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EFFECT OF CURRENT DENSITY ON MORPHOLOGY AND CORROSION RESISTANCE OF EPOXY RESIN /Zn LAYERS

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ABSTRACT

In this research we intended to obtain and characteriz composite layers by using epoxy resin (disperse phase) electrodeposited with zinc (metal matrix). The epoxy resin/Zn layers were electrodeposited at two values of current densities: 3A/dm^2 and 5A/dm^2 from a suspension of epoxy resin particles with two mean diameter size particles (0.1 – 5.0µm and 6 – 10µm) in aqueous zinc sulphate electrolyte. Suspension was prepared by adding 10g/L epoxy resin particles into electrolyte solution. The morphology of the layers was investigated by scanning electron microscopy method. The regular crystal structure characteristic of electroplated zinc layers was disturbed by epoxy resin particles that perturb the zinc growth during electrodeposition. The corrosion behavior of the layers in the corrosive solution was investigated by potentiodynamic polarization method. As corrosion test solution 0.5 M sodium chloride was used. The rate of corrosion for layers obtained at 3A/dm^2 was 6.21µm/year for layers with means diameter size particles of 0.1 – 5.0µm, respectively 16.18µm/year for layers with means diameter particles size of 6 – 10µm. It was observed that by increasing the current density to 5A/dm^2 the rate of corrosion for layers was 16.11µm/year for layers with means diameter size particles of 0.1 – 5.0µm, respectively 24.37µm/year for layers with means diameter size particles of 6 – 10µm.

KEYWORDS: epoxy resin particles, electrodeposition, epoxy resin/Zn composite coatings, layers morphology, corrosion rate

1. Introduction

Zinc is an important element in industrial world; it is used in a wide range from metal products to rubber, paint and agricultural industries. Zinc deposits are essentially used to protect steel against corrosion. The protection is principally a result of the zinc's anodic behavior in any electrochemical reaction. Under the same conditions (3.5% sodium chloride solution), the potential of zinc deposits is more negative (-1050mV/SCE) than that of steel (-650mV/SCE). Thus, zinc deposits behave as sacrificial anodes and offer cathodic protection [1, 2]. Surface layers are used to increase the lifetime of components exposed to corrosion and wear condition. It is well known that surface morphology and texture which are both influenced by bath composition and processing parameters have significant effects on the corrosion resistance of zinc electrodeposits [3-5].

Epoxy resins are considered as one of the most important classes of thermosetting polymers and find extensive use in various fields of coating, high performance adhesives and other engineering applications.

Epoxy resins are network-forming polymers displaying several interesting characteristics, e.g. good chemical resistance, adhesion to the most varied substrates, good electrical resistance and mechanical properties. Because of these attributes they have found many applications in different industries (e.g. electronics, aeronautics or astronautics) as protective layers, fiber reinforced plastics, adhesives etc. [6-7].

Considerable efforts have been made not only to improve corrosion resistance property of zinc layers but also to impart other beneficiary properties. One of the possible solutions for this is the incorporation of inert particles (nano or micro sized) into a growing zinc metal matrix during electrodeposition.

The resulted coating generally referred to as metal matrix composite has attracted interest due to its unique functional properties such as higher corrosion and wear resistance, hardness, super conduction and magnetic properties, semiconductor properties, photo catalytic properties compared to pure metal or alloy coatings [8]. However these properties depend on process parameters such as current density, concentration of salts, additives, surfactants and their nature and type of applied current (pulsed current, direct current) [9].

In the present research, efforts have been made to develop a bath solution without additive because they could give reactions with epoxy resin particles and the results could not be interpreted properly. So that, it was proposed to obtain composite layers using epoxy resin type Dinox 110L electrodeposited with zinc.

2. Experimental part

For electrodeposition of coating layers we used an electrochemical cell. The zinc metal plate of 99.99% purity (anode) and DC04 steel plates of 6×3×0.1cm (cathode) were employed. Before electrodeposition mild steel plates were mechanically polished with different grades of emery paper, degreased with alkaline solution and washed with distilled water. Anode was activated by dipping in 10% dilute hydrochloric acid solution for few seconds, washed with water and then placed in bath solution with the composition reported before [10].

