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Obtaining and comparative corrosion characterization of composite zinc and zinc alloy coatings with embedded stabilized polymeric micelles

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Abstract: The results concerning the electrochemical obtaining of composite zinc and some composite zinc alloy coatings (Zn-Co and Zn-Mn) with embedded core-shell type stabilized polymeric micelles (SPMs, based on poly-propylene oxide and poly-ethylene oxide) are presented and discussed. The deposition and dissolution processes of the zinc and both zinc based alloys in the presence or absence of SPMs are investigated by using of cyclic polarization (cyclic voltammetric curves). The influence of the incorporated in the metal or alloy matrix SPMs on the surface morphology of the obtained coatings is shown and commented. The corrosion behavior and protective ability of the composite coatings are evaluated in a model medium containing chloride ions as corrosion activators and are compared to the same characteristics of the non-composite coatings. The influence of the SPMs on the corrosion resistance and protective properties of the zinc and zinc alloy coatings in that medium is analyzed and discussed.

Key words: corrosion, composite coatings, zinc, zinc alloys, stabilized polymeric micelles

1. INTRODUCTION

The electrodeposition of Zn and zinc alloy coatings on steel substrates has been for a long time applied to achieve high corrosion resistance [1-3]. Zinc is generally used as a sacrificial coating with an aim to protect the steel from corrosion damages. However, the safe exploitation of these coatings is to a certain degree limited due to the aggressive nature of environment containing industrial pollutants. As a result, additional efforts must be done in order to improve their corrosion resistance [4,5].

Electrodeposition of different composite coatings is a highly advanced method in material science leading to obtaining of materials with desired properties at easy conditions. Another important application is the possibility to co-deposit metal with metallic, non-metallic, polymeric particles etc. The demand for newly developed materials based on metal matrix composites shows an increasing tendency due to their potential applications in many industrial and other sectors [6-10].

Composite zinc and zinc alloy coatings can be also applied for corrosion prevention since it is well known that most of them exhibit very high corrosion resistance [11-16]. Aiming at increasing the protective ability of the zinc and its alloys different attempts have been realized in order to incorporate non-organic or organic micro- or nano-sized particles in them [17-29].

The aim of the present work is to obtain via electrochemical method composite Zn and zinc alloy coatings, to characterize and evaluate their protective parameters and to compare the obtained results with these of the galvanic ones.

2. EXPERIMENTAL

2.1. Sample preparation

The selected zinc based alloy coatings have been previously investigated by us and have been classified as protective coatings with high corrosion resistance in 5% NaCl solution. The aim of the investigation is to clarify if the presence of SPMs in the alloy matrix will improve their protective ability toward the substrate.

All samples (composite and non-composite) are electrodeposited on low carbon steel substrates with sizes 20 x 10 x 1 mm, whole surface area of 4 cm^2 and coating thickness of approximately 12 µm. Deposition conditions are: current density 2 A/dm^2; room temperature – 22 °C; metallurgical zinc anodes. In the case of Zn-Mn electrodeposition process the electrolyte is circulated.

2.2. Galvanic coatings

2.2.1. Zinc coatings are electrodeposited from electrolyte with a composition 150 g/l $ZnSO_4.7H_2O$, 30 g/l NH_4Cl, 30 g/l H_3BO_3, additives AZ-1 (wetting agent) - 50 ml/l and AZ-2 (brightener) - 10 ml/l, pH value 4,5–5,0.

2.2.2. Zn-Co (1 wt.%) alloy coatings are obtained from electrolyte containing 100 g/l $ZnSO_4.7H_2O$; 120 g/l $CoSO_4.7H_2O$; 30 g/l NH_4Cl; 25 g/l H_3BO_3; additives ZC-1 (wetting agent) - 20 ml/l and ZC-2 (brightener) - 2 ml/l; pH 3,0–4,0.

2.2.3. Zn-Mn (11 wt.%) alloy coatings are electrochemically received from the following

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electrolyte: $ZnSO_4.7H_2O$ - 10 g/l; $MnSO_4.7H_2O$ - 100 g/l; $(NH_4)_2SO_4$ - 60 g/l, additive AZ-1 – 40 ml/l.

