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Corrosion performance of composite galvanic coatings with variable concentration of polymeric nano-aggregates and/or Cr(III) conversion layers

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This paper reports on the corrosion performance of composite zinc layers (~ 8μm) on a steel substrate, considering the influence of nano-aggregates and Cr(III) conversion layers, compared to control (only Zn layers) conditions. The main factors, influencing the corrosion performance of Zn in this study are: a) the effect of two concentrations of polymeric nano-aggregates (0.1g/l and 0.3g/l PEO_{113}-b-PS_{218} core-shell micelles in the starting electrolyte); b) the effect of Cr(III) conversion layers on both pure Zn and composite Zn layers. For most of the hereby investigated time intervals i.e. treatment in aerated 5% NaCl from 2h until 120h, the composite coatings present higher corrosion resistance, especially within longer treatment. Corrosion current densities are similar to Zn, however, anodic currents are significantly lower. After treatment in NaCl, the composite Zn coatings present a more homogenous product layer, formed as a result of the presence of the nano-aggregates. The additional Cr(III) treatment does not significantly improve the corrosion resistance of the composite coatings for the hereby investigated time intervals.

INTRODUCTION

Improving a zinc coating performance is desirable in terms of increasing its' service life, which can be achieved with or without the combination of a novel composite coating and an environmentally friendly conversion layer. Various methods and techniques are reported with this respect [1-10]; including the utilization of environmentally friendly compounds [11-13]. Composite coatings incorporating micro- or nano-sized aggregates are a more recent approach [14-16]. In previous works, the effect of different nano-aggregates on the corrosion performance of galvanic Zn coatings has been investigated. The approach is based on incorporation of very low concentration of micelles within the

electrodeposition process. Already reported is increased corrosion resistance of composite Zn (compared to pure galvanic Zn) in the presence of: $PHEMA_{15}PPO_{34}$-$PHEMA_{15}$ micelles (formed from the amphiphilic tri-block copolymer poly (2 – hydroxy-ethyl methacrylate) – b – poly (propylene oxide) – b – poly (2 - hydroxyethyl metha-crylate), micelles concentration of 1 g/l to the starting electrolyte) [17]; similarly, 1 g/l to 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 [16]; recently, 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 [18].

The nano-composite coatings were proven to have increased corrosion resistance in terms of reversible, rapidly changing initial corrosion activity (anodic/cathodic currents) as a response to altered environment and increased barrier properties, while still maintaining sacrificial activity of the Zn matrix. In general, the main result was a more pronounced cathodic activity, compared to conventional Zn and therefore impeded anodic reaction and increased protective ability, even in very aggressive environment as 5% NaCl.

Further improvement of the corrosion resistance of the nano-composite coatings, and pure zinc coatings respectively, can be achieved by an additional treatment in chromate or phosphate solutions. To this end, the objective of this work was to investigate the influence of Cr(III)-based conversion treatment (as an eco-friendly variety of the traditional (CrVI) treatment) on the corrosion performance of nano-composite and pure galvanic Zn coatings.

EXPERIMENTAL

Galvanic coatings: Both zinc (Zn) and composite zinc (i.e. Zn + polymeric nano-aggregates, designated further as zinc-polymer or ZnP) coatings were electrodeposited on a steel substrate (low carbon steel, surface area of $4cm^2$) from slightly acidic sulfate-chloride electrolyte with the following 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. For the ZnP coating, the electrolyte also contains the previously stabilized in demi-water PEO_{113}-b-PS_{218} micelles in 2 different concentrations: 0.1g/l and 0.3g/l to the starting electrolyte. The electrodeposition conditions were realized at current density of 2 A/dm^2, pH 4.5-5.0, to – 22°C, no stirring or agitation. The coating thickness for both Zn and ZnP layers was approximately 8 μm.

Conversion layers: The solution for obtaining the "hell-green" conversion film contains Cr^{3+} ions, introduced as a complex salt of chromium with oxalic acid. Another component is concentrated H_3PO_4. Nitrate (NO^{3-}) ions from nitric acid (concentration 50%) are used as oxidizers leading to pH values of the solution of about 1.5.

Sample designation: As aforementioned, conventional galvanic Zn and nano-composite Zn are hereby investigated, thus forming the groups of samples Zn and ZnP respectively (ZnP designed as an abbreviation for Zn and polymer). The specimens from group ZnP form 2 sub-groups: groups ZnP0.1% and ZnP0.3%, which are samples electrodeposited from a starting electrolyte with 0.1 g/l and 0.3 g/l micelles respectively. Further, specimens from groups Zn and ZnP were treated in the conversion layer for "green passivation" (GP) and these types of investigated samples are designated: ZnGP,

ZnP0.1GP and ZnP0.3GP Three replicates per type and per investigated time interval were tested.

