THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2014, ISSN 1453 – 083X

EFFECT OF ZnO NANOPARTICLES ON THE ANTICORROSION PROPERTIES OF EPOXY COATING[1]

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ABSTRACT

Homogeneous epoxy coating obtained by embedding ZnO nanoparticles (≤50 nm) in the epoxy matrix, was applied on Grade A naval steel substrates by dip-coating method. The morphology and microstructure of the coatings were characterized by optical microscopy, scanning electron microscopy with electron diffraction spectroscopy (SEM-EDS) and X-ray diffraction (XRD) analysis. The effect of nanoparticles on the corrosion resistance of the hybrid coatings was investigated by potentiodynamic polarization method. The coated steel samples were electrochemically monitored over the 30 days of immersion in 5 wt.% NaCl solution. The incorporation of a small amount of ZnO nanoparticles (1 wt.%) has a beneficial effect, significantly improving the anticorrosion behavior of coating in terms of polarization resistance and corrosion rate, parameters estimated from Tafel curves.

KEYWORDS: ZnO nanoparticles, epoxy coating, Tafel curves, corrosion parameters

1. Introduction

Epoxy based coatings have been used for a long time and appear to be the most convenient method for preventing corrosion and fouling of steel surfaces, structures which work in very severe conditions. Generally, epoxy coatings reduce the corrosion of a metallic substrate subject to an electrolyte, in two ways: they act as a physical barrier layer against the ingress of a deleterious species; second, they can serve as a reservoir for corrosion inhibitors to aid the steel surface in resisting to the attack initiated by aggressive species [1]. Unfortunately, the epoxy coatings have susceptibility to damage by surface abrasion and wear [2, 3] and also they show poor resistance to the propagation of cracks [4].

The defects appeared on coating surface can act as pathways, accelerating the ingress of water, oxygen and chloride anions onto metallic substrate. Being hydrophilic in nature, the epoxy coatings have large volume shrinkage upon curing and can absorb water from surroundings [5, 6], leading to the increasing of the number of pores and crevices, defects that create corrosion products.

The barrier features of epoxy coatings can be enhanced by the incorporation of nanosized inorganic filler particles, dispersed within the epoxy matrix, to form an epoxy based nanocomposite.

Thereby, the following benefits can be obtained:

- improving of the integrity and durability of coatings by dispersion of fine particles in the cavities of epoxy matrix [7-9].
- preventing epoxy disaggregation, obtaining a more homogeneous coating, due to the tendency of nanoparticles to occupy small hole defects, interconnecting more molecules, reducing total free volume and increasing cross-linking density [10-12].
- offering significant barrier properties for corrosion protection [13-14] and reducing the tendency of coating for blistering or delaminating.

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[1] Papers presented at the second edition of the Scientific Conference of Doctoral Schools from "Dunarea de Jos" University of Galati, CSSD-UDJG 2014, Galati, May 15-16, 2014.

In this paper, we present the effect of ZnO nanoparticles on the surface morphology and anticorrosion parameters of epoxy coatings for better understanding the mechanisms through which nanoparticles interact with epoxy matrix, for obtaining coatings with high performances in the corrosion protection of steel.

2. Experimental details

2.1. Materials

The epoxy resin, the hardener and the solvent used for coating deposition, commercially known as DER 353, I 3100 and D 309 respectively, were obtained from S.C. “Policolor” S.A. (Bucharest). The DER 353 liquid epoxy resin is an aliphatic glycidyl ether modified bisphenol A/F based epoxy resin, whereas I 3100 hardener is a polyaminoamidic hardener. ZnO nanoparticles with diameter below 50 nm were purchased from Sigma Aldrich (Steinheim, Germany).

Sodium chloride (NaCl) used for corrosion test was purchased from S.C. Silal Trading S.R.L. (Bucharest). As substrates were used rectangle steel samples (50x20 mm) of grade S235JR+AR according to EN 10025-2004 with the following composition: 0.12% C, 0.48% Mn, 0.015% Si, 0.013% P, 0.006%S, 0.039% Al, 0.016% Cu, 0.029% Cr, 0.024% Ni, 0.001% V, 0.003% Mo, 0.001% Ti, 0.001% Nb and Fe.

