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MORPHOLOGICAL ASPECTS AND CORROSION BEHAVIOUR OF PHENOL FORMALDEHYDE/Zn COMPOSITE COATINGS

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ABSTRACT

The present work has the purpose of studying morphological aspects and corrosion behaviour of pure zinc and composite coatings having zinc as metal matrix and phenol – formaldehyde resin type Novolac (RESITAL 6358/1) as dispersed phase obtained during the electrodeposition process of zinc. The phenol – formaldehyde resin/Zn composite coatings were electrodeposited from a suspension of phenol – formaldehyde resin particles in aqueous zinc sulphate electrolyte by adding 10g/L and 25g/L of phenol – formaldehyde resin particles in the electrolyte solution. The dimensions of resin particles were 0.1 - 5µm. The morphological aspects of the coatings were investigated by scanning electron microscopy method. While the pure zinc coatings have a rather regular surface, the composite coatings surfaces have finer grains and different morphologies. The electrochemical behaviour of the coatings in the corrosive solution was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy methods. As electrochemical test solution, 0.5M NaCl was used in a three electrode open cell. The polarization resistances of phenol – formaldehyde resin/Zn composite coatings are bigger than that of pure zinc coatings obtained under the same condition for electrodeposition.

KEYWORDS: PF resin/Zn composite coatings, electrodeposition, scanning electron microscopy, polarization resistance

1. Introduction

Composite materials are material systems that consist of a discrete constituent (the reinforcement) distributed in a continuous phase (the matrix) and that derive their distinguishing characteristics from the properties and behavior of their constituents, from the geometry and arrangement of the constituents, and from the properties of the boundaries (interfaces) between the constituents.

Composites are classified either on the basis of the nature of the continuous (matrix) phase (polymer-matrix, metal-matrix, ceramic-matrix, and intermetallic-matrix composites), or on the basis of the nature of the reinforcing phase (particle reinforced, fiber reinforced, dispersion strengthened, laminated, etc.). The properties of the composite can be tailored, and new combinations of properties can be achieved [1]. Metal matrix composites offer a number of advantages compared to their base metals, such as higher specific strengths and moduli, higher elevated temperature resistance, lower coefficients of thermal expansion, and, in some cases, better wear resistance. From this potential, metal matrix composites fulfil all the desired conceptions of the designer [2 – 5].

Composite coatings on zinc are finding increased interest in surface technology and corrosion protection. Potential fields of application are improved corrosion and wear resistance of zinc composite layers with extended lifetime [6].

Electrochemical deposition of composite coatings can bring many advantages as compared to other methods. Electrodeposition of zinc on steel is carried out to protect steel from corrosion. The reason for the pre-eminence of zinc in the world of electrodeposition can be attributed to its relative readiness of deposition and better corrosion resistance [7 – 9].

The application of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods to coated metals has resulted in provisions of new information concerning their degradation in corrosive environments [10, 11]. EIS has been shown to be a useful technique in the study of the corrosion performance of surface coated metals in recent years [12–21].

The present work has the purpose of studying the morphological aspects and corrosion behaviour of pure zinc and composite coatings having zinc matrix and phenol – formaldehyde (PF) resin type Novolac with commercial name RESITAL 6358/1 synthesized by Hüttenes – Albertus Group (Germany) as dispersed phase obtained during electrodeposition process of zinc.

2. Experimental

For electrodeposition it was used zinc sulphate plating bath [22]. The pH of the solution was 3.8. Zinc plate of 99.9% purity was used as anode. As cathode we used carbon steel type DC04. Before deposition, the samples were degreased with alkaline solution at 80 – 90^{0}C during 10min. After decreasing, the surfaces were etched with 15% HCl for 1 – 2min and washing with distilled water.

The PF resin/Zn composite coatings were electrodeposited from a suspension of PF resin particles in aqueous zinc sulphate electrolyte by adding 10g/L and 25g/L PF resin dispersed particles with dimensions 0.1 – 5μm.

