

The influence of steel surface modification by electrodeposited Zn–Fe alloys on the protective behaviour of an epoxy coating

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Abstract

The electrochemical and transport properties of epoxy coatings electrodeposited on steel and steel modified by Zn–Fe alloys were investigated during exposure to 3% NaCl. The Zn–Fe alloys were deposited on steel surface from alkaline bath galvanostatically using different current densities. From the time dependence of pore resistance of epoxy coating (impedance measurements), diffusion coefficient of water through epoxy coating (gravimetric liquid sorption measurements) and water content in the epoxy coating (thermogravimetric analysis), it was shown that Zn–Fe sublayer could improve the corrosion stability of the protective system based on epoxy coating. The values of the pore resistance were almost unchanged over the long period of immersion time for epoxy coating on steel modified by Zn–Fe alloy deposited by 4 A dm^{-2} , indicating the great stability of this protective system. The values of diffusion coefficient of water through epoxy coating on this alloy and water content inside the epoxy coating were the smallest, indicating the low porosity of the coating. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Electrodeposition; Zn–Fe alloys; Steel; Epoxy coatings; Corrosion; EIS

1. Introduction

It has been shown [1,2] that zinc alloys can provide improved corrosion resistance compared to pure zinc in the protection of ferrous-based metals. The most common zinc alloys are zinc–nickel, zinc–cobalt and zinc–iron [1,2]. The Zn–Fe alloys have been used a lot recently, since they showed excellent corrosion resistance (due to the nature of the zinc–iron phase), good paintability, formability and weldability (due to the high hardness and melting point of the zinc–iron phase in comparison to pure zinc) and ease of formation of the coating [3,4]. On the other hand, it is well known that surface modification can significantly improve the stability of a polymer/metal system against corrosion [5].

In our previous work, the effect of steel surface modification by Zn–Ni and Zn–Co alloys were investigated [6–10]. The aim of this work was to modify a steel surface by Zn–Fe alloys electrodeposited from alkaline bath using different current densities and to investigate the corrosion behaviour of the Zn–Fe alloy/epoxy coating protective system. Thin, non-pigmented epoxy coatings (primers) were elec-

trodeposited on Zn–Fe alloys of different composition and morphology, as well as on a steel surface, as a reference.

2. Experimental

2.1. Electrodeposition of Zn–Fe alloys

Zn–Fe alloys were deposited galvanostatically by 2.0, 4.0 and 10.0 A dm^{-2} on a steel panel or on a rotating disc electrode at 25°C from alkaline bath: $0.09 \text{ mol dm}^{-3} \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $0.01 \text{ mol dm}^{-3} \text{ FeSO}_4 \cdot 6\text{H}_2\text{O}$, 0.01 mol dm^{-3} ascorbic acid, $\sim 0.2 \text{ mol dm}^{-3}$ triethanolamine, $30 \text{ g dm}^{-3} \text{ Na}_2\text{SO}_4$ and $80 \text{ g dm}^{-3} \text{ NaOH}$ ($\text{pH} \geq 14$) [4]. The employed electrolyte was prepared using p.a. chemicals and double distilled water.

The working electrodes (steel panels $20 \text{ mm} \times 20 \text{ mm} \times 0.25 \text{ mm}$) were pretreated by mechanical cleaning (polishing) and then degreased in a saturated solution of sodium hydroxide in ethyl alcohol, pickled with hydrochloric acid solution at 1:1 dilution for 30 s and rinsed with distilled water. Prior to each electrodeposition the Pt disc surface was mechanically polished with a polishing cloth (Buehler Ltd.), impregnated with a water suspension of alumina powder ($0.3 \mu\text{m}$ grade) and then rinsed with pure water in an ultrasonic cleaner. Counter electrode was either a Zn spiral

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ribbon (high purity Zn), placed parallel to the RDE at a distance of 1.5 cm (for plating on a rotating disc electrode), or Zn panels (high purity Zn 30 mm × 30 mm × 0.2 mm for plating on a steel panel), placed parallel to the working electrode at a distance of 1.5 cm. The thickness of Zn–Fe alloys was 10 μm .

