

Adhesion of epoxy cataphoretic coatings on Zn alloys

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Abstract: One of the most important factors in corrosion prevention by protective coatings is the loss of coating adhesion under environmental influence. In this work, the adhesion of epoxy cataphoretic coatings was examined on steel and steel modified by Zn–Fe and Zn–Co alloys. The dry and wet adhesions of epoxy primers were measured by the direct pull-off standardized procedure, as well as indirectly by the NMP test. The corrosion stability of the coated samples was investigated by electrochemical impedance spectroscopy. It was shown that under dry testing conditions all the samples exhibited very good adhesion. However, different trends of adhesion loss of different protective systems during exposure to a corrosive agent (3 % NaCl solution) were observed. The lowest adhesion values were obtained for epoxy coating on the steel substrate. The change in adhesion of the epoxy coating on steel modified by Zn–Co alloy during immersion in 3 % NaCl solution for 24 days was the smallest of all the investigated samples. Electrochemical impedance measurements in 3 % NaCl solution confirmed the good protective properties of this protective system, *i.e.*, greater values of pore resistance were obtained.

Keywords: adhesion, Zn–Fe alloy, Zn–Co alloy, epoxy coating, electrochemical impedance spectroscopy.

INTRODUCTION

The most important properties of a protective coating are the anticorrosive action and the adhesion to the substrate.^{1–4} Thus, the determination of adhesion is often used when characterizing protective properties of organic coatings on a metal substrate. In principle, paint adhesion can be improved by providing a substrate with a pre-treatment layer, followed by the application of a corrosion-inhibiting primer and a topcoat paint. One of the frequently used steel pre-treatments is electrochemical deposition of Zn alloys,^{5–8} especially in the automotive industry, because of the increased requirements for coatings with longer service life, as well as being good replacements of toxic cadmium coatings.⁹

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In this work, different methods were used to determine if and to what extent the adhesion of epoxy coatings depends on the modification of a steel substrate with zinc alloys. In addition, the results of the various methods (pull-off test, NMP test and EIS) were compared to determine whether they showed the same tendency.

EXPERIMENTAL

Electrodeposition of Zn alloys

The steel panels (40 mm×40 mm×0.25 mm employed for the adhesion pull-off measurements and 14 mm×14 mm×0.25 mm for the NMP test) were pretreated by mechanical cleaning (polishing successively with emery papers of the following grades: 280, 360, 800 and 1000) and then degreased in a saturated solution of sodium hydroxide in ethanol, pickled with a 1:1 hydrochloric acid solution for 30 s and finally rinsed with distilled water.

Zn-Fe Alloys were deposited galvanostatically at 4.0 A dm⁻² on a steel panel at 25 °C from an alkaline bath: 0.09 mol dm⁻³ ZnSO₄, 0.01 mol dm⁻³ FeSO₄, 0.01 mol dm⁻³ ascorbic acid, ≈ 0.2 mol dm⁻³ triethanolamine, 30 g dm⁻³ Na₂SO₄ and 80 g dm⁻³ NaOH (pH ≈ 14).¹⁰ Zn-Co Alloys were deposited galvanostatically at 5.0 A dm⁻² on a steel panel from a chloride bath¹¹ at 25 °C: 80 g dm⁻³ ZnCl₂, 16 g dm⁻³ CoCl₂·6H₂O, 25 g dm⁻³ H₃BO₃ and 210 g dm⁻³ KCl.

The employed electrolytes were prepared using p.a. chemicals (Merck, Aldrich, and Fluka) and double distilled water. The thickness of the Zn alloys was 10 μm.

Surface roughness

The surface roughness of the steel surface, Zn-Fe and Zn-Co alloys, as substrates for the deposition of an epoxy coating, was determined by a TR-200 handheld roughness tester.

