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Pattern formation during electrodeposition of alloys

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Abstract The increase in the content of the alloying element in electrodeposited alloys reflects in the changes of their phase composition, when the saturation limit of the lattice of the basic metal is reached. At higher percentages, the excess amount of the alloying element forms one or more new, richer in this element phases. The coatings become multi-phase, heterogeneous and their physical–mechanical properties change. Sometimes an ordered distribution of the different phases of the heterogeneous alloy coating could be observed. Examples of selforganization phenomena during electrodeposition of different alloy systems, such as Ag-Sb, Ag-Bi, Ag-In, Ag-Sn, Ag-Cd, Cu-Sb and In-Co, resulting in pattern formation and formation of spatio-temporal structures on the surface of the obtained coatings are presented and compared. Instabilities resulting in potential or current oscillations are registered in most of the investigated systems. The phase composition of the alloy coatings and especially of the observed pattern is determined and some similarities in the structure of the phases forming the pattern are registered. The pattern formation is registered on the cathode not only in cyanide silver alloys electrolytes, but also during deposition of other alloy systems in acidic electrolytes like Cu-Sb and In-Co. The effect of the natural convection in nonagitated electrolytes on the pattern formation is discussed. The possibility of formation of periodic structured coatings without applying external electrical pulses which could result in appropriate modification of some properties of the electrodeposited alloys is demonstrated. The hypothesis that similar pattern formation could be observed in agitated electrolytes at different hydrodynamic and electrolysis

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conditions, when the same percentage or the same phase composition of the alloy is reached was examined for Ag-Cd, In-Co and Ag-Sb alloys in jet-plating experiments.

Keywords Alloys . Electrodeposition . Pattern formation . Self-organization

Introduction

The electrodeposition of alloys is aimed at the improvement of the surface properties of metallic articles. To obtain the desired surface properties, different metals are co-deposited in different ratios, depending on the electrolysis conditions, so that different alloy phases could be formed during electrodeposition. This results in different physical, chemical, mechanical etc. properties of the obtained coatings. The main task in the electrodeposition of alloy coatings is the determination of appropriate complex forming agents for the different metals able to bring their deposition potentials close to each other. In the normal case, the more positive element in the alloy system deposits preferentially and depending on the electrolysis conditions, there is a region of potentials or current densities where the obtained coatings consist only of this element. At higher potentials or current densities the co-deposition of the less positive element starts and in the "regular case", according to Brenner [[1\]](#page-7-0), its content in the deposited coatings increases at further deviation from the equilibrium state. Depending on its concentration in the electrolyte, the basic element deposits mostly under diffusion-controlled conditions. The increase in the content of the alloying element reflects in the changes of the phase composition of the deposited alloy coating. Depending on the solubility of the less positive element in the more positive one, i.e. of the alloying element in the basic metal, at its low contents solid solutions (homogeneous single-phase alloys) are formed. At higher

current densities, the amount of the deposited alloying element increases and the limit of its solubility in the basic metal is reached. This situation corresponds to extreme values of some properties of the obtained material, like internal stress, hardness, wear resistance, electrical resistance etc. When higher percentages are reached, the excess amount of the alloying element forms one or more richer in this element phases. The coatings become multi-phase, heterogeneous and their physical–mechanical properties change. The distribution of the different phases in the coating, as well as on its surface, is an object of many investigations, because the properties of the heterogeneous alloy coatings are a mixture of the properties of the different phases presented therein.

In most cases, the different phases are chaotically distributed in the bulk, as well as on the surface of the electrodeposited alloy and the electrodeposition process becomes very complex and case specific, because the co-deposition of both metals is performed simultaneously on substrate elements with different elemental and/or phase composition where some preferential deposition or underpotential deposition could be possible.

