THE INFLUENCE OF WORKING PARAMETERS AGAINST COMPOSITION OF ZINC-COBALT ALLOY CO-DEPOSITED LAYERS

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Abstract

Electrodeposited alloys are important in industry due to their properties which are superior to those of single metal layer. Zinc-cobalt alloys were co-deposited on gold substrate. Composition of the layers was established using SEM-EDX techniques. The influence of working parameters against stoichiometric composition of alloys was studied in order to find optimal conditions to achieve a desired final product. Some discussion about reaction mechanism was opened based on EIS diagrams.

Keywords: zinc-cobalt alloy, co-deposition, SEM-EDX technique, EIS

1. INTRODUCTION

In machine building industry zinc remains the principal metal for anti-corrosion applications, especially for protection of steel products. In the last years there were registered a significant increasing of electrodeposited alloys, because it was an important market demand for products with high quality coatings. In the front of list there are the automotive industry and the aerospace industry, also those applications for electrical components and for fixing devices.

In anticorrosion protection, cadmium is more used together with zinc. Because consumption of heavy metals has to be reduced year by year, until total elimination, there are researching to creates new technologies and one of them is based on alloys electrochemically deposited, such as Zn-Ni, Zn-Co, Zn-Fe.

The electrochemical reactions which occur on cathode surface could be considered having evolution on two steps, after Matlosz. Zinc ions are deposited on their own substrate, on gold substrate used and on cobalt substrate. Also, cobalt ions are deposited on their own substrate, on gold substrate and on the zinc substrate. More, there have to be considered secondary reactions, those where ions Zn^{2+} combine with hydrogen to form ZnH^{+}, as well as ions Co^{2+} combine with hydrogen to form CoH^{+}. Those intermediary species, formed in the adsorption process, will decompose finally in metallic Zn, and metallic Co respectively [1, 2].

The reactions mechanism may be written as follow:

$$Co^{2+} + e^{-} \rightarrow Co^{+}_{ads}$$
$$Co^{+}_{ads} + e \rightarrow Co$$
$$Co + H^{+} \rightarrow CoH^{+}_{ads}$$
$$CoH^{+}_{ads} + H^{+} + 2e^{-} \rightarrow Co + H_2$$

$$\begin{aligned} Zn^{2+} + e^- &\rightarrow Zn^+_{ads} \\ Zn^+ + e^- &\rightarrow Zn \\ Zn + H^+ &\rightarrow ZnH^+_{ads} \\ ZnH^+_{ads} + H^+ + 2e^- &\rightarrow Zn + H_2 \end{aligned} \qquad (1)$$

Co^{2+} and Zn^{2+} are dissolved as metallic ions, hydrolyzed or not. Co^+_{ads} and Zn^+_{ads} which could or couldn't contain the hydroxyl group, are adsorbed univalent in intermediary reactions. Co and Zn form the metallic layers of nickel and zinc respectively.

The kinetic of mass transfer is supposed respects the Butler-Volmer equation:

$$i = i_0 \left\{ \exp\left[\frac{(1-\beta)F\eta}{RT} \right] - \exp\left[\frac{-\beta F\eta}{RT} \right] \right\} \quad , \qquad (2)$$

where η is the over potential which measures the difference between the potential value when through interface is passed a current and the equilibrium potential; β is called coefficient of symmetry; F is the Faraday's constant, R - universal constant of gases, T – absolute temperature; i is effective cathode current density and i_0 is the exchange current density [3].

In far away equilibrium conditions the anode reactions could be neglected.

2. EXPERIMENTAL DETAILS

The deposition of Zn-Co thin films was electrochemically performed at INCDFM-Bucharest-Magurele (National Institute of Researches and Development for Physics of Materials). To obtain layers with desired properties it was necessary to investigate the influence of deposition conditions (like discharging potential, bath composition, temperature and stirring of the electrolyte during the deposition process) against structure, morphology, composition, aspect and optical properties of the layers.

We used the following compositions to prepare the electrolyte low acid for deposing of Zn-Co alloys: (the first solution) zinc chloride ($ZnCl_2$) 63 $g \cdot L^{-1}$, cobalt chloride ($CoCl_2 \cdot 6H_2O$) 15.32 $g \cdot L^{-1}$, potassium chloride 225 $g \cdot L^{-1}$, boric acid (H_3BO_3) 15-25 g·L, pH 5-6, t(°C) 21-38°C; (the second solution) zinc chloride ($ZnCl_2$) 63 $g \cdot L^{-1}$, cobalt chloride ($CoCl_2 \cdot 6H_2O$) 8.16 $g \cdot L^{-1}$, potassium chloride 225 $g \cdot L^{-1}$, boric acid (H_3BO_3) 15-25 g·L, pH 5-6, t(°C) 21-38°C.

