PROTECTIVE PROPERTIES OF Zn-Mn COMPOSITE COATINGS

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Abstract

Galvanic and nanocomposite Zn-Mn(11 wt.%) alloy coatings are obtained from a simple sulfate bath at electrodeposition conditions. The nanocomposite coatings contain stabilized polymeric micelles – SPM - the latter added to the electrolytic bath in concentration of 0,1 wt.%. Some of the coatings are additionally treated in Cr^{3+}-based solution for obtaining of surface conversion layer. The protective ability of the coatings is evaluated in a model corrosion medium of free aerated 3% NaCl solution by potentiodynamic polarization curves and polarization resistance measurements. The surface morphology of the coatings is investigated by SEM images. The results show the better corrosion resistance and greater protective ability of the nanocomposite Zn-Mn alloy coatings compared to the ordinary ones. The influence of the Cr^{3+}-based conversion layers on the coating characteristics is also commented and discussed.

Keywords: *Zn-Mn, nanocomposites, corrosion, conversion Cr(III) layers, polarization*

1. INTRODUCTION

The galvanic coatings based on Zn and Mn belong to the most corrosion resistant alloys [1]. The classic mode for their obtaining is related to the application of sulfate-citric or fluoride-borate electrolytes [2 – 4]. These coatings find application in different industrial areas at heavy conditions which is one reason for their further investigation regardless of the difficulties related to their electrodeposition.

In the last two decades the interest concerning the obtaining and technical application of Zn-Mn alloy steadily increases [5 - 21]. As well-known Mn possesses more negative potential compared to the most of the metals so the obtained alloy is less noble compared to the ordinary Zn. It demonstrates a passivating behavior forming insoluble products on the surface which impede the penetration of the corrosion medium deeply inside [9, 15, 22].

Additional way to improve the protective ability of Zn-Mn alloy coating is its treatment in chemical solutions based on phosphates, Cr(III) containing compounds etc. [5-7, 23-25]. This leads to appearing of a surface conversion layer (CL) with lower susceptibility against aggressive corrosion media. Chromium(III) based layers decrease the dissolution rate and slows down the rate of the oxygen reduction reaction [26 – 34].

The new tendency in the electrodeposition is characterized with a massive influx of nanotechnologies which leads to obtaining of new materials with desired properties and better protective ability against corrosion. Main feature of these materials is the incorporation of different particles (non-organic or organic based) which determines some specific characteristics of the final product [35 – 41].

Our previous investigations demonstrate the application of different types of stabilized polymeric micelles (SPM) based on polyethylene oxide, polypropylene oxide, polyhydroxy–methylmetacrylate, polystyrene [42 - 47]. All investigated SPM are “core-shell” type where the core is the hydrophobic part and the shell – the hydrophilic one.

In the present study the obtaining of nanocomposite Zn-Mn(11wt.%) alloy coatings containing core-shell type SPM with composition $PEO_{75}PPO_{30}PPO_{75}$ is demonstrated and discussed. Composite and ordinary Zn-Mn coatings are additionally treated in Cr(III)-based solutions for chemical passivating, i.e. for obtaining of transparent conversion layers.

The corrosion behavior of Zn-Mn alloy and its nanocomposite (with or without additional conversion layer) is investigated and estimated in a model corrosion medium with chlorine ions as corrosion activators.

2. MATERIALS AND METHODS

2.1. Sample preparation

Low-carbon steel plates with dimensions 20 x 10 x 1 mm are used as substrates. Prior to each experiment the latter were mechanically polished, thereafter degreased, washed with tap water, rinsed with distilled water and dried at room temperature.

2.2. Electrolytes and electrodeposition conditions

The electrodeposition was performed at room temperature in double-chamber electrolytic cell of 300 ml volume, at current density of 2 A/dm^2, pH 5 and circulation speed of 150 rpm. The starting electrolyte used was with composition, g/l: $ZnSO_4.7H_2O$ – 10,0; $MnSO_4.H_2O$ – 100,0, $(NH_4)_2SO_4$ – 60,0. Wetting agent was the additive AZ1 (40 ml/l) the latter containing mainly polyethylene glycol and benzoic acid.

Metallurgical zinc was used as anode, the steel plates as cathode and a platinum plate serves as a counter electrode. Under these conditions the alloy Zn-Mn with 11wt.% manganese in it was obtained. This alloy contains mainly the intermetallic phase δ1 the latter well known from the phase diagram of the metallurgical alloy and small amounts of pure zinc.