Electrodeposition of epoxy coatings

Epoxy (pigmented) coatings were electrodeposited from an epoxy resin emulsion modified by amine and isocyanate on steel and a steel surface previously modified by Zn-Fe and Zn-Co alloy, using the constant voltage method (CATOLAC emulsion 543.052, produced by PPG). The resin concentration in the electrodeposition bath was a 10 wt. % solid dispersion in water at pH 5.7; the temperature was 26 °C and the applied voltage was 250 V.¹² After coating for 3 min, the coatings were rinsed with distilled water and cured at 180 °C for 30 min. The film thickness, determined by a Fischer Dualscope-Mpor, was 17±1 μm.

Adhesion measurements

The adhesion strength of the epoxy coatings on the metal substrates was determined by two methods: by the direct pull-off standardized procedure and by determining the NMPRT (*N*-methylpyrrolidone retention time).

Pull-off test

The adhesion strength of the epoxy coatings on steel and steel modified by Zn-Fe and Zn-Co alloys was determined by an Erichsen Adhesionmaster 513 MC/525 MC. The adhesion measurements were performed prior to exposure to 3 % NaCl solution ("dry" adhesion), as well as at certain time intervals during exposure to a 3 % NaCl solution at room temperature for a period of 24 days ("wet" adhesion).

For each type of protective system, five samples were tested and the average value of these measurements was taken. For all measurements only the ones with adhesive failure were taken into account.

NMP Test

The employed *N*-methylpyrrolidone (NMP) was of p.a. purity. In the NMP delamination test¹³ panels of 2 cm² area were immersed in NMP at 60 °C. The paint always delaminated from the edges inwards. The time when the paint had completely delaminated was recorded. The experiment

was performed five times per panel and the average value was calculated as the NMPRT (NMP retention time, or the time for the paint film to delaminate completely from the substrate) for a particular primer–metal combination. Each panel was always treated in a fresh solvent.

Electrochemical impedance spectroscopy (EIS)

For the a.c. impedance measurements, the coated samples were exposed to 3 % NaCl in distilled water for 24 days. A three-electrode cell arrangement was employed for 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 performed over a frequency range of 100 kHz to 10 mHz using a 5 mV amplitude sinusoidal voltage. The impedance spectra were analyzed using a suitable fitting procedure.¹⁴

RESULTS AND DISCUSSION

Adhesion measurements

Adhesion is based on the chemical and physical forces between the top side of the metal substrate and the under side of the paint which covers the metal surface. To understand more about the forces between these two phases, *i.e.*, the metal substrate and the paint film, these forces should be measured. Two different adhesion tests were applied in order to gain some insight as to what kind of substrate would provide the best adhesion and for a more fundamental reason, to show how a surface roughness along with the surface wettability affect the adhesion as well as the corrosion resistance of protective systems.

NMP Test

NMP is a highly polar solvent and it is capable of forming strong hydrogen bonds, allowing it to rapidly diffuse into organic coating and causing extensive swelling.¹³ Due to the swelling, shear stresses are imposed at the metal/coating interface. These shear stresses are, in most cases, relaxed by delamination of the coating. Thus longer the time until delamination, the better is the adhesion. The time for the paint film to delaminate completely and intact from the substrate, defined as NMP retention time (NMPRT), was recorded.

NMP Adhesion tests were performed initially before exposure to 3 % NaCl, *i.e.*, on the dry films, and the results are presented in Table I.

The highest NMP retention time (NMPRT) was obtained for the epoxy coating on steel modified by Zn–Co alloy. For epoxy coating on steel modified by Zn–Fe alloy, the delamination time was slightly shorter. These results point to higher initial adhesions of the epoxy coating on steel modified by Zn alloys as compared to the bare steel substrate.

Pull-off measurements

Wet adhesion, or the adhesion of a coating which is exposed to moisture, water or a corrosive agent, is very important because in the presence of moisture

the conditions can be simulated which occur in practical conditions.⁴ For this reason, it is important to also know the adhesion strengths of protective systems which are exposed to a corrosive media.

