

The effect of Zn-Ni sublayers on the corrosion behaviour and thermal stability of epoxy coatings electrodeposited on steel

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The electrochemical and transport properties, as well as the thermal stability of epoxy coatings electrodeposited on steel and steel modified by Zn–Ni alloys were investigated during exposure to 3 % NaCl. The Zn–Ni alloys were electrodeposited on steel using direct and pulse current. From the time dependence of the pore resistance of the epoxy coating (impedance measurements), the diffusion coefficient of water through the epoxy coating (gravimetric liquid sorption measurements) and the thermal stability of the epoxy coating (thermogravimetric analysis), it was shown that Zn–Ni sublayers significantly improve the corrosion stability of a protective system based on an epoxy coating. The values of the pore resistance were almost unchanged over a long period of immersion time for epoxy coatings on steel modified by Zn–Ni alloys, indicating the great stability of these protective systems.

Keywords: electrodeposition, epoxy coatings, Zn–Ni alloys, steel, corrosion, EIS.

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.³ Zinc–nickel alloys are mostly used because of their high degree of corrosion resistance and their good mechanical properties.^{4–7} Zn–Ni alloys with a Ni content in the range of 12–14 wt. % exhibit the best corrosion properties and can be several times better than a pure zinc coating of the same thickness.⁸

On the other hand, it is also known that the application of pulse plating leads to improvements in the quality of electrodeposits: smooth deposits are achieved, with decreased porosity, better ductility, hardness and surface roughness.⁹

The aim of this work was to modify a steel surface by Zn–Ni alloys electrodeposited using the direct and pulse current techniques and to investigate the corrosion be-

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haviour of the Zn–Ni alloy-epoxy coating protective system. The corrosion behaviour of the epoxy coating on steel was also examined, as a reference. Thin, non-pigmented epoxy coatings (primers) were electrodeposited in order to investigate more accurately the effect of the metal surface on the epoxy coating.

EXPERIMENTAL

Electrodeposition of Zn–Ni alloys

Zn–Ni alloys were electrodeposited on a steel panel or on a rotating disc electrode from a bath¹⁰ containing: 15 g dm⁻³ ZnO, 60 g dm⁻³ NiCl₂·6H₂O, 250 g dm⁻³ NH₄Cl and 20 g dm⁻³ H₃BO₃, at 40 °C. The pH of this solution was 6.0. The working electrode was steel panel (20×20×0.25 mm) pretreated by mechanical cleaning (polishing) and then degreased in a saturated solution of sodium hydroxide in ethanol, pickled with a hydrochloric acid solution at 1 : 1 dilution for 30 s and rinsed with distilled water. The counter electrode was either a Ni spiral wire, placed parallel to the RDE at a distance of 1.5 cm (for plating on a rotating disc electrode) or a platinum anode (for plating on a steel panel) placed parallel to the working electrode at a distance of 1.5 cm. The reference electrode was a saturated calomel electrode (SCE). The Zn–Ni alloys were deposited either by direct current (DC) with a current density of 10, 20 and 50 mA cm⁻² or by pulse current (PC) with an average current density of 20 mA cm⁻², and with a cathodic deposition time (on period, T_{on}) and pause period (off period, T_{off}) of $T_{\text{on}} = T_{\text{off}} = 1$ ms. The thickness of the Zn–Ni alloys was 10 μm.

Anodic linear sweep voltammetry (ALSV)

For the determination of the phase structure of the alloys, the alloys were dissolved anodically at room temperature (23±1 °C) using the slow sweep voltammetry technique (sweep rate 1 mV s⁻¹ and rotation of 2000 rpm) in a N₂ saturated 0.5 mol dm⁻³ Na₂SO₄ + 0.05 mol dm⁻³ EDTA solution. The working electrode used in this experiment was a Pt rotating disc electrode ($d = 8$ mm, at 2000 rpm). 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 μm grade) and then rinsed with pure water in an ultrasonic cleaner. The counter electrode used in these experiments was a Pt spiral wire and the reference electrode was a saturated calomel electrode (SCE). All potentials are referred to the SCE.

The chemical composition of the Zn–Ni alloys was determined by atomic absorption using a Perkin Elmer spectrophotometer (AAS-1100).