The Zn-Mn composite coatings were obtained from the same electrolyte and at the same electrodeposition conditions but with an addition of 1g/l of the stabilized polymeric particles (described below), respectively.

The obtained alloy and nanocomposite Zn-Mn coatings were electrodeposited with approximately 12 μm thickness.

2.3. Stabilized polymeric micelles (SPM)

The SPM with nanosizes used in the present investigation are obtained from commercially available products. These are amphiphilic three block co-polymers of the type $PEO_{75}PPO_{30}PEO_{75}$ [poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)]. The latter can form spontaneous core-shell micelles in aqueous media. The hydrophobic core consists of PPO segments while the shell is dominated by hydrated PEO chains [48].

2.4. Chemical passivating

The solution for chemical passivating is based on environmentally friendly complex of tri-valence chromium salt with oxalic acid - potassium oxalate chromium (III) complex, $K_3[Cr(C_2O_4)_3]$. Conversion layer is colorless (transparent) and is obtained at immersion time of 30 sec., the latter been selected as optimal from previous laboratory investigations. This solution is applied at pH value 1,6 - 2,0 (after treatment with 50%-HNO_3).

Thereafter the alloy and the composite samples are rinsed with distilled water and dried at about 60-65 ^oC for a short time. Chemically passivated samples are ready for corrosion treatment after 24 h which is known as “time for ripen”. During this period the conversion layers become more hard, hydrophobic and wear-resistant.

2.5. Corrosion medium/Reproducibility

A model corrosion medium of 3% NaCl solution at ambient temperature was used during the investigations. The results from the applied tests are an average of 5 samples per type i.e. for each measurement 5 replicates of a Zn-Mn coatings and its composites are conditioned for the investigations.

2.6. Sample characterization

The investigations are carried out in a three-electrode experimental cell with Luggin capillary for minimizing the ohmic resistance of the medium. Corrosion potentials are measured with respect to the saturated calomel electrode (SCE).

Following methods are applied:

2.7.1. Scanning electron microscopy (SEM)

A scanning electron microscope JEOL JSM-6390, Japan was used for the investigation of the elemental composition of the ordinary Zn-Mn alloy, its composite as well as for the surface morphology changes of chromated and nonchromated samples before and after exposure in the model medium.

2.7.2. Potentiodynamic polarization curves

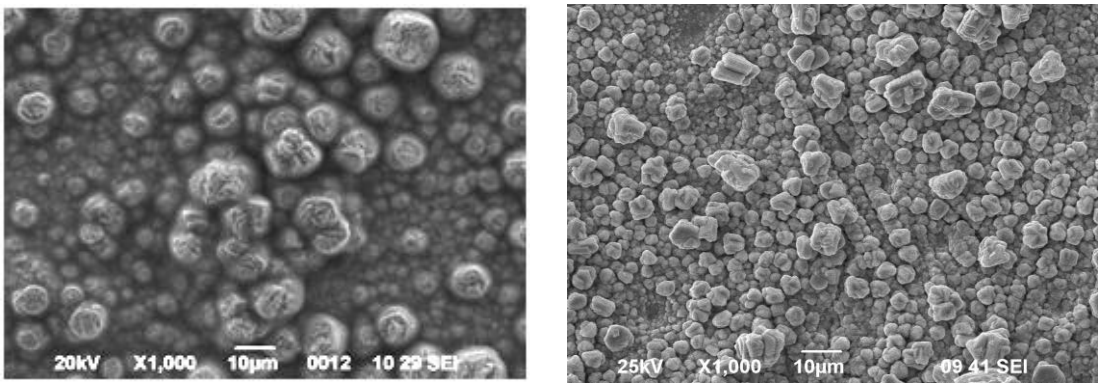
Aiming at application of accelerated corrosion tests potentiodynamic polarization investigations were carried out using an apparature VersaStat at polarization step of 1 mV/s.

2.7.3. Polarization resistance (Rp) measurements

The protective ability of the electrodeposits are estimated by applying of polarization resistance (Rp) measurements for a prolonged periods of time (16 days) in the range of +/- 25 mV relative to the corrosion potential using the Stern-Geary equation [49]. As a rule higher Rp value corresponds to higher corrosion resistance and to lower corrosion rate as well.

