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Zn-Ni ALLOY COATINGS FROM ALKALINE BATH CONTAINING TRIETHANOLAMINE. INFLUENCE OF ADDITIVES

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ABSTRACT. The Zn-Ni alloys have been electrodeposited from an alkaline bath containing triethanolamine as complexing agent for Ni^{2+} ions. Polyethyleneglicol (PEG), in combination with either coumarin, piperonal or vanillin have been tested as brightening agents. Their effect on the codeposition process and on the corrosion resistance of the resulted coatings was investigated. Under the examined conditions, the electrodeposition was of anomalous type. The effect of plating bath conditions on the corrosion resistance was studied by Tafel polarization measurements. It was found that the tested compounds had a beneficial effect both on deposits quality and on their corrosion resistance.

Keywords: *zinc - nickel alloys, electrodeposition, corrosion, triethanolamine*

INTRODUCTION

Zn-Ni alloys replace successfully cadmium coatings in the automotive industry [1] and provide superior sacrificial protection to steel than pure zinc since they corrode more slowly. Moreover, adhesion of chromate onto Zn-Ni alloy is superior to zinc.

Zinc-nickel can be plated from acid [2-12] or alkaline noncyanide solutions [13-21]. Although Ni is nobler than Zn, the codeposition of Zn-Ni in both cases is anomalous and Zn is present in a higher percent than Ni in the final deposit [2].

The acid bath typically gives a higher Ni content than the alkaline one (*i.e.* 10-14% *vs.* 6-9 %), with high current efficiency, but the distribution of the plated alloy is poor. In contrast, alkaline electrodeposition is less efficient, but gives more uniform plating in both thickness and alloy composition [14]. Moreover, alkaline baths are non-corrosive.

Basic alkaline baths usually contain Zn^{2+} and Ni^{2+} ions, an alkali metal hydroxide and a complexing agent for nickel, such as polyethyleneimine [13, 21], di-, or triethylenetriamine [14], N,N'-bis(3-amino-propyl)ethylenediamine [14], tetraethylenepentamine [14], triethanolamine [19, 20, 22], tartrate [15], ammonia [17-18] etc.

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Electrodeposited Zn–Ni alloys exhibit three main phases: the *α*-phase, which is a solid solution of zinc in nickel with an equilibrium solubility of about 30% Zn, the *γ*-phase, an intermediate phase with a composition Ni_5Zn_{21} and the *η*-phase, which is a solid solution of nickel in zinc with a very low amount of nickel [23].

The use of additives in electrodeposition baths is extremely important due to their influence on the growth and structure of the cathodic deposits [24]. They influence the physical and mechanical properties of the coatings as well as their chemical composition and their corrosion resistance.

In this context, the aim of this work is to investigate the effect of piperonal, coumarin and vanillin in combination with polyethyleneglicol (PEG) on Zn-Ni electrodeposition from an alkaline bath containing triethanolamine.

X ray diffraction (XRD) was used for determination of phase structure of the deposits and electrochemical measurements were carried out in order to characterize their corrosion behavior by using Tafel method.

RESULTS AND DISCUSSION

Electrodeposition

Table 1 presents the results of the visual observation made on Zn-Ni electrodeposits obtained in the absence or in the presence of different additives.

Table 1. Effect of additives on the visual aspect of the alloy deposit. Electrolyte: ZnO 15 g/l + NaOH 130 g/l + $NiSO_4$ 6 H_2O 6 g/l + Triethanolamine (TEA) 80 g/l (pH 14); i = 40 mA/cm^2; t = 35 min; t^0 20 ± 2 ^0C.

No.	Additives	Aspect of the deposit
1	-	dark grey, rough, mat
2	3 ml/l PEG +1 mg/l piperonal	grey, semi bright
3	3 ml/l PEG + 1 mg/l coumarin	grey, semi bright
4	3 ml/l PEG +1 mg/l vanillin	grey, uniform, smooth
5	3 ml/l PEG +5 mg/l vanillin	grey, uniform, semi bright
6	3 ml/l PEG +10 mg/l vanillin	light grey, uniform, bright

It was observed that the most leveled and bright deposits were obtained in presence of the combination of PEG and vanillin and, as expected, the brightness of the deposits increased with the vanillin concentration. All additives improved the quality of the deposits in terms of adherence, grain size and homogeneity.

Corrosion measurements

Linear polarization tests in a potential range of ± 200 mV *vs.* the open circuit potential (ocp) have been made employing the Zn-Ni coated steel electrodes obtained in presence of different additives (Figure 1). PEG was used in all cases as a “carrier”. “Carriers” are compounds with large molecules suffering rapid adsorption - desorption that are usually used in conjunction with compounds having small molecules and suffering specific adsorption at the electrodic interface, in order to obtain leveled and bright metallic deposits [24].

As can be observed, the Zn-Ni alloy becomes nobler than zinc (the corrosion potential is shifted in the positive direction) and hence, the corrosion rate of alloy is hindered. At the same time, the deposit remains still sacrificial with respect to steel.