As working electrode we used a glass lamella having a gold thin layer deposed using sputtering method (using a Hummer 6 installation). The pH level was maintained between 5 and 6 naturally without addition of acids, because the salts were chlorides which after electrolytic dissociation have an acid character (excepting KCl, salt of a strong acid and a strong base). The working temperature was between 21°C and 38°C.

A good adhesion was obtained using the next described method. The glass lamella was first polished, then gold plated in a sputtering installation. Also there were tried some proves with bright glass, but the result was negative because all the gold dissolved themselves in solution.

As reference electrode it was used the calomel electrode immersed directly in the electrolytic cell.

Co-deposition of zinc-cobalt layers was performed using a potentiostat-galvanostat VoltaLab 40 and soft-

ware VoltaMaster 4.

Layers were analyzed with an EDX Shimadzu 720, at Stefan cel Mare University of Suceava and with a SEM VEGA II LSH, at Al.I.Cuza University of Iaşi. Other measurements were performed with a SEM Zeiss EVO 20 with EDX-Bruker detector, at INCDFM Bucharest-Magurele. To measure the structural and morphological properties, it was used an optic microscope Zeiss DSM 982 Gemini, at INCDFM.

3. RESULTS AND DISCUSSIONS

Figures 1 shows the polarization curve for solution of electrolyte used for Zn-Co co-deposition recorded for the potential range between -100 mV and -1200 mV at 32ºC, with a scanning velocity of 5 mV/s. Studying the behavior of solution there was decided to perform deposition at -1000 mV, -1100 mV and -1200 mV.

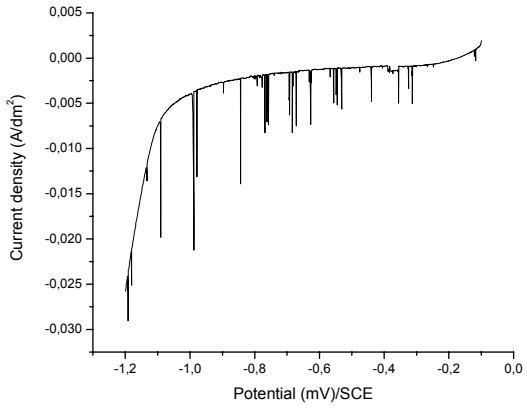

Fig.1. Polarization curve for described solution of electrolyte used for Zn-Co co-deposition recorded for the potential range from -100 mV to -1200 mV, 32ºC temperature, with magnetic stirring of the electrolyte

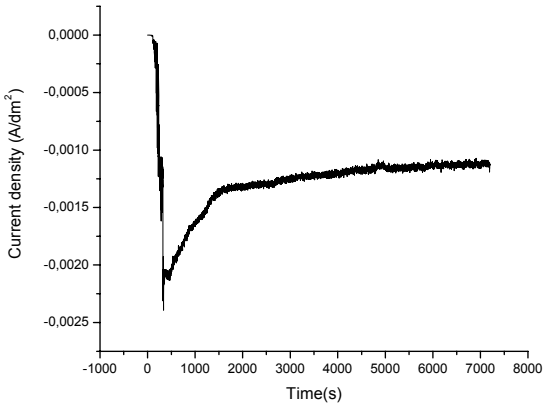

Fig.2. Crono-amperograme recorded during Zn-Co alloy co-deposition at -1000 mV potential and 32ºC, with magnetic stirring of the electrolyte

Figure 2 presents the evolution of current density during electrodeposition. During the first 20 minutes of the process the decreasing of the current in faster, then slowly decreasing was recorded. The behavior is similar those signed in other experiments and is closely with the diminishing of ions concentration in solution.

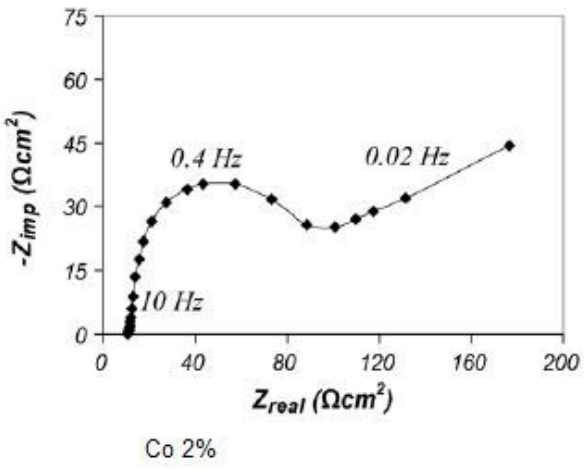

Fig.3. Nyquist impedance curve obtained for the second solution (low concentration of Co ions)

