



## Corrosion behavior and protective ability of Zn and Zn–Co electrodeposits with embedded polymeric nanoparticles

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### ABSTRACT

The anodic behavior, corrosion resistance and protective ability of Zn and alloyed Zn–Co (~3 wt.%) nanocomposite coatings were investigated in a model corrosion medium of 5% NaCl solution. The metallic matrix of the layers incorporates core–shell nano-sized stabilized polymeric micelles (SPMs) obtained from poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) block co-polymers. The protective properties of the composite coatings were evaluated using potentiodynamic polarization technique, polarization resistance measurements and powder X-ray diffraction. The sizes and distribution of the stabilized polymeric micelles in the starting electrolytes used as well as in the metal matrices of the layers were investigated using scanning and transmission electron microscopy. The results obtained are compared to those of electrodeposited Zn and Zn–Co (~3 wt.%) alloy coatings at identical conditions and demonstrate the enhanced protective characteristics of the Zn nanocomposites during the investigating period. The influence of the SPMs on the corrosion resistance of the nanocomposite layers is commented and discussed.

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## 1. Introduction

Electrodeposited zinc coatings are widely used in practice for preventing the corrosion of steel [1,2]. For example, the usage of zinc-coated steel in the automotive industries improves significantly its corrosion resistance. The latter depends in particular on the deposition technology, but it is also affected by the morphology and crystallographic orientation in the Zn layer [3,4]. Many researchers [5–11] comment and discuss the high protective properties of the zinc in the conditions of wet (aqueous) corrosion.

Improvement of the corrosion resistance of the zinc coating can be achieved by an additional treatment in chromate or phosphate solutions, alloying with other metals [12–18] or, recently, obtaining of nanocrystalline deposits [19].

Development of novel galvanic layers with improved corrosion resistance is demanded by the increasing industrial requirements for longer service life or reduced coating thickness. Recently, a new approach for the preparation of zinc coatings with higher corrosion resistance and protective ability in corrosive environments was reported [20–24]. This approach is based on the formation of nanostructured Zn-based coatings with embedded stabilized polymeric micelles (SPMs) consisting of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO co-polymers) [25]. The latter are commercially available surfactants (pluronic, synperonic, poloxamers) that spontaneously form nano-sized core–shell micelles in water having a predominantly hydrophobic PPO-composed core and a shell dominated by hydrated PEO segments. The micellar structure is locked by formation of an interpenetrating network of polyether chains and a tetrafunctional cross-linking agent to improve the micellar stability in a broad range of experimental conditions. The incorporation of the above-mentioned SPMs in the galvanic coating changes partially the metal matrix leading to a mixed

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metallic/polymeric structure. In the case of corrosion attack a preventing barrier consisting of corrosion products with a low product of solubility (PS) and SPMs appears spreading the damages on greater surface area and impeding the penetration of the aggressive components into the depth of the coating [21,22].

The present contribution is aimed to present the preparation procedure of Zn and Zn–Co nanocomposite coatings with embedded stabilized PEO<sub>75</sub>PPO<sub>30</sub>PEO<sub>75</sub> micelles and to investigate their protective properties in a model corrosion medium containing Cl<sup>-</sup> ions.

## 2. Experimental

### 2.1. Galvanic coatings

#### 2.1.1. Zinc coatings

Zinc galvanic coatings were obtained using a slightly acidic starting electrolyte with a composition (in mol dm<sup>-3</sup>): ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.6; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.2; H<sub>3</sub>BO<sub>3</sub>, 0.5 and deposition conditions: current density 2 A/dm<sup>2</sup>, pH value 4.5–5.0, room temperature of 22 °C, metallurgical zinc anodes. Two laboratory additives were used: AZ-1 (wetting agent: 50 ml/l; contains polyethyleneglycol derivative, Na-salt of benzoic acid, etc.) and AZ-2 (brightener: 10 ml/l; contains benzalacetone, etc.).

#### 2.1.2. Zinc–cobalt alloy coatings

Galvanic Zn–Co (3 wt.%) alloy coatings were electrodeposited from a starting electrolyte having a composition (in mol dm<sup>-3</sup>): ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.35; CoSO<sub>4</sub>·7H<sub>2</sub>O, 0.4; NH<sub>4</sub>Cl, 0.6; H<sub>3</sub>BO<sub>3</sub>, 0.4. The process was carried out at current density 2 A/dm<sup>2</sup>, pH value 3.0–4.0, room temperature of 22 °C using metallurgical zinc anodes. Laboratory additives named ZC-1 (wetting agent: 20 ml/l; contains nicotinic and salicylic acids, monoethanolamin, etc.) and ZC-2 (brightener: 2 ml/l; contains benzalacetone, etc.) were applied in this case.

