The initial potential of the voltammetric scan was 0 mV vs. Ag/AgCl. The registered curves are presented in the window −0.4 V to −2.4 V for better visualization of the obtained results.

Curve *a* in Fig. 1 is the polarization curve on the stationary vertical electrode. It is characterized by the wave at about −1.4 V. The current density level of the wave could be assumed as a limiting current density for the cadmium reduction process. At potentials more negative than −1.8 V oscillations of the current appear. It was suggested that the oscillations start at a potential determined by the onset of the hydrogen evolution during the cadmium deposition [7], which corresponds to the mechanism proposed by Kaneko et al. [18].

Curve *b* in Fig. 1 shows the polarization curve registered on the rotating disc electrode (RDE) without rotation at 0 rpm. In this case

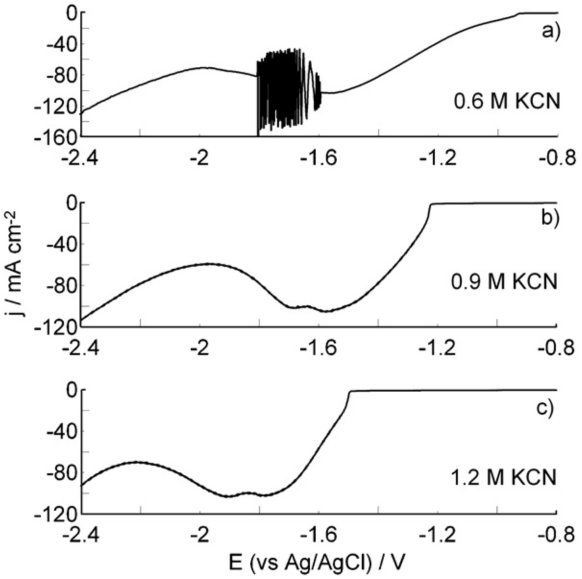

Fig. 2. Polarization curves on RDE at different concentrations of cyanide ions in the electrolyte for deposition of pure cadmium: (a) 0.6 M; (b) 0.9 M; (c) 1.2 M. Sweep rate of 25 mV s^{-1}.

the natural convection is embarrassed and the free removal of the hydrogen bubbles is hindered. A peak, connected with the cadmium reduction is observed at the potential of about −1.25 V and current oscillations are not observed.

The rotation of the electrode causes a definite hydrodynamic flow resulting in a constant thickness of the diffusion layer over the entire surface of the electrode. This ensures the removal of the hydrogen bubbles with a constant speed corresponding to the rotation speed of the electrode, so that the pulsating hydrogen evolution should be in part or whole eliminated. At 1000 rpm in the potential interval between −1.6 V and −1.8 V current oscillations are registered (Fig. 1, curve *c*). By increasing the rotating speed the onset of the oscillations moves to more negative potentials. At 2000 rpm the oscillations start at −1.7 V and continue almost to the potential of −1.9 V (Fig. 1, curve *d*). At the higher rotation speed of 3000 rpm the oscillations start at −1.75 V and continue to −1.95 V (Fig. 1, curve *e*).

From these experiments it could be concluded that depending on the improved mass transport conditions (by using rotating disc electrode) in spite of the partial removal of the hydrogen bubbles by the tangential hydrodynamic flow, current oscillations could be registered at linear polarization experiment in different potential regions (at low rotation speed between −1.6 and −1.8 V and at high rotation speed – at potentials more negative than −1.7 V).

The existence of oscillations with different origin in the one and the same system (for example during reduction of hydrogen peroxide onto platinum electrode) due to formation/destruction of passive films in the potential region just before hydrogen evolution or due only to the hydrogen evolution were claimed by other authors [22,23].

In the investigated system the formation of passive films leading to oscillation according to the mechanism proposed by Vishomirskis [17] could be possible because of the absence of free complex forming agent. The minimal molar ratio of cadmium to cyanide ions in the electrolyte should be 1:4 which ensures the formation of soluble cyanide complexes of cadmium.

The possibility of formation of passive films is confirmed by the results presented in Fig. 2. In absence of free cyanide current oscillations can be registered on the rotating disc electrode (curve *a*). In the presence of free cyanide (0.3 M or more) the oscillations disappear (curves *b* and *c*) in spite of the hydrogen evolution at high cathodic potentials. This fact allows the conclusion, that the observed instability is more complicated than in the case reported by Kaneko et al. in the presence of 1.6 M free cyanide ions in the electrolyte [18].

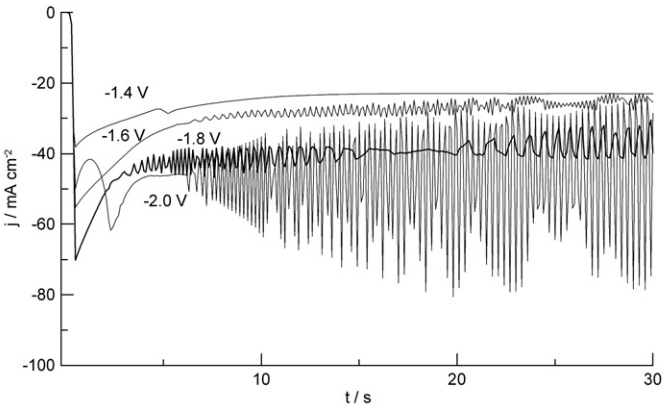

Fig. 3. Chronoamperometric curves, obtained at different potentials in the electrolyte for deposition of cadmium.

