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CORROSION BEHAVIOR OF ELECTROCHEMICALLY DEPOSITED Zn-TiO$_2$ NANOCOMPOSITE COATINGS

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ABSTRACT. Zn-TiO$_2$ nanocomposite films were successfully formed on carbon steel by rapid plating from a ZnSO$_4$-based bath (i = 10 A dm^{-2}). The corrosion resistance of the composite coatings was studied by polarization and electrochemical impedance spectroscopy measurements. In the presence of TiO$_2$, simultaneously with the negative shift of the corrosion potential, a decrease of the corrosion current density was observed as compared to pure zinc coatings, reflecting the beneficial effect of TiO$_2$ nanoparticles on the corrosion resistance of zinc coatings.

Keywords: nanocomposite coatings, zinc, titanium oxide, corrosion

1. INTRODUCTION

Electrodeposition of Zn films on steel is widely practiced for corrosion resistance increase. However, the life span of such coatings is limited due to the aggressive nature of some environments, particularly those containing industrial pollutants. Consequently, considerable efforts are being made to improve their corrosion resistance [1].

TiO$_2$ can reinforce metallic coatings including zinc electroplate to improve corrosion and wear resistance, hardness and other properties of the coating such as semiconductor and magnetic properties, lubricity etc. [2-5].

One of the methods used for entrapment of TiO$_2$ micro- or nanoparticles in the metallic matrix is the electrolytic co-deposition. The main advantages of this method over other coating methods are the uniformity of deposition for complex shapes, reduction of waste encountered in dipping or spraying techniques, low level of contamination, high production rates, low initial capital investment requirements and easy transfer from the research laboratory to existing infrastructure in electroplating and electroforming industries [6].

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The present paper seeks to investigate the corrosion behavior of Zn-TiO_2 coatings obtained by electrolytic co-deposition of zinc with TiO_2 nanoparticles, on steel substrate (OL 37 / Zn-TiO_2). The investigation methods were open circuit potential measurements, hydrodynamic voltammetry and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

Materials

TiO_2 aerogel (surface area 305 m^2/g) was obtained by the sol-gel method and was a kind gift from Dr. Virginia Danciu (Laboratory of Electrochemical Research, Faculty of Chemistry and Chemical Engineering Cluj-Napoca).

Zn and Zn-TiO_2 films were co-deposited on OL 37 steel substrate (S = 0.78 cm^2) using a rotating disc electrode (1000 rpm) from solutions containing 350 g/l $ZnSO_4 * 7\ H_2O$ and 30 g/l $(NH_4)_2SO_4$ (pH 4) without or with 20 g/l TiO_2, at a current density of 100 mA/cm^2, during 30 minutes.

Corrosion experiments were carried out in 0.2 g/l aerated Na_2SO_4 solution (pH 3), at room temperature.

Methods

Potentiodynamic polarization measurements were conducted using an electrochemical analyzer (PARSTAT 2273, USA) connected to a PC for potential control and data acquisition. Open-circuit potential (*ocp*) measurements were performed as a function of time.

The electrochemical experiments were performed in a three-electrode cell with a separate compartment for the reference electrode connected with the main compartment *via* a Luggin capillary. The working electrode was a rotating disc, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum foil.

Anodic and cathodic polarization curves were recorded in a potential range of $E = E_{corr} \pm 200$ mV with a scan rate of 0.25 mV s^{-1}. The rotation speed of the working electrode was fixed at 1000 rpm.

Impedance measurements were performed at the open circuit potential in the moment of immersion of the samples in the Na_2SO_4 solution during 30 h from this moment. The impedance spectra were acquired in the frequency range 10 kHz to 10 mHz at 10 points per hertz decade with an AC voltage amplitude of ± 10 mV.

3. RESULTS AND DISCUSSION

3.1. Open-circuit potential (ocp) measurements

The open-circuit potentials evolution in time for OL 37/Zn and OL 37/Zn-TiO_2 electrodes, recorded immediately after 60 minutes immersion in the corrosive medium is presented in Figure 1.