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 (SE*M), 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. The current density maps from SVET measurements were recorded after 2h in the corrosion medium of 0.01M NaCl.

RESULTS AND DISCUSSION

Impedance spectroscopy (EIS) was performed at open circuit potential for all specimens: Zn, ZnP0.1%, ZnP0.3%, ZnGP, ZnP0.1GP and ZnP0.3GP in 5% NaCl. The EIS response was recorded after immersion times of 2h, 24h, 96h and 120h. Figures 1 and 2 present the EIS experimental curves as an overlay of the response for each coating at the time interval of 2h and 120h. 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_fQ_f), denoted to the electrochemical reaction; both constants in series with the electrolyte resistance (R_{el} ~ 3hm). The best fit parameters for the different immersion periods 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).

Initially (after 2h treatment), higher magnitude of impedance |Z| was recorded for Zn, compared to the composite ZnP0.1% coating, whereas the highest |Z| appears to be characteristic for the ZnP0.3% coating, the EIS response clearly depicting two time constants i.e. a larger contribution of the surface layer for ZnP0.3%, compared to ZnP0.1% and pure Zn; the global Rp for ZnP0.3% after 2h treatment is the highest (Table 1, 630 Ohm.cm^2). If a comparison is made between the chromated coatings (designation GP), the composite coatings appear to be with similarly higher resistance (280 – 490 Ohm.cm^2) after 2h treatment, compared to pure galvanic Zn (360 Ohm.cm^2). Further, with prolonged treatment, the non-chromated and chromated composite coating ZnP0.3% appears to be with the best corrosion resistance. It should be noted, however, that the "green passivation" does not lead to better properties for the composite coatings, since the highest Rp values after 120h, are recorded for non-chromated ZnP0.3% - 1720 Ohm.cm^2. The effect is attributed to both increased barrier effects (due to the presence of micelles in the metallic matrix), as well as increased charge transfer resistance. The most plausible mechanisms, related to the lower resistance of the chromated composite coatings is discussed further below.

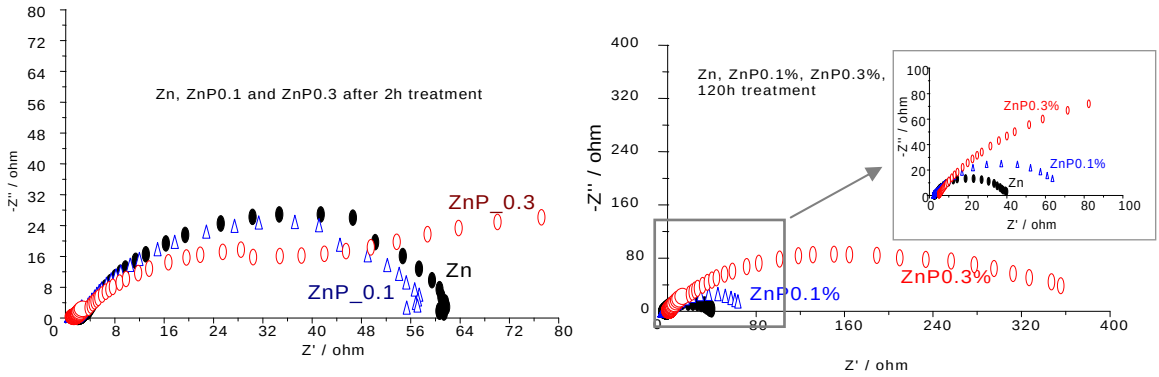

Fig.1 EIS response after 2h (left) and 120h (right) for Zn, ZnP0.1 and ZnP0.3 in 5% NaCl

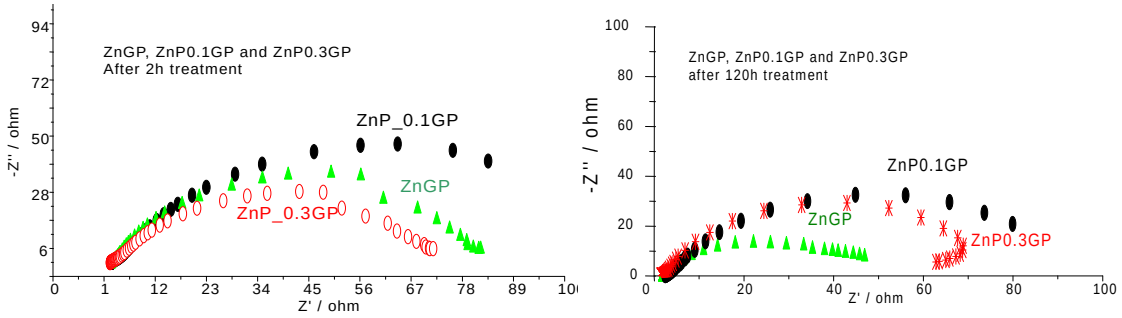

Fig.2 EIS response after 2h (left) and 120h (right) for ZnGP, ZnP0.1GP and ZnP0.3GP in 5% NaCl