Possibly the suggested formation of passive films on the electrode surface is the reason for the observed current oscillations in potentiostatic regime. Similar oscillations were not observed by Kaneko et al. as well as by Vishomirskis, because both of them performed experiments with high concentration of free cyanide ions in the electrolyte.

Fig. 3 shows the current density oscillations in the chronoamperometric curves, registered on the vertical electrode at different applied potentials. The investigated potentials were chosen on the basis of the linear polarization curves – from −0.8 V to −2.0 V with a step of 0.2 V. Coulometric technique with set potential was used, i.e. the deposition was performed with the charge of 2 C cm^{-2}. After applying the respective potential and after a short transition time the reduction of cadmium starts.

Up to the applied potential of −1.4 V (the first presented curve in Fig. 3 there are not any oscillations registered on the vertical stationary electrode). At more negative potentials (−1.6 V) the oscillations start with very small amplitude, about 1–3 mA cm^{-2}. The change of the applied potential to −1.8 V results in an increase in the amplitude of the observed oscillations in the range between 2 and 10 mA cm^{-2} and at the potential of −2 V the amplitude reaches 50 mA cm^{-2}.

The observed behavior of the chronoamperometric curves does not elucidate the reason of the oscillations – it could be some changes in the active surface of the working electrode due to its blocking by passive layers or hydrogen bubbles.

Fig. 4 shows the chronopotentiometric curves, on stationary vertical electrode obtained at different current densities, chosen according to the linear polarization curves: at current densities up to 15 mA cm^{-2} which are smaller than the limiting current density the oscillations do not appear (curve *a*). The increase of the applied current to 20 mA cm^{-2} leads to the appearance of potential oscillations with amplitude of about 600–800 mV. The period of the oscillations is 19–23 s. At the higher current density (25 mA cm^{-2}) the amplitude of the oscillations increases to more than 1.2 V and the period decreases to 10–12 s. When potentials between −1.2 and −1.5 V are reached the oscillations appear. In this case, pulsating evolution (not massive) of hydrogen bubbles from the cathode surface could be observed by naked eyes. At increased current densities the oscillations stop as earlier, as higher current density is applied, possibly due to the massive hydrogen evolution.

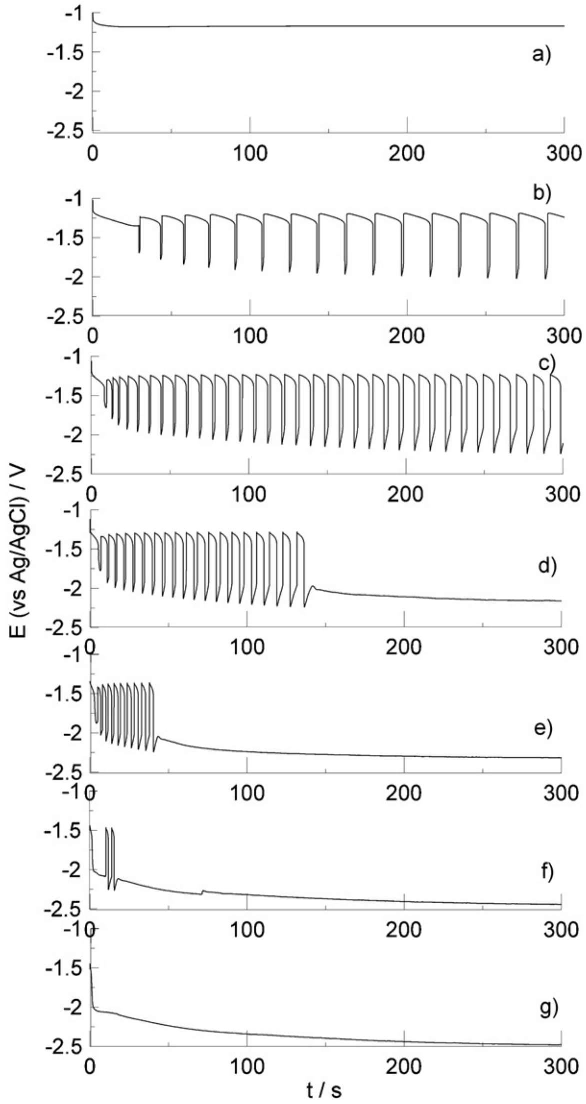

Fig. 4. Chronopotentiometric curves, obtained at different current densities in the cadmium electrolyte: (a) 15 mA cm^{-2}; (b) 20 mA cm^{-2}; (c) 25 mA cm^{-2}; (d) 3 mA cm^{-2}; (e) 40 mA cm^{-2}; (f) 50 mA cm^{-2}; (g) 60 mA cm^{-2}.