Electrodeposition of the epoxy coatings

The epoxy coatings were electrodeposited from an epoxy resin emulsion modified by amine and isocyanate, on steel and on steel previously modified by Zn–Ni alloys, using the constant voltage method (CATOLAC emulsion 543.052, produced by Industrie Vernici Italiane under a Pittsburg Paint and Glass (PPG) licence). 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. After coating for 3 min, the coatings were rinsed with distilled water and cured for 30 min. The measured thickness of the coatings was 22±1 μm.

Electrochemical impedance spectroscopy (EIS)

For AC impedance measurements the coated samples were exposed to 3 % NaCl in distilled water for 48 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). AC 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 analyzed using a suitable fitting procedure.¹¹

Determination of the rate of the H₂ evolution reaction

The rate of the hydrogen evolution reaction in the polymer solution on steel and Zn–Ni surfaces was determined on Pt rotating disc electrode using a slow sweep voltammetry (rotation of 2000 rpm, sweep rate 0.5 mV s⁻¹). The working electrode used in this experiment was a Pt rotating disc electrode. The Pt disc surface was prepared the same way as in the ALSV experiments. The counter electrode was a Pt spiral wire and the reference electrode was SCE.

Gravimetric liquid sorption measurements

Gravimetric liquid sorption measurements were performed by weighing samples on an analytical balance following immersion in 3 % NaCl at 25 °C. The samples were periodically removed from the electrolyte and weighed. Sorption curves were used to evaluate the diffusion coefficient of water across the epoxy coatings.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Perkin-Elmer TGS-2 instrument. The experiments were performed in a dynamic nitrogen atmosphere (30 cm³ min⁻¹) at a heating rate of 10 °C min⁻¹ over the temperature range of 23–600 °C. The thermal stability of the epoxy coatings were determined from the TG data.

RESULTS AND DISCUSSION

Alloy characterization

It is well known that the deposition of a Zn–Ni alloy is anomalous from most baths^{12,13} and due to this fact it is possible to deposit Zn rich alloys, where the γ or δ phase prevail. The results of chemical analysis showed that the Ni content was almost the same for all the investigated Zn–Ni alloys. The overall alloy composition determined by atomic absorption was 13 wt. % Ni for the alloys deposited by direct current (Zn₈₇Ni₁₃), whereas the alloys deposited by pulse current had 12 wt. % Ni (Zn₈₈Ni₁₂).

Anodic linear sweep voltammetry (ALSV) was used in determining the phase structure of the Zn–Ni alloys.¹⁴ When an alloy film is anodically polarized under potentiodynamic conditions, the components dissolve at various potentials, depending on their equilibrium and kinetic properties. The various phase structures and chemical forms present in the alloy produce various current peaks. Therefore, an obtained peak is a characteristic of the alloy components and the phase structure of the deposit. All the ALSV traces, obtained in Na₂SO₄ + EDTA solution, for the Zn–Ni alloys deposited by direct current (Fig. 1) and for the Zn–Ni alloy deposited by pulse current (Fig. 2) consisted of two current peaks, I and II, which were assumed to be the δ -phase or Ni₃Zn₂₂ (peak I) and the γ -phase or Ni₅Zn₂₁ (peak II). There was also an increase of the relative amount of electricity under the peaks for the alloys deposited by DC (Fig. 2), which is the result of the higher current efficiency in direct plating.

The phase structures present in the Zn–Ni alloys were identified on the basis of the chemical composition of alloys, X-ray diffractograms (XRD) and equilibrium phase diagram of the binary Zn–Ni system.^{15,16} The X-ray diffractograms recorded for the Zn–Ni alloys deposited by direct and pulse current indicate¹⁶ the presence of the γ -phase, or Ni₅Zn₂₁, with different crystallographic orientations: (411, 330), (422) and (442, 600) and the Zn rich δ -phase or Ni₃Zn₂₂. It can be concluded that the deposition current density has little effect on the alloy phase structure (Fig. 1).