TABLE I. NMPRT Values for epoxy coatings on steel and steel modified by Zn-Fe and Zn-Co alloys before exposure to 3 % NaCl

| Substrate | NMPRT / min |
|---------------------|-------------|
| Steel | 3.0 |
| Steel + Zn-Fe alloy | 4.7 |
| Steel + Zn-Co alloy | 6.3 |

The pull-off results of the change of adhesion strength with time of immersion in NaCl solution for epoxy coatings on different substrates are shown in Fig. 1.

A general trend of decreasing adhesion strength with increasing exposure time was observed for all samples. The best performance was obtained for the epoxy coatings on steel modified by Zn-Co alloy, throughout the whole investigated time. The lowest values for both dry and wet adhesion were obtained for the epoxy coating on the steel substrate. Initially, during the first few days, the values of the adhesion strengths for epoxy coating on steel modified by Zn-Fe and Zn-Co alloy were very similar. However, after about 7 days, the adhesion strength of the epoxy coating on steel modified by Zn-Fe alloy drops sharply, whereas that of the epoxy coating on steel modified by Zn-Co alloy decreases only slowly, indicating a more stable protective system during exposure to a corrosive agent.

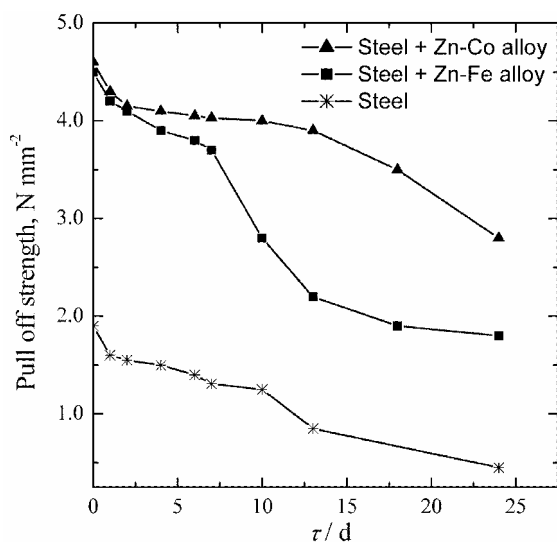


Fig. 1. The pull-off strength for epoxy coatings on steel and steel modified by Zn-Co and Zn-Fe alloys during exposure to 3 % NaCl solution.

The reductions of adhesion after one day of exposure to the corrosive agent and after the whole investigated time period are shown in Table II. Of all the protective systems investigated in this work, the smallest reduction of adhesion

was obtained for the epoxy coating on steel modified by Zn–Co alloy. After one day of exposure, the reduction of adhesion was very similar for epoxy coatings on both Zn alloys, but after 24 days of exposure to 3 % NaCl, the reduction of adhesion for epoxy coating on Zn–Co alloy was significantly lower (40 %) as compared to Zn–Fe alloy (60 %).

TABLE II. Dry and wet adhesion (in N mm^{-2}) and percentage of adhesion reduction after one day and 24 days of exposure to 3 % NaCl

| | | Substrate | | |
|--------------------|---------|-----------|---------------------|---------------------|
| | | Steel | Steel + Zn–Fe alloy | Steel + Zn–Co alloy |
| Dry adhesion | | 1.9 | 4.5 | 4.6 |
| Wet adhesion | one day | 1.6 | 4.2 | 4.3 |
| | 24 days | 0.45 | 1.8 | 2.8 |
| Adhesion reduction | one day | 15.8 | 6.7 | 6.5 |
| | 24 days | 76.3 | 60 | 40 |

The obtained initial values of adhesion strength (dry adhesion, Table II) compare very well with the results obtained using the NMP test (Table I), where it was also shown that the lowest adhesion was obtained for the epoxy coating on the steel substrate.

Surface roughness and wettability

Theoretically, for optimal adhesion, it would be important for the polymer solution to fully penetrate into the pores of the surface layer. Penetration of the polymer solution into the pores on a rough surface, *i.e.*, surface wettability by the polymer solution, depends on the contact angle and the shape of the pores. If these are favorable, which means greater surface roughness and smaller contact angle, *i.e.*, better wettability, a significant penetration may occur at equilibrium.