3. RESULTS AND DISCUSSION

3.1. Scanning electron microscopy (SEM) and EDX analysis



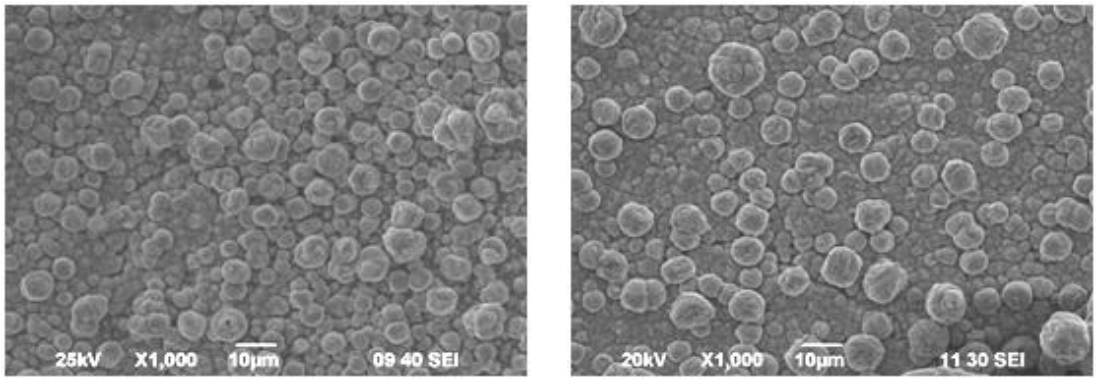
A B

Figure 1. SEM images of galvanic and composite Zn-Mn coatings:
A – Zn-Mn(~11 wt.%) coating; B – Zn-Mn(~11 wt.%) composite coating.

As well known the surface morphology is of great importance for the protective properties of the metal and alloy coatings. When CL also exists on the surface of the metallic or composite coating the time for the first corrosion damages will be prolonged. Typical surface morphology of the as received Zn-Mn alloy and its nanocomposites is presented in Fig. 1(A,B). The addition of 1g/l SPMs to the starting electrolyte leads to some changes in the surface morphology of the alloy. The structure consists in that case of smaller grains and the surface looks more uniform compared to the previous case – Fig. 1B.

Figure 2 demonstrates the surface of the Zn-Mn alloy and composite coatings treated in the chemical solution for obtaining of a transparent conversion layer (TCL). The surface of the galvanic alloy looks

more smoothed probably of the slicking action of the passivating solution and its low pH value. Very close in that case, i.e. after this additional chemical treatment is the surface image of the composite Zn-Mn alloy.



A B

Figure 2. SEM images of galvanic and composite Zn-Mn coatings with transparent CL: A – Zn-Mn(~11 wt.%) coating; B – Zn-Mn(~11 wt.%) composite coating.