PF resin is a highly cross linked thermosetting material that is produced by the poly-condensation of phenol and formaldehyde in the presence of either acidic or basic catalyst. An acid catalyst is usually used in preparing Novolac type resin (see Fig. 1).

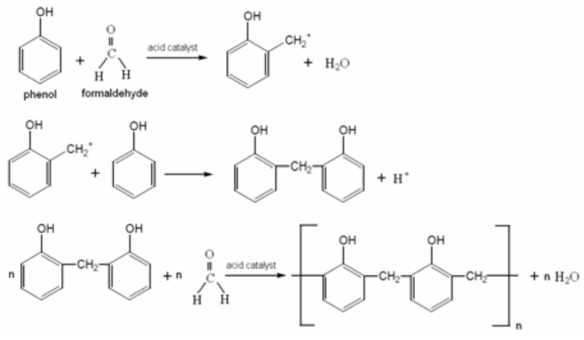

Fig. 1. *The schematic formation of the Novolac type structures*

The term novolac refers to the early use of phenolic to replace expensive shellac-based coatings. Novolacs are now those resins made at formaldehyde to- phenol molar ratios of less than one-to-one [23, 24].

The pure zinc and composite coatings were obtained at current density of 5A/dm^2, time for electrodeposition 60min, a stirring rate of 1000 rpm and an electrolyte temperature of 25^{0}C. Polished, degreased and cleaned cathodes of 2.5cm^2 exposed areas were used.

Before electrochemical corrosion investigations, the morphologies of deposits were examined by Scanning Electron Microscope type JEOL, JSM-T220A.

For electrochemical corrosion measurements were used a Solartron 1286 Electrochemical Interface coupled with a 2895 Solartron Frequency Response Analyser and the Z-Plot / Z-View SOFTWARE. A three - electrode open cell with pure zinc and PF resin/Zn composite coatings layers as working electrode (W.E.), a platinum gauze as counter electrode (C.E.) and mercury – mercurous sulphate electrode Hg/Hg_2SO_4/ saturated K_2SO_4 as reference electrode (R.E.; E = + 658mV/NHE). As test solution, 0.5M NaCl were used at room temperature (20±1^{0}C).

EIS measurements used initial frequency (I. F.) 65000Hz, final frequency (F. F.) 0.001Hz, AC sine wave amplitude of 10mV, frequency per decade: 10Hz, delay before integration 1s. The electrochemical impedance spectroscopy diagrams were recorded after 30min of immersion. All the recorded impedance spectra were analyzed as Nyquist Diagrams.

For potentiodynamic polarization measurements were used initial potential (I. P.) – 1900mV (Hg/Hg_2SO_4), final potential (F. P.) – 1200mV (Hg/Hg_2SO_4) and a scan rate of 1.66mV/s. The polarization potentiodynamic curves were recorded after 30min of immersion. The corrosion current density (i_{corr}) for the particular specimens was determined by extrapolating the anode and cathode Tafel curves.

3. Results and discussions

The thicknesses of pure zinc and composite coatings obtained by electrodeposition at 5A/dm^2 current density, 60min deposition time and 1000rpm are shown in Fig. 2.

From Fig.2 it can be observed that by adding PF resin particles the thickness of the coatings is a little beat smaller. Decreases of the thickness could be possible because the resin particles determined smoother and fine structure of PF resin /Zn composite coatings than pure zinc electrodeposited.

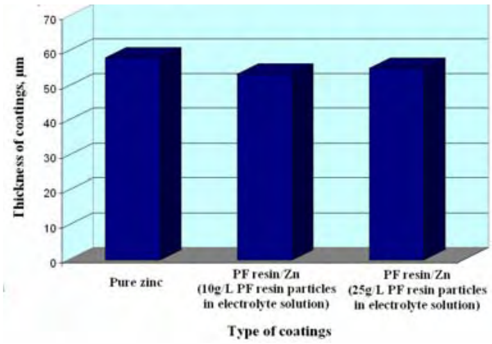

Fig. 2. *The thickness of pure zinc and composite coatings obtained by electrodeposition at 5A/dm^2 current density, time 60min, 1000rpm*

Figs. 3 – 5 compares morphological aspects of pure zinc coating and PF resin/Zn composite coatings by scanning electron microscopy method.