Table 1: Best fit parameters from EIS measurements*

Cell	*time*	*Rp.l* Ωcm^2	*Rf* Ωcm^2	$Q_{pr.l}, Y_0$ $\times 10^{-5}\ \Omega^{-1}s^n$	*n*	Q_f, Y_0, $\times 10^{-5}\Omega^{-1}s^n$	*n*	*Rp* Ωcm^2
Zn	2h	60	280	0.72e-5	0.31	0.59e-4	0.82	340
	120h	4	140	0.56e-4	0.89	0.36e-3	0.83	140
ZnP0.1%	2h		230			0.47e-3	0.76	230
	120h		290			0.42e-2	0.71	290
ZnP0.3%	2h	490	140	0.45e-3	0.53	0.88e-4	0.74	630
	120h	1060	660	0.21e-4	0.62	0.83e-5	0.79	1720
ZnGP	2h	100	260	0.60e-4	0.47	0.85e-4	0.89	360
	120h	4	180	0.78e-3	0.78	0.25e-2	0.72	180
ZnP0.1%GP	2h	20	470	0.11e-4	0.65	0.32e-4	0.84	490
	120h	34	330	0.28e-3	0.41	0.15e-2	0.84	360
ZnP0.3%GP	2h	12	270	0.19e-4	0.63	0.57e-4	0.82	280
	120h	48	300	0.13e-2	0.54	0.14e-2	0.84	340

*Equivalent electrical circuit R(RQ)(RQ); (fitting error % < 3.5%). Rel ~ 2-3 Ohm

Potentio-dynamic polarization: The results from EIS measurements are supported by PDP tests. Figure 3 depicts an overlay of PDP curves for all coatings after 2h and 120h treatment. Initially, after 2h, both groups of chromated and non-chromated coatings present similar behavior with external polarization (Fig.3a,c) with a prolonged region of slightly increasing anodic currents (between -1V and -250 mV) for the composite coatings i.e. the composite coatings present higher corrosion resistance (Fig.3a). For the chromated coatings (Fig.3c), the 2h time interval depicts highest corrosion resistance for the ZnP0.1GP coating (current drop around +125mV), which is consistent with the derived highest Rp value from EIS measurements for this coating in the group of

chromated coatings for the 2h time interval (490 Ohm.cm^2, Table 1). Further, within longer treatment the chromated composite coatings ZnP0.1GP and ZnP0.3GP (Fig.3d) present higher resistance with external polarization (current drop around 0V), which is again in line with the EIS response, where similarly higher (360 and 340 Ohm.cm^2) Rp values were recorded for the chromated composite coatings, compared to chromated pure Zn (for ZnGP 180 Ohm.cm^2 was recorded). The best corrosion resistance after 120h, however, is recorded for the non-chromated composite coating ZnP0.3 (Fig.3b), exhibiting significantly lower anodic current in the region after corrosion potential (similarly, the highest Rp values were recorded for this coating via EIS i.e. 1720 Ohm.cm^2).