2.3. Composite coatings

The composite coatings are electrochemically deposited from the same electrolytes and at the same electrodeposition conditions described above but with an addition of powdered stabilized nano-sized polymeric micelles (SPMs) in selected concentrations. The applied SPMs are based on $PEO_{75}PPO_{30}PEO_{75}$ (poly-ethylene oxide – poly-propylene oxide – poly-ethylene oxide) tri-block copolymer where PPO is the hydrophobic core and PEO – the hydrophilic shell.

2.4. Stabilized polymeric micelles (SPMs)

The main procedure for preparation of these SPMs is described elsewhere [30] and includes the formation of core–shell type micelles in aqueous media at 60 °C and immobilization of tetra-functional hydrophobic monomer - pentaerythritol tetra-acrylate (PETA) – followed by UV-induced polymerization and formation of a semi-interpenetrating polymer network. The stabilized micelles are dialyzed against distilled water and then added to the electrolytes described above. The sizes and shape of the applied SPMs are presented elsewhere [27].

2.5. Corrosion medium and reproducibility

A model corrosion medium of 5% NaCl solution with pH 6.7 at ambient temperature of about 30 °C is used for the investigations. The results from the electrochemical investigations are an average of 5 samples per type i.e. for each measurement 5 replicates of a Zn, zinc based alloys or their composites. Aiming at receiving of better reproducibility prior to the test all samples are temporized for a definite period in the model medium at conditions of open circuit potential (OCP).

2.6. Sample characterization

The sample characterization is realized by using of electrochemical workstation PAR ‘‘VersaStat 4” and application of the following methods:

- Cyclic voltammetry curves – to investigate the influence of the SPMs added to the electrolytes on the cathodic and anodic processes. The measurements are performed at scan rate of 10 mV/s.
- Potentiodynamic (PD) anodic polarization – the aim is to compare and evaluate the peculiarities of the anodic behavior of galvanic and composite coatings. The measurements are performed at a scan rate of 1 mV/s.

In addition, polarization resistance (R_p) measurements are carried out for a test period of 312 hours by using of ‘‘Corrovit’’ equipment in the range of ±25 mV relative the corrosion potential. From the Stern–Geary equation [31] it is known that higher Rp value (in $\Omega.\ cm^2$) corresponds to higher corrosion resistance and to lower corrosion rate.

The surface morphology of the samples is investigated with Scanning (SEM) electron microscopy by using of INCA Energy 350 unit.

All electrochemical measurements are carried out in a common three-electrode experimental cell (volume of 250 ml) with a Luggin-capillary for minimizing the ohmic resistance of the corrosion medium. Platinum plate is taken as a counter electrode and the potentials are measured with respect to the saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

The results obtained by this method are presented in Figure 1(A-C). It is well visible that the presence of the SPMs in the zinc electrolyte facilitate the cathodic deposition process – the difference between the cathodic current density value of the electrolyte without SPMs (curve 1) and electrolyte with 0,1 wt.% SPMs (curve 3) is about 12-14 mA/cm^2 – (Figure 1A).

The presence of SPMs in the solution does not affect the polarization of the cathodic process at the initial stage but it is more intensive which means that the SPMs do not burden the electrodeposition. The weight of the obtained galvanic and composite coatings and their thicknesses are very close. Visually, no changes are observed concerning the hydrogen evolution rate.

In general, the SPMs are regarded as electro neutral but the zinc ions can realize a coordination bond with the oxygen from the hydrophilic PEO chains. In addition, due to their very small sizes zinc ions can find place in the internal volume of the hydrophilic shell. As a result the SPMs transform in micelle-metallic (SPM-Zn) aggregates with partial positive charge due to the available Zn^{2+}. When the electrodeposition begins these aggregates will move electro-phoretically to the cathode and deposit there together with the individual zinc ions i.e. competitive electrodeposition of the zinc ions and of the zinc-SPMs aggregates occurs. The latter are much greater compared to the sizes of the zinc ions and thus discharge on (cover) greater surface of the cathode. In addition, a possible interaction of PEO-chains with the additive AZ1 (based on PEO-derivative) could be proposed which will mitigate the wetting of the cathode.