The deposition of alloys is often accompanied by electrochemical instabilities resulting in current or potential oscillations, comprehensively treated in the review papers of Wojtowich [[2\]](#page-7-0), Krischer [[3\]](#page-7-0), Koper [[4\]](#page-7-0) and many other scientists, and explained on the basis of autocatalytic processes, negative electrical resistance of the system, etc. The oscillatory processes result in a specific structure of the obtained alloy deposits, like spontaneous formation of layered structures without applying external electrical pulses. In this case the different sublayers have different metal percentages and are well recognizable by optical or electron microscopy in cross-sections of the deposits. Similar deposits are observed in many systems, like Ni-P [\[5](#page-7-0)], Ag-Pb, Ag-Cd, Cu-Pb, Ni-Fe [[6\]](#page-7-0), Ag-Sb [[7\]](#page-7-0), Ag-Sn [[8\]](#page-7-0) and many other alloy systems [[9\]](#page-7-0). In some cases the period of the structures could be directly related to the period of the registered oscillations [\[10\]](#page-7-0). In the Ag-Sb system, the limit of the sensitivity of the registration of current oscillations is set by the relation of the scale of the observed periodic structures to the diameter of the Haber-Luggine capillary in front of the electrode. The layered structures could be easily related to global oscillations of the system where the surface of the coating is more or less homogeneous for a certain time at the conditions of the extreme values of the oscillating electrochemical parameter. The formation of gradient layers does not correspond to systems showing bi-stability, where the registered electrochemical parameter changes abruptly.

Sometimes an ordered distribution of the different phases of the heterogeneous alloy coating could be observed. Having in mind that the electrochemical cell is an open non-linear system, electrochemically driven far from equilibrium, where co-operative phenomena, synergetic effects and ordered structure formation are possible, self-organization phenomena and formation of spatio-temporal structures during electrodeposition of several alloys could be expected.

The aim of this paper is to present and to compare some examples of self-organization phenomena during electrodeposition of alloys resulting in the formation of spatiotemporal structures on the surface of the obtained coatings.

Experimental

The deposition of the alloy coatings is performed at galvanostatic and in some cases also under potentiostatic conditions. The deposition of different alloy systems, like Ag-Sb [\[11](#page-7-0), [12](#page-7-0)], Ag-In [\[13](#page-7-0)], Ag-Bi [\[14](#page-7-0)], Ag-Sn [\[15](#page-7-0)], Ag-Cd [[16,](#page-7-0) [17](#page-7-0)], Cu-Sb [[18\]](#page-7-0), In-Co [\[19](#page-7-0), [20](#page-7-0)] etc. was thoroughly investigated and the electrolyte compositions and electrolysis conditions are given in the respective papers. Apart from electrochemical processes, the elemental as well as the phase composition of the deposited layers, their structure and the resulting physical–mechanical properties were investigated and reported elsewhere. The experiments in flowing electrolytes were performed in a special experimental jet-plating device. The construction of the cell is described elsewhere [[21](#page-7-0)]. The cathodes were brass sheets with a surface of 2.2×3.3 cm and the localized area for deposition was 1.77 cm². The coatings with a thickness between 1 and 100 μm were deposited at room temperature at a flow speed of the electrolyte of 400 $dm³h⁻¹$. The electrolyte was injected into the cell trough a titanium nozzle, connected as anode [\[21](#page-7-0)].

Results and discussion

More than 70 years ago in 1938, E. Raub and A. Schall [\[22](#page-7-0)] published in Germany results about the electrodeposition of silver-indium alloy coatings showing the transition from chaotically distributed phases of the alloy into well defined periodic spiral structures. According to their observation, the indium-rich phase sometimes forms well-defined crystallization spirals on the surface of the indium-poorer alloy coating. To our knowledge, it is the first known report of the self-organized formation of spatio-temporal structures and patterns on the surface of the cathode. The authors have not performed any in situ observation of the formation and spreading the structures on the electrode surface.

