Influence of particles size on the morphology and corrosion behaviour of phenol – formaldehyde/Zn composite coatings obtained by electrodeposition

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The present work has the purpose of studying the structure and corrosion behaviour of composite coatings having zinc as matrix, and phenol – formaldehyde resin type Novolac (RESITAL 6358/1) as dispersed phase obtained during 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 of phenol – formaldehyde resin particles in the electrolyte solution. Two dimensions of dispersed particles were used: 0.1 - 5µm and 6 - 10µm respectively. The surface morphologies of the coatings were investigated by scanning electron microscopy (SEM – EDS) and atomic force microscopy (AFM) methods. The pure zinc coating has a rather regular surface, whereas the composite coating surfaces have finer grains and different morphologies. The electrochemical behaviour of the coatings in the corrosive solutions was investigated by electrochemical impedance spectroscopy (EIS) method. As electrochemical test solution 0.5M sodium chloride was used in a three electrode open cell. The corrosion potential is shifted to more negative values for composite coatings than that of pure zinc coating. The polarization resistances of phenol – formaldehyde resin/Zn composite coatings are bigger than that of pure zinc coating obtained in the same condition for electrodeposition.

1. Introduction

Composite materials consist of a discrete constituent (the reinforcement) distributed in a continuous phase (the matrix) and that derive their distinguishing characteristics from the properties and behaviour of their constituents, from the geometry and arrangement of the constituents and from the properties of the boundaries (interfaces) between the constituents [1]. These innovative materials open up unlimited possibilities for modern materials science and development; the characteristics of metal matrix composites can be designed into the material, custom-made, dependent on the application. From this potential, metal matrix composites fulfil all the desired conceptions of the designer [2 – 4].

Metal matrix composites are only at the beginning of the evolution curve of modern materials (see Fig. 1) [5]. Zinc is more corrosion resistant than steel in most natural atmospheres, the exceptions being ventilated indoor atmospheres where the corrosion of both steel and zinc is extremely low and certain highly corrosive industrial atmospheres. The major drawback of thick coatings is the poor weldability and the difficulty to achieve uniform finishing after painting. This provides the need to develop thinner electrodeposited coatings with improved properties such as hardness, ductility, corrosion resistance, etc [6].
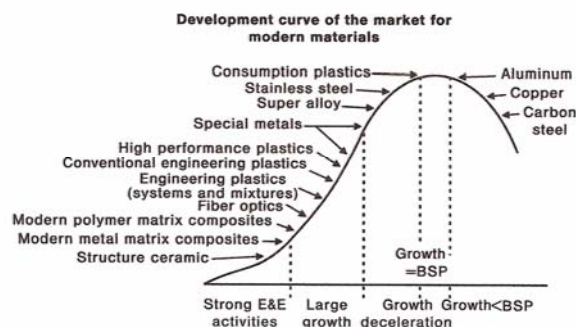

Fig. 1. Development curve of the market for modern materials

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 readily of deposition and better corrosion resistance [7 – 9].

EIS has been successfully applied to the study of corrosion systems for thirty years and been proven to be a powerful and accurate method for measuring corrosion

rates. But in order to access the charge transfer resistance or polarization resistance that is proportional to the corrosion rate at the monitored interface, EIS results have to be interpreted with the help of a model of the interface.

An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal, usually a voltage between 5mV to 10 mV, is applied to a specimen over a range of frequencies from 100 000 Hz to 0.001 Hz [10, 11].

The present work has the purpose of studying the surface structure and corrosion behaviour of composite coatings having zinc matrix and 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.

It is necessary to note that by involving the particles of PF resin in a zinc matrix, we can obtain new materials with properties differing from those of the individual materials.

2. Experimental

For electrodeposition it was used zinc plating bath with following composition: 310g/L $ZnSO_4$ x $7H_2O$; 75g/L Na_2SO_4 x $10H_2O$; 30g/L $Al_2(SO_4)_3$ x $18H_2O$. 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 (50 – 60 g/L Na_2HPO_4 x $12H_2O$; 25 – 30g/L Na_2SiO_2 x $5H_2O$; 2 – 3g/L liquid soap at a temperature o 80 – 90^0C during 10 minutes. After decreasing the surfaces were etched with 15% HCl for 1 – 2 minutes and washing with distilled water.

The PF resin/Zn composite coatings were electrodeposited from a suspension of phenol – formaldehyde (PF) resin particles in aqueous zinc sulphate electrolyte by adding 10g/L PF resin dispersed particles. The size of dispersed particles were 0.1 – 5 μm and 6 – 10 μm.

Phenol-Formaldehyde 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. A Novolac resin is produced if the mole ratio of formaldehyde to phenol (F/P) is greater than one [12]. This method produces relatively linear chains with molecular weights typically between 500 g/mol and 1000 g/mol (see Fig. 2).