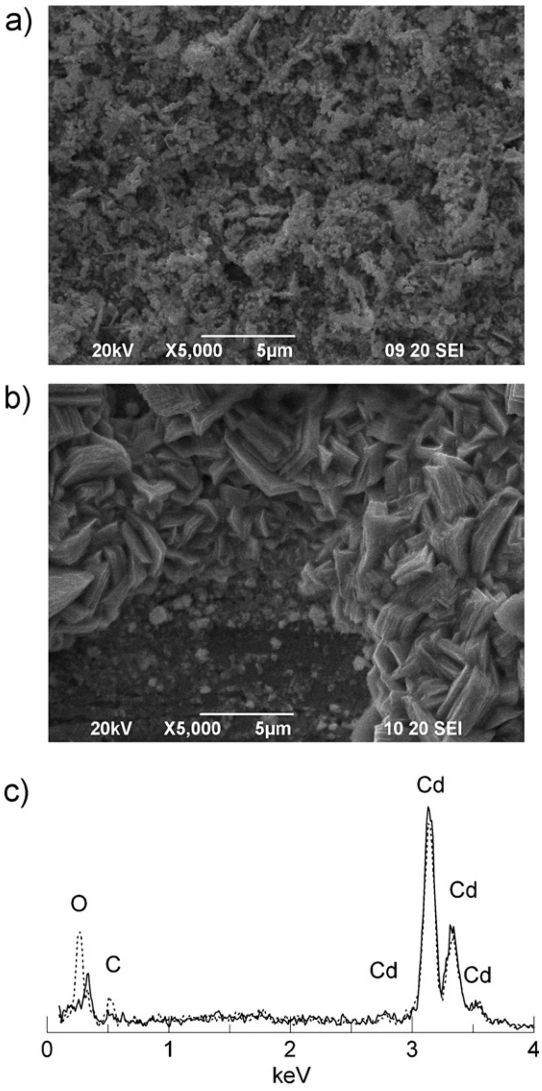

Fig. 5. (a) SEM image of the sample, deposited at −1.2 V in the electrolyte for cadmium deposition. (b) SEM image of the sample, deposited at −1.8 V in the electrolyte for cadmium deposition. (c) Comparison between distributions of the elements on the surface of both samples, determined by EDX (dashed line – at −1.2 V; solid line – at −1.8 V).

In order to answer the question what happens at the most positive potential of the oscillations, and what – at the most negative one, following experiments were performed: Two samples were deposited in the investigated cadmium electrolyte at the potentials of −1.2 V and −1.8 V (the most positive and most negative potentials in the oscillation curve (for instance, corresponding to Fig. 3c – 25 mA cm^{-2})) for 300 s.

The appearance of the coatings was different – the deposited one at −1.2 V was dark gray and the other, deposited at −1.8 V was silvery white with the metallic color of cadmium.

The morphology of these coatings is shown in Fig. 5. The composition of the deposit, obtained at −1.2 V contains about 85 wt.% of Cd, 8 wt.% of O and 6.9 wt.% of C, and of the deposit obtained at −1.8 V – about 96 wt.% of Cd, 3.3 wt.% of O, and absence of carbon.

The sponge-like morphology of the coating, obtained at −1.2 V is shown in Fig. 5a. In contrary, the coating, deposited at −1.8 V has morphology with well-defined crystals of cadmium onto the almost whole surface (Fig. 5b).

The comparison between the spectra of above mentioned samples is presented in Fig. 4c. The different content of the carbon and oxygen together with optical and morphological differences suggests presence of some passive film on the surface of the electrode. To clarify the nature of the formed film the sample with the coating, obtained at −1.2 V was investigated by X-ray photoelectron spectroscopy – a technique, which could perform not only quantitative and qualitative analysis of the present elements, but also their chemical state [21].

Fig. 6 shows the XPS spectra of the ascertained in the coatings elements – cadmium (Fig. 6a), oxygen (Fig. 6b) and carbon (Fig. 6c).

As typically for the d-elements the cadmium peak is split [21]. The maximum of the peak at the 401 eV (N1s) belongs to the C—N bond, the peak with maximum at the 404.8 eV indicate the existence of $Cd(OH)_2$ (Fig. 6a). Almost all oxygen is bonded in the hydroxide group – the peak with a maximum at 531 eV in the oxygen spectrum (Fig. 6b, peak 1) corresponds to hydroxide bonds and the peak at 533 eV (Fig. 6b, peak 2) could be assigned to the complicated structure of N—O—Cd compounds. Two peaks are registered in the carbon spectrum (Fig. 6c) – the first big one (peak 1) at 285 eV corresponds to carbon–hydrogen bonds, the second one (peak 2) at 287 eV (resulting from the de-convolution of the spectra) refers to the carbon–nitrogen bonds (typical bonds in the cyanide group) and