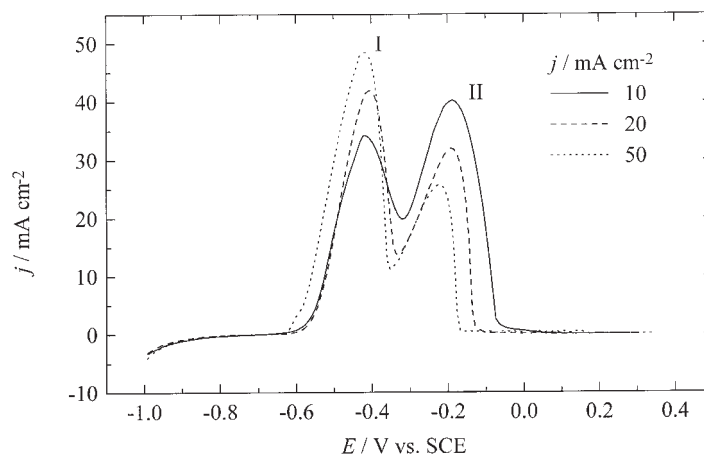


Fig. 1. ALSV voltammograms in a $\text{Na}_2\text{SO}_4 + \text{EDTA}$ solution of the dissolution of Zn–Ni (DC) alloys, deposited at different current densities; $\omega = 2000 \text{ rpm}$, $\nu = 1 \text{ mV s}^{-1}$.

In order to investigate the corrosion resistance of the Zn–Ni (DC) alloys, the open circuit potential (E_{Opc}) was measured daily.¹⁶ It was found that the Zn–Ni alloy deposited at a current density of 20 mA cm^{-2} exhibited the best corrosion resistance. Due to this fact, this alloy and the one deposited by pulse current of the same average current density ($j_{\text{av}} = 20 \text{ mA cm}^{-2}$) were used for modification of the steel surface. The electrochemical and transport properties, as well as thermal stability of the epoxy coating electrodeposited on steel modified by Zn–Ni (DC) and Zn–Ni (PC) alloys were investigated during exposure to 3 % NaCl.

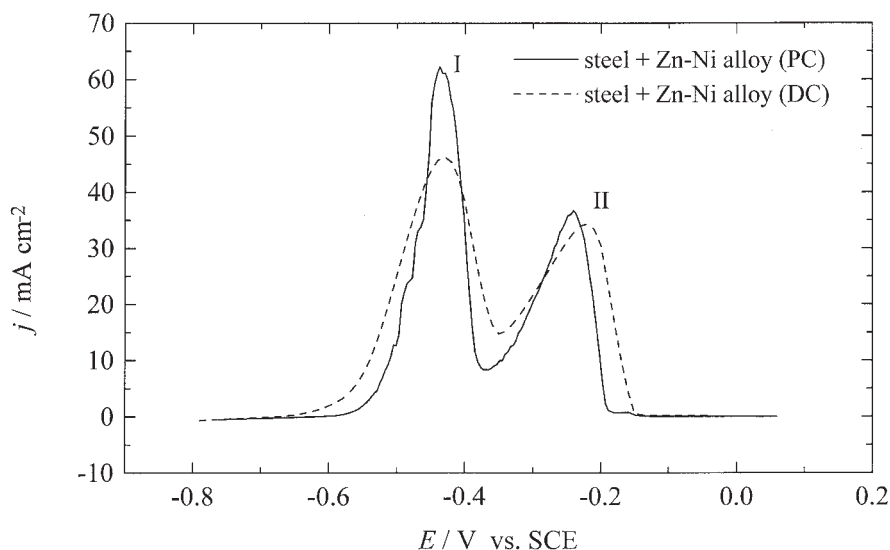


Fig. 2. ALSV voltammograms in a $\text{Na}_2\text{SO}_4 + \text{EDTA}$ solution of the dissolution of Zn–Ni alloys, deposited by a pulse and direct current of 20 mA cm^{-2} ; $\omega = 2000 \text{ rpm}$, $\nu = 1 \text{ mV s}^{-1}$.

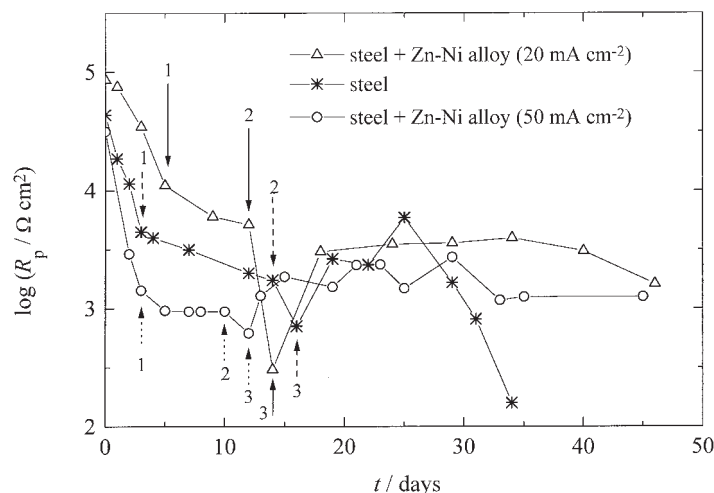


Fig. 3. The time dependence of the pore resistance for epoxy coatings on steel and steel modified by Zn–Ni (DC) alloys deposited at different current densities, during exposure to 3 % NaCl.