Zinc sulphate electrolyte has cathodic polarization bigger than zinc chloride electrolyte so that it was used sulphate electrolyte for electrodeposition. Sodium sulphate increase the conductibility and ability for dispersing and aluminium sulphate was used as buffering agent which stabilized the acidity of electrolyte. Concomitantly we obtain more shining layers.

The pH of the solution was 3.8. Deposition was carried out at current density of 3A/dm^2 and 5A/dm^2, deposition time of 60 minutes and stirring rate of 1000rpm. Electrodeposition experiments were performed at room temperature. In bath solution it was added epoxy resin to give a solution concentration of 10g/L epoxy resin particles with means diameter size particles of 0.1 – 5.0μm and 6–10μm. Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and crosslinks) when mixed with a catalyzing agent or "hardener". Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A (Fig. 1). The value of n varies from 0 to 25. The resin is liquid when n < 1 and solid when n > 2 [11].

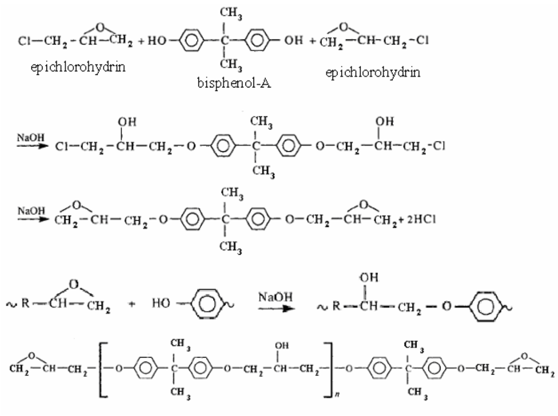

***Fig. 1.** Schematic illustrating the formation of the epoxy resin type structures*

Properties of epoxy resin type Dinox 110L used as disperse phase for electrodeposition are presented in Table 1.

The thickness of layers was calculated using gravimetric method.

The morphology of deposits was examined by scanning electron microscopy (SEM) using a microscope type Phylips FEI; QUANTA 200.

***Table 1.** Properties of epoxy resin type Dinox 110L*

Molecular weight	500 g/mol
Density	1.18 – 1.25 g/cm^3
Epoxide number	1.85 – 2.20 Eq/kg
Melting point	64 – 76 ºC
Volatile compounds	Max. 1%

For potentiodynamic polarization measurements it was used a three-electrode open cell with epoxy resin/Zn layers as working electrode (WE), a platinum gauze as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode (SCE = +241mV/NHE). Initial potential (I.P.) was –1.6 V (Hg/Hg_2Cl_2), final potential (F.P.) was –0.9 V (Hg/Hg_2Cl_2) and a scan rate of 0.5 mV/s. The polarization potentiodynamic curves were recorded after 30 min of immersion. The Tafel parameters for the particular specimens were determined by extrapolating the anode and cathode Tafel curves. As test solution 0.5 M sodium chloride was used.

3. Results and discussions

3.1. SEM analysis

The thickness of epoxy resin/Zn composite layers obtained at 3A/dm^2 was 42.32μm for layer obtained with particles by means diameter size of

0.1 – 5µm and 51.45µm for the layer obtained with particles by means diameter size of 6 – 10µm.

If we increased the current density to 5 A/dm^2 it was found a thickness layer of 70.14µm for the layer obtained with particles by means diameter size 0.1–5µm and 78.34µm for the layer obtained with particles by means diameter size 6 – 10µm (Fig. 2).

It could be observed that by increasing the current density the layers thickness increases. Also it has been observed that by increasing the mean diameter size of epoxy resin particles the layers thickness increased.

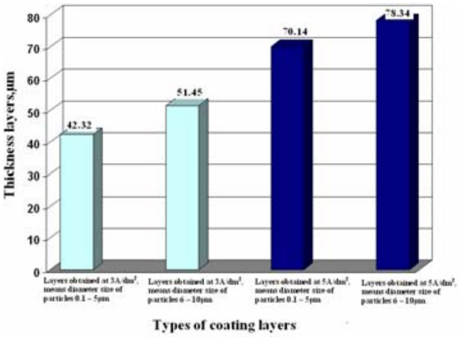

Fig. 2. *Comparative thickness of epoxy resin/Zn layers*

Figs. 3 - 8 compare morphological aspects of pure zinc coatings and epoxy resin composite layers obtained of different current density and different mean diameter particles size under scanning electron microscopy method.

