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This study reports on a comparative investigation of the corrosion behavior of zinc (Zn) and nano-composite zinc (ZnC) galvanic layers in 5% NaCl solution. The metallic matrix of the ZnC layers incorporates nano-sized, stabilized polymeric aggregates, formed from the amphiphilic tri-block co-polymer: poly(2-hydroxyethyl methacrylate) – poly (propylene oxide – poly (2-hydroxyethyl methacrylate) (PHEMA\textsubscript{15}PPO\textsubscript{34}PHEMA\textsubscript{15}). The main objective was to evaluate the electrochemical properties and surface characteristics of both coatings, thus further to investigate if the nano-composite layers will have better corrosion resistance, compared to pure galvanic zinc. The electrochemical behavior, investigated by Impedance spectroscopy (EIS) and Scanning vibrating electrode technique (SVET), supported by surface analysis, using Atomic-force microscopy (AFM) and Scanning electron microscopy (SEM), reveals higher corrosion resistance and consequently better performance of the nano-composite layers, compared to pure galvanic zinc. The mechanism of incorporation of the polymeric nano-aggregates in the coating and their influence on the barrier properties of the composite layers are also briefly discussed.

Introduction

Zinc electrodeposition is an industrial process with wide application and of high importance for the corrosion protection of carbon steel. An adherent zinc coating on a steel substrate has many times the corrosion resistance of the carbon steel; in natural environments zinc corrodes by a factor of 10 to 100 times less than steel \cite{1}. The protection of steel by zinc coating is thus through a barrier effect. Furthermore, in locations where the zinc coating is removed or defective, thus leaving the steel substrate exposed, the galvanic action between steel and zinc can still protect the exposed steel surface from corrosion. In other words, the galvanic corrosion of zinc, unlike many other metals, is desirable for zinc because it is required to protect the steel from corrosion \cite{2}. 

\cite{1}

\cite{2}
Extending the service life of a zinc coating however, will provide longer protection and increased service life for the protected steel.

Therefore, a variety of methods and techniques are available for improving the zinc coatings performance and increasing their corrosion resistance e.g. alloying with other metals [3, 4], conversion coatings [5 - 7] and more recently, composite coatings, incorporating micro- or nano-sized polymeric aggregates [8, 9]. Another, also recent, approach is the electrodeposition of nanocrystalline coatings by using generally applied (as levelers and brighteners) organic additives or pulse deposition techniques [10].

The corrosion resistance of a galvanic zinc layer depends, among other factors, on the morphology and crystallographic orientation in the layer [11, 12]. It is also well known that electrocrystallization occurs by growth of existing crystals or formation of new nuclei [13]. The latter is favored at high overpotentials and low surface diffusion rates of adsorbed metallic ions on the growing zinc layer, which in turn benefits formation of nano-crystals [14 - 16]. For the latter purpose, organic additives are normally used in the zinc electroplating baths. These conditions and in particular grain refinement of the zinc layer, may be also achieved by means of incorporating polymeric nano-sized aggregates, which on one hand act as new nucleation sites and on the other hand, increase the corrosion resistance of the zinc layers in aggressive environment, due to the amphiphilic nature of the used polymer. Therefore, the main objective of the present work was to investigate the electrochemical properties and corrosion performance of composite zinc coatings, incorporating polymer nano-aggregates from the amphiphilic tri-block copolymer PHEMA15PPO34PHEMA15, in comparison with pure galvanic zinc, both electrodeposited from acidic sulfate-based electrolytes.

The approach is based on the formation of nano-structured zinc composite layer, by embedding the stabilized PHEMA15PPO34PHEMA15 micelles in the process of electrodeposition. Thus, the composite coating contains practically insoluble polymer micelles and metallic grains, which leads to an altered zinc matrix. In the case of exposure to highly aggressive corrosion medium, the composite layer will behave differently, compared to the pure galvanic zinc. The composite ZnC coating will have increased barrier properties due to the insoluble polymer micelles on one hand. On the other hand, the ZnC matrix will consist of a larger amount of interfacial boundaries, compared to pure Zn, which will probably lead to alteration of anodic and cathodic areas on the surface in the event of corrosion attack. To this end, the paper presents a comparative investigation of electrochemical parameters and surface properties of both Zn and ZnC layers before and after exposure to 5% NaCl solution. Further, the mechanism of polymer incorporation in the metal matrix, as well as the phenomena, related to the increased barrier properties and a kind of “self-healing” of the composite coating in the event of corrosion attack, are also discussed.

