



COBALT-INDIUM ALLOYS ELECTRODEPOSITION FROM CITRATE ELECTROLYTE AND SPATIO-TEMPORAL PATTERNS FORMATION

ELECTRODEPÓSITO DE ALEACIONES COBALTO-INDIO A PARTIR DE ELECTROLITOS DE CITRATO Y FORMACIÓN DE PATRONES ESPACIO-TEMPORALES

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Abstract

Cyclic voltammetry technique was used to compare the mechanism of the deposition of In, Co and Co-In from citrate electrolytes. Samples of Co-In coatings were electrodeposited at different current densities to permit the subsequent investigation of their physicochemical characteristics. It was established a strong relation between Co-In phase composition and the electrolysis conditions. At low current densities below the limiting current only In was deposited. At higher current the alloy phase of CoIn₃ was formed, besides that of In, and minority phases were Co and Co(OH)₂. At higher current densities of about 0.8-1.5 A/dm², when intensive hydrogen evolution was observed, specific patterns (spirals, waves, targets) were visible onto the Co-In coating surfaces, considered as spatio-temporal structures. The pattern formation could be promoted by the specific hydrodynamic conditions close to the cathode-electrolyte interface and by the concentration fluctuation of the ionic species.

Keywords: electrodeposition, cobalt-indium alloy, cyclic voltammetry, spatio-temporal patterns, XRD, SEM-EDX.

Resumen

La técnica de voltametría cíclica fue utilizada para comparar el mecanismo de deposición de In, Co y Co-In a partir de electrolitos de citrato. Muestras de los recubrimientos de Co-In fueron electrodepositados a diferentes densidades de corriente para poder realizar una investigación posterior de sus características fisicoquímicas. Se estableció que hay una fuerte relación entre la composición de las fases Co-In y las condiciones de la electrólisis. A densidades de corriente por debajo de la corriente límite, solo fue depositado In. A densidades de corriente mayores se formó la fase CoIn₃, al igual que In, y como fases minoritarias fueron Co y Co(OH)₂. A mayores densidades de corriente entre 0.8-1.5 A/dm², cuando se da una intensiva evolución de hidrógeno, patrones específicos visibles (ondas, espirales y *targets*) fueron observados sobre la superficie de los depósitos de Co-In, que son considerados como estructuras espacio-temporales. La formación de estos patrones podría ser promovida por las condiciones hidrodinámicas específicas cerca de la interfase del cátodo-electrolito y por la fluctuación de la concentración de las especies iónicas.

Palabras clave: electrodeposición, aleaciones cobalto-indio, voltametría cíclica, patrones espacio-temporales, XRD, SEM-EDX.

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1 Introduction

The study of the metal electrodeposition processes is an important area in electrochemistry because the modern technology requires the development of new materials with specific properties to specific applications. The knowledge of the electrodeposition mechanism and the structure of obtained coatings are of the prime importance, since by this way, it is possible to modify the properties of the material. The electrodeposition process is much more complicated when it comes to the electrodeposition of two metals, forming an alloy (Brenner, 1963; Skirstymonskaya, 1964; Srivastava and Nigam, 1979; Paunovich and Schlesinger, 1998).

During recent years studies reported that the electrodeposition of several silver alloys, such as Ag-In (Dobrovolska, *et al.*, 2005) Ag-Bi (Krastev, *et al.*, 2004), Ag-Sb (Krastev and Nikolova, 1986; Krastev, *et al.*, 1989; Krastev and Koper, 1995) and Ag-Sn (Hrussanova and Krastev, 2009), presented the formation of the interesting and novel patterns on alloy surfaces, known as spatio-temporal structures. They are usually observed in electrolysis conditions when the process is very complicated, characteristic for non-linear dynamic processes, under natural convection flow and kept far from electrochemical equilibrium (Krastev and Nikolova, 1986; Krischer, 1999). The interest in such patterns arises in a wide variety of fields of the natural sciences. Particularly, in physical chemistry the observation of wave propagation, target patterns and spiral waves of chemical activity is not at all uncommon (Cross and Hohenberg, 1993; Epstein, 1991; Ataullakhanov, *et al.*, 2004). The spatio-temporal structures are considered as spontaneous self-organization of the system that is composed of few or many components. Self-organization phenomena in the case of electrodeposition of alloys can be considered as concentration fluctuation of the metal ions on the electrode surface and this is spontaneously amplified by the coupling between the autocatalytic nature of the electrodeposited ions and the flow of the electrolyte solution (flow induced electrochemical instability).

