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ELECTRODEPOSITION AND CHARACTERIZATION OF ZINC-COBALT ALLOY COATINGS

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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. Application properties important for coating systems used in the automotive industry, such as friction behavior, adhesion, and corrosion behavior, were investigated on coatings with varying cobalt content. The corrosion resistance of the Zn-Co alloy layers was found to be better than the one of pure zinc coatings.

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

1. Introduction

There is a growing interest in zinc coatings combined with elements of the iron-group metals (Fe, Ni and Co) on steel substrate thanks to results reported in the literature. These results show that the corrosion performance of these electrodeposits is superior to that of plain Zn coatings.

In machine building industry, zinc remains the principal metal for anti-corrosion applications, especially for protection of steel products. On top of the years, it has registered a significant increasing of electrodeposited alloys, because it was an important market demand for products with high quality coatings. In the front of the 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 researches meant to create 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 as having evolution in two steps, according to 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 Zn^{2+} ions combine with hydrogen to form ZnH^+, as well as where Co^{2+} ions combine with hydrogen to form CoH^+. Those intermediary species, formed in the adsorption process, will decompose finally in metallic Zn, and metallic Co respectively. The reactions mechanism may be written as follows [1, 2].

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

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 cobalt and zinc respectively.

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

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

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].

Under 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 $g{\cdot}L$, 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 $g{\cdot}L$, 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 (except for 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 samples with bright glass, but the result was negative because all the gold dissolved itself 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

Figure 1 show 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, it was decided to perform deposition at -1000 mV, -1100 mV and -1200 mV.

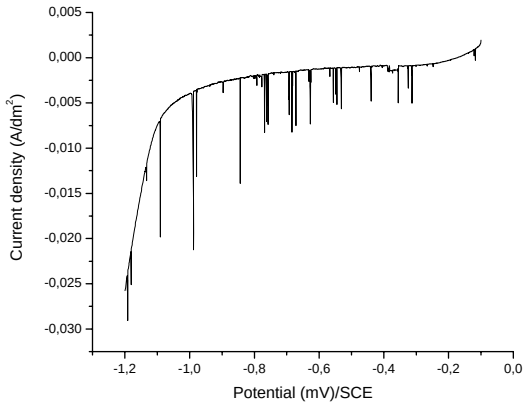

Fig.1. *Polarization curve for described solution of electrolyte used for Zn-Co co-deposition recorded for the potential range from -100 mV to -1200 mV, 32ºC temperature, with magnetic stirring of the electrolyte.*

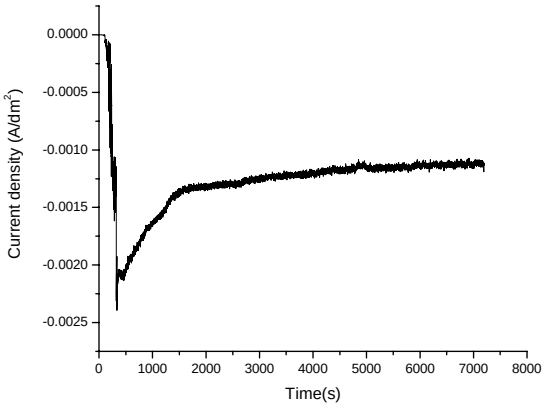

Fig.2. *Crono-amperograme recorded during Zn-Co alloy co-deposition at -1000 mV potential and 32ºC, with magnetic stirring of the electrolyte.*

Figure 2 presents the evolution of current density during electrodeposition process. As it could be seen, during the first 20 minutes of the process the decreasing rate of the current density is faster comparing with the decreasing rate recorded for the rest of the time.

The behavior is similar to those signed in other experiments and is close to the diminishing of ions concentration in solution. Figures 3 and 4 show Nyquist representation of Electrochemical Impedance Spectroscopy (EIS) diagrams obtained for those two solutions and it could be observed 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.

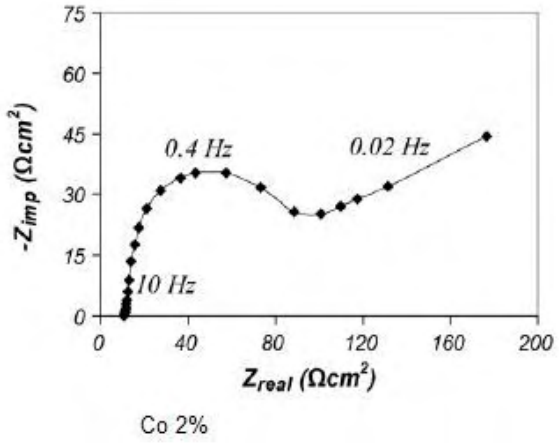

Fig.3. *Nyquist impedance curve obtained for the second solution (low concentration of Co ions).*

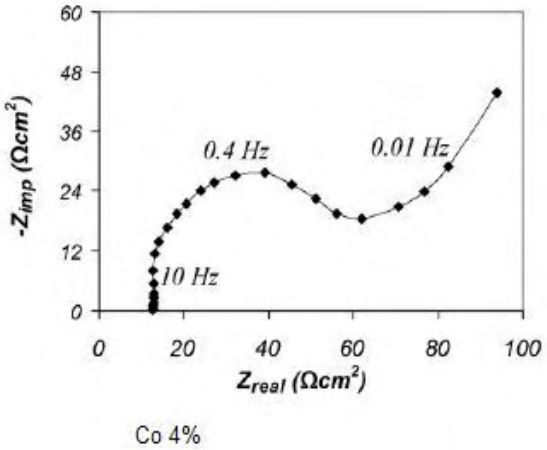

Fig.4. *Nyquist impedance curve obtained for the first solution (higher concentration of Co ions).*

The capacitance of double layer (C_{dl}) could be calculated from the next relation:

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

where i is the complex exponent ($i=(-1)^{1/2}$), ω is the angular frequency ($\omega = 2\pi f$) and n is an exponent higher than 0.5 and smallest than 1.

We found for those two solutions the following 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 regarding the influence of concentration of Co ions [4, 5, 6, 7].

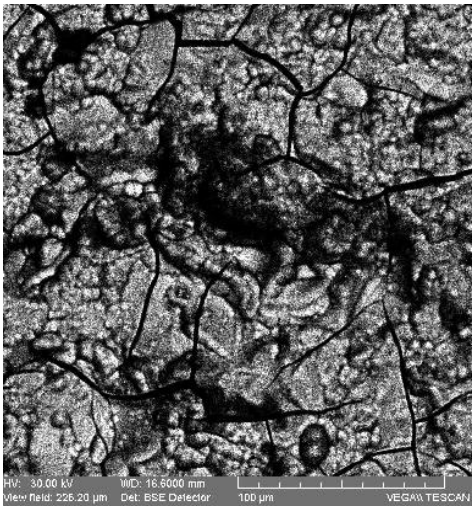

Fig.5. *SEM image of a zinc-cobalt layer electrodeposited at -1000 mV and 24ºC (first solution, 4% Co), with magnetic stirring of the electrolyte. Optical magnitude 1000X, VEGA TESCAN device.*

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.*

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 a 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 obtaining a superior protection against corrosion. At 38ºC there were situations of dissolution of gold layer from lamella and exfoliation. Anyway, these experiments have to be reevaluated because there are only at the beginning in our collective themes.

4. Conclusions

The deposition of Zn-Co alloys has 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 electrochemical reactions seems to be the same.

The analyses confirm that zinc-cobalt alloys were formed. Also it is confirmed that the percentage 58.710% Zn and 27.818% Co, Cl 5.676%, of those two metals in the deposited alloys depends on the working conditions.

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

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