Electrochemical properties of the epoxy coatings

The pore resistance, R_p , was determined from the impedance plots in the complex plane for the epoxy coatings electrodeposited on steel and steel modified by Zn–Ni alloys. The fitting of the experimental data was accomplished using the fitting procedure elaborated by Boukamp.¹¹ The pore resistance is plotted as a function of time in Fig. 3, for epoxy coatings on steel and steel modified by Zn–Ni (DC) alloys deposited using different current densities.

Initially, during the first few days for all coatings, the pore resistance decreases over time (Fig. 3, period up to point 1) denoting the entry of the electrolyte into the epoxy coating.^{17–19} This is the first step of electrolyte penetration through an organic coating 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.²⁰ After this period, the values of the pore resistance reach a plateau and remain almost constant over a longer period of time (Fig. 3, period 1 – 2) indicating the maintenance of good protective properties of the epoxy coating.²¹ This is the second step of electrolyte penetration and it refers to the 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.²⁰ This leads to the beginning of electrochemical processes on the metallic interface and, as a consequence, to the loss of adhesion. This detachment of the coating is characterized by a decrease of the pore resistance (Fig. 3, point 3).

During this time interval, the epoxy coating on the Zn–Ni (DC) alloy electrodeposited using a current density of 20 mA cm^{-2} has larger values of R_p than epoxy coating on steel and the Zn–Ni (DC) alloy electrodeposited using a current density of 50 mA cm^{-2} . This means that the Zn–Ni alloy deposited using a current density of 20 mA cm^{-2} exhibits better protective properties and was used for further investigations.

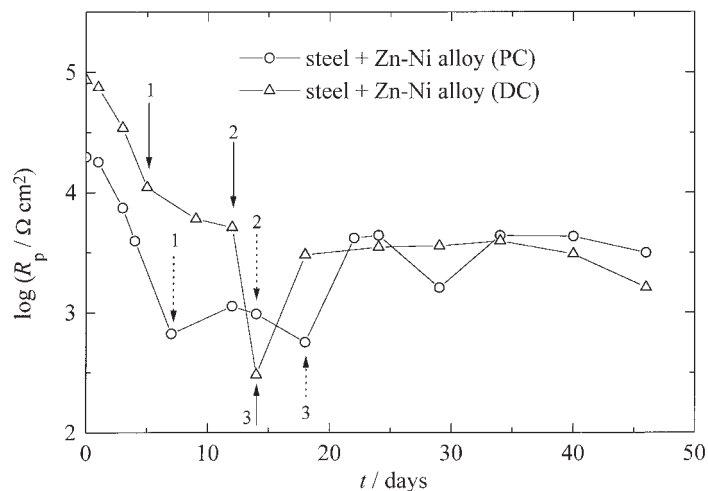


Fig. 4. The time dependence of the pore resistance for epoxy coatings on steel modified by Zn–Ni alloys, deposited by pulse and direct current of 20 mA cm^{-2} , during exposure to 3 % NaCl.

Comparing the values of the pore resistance of an epoxy coating on a Zn–Ni alloy (DC) with that on a Zn–Ni (PC) alloy deposited using the same current density (20 mA cm^{-2}), the value of the R_p for the epoxy coating on the Zn–Ni (DC) alloy was larger (Fig. 4, period up to point 2) but the beginning of the epoxy coating detachment (Fig. 4, point 3) occurs later in the case of the epoxy coating on an Zn–Ni (PC) alloy. Direct current plating produces deposits with a higher surface roughness than those produced by pulse plating⁹ and the longer corrosion protection by an epoxy coating on a Zn–Ni (PC) alloy can be explained by a better adhesion to the smoother surface.²² Both the investigated Zn–Ni alloys had almost the same chemical composition and phase structure, so the adhesion differences arise from the different surface topography.