The pure zinc and composite coatings were obtained at current density o 4 A/dm^2, time for electrodeposition 30 minutes, a stirring rate of 1000 rpm and an electrolyte temperature of 25^0C. Polished, degreased and cleaned cathodes of 2.5 cm^2 exposed areas were used.

Before electrochemical corrosion investigations the morphologies of deposits were examined by Scanning Electron Microscope type JEOL, JSM-T220 A and atomic force microscope type NanoWizard II.
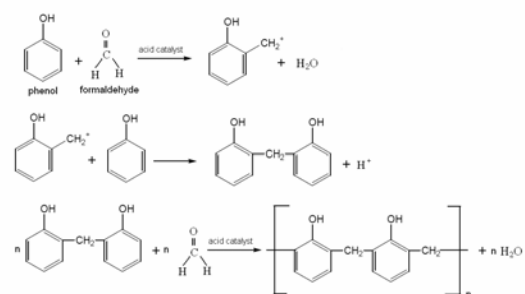

Fig. 2. The schematic formation of the Novolac type structures

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 PF resin/Zn layers as working electrode (W.E.), a platinum gauze as counter electrode (C.E.) and mercury – mercurous sulphate Hg/Hg_2SO_4 electrode as reference electrode (R.E.; E = + 658mV/ENH). As test solution 0.5 M sodium chloride were used at room temperature (20±1 ^0C). EIS measurements used initial frequency (I.F.) 65000Hz, final frequency (F.F.) 0.001Hz, AC sine wave amplitude of 10mV, frequency per decade: 10 Hz, delay before integration 1s. All the recorded impedance spectra were analyzed as Nyquist Diagrams.

3. Results and discussions

The thicknesses of pure zinc and composite coatings obtained by electrodeposition at 4A/dm^2 current density and 30minutes deposition time are shown in fig. 3.
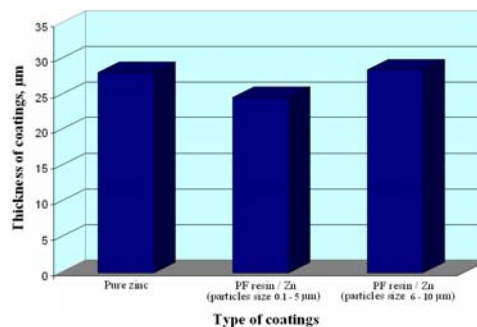

Fig. 3. The thickness of pure zinc and composite coatings obtained by electrodeposition at 4A/dm^2 current density and time 30minutes

Fig. 4 – 6 (A and B) compare the surface morphology of pure zinc coating and PF resin/Zn composite coatings by scanning electron microscopy images and atomic force microscopy images.

The surface of zinc is made up of regular hexagonal crystals with a uniform grain size. 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.
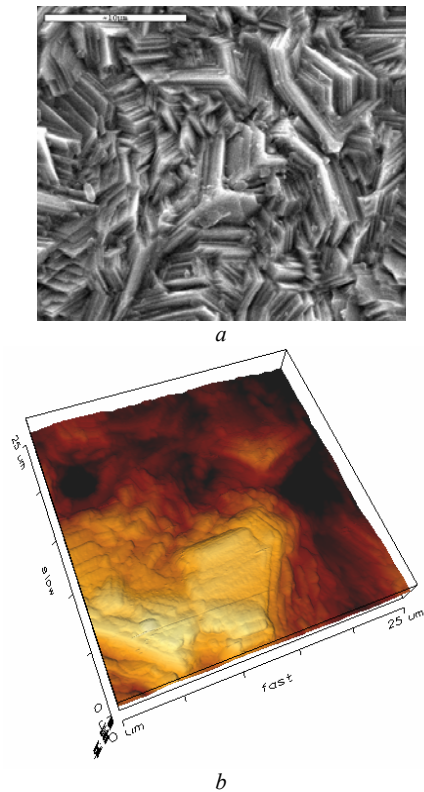
Fig. 4. Surface morphology of pure zinc coating:
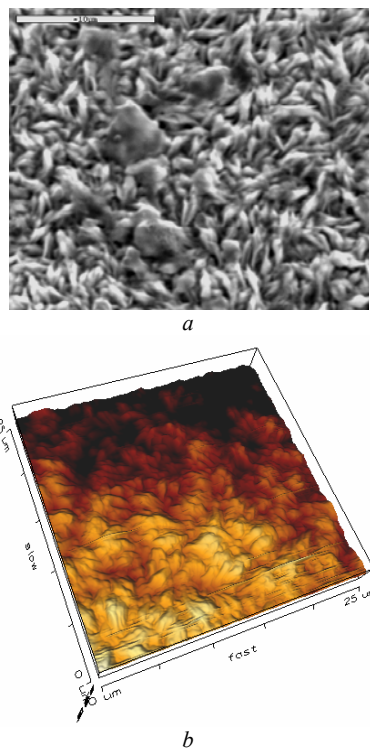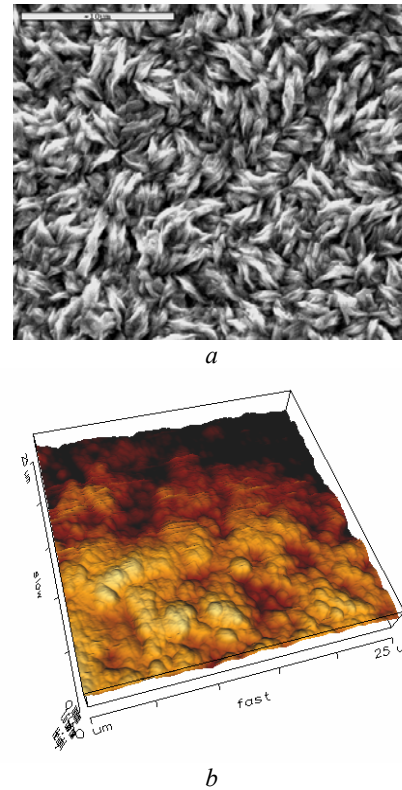*A – SEM image (x 5000), B - AFM image (25µm x 25µm)*