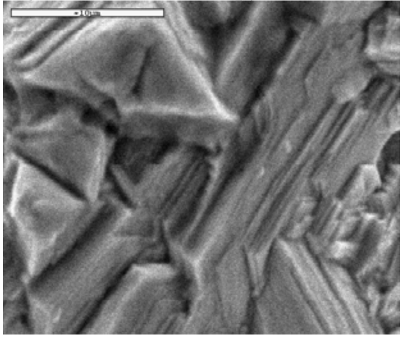

Fig. 3. *SEM surface morphology of pure zinc electroplating (x 5000)*

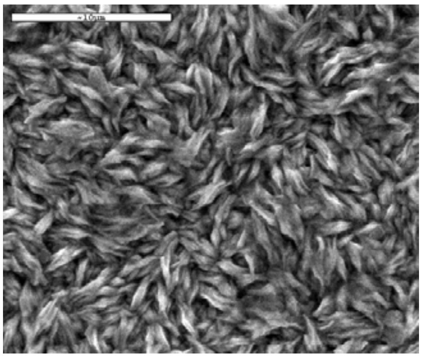

Fig. 4. *SEM surface morphology of PF resin/Zn composite coatings (10g/L PF resin particles in electrolyte solution) (x 5000)*

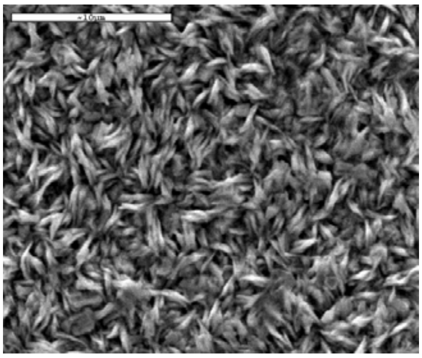

Fig. 5. *SEM surface morphology of PF resin/Zn composite coatings (25g/L PF resin particles in electrolyte solution) (x 5000)*

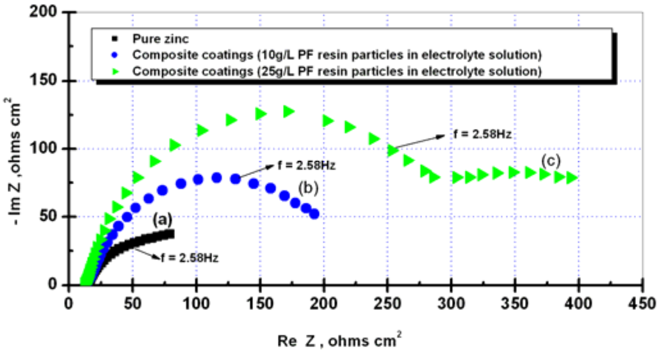

Fig. 6. *Nyquist diagrams of impedance spectrum for pure zinc and PF resin/Zn composite coatings in 0.5M NaCl after 30 min from immersion:*
(a) – pure Zn, (b) – PF resin/Zn composite coatings (10g/L PF resin particles in electrolyte solution), (c) - PF resin/Zn composite coatings (25g/L PF resin particles in electrolyte solution)