### 2.2. Stabilized polymeric micelles

The main procedure for preparation of stabilized PEO<sub>75</sub>PPO<sub>30</sub>PEO<sub>75</sub> micelles was described elsewhere [25] and includes the following steps:

- Formation of core–shell type micelles from PEO<sub>75</sub>PPO<sub>30</sub>PEO<sub>75</sub> triblock co-polymer in aqueous media at 60 °C and immobilization of a tetrafunctional monomer, pentaerythritol tetraacrylate (PETA), in the micelles.
- UV-induced polymerization of PETA leading to the formation of a semi-interpenetrating polymer network.

The stabilized micelles were dialyzed against distilled water (DW) and, then, incorporated in the metal coatings at the electrodeposition conditions described above.

### 2.3. Composite coatings containing polymeric particles with nanosizes

The composite coatings with incorporated polymeric nanoparticles were obtained in two different ways using the same electrolytes and electrodeposition conditions presented in Section 2.1 and following some preliminary preparation requirements:

I approach: SPMs (1 g/l) were first dissolved in DW and after 24 h period of temporizing were added to the electrolytes for Zn and Zn–Co, respectively; the obtained coatings are designated as ZnI or Zn–CoI.

II approach: the powdered SPMs (1 g/l) were added directly under stirring to the electrolytes for Zn and Zn–Co, respectively; these coatings are designated as ZnII or Zn–CoII.

### 2.4. Sample preparation

Both sides of the steel substrate plates, with dimensions 20 mm × 10 mm × 1 mm (total area of 4 cm<sup>2</sup>) were electrochemically coated with Zn or Zn–Co galvanic and nanocomposite coatings. The thickness of all layers obtained was approximately 12 μm.

### 2.5. Corrosion medium

A model corrosion medium of 5% NaCl solution with pH ~ 6.7 at ambient temperature of 32 °C was used for the investigations.

### 2.6. Sample characterization

#### 2.6.1. Microprobe analysis

The elemental composition of the Zn–Co alloy samples was determined using microprobe analyzer JEOL Superprobe 733, Japan.

#### 2.6.2. Scanning (SEM) electron microscopy

The surface morphology of the samples was investigated using scanning electron microscope JEOL JSM-5300 (Japan).

#### 2.6.3. Transmission (TEM) electron microscopy

The size and the distribution of SPMs in the starting electrolytes (SEs) as well as in DW were observed, using PHILIPS CM 100 TEM apparatus. A drop of the SPMs dispersed in DW or (SEs), respectively, was deposited on a TEM copper grid (3.05 mm, 200 meshes) coated with a Formvar film. The solvent was evaporated under vacuum thereafter.

#### 2.6.4. Corrosion investigations

Potentiodynamic (PD) anodic polarization measurements were performed in the model corrosion medium at a scan rate of 1 mV/s, using an "AUTOLAB PGSTAT 30" unit. Prior to performing the measurements, all investigated samples were maintained (temporized) for a definite period in the model corrosion medium at conditions of open circuit potential (OCP).

Polarization resistance ( $R_p$ ) values were measured at selected intervals of time during the investigating period of 4 days immersion in the corrosion medium in the range of ±25 mV relative the corrosion potential. Taccusel equipment (apparatus "Corrovit") was used for this purpose. From the Stern–Geary equation [26] it follows that higher  $R_p$  value (in Ω cm<sup>2</sup>) corresponds to higher corrosion resistance and to lower corrosion rate, respectively.

All electrochemical measurements were carried out in a common three-electrode experimental cell with a Luggin-capillary for minimizing the ohmic resistance of the corrosion medium. Platinum plate was taken as a counter electrode. The corrosion potentials were measured with respect to the saturated calomel electrode (SCE).

#### 2.6.5. X-ray diffraction (XRD)

The phase composition of the corrosion products formed on both galvanic and nanocomposite samples after 4 days immersion in 5% NaCl solution was determined using automatic X-ray diffractometer DRON-3 (Bragg–Brentano arrangement, Cu Kα-radiation and scintillation counter). XRD patterns were recorded in a step scanning mode, in steps of 0.02° (2θ) and counting time of 1 s step<sup>-1</sup>. The PowderCell program [27] was used in data processing.

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