Fig. 6. Surface morphology of PF resin/Zn composite
coatings (size of PF resin particles 6 - 10µm): A – SEM
image (x 5000) B - AFM image (25µm x 25µm)

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.

Roughness is a measure of the texture of a surface and plays an important role in determining how a real system will interact with the environment. It is quantified by the vertical deviations of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth. The following roughness parameters were determinate for zinc and PF resin/Zn composite coatings: R_a - arithmetic average of absolute values; R_q - root mean squared; R_t - maximum height of the profile (see table 1).

Table 1. The values of roughness parameters for pure
zinc and composite coatings

Type of coatings	R_a (nm)	R_q (nm)	R_t (µm)
Pure zinc	627.1	766.2	3.238
PF resin/Zn (0.1 – 5µm)	455.2	547.3	2.767
PF resin/Zn (6 – 10µm)	209.8	255.7	1.505

Fig. 5. Surface morphology of PF resin/Zn composite
coatings (size of PF resin particles 0.1 - 5µm): A – SEM
image (x 5000)B - AFM image (25µm x 25µm

By adding the PF resin particles in the zinc electrolyte the parameters of roughness decrease. For this reason the surface structure of composite coatings was changed more to finer crystallites and becomes smooth. The PF resin acts as reducing the crystals size of electrodeposited zinc during co-deposition. The PF resin could have an inhibition effect of zinc crystals growth and a catalytic effect in increasing the nucleation sites.

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 (see table 2).

Table 2. The OCP values for pure zinc and composite coatings in 0.5M sodium chloride

Type of coatings	Time for OCP, min	OCP, V
Pure zinc	10	- 1.47
PF resin/Zn (0.1 – 5μm)	10	- 1.52
PF resin/Zn (6 – 10μm)	15	- 1.53

From the experimental data can say that the corrosion potential is shifted to more negative values for composite coatings (– 1.53V and – 1.52V) than pure zinc coatings (– 1.47V).

The Nyquist plot representation of impedance spectra performed in 0.5M sodium chloride for pure zinc and PF resin/Zn composite coatings after 30min of immersion it is shown in fig. 7.

Two equivalent electrical circuits were proposed to fit the experimental impedance data [13 – 15]. In most cases, these circuits, represented in the Fig. 8 (a and b) allow 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 represents 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.

The impedance could be described by the following equation:

$$Z = R_e + \frac{R_p}{1+(j\omega\tau)^\beta} \quad \text{(with } 0 < \beta \leq 1) \quad (1)$$

The value of β determines the amplitude of the semi - circle depression. The importance of the discrepancy between the Randles' circuit model with a pure capacitor. C_{DL} and the circuit with the CPE: the borderline case of the Randles' circuit is found if β = 1.

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.
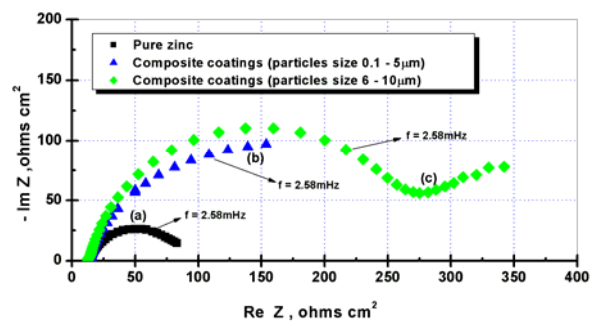