The chemical composition of the Zn–Fe alloys was determined by EDX analysis of the deposits using scanning electron microscopy (SEM) type PHILIPS XL 30.

2.2. Electrodeposition of epoxy coatings

The epoxy coatings were electrodeposited from an epoxy resin emulsion modified by amine and isocyanate, on steel and steel surface previously modified by Zn–Fe alloys, using a constant voltage method (CATOLAC emulsion 543.052, produced by PPG). The resin concentration in the electrodeposition bath was 10 wt.% solid dispersion in water at pH 5.7; the temperature was 26 °C and the applied voltage was 250 V [11]. After coating for 3 min, coatings were rinsed with distilled water and cured for 30 min and the measured thickness was $22 \pm 1 \mu\text{m}$.

2.3. Electrochemical impedance spectroscopy (EIS)

For a.c. impedance measurements the coated samples were exposed to 3% NaCl in distilled water for 35 days. A three-electrode cell arrangement was used in the experiments. The working electrode was a coated sample situated in a special Teflon holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was a saturated calomel electrode (SCE). The a.c. impedance data were obtained at the open-circuit potential using a PAR 273 potentiostat and PAR 5301 lock-in amplifier. The impedance measurements were carried out over a frequency range of 100 kHz to 10 mHz using a 5 mV amplitude of sinusoidal voltage. The impedance spectra were analysed using a suitable fitting procedure [12].

2.4. Determination of the rate of H_2 evolution reaction

The rate of hydrogen evolution reaction in the polymer solution on steel and Zn–Fe surfaces was determined using a slow sweep voltammetry (rotation of 2000 rpm, sweep rate: 0.5 mV s^{-1}). The working electrode used in this experiment was either a steel or a Pt rotating disc electrode ($d = 8 \text{ mm}$). The steel disc surface was prepared the same way as the steel panels. The counter electrode was a platinum spiral wire and the reference electrode was SCE.

2.5. Gravimetric liquid sorption measurements

Gravimetric liquid sorption measurements were performed by weighing samples on an analytic balance following immersion in 3% NaCl at 25 °C. The samples were

periodically removed from electrolyte and weighed. Sorption curves were used to evaluate the diffusion coefficient of water across epoxy coatings electrodeposited on steel and steel modified by Zn–Fe alloys.

2.6. Thermogravimetric analysis (TGA)

TGA was carried out using Perkin-Elmer TGS-2 instrument. The experiments were performed in a dynamic nitrogen atmosphere (30 ml min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ over the temperature range of 23–200 °C. The water content inside the epoxy coatings was determined from TG data.

3. Results and discussion

3.1. Electrochemical properties of epoxy coatings

Fig. 1a and b shows the Nyquist and Bode plots, respectively, for the impedance of the epoxy coatings