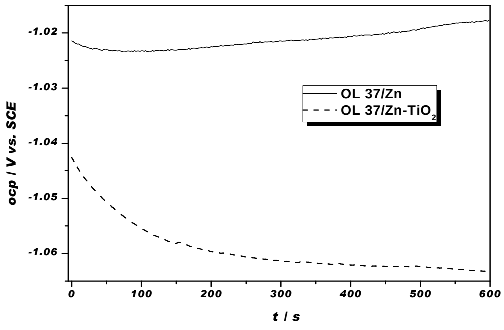

Figure 1. Open-circuit potentials evolution for the OL37/Zn and OL37/Zn-TiO_2 electrodes immersed in 0.2 g/l Na_2SO_4 (pH 3).

In the case of OL 37/Zn-TiO_2 electrode, the *ocp* values gradually increase in the negative direction during the first minutes to reach a stationary state characterized by -1.065 V *vs.* SCE. This evolution of the potential toward more negative values with the increase of immersion time can be explained by taking into account the growth of a corrosion products layer. According to this growth, the cathodic reaction is hindered and consequently the corrosion potential becomes more negative [7]. The *ocp* value is more negative in the presence of TiO_2 in the zinc deposit than in its absence, suggesting an intervention of these particles in the cathodic process (oxygen reduction).

3.2. Potentiodynamic polarization measurements

The cathodic and anodic polarization curves of OL 37/Zn and OL 37/Zn-TiO_2 electrodes recorded after their immersion during 60 minutes in Na_2SO_4 solution are shown in Figure 2.

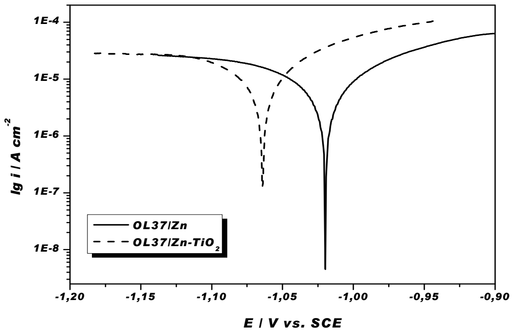

Figure 2. Influence of TiO_2 presence in the zinc deposit on the anodic and cathodic polarization curves.

The same shift of the corrosion potential towards more negative values is noticed in the case of OL 37/Zn-TiO_2 electrode as compared to OL37/Zn electrode. A similar behavior was reported in the case of Cu-ZrO_2 composite films immersed in 0.5 M H_2SO_4 solution [8], when the oxide nanoparticles were proved to retard or inhibit the oxygen reduction on the composite surface.

The corrosion parameters were calculated from the potentiodynamic polarization curves on the basis of the Tafel extrapolation, according to the equation:

$$i = i_0 \exp\left[\frac{2{,}303}{b_a}(E - E_{corr})\right] - \exp\left[-\frac{2{,}303}{b_c}(E - E_{corr})\right]$$

where b_a and b_c are anodic and cathodic Tafel slopes, E_{corr} is the corrosion potential and the other parameters have their usual meaning.

Table 1.

Electrochemical parameters of the corrosion process determined by Tafel method

Electrode	E_{corr} (mV *vs.* ESC)	i_{corr} (μA/cm^2)	- b_c (mV/dec)	b_a (mV/dec)
OL37/Zn (0h)	-1025	15,96	240	153
OL37/Zn-TiO_2(0h)	-1063	15,20	155	84

As can be seen, the presence of TiO_2 in the zinc deposit gives rise to decreases of corrosion current densities and of the Tafel coefficients as compared to the pure zinc coating.

3.3. Electrochemical impedance spectroscopy

The Nyquist impedance diagrams recorded on OL 37/Zn and OL 37/Zn-TiO_2 electrodes are presented in Figure 3.

The impedance spectra recorded in the absence and in the presence of TiO_2 nanoparticles in the zinc coatings exhibit a predominant capacitive behavior. The low frequency loop is characteristic of convective diffusion impedance. In agreement with the polarization measurements, it is necessary to consider that this loop is representative of the diffusion process in the electrolyte and through the porous layer [7].