The profound influence of the surface modification is expressed during prolonged exposure to 3 % NaCl (Figs. 3 and 4). The period of increase and then decrease of the pore resistance for an epoxy coating on steel (Fig. 3, period after point 3) can be explained by the plugging of the pores with corrosion products on steel during the extended time of exposure, followed by subsequent dissolution or desorption of the corrosion products.¹⁹ On the other hand, the almost unchanged values of the pore resistance for epoxy coatings on Zn–Ni alloys during long exposure time (Figs. 3 and 4 period after point 3) indicate the great stability of these protective system due to the existence of a passive layer on Zn–Ni alloys. Namely, it is well known that the corrosion products on Zn and Zn–Ni alloys usually consist of two layers: an inner oxide phase layer²³ and an outer layer consisting of basic salts, mainly $\text{ZnCl}_2 \cdot 4\text{Zn(OH)}_2$.²⁴ So, the unchanged values of the pore resistance during prolonged exposure times can be explained by the plugging of the epoxy coating pores with corrosion products. The obtained results demonstrate a decreased corrosion rate on a steel modified by Zn–Ni alloys and that the two layers of corrosion products form a good barrier to the transport of water, oxygen and electrolyte ions.

Transport properties of epoxy coatings

The influence of surface modification of steel on the sorption characteristics of epoxy coatings (first step of electrolyte penetration) was investigated by gravimetric liquid sorption experiments.²⁵ The reduced sorption curves (Fig. 5) are 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 times²⁶ is

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

where m_t is the amount of absorbed water at time t , m_∞ is the amount of absorbed water in equilibrium, D is 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 confirms the assumption that the sorption is controlled by Fickian diffusion. The diffusion coefficient of water through an epoxy coating on steel modified by Zn–Ni alloys was calculated from the slope of the initial linear region of the reduced sorption curve (Table I). The contact angle, ϕ , between a polymer solution and different substrates was determined by the drop test and the results are also given in Table I.

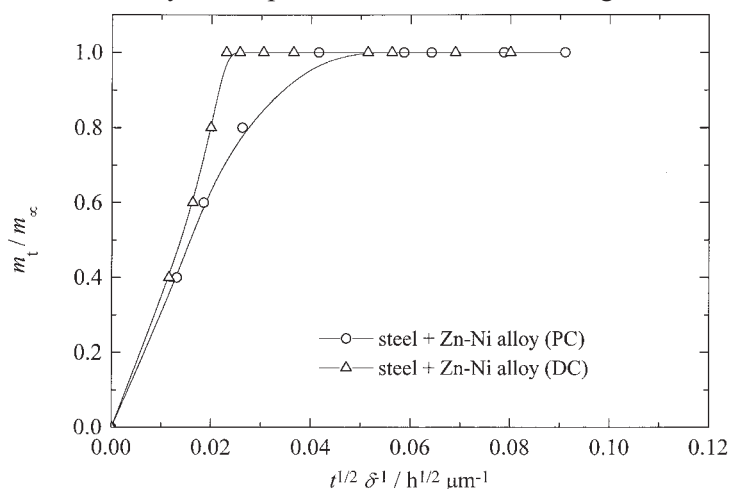


Fig. 5. The reduced sorption curves at 25 °C for epoxy coatings on steel modified by Zn–Ni alloys, deposited by a pulse and direct current of 20 mA cm⁻², during exposure to 3 % NaCl.

The smaller value of the diffusion coefficient of water for the epoxy coating on steel modified by the Zn–Ni (PC) alloy than for steel modified by the Zn–Ni (DC) alloy is the consequence of the less porous epoxy structure on steel modified by the Zn–Ni (PC) alloy.

The differences in $D(\text{H}_2\text{O})$ can be explained by the different rates of hydrogen evolution from Zn–Ni alloys during cathodic epoxy coating deposition, since hydrogen evolution by H_2O discharge is the first step in the deposition of an epoxy coating, as