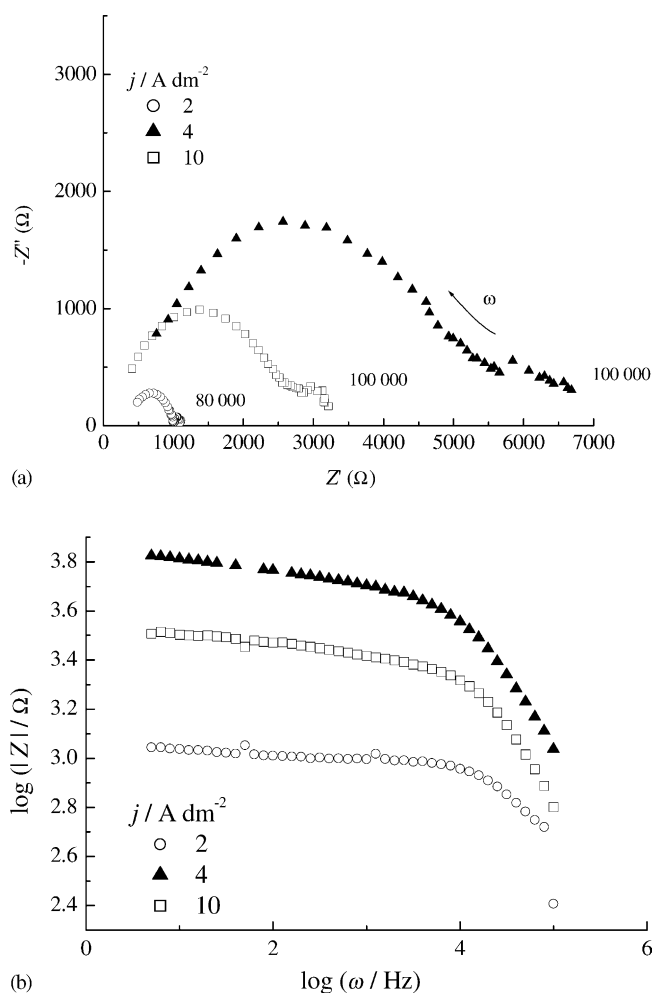


Fig. 1. (a) Nyquist and (b) Bode plots for epoxy coatings on steel modified by Zn–Fe alloys electrodeposited at different current densities after 1 day of exposure to 3% NaCl.

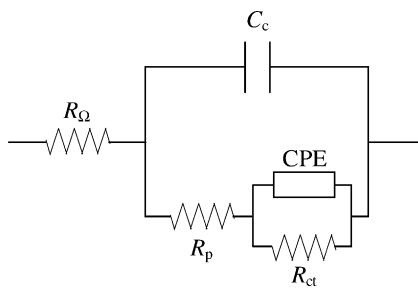


Fig. 2. Equivalent electrical circuit of a polymer-coated metal.

electrodeposited on steel modified by Zn–Fe alloys obtained at different current densities after 1 day of exposure to 3% NaCl. It can be seen from Fig. 1 that epoxy coating on steel modified by Zn–Fe alloy obtained by 4 A dm⁻² has greater values of pore resistance than epoxy coating on steel modified by other Zn–Fe alloys. A general equivalent electrical circuit model for the behaviour of polymer-coated metal in corrosive environments has been used (Fig. 2) [13,14], where R_{Ω} is the electrolyte resistance, R_p the coating pore resistance, C_c the coating capacitance, R_{ct} the charge-transfer resistance and CPE is a constant phase element, which represents all the frequency dependent electrochemical phenomena, namely double-layer capacitance and diffusion processes. The fitting of experimental data obtained, using the procedure elaborated by Boukamp [12], enabled the determination of pore resistance, R_p , and coating capacitance, C_c , for films formed on steel and steel modified by Zn–Fe alloys. The pore resistance and coating capacitance are plotted as a function of time in Figs. 3 and 4, respectively.

Initially, during the first few days for epoxy coatings on steel and steel modified by Zn–Fe alloys obtained at 2 and 4 A dm⁻², the pore resistance decreases (Fig. 3, period up to point 1), while coating capacitance increases over time (Fig. 4, period up to point 1), denoting the entry of electrolyte into the epoxy coating [11,15,16]. This is the first step of electrolyte penetration through an organic coating

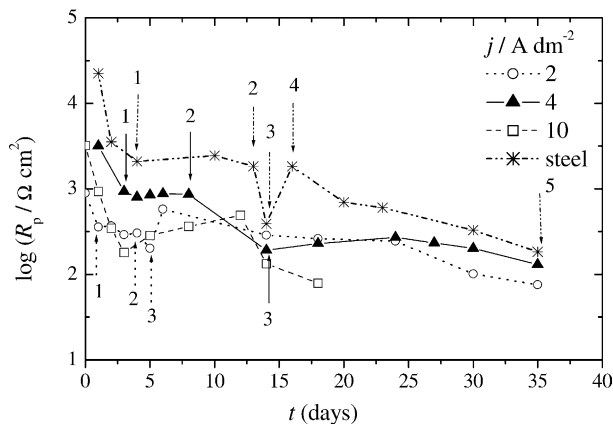


Fig. 3. Time dependence of pore resistance for epoxy coatings on steel and steel modified by Zn–Fe alloys during prolonged time of exposure to 3% NaCl.