2.2. Sol preparation and coating deposition

The hybrid sols were prepared in two steps. In the first step was prepared the epoxy precursor solution with a weight ratio of 1.6:1 epoxy resin to hardener. To the obtained solution were added ZnO nanoparticles (1 wt.%) under energical stirring (1400 rpm) and sonnication. Before the deposition of coatings, the steel substrates were cleaned with acetone, sand-blasting to the grade “Sa 2½” and finally immersed in acetone and dried. To remove the microparticles remained on the surface after sand-blasting, the substrates were sonicated in acetone for 10 minutes.

The coatings were deposed by dip-coating technique, using a home-made dip-coater. After each layer deposition, the samples were kept at room temperature for 30 min, placed in an oven (Model FN 055 Nüve) at 90ºC for 30 min and then again at room temperature for 30 min.

In order to compare the effect of the nanoparticles, unmodified epoxy coating (*type I*) and ZnO-modified epoxy coating (*type II*), with approximately the same thickness, around 5 0μm, have been prepared.

2.3. Characterization of coatings

The film thickness (Dry Film Thickness - DFT) was measured by a nondestructive testing method, using a 345 type Elcometer device.

The surface morphology and chemical composition of the coatings were analyzed by Scanning Electron Microscopy with Electron Diffraction Spectroscopy (SEM-EDS) using a Zeiss EVO MA 15 model microscope. *The anticorrosive behaviour* of the nanocomposite coatings was investigated by potentiodynamic weak polarization method. The samples were kept immersed in corrosive solution (5 wt.% aqueous NaCl solution) over the 30 days and the measurements of corrosion parameters were carried out periodically using Voltalab PGP 201 Radiometer Analytical equipment, with three electrodes: the epoxy coated steel sample served as the working electrode, whereas the counter electrode and the reference electrode were used a platinum plate and Ag/AgCl, respectively. A special cell assures the reproducibility of the experimental parameters, especially the distances between electrodes and the free sample surface (0.5024 cm^2) in contact with the corrosive solution. The steel was polarized around its corrosion potential, in general in the potential range of -1000 mV÷ +200 mV by a direct current (DC) signal, at a scan rate of 2 mV/s. The results were processed with the VoltaMaster software application-version 4, using the following experimental parameters: diameter of the free surface of the sample (8 mm), solution exposed surface aria (50.24 mm^2), steel sample density (7.8 kg/dm^3) and iron valence (2).

3. Results and discussion

3.1. Structure and morphology

Optical top-view images of the investigated samples are shown in Figure 1, which indicates that the cured epoxy coating has a relatively homogeneous morphology, without cracks (Figure 1a) and the ZnO modified epoxy coating is slightly rough and apparently showed no sign of nanoparticles agglomeration (Figure 1b). *Topographic analysis* of deposited films was realized by the technique of obtaining and overlapping of three-dimensional imaging (Figure 2). One can observe that simple epoxy coating has a smaller surface roughness than the nano-ZnO modified epoxy coating, thing that can be explained by the presence of a higher number of layers deposited. In Figure 3 are shown SEM images of the surface of nano-ZnO modified epoxy coating (Figure 3a) and chemical EDX analysis on the selected area (Figure 3b); one can observe the presence of some agglomeration of nanoparticles inside the coating, but no crack. The results of elemental EDX analysis in the area marked are displayed in Figure 4. Although SEM image of agglomerated nanoparticles is observed, EDX mapping on the same area shows a uniform distribution of zinc and oxygen, demonstrating a good dispersion of ZnO nanoparticles inside the composite coatings.

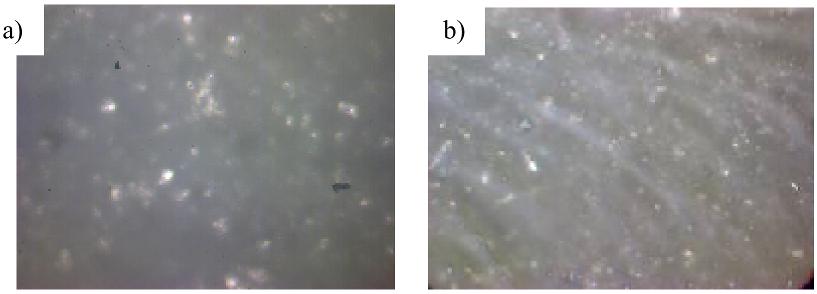

Fig. 1. *Optical micrographs of: simple epoxy coating (type I) (a); nano-ZnO modified epoxy coating (type II) (b) (magnification 12.5x8x)*