The anodic peaks of the composite zinc coating are much greater (up to 4 times) compared to the peak of the pure zinc – curves 1 and 3 – which qualitative corresponds to the cathodic part of the curves. In addition, an area with gradual increase of the anodic current appears in the potential zone between -990 and -740 mV which is most strongly expressed for the coating from the electrolyte with 0,1 wt.% SPMs. Possible reason for this phenomenon might be the accelerated dissolution of the zinc around the embedded SPMs and the following increase of the anodic current.

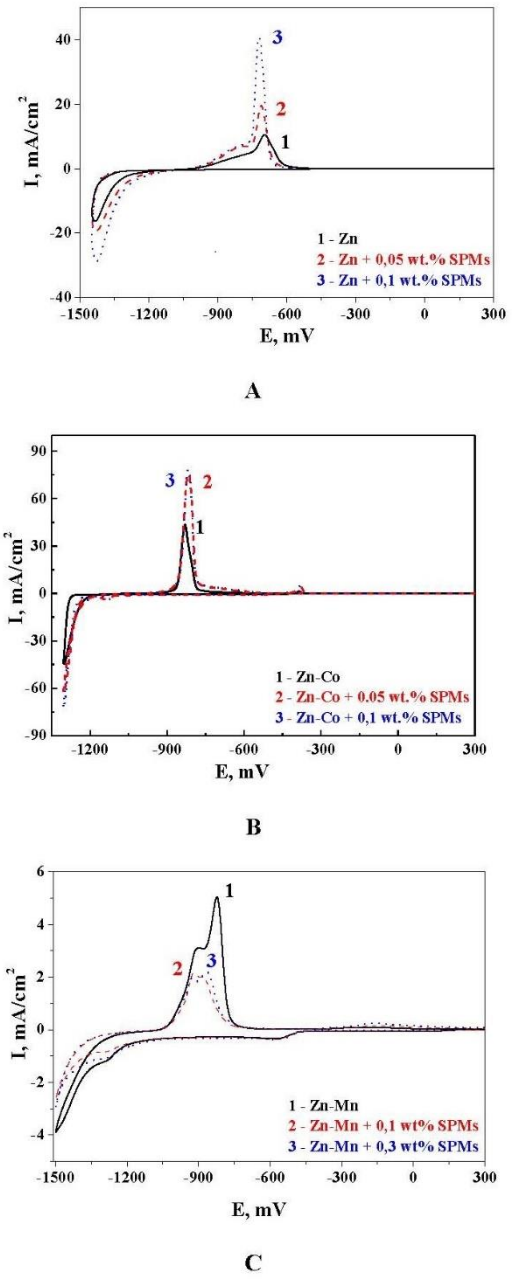


Figure 1. Cyclic voltammetry (CVA) curves of: A - Zn coating and its composites; B - Zn-Co(1 wt.%) coating and its composites; C - Zn-Mn(11 wt.%) coating and its composites.

Figure 1B demonstrates the influence of the SPMs on the cathodic and anodic processes (deposition and dissolution) of Zn-Co (1 wt.%) alloy. A depolarization can be registered in the cathodic part in the case of both alloy composites compared to the galvanic Zn-Co with about 80 mV (from -1270 mV up to -1190 mV). Also here, greater current density values are observed for the composites – about 60-70 mA/cm^2 compared to 40 mA/cm^2 for the galvanic alloy. According to this, greater anodic current density values for the composites and lower for the galvanic alloy can be registered.

The reasons for these results can be also attributed to the comments presented above for the electrodeposition of the composite and non-composite zinc.

The CVA curves for both galvanic and composite Zn-Mn (11 wt.%) alloy are shown in Figure 1C. In the cathodic area the addition of SPMs leads to an overvoltage with about 80 mV for the composites compared to the non-composite Zn-Mn and in addition, the current density value of the latter is greater. In the anodic part the current density of the galvanic coating is also greater than that of both composites. Characteristic for all samples is the presence of two anodic dissolution peaks which most probably follow from the fact that Mn can appear in different valences.

