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PROTECTIVE ABILITY OF NANO-COMPOSITE GALVANIC COATINGS WITH VARIABLE TYPE AND CONCENTRATION OF POLYMERIC MICELLES

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Abstract

The corrosion resistance of galvanic coatings (e.g. electrodeposited Zinc, as hereby presented) largely depends on their morphology and crystallographic orientation. The presence of organic nano-aggregates was found to positively alter the aforementioned characteristics, resulting in increased corrosion resistance due to enhanced barrier properties, favorable composition (e.g. formation of zinc oxides rather than zinc oxy(hydroxy)chlorides) and self-healing mechanisms. The paper presents a comparative study on recently developed nano-composite galvanic zinc layers, discussing their electrochemical behavior (recorded via Electrochemical Impedance Spectroscopy, Scanning Vibrating Electrode Technique and Potentio-dynamic Polarization) and surface morphology (via Scanning Electron Microscopy) after treatment in 5% NaCl.

Key words: *zinc; nano-aggregates; SVET; EIS; PDP; SEM*

1. INTRODUCTION

Galvanic zinc and zinc alloy coatings on steel find practical utilization in various industrial applications, providing protection of the steel substrate as a result of impeded steel corrosion initiation and/or propagation [1-5]. Each year over 40 million tones of steel are coated with zinc or zinc alloys and more than 2.2 million tones of zinc are used worldwide for coatings [6]. Zinc coatings have many times the corrosion resistance of carbon steel, in natural environments zinc corrodes by a factor of 10 to 100 times less than steel [7]. The protective properties of Zn, however, are mainly due to a galvanic, sacrificial action (corrosion of Zn instead of the steel substrate), resulting from the electronegative state of Zn (-1.07 V SCE), compared to steel (e.g. AISI 4340 with potential of −0.68 V vs. SCE in 0.6 M NaCl). Consequently, extending the service life of zinc coatings (or zinc alloyed such) will provide longer protection and increased service life for the protected steel. Additionally, a zinc composite coating with significantly extended service life and reduced thickness (compared to conventional Zn) will bring economical and environmental benefits.

Nano-composite coatings incorporating micro- or nano-sized aggregates were reported as better alternatives in more recent studies [8-10]. Related to this work, hereby briefly summarized are already reported investigations on improving the corrosion resistance of zinc coatings, incorporating (within the electro-deposition process) polymeric nano-aggregates of different type and concentration: micelles from the amphiphilic tri-block copolymer poly (2 - hydroxyethyl methacrylate) – b – poly (propylene oxide) – b – poly (2 - hydroxyethyl methacrylate) ($PHEMA_{15}PPO_{34}$-$PHEMA_{15}$), in

concentration of 1 g/l to the starting electrolyte, co-deposited within the Zn matrix were reported to result in higher corrosion resistance [11]; similarly, 1 g/l starting electrolyte of poly (ethylene oxide) – poly (propylene oxide) – poly (ethylene oxide) micelles (PEO-PPO-PEO) also resulted in increased protective properties of the composite Zn compared to conventional galvanic Zn [10]; the addition of 0.5 g/l PEO_{113}-b-PS_{218} (poly (ethylene oxide)-b-polystyrene) micelles proved to result in superior electrochemical performance and better (compact and more uniform) surface layer morphology and composition, compared to galvanic Zn [12]; further, even lower concentrations of PEO_{113}-b-PS_{218} micelles (0.1 and 0.3g/l to the starting electrolyte) were found to result in increased corrosion resistance, compared to zinc [13].

The mechanism, responsible for the higher corrosion resistance of the nano-composite zinc coatings, compared to pure zinc, was found to be related to rapidly changing initial corrosion activity (anodic/cathodic currents) as a response to altered environment and increased barrier properties, while still maintained sacrificial activity. The higher corrosion resistance of the composite coating was denoted to an enhanced barrier effect, resulting from the presence of the polymer nano-aggregates themselves, but is also denoted to a kind of "self-repairing" mechanism, resulting from the specific properties of the aggregates' core and shell in chloride containing environment (for more details on the nano-aggregates, as well as the related "self-healing' mechanisms, pls see [10-14].