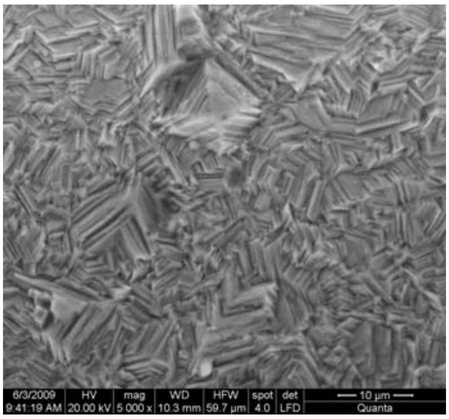

Fig. 3. *SEM surface morphology of pure zinc layers obtained at 3A/dm^2 (x 5000)*

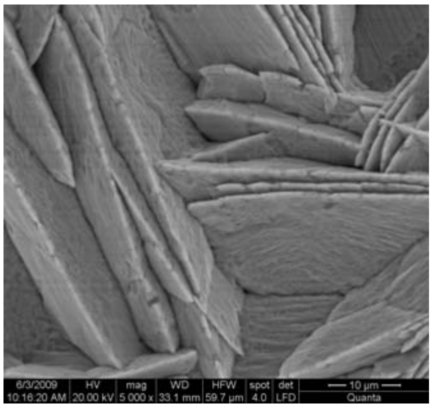

Fig. 4. *SEM surface morphology of pure zinc layers obtained at 5A/dm^2 (x 5000)*

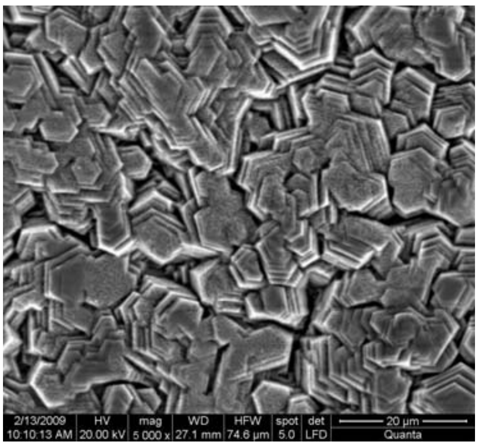

Fig. 5. *SEM surface morphology of epoxy resin/Zn composite layers obtained at 3A/dm^2 with means diameter particles size in electrolyte solution 0.1 – 5 µm (x 5000)*

Fig. 6. *SEM surface morphology of epoxy resin/Zn composite layers obtained at 3A/dm^2 with mean diameter particles size in electrolyte solution 6 – 10 µm (x 5000)*

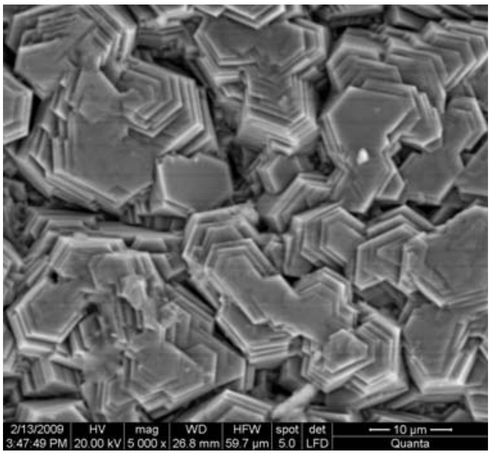

Fig. 7. *SEM surface morphology of epoxy resin/Zn composite layers obtained at 5 A/dm^2 with means diameter particles size in electrolyte solution 0.1 - 5µm (x 5000)*

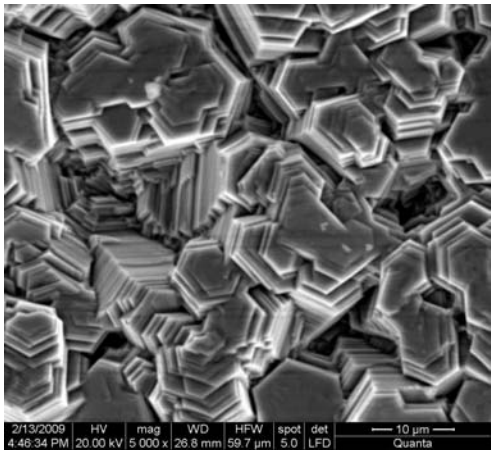

Fig. 8. *SEM surface morphology of epoxy resin/Zn composite layers obtained at 5A/dm^2 with means diameter particles size in electrolyte solution 6 - 10µm (x 5000)*