The polarization resistance R_p corresponding to the lower frequency limit of the impedance spectra increases in parallel with the thickness of the corrosion products layer. The increase of R_p can be explained by a limitation of the active area by this layer, more important when the layer is more developed (thicker and/or more compact) [7]. As can be seen from figure 3, in the moment of immersion, the highest value of R_p is noticed in the case of pure zinc coating, while after 12 h of immersion, R_p is higher in the case of the composite layer.

This behavior suggests a different evolution of the corrosion products layer in the two cases. Further work will address the chemical composition of these layers.

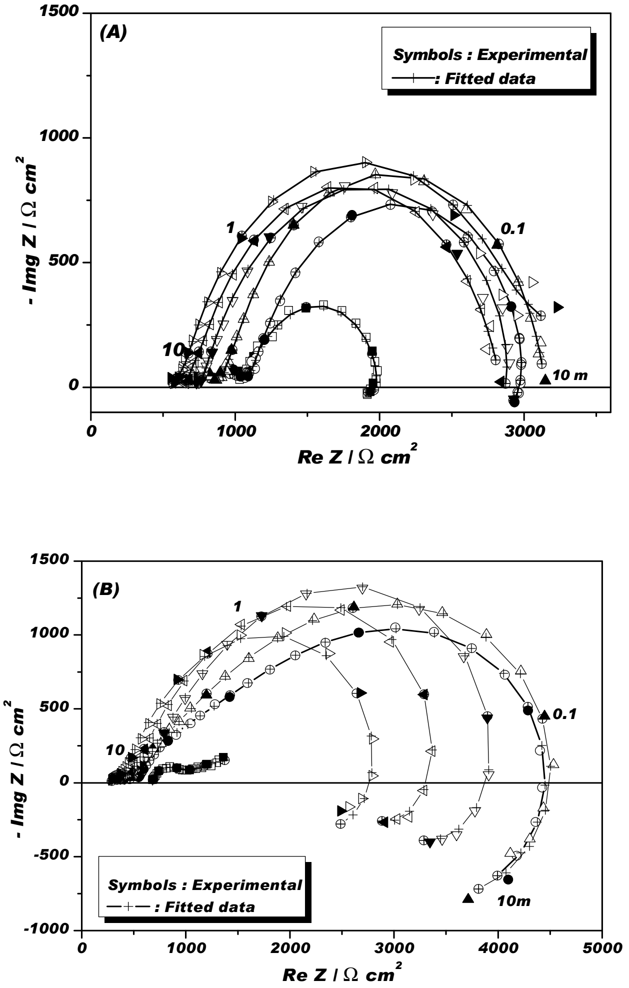

Figure 3. Nyquist impedance diagrams for OL 37/Zn (A) and OL 37/Zn-TiO$_2$ (B) electrodes in 0.2 g/l Na$_2$SO$_4$ solution (pH 3) at different immersion times: (■) 0 h; (●) 6h; (▲) 12h; (▼) 18h; (◀) 24h; (▶) 30h.

The inductive behavior is almost inexistent in the case of pure Zn coating and more pronounced in the case of Zn-TiO$_2$ nanocomposite film. It should be mentioned that this behavior becomes more important with the increase of immersion time, suggesting that the inductive loop could be due to the potential dependence of some inhibiting species present on the electrode surface (hydrogen or corrosion products involving metal ions) [9].

The equivalent electrical circuits used for non-linear regression calculations with a simplex method are presented in Figure 4.