Experimental materials and methods

**Galvanic coatings**: Both pure zinc (Zn) and composite zinc (ZnC) coatings were electrodeposited on a steel substrate (samples from carbon steel type 304, surface area of 1cm²) from slightly acidic electrolyte with the following composition: 175 g/l ZnSO₄, 7H₂O, 25 g/l (NH₄)₂SO₄, 30 g/l H₃BO₃, additives AZ-1 (wetting agent) 50 ml/l and AZ-2 (brightener) 10 ml/l. For the ZnC coating, the electrolyte also contains the previously dissolved in demi-water polymer micelles (concentration of the micelles in the electrolyte is 1 g/l). The following deposition condition applied: current density of 2
A/dm², pH 4.5-5.0, t⁰ – 22 °C, no stirring or agitation. The coating thickness for both Zn and ZnC layers was 12 µm.

Methods: The corrosion resistance of both Zn and ZnC coatings were investigated using electrochemical techniques (EIS and SVET); surface analysis was performed using AFM and SEM investigation.

The EIS measurements were 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, using GPES and FRA interface.

The SVET measurement provides detailed information which is not obtainable by other techniques, since it permits the mapping of current density in an electrolyte immediately above a substrate surface. The instrument used in this study was from Applicable Electronics (Forestdale, MA).

The AFM investigation was performed with a Digital Instrument Nanoscope III Multimode; the SEM investigation was done, using ESEM Philips XL30.

Corrosion medium: The corrosion behavior of both Zn and ZnC coatings was investigated in NaCl solution in concentrations of: 0.001M for the SVET measurements and 5% for EIS and polarization resistance measurements. The AFM and SEM investigation was performed before and after immersion in 5 % NaCl.

Results and discussion

Electrochemical measurements and Surface investigation: Impedance spectroscopy (EIS) measurements were performed at open circuit potential for both Zn and ZnC coatings in 5% NaCl solution.

The impedance response was recorded after different immersion times of 1h, 24h, 48h and 120h. Figures 1 and 2 present the EIS response in Nyquist and Bode format after 1h and 120h exposure (at OCP) to 5% NaCl solution. The equivalent electrical circuit for fitting the EIS data is given in Fig.2a); it consists of two time constants in series with the electrolyte resistance (R_{el} ~ 3Ohm). The first time constant (R_{ct}Q_{1}) is denoted to the

Fig.1 EIS response for Zn and ZnC coating after 1h immersion in 5% NaCl solution.

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electrochemical reaction, the second \((R_fQ_2)\) to the properties of the surface layer. The best fit parameters for the different immersion periods (1h, 24h, 48h and 120h) are given in Table 1 (values are given in Ohm, since the surface area of all samples is equal). Figure 3 presents the polarization resistance \(R_p\) in Ohm.cm\(^2\), calculated on the basis of the derived values for \(R_{ct}\) and \(R_f\).

Fig.2 EIS response for Zn and ZnC coating after 120h immersion in 5% NaCl solution.

Table 1 Summarized data for the best fit parameters, derived on basis of the experimental EIS results, using simulation and fitting procedures and the equivalent circuit type R(Q(R(Q)))

<table>
<thead>
<tr>
<th></th>
<th>(R_{ct}) ohm</th>
<th>(Q_1 \times 10^{-2})</th>
<th>(n)</th>
<th>(R_f) ohm</th>
<th>(Q_2 \times 10^{-5})</th>
<th>(n)</th>
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<tbody>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1h</td>
<td>554</td>
<td>0.0280</td>
<td>0.8612</td>
<td>536</td>
<td>0.2143</td>
<td>0.7649</td>
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<tr>
<td>24h</td>
<td>266</td>
<td>0.3497</td>
<td>0.9097</td>
<td>360</td>
<td>0.9002</td>
<td>0.6568</td>
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<tr>
<td>48h</td>
<td>122</td>
<td>0.1720</td>
<td>0.9879</td>
<td>519</td>
<td>0.5626</td>
<td>0.5892</td>
</tr>
<tr>
<td>120h</td>
<td>195</td>
<td>0.2383</td>
<td>0.9976</td>
<td>469</td>
<td>0.2155</td>
<td>0.5477</td>
</tr>
<tr>
<td>ZnC</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>534</td>
<td>0.0013</td>
<td>0.8994</td>
<td>320</td>
<td>0.4918</td>
<td>0.6802</td>
</tr>
<tr>
<td>24h</td>
<td>274</td>
<td>0.0281</td>
<td>0.7541</td>
<td>197</td>
<td>0.0769</td>
<td>0.6510</td>
</tr>
<tr>
<td>48h</td>
<td>535</td>
<td>0.1784</td>
<td>0.9842</td>
<td>408</td>
<td>0.0853</td>
<td>0.6108</td>
</tr>
<tr>
<td>120h</td>
<td>589</td>
<td>0.0335</td>
<td>0.7858</td>
<td>698</td>
<td>0.1832</td>
<td>0.6410</td>
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</table>