The surface of zinc is made up of regular crystals. The PF resin particles codeposit with zinc radically change the structure of the metal: disorder the regular crystal structure and the structure of the zinc matrix becomes finely crystalline. The pure zinc coatings have a rather regular surface, whereas the composite coating surfaces have finer grains structure with particles of PF resin uniform distributed on the surfaces. The electrochemical investigation of each sample began with monitoring the open circuit potential (OCP). OCP changes immediately after the immersion into the testing solutions till reaching relatively stable stationary values. The Nyquist plot representation of impedance spectra performed in 0.5M NaCl for pure zinc and PF resin/Zn composite coatings after 30min of immersion it is shown in Fig. 6. Two equivalent electrical circuits were proposed to fit the experimental impedance data [25 – 26]. In most cases, these circuits, represented in Fig. 7 (a and b) allows to obtain an excellent agreement between experimental and simulated impedance plots. The experimental data of our work was simulated with these equivalent circuits where: R_e – electrolyte resistance between the reference electrode and the working electrode; CPE1 – the double layer capacitance of pure zinc coatings depending on frequency in parallel with the polarization resistance R_p. R_r could represent the resistance of resin dispersed particles, C_c the coating capacitance due to resin particles and CPE2 the double layer capacitance of composite coatings depending on frequency.

CPE are a constant phase elements, accounting for the fact that the centres of the capacitive arcs of the circle are under the axis of real part. This feature of capacitive arcs is encountered in all electrochemical impedance studies performed on inhomogeneous surfaces and has given rise to extensive studies. CPE are not pure capacitors, but components depending on frequency.

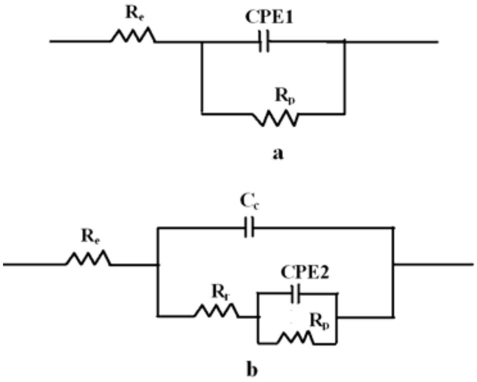

***Fig. 7**. Equivalent circuits to calculate the polarization resistance from impedance data*

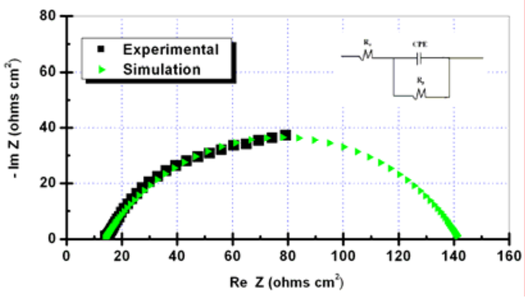

***Fig. 8.** Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (triangle points) for pure zinc coatings in 0.5M NaCl solution after 30min of immersion*

On the Figs. 8 and 9 were represented the experimental diagrams together with the simulation curves described by the equivalent circuits from fig. 7. It could be observed that the experimental impedance data fit very well with the equivalent circuit proposed.

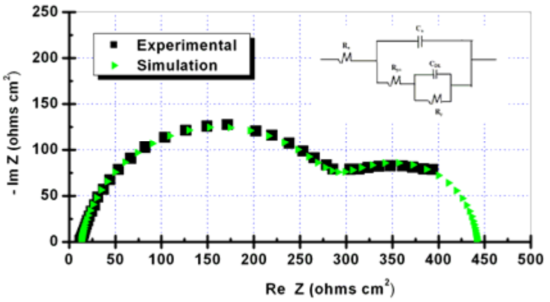

***Fig. 9.** Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (triangle points) for PF resin/Zn composite coatings in 0.5M NaCl solution after 30min of immersion*

The corresponding calculated polarization resistance values from impedance diagrams for pure zinc and PF resin/Zn composite coatings in 0.5M NaCl solution using the equivalent circuits from Fig. 7 are presented in the Fig. 10.