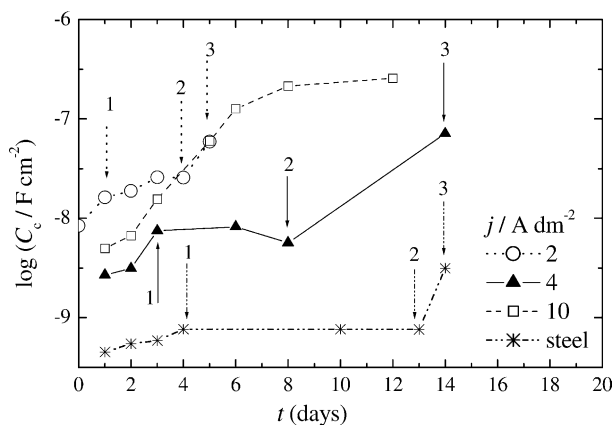


Fig. 4. Time dependence of coating capacitance for epoxy coatings on steel and steel modified by Zn–Fe alloys during initial time of exposure to 3% NaCl.

and it is related to water uptake when molecules of pure water diffuse into the micropores of the polymer net according to Fick’s law [17]. After this period, the values of pore resistance and coating capacitance reach a plateau (except for epoxy coating on Zn–Fe alloy deposited at 10 A dm⁻² which continuously keeps increasing for C_c), and remain almost constant over a longer period of time (Figs. 3 and 4, period 1–2) indicating the maintenance of good protective properties of the epoxy coating [18]. This is the second step of electrolyte penetration and it refers to penetration of water and ions through the macropores of the coating which become deeper with time, until they finally pass through the epoxy coating and reach the metal surface [11,16]. This leads to contact between the electrolyte and the metal surface and to the beginning of electrochemical processes on the metallic interface. The next period of increase in coating capacitance (Fig. 4, point 3) and decrease in pore resistance (Fig. 3, point 3) after a longer period of plateau (third step of electrolyte penetration) indicates the beginning of detachment of the coating from the substrate as a result of the adhesion loss and the start of underfilm corrosion reactions. In the case of epoxy coating on steel, the beginning of the electrochemical process on basic substrate occurred later than on steel modified by Zn–Fe alloys.

The time dependences of pore resistance and coating capacitance show that an epoxy coating electrodeposited on steel has better protective properties during this initial time interval of exposure to 3% NaCl. It has longer period of plateau at $\log R_p-t$ and $\log C_c-t$ curves, higher values of pore resistance and lower values of coating capacitance, which indicates better corrosion stability with respect to the coating electrodeposited on Zn–Fe sublayers.

The influence of substrate type on the electrochemical properties of epoxy coatings is pronounced during prolonged exposure to a corrosive agent. The period of increase and then decrease in pore resistance for epoxy coatings on steel (Fig. 3, period 3–5) can be explained by plugging of the pores with corrosion products, followed by further

dissolution and desorption of corrosion products [11,16]. On the other hand, there are almost unchanged values of pore resistance during a long time of exposure in the case of epoxy coating on steel modified by Zn–Fe alloys obtained at 2 and 4 A dm⁻², indicating greater stability of these protective systems (Fig. 3, period after point 3). This behaviour of epoxy coating on steel modified by Zn–Fe alloys obtained at 2 and 4 A dm⁻², during extended time of exposure, can be explained by plugging of the epoxy coating pores with corrosion products, which form a pseudo-passive layer on Zn–Fe surfaces, mainly consisting of ZnCl₂·4Zn(OH)₂ [19–21].