About 50 years later similar structure formation was observed during deposition of Ag-Sb alloys on copper substrates in non-agitated electrolytes [[12](#page-7-0)]. The role of the substrate during deposition of the silver alloys is negligible, because in all of them, in spite of the cyanide formulation,

the silver is the more positive element and the first layer formed on the foreign substrate is a layer consisting of pure silver. At low current densities pure silver coatings are formed, and reaching the deposition potential of antimony, the antimony starts to co-deposit, a region with a negative slope is registered on the stationary polarization curve [\[7](#page-7-0)]. At higher antimony contents the transition of the alphaphase (solid solution of Sb in Ag) of the deposit into a heterogeneous mixture of different textured phases of this alloy system is observed [\[11\]](#page-7-0). Considering the antimony percentage in the coatings, the texture and the phase composition of the alloy coatings with well-expressed spatiotemporal structures, the conclusion could be made, that the structures appear in the transition region of the alpha phase to the hexagonal ξ-phase and maybe are formed by these two phases. Moreover, there is a correspondence between the basic planes of the texture orientations $\langle 11 \rangle$ of the α phase and <0001> of the ξ-phase, which could contribute to the observed bi-stability. An example of the surface of an Ag-Sb coating with spatio-temporal structures is shown in Fig. 1.

Under potentiostatic conditions, current oscillations are registered in the Ag-Sb deposition system. The oscillations are observed in the region of negative slope of the stationary polarisation curve and their magnitude and their period decrease with increased potential, i.e. with increased deviation from the equilibrium state. In this case the oscillations correspond to the formation of coarse travelling waves consisting of phases with different antimony content and their propagation in front of the Haber-Luggin capillary, leading to the formation of layered structures visible in the crosssections of the deposit [\[10](#page-7-0)]. At higher potentials the waves become finer, a certain number of them cover the cathode surface in front of the capillary and the oscillations cannot be registered more with this configuration of the capillary. In this case the formation of smaller waves, spirals with different number of arms and target patterns is microscopically

Fig. 1 Optical image of a Ag-Sb alloy coating; 1.5 Adm⁻²; 12 wt.% Sb; 10 μm

observed. The deposition of antimony on its own substrate is easier than the one on the silver substrate [\[23](#page-7-0)], which ensures the necessary autocatalytic step for the appearance of the self-organization phenomenon. The movement of the coarse waves in vertical direction on the electrode surface suggested the assumption that the upwards flow of the electrolyte due to the natural convection is one of the crucial factors or necessary conditions for the appearance of this instability and the periodical pattern formation. The hypothesis was confirmed by experiments in a strong magnetic field (5 T) [[23\]](#page-7-0) where the natural convection was suppressed by the magnetohydrodynamic flow in horizontal direction at an appropriate orientation of the cell to the magnetic field. The results showed that the waves are situated perpendicularly to the flow of the electrolyte and moves in the direction of the flow. The observed instability was called "flow-induced electrochemical instability" [\[23](#page-7-0)].

The appropriate combination of the different factors during electrodeposition and the resulting velocity of the wave propagation probably play a very important role for the formation of the periodic structures as well. The waves in the case of the Ag-Sb spatio-temporal structures move with a velocity of several micrometers per second and the rotation speed of the spiral structures is of about 8° per second.

The spatio-temporal structures in the case of deposition of Ag-Bi alloy coatings are very different and clumsy, compared to these in the Ag-Sb system (Fig. 2).

Bismuth is deposited on copper or silver substrates reluctantly forming island coatings, it deposits on its own substrate easier than on silver, but the necessary autocatalytic step for the spatio-temporal structure formation is not so expressed. The deposition potentials of both metals are close to each other and playing with the concentration of free cyanide it is possible to shift the deposition potential of silver to more negative values compared to the deposition