More recently, the above commented nano-composite coatings (containing varying concentration of nano-aggregates) were additionally treated in chromate solutions (top conversion layers) [13,15]. The influence of Cr(III)-based conversion treatment was evaluated on two type of composite coatings (incorporating $PEO_{75}PPO_{30}PEO_{75}$ micelles and PEO_{113}-b-PS_{218} micelles) and compared to Cr(III) treated galvanic zinc. The expected significant increase of corrosion resistance as a result of the additional Cr(III) was not observed within the investigated time intervals of 1h – 240h. On the contrary, initial improvement was observed only for the chromated pure Zn. Further on, within 240h of treatment a positive effect was not observed and the coatings with best corrosion performance and superior corrosion resistance remained to be the non-chromated nano-composite coatings.

This work aims to give a comparison of the corrosion resistance and surface morphology of nano-composite zinc coatings, containing two types of micelles ($PEO_{75}PPO_{30}PEO_{75}$ and PEO_{113}-b-PS_{218}) in various concentrations. Thus on one hand the superior electrochemical behavior of nano-composite zinc, compared to pure zinc is discussed; on the other hand this study provides information on which type of micelles (also related to different concentration) exerts better corrosion performance of the zinc layers.

2. EXPERIMENTAL

2.1 Materials

Galvanic coatings: Zinc (Zn) and composite zinc (ZnP and ZnB) coatings were electrodeposited on a steel substrate (low carbon steel, surface area of 4cm^2) from slightly acidic sulfate-chloride electrolyte: 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. For the ZnP and ZnB coatings, the electrolyte also contains the previously stabilized in demi-water PEO_{113}-b-PS_{218} micelles (for ZnP) and $PEO_{75}PPO_{30}PEO_{75}$ micelles (for ZnB) (concentration of the micelles in the electrolyte is 1g/l for ZnB and varying i.e. 0.5, 0.3 and 0.1 g/l for ZnP). The electrodeposition conditions were: current density of 2 A/dm^2, pH 4.5-5.0, t^o – 22°C, no stirring or agitation. The coating thickness for all layers was approximately 8 μm. The results from the electrochemical tests are an average of 3 replicates per type and per stage. Corrosion medium was 5% NaCl solution.

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Polymeric micelles: Micelles from PEO_{113}-b-PS_{218} di-block copolymer and $PEO_{75}PPO_{30}PEO_{75}$ tri-block copolymer were added in various concentrations to the starting electrolyte. Thus, composite coatings with different amounts of micelles, incorporated in the metallic matrix were obtained. The hydrodynamic radius of the $PEO_{75}PPO_{30}PEO_{75}$ micelles was 50 – 150 nm; for the PEO_{113}-b-PS_{218} micelles a hydrodynamic radius of 50 nm is relevant. For more information on the micelles preparation and characterization, please see [10, 12,14,16].

Sample designation: The hereby investigated samples (3 replicates per group and condition) are designated as follows:

Zn – pure galvanic zinc;

ZnB – composite zinc coating, containing 1g/l $PEO_{75}PPO_{30}PEO_{75}$ micelles;

ZnP0.1, ZnP0.3 and ZnP0.5 – composite zinc coatings, containing 0.1 g/l, 0.3g/l and 0.5 g/l respectively of PEO_{113}-b-PS_{218} micelles.

2.2. Methods

Potentio-dynamic polarization (PDP) was performed in the range of -0.15 V to +1.2 V vs OCP at scan rate of 1mV/s (in a common three-electrode electrochemical cell, all readings are versus SCE reference electrode, using EcoChemie Autolab).

Electrochemical Impedance Spectroscopy (EIS) was carried out in the frequency range of 50 kHz to 10 mHz by superimposing an AC voltage of 10 mV, using EcoChemie Autolab - Potentiostat PGSTAT30, combined with FRA2 module.

Scanning vibrating electrode technique (SVET) measurement: the instrument used was from Applicable Electronics (Forestdale, MA); the scanned area was 3.4 × 2.6 mm at a distance of 100 μm between the samples surface and the microelectrode.