The values of surface roughness, R_a , on the steel substrate and the steel modified by electrochemically deposited Zn–Co and Zn–Fe alloys are given in Table III. Contact angle, ϕ , between the polymer solution and the different substrates was determined by the drop test and the results are also given in Table III.

TABLE III. The values of surface roughness, R_a , and contact angle, ϕ , for epoxy coatings on steel and steel modified by Zn–Co and Zn–Fe alloys

| | Substrate | | |
|---------------------|-----------|---------------------|---------------------|
| | Steel | Steel + Zn–Fe alloy | Steel + Zn–Co alloy |
| $R_a / \mu\text{m}$ | 0.250 | 1.77 | 0.913 |
| $\phi / ^\circ$ | 45 | 10 | Complete |

The high value of surface roughness for the steel modified by Zn–Co alloy and the complete wettability by the epoxy emulsion could explain the good initial adhesion of this protective system. On the other hand, the large contact angle on

the steel surface, indicating the poor wettability of this substrate, together with the smallest surface roughness result in poor bonding of the epoxy emulsion with the steel surface and, as a consequence, the smallest adhesion was obtained for this protective system (Tables I and II, Fig. 1). A higher value of R_a but also a larger φ , results in almost the same value of dry adhesion (Table II).

The better adhesion of the epoxy coating on steel modified by Zn alloys compared to the same epoxy coating on steel can be explained as follows. Namely, it is well known the metal surfaces are generally covered with oxides and contain some hydrated polar groups, which is favorable in respect to bonding to an organic coating. In order to wet the surface and bond to the metallic substrate, polar primers require an oxide layer. It is well known that hot-dip galvanized steel, *i.e.*, Zn coatings, and Zn alloy coatings form zinc oxide and zinc hydroxide on their surfaces immediately after galvanizing. The results shown in Fig. 1 and Tables I and II indicate that bonds between the epoxy coating used in this work and zinc oxide and/or zinc hydroxide are stronger than the ones formed with iron oxides, which normally cover a steel surface.

Electrochemical properties

The Nyquist plots for the impedance of the epoxy coatings electrodeposited on steel and steel modified by Zn–Co and Zn–Fe alloys on the first day (after 2 hours) and after 8 days of exposure to 3 % NaCl are shown in Figs. 2 and 3, respectively. It can be seen from Figs. 2 and 3 that the epoxy coating on steel modified by Zn–Co alloy has larger values of the pore resistance than the epoxy coating on steel and steel modified by Zn–Fe alloy.

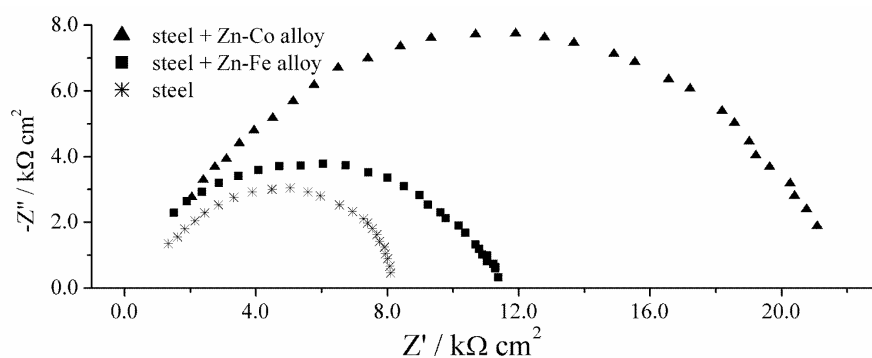


Fig. 2. Nyquist plots for epoxy coatings on steel and steel modified by Zn–Co and Zn–Fe alloys, on the first day of exposure to 3 % NaCl.