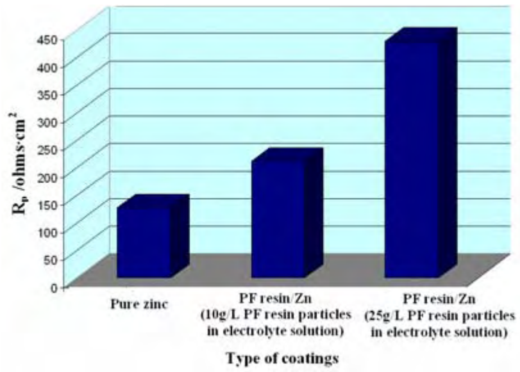

***Fig. 10**. Variation of polarization resistance for pure zinc and PF resin/Zn composite coatings in 0.5M NaCl after 30min from immersion*

For pure zinc coatings the polarization resistance was 127.37Ω·cm^2.

For PF resin/Zn composite coatings layers obtained by adding 10g/L PF resin particles in electrolyte solution the polarization resistance was 211.38Ω·cm^2 and with increasing the concentration of the particles in electrolyte solution to 25g/L the polarization resistance increase to the value of 428.69Ω·cm^2.

It was observed that o good polarization resistance was found for PF resin/Zn composite coatings with 25g/L PF resin particles in electrolyte solution. The value of polarization resistance for this type of coatings is about four times bigger than polarization resistance of pure zinc coating obtained at the same electrodeposition conditions.

The performed potentiodynamic diagrams for pure zinc and PF resin/Zn composite coatings in 0.5M NaCl after 30min of immersion are presented in Fig. 11.

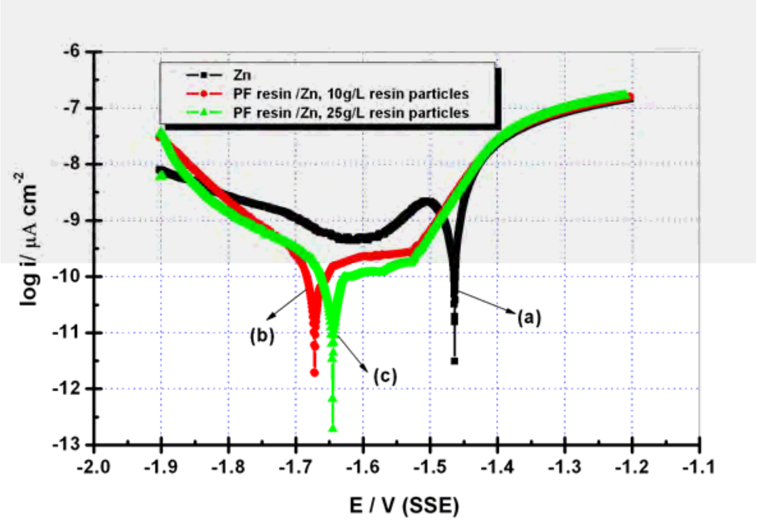

Fig. 11. *Comparative polarization potentiodynamic curves for pure zinc and PF resin/ Zn composite coatings in 0.5M NaCl solution obtained after 30minutes from immersion time (log scale): (a) – pure Zn, (b) – PF resin/Zn composite coatings (10g/L PF resin particles in electrolyte solution), (c) - PF resin/Zn composite coatings (25g/L PF resin particles in electrolyte solution)*

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation, as follows [27]:

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

- i_{corr} is the corrosion current density in Amps/cm^2;
- R_p is the corrosion resistance in ohms cm^2;
- β_a is the anodic Tafel slope in Volts/decade or mV/decade of current density;
- β_c is the cathodic Tafel slope in Volts/decade or mV/decade of current density;
- the quantity, $(\beta_a \cdot \beta_c)/(\beta_a + \beta_c)$, is referred to as the Tafel constant.

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarisation resistance (R_p), which were obtained from the potentiodynamic polarisation curves are summarized in Table 1.