3.2. Potentiodynamic (PD) polarization curves

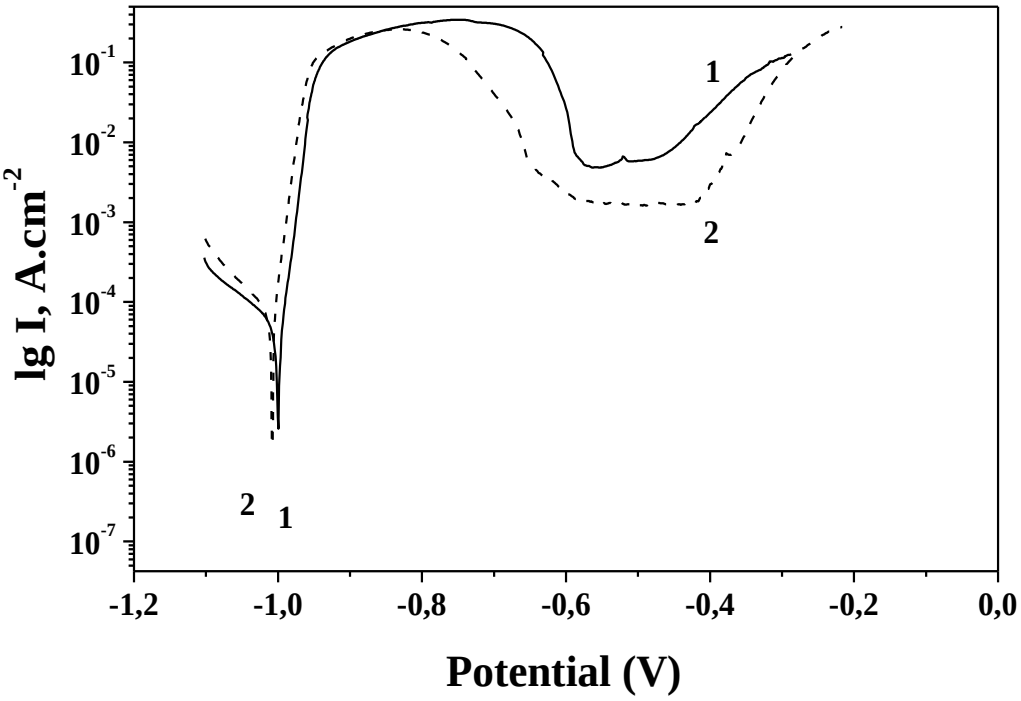


Figure 3. PD curves of galvanic and composite alloys Zn-Mn(~11 wt.%): 1 – Zn-Mn(~11 wt.%); 2 – composite Zn-Mn(~11 wt.%).

The results from the potentiodynamic investigations of Zn-Mn(11wt.%) and its composite in the model medium are presented in Figure 3. The corrosion potentials and corrosion current densities of both samples are very close most probably due to their nature – alloy matrix containg both metals Zn

and Mn. However, some differences appear due to the presence of SPM in the composite sample – this is the earlier susceptibility for passivation of the composite as a result of the ongoing anodic dissolution process leading to appearing of corrosion products the latter containing some residues of SPM. This mixed layer (corrosion products and SPM) will cover the surface to a certain degree leading to slow down of the penetration rate of the corrosion agents toward the steel substrate.

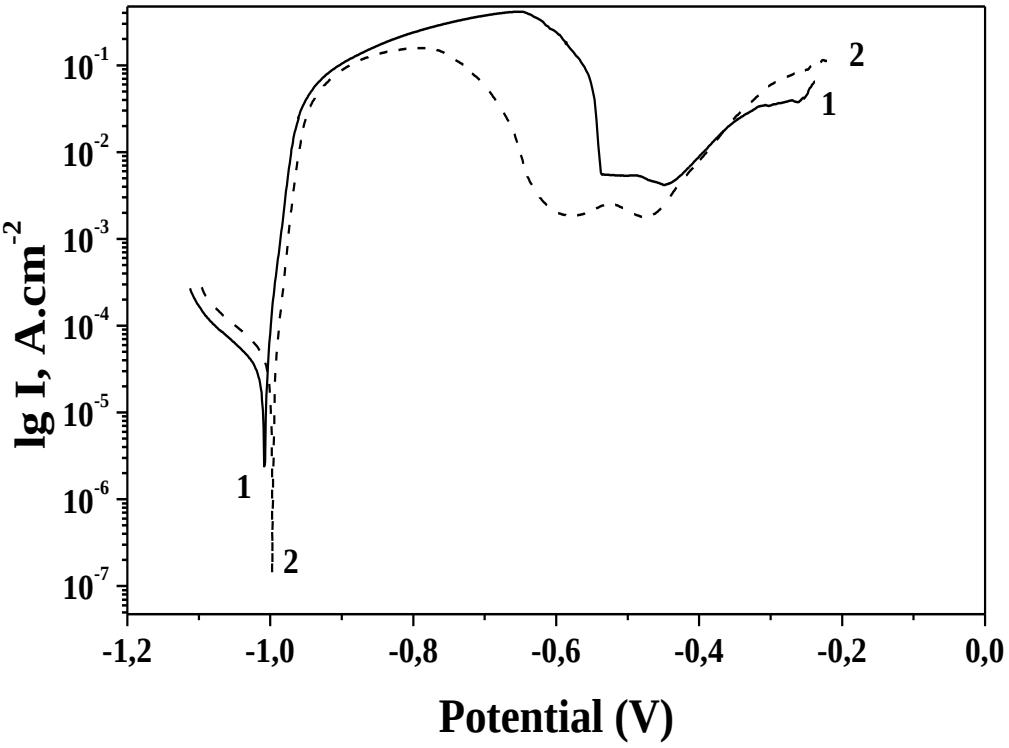


Figure 4. PD curves of galvanic and composite alloys Zn-Mn(~11 wt.%) with transparent conversion layer (CL): 1 – Zn-Mn(~11 wt.%); 2 – composite Zn-Mn(~11 wt.%).