Fig.3 Polarization resistance values, derived from EIS measurements
The initial drop of the $R_p$ ($R_{ct}$ respectively) values after 1h to 24h of immersion is more pronounced for the composite coating. After 48h and up to 120h however, the $R_{ct}$ values for the composite coating increase, while the $R_{ct}$ values for the pure Zn coating decrease and remain lower. This performance is due to the rapid dissolution of the pure Zn coating, while the corrosion product layer, formed in the case of the nano-composite, is more resistant, probably acting as a “barrier” layer, denoted to the presence of the polymer nano-particles and evidenced by increased $R_{ct}$, as well as increased resistance of the product layer $R_f$ with time of conditioning. The results from EIS measurements are supported by the performed SVET analysis, Fig.4.

Fig.4 Current maps, recorded above the surfaces of ZnC and Zn after 0.5h (left) and 2h (right) immersion in 0.001M NaCl solution

After 0.5h in 0.001M NaCl solution (during SVET analysis), the current density map for the nano-composite layer (ZnC) depicts higher local anodic currents, compared to the pure Zn (Fig.4a); after 2h however, there is a significant drop of the anodic current for ZnC and an increase for the pure Zn (Fig.4b).

Fig.5 3D AFM images of ZnC (a,c) and Zn (b,d) electrodeposits on a steel substrate, before and after 120h immersion in 5% NaCl solution
The initially high anodic current for ZnC is due to a more rapid dissolution of the coating in the interfacial zones between the nano-polymer particles and the zinc matrix, while the pure Zn dissolves more uniformly. With time, the anodic current decreases significantly for the composite, which is due to the formation of a “barrier” layer with higher corrosion resistance, as evidenced also by EIS. The corrosion mechanism for the composite is most likely transforming from localized corrosion to a more general corrosion, which lowers the overall corrosion current and retards further propagation of the corrosion medium to the steel substrate.

The above considerations are evidenced and supported by the surface morphology of both galvanic and nano-composite coatings before and after 120h immersion in 5% NaCl.

Fig.6. SEM images of ZnC (a,c) and Zn (b,d) electrodeposits before and after 120h immersion in 5% NaCl solution

The AFM studies (Fig.5) reveal a more homogeneous surface for the ZnC sample before treatment and lower percentage of rough regions after treatment. SEM investigation shows that the ZnC layer consists of finer grains before treatment (Fig.6a) and a more uniformly deposited layer of smaller in crystallites’ size corrosion products after treatment (Fig.6c). In contrast, the Zn coating exhibits larger grains before and after treatment (Fig.6b), higher surface roughness and larger deposits (Fig.6d).

Mechanisms, related to the ZnC coating: The possible mechanisms of incorporation of the polymeric micelles and the most likely phenomena, related to the increased barrier effects of the nano-composite ZnC layer are briefly discussed in what follows.

The polymeric micelles are initially added to the electrolytic bath (in concentration of 1 g/l). The micelles are electro-neutral in nature and present formations of a hydrophobic core (PPO) and a hydrophilic shell (PHEMA). Since the micelles are initially stabilized (details for micelles synthesis as reported in [17]), there will not be an interaction of the hydrophilic shell with the electrolyte in rest conditions (i.e. when there is no current flow in the cell before electrodeposition). A possible mechanism however, is the attraction of
OH- groups by the hydrophilic shell, since a fundamental property of polymer aggregates in acidic solutions (electrolyte pH 4.5) is hydration of the polymers. Further, in the time of electrodeposition, the following mechanisms can apply:

- co-deposition of the polymeric micelles (for simplicity denoted as particles) in the zinc matrix, driven by particle-electrode interactions due to a force balance [8] of adhesion forces (electroosmotic, electrophoretic, London-van der Waals), friction forces (in the process of particle incorporation) and removal forces (in the process of particle-to-particle or particle-to-electrode interactions, since not all particles incorporate in the coating);

- co-deposition as a result of the influence of the DC current flow (in the time of electrodeposition) on the hydrophilic shell. As reported in [18] a DC current causes a decrease of the shell tension and therefore leads to an increase in the number of defects, thus inducing periodic motion (mechanical stress) or increasing interlayer repulsion through electroviscous/electrostatic effects. These latter mechanisms, acting separately or in combination with the process of initially generated hydration of the micelle (OH- groups coordinated in the shell) in rest conditions, will be responsible for attraction of zinc ions in the shell of the micelles. The result will be nano-particle (polymer micelle, incorporating zinc ions) migration and deposition at the cathode.