Fig. 2 Optical image of a Ag-Bi alloy coating; 0.6 Adm⁻², 40 wt.% Bi, 22 μm

potential of bismuth. The obtained coatings are heterogeneous and consist of the α -phase of the alloy system (silver lattice) with a small amount of bismuth due to its low solubility in silver and pure bismuth [[14\]](#page-7-0). Instead of lamellar, like in the silver–antimony system, the cross-sections of the deposits show a columnar structure with white columns of the silver-rich phase and dark columns of the bismuthrich one. The structures on the electrode surface are not observed in the transition region between the α -phase and the next, richer in the alloying element phase of the alloy of several percents of bismuth, as it is in the case of silver– antimony alloys, but in a region of bismuth contents in the deposit of about 40–50 wt.%. Moreover, there are no crystallographic similarities in the structure of both phases forming the alloy. Oscillatory reactions are not typical for the system and all these factors contribute to the simple behaviour of the system concerning the variety of spatio-temporal structures.

The spatio-temporal structure formation during Ag-In alloy electrodeposition was re-discovered some years later [\[13](#page-7-0), [24](#page-7-0), [25\]](#page-7-0). The possibility to prepare clear, stable with time indium and silver–indium electrolytes was found, overcoming the difficulties originating from the low solubility of indium hydroxide in alkaline media [[26,](#page-7-0) [27\]](#page-7-0). A useful linear relationship between the molar ratio of both metals in the electrolyte and the current density was established, representing the area of conditions where the structures can be obtained. Waves, left- and right-handed spirals with different number of arms, and target patterns can be observed on the coatings surface [[13\]](#page-7-0). The solubility of indium in silver is about 19–20 wt.%, i.e. there is a wide region of indium percentages covering the deposition of homogeneous coatings consisting of the α -phase of the alloy. At higher indium percentages the spatio-temporal structure formation is registered, but the X-ray investigations reveal several alloy phases present in the coating, such as Ag (α-phase), Ag₃In, $In₄Ag₉$ and AgIn₂ phases, so that the question appears which phases have the optical contrast to allow the visibility of the detected structures. EDAX analysis shows similar results in both dark and light areas of the structures due to the higher penetration depth of the electron beam compared to the thickness of the alternatively formed layers of different composition during the fast spreading of the waves over the surface. The distance between two fronts of the structures $(\sim 100 \mu m)$ is about one order of magnitude higher than in the case of the Ag-Sb structures and the rotation speed is about two times lower (about 4° per second), that means the structures appear at another ratio of the space–time parameters. The determination of the phases forming the observed structures was possible by an appropriate combination of different X-ray, microscopic and electrochemical methods. The comparison between the obtained results by anodic linear sweep voltammetry, dissolving step by step the

different phases of the alloy coating with the X-ray measurements allows the conclusion that the structures are formed by the α -phase and the Ag₃In phase of the alloy [\[28](#page-7-0)]. In this case, similar to the spatio-temporal structures in the Ag-Sb system, the similarity of the dense packed (111) planes of the fcc lattice of the α -phase and the basic plane (0001) of the hexagonal lattice of the Ag_3In phase possibly contributes to the easy local transition from phase to phase during deposition [[29\]](#page-7-0).

Potential oscillations during galvanostatic deposition of the alloy are observed in contrast to the current oscillations in potentiostatic regime in Ag-Sb alloy electrodeposition [\[24\]](#page-7-0). The difference in the behaviours of both systems, allows the assumption of possible passivation effects on the surface during Ag-In alloy electrodeposition.