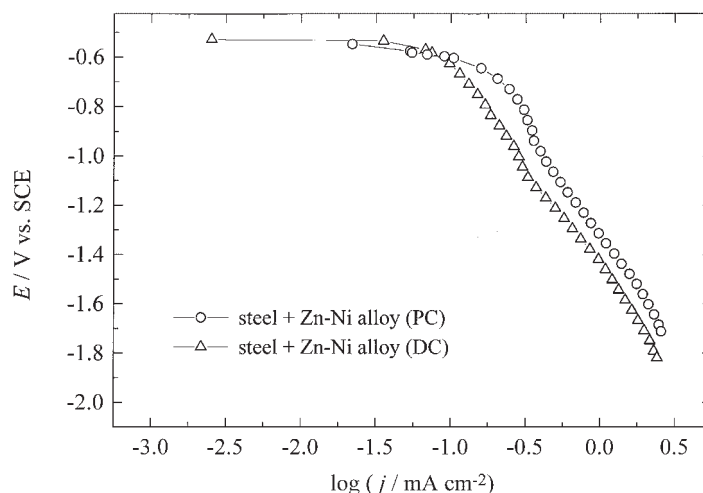


Fig. 6. Polarization curves for hydrogen evolution on steel modified by Zn–Ni alloys, deposited by a pulse and direct current of 20 mA cm^{-2} , in a polymer solution at 25°C , N_2 saturated, $\omega = 2000 \text{ rpm}$, $\nu = 0.5 \text{ mV s}^{-1}$.

well as by the different surface tension of the polymer solution on different substrates. The rate of hydrogen evolution from a polymer solution on both the Zn–Ni alloys is almost the same (Fig. 6) but the contact angle between the polymer solution and the Zn–Ni (DC) alloy is greater than the contact angle on Zn–Ni (PC) alloy (Table I). This indicates the better wettability of the Zn–Ni alloy obtained by PC than the Zn–Ni alloy obtained by DC deposition. The larger contact angle on the Zn–Ni (DC) alloy than on the Zn–Ni (PC) alloy, although the rate of H_2 evolution was the same, causes accumulation of H_2 on the cathode during electrodeposition of the epoxy film and, as a consequence, a more porous epoxy coating structure is formed on the Zn–Ni (DC) alloy. During further curing at 180°C during the formation of the epoxy film, H_2 goes out leaving more vacancies in the polymer network resulting in a more porous structure of the epoxy coating²⁷ on steel modified by the Zn–Ni (DC) alloy, *i.e.*, a larger $D(\text{H}_2\text{O})$, in respect to the same epoxy coating on steel modified by the Zn–Ni (PC) alloy.

TABLE I. The values of the diffusion coefficient of water at 25°C , $D(\text{H}_2\text{O})$, contact angle, ϕ , between a polymer solution and the investigated surfaces and the integral procedure decomposition temperature (*ipdt*) for epoxy coatings electrodeposited on steel modified by Zn–Ni alloys

Substrate	Steel + Zn–Ni (DC) alloy	Steel + Zn–Ni (PC) alloy
$D(\text{H}_2\text{O}) \times 10^{10} / \text{cm}^2\text{s}^{-1}$	7.2	5.6
$\phi / ^\circ$	35	27
<i>ipdt</i> / $^\circ\text{C}$	429	391

Thermal stability of epoxy coatings

The thermal stability is a description of the chemical stability of a polymer at high temperatures, since the chemical processes that occur at elevated temperatures result in

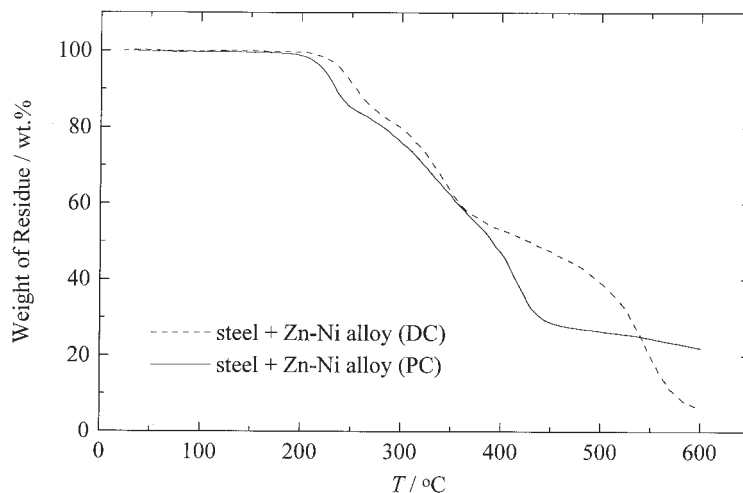


Fig. 7. TG curves for the determination of the thermal stability of epoxy coatings on steel modified by Zn–Ni alloys, deposited by a pulse and direct current of 20 mA cm^{-2} (heating rate $10 \text{ }^\circ\text{C min}^{-1}$).

the thermal degradation or crosslinking of high polymers. A qualitative characterization of the degradation process is, among other values, illustrated by the integral procedure decomposition temperature (*ipdt*), or the temperature corresponding to a 50 % weight loss, as an indication of the rate of thermal degradation.²⁸