As a result of the reported research works on silver alloys (Dobrovolska, *et al.*, 2005; Krastev, *et al.*, 2004; Krastev and Nikolova, 1986; Krastev, *et al.*, 1989; Krastev and Koper, 1995; Hrussanova and Krastev, 2009) aroused the interest to study the possibility of Co-In alloy, formed by magnetic and diamagnetic metals, and to find the electrolysis conditions for specific patterns and self-organized

structure formation. Electrodeposited Co-In alloys are not extensively studied and we found only the report of Sadana *et al.* (1975). The authors have established that the Co-In alloys, ranging in composition from 2.0 to 90.6% Co, could be electrodeposited from aqueous solutions.

The aim of our research was to obtain an electrodeposited Co-In in a wide compositional range from citrate electrolyte, allowing searching for their physicochemical properties.

2 Experimental

The indium, cobalt and alloy coatings were deposited from citrate electrolytes that contain 0.088 M diammonium hydrogen citrate (DAHC): indium from solution of 0.044 M In as InCl_3 and DAHC; cobalt from 0.51 M Co as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and DAHC; Co-In alloy coatings from solution containing 0.044 M In as InCl_3 , 0.51 M Co as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and DAHC. The hydroxycarboxylic acid DAHC was used as pH buffer agent (Adin, *et al.*, 1970), promoting better cathode current efficiency (Sadana *et al.*, 1975). The electrolytes were prepared using chemicals of *pro analysis* purity and distilled water. The cyclic voltammetry (-1.8V to +1.8V) were performed using computerized potentiostat/galvanostat (GAMRY 600, PHE 200), in 100 cm³ tri-electrode glass cell at room temperature and 5 mV/s scan rate. The working electrode (1 cm²) and the two counter electrodes (4 cm²) were made from Pt; as reference electrode Ag/AgCl was used. The cathode current efficiency of Co, In and Co-In coatings, deposited at different current density on copper substrates (2x1 cm), were determined gravimetrically. Samples of Co-In coatings with thickness about 5-7 μm were deposited also on copper substrates and used for SEM-EDX and XRD phase analysis (at 2θ angles from 25° to 70° with monochromatic $\text{CuK}\alpha$ irradiation, $\lambda = 1.5405 \text{ \AA}$).

3 Results and discussions

3.1 Cyclic voltammetry of Co, In and Co-In processes

The emphasis in the discussion of the electrodeposition mechanism is based on the CV's curves principally in the cathodic part, where the process of the electrodeposition takes place. The CV's

were also reordered in electrolytes in absence of citrate (DAHC), which are not presented in this report.

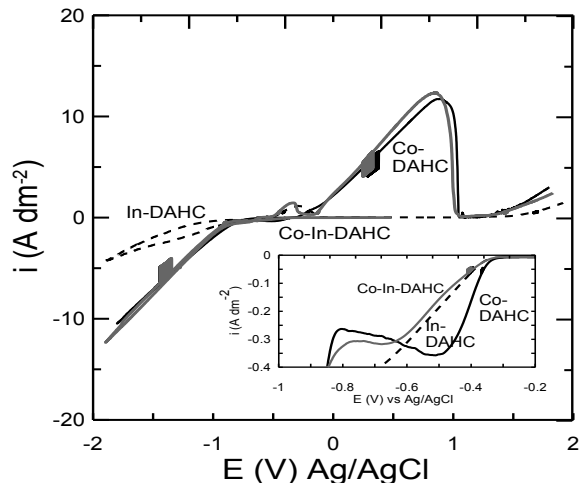


Fig. 1. Cyclic voltammety curves of Co-In in citrate electrolyte (DAHC), compared with the CV's Co (Co-DAHC) and In (In-DAHC).

Figure 1 compares the cyclic voltammety curves of Co (solid line), In (dashed line) and Co-In alloy (grey line) deposition from citrate electrolytes (DAHC). The discussion is more focused on Co-In deposition. As can be seen, the Co-In deposition starts at potential of -400 mV that is very closely to those indium (-400 mV) and cobalt (-350 mV) in citrate electrolytes. The Co-In cathodic curve runs further up to -650 mV in a parallel form to that of In, however at -0.35 A/dm² reaches the limiting current density forming plateau, characteristic also for Co-DAHC cathodic curve. The cathode efficiency of the indium electrodeposition in presence of DAHC was almost constant between 19% (0.3 A/dm²) and 23% (2 A/dm²).