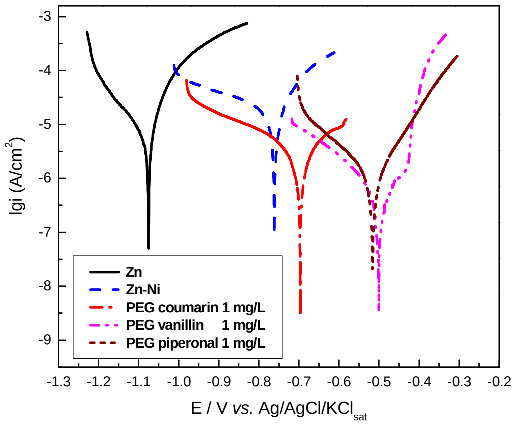

Figure 1. Polarization curves for Zn-Ni coated steel obtained from a bath containing different additives. Experimental conditions: electrolyte Na_2SO_4 0.2 g/l (pH 5); scan rate, 0.166 mV/s; PEG concentration, 3 ml/l.

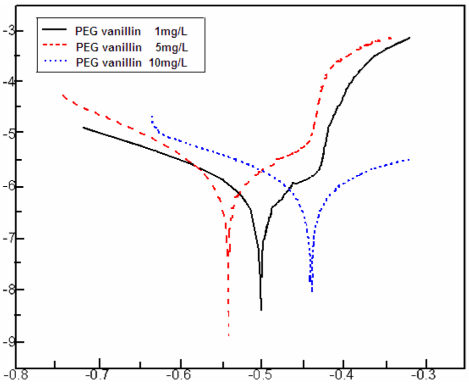

Figure 2. Polarisation curves for Zn-Ni coated steel obtained from a bath containing different concentrations of vanillin. Experimental conditions: electrolyte Na_2SO_4 0.2 g/l (pH 5); scan rate, 0.166 mV/s; PEG concentration, 3 ml/l.

The addition of additives gives rise to significant decreases of corrosion current densities as compared to Zn and Zn-Ni obtained without additives. This indicates that, as expected, the investigated organic compounds strongly modified the quality of the cathodic deposit in terms of structure and morphology, producing more compact, fine-grained and consequently more corrosion resistant coatings.

For a given additive (*e.g.* vanillin) the effect depends on the compound concentration (Figure 2). However, the dependence of the corrosion current density on the additive concentration in the plating bath is not monotone, probably due to the fact that in every electrodeposition process, there is an optimal additive concentration for which the deposit quality is the best [25]. This aspect should be investigated in more details in the future.

The values of the corrosion parameters of the coatings prepared in the absence and in the presence of additives were calculated from the polarization curves by using the Stern - Geary theory [26] and Tafel interpretation and are presented in Table 2.

As can be seen from Table 2, the additives shift the corrosion potential towards more positive values and decrease the corrosion current with about one order of magnitude. When used in concentration of 1 mg/l in combination with PEG, coumarin and vanillin led to similar results concerning the corrosion rate, but the deposits obtained in the presence of vanillin present higher polarization resistance than those obtained in the presence of coumarin and were brighter.

Table 2. Parameters of the corrosion process of the Zn and Zn-Ni coatings

Parameters	**Zn**	**Zn-Ni**	**Zn-Ni+PEG +coumarin**	**Zn-Ni + PEG + piperonal**		**Zn-Ni + PEG + vanillin**		
			1mg/l	**1mg/l**	**5mg/l**	**1mg/l**	**5mg/l**	**10mg/l**
i_{corr}(A/cm^2)	5.80E-06	1.68E-06	3.44E-07	1.68E-06	1.00E-06	3.34E-07	4.95E+0	4.07E-07
b_c (V/dec)	0.034	0.074	0.040	0.085	0.118	0.056	0.034	0.053
b_a(V/dec)	0.084	0.047	0.050	0.112	0.048	0.046	0.038	0.005
R_p (Ohm)	438	441	911	618	9976	6948	3315	4865
E_{corr}(mV)	-1075	-761	-622	-516.0	-530	-501	-541	-438
V_{corr} (mm/year)	1.16E-01	2.51E-02	5.13E-03	2.51E-02	1.49E-02	4.98E-03	7.38E-03	6.05E-03

*b_a and b_c are the anodic and cathodic activation coefficients, respectively.

XRD analysis

In order to put on evidence the formation of Zn-Ni alloy by electrodeposition and to correlate the electrochemical results with the structural data of the coatings, XRD investigations were carried out on the coated steel electrodes obtained with PEG and 1 mg/l of different additives (Figure 3).

The XRD patterns of the Zn-Ni coatings obtained from a bath containing PEG (3 ml/l) in combination with either piperonal, vanillin or coumarin 1 mg/l (Figure 3) have revealed the formation of the ZnNi cubic alloy, space group P 4/m, PDF card no. 65-3203; a = 0.295(6) nm and V= 0.259(2) nm^3. The unit cell parameters and the unit cell volumes of the ZnNi cubic alloy, calculated using the PowderCell software [27] from the whole X-ray diffraction pattern refinement of the above-mentioned Zn-Ni coatings, are presented in the Table 3.