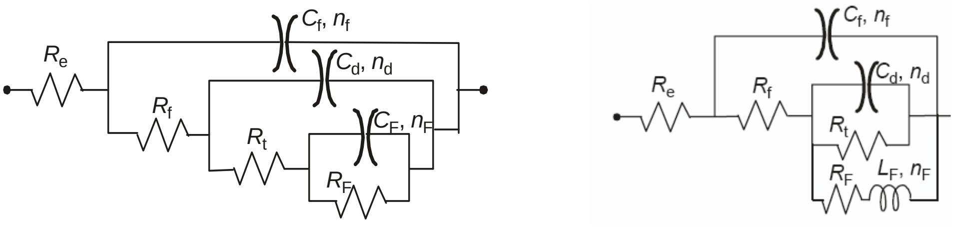

Figure 4. The equivalent electrical circuits used for computer fitting of the experimental data

When the impedance spectra contained only capacitive loops, the fitting was performed using a 3RC equivalent circuit, while when an inductive loop was present, an equivalent 2RC-LC circuit was used. The significance of the different variables is the following [10]:

- R_e: Electrolyte resistance
- C_f: Capacitance due to the dielectric nature of surface film (corrosion products)
- R_f: Resistance representing the ionic leakage through pores of the dielectric film
- C_d: Double layer capacitance at the zinc / electrolyte interface
- R_t: Charge transfer resistance
- C_F: Faradic capacitance due to an oxidation - reduction process taking place at the electrode surface, probably involving the corrosion products.
- R_F: Faradic resistance of the corrosion products accumulated at the interface.
- n_f, n_d, and n_F: Coefficients representing the depressed characteristic of the three capacitive loops in the Nyquist diagrams.

The values of the corrosion parameters obtained by fitting of the experimental impedance data are presented in Table 2.

Table 2.

Parameter values for OL 37/Zn and OL 37/Zn-TiO_2 electrodes corrosion calculated by non-linear regression of the impedance data from figure 3 using the 3RC or 2RC-LC models

Electrode	**Immers. time (h)**	**R_f (Ω cm^2)**	**C_t (μF cm^{-2})**	**n_f**	**R_t (Ω cm^2)**	**C_d (μF cm^{-2})**	**n_d**
OL 37/Zn	0	152.48	2.10	0.75	1164.3	17.24	0.75
	6	194.94	3.02	0.59	4052.2	113.77	0.80
	12	346.25	73	0.88	1731.3	103.24	0.86
	18	124.94	29.65	0.85	983.4	96.62	0.85
	24	462.01	89.4	0.84	1470.9	117.74	0.87
	30	197.65	49	0.84	1777.4	129.65	0.83
OL 37/ Zn-TiO_2	0	290.61	15.36	0.76	454.33	3430	0.51
	6	1277.1	5.04	0.63	3840.7	70.45	0.58
	12	1493.9	10.87	0.55	4365.7	20.67	0.61
	18	377.53	4.11	0.68	3537.6	62.12	0.80
	24	252.04	5.35	0.71	3017.1	105.62	0.83
	30	196.43	7.48	0.69	2579.3	141.32	0.83

As can be observed from figure 3, between the experimental and the calculated regression data exists a good accordance. The analysis of the results presented in table 2 led to the following conclusions:

(i) The charge transfer resistance R_t (of 10^3 Ω cm^2 order of magnitude) suggests that the layer of corrosion products is not very compact [11]. Generally, if the composition of the corrosion products does not change during the experiments, an increase of R_t values can be correlated with an increase of the thickness of non-conductive corrosion products layer. Thus, the higher R_t values in the presence of TiO_2 nanoparticles than in their absence suggests a better corrosion resistance in the first case. The decrease of R_t during long-term measurements could be attributed to the formation of less protective corrosion products.

(ii) The double layer capacitance values of the corrosion products layer C_f are also characteristic to a porous layer (10^{-4} F/cm^2). In the case of OL 37/Zn electrode, the relative constancy of C_f after 12 h of immersion points to a certain stabilization of the composition of the corrosion products layer. The decrease of C_f in the case of OL 37/Zn-TiO_2 electrodes could be attributed to the thickening of the corrosion products layer, which leads to a change of permittivity of the environment [11].

4. CONCLUSIONS

The electrochemical measurements showed that the corrosion process on zinc-titania composite surface is slower than on pure zinc surface, because of oxide particles embedded in the zinc matrix.

The titanium oxide particles retard or inhibit the oxygen reduction on the composite surface.

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