Microscopic investigation (SEM), using ESEM Philips XL30.

Corrosion medium: for the PDP and EIS tests, as well as for treatment before surface analysis, a corrosion medium of 5% NaCl was used (solutions were aerated, no stirring was involved). The SVET measurements were performed in corrosion medium of 0.001M NaCl.

Time intervals: The electrochemical behavior of all hereby investigated coatings was recorded after 2h, 24h, 96h and 120h immersion in the corrosion medium (hereby presented are only 2h and 120h). The current density maps from SVET measurements were recorded after 2h in the corrosion medium of 0.01M NaCl.

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

Impedance spectroscopy (EIS) was performed at open circuit potential for all specimens: Zn and composite Zn (ZnB, ZnP0.1, ZnP0.3, ZnP0.5) in 5% NaCl. The EIS response was recorded after immersion times of 2h, 24h, 96h and 120h (first and last time interval hereby presented and discussed). Figures 1 and 2 present the EIS experimental curves as an overlay of the response for 2h and 120h respectively. The equivalent electrical circuit consists of two time constants: ($R_{p.l}Q_{p.l}$), denoted to the properties of the surface layer and ($R_{ct}Q_{ct}$), denoted to the electrochemical reaction; both constants in series with the electrolyte resistance (R_{el} ~ 3hm). Additionally, Warburg impedance was incorporated within the circuits for some responses to account for diffusion phenomena (for simplicity, W is not hereby discussed). The best fit parameters for the immersion periods of 2h and

120h are given in Table 1 (the EIS plots depict the response in Ohm, since the surface area of all samples is equal; Table 1 presents the best fit parameters as normalized values).

As seen from the plots, initially (and for simplicity) one time constant only can be used to fit the response after 2h, except for coating ZnP0.3, where a larger contribution of the product layer, formed on the surface of the electrodes is relevant. Further, after 120h of immersion, generally 2 (or 3) time constants were employed. The EIS response indicates that although the ZnB coating was deposited from an electrolyte containing 1g/l micelles, the properties of this coating with time are similar to pure galvanic Zn. On later stages, corrosion resistance is increased for ZnB, compared to Zn, but not as significant as observed for the ZnP coatings. The best performance at 2h stage is for the ZnP0.5 coating, similar to ZnP0.3 (Fig.1, Table 1). After 120h of treatment, the ZnP0.5 coating exhibits still the highest Rp values, although more than two time constants are present, in contrast to ZnP0.1 (and similar to ZnP0.3), (Fig.2, Table 1). In other words, product layer transformation occurring within the Zn corrosion products denote for higher diffusion limitations and increased corrosion resistance on one hand. On the other hand, the specific properties of the incorporated micelles account for corrosion delay due to self-healing phenomena, a mechanism which is largely discussed and reported [10-14]. With relevance to the aims of this study, it can be stated that higher concentration of micelles in the electrolyte (and embedded in the metallic matrix respectively) does not necessarily mean better corrosion resistance (compare ZnB and ZnP). As hereby observed twice or more lower (0.5g/l and 0.3g/l respectively) concentration of micelles results in a composite coating with significantly improved characteristics. Of course, the electrochemical behavior and surface properties will be dependent on the type of micelles used. What can be stated at this stage is that most likely the size of the micelles plays an important role – the ZnB coating contains PEO-PPO-PEO micelles of 50 – 150 nm size, whereas all ZnP coatings contain PEO-b-PS micelles of 50 nm. Although different micelle formations would certainly affect differently the monitored behavior (which will be subject to further investigation), it can be stated that the size of the nano-aggregates determines the crystallographic orientation in the coating. Further, with respect to the influence of different micelle concentration (ZnP coatings), apparently the higher concentration results in higher corrosion resistance. For determining an optimum concentration, however, a more thorough investigation is needed.