The thermal stability of epoxy coatings electrodeposited on steel modified by Zn–Ni alloys deposited by DC and PC was investigated by thermogravimetry, TGA. The difference in the temperatures of degradation of epoxy coatings on steel modified by Zn–Ni alloys is shown in Fig. 7 and Table I. As can be seen, the *ipdt* value is greater for the epoxy coating on steel modified by the Zn–Ni (DC) alloy. The different thermal properties are a consequence of the accumulation of hydrogen during the electrodeposition of the epoxy coating, as described earlier. The smaller wettability of the polymer solution on the Zn–Ni (DC) alloy causes an accumulation of H_2 on the cathode, although the rate of hydrogen evolution for both Zn–Ni alloys is almost the same (Fig. 6). The greater amount of the accumulated hydrogen reacts with oxygen in the polymer chains causing an increased number of hydrogen bonds, and, consequently, an increase of *ipdt* value for the epoxy coating on the Zn–Ni (DC) alloy.

CONCLUSIONS

On the basis of all the experimental results, it can be concluded that modification of a steel surface by Zn–Ni alloys improves the corrosion stability of the protective system based on an epoxy coating in respect to an epoxy coating on steel. The deposition current density has a great influence on the corrosion resistance of Zn–Ni alloys. The best corrosion properties are obtained with a Zn–Ni alloy deposited by 20 mA cm^{-2} and this alloy was compared to a Zn–Ni alloy deposited by pulse current with the same average current density.

During the initial time of exposure to 3 % NaCl the epoxy coating on steel modified by Zn–Ni (PC) has smaller values of the pore resistance, but the beginning of the detachment of the coating occurs later. The difference in the electrochemical properties of epoxy coatings on Zn–Ni (DC) and (PC) alloys arises from the different adhesion of the epoxy coatings, as a consequence of the different surface roughness of the alloys obtained by DC and PC. Since the Zn–Ni (PC) alloy surface is smoother, the adhesion of the epoxy coating is better.

During prolonged exposure to 3 % NaCl almost unchanged values of R_p were observed for the epoxy coating on both Zn–Ni alloys. This indicates the great stability of these protective systems due to the formation of two passive layers of corrosion products, which are good barrier to the transport of water, oxygen and electrolyte ions.

The type of substrate also effects the sorption characteristics and thermal stability of the epoxy coating. The smaller value of $D(H_2O)$ for the epoxy coating on the Zn–Ni (PC) alloy could be explained by the less porous structure of the epoxy coating on this surface, which is caused by the better wettability of this alloy surface by the polymer solution, although the rate of hydrogen evolution during the deposition of the epoxy coating is the same on both the Zn–Ni alloys. As a result, a smaller quantity of H_2 is accumulated on the cathode and thus there are less hydrogen bonds in the epoxy coating on the Zn–Ni (PC) alloy; consequently the thermal stability is decreased. So, the epoxy coating on the Zn–Ni (PC) alloy exhibits better corrosion stability during the initial immersion time, while the epoxy coating on the Zn–Ni (DC) alloy exhibits improved thermal stability.

ИЗВОД

УТИЦАЈ Zn–Ni ПОДСЛОЈЕВА НА КОРОЗИОНО ПОНАШАЊЕ И ТЕРМИЧКУ СТАБИЛНОСТ ЕПОКСИДНИХ ЕЛЕКТРОФОРЕТСКИХ ПРЕВЛАКА НА ЧЕЛИКУ

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Проучаване су електрохемијске и транспортне карактеристике и термичка стабилност епоксидних електрофоретских превлака на челику и челику модификованом Zn–Ni легурама током деловања 3 % раствора NaCl. Легуре Zn–Ni су таложене на челику константном и пулсирајућом струјом. На основу временске зависности отпорности у порам епоксидне превлаке (импедансна мерења), коефицијента дифузије воде кроз епоксидну превлаку (гравиметријско одређивање сорпционих карактеристика) и њене термичке стабилности (термогравиметријска анализа), показано је да Zn–Ni подслојеви значајно повећавају корозиону стабилност заштитног система на бази епоксидне превлаке. Скоро непромењене вредности отпорности у порам током дугог периода деловања корозионог агенса код епоксидних превлака на челику модификованом Zn–Ni легурама указују на велику стабилност ових заштитних система.

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