It can be see also (Fig. 1) that the cathodic process of Co-DAHC occurs with lower overvoltage than those of In-DAHC and Co-In co-deposition. Later (at -780 mV) the cathodic current of Co-In-DAHC increases abruptly, when the hydrogen evolution goes more intensively (with bubble formation). The simultaneous hydrogen evolution could change the pH of the cathode-electrolyte interface, getting a local alkalization that could promote the formation of oxide/hydroxides of In or Co. To verify the appearance of any hydroxide over the electrode surface, Co-DAHC coatings were electrodeposited at different cathodic densities and analyzed by XRD; the results are discussed further in this report.

During the anodic period a small peak at -350 mV

is observed, corresponding probably to the dissolution of the formed in the cathodic period Co-In alloy. The second high anodic peak at more positive potential (867 mV) is almost in coincidence with that of Co-DAHC anodic peak (Fig. 1) and for this reason it could be attributed to the active dissolution of pure Co, as a part of the Co-In alloy.

The cathode current efficiencies for Co-In deposits at 0.3 A/dm² up to 2.0 A/dm² were changing in a small interval, from 64% to 74%, respectively. The efficiency of Co process revealed values from 25% to 74% in the same interval of cathodic densities, while the efficiency of In-DAHC depositions was almost lower and relatively constant (19% - 23%). As was noted before, the deposition process is followed by simultaneous hydrogen evolution that consumes a part of cathodic current.

3.2 Phase composition (XRD) of Co-In deposits

In the reported studies about Co-In metallurgical system, using data of enthalpy formation and phase diagrams, there exists considerable disagreement about Co-In composition. According to Khlaporova (1954) and Elliot (1965), there are three intermediate compounds: Co_3In_2 , CoIn and CoIn_2 . But later, Dasarathy (1967) claimed the existence of only two intermediate phases, Co_3In_2 and CoIn . However, later Schoebel and Stadelmaier (1970), and more recently Bros *et al.* (1966) reported that the intermediate compounds in this system were CoIn_3 and CoIn_2 . According to Sadana *et al.* (1975) no evidence for the existence of CoIn_2 or CoIn was found during the study of annealed and unannealed alloys deposits: the authors reported Co_3In_2 and CoIn_3 alloy phases.

The registered XRD patterns of Co-In alloy coatings (Fig. 2), electrodeposited at different cathodic densities, revealed that there is a strong relation between phase composition and the cathodic current density, e.g. electrolysis conditions.

For example, at low current of 0.3 A/dm² only metallic indium phase (tetragonal structure) was detected. This fact could be understood considering that at that current density the Co-In cathodic curve is closer to the indium one (Fig. 1). However, at higher current density of 0.5 A/dm² the XRD relative intensity of pattern suggest two crystalline phases: CoIn_3 alloy (tetragonal structure; $a=b=0.683$ nm, $c=0.0519$ nm) and indium. As a minority phase was found Co(OH)_2 , as a consequence of local alkalization of electrode-electrolyte interface. The CoIn_3 phase

coincides with the reported one for metallurgical Co-In alloys [20,21].

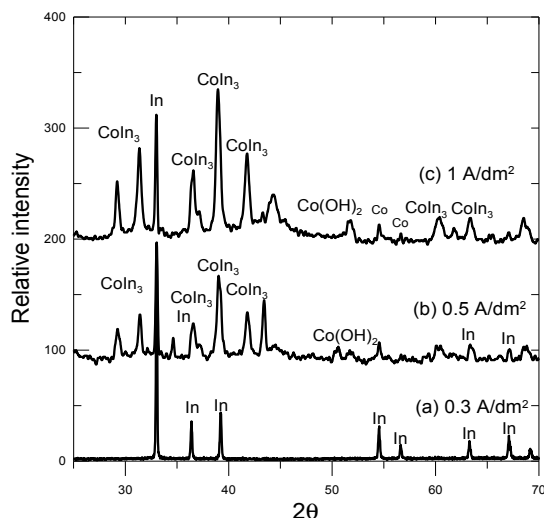


Fig. 2. XRD patterns of Co-In alloy samples electrodeposited at (a) 0.3 A/dm² (30 min); (b) 0.5 A/dm² (60 min); (c) 1 A/dm² (60 min).