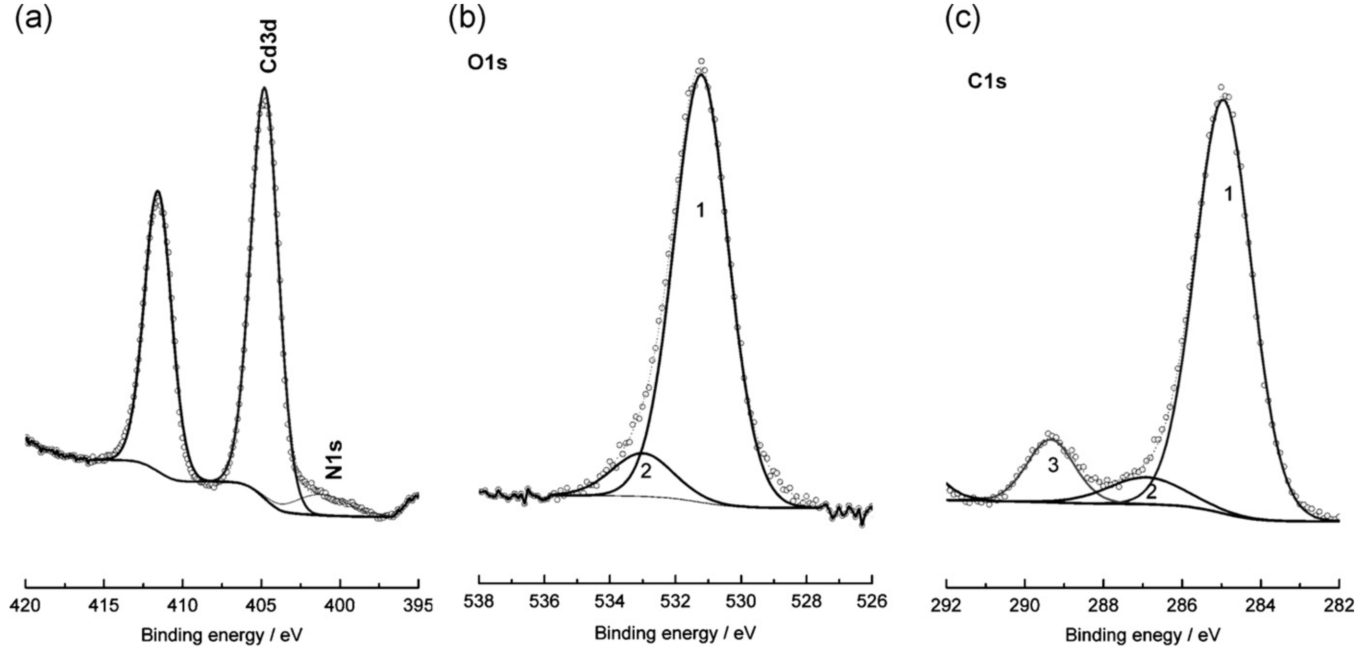

Fig. 6. XPS spectra, obtained in the coating, deposited at −1.2 V (SEM image of the sample is shown at Fig. 5a). a – cadmium; b – oxygen; c – carbon. Dotted line – experimental results, solid lines – deconvolution.

the third one (peak 3), with a maximum about 289 eV corresponds to complicated structures of C with N, O and H [21].

Therefore it could be stated, that at the most positive potential of the oscillations some passive film of cadmium hydroxide and cadmium cyanide is formed. Most probably, the passive film is a result of formation of some insoluble cadmium compounds due to some alkalization at the electrode/electrolyte interface and insufficient amount of complex forming cyanide ions. This film needs time to be formed in sufficient amount to be able to block the active surface (Fig. 4b–d). When the active surface is blocked, the potential increases rapidly to a level enough high to destroy the film and to start the hydrogen evolution. This could be the explanation why at higher current densities, which ensure a potential, more negative than the region of "passivity" the oscillations stop, independently of the visible massive hydrogen evolution under galvanostatic conditions.

3.2. Electrodeposition of silver–cadmium alloy

Fig. 7 presents the polarization curve, obtained in the Ag–Cd alloy electrolyte. A shoulder representing the diffusion-controlled deposition of Ag appears at −0.55 V and the limiting current density for the silver deposition in this electrolyte could be determined as 7 mA cm^{-2}. The co-deposition of Cd starts at the potentials, more negative than −1.0 V and the next shoulder appears at the potential of −1.3 V with a current density of 15 mA cm^{-2}, which could be assigned to the maximum rate of the reaction of co-deposition of Cd. The next increase in the current density, which could be connected with the massive hydrogen evolution. The electrode processes during deposition of both metals – silver and cadmium from cyanide complexes were discussed in a previous paper [7]. The galvanostatic chronoamperometric curves, obtained

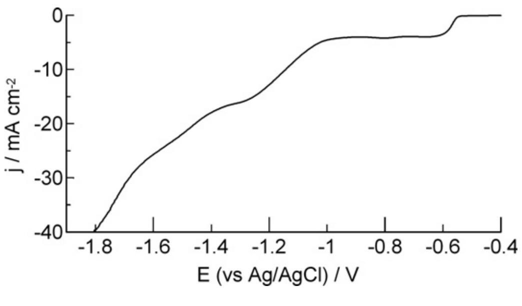

Fig. 7. Linear polarization curve for an electrolyte for silver–cadmium alloy deposition, scan rate 25 mV s^{-1}.