The electrochemical and corrosion behavior of the samples with transparent CL under the same polarization conditions are shown in Figure 4. The main conclusion is that both corrosion current density values are lower compared to the non-chromated coatings (compare with Figure 3) due to the availability of the conversion layer.

3.3. Polarization resistance measurements

The experimental results for Rp values obtained for galvanic Zn-Mn alloy and its composite coating obtained from the starting electrolyte are presented in Fig. 5. It is clearly seen from the figure that the incorporation of the SPM into the alloy matrix leads to increased Rp values of the composite coating with additional finishing conversion layer.

During the whole period of investigation the polarization resistance of the chromated composite alloy coating is higher compared to the chromated alloy Zn-Mn coating without incorporated SPM. The most probable reason for this seems to be the SPM which polymeric parts are available in the layer of the newly appeared corrosion products with low product of solubility value - in that case most probably these are zinc hydroxide chloride, well known from other our investigations [42 - 47]. These corrosion products are typical for zinc and most of its alloys in chloride containing media and play very important role for its corrosion resistance and protective ability due to reasons mentioned above [42-44].

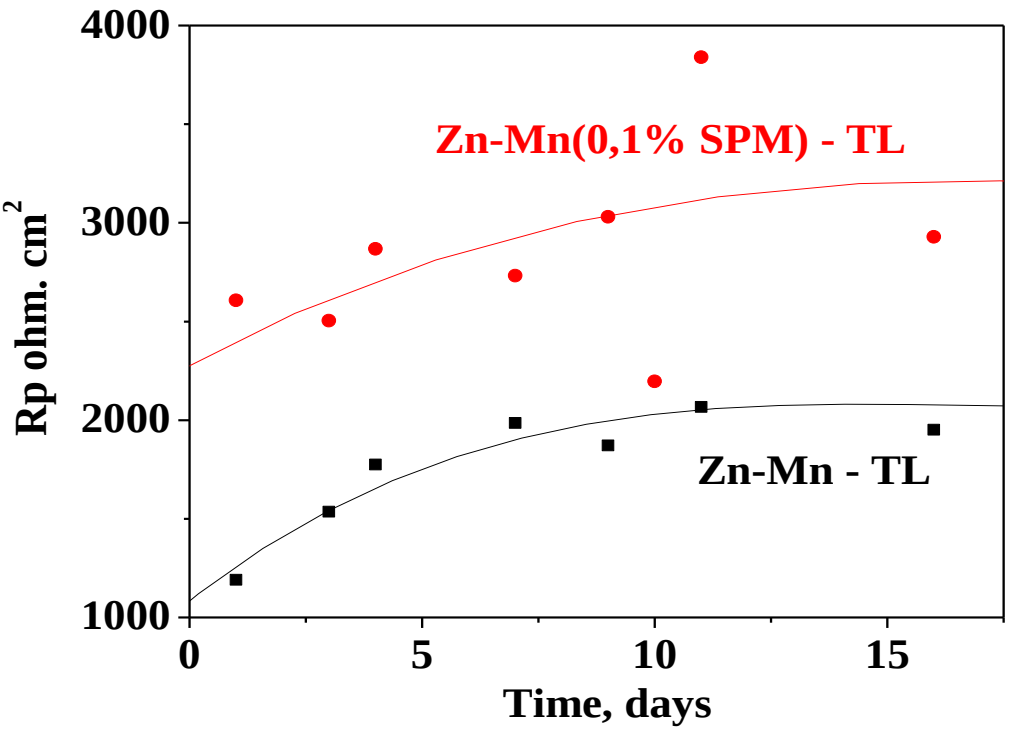


Figure 5. Rp data of galvanic and composite alloys Zn-Mn(~11 wt.%)

1 – Zn-Mn(~11 wt.%); 2 – composite Zn-Mn(~11 wt.%).

4. CONCLUSIONS

The presented results show the positive influence of the incorporation of stabilized polymeric micelles in the alloy matrix of the Zn-Mn(11 wt.%) alloy. SEM investigations lead to the conclusion that these micelles decrease the crystallite sizes of the alloys and make the surface morphology more even.

The composite alloy coatings can be additionally treated with solutions for obtaining of surface conversion layers the latter showing increased corrosion resistance and protective ability in model medium containing chlorine ions as corrosion activators.

The increased protective characteristics of the chromated composite Zn-Mn alloy coatings follow from the simultaneous action of the conversion layer and from the appearance of a mixed layer of corrosion products and SPM which protects better the steel substrate.

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