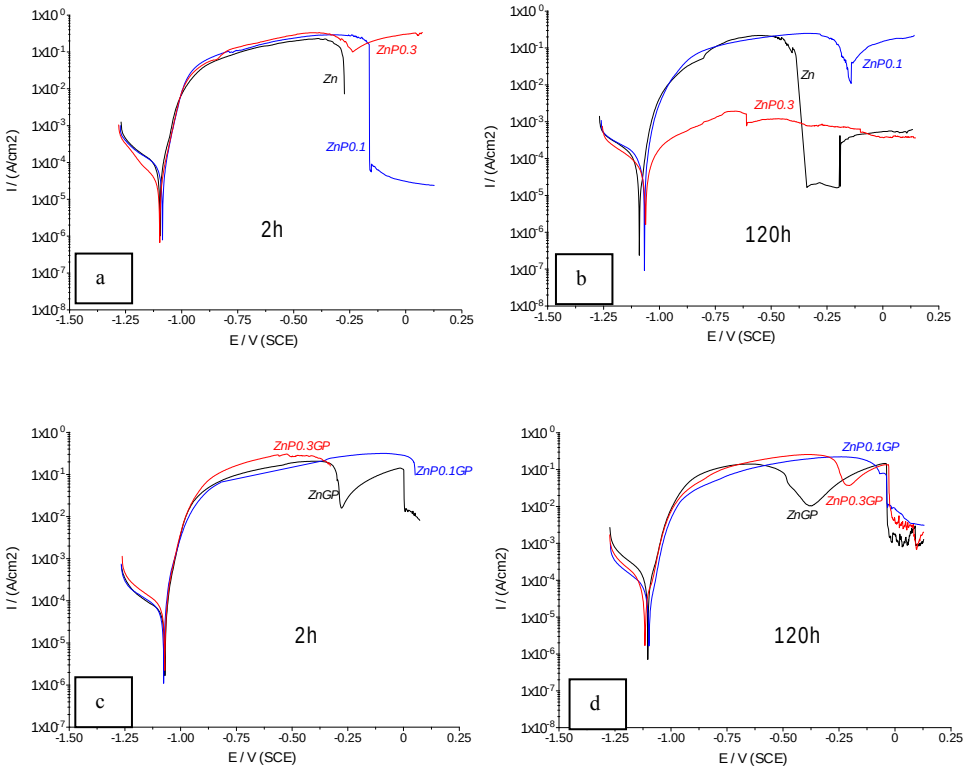

Fig.3 PDP curves for Zn, ZnP0.1 and ZnP0.3 after 2h and 120h treatment (a,b) and ZnGP, ZnP0.1GP and ZnP0.3GP after 2h and 120h treatment (c,d)

According the EIS response and behavior with external polarization (PDP tests), the chromated coatings (ZnGP, ZnP0.1GP and ZnP0.3GP) did not perform significantly better, compared to the non-chromated such. The most plausible reason for this behavior is as follows: the solution for "green passivation" is with a pH of 1.5; When the zinc (composite zinc respectively) coating is immersed in this medium an oxidation process begins (dissolution of zinc) accompanied by reduction of the NO^{3-} ions. The reaction is accompanied by consumption of H^+, the solution near the zinc surface is alkalized and some of the newly appeared Zn^{2+} and Cr^{3+} ions are deposited on the surface in the form of low soluble hydroxide containing compounds, the latter thus forming the conversion chromating film. This process is altering the composition, compactness and properties in general of the zinc matrix, especially when the nano-aggregates are involved. As a result, for the hereby relatively short periods of treatment, the general Rp values of the chromated coatings end up lower (the couple ZnP0.3 and ZnP0.3GP) or slightly higher (the couples Zn and ZnGP and Zn0.1P and ZnP0.1GP) compared to the non-chromated ones. However, and since the best performance remains to be for the non-chromated

ZnP0.3 coating at the end of the test, the hereby tested time intervals appear to be insufficiently long for the final evaluation of the influence of Cr (III) –based conversion layers on the Zn coated steel. Tests are still on-going and final conclusions will be reported in a future contribution.

SVET: The results from SVET measurements support the above findings, revealing the higher corrosion activity of Zn and ZnGP, compared to the composite coatings ZnP and ZnPGP in the relevant model medium (which for SVET is 0.01M NaCl) after 2h. Fig. 4 presents the current density maps for the couples: Zn and ZnP0.1 (a); ZnP0.1 and ZnP0.3 (b) and ZnGP and ZnP0.1GP (c). The composite coating is cathodic, compared to Zn (Fig.4a); similarly for chromated coatings, ZnGP is with lower corrosion resistance, compared to the chromated composite coating (Fig.4c). A comparison between the composite coatings ZnP0.1 and ZnP0.3 (Fig.4b) reveal higher anodic currents for the ZnP0.1 coating, which is again supporting the results, derived from EIS and PDP tests.