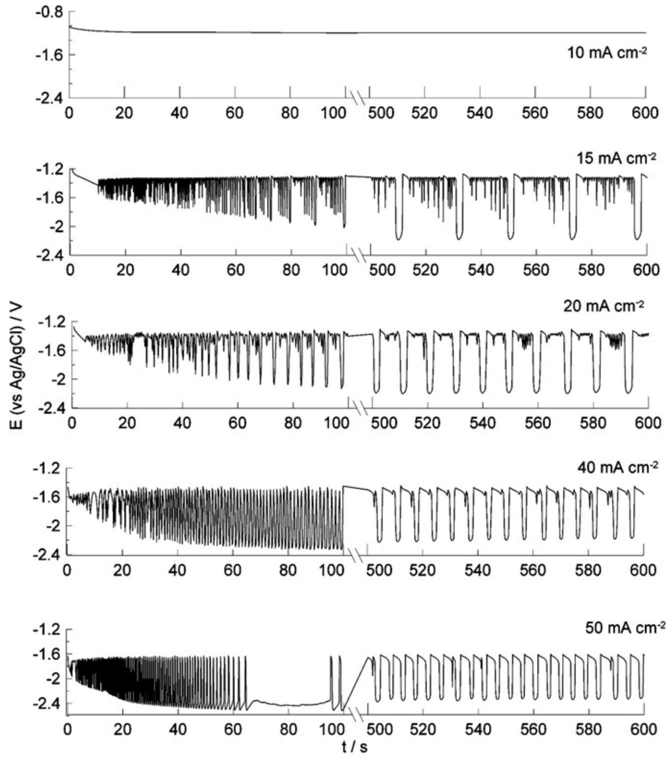

Fig. 8. Chronopotentiometric curves, obtained at different current densities in the alloy electrolyte onto vertical platinum electrode.

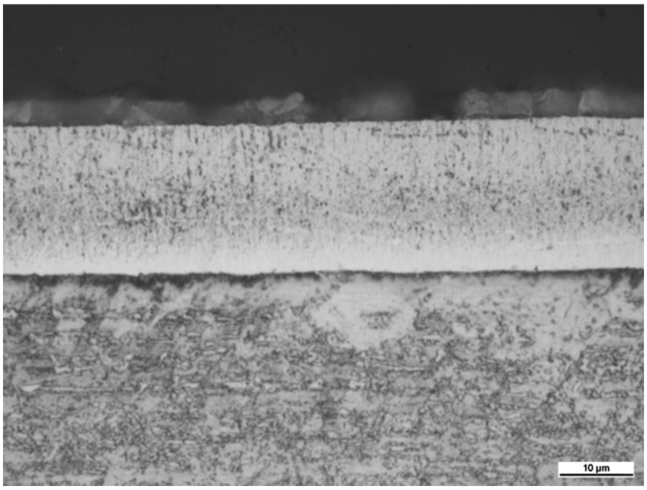

Fig. 9. Cross section of a silver–cadmium deposit, obtained in the electrolyte for silver–cadmium alloy deposition, 20 mA cm^{-2}, 30 min.

during deposition of silver–cadmium alloys from the investigated electrolyte are shown in Fig. 8.

At a current density of 10 mA cm^{-2} the obtained coatings have an average content of about 15–17 wt.% of Cd. Potential oscillations were not registered. The coatings are silver-white.

At an increased current density of 15 mA cm^{-2} the coating contains about 48–50 wt.% of Cd. The surface is bright and pronounced oscillations are observed. The increase of the current density leads to an increase in the content of Cd as follows: at 20 mA cm^{-2} – 80 wt.%, at 30 mA cm^{2} – 87 wt.%, and at 40 mA cm^{-2} – almost 96 wt.% of Cd. At higher cadmium content the morphology of the coatings become smoother. The potential oscillations start when the cadmium content of the deposit becomes sufficiently high (more than 45 wt.%). They are possibly connected with the decreased hydrogen overvoltage on the cadmium-rich alloy substrate and the formation of passive films which most probably have the same nature as those observed during pure cadmium electrodeposition. The contribution of the different possible reasons cannot be distinguished because of the formation of different alloy phases during deposition.