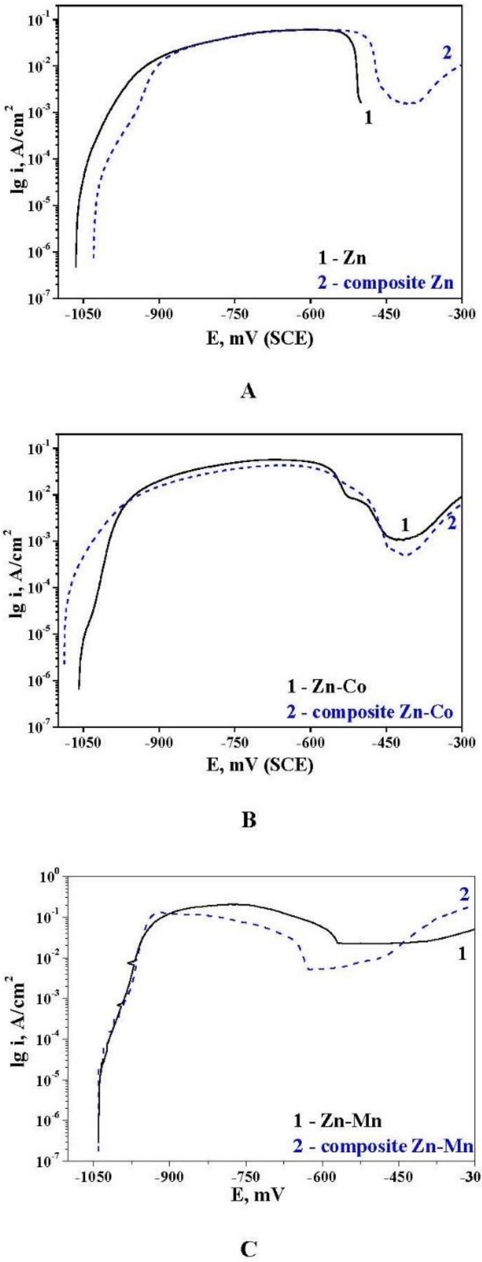
It can be summarized that the presence of SPMs does not facilitate the electrodeposition of the Zn-Mn composite coatings comparing to the case of the Zn and Zn-Co. One reason for this observation could be the different valent values of Mn as well as the inhibited interaction of the manganese ions with the SPMs i.e. with their hydrophilic part.

3.2. Potentiodynamic anodic polarization

The anodic curves of the investigated Zn and its composite obtained from electrolyte with 0,1 wt.% SPMs in the model corrosion medium of 5% NaCl are presented in Figure 2 (A-C) The difference between them is the curve's length the latter being longer for the composite coating which means that it lasts more under external anodic polarization. In order to reduce possible errors from the substrate dissolution and appearance of a mixed current the sample was checked during the experiment to register if the coating still exist or is already dissolved.

As seen from Figure 2A the galvanic zinc coating is totally dissolved at potential values of about -500 mV while the composite Zn lasts up to about -300 mV. The composite Zn characterizes also with a pseudo-passive zone (since the anodic current is relative high – 2.10^{-3} A/cm^2) in the potential area between -380 mV and -460 mV which means that in this zone the anodic dissolution process is hampered.

Since the Zn does not characterize with a passive zone in such medium the obtained results can be regarded as a sign for the positive influence of the SPMs on the protective properties.