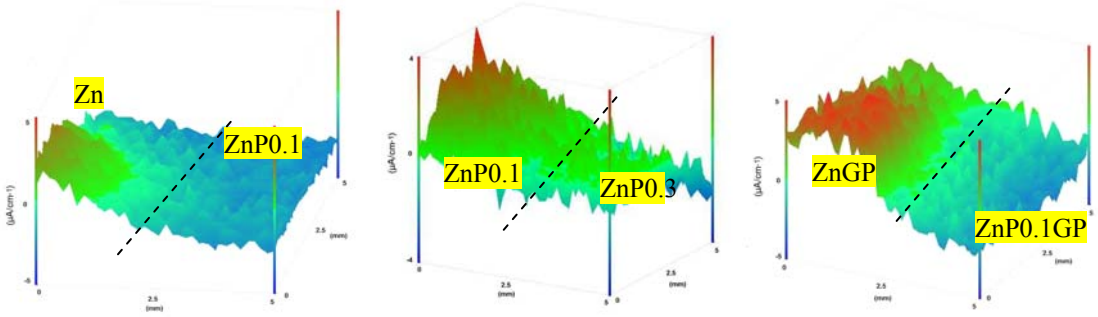

Fig.4 Current density maps (SVET) after 2h treatment in 0.01M NaCl

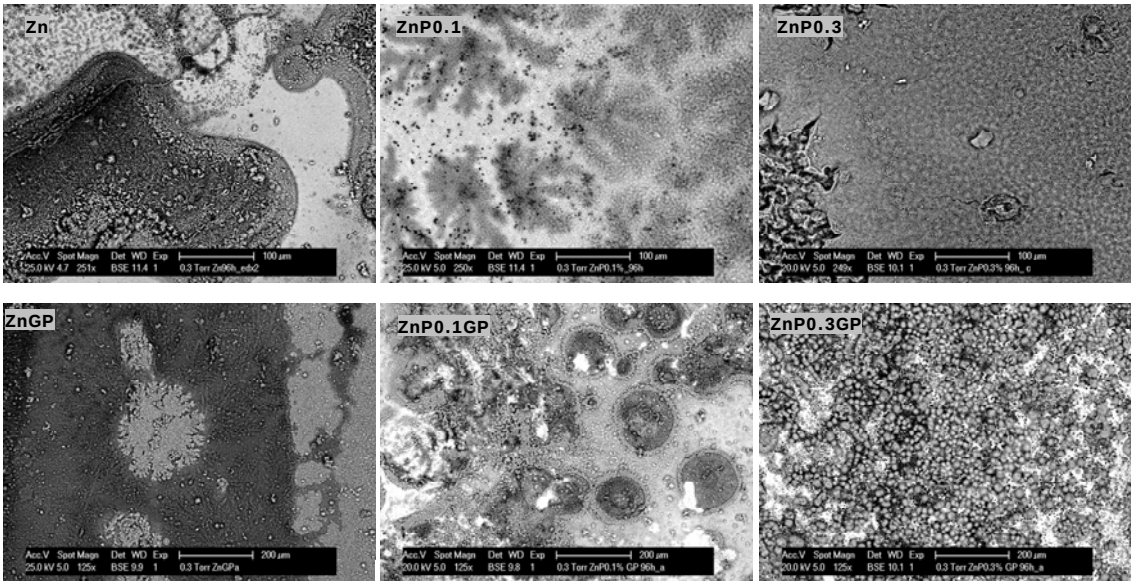

Fig.5 ESEM micrographs of ZnP0.1 (left) and Zn (right) after 96h treatment in 5% NaCl

Morphology (SEM): Morphological observations of the product layer, formed after 96h of treatment in the corrosion medium of 5% NaCl were recorded by SEM. Fig. 5 depicts a comparison of specimens Zn, ZnP0.1 and ZnP0.3 (top) and the chromated such (bottom). The micrographs depict a variety of corrosion products on the surface of all treated samples (mainly ZnO and Zinc-oxy-hydroxi-chloride (ZHC) as detected by EDX

and XRD (not hereby presented), but with visually more homogeneous and compact layer for the composite coatings. The product layer in ZnP0.3 coating contains mainly ZnO of uniform distribution, which denotes for higher corrosion resistance, as actually recorded for this coating.

CONCLUSIONS

Conventional galvanic Zn and nano-composite Zn (ZnP coatings with 2 different initial concentrations of micelles to the starting electrolyte i.e. ZnP0.1 and ZnP0.3) were investigated in comparison to chromated such (ZnGP and ZnPGP). Both types of composite coatings present higher corrosion resistance, compared to pure galvanic zinc. The expected significant increase of corrosion resistance as a result of the treatment with a solution for "green passivation" was not observed at this stage. A more pronounced effect of the Cr(III) conversion layer (initial (2h) and with prolonged treatment (120h)) was observed only for ZnGP and ZnP0.1GP coatings. The coating with the best corrosion resistance was the non-chromated, composite coating ZnP0.3.

Considering the alterations in the surface layers as a result of the combined effect of incorporated micelles and the mechanism of products formation due to Cr(III) passivation, it is concluded, that the results so far present the initial alterations of corrosion activity of the composite and chromated coatings in chloride-containing medium, but for a thorough and final conclusion on the influence of Cr(III) conversion layers on Zn (and especially composite Zn respectively), investigation within prolonged time intervals has to be considered.

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