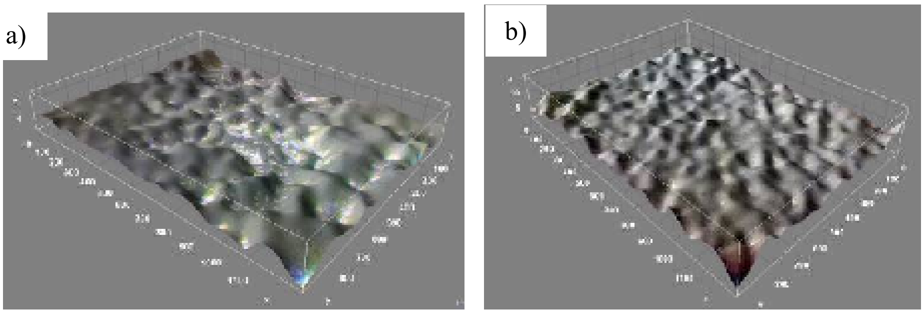

Fig. 2. *3D image of: simple epoxy coating (type I) (a); nano-ZnO modified epoxy coating (type II) (b)*

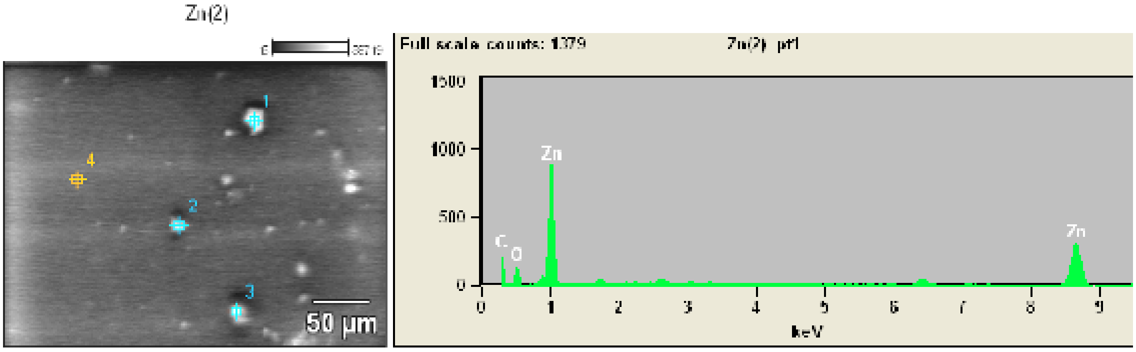

Fig. 3. *SEM image of nano-ZnO modified epoxy (type II) coating (a); chemical analysis specific to region 1 (b)*

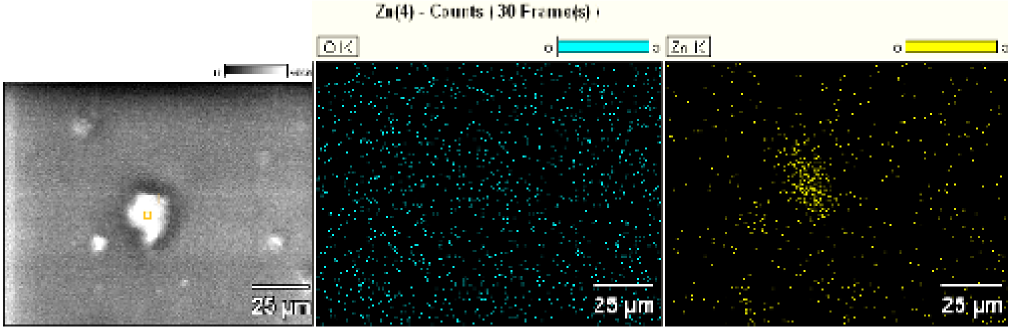

Fig. 4. *Elemental contents of oxygen and zinc mapped by EDX on an area of the nano-ZnO modified epoxy coating (type II)*

The film thickness (DFT)

The medium values obtained for thickness of two epoxy coatings, unmodified (*type I*) and modified with ZnO nanoparticles (*type II*) were of 43 µm and 50 µm, respectively.