Heterogeneous coatings consisting of different phases could also be obtained during silver–cadmium alloy electrodeposition. According to the phase diagram of the system a relatively large number of phases could be expected at higher Cd contents of the deposit. The alloy can be easily deposited from simple cyanide electrolytes with sufficient amount of free cyanide. The deposition is of regular type according to Brenner [\[1](#page-7-0)], so that at low current densities silver-rich coatings are obtained and the cadmium content in the alloy increases with increasing current density. As a result, after saturation of the silver lattice with cadmium, again heterogeneous multi-phase coatings are deposited. The X-ray investigations show the presence of the α -phase of the alloy together with the phases AgCd, $Cd₃Ag$ and pure Cd in the deposits [[17\]](#page-7-0). By comparative ALSV and X-ray experiments, it was possible to determine the dissolution potentials of the galvanostatically or potentiostatically deposited heterogeneous alloy coatings [[30\]](#page-7-0). Moreover, intensive hydrogen evolution is observed when cadmium-rich phases form the coating, which leads to instabilities and intensive potential oscillations under galvanostatic conditions. Potentiostatic and galvanostatic oscillations during electrodeposition of pure cadmium are registered and reported elsewhere [[31\]](#page-7-0). The results allow the conclusion that not only the hydrogen evolution, but also the formation of passive layers on the cathode surface contribute to the observed oscillation behaviour. During electrodeposition of the alloy, potential oscillations are observed at high current densities when the cadmium content exceeds 45 wt.%. They are connected with the decreased hydrogen overvoltage on the cadmium-rich alloy substrate and the formation of passive films. A direct connection between oscillations and spatio-temporal structure formation was not established.

At cadmium contents higher than 65 wt.% the coatings become light and shiny and pattern formation is observed on their surface [[16,](#page-7-0) [31](#page-7-0), [32\]](#page-7-0).

Periodical spatio-temporal structures are formed at cadmium contents of about 80 wt.% (Fig. [3](#page-4-0)). Detailed X-ray

Fig. 3 Optical image of a Ag-Cd alloy coating; 1.2 Adm⁻², 69 wt.% Cd, 9 μm

investigations revealed, that in this case textured coatings consisting of the cadmium-rich hexagonal phase $Ag_{1.05}Cd_{3.95}$ and the pure cadmium phase are obtained. In this case the <101>—reflexes of the highly oriented alloy phase coincide with the <101>—reflexes of the highly oriented pure cadmium phase, i.e. the similarities in the basic crystallographic planes contribute to the spatiotemporal structure formation again. Moreover, in this case the structure formation is observed not in silver-based, but in the cadmium-based alloy [\[31](#page-7-0)]. The period of the observed structures is about 30 μ m, i.e. about three times larger than in the case of Ag-Sb and about three times smaller than in the case of Ag-In patterns. The formation and the spreading of the structures can be observed in situ in this system, too.

Taking into account the experience with the Ag-Sb, Ag-Bi, Ag-In and Ag-Cd alloy systems and performing the experiment under similar electrodeposition conditions (vertical electrode, non-agitated electrolyte with natural convection, diffusion-controlled deposition of the more positive element, high current densities allowing deposition of multi-phase heterogeneous coatings etc.), spatio-temporal structure formation was registered in some other alloy systems in alkaline electrolytes on silver basis (Ag-Sn) or in acid electrolytes in absence of silver (Cu-Sb and In-Co).

The saturation limit of the silver lattice with Sn is according to the phase diagram of the alloy of about 12 wt.% and in electrodeposited alloy higher contents of about 18 wt.% Sn [\[33](#page-7-0)] could be reached. The system is of regular type again, according to Brenner [[1\]](#page-7-0). The electrodeposition of Ag-Sn alloys with a tin content up to 40 wt. $%$ is possible from pyrophosphate-cyanide electrolytes [\[15](#page-7-0)]. At Sn contents higher than 16 wt.% tin-richer phases can be deposited together with the silver-rich α-phase of the alloy [[8](#page-7-0)]. X-ray investigations show the presence of pure Ag and Sn phases, as well as the presence of the orthorhombic Ag3Sn phase at higher Sn contents in the coatings which are well textured again. The phase heterogeneity is optically well visible and at Sn contents of about 35 wt.% a more or less ordered distribution of the different phase over the cathode surface can be observed [\[8](#page-7-0)]. All presented phases in the coating are crystallographically different, so that at this stage it is not possible to discuss any similarities in certain crystallographic planes which could contribute to the formation of the spatio-temporal structures. The movement of the spatiotemporal structures in vertical direction, which is possibly connected with the effect of the natural convection during electrodeposition results in layered coatings (Fig. 4). In the case of Ag-Sn alloy deposition possibly some additional factors should be taken into account, or some parameters should be changed in order to find well-formed spirals and target patterns in the electrodeposited coatings. Similar patterns are still not observed in this system.