The values of pore resistance are slightly greater in the case of epoxy coating on steel modified by Zn–Fe alloy deposited at 4 A dm⁻² with respect to epoxy coating on steel modified by Zn–Fe alloy deposited at 2 and 10 A dm⁻². The differences in electrochemical properties among epoxy coatings on different Zn–Fe alloys arise from different chemical composition and surface morphology of alloys obtained by different deposition parameters [22]. Namely, it is well known that Zn coatings deposited from baths of various compositions have differences in porosity, structure and other characteristics, which, in turn, affect the corrosion resistance of the coatings [23]. The other possible reason for better electrochemical properties of epoxy coating on Zn–Fe alloy deposited at 4 A dm⁻² is the presence of thinner oxide layer on this Zn–Fe surface. Namely, the EDX analysis reported the presence of oxygen in Zn–Fe deposits where the Zn–Fe alloy deposited at 4 A dm⁻² had the least oxygen content and the one deposited at 10 A dm⁻² had the highest oxygen content. It was assumed that adhesion of epoxy coating to surface with thicker oxide layer is poor, as compared to one with a thin oxide layer, as it is expected to be on Zn–Fe alloy surface obtained at 4 A dm⁻². On the basis of the results presented so far, it could be seen that the Fe content in the alloy determined by EDX (Table 1) is one of the factors determining also corrosion stability of protective systems based on Zn–Fe alloy and epoxy coating. The alloy with the highest Fe content, i.e. the one obtained at 10 A dm⁻², is the one with the worst electrochemical properties.

3.2. Transport properties of epoxy coatings

The influence of surface modification of steel by Zn–Fe alloys on the sorption characteristics of epoxy coatings (first

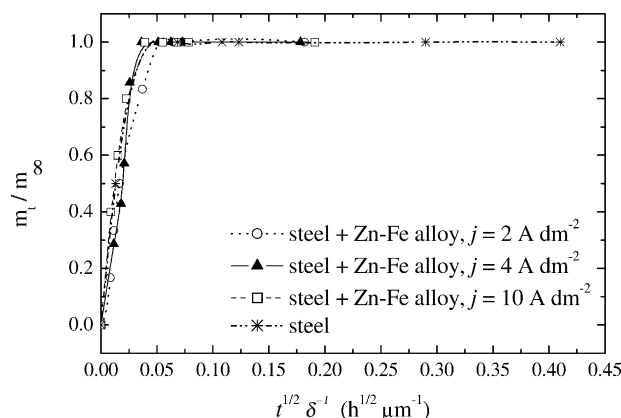


Fig. 5. Reduced sorption curves at 25 °C for epoxy coatings on steel and steel modified by Zn–Fe alloys in 3% NaCl.

step of electrolyte penetration) was investigated by gravimetric liquid sorption experiments. The reduced sorption curves (Fig. 5) plotted as the dependence of m_t/m_∞ on $t^{1/2}/\delta$, since the second Fickian diffusion law, for a flat plane and short times is [24]:

$$\frac{m_t}{m_\infty} = \frac{4D^{1/2}}{\delta\pi^{1/2}} t^{1/2}$$

where m_t is the amount of absorbed water at time t , m_∞ the amount of absorbed water in equilibrium, D the diffusion coefficient of water through the epoxy coating and δ is the film thickness. As can be seen from Fig. 5 the initial absorption of water is linear until a steady state is achieved. The initial linear dependence of the reduced sorption curves confirm the assumption that the sorption is controlled by Fickian diffusion. The diffusion coefficient of water through a non-pigmented epoxy coating on steel and steel modified by Zn–Fe alloys was calculated from the slope of the initial linear region of the reduced sorption curves (Table 1).

The value of $D(\text{H}_2\text{O})$ obtained for epoxy coating on steel is greater than for epoxy coatings on steel modified by Zn–Fe alloys, indicating more porous structure of epoxy coating on steel. The epoxy coating on Zn–Fe alloy obtained at 4 A dm⁻² has the smallest $D(\text{H}_2\text{O})$ suggesting the smallest porosity of this protective system. The epoxy coating on Zn–Fe alloy obtained at 10 A dm⁻² has the greatest $D(\text{H}_2\text{O})$ among Zn–Fe alloys investigated. These results are in

Table 1

The values of iron content, diffusion coefficient of water at 25 °C, $D(\text{H}_2\text{O})$, absorbed water content and contact angle, ϕ , for epoxy coatings electrodeposited on steel and steel modified by Zn–Fe alloys