At the beginning of the process preferentially silver as more positive metal in the system [7,24] is deposited and the

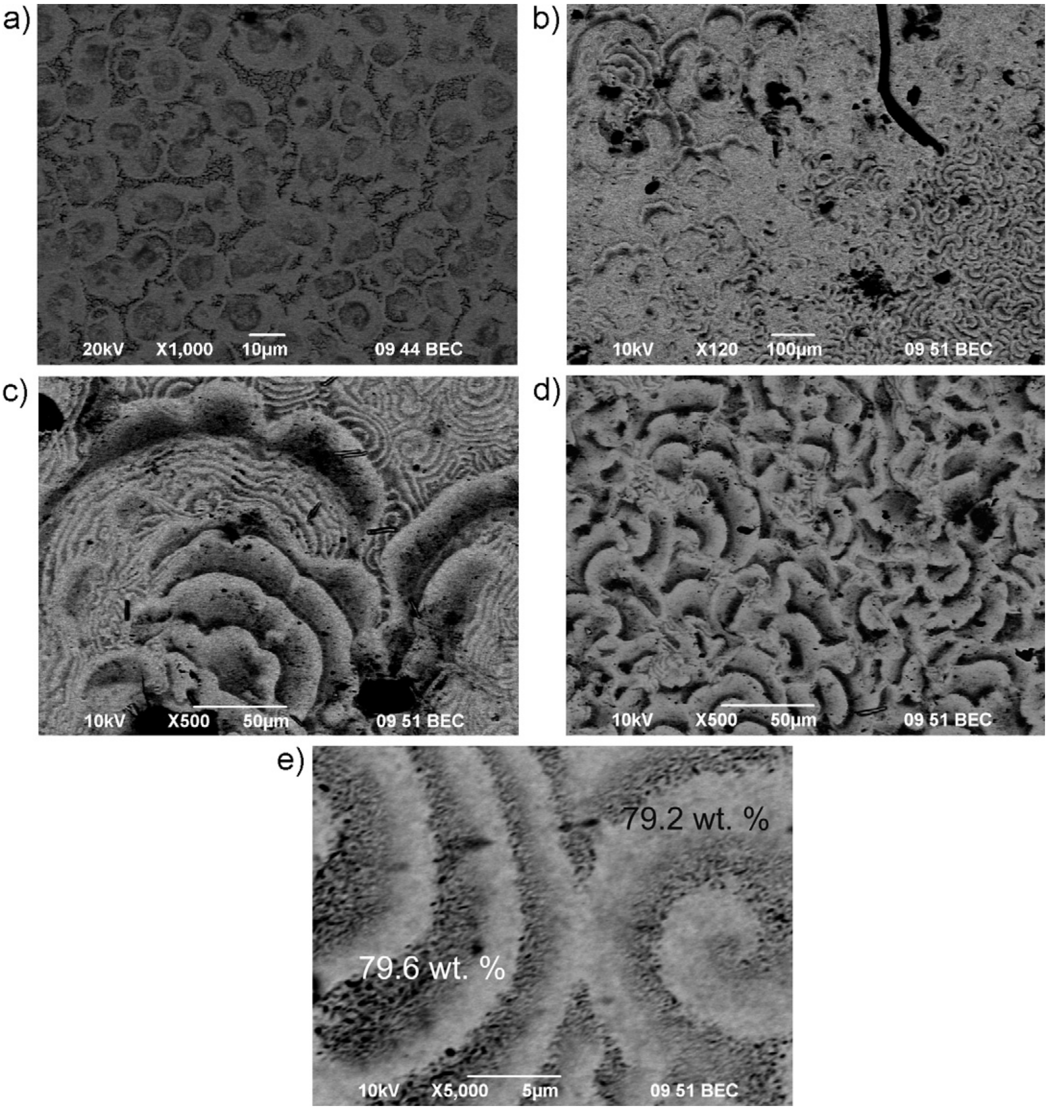

Fig. 10. Scanning electron microscopy images of the coatings obtained at different potentials: (a) −1.2 V; (b) −1.5 V; (c) and (d) different areas of the sample of Fig. 10b; (e) part of the area shown in Fig. 10c under higher magnification.