The composite ZnC layer, already formed on the steel substrate, will be expected to act differently, compared to pure galvanic Zinc, as obvious from the above presented experimental results. What is actually expected, is that the ZnC coating will have higher corrosion resistance, compared to Zn, in the highly aggressive medium of 5 % NaCl. However, although the corrosion resistance of ZnC proves to be higher than Zn after treatment of 120 h, this is not the case in the beginning of the tests, where ZnC coating exhibits higher corrosion rates (see EIS and SVET measurements above). The mechanisms, responsible for the latter observations are most likely as follows:

- At first, the co-deposition of the particles in the zinc metallic matrix is affected by the hydrophilic nature of the vesicle shell. As reported in [19] hydrophilic particles can be easily incorporated in a metal matrix, however there is always a gap under the particle, where the metal layer still grows; this is due to intermittent occurrence of particle riding and incorporation. For hydrophobic particles, metal deposition does not take place underneath the particle and they incorporate without forming gaps.

- Secondly, the hydrophilic shell acts differently in relation to the environmental conditions e.g. open air and humidity i.e. there could be competing processes of reversible swelling and collapse of the shell, depending on the external or internal humidity. In the former case (swelling) there will be a barrier (polymers and zinc oxides/hydroxides, carbonates) protective layer. In the latter case of collapsing of the shell, the products leaving the shell will be released at the interfacial boundaries of the particles as well as on adjacent “pure” zinc surface, which along with the remaining hydrophobic parts of the polymers, again leads to protection of the substrate. In the case of chloride environment, a collapse of the hydrophilic shell of the particle and hence faster propagation of chloride ions in depth of the coating and consequently to the steel surface is possible. The collapse of the shell in this case is due to certain properties of the particles, reported for micelles of co-polymers in the presence of chlorides [20], which are as follows: salts are reported to alter the surface activity, micellisation and thermoreversible gel transition of co-polymers. Chlorides (as in this case the external 5 % NaCl solution) act as water structure makers, leading to an increase in self-hydration of water through hydrogen bonding, thereby reducing the hydration of the co-polymer. Consequently, there will be de-hydration of the particle shell and the latter will collapse
over the core, ending up with a hydrophobic polymeric structure, still incorporated in the metallic matrix.

Therefore, when the composite coating is exposed to NaCl solution, there is an initial accelerated corrosion rate (compared to the pure galvanic zinc), denoted to opening gaps between the particle and the zinc matrix (in addition to the underneath voids, formed in the process of deposition, as previously discussed). On one hand in this interconnected void network around the particle, there could be deposition of previously (before immersion in NaCl) formed zinc oxides(hydroxides), which would be released upon collapsing the shell. On the other hand however, there will be also fresh anodic surface, where corrosion preferentially will take place. Consequently, corrosion rate of the composite coating is initially higher, compared to galvanic zinc. With time of treatment, the corrosion process slows down significantly and further the composite coating exhibits much higher corrosion resistance. This will be the case, since the preferential corrosion around the polymer particles takes place intensively (fresh surface) but on a very small area, compared to the total surface. This makes a large ratio of anodic/cathodic areas and once the fresh anodic areas (comparatively too small) are covered with products, the corrosion rate will decrease significantly. The process is of course supported by the hydrophobic parts of the particles in the film, which additionally enhances the barrier properties of the coating.

**Conclusions**

In conclusion, it can be stated that the electrochemical behavior, investigated by EIS and SVET, supported by AFM and SEM surface analysis, reveal higher corrosion resistance and consequently better performance of the nano-composite layers, compared to pure galvanic Zn.

Additionally, the following can be stated: an important aspect of this study relates to considerations, relevant to the mechanism of sacrificial/barrier properties of the composite. Fundamentally, a zinc coating is meant to protect the steel surface by desirable galvanic corrosion of the zinc itself. Retarding the zinc galvanic corrosion however is also advantageous, since this will increase service life of the coating. The improved properties of a zinc coating however, should not induce full passivation, since then the galvanic action will not be to a sufficient. In this aspect, the nano-composite coating exhibits a kind of “self-healing” properties, denoted to the special characteristics of the incorporated polymers. The reversible mechanisms of collapse and swelling of the particle shell, along with the constantly remaining hydrophobic core, provide reversible corrosion mechanisms (depending on the environment) and allow for better corrosion resistance along with avoiding fast dissolution or full passivation of the coating.

**References**