As it can be seen in Fig. 3 - 8, the addition of epoxy resin particles in electrolyte bath significantly changes the morphology of the zinc deposits as compared to those obtained from solutions without disperse phase. The morphology of coatings layers is different compared to pure coated zinc. The pure zinc coating has a rather regular surface, is bright but not smooth and consists of hexagonal platelets of moderate size having the degree of orientation perpendicular to the substrate surface (Fig. 3 - 4). The morphology of zinc layers obtained at 5A/dm^2 presents a significant increase in the size of the zinc platelets.

For composite layers obtained at 3A/dm^2 it could be observed that the morphology of the surfaces is different function means diameter particles size. It is noted that with increasing means diameter size from 0.1 – 5µm to 6 – 10µm the morphology of the layers is different needle more orderly and smooth (Figs. 5 – 6).

If we increased the current density up to 5 A/dm^2 it was observed that the morphology of the surfaces is changed more to finer crystallites (Figs. 7 – 8). The crystals of coatings were parallelly orientated to the substrate and the hexagonal planes are clearly observed.

The epoxy resin particles act as reducing the crystals size and orientation of electrodeposited zinc during co-deposition.

3.2. Potentiodynamic polarization measurements

The electrochemical investigation of each sample began with the monitoring of the open circuit potential change immediately after the immersion into the testing solutions till reaching a relatively stable stationary value.

The performed potentiodynamic diagrams for epoxy resin/Zn composite coatings in 0.5 M sodium chloride after 30 minutes of immersion are presented in Figure 9.

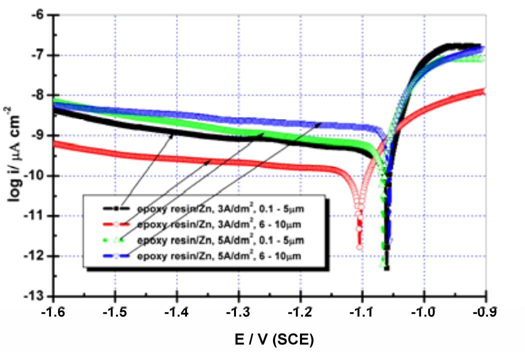

Fig. 9. *Potentiodynamic polarization curves for epoxy resin/Zn layers in 0.5 M sodium chloride solution obtained after 30 minutes of immersion time (log scale)*

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation [12]:

$$i_{corr} = \frac{1}{2.303R_p}\left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c}\right) \qquad (1)$$

i_{corr} = corrosion current density;
R_p = polarization resistance;
β_a = anodic slope;
β_c = cathodic slope.

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Different parameters such as corrosion current density (i_{corr}) and corrosion potential (E_{corr}), cathodic (β_c) and anodic (β_a) Tafel slopes derived from Fig. 9 using Tafel extrapolation are summarized in Table 2.

Corrosion rates (CR) were calculated by the following equation:

$$CR(\mu m / year) = \frac{0.051 \cdot i_{corr} \cdot (E_q.wt.)}{d} \qquad (2)$$

i_{corr} – corrosion current density calculated from Stern – Geary equation;

E_q.wt. is the equivalent weight;

d is the density of the zinc metal in g/cm^3.

The corrosion potential for all types of composite layers is not greatly different; it was observed a very small difference by 30mV.

From potentiodynamic polarization curves the polarization resistance of epoxy resin/Zn layers were been found between 484.82Ωcm^2 (composite layers obtained at 3 A/dm^2 with mean diameter size of resin particles 0.1 – 5μm) and 179.68Ωcm^2 (composite layers obtained at 5A/dm^2 with mean diameter size of resin particles 6 – 10μm).

If we compare corrosion rate of epoxy resin/Zn composite layers with corrosion rate of pure zinc layers [13, 14] we can conclud that by adding epoxy resin particles in zinc electrolyte were obtained epoxy resin/Zn composite layers most resistant to the corrosive attack of the 0.5 M sodium chloride solution than pure zinc obtained from electrodeposition at the same parameters (Fig. 10).