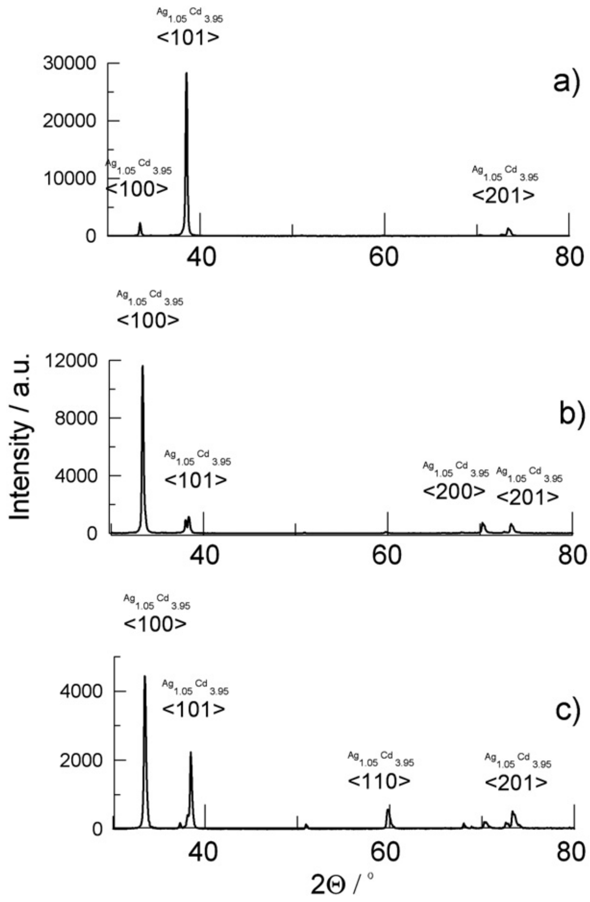

Fig. 11. XRD spectra of the potentiostatic deposited coatings: (a) −1.2 V, (b) −1.5 V and (c) −1.8 V.

oscillations are irregular possibly due to its influence. With increased deposition time they become more regular and reproducible and their period increases. With increased cadmium content the oscillations become again more regular, similar to the case of pure cadmium. Layered structures from different alloy phases could not be observed in the cross section of the electrodeposited silver–cadmium coatings by optical microscopy (Fig. 9).

Spatio-temporal structure formation was observed during electrodeposition of silver–cadmium alloys. Alloy coatings were deposited at 3 different potentials: at −1.2 V; −1.5 V and −1.8 V (potentials of just before the most positive, middle and most negative part of the oscillation curve obtained at 15 mA cm^{-2}) (Fig. 8). The obtained coatings were compact, dark-gray and bright.

Fig. 10a shows the morphology of the coating, obtained at the most positive potential of the oscillations (−1.2 V) during electrodeposition of Ag–Cd alloy in the investigated electrolyte. The deposit contains about 65 wt.% of Cd. Spots and details from not very well formed targets are visible on the electrode surface.

At the higher potentials of −1.5 V and −1.8 V the whole surface of the coatings is covered by periodical spatio-temporal structures in different scales (Fig. 10b–d). Because of the similarities in appearance and morphology between the samples obtained at −1.5 V and −1.8 V the morphology of the latter is not presented.

EDX analysis show, that in the both different morphological areas of the spatio-temporal structures the content of cadmium is almost the same – about 79 wt.% (Fig. 10e).

The XRD spectra of the samples, deposited at −1.2 V, −1.5 V and −1.8 V are presented in Fig. 11. In spite of the believed multiphase heterogeneity of the coatings, only reflections with a very strong preferred orientation of the crystallites of the hexagonal

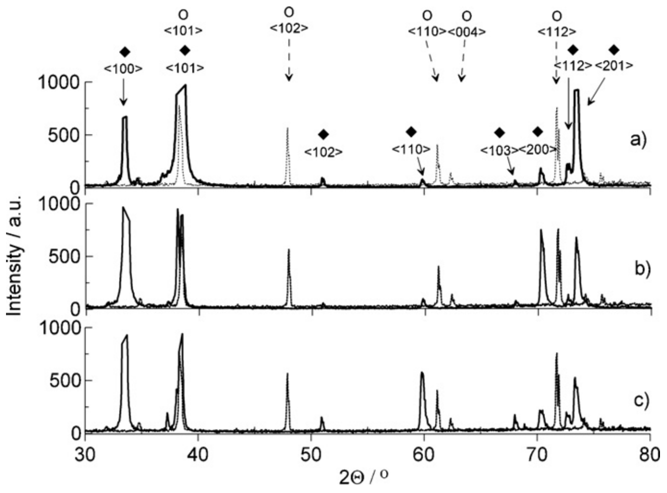

Fig. 12. Cut-outs (2Θ interval between 30° and 80°; intensity interval between 0 and 1000 counts) of the X-ray patterns presented in Fig. 11 (♦), overlaid by the XRD pattern of pure cadmium coatings (O), obtained at −1.5 V.