Spiral and target patterns are still not observed in the Cu-Sb alloy system, too. The system is also from a regular type according to Brenner [[1\]](#page-7-0). Copper is the more positive element during electrodeposition from methanesulfonate-tartrate electrolytes and with increased current density antimony contents of about 50 wt.% could be reached [\[18](#page-7-0)]. The solubility of Sb in Cu according to the phase diagram is about 10 wt.% and heterogeneous multi-phase semi-bright coatings can be deposited with an antimony content exceeding the amount needed for the α -phase. X-ray investigations show the presence of the α -phase, pure antimony and the tetragonal phase Cu₂Sb in the deposits. At Sb contents of about 40 wt.% in the coating wave structures consisting of pink copper- and violet antimonyricher stripes can be observed on its surface [\[18\]](#page-7-0). A detailed analysis of the phase composition of the different areas is not conducted yet. Possibly X-ray investigations should be complemented with optical observations and ALSV electrochemical techniques to determine the phase composition of the violet stripes of the coatings.

The movement of the waves under the contribution of the natural convection over the electrode surface result in a

Fig. 4 Cross-section of a Ag-Sn coating; 1.4 Adm−² , 35 wt.% Sn, 30 μm

multilayered deposit combining the properties of the phases presented in the separate layers [[18\]](#page-7-0). The results allow the important conclusion that the formation of ordered periodic patterns can be also observed in silver-free and cyanide-free systems.

Such a system is the rare In-Co alloy one, deposited from acid citrate electrolytes [\[19](#page-7-0), [20,](#page-7-0) [32\]](#page-7-0). The deposition potentials of In and Co are close together and it is difficult to say which element is the more positive one in this system. Even at low current densities cobalt is co-deposited with indium and the indium content of the coatings decreases at higher current densities [[19,](#page-7-0) [20](#page-7-0)]. The obtained coatings are darkgrey and matt and with increased cobalt content their heterogeneity becomes more visible. When the content of indium is in the range between 50 and 30 wt.%, different areas of the electrode surface are covered by spatio-temporal structures in form of targets, waves and spirals (Fig. 5). The EDX analysis shows that the indium contents in the different dark and light zones do not differ so much and vary between 38 and 32 wt.%. Most possibly, the wave fronts move with a sufficiently high speed during deposition, so that the thickness of the dark and light layers formed during deposition is substantially smaller than the penetration depth of the electron-beam during EDX analysis. As a result, the beam penetrates through several light and dark layers, and the estimated average content of indium in both zones is similar. The coatings are stressed and cracked in spite of the contribution of the "soft" metal indium to the "hard" cobalt.

X-ray investigations show the presence of the three phases at high contents of cobalt in the coatings—In, Co and CoIn₃ [\[20](#page-7-0)]. It can be assumed that the phase CoIn₃ is one of the phases forming the spatio-temporal structures. A similarity in the structure between the In and CoIn₃ phases exist—both of them have a tetragonal lattice, but the dissolution experiments of the coating using ALSV show that the

Fig. 5 Optical image of the In-Co alloy coating; 1 Adm⁻², 62 wt.% Co, 3 μm

structures exist and are visible on the electrode surface after dissolution of the pure indium phase [\[32\]](#page-7-0). There is no similarity in the hexagonal lattice of cobalt and the tetragonal lattice of CoIn₃ which lead to the conclusion that such a similarity is not a crucial factor for the spatio-temporal structure formation in the alloy systems. Moreover, it should be the same deposition potential of the different phases forming the structure under the same electrolysis conditions.