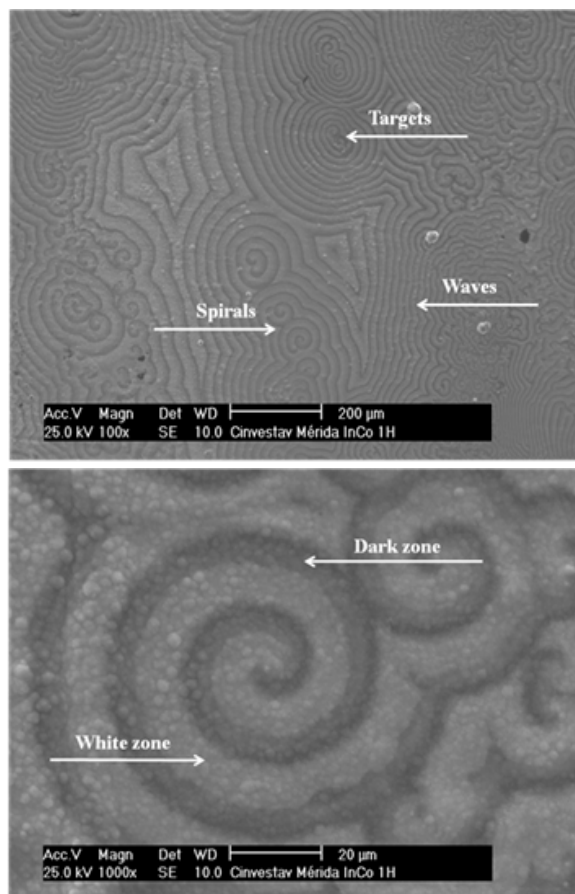


Fig. 3. SEM surface image (100x) of Co-In coating deposited during 60 min at 1 A/dm²: spirals (left and

right hand), waves and targets (a); dark zone in spirals and clearer (“white”) zones (b).

At more higher current density of 1 A/dm² (Fig. 1), after limiting current where an intensive hydrogen evolution is observed, the XRD pattern revealed that CoIn₃ alloy is the majority phase, followed by In; Co and Co(OH)₂ were detected as minority ones. The formed hydrogen bubbles near the electrode interface produce a specific natural convection flow (agitation) that could facilitate the diffusion process of both metal species deposited on the cathode. The reported results indicate that there is a strong relation between Co-In phase composition and the electrolysis conditions, which control the co-deposition process of both metals. At low current densities (before diffusion limit) it was not possible to obtain Co-In alloy. When the current density shifts to values closer to the diffusion limit the alloy deposition (CoIn₃) was reached, besides the phase of In.

4 Spatial-temporal pattern formation

Co-In samples were deposited at 1 A/dm² (5 to 90 min), when co-deposition process is strongly controlled by the diffusion of the ionic species and by the simultaneous intensive hydrogen evolution (Fig. 1). Even in a short time of 5 min, the surface of Co-In deposit showed specific patterns: left and right hand spirals, waves, targets. The patterns (in darker color) were visible *in situ* and also after switching off the current, and removing the coating sample from the electrolyte; they are stable during a long time of storage at room temperature and do not changed for months. Figure 3 shows SEM image (100x) of well-defined patterns on the Co-In surface. The surface elemental analysis SEM-EDX revealed that both zones (Fig. 3b), spiral pattern (darker) and clearer (“white”) one contain twice higher Co (60-64%) than that of In (30%-26%). Probably the difference in colour is due to the existence of two textured phases. These facts still need their explanation. It can be seen also (Fig. 3b) that the surface morphology of the Co-In deposit is very homogeneous, presenting similar grain (cluster) size. The EDX detected also the presence of oxygen (10%) that could be related to the formed cobalt oxyhydroxide. White crystalline clusters were formed at higher time of deposition (more than 90 min), which elemental analysis revealed pure In (100%).

The formed patterns are more visible at the bottom of the sample, where the intensive hydrogen bubble evolution promotes natural agitation and the flow dynamics in this area of the electrode is very specific. According to Raub and Schall (1938), whose have first observed similar structures during the deposition of Ag-Sb, was necessary electrolyte agitation.

Conclusions

Cyclic voltammetry technique was used to compare the mechanism of the deposition of In, Co and Co-In from citrate electrolytes. It was established a strong relation between Co-In phase composition and the electrolysis conditions. At low current densities below the limiting current only In is deposited. At higher current the alloy phase of CoIn₃ is formed, besides that of In. Minority phases are Co and Co(OH)₂. At galvanostatic conditions, at current higher than the limiting current density and in the presence of intensive hydrogen evolution, it was possible to obtain visible specific space-time structures (spirals, wave, targets) onto the Co-In samples, considered as spatio-temporal structures.

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