Surface analysis and electrochemical behavior of zinc composite layers, incorporating polymer nano-micelles.

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This study presents a comparative investigation of the corrosion behavior of zinc (Zn) and nano-composite zinc (ZnC) galvanic layers on a steel substrate in 5% NaCl solution as a corrosion medium. The metallic matrix of the nano-composite layers incorporates nano-size stabilized polymer micelles of a mixed poly(ethylene oxide) (PEO)/poly(2-hydroxyethyl methacrylate) (PHEMA) shell and a thermo-sensitive poly(propylene oxide) (PPO) core. The micelles were prepared in aqueous media and stabilized by UV-induced free radical polymerization of pentaerythritol tetra-acrylate (PETA). The Zn and the composite Zn coatings were electrodeposited from a slightly acidic basic electrolyte (BE: 175.0 g/l ZnSO₄ · 7H₂O; 25.0 g/l (NH₄)₂SO₄; 30.0 g/l H₃BO₃; 50 ml/l AZ-1 wetting agent; 10 ml/l AZ-2 brightener; current density 2 A/dm²; pH4.5-5.0; t⁰ 22°C; cast Zn anodes); the stabilized micelles were dialyzed in distilled water and added to the BE, thus incorporated (electrophoretically) in the matrix of the coating during the electro-deposition process.

The main objective of this study was to evaluate the electrochemical properties and surface characteristics of both coatings, thus further to investigate if the nano-composite layers will have better performance, compared to pure galvanic zinc. The electrochemical properties of both (nano-composite and pure galvanic) zinc coatings were studied using EIS and SVET methods. The surface characteristics before and after exposure to 5% NaCl solution were examined, using SEM and AFM.

Fig.1 EIS response (a) and derived Rp values (b)

Fig.1a) presents the EIS response in Nyquist format after 120h exposure (at OCP) to 5% NaCl solution. The el. circuit for fitting the EIS data is given in Fig.1a), it consists of two time constants in series with the electrolyte resistance (R_{el} ~30ohm). The first time constant ($R_{ct}Q_1$) is denoted to the electrochemical reaction, the second (R_fQ_2) to the properties of the surface layer.

Zn						
Table 1 Best fit parameters						
time	R_{ct} ohm	$Q_1 \times 10^{-2}$ Y_0 l/ohm	n	R_f ohm	$Q_2 \times 10^{-3}$ Y_0 l/ohm	n
1h	554	0.0280	0.8612	536	0.2143	0.7649
24h	266	0.3497	0.9097	360	0.9002	0.6568
48h	122	0.1720	0.9879	519	0.5626	0.5892
120h	195	0.2383	0.9976	469	0.2155	0.5477

ZnC						
time	R_{ct} ohm	$Q_1 \times 10^{-2}$ Y_0 l/ohm	n	R_f ohm	$Q_2 \times 10^{-3}$ Y_0 l/ohm	n
1h	534	0.0013	0.8994	320	0.4918	0.6802
24h	274	0.0281	0.7541	197	0.0769	0.6510
48h	535	0.1784	0.9842	408	0.0853	0.6108
120h	589	0.0335	0.7858	698	0.1832	0.6410

The best fit parameters for different immersion periods of 1h, 24h, 48h and 120h are given in Table 1 (values are given in Ohm, since the surface area of all samples is equal). Fig.1b) presents the polarization resistance R_p in Ohm.cm², calculated on the basis of the derived values for R_{ct} and R_f .

The initial drop of the R_p (R_{ct} resp.) values after 1h to 24h of immersion is more pronounced for the composite coating. After 48h and up to 120h however, the R_p values for the composite coating increase, while the R_p 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.3a).

Fig.3 SVET analysis (a); surface morphology (AFM) maps (b)

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; after 2h however, there is a significant drop of the anodic current for ZnC and an increase for the pure Zn. The initially high anodic current for ZnC is probably 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 in 5%NaCl. The AFM studies (Fig.3b) 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.4a) and a more uniformly deposited layer of smaller in crystallites’ size corrosion products after treatment (Fig.4c). In contrast, the Zn coating exhibits larger grains before and after treatment (Fig.4b), higher surface roughness and larger deposits (Fig.4d).

Fig.4 (a) ZnC before and (c) after treatment; (b) Zn before and (d) after treatment.

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.