A

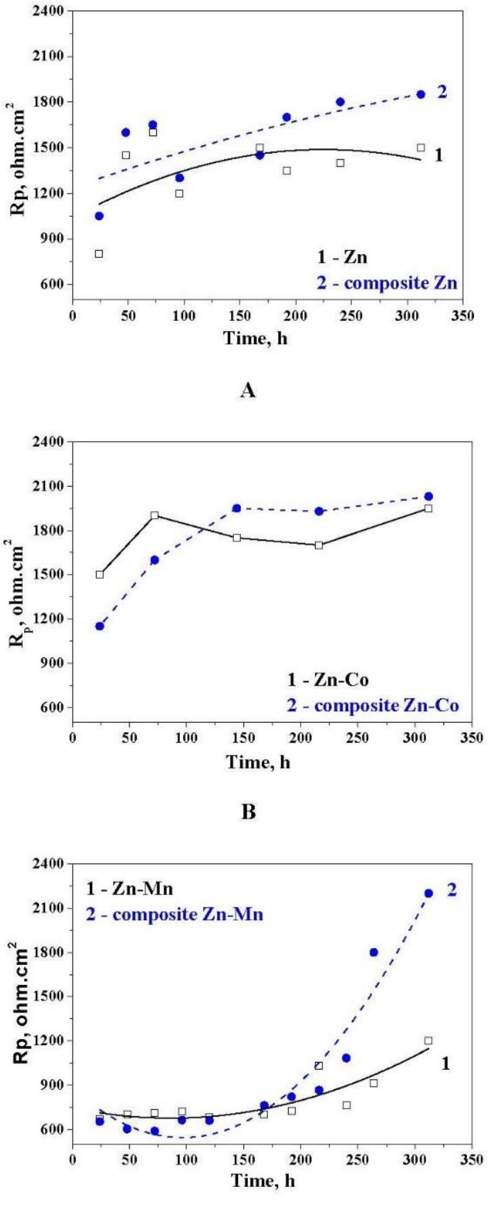
B

C

Figure 2. Potentiodynamic polarization curves of:
A – Non-composite and composite Zn obtained from electrolyte with 0,1wt% SPMs; B - Non-composite and composite Zn-Co(1 wt.%) obtained from electrolyte with 0,1wt% SPMs; C - Non-composite and composite Zn-Mn(11 wt.%) obtained from electrolyte with 0,1wt% SPMs

Figure 2B represents the anodic PD curves of the Zn-Co alloy and its composite obtained from electrolyte containing 0,1 wt.% SPMs in the model medium used. Contrary to the previous case no significant positive influence of the SPMs on the disposal and on the length of the anodic curve of the composite coating can be registered. Both curves are of the same length, have very close anodic current density values and show almost equal passive zones, i.e. pseudo-passive zones since the current density registered is very high – in the range of about 10^{-3} A/dm^2.

The results obtained for the galvanic and composite coatings of Zn-Mn alloy the latter obtained from electrolyte with 0,1 wt.% SPMs are demonstrated in Figure 2C. The positive influence of the embedded SPMs on the electrochemical behavior of the composite is to a certain degree controversial. The length of both curves is almost



A

B

C

Figure 3. Polarization resistance (Rp) measurements of: A – Non-composite and composite Zn obtained from electrolyte with 0,1wt% SPMs; B - Non-composite and composite Zn-Co(1 wt.%) obtained from electrolyte with 0,1wt% SPMs; C - Non-composite and composite Zn-Mn(11 wt.%) obtained from electrolyte with 0,1wt% SPMs.

equal and the current density values in the area after the corrosion potential have close slopes and beta constants. A difference can be registered in the zone of the maximal anodic dissolution where the rate of the anodic process of the composite gradually decreases forming a pseudo-passive zone at relative high anodic current densities.

3.3. Polarization resistance (Rp) measurements

The results obtained by this method for galvanic and composite zinc coating (from bath with 0,1 wt.% SPMs) are shown in Figure 3A. After 312h it can be observed that the Rp of the Zn composite shows an increasing tendency and at the end is with about 350 ohms higher than that of the galvanic zinc. At the end of the test both coatings do not have remarkable damages on the surface but the composite one shows better decorative appearance. The reason for this can be explained with the formation of a mixed surface layer which consists of newly formed corrosion product – zinc hydroxide chloride (ZHC, registered also previously by us with XRD method) and SPMs. As well known ZHC characterizes with a low product of solubility (~ 10^{-14}) which has a barrier effect toward the penetration of the corrosion medium into the depth of the coating. In the case of a mixed layer the hydrophobic part of the SPMs additionally increases this inhibiting effect.

The polarization resistance results concerning the Zn-Co galvanic alloy and its composite (from bath with 0,1 wt.% SPMs) is presented in Figure 3B. Both coating types show an increasing tendency of Rp during the first 72 hours but thereafter the composite one characterizes with higher Rp values. However, the difference between both coatings at the end of the period is very close - in the frames of about 70-80 ohms. This result partially corresponds to the PD investigations which do not show any significant difference between the potentiodynamic polarization curves of the galvanic and composite coating. The reason for this could be explained with the fact that the structure and surface morphology of the composite differ compared to the non-composite Zn and Zn-Co [27]. The surface morphology of the composite Zn-Co can be regarded as a net of SPMs-‘‘chains’’ (‘‘worm-like’’ shape), separating the alloy matrix in some kind of individual areas (see Fig. 4). At lower ambient temperature the alloy transforms readily to ZHC forming a protective surface layer. This process is accompanied by an increase of the volume fraction of the product. Since at higher temperatures the rate is higher mechanical stresses appear and they cannot (there is not enough time to) relax. The resulting stresses lead to more ruptures so the final effect cannot be classified unambiguously as positive for the increasing of the protective ability of the coating.