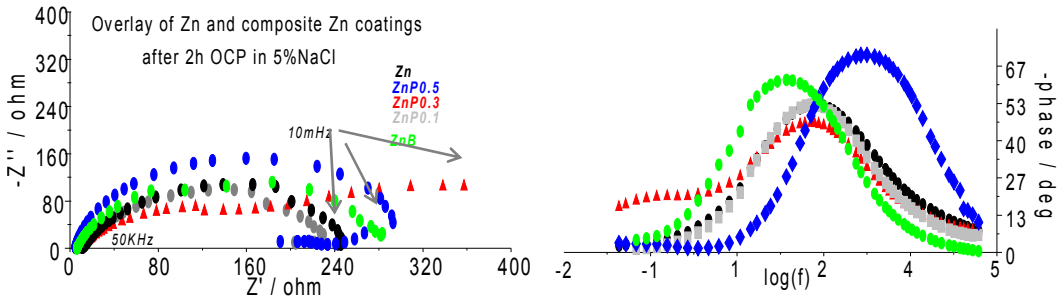

Fig.1 EIS response for Zn, ZnB, ZnP0.1, ZnP0.3 and ZnP0.5 after 2h treatment in 5%NaCl

The EIS results are in line with the electrochemical behavior with external polarization. Fig.3 depicts and overlay of the PD curves for all hereby discussed coatings after 2h conditioning (a) and 120h conditioning (b) in 5% NaCl.

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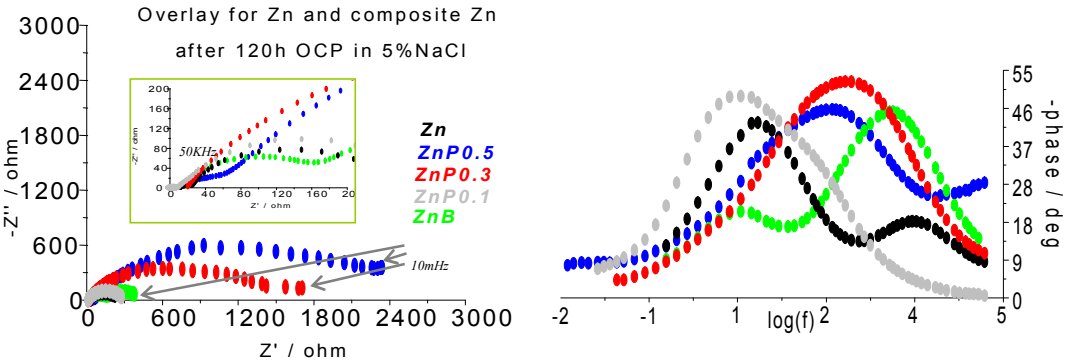

Fig.2 EIS response for Zn, ZnB, ZnP0.1, ZnP0.3 and ZnP0.5 after 120h treatment in 5%NaCl

Table 1: Best fit parameters from EIS measurements*

Cell	*time*	*Rp.l* $k\Omega cm^2$	*Rct* $k\Omega cm^2$	*Y_0, Qp.l.* $1/\Omega.s^n$	*n*	*Y_0, Qct* $1/\Omega.s^n$	*n*	*Rp* $k\Omega cm^2$
	2h							
Zn			0.28			0.21e-3	0.9123	0.28
ZnB			0.30			0.83e-3	0.8504	0.30
ZnP0.1			0.28			0.47e-3	0.7602	0.28
ZnP0.3		0.49	0.14	0.45e-3	0.53	0.88e-4	0.7487	0.63
ZnP0.5			0.65			0.38e-7	0.9221	0.65
	120h							
Zn		0.03	0.14	0.12e-4	0.7952	0.37e-3	0.8955	0.17
ZnB		0.16	0.26	0.49e-5	0.7031	0.26e-3	0.8601	0.46
ZnP0.1			0.29			0.42e-2	0.7122	0.29
ZnP0.3		1.06	0.67	0.21e-4	0.6253	0.83e-5	0.7901	1.73
ZnP0.5		1.40	0.72	0.52e-7	0.3941	0.17e-6	0.8593	2.12

*Equivalent electrical circuits R(RQ) and/or R(RQ)(RQ), incl. W where necessary;. Rel ~ 2-3 Ohm