3.2. Effect of nanoparticles on the corrosion resistance of the coated steel

The experimental corrosion parameters (corrosion potential, corrosion current, polarization resistance and instantaneous corrosion rate) of the steel samples coated with metal oxide-epoxy nanocomposite were estimated from Tafel curves. Figure 5 shows the temporal evolution of instantaneous corrosion rate (Figure 5a) and polarization resistance, Rp, (Figure 5b) of the steel samples coated, during more than 30 days of immersion in 5 wt.% NaCl solution.

One can notice that both diagrams show that in case of simple epoxy coating there is a continuing trend of increasing instantaneous corrosion rate (Figure 5a), respectively of decreasing polarization resistance (Figure 5b).

This could be attributed to the fact that in the case of this type of coating, once activated the destruction of physical barrier, the corrosion process continuously develops.

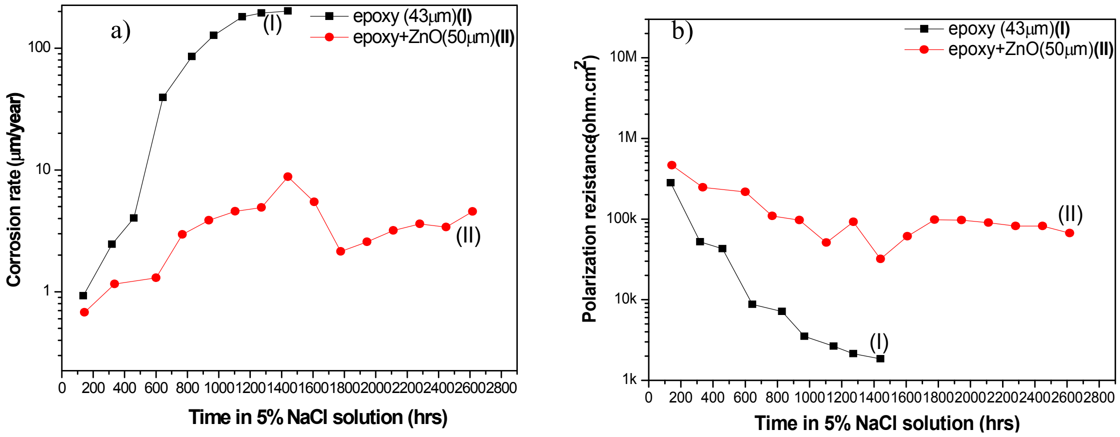

Fig. 5. *Time evolution of: corrosion rate (a) and polarization resistance (b), of epoxy-coated steel in 5 wt.% aqueous NaCl solution, at different time of immersion*

In case of nano-ZnO modified epoxy coating, for both diagrams in Figure 5 one can distinguish three steps: from the beginning to around 800 hours of immersion (Step I) in which the corrosion rate grows up in an accelerated way from 800 to about 1400 hours of immersion (Step II) in which there is a lower growth of instantaneous corrosion rate and the last (Step III) in which the corrosion rate decreases or it is maintained within close limits. Consequently, the trend of decreasing is similar in case of polarization resistance. The incorporation of a small amount of ZnO nanoparticles (1 wt.%) into the epoxy coating significantly reduced the corrosion rate of the epoxy-coated steel over the 30-day immersion in 5 wt.% NaCl solution, by 2 to 40 times, after 1272 hours and consequently leads to the adequate improving corrosion resistance of the epoxy-coated, by 2 to 43 times, for the same period of immersion.

The tendency of nano-ZnO modified epoxy coating to keep a constant good level for anticorrosion resistance on long-term (until 2600 hours of immersion) could be explained both by the occurrence of corrosion products that can slow the corrosion process but also by the beneficial presence of ZnO nanoparticles which can act as reservoir for corrosion inhibitors of the steel surface in resisting to the attack of aggressive species.

4. Conclusions

ZnO nanoparticles were successfully dispersed in epoxy resin matrix at a concentration of 1%. The samples obtained after dipping the steel substrate into the hybrid sol show smooth surface and compact coating, a good compliance and adherence to the substrate, no cracks and no boundaries between the deposited layers. The electrochemical monitoring over the 30 days of immersion in 5 wt.% NaCl aqueous solution suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel. For future research, it is important to investigate ways to improve the dispersion of a mix of nanoparticles to provide different features of the epoxy coating, to increase the content of ZnO nanoparticles and the potential application of the nanoparticles as reservoirs of corrosion inhibitors.

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