A general equivalent electrical circuit model for the behavior of polymer-coated metal in corrosive environments was used (Fig. 4),^{15,16} where R_{Ω} is the electrolyte resistance, R_p is the coating pore resistance, C_c is the coating capacitance, R_{ct} is the charge transfer resistance and CPE is a constant phase element,

which represents all the frequency-dependent electrochemical phenomena, namely the double-layer capacitance and diffusion processes. The fitting of experimental data obtained using the procedure elaborated by Boukamp¹⁴ enabled the determination of the pore resistance, R_p for the films formed on steel and steel modified by Zn alloys. The values of pore resistance for different protective systems, as a function of time of exposure to 3 % NaCl, are given in Table IV.

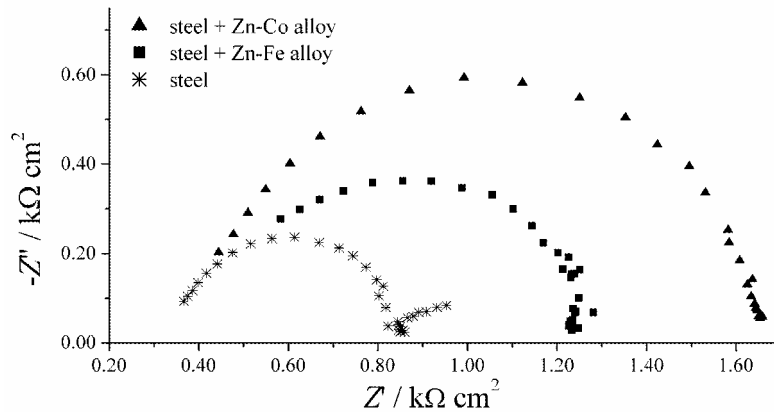


Fig. 3. Nyquist plots for epoxy coatings on steel and steel modified by Zn-Co and Zn-Fe alloys, after 8 days of exposure to 3 % NaCl.

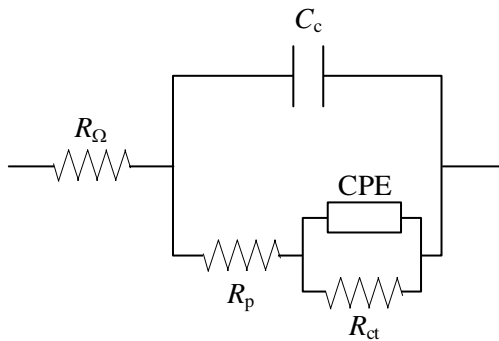


Fig. 4. Equivalent electrical circuit of a polymer-coated metal.

It can be seen that the values of the pore resistance for the epoxy coating on steel modified by Zn-Co alloy are larger compared to the epoxy coating on steel and steel modified by Zn-Fe alloy, indicating again the good corrosion stability of this protective system. This result is in good agreement with the adhesion measurements (Fig. 1, Tables I and II), where it was shown that this protective system had the highest adhesion values.

The smaller values of the pore resistance for the epoxy coating on Zn-Fe alloy as compared to the epoxy coating on Zn-Co alloy can be explained by local heating of the Zn-Fe cathode during the deposition of the epoxy coating, which could cause cratering of the epoxy coating. Namely, it is well known that a zinc

and zinc alloy-plated cathode attain higher temperatures during deposition as compared to a steel cathode, with a tendency for some erratic temperature variation, caused by local film ruptures (cratering).¹⁷ Such a local heating of the cathode during the deposition process causes the formation of different structure of electrodeposited epoxy coating on zinc and zinc alloy-plated cathode as compared to the steel substrate, where local heating is significantly lower.^{17,18} The results of Schoff^{19,20} indicate that there is a greater tendency to crater over Zn–Fe alloy than over galvanized steel, Zn–Ni alloy and steel.