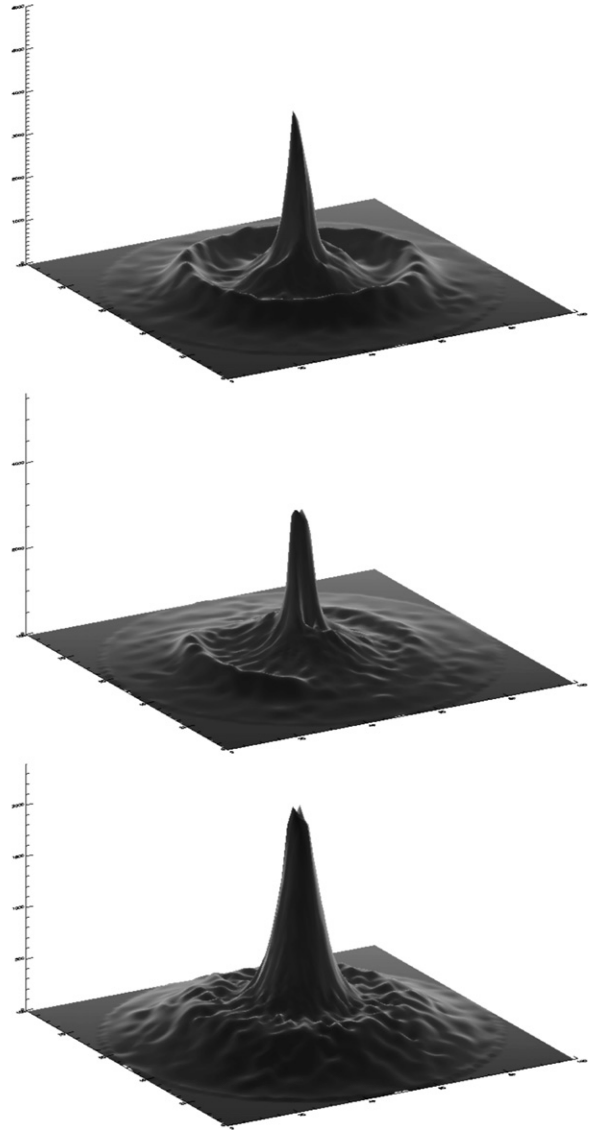

Fig. 13. 3D pole figures in direction ⟨1 0 1⟩ of the $Ag_{1.05}Cd_{3.95}$-phase in the alloy coatings, shown in Figs. 10 and 11 deposited at: (a) −1.2 V, (b) −1.5 V and (c) −1.8 V.

$Ag_{1.05}Cd_{3.95}$ phase (PDF 065-7991) are presented in all three spectra. The intensities of the reflexes in the three spectra are different. In the spectrum of the coating, deposited at −1.2 V the highest intensity is registered of the reflex corresponding to the ⟨1 0 1⟩ orientation, which reaches about 30 000 counts (a.u.). In the next two samples the highest reflex intensity corresponds to the ⟨1 0 0⟩ orientation and reaches 12 000 counts for the coatings, deposited at −1.5 V and 5000 counts for the coatings, deposited at −1.8 V.

The question which needs to be answered at this stage is: are the observed structures formed only by the phase $Ag_{1.05}Cd_{3.95}$ or by two phases – the phase $Ag_{1.05}Cd_{3.95}$ and the pure Cd phase, which peaks are possibly overlapped?

Fig. 12 presents the cut-outs ((*2Θ*)- in the same *2Θ* interval but with the upper limit of intensity counts (a.u.) of 1000) of the X-ray spectra presented in Fig. 11, overlaid by the spectrum of the cadmium coating, deposited at −1.5 V (dashed curve). The comparison between the spectra of pure cadmium coatings and each spectrum of the alloy coatings shows, that only one cadmium peak could appear on the same position as a peak of the ⟨1 0 1⟩-peak of the $Ag_{1.05}Cd_{3.95}$ phase (⟨1 0 1⟩). It could be presumed that the pure cadmium phase has a very strong preferred orientation along the axis ⟨1 0 1⟩ (PDF 03-065-3363) and due to the same type of crystal lattices (hcp) of both phases the coincidence of the corresponding maxima would be possible.

Texture investigations were performed along the ⟨1 0 1⟩-reflexes of the $Ag_{1.05}Cd_{3.95}$ phase in the three samples, deposited at −1.2 V, −1.5 V and −1.8 V (see Figs. 11 and 12). The 3D pole figures are presented in Fig. 13a–c. The split peak in the pole figures of the coatings, deposited at −1.5 V and −1.8 V at higher cadmium content in the coatings is visible (Fig. 13b and c). On this basis it could be assumed, that in the case of potentiostatic deposition, when the spatio-temporal structures cover the entire electrode surface they are formed by crystallites of the $Ag_{1.05}Cd_{3.95}$ phase and the highly oriented along the ⟨1 0 1⟩-axis pure Cd-phase.

4. Conclusions

During electrodeposition of cadmium both potentiostatic and galvanostatic oscillations are registered. Potentiostatic oscillations were observed for the first time. Experiments with different electrodes under different hydrodynamic conditions show the possibility of formation/destruction of passive layers on the electrode surface, which besides the hydrogen evolution under limiting current density conditions could be an additional promoter of the oscillation behavior of the system. The duration of the observed potential oscillations decreases with increased current density, due to massive hydrogen evolution. XPS investigations confirm the existence of passive films at potentials corresponding to the onset oscillations.

Potential oscillations are observed again during electrodeposition of Ag–Cd alloys at high current densities. They appear when the cadmium content in the deposits is more than 45 wt.% and they have possibly the same origin as the oscillations during cadmium electrodeposition. The period and regularity of the oscillations depend on the current density, respectively on the cadmium content.

At high cadmium content during alloy deposition, the formation of periodical structures consisting of different phases of the alloy is registered. The cadmium content of the different morphological areas of the patterns is almost identical. The XRD spectra of the obtained structured coatings suggest the existence of two textured phases, with very strong preferred orientations of the crystallites in the direction ⟨1 0 1⟩ of $Ag_{1.05}Cd_{3.95}$ and the pure cadmium phase.

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