Substrate	Steel	Steel + Zn–Fe alloy, $j = 2 \text{ A dm}^{-2}$	Steel + Zn–Fe alloy, $j = 4 \text{ A dm}^{-2}$	Steel + Zn–Fe alloy, $j = 10 \text{ A dm}^{-2}$
Fe content (wt.%)		1.0	1.3	2.2
$D(\text{H}_2\text{O}) (\times 10^{10} \text{ cm}^2 \text{ s}^{-1})$	7.83	5.0	3.7	6.8
Water content (wt.%)	0.40	0.40	0.25	0.50
ϕ (°)	48	4	Complete	10

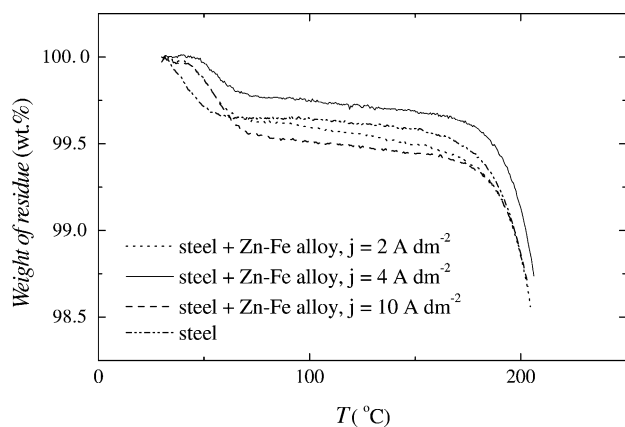


Fig. 6. TG curves of the dehydration process for epoxy coatings on steel and steel modified by Zn–Fe alloys after 1 day of exposure to 3% NaCl (heating rate $10^{\circ}\text{C min}^{-1}$).

accordance with impedance measurements (Fig. 3), where it was also shown that this system had the worst electrochemical properties.

The quantity of absorbed water inside the epoxy coating, as a measure of corrosion stability, was determined by thermogravimetric (TG) measurements. The dehydration process is represented by TG curves for epoxy coatings on all surfaces (Fig. 6). Two weight loss steps could be observed in Fig. 6 for all investigated systems, with a total weight loss of ~ 1.5 wt.% which is completed at $\sim 200^{\circ}\text{C}$. The first step (at $\sim 55^{\circ}\text{C}$ for epoxy coating on steel and at $\sim 65^{\circ}\text{C}$ for epoxy coating on steel modified by Zn–Fe alloys) is related to the more or less free water loss from the macropores of epoxy coating. The second step takes place between temperatures 55 and 190°C and it is characterized by a gradual, slow decrease in weight loss, which is probably due to the delivering of chemically linked water. The values of water content inside the epoxy coatings on steel and steel modified by Zn–Fe alloys are given in Table 1.

The smallest value of water content is inside the epoxy coating on steel modified by Zn–Fe alloy deposited at 4 A dm^{-2} , indicating again the least porous epoxy structure and, thus, the most stable system in corrosive environment. The value of water content inside the epoxy coating on Zn–Fe alloy deposited at 10 A dm^{-2} is the greatest.

The differences in $D(\text{H}_2\text{O})$, amount of absorbed water and, consequently, in electrochemical properties could be explained by different rates of hydrogen evolution from steel and Zn–Fe alloys during cathodic epoxy coating deposition, since hydrogen evolution by H_2O discharge is the first step in the deposition of an epoxy coating [25], as well as by the different surface tension of the polymer solution on different substrates [6,7]. Fig. 7 shows that the rate of hydrogen evolution reaction is almost the same for all Zn–Fe surfaces and it is higher than steel surface. Surface tension of polymer solution on steel and Zn–Fe alloys is also different. Contact angle, ϕ , between polymer solution and different substrates

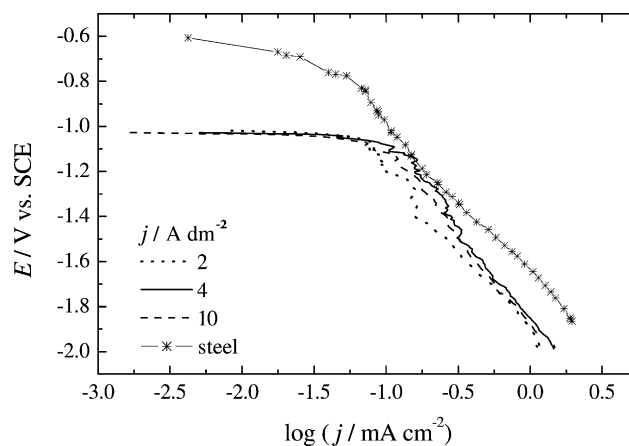


Fig. 7. Polarization curves for hydrogen evolution on steel and steel modified by Zn–Fe alloys in polymer solution at 25°C , N_2 saturated, $\omega = 2000\text{ rpm}$, $\nu = 0.5\text{ mV s}^{-1}$.