The microstructural parameters, the effective crystallite mean size, D_{eff} (nm) and the mean root square (rms) of the microstrains, ($<\varepsilon^2>^{1/2}_m$), of the ZnNi cubic crystalline phase of the Zn-Ni coatings are also presented in Table 3.

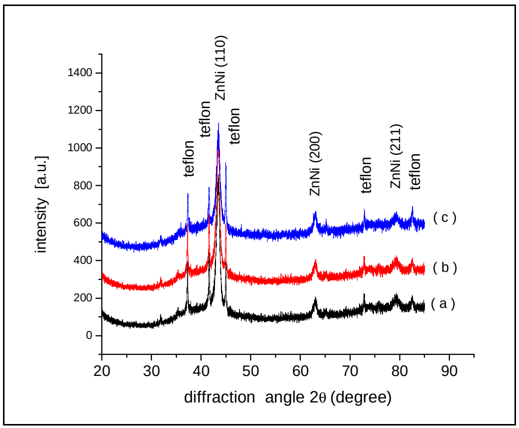

Figure 3. X-ray diffractograms of Zn-Ni coatings obtained from a bath containing PEG (3 ml/l) in combination with piperonal (a), vanillin (b) and coumarin (c) in concentration 1 mg/l.

Table 3. The unit cell parameters, the unit cell volumes of the ZnNi cubic alloy and the microstructural parameters of the Zn-Ni coatings obtained from a bath containing PEG (3 ml/l) in combination with piperonal (a), vanillin (b) and coumarin (c) in concentration 1 mg/l

Samples	Unit cell parameter a [nm]	Unit cell volume [nm3]	Effective crystallite mean size Deff (nm)	Rms of the microstrains <ε2>1/2m x 103
Zn-Ni + PEG + piperonal	0.2958(2)	0.2588(7)	8.85	5.093
Zn-Ni + PEG + vanillin	0.2955(6)	0.2581(9)	8.45	4.574
Zn-Ni + PEG +coumarin	0.2957(7)	0.2587(4)	9.62	2.424

The nanostructured Zn-Ni coatings prepared in the presence of additives piperonal and vanillin showed a smaller average size of the crystallites (8.6 nm), than the nanostructured Zn-Ni coatings prepared in the presence of coumarin (9.6 nm). At the same time, the lattice microstrain $< \varepsilon^2 >^{1/2}$ of nanostructured Zn-Ni coatings prepared in the presence of piperonal and vanillin shows a larger value of the intercrystallite zones that suggests a higher interaction between the nanoparticles of the coating and the steel support and, consequently, a higher corrosion resistance of the coatings.

CONCLUSIONS

The Zn-Ni coatings showed an excellent corrosion resistance as compared with conventional Zn coatings obtained from an alkaline bath. Using of additives allowed obtaining more corrosion resistant Zn-Ni deposits than in their absence.

The best corrosion behavior was exhibited by the coatings obtained in the presence of PEG in combination with piperonal or with vanillin, which presented a smaller average size of the crystallites than the nanostructured Zn-Ni coatings prepared in the presence of coumarin.

EXPERIMENTAL SECTION

Electrodeposition

The electrodeposition of the Zn-Ni coatings was carried out in a two compartments glass cell, with the capacity of 250 ml, using a steel (OL37) disk electrode (Ø =1cm) as working electrode, a $Ag/AgCl/KCl_{sat}$ as reference electrode and a Pt foil as counter electrode. Before electrodeposition, the working electrode was wet polished on emery paper of different granulations and finally on felt with a suspension of alumina. Before plating, the electrode was ultrasonicated during 2 minutes, washed with acetone and distilled water in order to remove the impurities from the surface.

The approximately 40 μm thick composite coatings were obtained at a constant current density (i = 40 mA/cm^2) by using a potentiostat / galvanostat (Voltalab PGP201, Radiometer analytical), during 35 minutes, at room temperature (25 +/- 2^{0}C).

Corrosion measurements

The corrosion measurements were performed with a potentiostat Autolab-PGSTAT 10, (Eco Chemie BV, Utrecht, Netherlands). Before the polarization measurements, the open circuit potential (OCP) was recorded during 1 hour, until it was stabilized.

XRD measurements

The powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance powder diffractometer working at 40 kV and 40mA, using CuKα wavelength, with a germanium monochromator. The measurement was performed in the range angle 2θ=20-85^0 and in a step-scanning mode with a step $\Delta 2\theta = 0.01^0$. Pure corundum powder standard sample was used to correct the data for instrumental broadening.

The Warren-Averbach X-ray Fourier analysis [28] of the ZnNi (1 1 0) (2θ = 43.42 degree), ZnNi (2 0 0) (2θ = 63.02 degree) and ZnNi (2 1 1) (2θ = 79.22 degree) cubic ZnNi alloy structure diffraction profiles were used in order to determine the microstructural parameters of the Zn-Ni coatings (the effective crystallite mean size, D_{eff} (nm) and the mean root square (rms) of the microstrains, $<\varepsilon^2>^{1/2}_m$.

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