***Table 2**. Tafel parameters for epoxy resin/Zn layers calculated from potentiodynamic polarization curves obtained after 30 min from immersion in 0.5 M sodium chloride solution*

Type of coatings	**E_{corr}, V; Hg/HgCl$_2$**	**β_a,**	**β_c,**	**i_{corr},**	**R_p ,**	**v_{corr},**
		[mV/decade]		[μA/cm^2]	[Ω cm^2]	[μm/year]
Epoxy resin/Zn 3A/dm^2, particles size 0.1 - 5μm	- 1.06	18.1	- 78.0	13.16	484.82	6.21
Epoxy resin/Zn 3A/dm^2 particles size 6 - 10μm	- 1.09	35.6	- 55.1	34.32	273.60	16.18
Epoxy resin/Zn 5A/dm^2, particles size 0.1 - 5μm	- 1.07	25.0	- 202.7	34.17	282.76	16.11
Epoxy resin/Zn 5A/dm^2 particles size 6 - 10μm	- 1.08	27.8	- 92.7	51.68	179.68	24.37

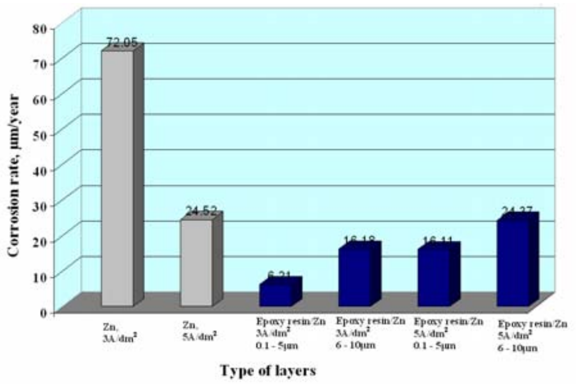

***Fig. 10.** Corrosion rate for pure zinc and epoxy resin/Zn composite layers obtained at different values of current densities*

From the results presented in Fig. 10, it can be concluded that, by including epoxy resin particles in zinc sulphate electrolyte bath, the layers obtained are more resistant to the corrosive attack of the 0.5 M sodium chloride. Corrosion rate for pure zinc was 72.05μm/year (layers obtained at 3A/dm^2) and 24.52μm/year (layers obtained at 5A/dm^2). Corrosion rate for epoxy resin/Zn composite layers was between 24.37μm/year (layers obtained at 5A/dm^2 with means diameter size particles of 6 – 10μm) and 6.21μm/year (layers obtained at 3A/dm^2 with means diameter size particles of 0.1 – 5μm) that demonstrate a significant increase of corrosion rate.

4. Conclusions

Our research proved that epoxy resin particles type Dinox 110L could be codeposited with zinc to obtain composite layers without using any surfactants.

It could be observed that by increasing the current density and the mean diameter size of epoxy resin particles the thickness layers increase.

Addition of epoxy resin particles in electrolyte bath significantly changes the morphology of the zinc deposits as compared with those obtained from solutions without disperse phase.

The pure zinc coating has a rather regular surface and consists of hexagonal platelets of moderate size having degrees of orientation perpendicular to the substrate surface. The morphology of the epoxy resin/Zn surfaces is changed more to finer crystallites and crystals of coatings were parallelly orientated to the substrate and the hexagonal planes are clearly observed.

The epoxy resin particles acts as reducing the crystals size and orientation of electrodeposited zinc during co-deposition. From potentiodynamic polarization curves the polarization resistance of epoxy resin/Zn layers has been found between 484.82Ωcm^2 (composite layers obtained at 3A/dm^2 with mean diameter size of resin particles 0.1 – 5µm) and 179.68Ωcm^2 (composite layers obtained at 5A/dm^2 with mean diameter size of resin particles 6 – 10µm). Corrosion rate for epoxy resin/Zn composite layers was between 24.37µm/year (layers obtained at 5A/dm^2 with mean diameter size particles of 6 – 10µm) and 6.21µm/year (layers obtained at 3A/dm^2 with means diameter size particles of 0.1 – 5µm) that demonstrate a significant increase of corrosion rate versus corrosion rate of pure zinc coatings obtained at the same parameters for electrodeposition. It was demonstrated that the new composite sobtained, epoxy resin/Zn composite layers, have a better corrosion properties than pure zinc layers.

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