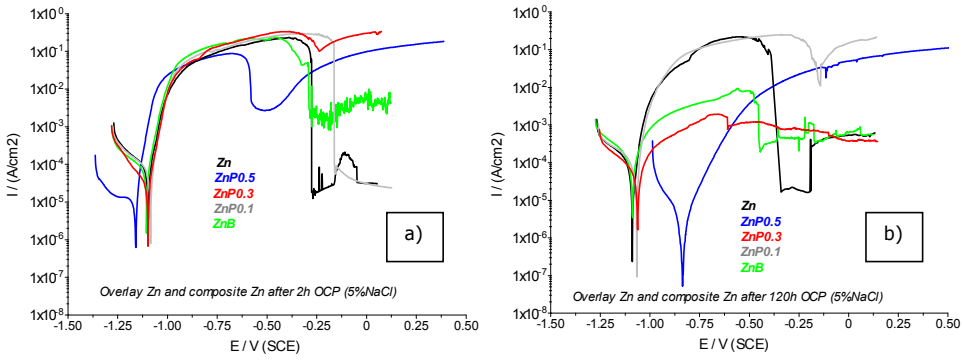

Fig.3 Overlay of PDP scans for all coatings after 2h (a) and 120h (b) of immersion in 5%NaCl

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As seen form the plots, corrosion current density after 2h is lowest for the ZnP0.5 coating (although a more cathodic corrosion potential was observed). Zn, ZnB, ZnP0.1 and ZnP0.3 exhibit similar corrosion current densities. The region of anodic currents between -1V and 0V is, however, prolonged for the composite ZnP coatings, denoting for higher corrosion resistance of the latter. The ZnB coating behaves similarly to Zn. After 120h of treatment, the lowest corrosion current density (as well as more anodic corrosion potential) is recorded for the ZnP0.5 coating. Similarly, significantly lower anodic currents i.e. better corrosion resistance is observed for ZnP0.3 and ZnB. The ZnP0.1 coating behaves similarly to Zn at this stage, although a prolonged anodic region after corrosion potential is observed for ZnP0.1 i.e. even 0.1% of PEO-b-PS micelles is able to increase the resistance of a Zn coating, but not as significantly as with higher concentrations (0.3 and 0.5 g/l). Here again (as within EIS measurements) it is obvious that the formation of product layers with immersion is altered in the presence of micelles and is affected by the micelles dimension and type respectively.