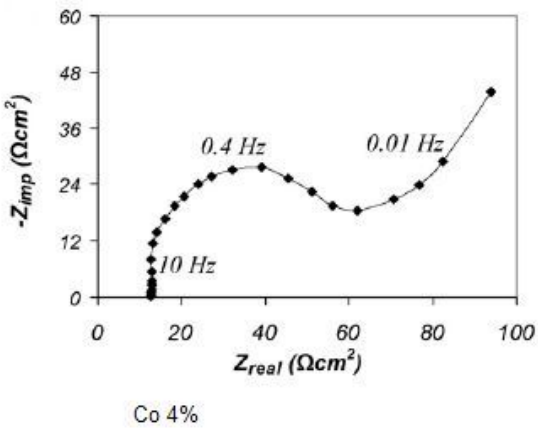

Fig.4. Nyquist impedance curve obtained for the first solution (higher concentration of Co ions)

Figures 3 and 4 show Nyquist diagrams obtained for those two solutions and it could be observe that there are not many differences between them. It is a single semicircle at high frequencies and the double radius (diameter) corresponds to the charge transfer resistance (R_{ct}). The resistance of the solution (R_s) is given by the distance between origin and the point where the semicircle begins. The capacitance of double layer (C_{dl}) could be calculated from the next relation:

$$Z(\omega) = \frac{1}{(i\omega C_{dl})^n} \quad , \qquad (3)$$

where i is the complex exponent ($i=(-1)^{1/2}$), ω is the angular frequency (ω = 2πf) and n is an exponent higher than 0.5 and smallest than 1. We found for those two solutions next values: R_{s1}=15.5 Ω·cm^2 and R_{s2}=17.5 Ω·cm^2, R_{ct1}=61 Ω·cm^2 and R_{ct2}=103 Ω·cm^2, C_{dl1}=97 μF·cm^{-2} and C_{dl2}=84 μF·cm^{-2}. The results confirm the fact there are not many differences as regard the influence of concentration of Co ions [4, 5, 6, 7].

Figures 5 and 6 show images of some samples of layers of Zn-Co electrodeposited using the first solution with a higher concentration of Co ions. Working at 32ºC there was obtained the better aspect of the layer. Some micro-cracks could be observed, but these are not exactly a negative fact, because there are situations when cracks are desired for obtain a superior protection against corrosion. At 38ºC there were situation of dissolution of gold layer from lamella and exfoliation. Anyway, these experiments have to be reevaluated because there are only at beginning in our collective themes.

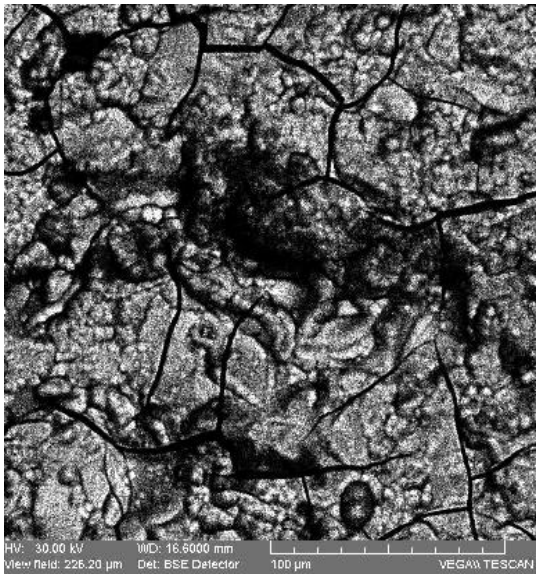

Fig.5. SEM image of a zinc-cobalt layer electrodeposited at -1000 mV and 24ºC (first solution, 4% Co), with magnetic stirring of the electrolyte. Optical magnitude 1000X, VEGA TESCAN device.

Fig.6. SEM image of a zinc-cobalt layer electrodeposited at -1000 mV and 32ºC (first solution, 4% Co), with magnetic stirring of the electrolyte. Optic magnitude 1000X, VEGA TESCAN device.

4. CONCLUSIONS

The deposed of Zn-Co alloys have a future in technique and the researches will offer new solutions for development.

EIS diagrams prove that there are not many differences between the solutions where Co ions concentration differs in the range of low values. So, the mechanism of electrochemically reactions seems to be the same.

The analyses confirm that zinc-cobalt alloys were formed. Also it is confirmed that the percents of those two metals in the deposited alloys depend by working conditions.

The quality of the deposited layers could be controlled through the electrolyte concentration, discharge potential and working temperature.

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