The results obtained by this method for the galvanic and composite coatings of Zn-Mn (from bath with 0,1 wt.% SPMs) are shown in Figure 3C. It can be registered that the Rp values of the galvanic alloy coating gradually increase up to about 1100 ohm.cm^2 while the same parameter for the composite one initially decreases and after 150 h sharply increases up to about 2200 ohm.cm^2. Also here, the reason could be find in the surface morphology – see Figure 4. The galvanic alloy consists of greater aggregates with sizes of about 5-10 μm while the incorporation of SPMs lead to fine and more arranged structure especially in the case when more SPMs are embedded in the Zn-Mn matrix. In the latter case the newly formed ZHC creates something like a net which connect to the individual grains making them in such a case more sustainable and increasing the barrier effect by covering the separate opening on the surface.

4.SCANNING ELECTRON SPECTROSCOPY

Typical surface morphology of non-composite and composite zinc and zinc alloy coatings are presented in Fig. 4.

It is seen that the sample surfaces of the presented coatings exhibit marked differences. The surface of the pure zinc and Zn-Co are relatively smooth and even and the boundaries between the individual grains are not well defined. Contrary to this the surface morphology of the composite zinc is more uneven and the embedded SPMs are easy to be registered. The surface of composite Zn-Co distinguishes with “worm-like” shape which could be explained with additional aggregation of SPMs at these experimental conditions.

The surface of the composite Zn-Mn is in general close to this of the galvanic alloy but seems to be more compact. The embedded SPMs are not well visible and seem to be incorporated in the individual grains. However, their presence is confirmed by the electrochemical test since the composite coatings show better protective properties.