Fig. 7. Nyquist plots of impedance spectrum for pure zinc and PF resin/Zn composite coatings in 0.5M sodium chloride after 30 min from immersion: (a) – pure Zn, (b) –PF resin/Zn composite coatings (particles size 0.1 - 5μm, (c) - PF resin/Zn composite coatings (particles size 6 - 10μm.
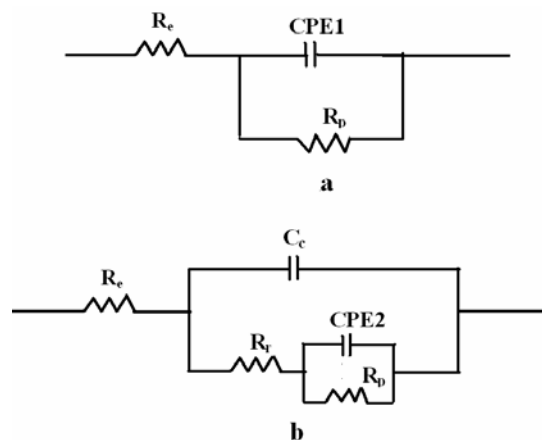

Fig 8. Equivalent circuits for the calculation of the polarization resistance from impedance data

On the Figs. 9 and 10 were represented the experimental diagrams together with the simulation curves described by the equivalent circuits from fig. 8. It could be observed that the experimental impedance data fit very well with the equivalent circuit proposed.
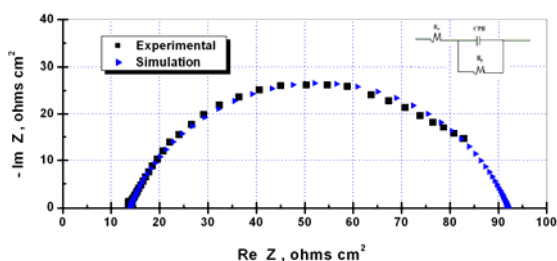
Fig. 9. Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (triangle points) for pure zinc coatings in 0.5 M sodium chloride solution after 30 min of immersion
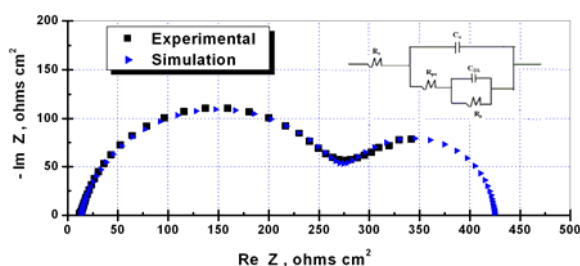

Fig. 10. Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (triangle points) for PF resin/Zn composite coatings in 0.5 M sodium chloride solution after 30min of immersion

The corresponding calculated polarization resistance values from impedance diagrams for pure zinc and PF resin/Zn composite coatings in 0.5M sodium chloride solution using the equivalent circuits from fig. 8 are presented in the Fig. 11.
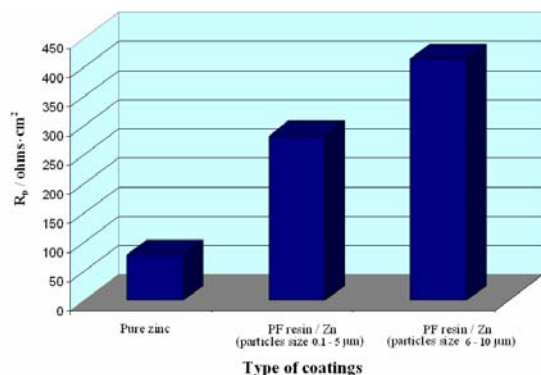

Fig. 11. Variation of polarization resistance for pure zinc and PF resin/Zn composite coatings in 0.5M sodium chloride after 30 min from immersion.

For pure zinc coatings the polarization resistance was $78.17\Omega\cdot cm^2$. For PF resin/Zn composite coatings layers obtained from resin particles with size $0.1 - 5\mu m$ the

polarization resistance was $281.90\Omega\cdot cm^2$ and with increasing the size of particles to $6 - 10\mu m$ the polarization resistance increase to the value of $413.71\Omega\cdot cm^2$.

It was observed that o good polarization resistance was found for PF resin/Zn composite coatings with particles size of $6 - 10\mu m$. The value of polarization resistance for this type of coating is about five times bigger than polarization resistance of pure zinc coating, so that the corrosion resistance of composite coating is about five times higher than pure zinc coating obtained at the same electrodeposition conditions.

3. Conclusions

It was 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 of 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.

The corrosion potential is shifted to more negative values for composite coatings than that of pure zinc coatings obtained in the same conditions of electrodeposition.

The PF resin/Zn composite coatings have a better corrosion resistance compared with pure zinc coatings obtained in same conditions of electrodeposition. 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 acting as insulators on composite surfaces.

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