Table 1. *Polarization resistances values of pure zinc and PF resin/Zn composite coatings calculated from polarization potentiodynamic curves obtained after 30min from immersion in 0.5M NaCl solution*

Type of coatings	**E_{cor}, V** Hg/Hg_2SO_4	**β_a** mV/decade	**β_c** mV/decade	**i_{cor},** μA/cm^2	**R_p** Ω·cm^2
Pure zinc	-1.47	53.95	21.26	52.00	127.34
PF resin/Zn composite coatings with 10g/L PF resin particles in electrolyte solution	-1.67	37.94	33.21	35.98	213.66
PF resin/Zn composite coatings with 25g/L PF resin particles in electrolyte solution	-1.64	26.31	26.93	13.43	430.19

The corrosion potential is shifted to more negative values for PF resin/Zn composite coatings (-1.67V for coatings obtained with 10g/L resin in electrolyte solution, respectively - 1.64V for coatings obtained with 25g/L resin in electrolyte solution) than pure zinc coatings (-1.47V).

From potentiodynamic polarization curves the polarization resistance for pure zinc coatings was 127.34Ω·cm^2. For PF resin/Zn composite coatings layers obtained by adding 10g/L PF resin particles in electrolyte solution the polarization resistance was 213.66Ω·cm^2 and with increasing the concentration of the particles in electrolyte solution to 25g/L the polarization resistance increase to the value of 430.19Ω·cm^2.

The polarisation resistance values calculated with Stern-Geary formula from potentiodynamic diagrams was in a good agreement with those obtained from impedance measurements.

From experimental data it was observed that corrosion current density (corrosion rate) has a big value for pure zinc coatings (52.00μA/cm^2) and small value for PF resin/Zn composite coatings (35.98μA/cm^2 for PF resin/Zn composite coatings layers obtained by adding 10g/L PF resin particles in electrolyte solution), respectively 13.43μA/cm^2 for PF resin/Zn composite coatings layers obtained by adding 25g/L PF resin particles in electrolyte solution).

It was observed that by adding PF resin particles in zinc electrolyte for electrodeposition it was obtained PF resin/Zn composite coatings most resistant at corrosive attack at 0.5M NaCl solution than pure zinc obtained from electrodeposition in same conditions.

This improvement of corrosion resistance could be due to the fine surface structure of composite coating compared with pure zinc coating as well as to the incorporation of PF resin particles into composite coatings.

3. Conclusions

It has been demonstrated that PF resin particles type Novolac with commercial name RESITAL 6358/1 could be codeposited with zinc to obtain composite coatings.

The surface morphology to PF resin/Zn composite layers is different compared with pure zinc coatings: the regular crystal structure characteristic of electroplated zinc coatings was disturbed. The PF resin particles embedded in the zinc matrix perturb the zinc crystals growth during electrodeposition.

By increasing the PF resin concentration in the zinc electrolyte the surface structure of composite coating is changed more to finer crystallites. The PF resin acts as reducing the crystals size of electrodeposited zinc during co-deposition.

Electrochemical impedance spectroscopy and polarisation potentiodynamic methods are powerful techniques to investigate the corrosion protection of pure zinc and PF resin/Zn composite coatings. The polarization resistance values obtained from both methods are in good agreement.

The corrosion potential is shifted to more negative values for composite coatings (-1.67V and -1.64V) than those of pure zinc coatings (-1.47V) obtained in the same conditions of electrodeposition.

For composite coatings, the polarization resistance is bigger than for pure zinc coatings obtained under the same condition for electrodeposition. It was observed that a good polarization resistance was found for PF resin/Zn composite coatings with 25g/L PF resin particles in electrolyte solution. The value of polarization resistance for this type of coating is about four times bigger than polarization resistance of pure zinc coatings.

From experimental data it was observed that corrosion current density (corrosion rate) is higher for pure zinc coatings and smaller for PF resin/Zn composite coatings.

The better corrosion resistance of PF resin/Zn composite coatings could be due to the fine surface structure of composite coating compared with pure zinc coating as well as to the incorporation of PF resin particles into composite coatings could have an inhibition effect of zinc crystals growth and a catalytic effect in increasing nucleation sites.

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