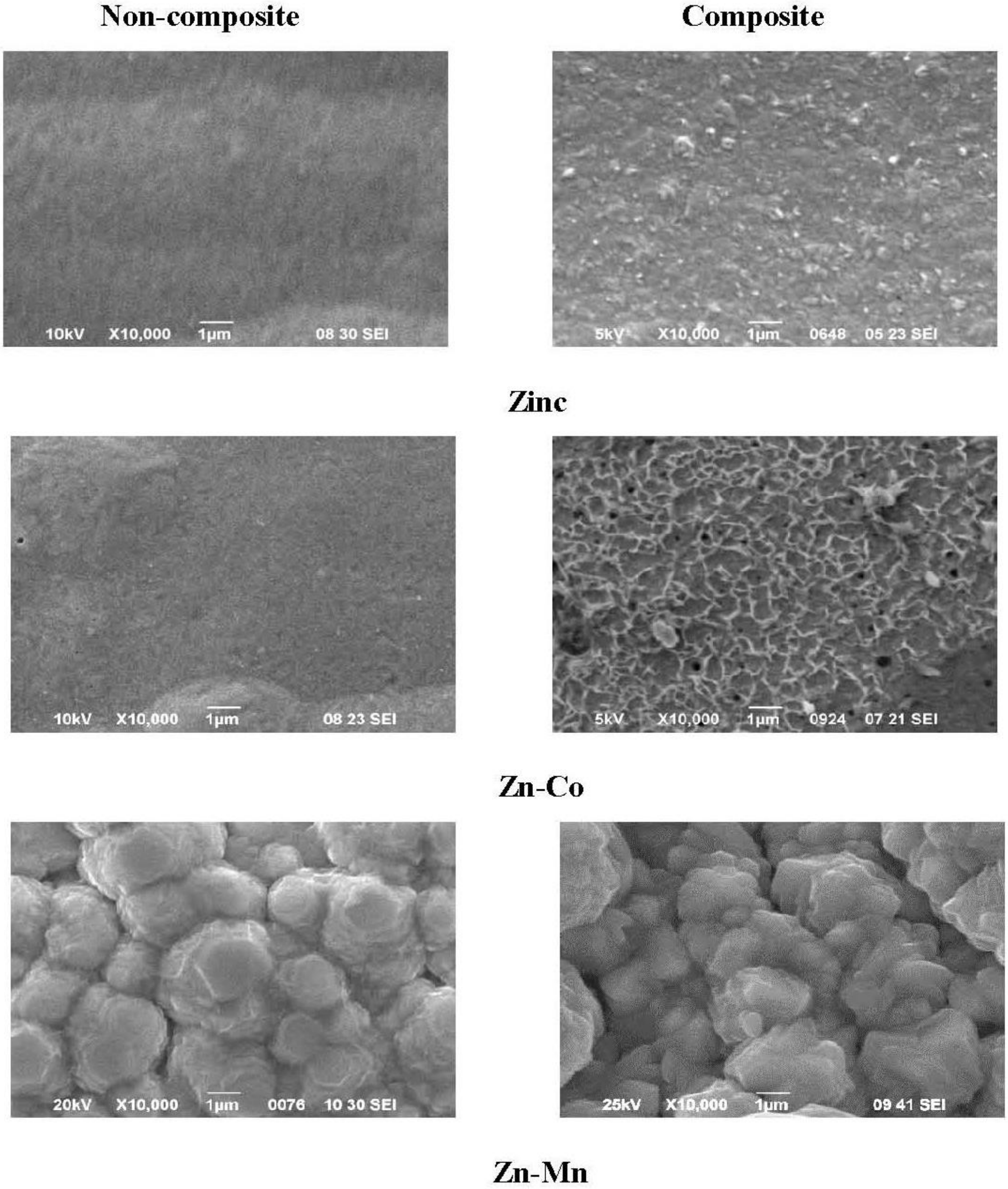


Figure 4. SEM images of non-composite (left) and composite (right) coatings of Zn and zinc based alloys.

5.CONCLUSIONS

The investigated galvanic and composite zinc and zinc based alloy coatings show different corrosion behavior and protective ability in a model medium of 5% NaCl and at ambient temperature of about 30 ^{o}C.

In the case of the zinc the incorporation of the SPMs leads to increase of the Rp and to appearance of a pseudo-passive zone at external anodic polarization which means that the composite Zn has better protective properties and susceptibility for passivating in that medium.

Contrary to this, the Zn–Co alloy and its nanocomposites demonstrate in general very close corrosion behavior at external anodic polarization and prolonged Rp measurements. In that case due to the specific incorporation and distribution of the SPMs into the alloy matrix their influence on the protective ability is controversial.

In the case of Zn-Mn the embedded SPMs show a positive influence leading to greater Rp and to appearance of a pseudo-passive zone at external anodic polarization.

The reasons for this behavior can be summarized mainly in two points:

- the influence of the surface morphology which differs for the individual composites;
- the formation of a mixed barrier layer consisting of corrosion products with a low product of solubility and SPMs, which seems to reinforce in some way the ZHC layer and slows down the progress of the destructive processes into the depth of the coating.

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ПОЛУЧАВАНЕ И СРАВНИТЕЛНО КОРОЗИОННО ХАРАКТЕРИЗИРАНЕ НА КОМПОЗИТНИ ЦИНКОВИ И СПЛАВНИ ЦИНКОВИ ПОКРИТИЯ С ВГРАДЕНИ СТАБИЛИЗИРАНИ ПОЛИМЕРНИ МИЦЕЛИ

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(Резюме)

Представени и дискутирани са резултати, свързани с електрохимичното получаване на композитни цинкови и цинкови сплавни покрития (Zn-Co и Zn-Mn) с вградени стабилизирани полимерни мицели (СПМ) на база полипропилен оксид и полиетилен оксид. Процесите на отлагане и разтваряне на цинка и двата вида цинкови сплави в присъствие и отсъствие на СПМ са изследвани с помощта на циклични волтамперометрични криви. Показано и коментирано е влиянието на включените в металната/сплавната матрица СПМ върху повърхностната морфология на получените. Изследвани са корозионното поведение и защитната способност на композитните и некомпозитните покрития в моделна среда, съдържаща хлорни йони като активатори на корозията. Анализирано е влиянието на СПМ върху корозионната устойчивост и защитните свойства на цинка и неговите сплави в тази среда.