Figure 6 shows the contents of the alloying elements that can be reached in the deposited coatings of the reported investigations, depending on the current density. These contents are different for the different alloy systems and they also depend on the electrolyte composition and on the concentrations of the metal ions, as well as on the concentrations of the complex forming agent used. At high current densities the curves reach a plateau region, corresponding to diffusion-limited deposition of both metals forming the alloy coating. The spatio-temporal structure formation is mostly registered in this region near to the maximal possible content of the alloying element in the deposit.

The content of the alloying element in the deposited alloy coatings can be drastically changed in agitated or flowing electrolytes. The facilitated mass transport process in agitated electrolytes results in the easier deposition of the more positive element and reduced content of the more negative one in the coating at the same current density. Consequently, the same elemental and phase composition of the alloy could be possibly achieved at higher current densities. The more intensive the agitation of the electrolyte, the higher is the current density. The hypothesis that performing the deposition in a flowing electrolyte at conditions leading to the same elemental composition that could result in the same or similar phase composition of the alloy like in the case of spatio-temporal structure formation on the electrode surface during deposition in non-agitated electrolytes, was proved in jet-plating experiments. AgCd, InCo and AgSb alloy systems were chosen as model systems. The deposition was

Fig. 6 Content of the alloying element in dependence of the current density in silent electrolytes

performed in electrolytes of the same composition as the ones in the case of silent electrolytes at ambient temperature with a flow speed of the electrolytes of 400 $\text{dm}^3 \text{h}^{-1}$. The contents of the alloying elements in the deposited coatings are presented in Fig. 7. The maximal contents are similar to those observed during deposition in silent electrolytes and they are reached at the much higher current densities of about 50 to 80 Adm^{-2} .

High-speed deposition experiments were performed with the Ag-Cd alloy system. Figure 8 shows the surface of a coating deposited at the high current density of 30 Adm⁻² and at the flow rate of the electrolyte of 400 dm^3h^{-1} with 65 wt.% of Cd. The formation of spatio-temporal structures is visible, maybe not so contrast-rich compared to the structures from the silent electrolyte, but leading to the conclusion, that the spatio-temporal structure formation can be observed under different hydrodynamic conditions in flowing electrolytes, when the elemental and the phase composition of the coatings correspond to those obtained in silent electrolytes.

Microscopic investigations of the obtained In-Co coatings in the jet-cell show spatio-temporal pattern formation onto the electrode surface (Fig. 9). The thickness of the coating is approximately 1 μm and the observed structures cover almost the whole surface of the deposit. A big variety of patterns, like spirals, waves, targets in different scales could be observed on the surface of the jet-cell cathode. The EDX analysis shows indium content of about 70–75 wt.% in the different areas of the observed structures which exceeds the values of the indium content in the spatio-temporal structures obtained in the silent electrolytes [[20\]](#page-7-0), but is still in the concentration interval where the phase $Coln₃$ is registered. The conclusion could be made that it is not necessary to have the same elemental composition in order to

Fig. 8 Optical image of a Ag-Cd alloy coating, obtained under highspeed plating conditions; 30 Adm⁻², 67 wt.% Cd, 6 μm

register the structures. This composition should be in the interval where the corresponding phases forming the structures could exist. In this case the effect of the natural convection on the pattern formation is not essential; moreover, at these flow rates of the electrolyte it should be neglected.

An exception was observed during electrodeposition under jet-plating conditions of Ag-Sb coatings. In this case, a spatio-temporal structure formation was not registered in flowing electrolytes. The appropriate conditions might not have been found (maybe other metal concentrations in the electrolyte should be used), or some additional factors should be taken into account, or the system differs markedly in its behaviour from the other two systems In-Co and Ag-Cd. Future investigations should give the answer.

Fig. 7 Content of the alloying element in dependence of current density under high-speed plating conditions

Fig. 9 Optical image of a In-Co alloy coating, obtained under highspeed plating conditions; 50 Adm⁻², 35 wt.% Co, 1.7 μm

 $100 \mu m$

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