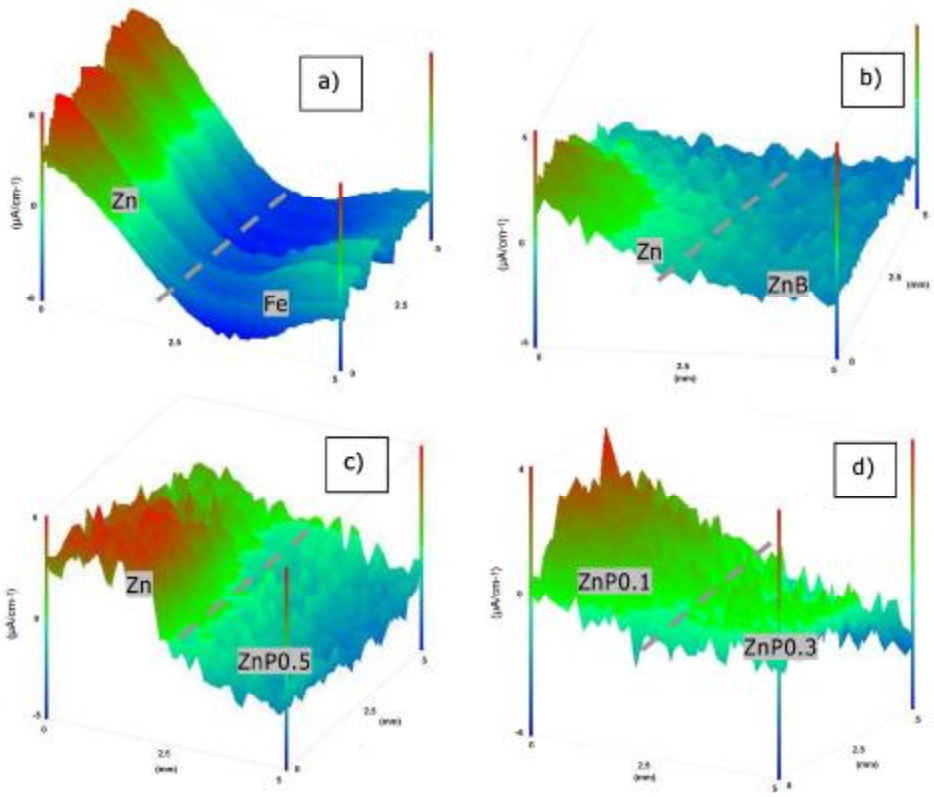

Fig.4 Current density maps (SVET) after 2h treatment in 0.001M NaCl

The electrochemical performance of the investigated coatings in terms of anodic/cathodic behavior with respect to pure Zn is illustrated best via SVET measurements. The technique allows monitoring the exact same location with time (hereby not presented). Fig.4 illustrates the SVET current density maps, recorded after 2h of treatment in 0.0001M NaCl. Fig4a) presents the couple Zn/Fe as an illustration of the extent of anodic dissolution of Zn (as anodic coating) over the substrate. Fig.4b) depicts the couple Zn/ZnB, where ZnB is cathodic with respect to Zn; Fig.4c) presents the couple Zn/ZnP0.5 – again, ZnP0.5 is far more corrosion resistant than Zn and finally, Fig. 4d) depicts the couple ZnP0.1/ZnP0.3 as a comparison of these two composite coatings. As seen from the plot,

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ZnP0.1 is significantly more anodic than ZnP0.3 and therefore with lower corrosion resistance, as previously recorded via EIS and PDP measurements.

3.2. Surface analysis

Figure 5 presents the morphological observation of all hereby investigated coatings after 96h treatment in 5%NaCl.