was determined by drop test and the results are also given in Table 1. Contact angle was not measurable on Zn–Fe alloy obtained at 4 A dm^{-2} , indicating the complete wettability of this substrate. The larger contact angle on steel surface and higher rate of H_2 evolution causes the accumulation of H_2 on the cathode during electrodeposition of epoxy coating. During the subsequent curing at 180°C of the epoxy coating, the H_2 goes out, leaving more vacancies in the polymer network and causing epoxy coating on steel to have a more porous structure. This is also in agreement with previously shown results of the greatest value of $D(\text{H}_2\text{O})$ on steel. Hydrogen evolves with almost the same rate for all examined Zn–Fe surfaces (Fig. 7), but surface tension of polymer solution on Zn–Fe alloys is different. The greater contact angle of Zn–Fe alloy obtained at 10 A dm^{-2} , although the rate of H_2 evolution is the same, causes some accumulation of H_2 on the cathode during electrodeposition of epoxy coating and, as a consequence, a more porous epoxy structure is formed on this alloy with respect to other Zn–Fe surfaces. That is why the most porous epoxy structure is formed on this Zn–Fe alloy (greater $D(\text{H}_2\text{O})$ and the greatest amount of absorbed water).

It could be concluded that although the values of R_p are smaller for epoxy coating on steel modified by Zn–Fe alloys than on steel, the Zn–Fe alloy layer could still provide steel surface protection by its barrier properties, postponing the time of electrolyte penetration to steel surface. This relates to Zn–Fe alloys obtained at 2 and 4 A dm^{-2} , while epoxy coating on steel modified by Zn–Fe alloy obtained at 10 A dm^{-2} shows poor protective properties (no plateau of constant R_p and C_c values, Figs. 3 and 4).

4. Conclusion

Using EIS, gravimetric liquid sorption experiments and TGA, the electrochemical and transport properties of epoxy

coatings electrodeposited on steel and steel modified by Zn–Fe alloys were monitored during exposure to 3% NaCl. It was shown that the plating current density in Zn–Fe alloy electrodeposition has a great influence on the corrosion resistance of protective systems based on Zn–Fe alloy/epoxy coating.

During the initial time of exposure to 3% NaCl better electrochemical properties were obtained for epoxy coating on steel: higher values of pore resistance, lower values of coating capacitance and longer period of plateau at time dependencies of these parameters. On the other hand, during prolonged exposure to 3% NaCl the steel modified by Zn–Fe alloy obtained at 4 A dm^{-2} significantly improves the corrosion stability of the protective system: almost unchanged values of R_p were observed due to the formation of a pseudo-passive layer of corrosion products, which is a good barrier to the transport of water, oxygen and electrolyte ions.

The highest value of $D(\text{H}_2\text{O})$ and the greatest amount of absorbed water for epoxy coating on steel and steel modified by Zn–Fe alloy obtained at 10 A dm^{-2} indicate the more porous epoxy structures obtained. This could be explained by the existence of hydrogen evolved during electrodeposition of epoxy coating, which, due to the smaller wettability of these surfaces by polymer solution, accumulates on the cathode, and during further curing goes out leaving more vacancies in the polymer network. The smallest values of $D(\text{H}_2\text{O})$ and the amount of absorbed water were obtained for epoxy coating on steel modified by Zn–Fe alloy obtained at 4 A dm^{-2} .

On the basis of all the experimental results, it can be concluded that steel surface modification by Zn–Fe alloy deposited at 4 A dm^{-2} improves the corrosion stability of a protective system based on an epoxy coating.

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