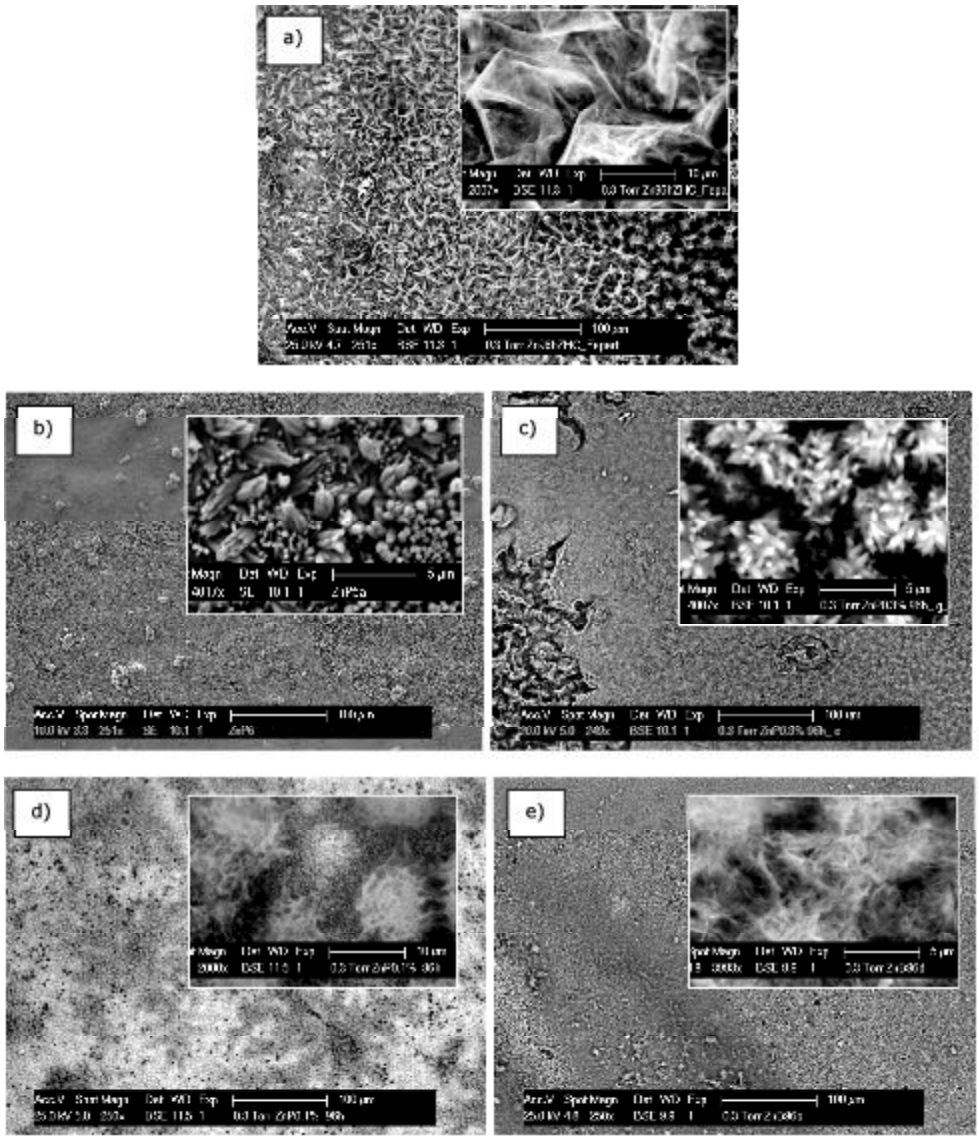

Fig.5. SEM micrographs of the product layers, formed after 96h immersion in 5% NaCl: (a) Zn; (b) ZnP0.5; (c) ZnP0.3; (d)ZnP0.1 and (e)ZnB

Characteristic for the Zn coating is the existence of iron oxides/hydroxides on the surface, meaning that a large portion of the Zn coating has already been dissolved (Fig.5a). For the ZnP0.5 and ZnP0.3 coatings, the surface is more uniform and compact, products from dissolution of the substrate (Fe oxides/hydroxides) were not detected; the product layer consists mainly of well compacted and low crystalline ZnO – Fig. 5b)c). For the ZnP0.1 and ZnB coatings (those with lower corrosion resistance,

compared to ZnP0.5 and ZnP0.3) the surface is largely covered by Cl-containg compounds (mainly $Zn_5(OH)_8Cl_2.H_2O$). This non-uniform layer, although with a low solubility product is not as protective as ZnO in terms of pure electrochemical mechanisms on one hand (Cl^- binding and release and thus pitting initiation and propagation and/or delay of pitting propagation) as well as product layer compaction and crystallinity on the other hand (larger and non-uniformly distributed formations, Fig.5d)e)).

4. CONCLUSIONS

The paper discussed a comparative study of Zn and composite Zn coatings, incorporating different type and concentration of polymeric nano-aggregates (micelles). The recorded electrochemical behavior, supported by surface analysis, denotes for the increased corrosion resistance of all composite coatings, compared to pure galvanic Zn.

With regard to the type of the nano-aggregates, PEO-PPO-PEO micelles appear to exert less pronounced effect on the protective properties of the layers, whereas PEO-b-PS micelles significantly increase corrosion resistance. Higher concentration of micelles does not necessarily mean higher corrosion resistance; however, these effects are related to the size of the micelles and their type. Apparently 1g/l PEO-PPO-PEO micelles to the starting electrolyte results in a zinc composite matrix with lower resistance (coatings ZnB), compared to the composite matrix, obtained by adding 0.3 and 0.5g/l of PEO-b-PS micelles to the starting electrolytes (coatings ZnP).

Since the size of PEO-PPO-PEO micelles (coatings ZnB) is larger (50 – 150 nm), compared to PEO-b-PS micelles (50 nm), coatings ZnP, it is strongly believed that the difference in corrosion resistance mainly originates from the different nucleation mechanisms, crystallographic orientation and homogeneity/compactness of the composite matrix, resulting from the presence of micelles of different size (and type). Therefore, a further and thorough comparative investigation is needed in order to fully clarify the previously postulated (in already reported works [10-14]) enhanced barrier effects and self-haling mechanisms for zinc composite nano-coatings of the hereby investigated types.

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