TABLE IV. The values of pore resistance, R_p , for epoxy coatings on steel and steel modified by Zn–Fe and Zn–Co alloy, during exposure to 3 % NaCl

| Substrate | $R_p / \Omega \text{ cm}^2$ | | |
|---------------------|-----------------------------|--------------|---------------|
| | 1 st day | After 8 days | After 24 days |
| Steel | 4365 | 316 | 250 |
| Steel + Zn–Fe alloy | 7586 | 562 | 282 |
| Steel + Zn–Co alloy | 13183 | 891 | 350 |

Another reason for the smaller values of the pore resistance for the epoxy coating on Zn–Fe alloy is blistering, since in the case of organic coatings on Zn–Fe alloys the presence of blisters is possible.²¹ In the case of the investigated epoxy coating on Zn–Fe alloy, blisters were visible after about one week of exposure to 3 % NaCl. It was shown that the corrosion products in the protective system Zn–Fe alloy/organic coating consist of Fe_3O_4 ,²¹ which probably lift the organic coating from the substrate and cause blister formation underneath. The more porous an organic coating is, the more easily will an electrolyte penetrate it, thus reaching the metal substrate below, *i.e.*, Zn–Fe alloy. Consequently, corrosion process will occur sooner and adhesion of the epoxy coating to the alloy substrate will be weakened. For this reason, a sharp decrease in the adhesion of the epoxy coating on Zn–Fe alloy occurs after 7 days of exposure to 3 % NaCl solution (Fig. 1).

The third reason of increased corrosion stability of epoxy coating on steel modified by Zn–Co alloy as compared to epoxy coating on steel modified by Zn–Fe alloy is the greater corrosion stability of Co as compared to Fe. Namely, the corrosion rate of pure Co in sea water is ten times slower than corrosion rate of pure Fe under the same conditions.²² Since the amount of both Co and Fe in the alloys was ≈ 1.2 wt. %, ²³ the amount of Co and Fe in the alloy is not the determining factor of the corrosion stability of an alloy, but rather the stability of the element itself.

All these results indicate a greater corrosion stability of the protective system based on the epoxy coating on steel modified by Zn–Co alloy.

CONCLUSIONS

Using EIS, pull-off adhesion measurements and the NMP test, the corrosion stability of an epoxy coating on steel and steel modified by electrodeposited Zn–Co

and Zn–Fe alloys were monitored during exposure to 3 % NaCl. It was shown that the substrate has a large influence on the corrosion resistance and adhesion strength of the protective systems based on an epoxy coating. The increased adhesion strength and higher values of the pore resistance for the epoxy coating on steel modified by Zn–Co alloy compared to the epoxy coating on steel and steel modified by Zn–Fe alloy indicate its higher corrosion stability.

The Zn–Co deposit on steel increased both the dry and wet adhesion strength of the epoxy coating. The overall increase in wet adhesion for this sample was maintained throughout the whole investigated time period.

The EIS results correlate well with the adhesion values obtained with both the pull-off and NMP test. The largest values of pore resistance were obtained for the epoxy coating on steel modified by Zn–Co alloy, then for the epoxy coating on steel modified by Zn–Fe alloy and the lowest values for the epoxy coating on steel. The adhesion strength decreased in the same manner.

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ИЗВОД

АДХЕЗИЈА ЕПОКСИДНИХ КАТАФОРЕТСКИХ ПРЕВЛАКА НА ЛЕГУРАМА ЦИНКА

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Један од најважнијих фактора у заштити од корозије органским превлакама је губитак адхезије органских превлака под утицајем корозионе средине. У овом раду проучавана је адхезија епоксидних катафоретских превлака на челику и челику модификованом легурама Zn–Fe и Zn–Co. Испитиване су тзв. сува и мокра адхезија стандардним pull-off поступком, као и NMP тестом. Корозиона стабилност свих узорака је испитивана спектроскопијом електрохемијске импеданције. Сви узорци су имали добру почетну адхезију, међутим током деловања корозионог агенса (3 % NaCl) промена адхезије се значајно разликовала код различитих заштитних система. Најмање вредности адхезије су добијене у случају епоксидне превлаке на челику. Укупно смањење адхезије током 24 дана испитивања је најмање за епоксидну превлаку на челику модификованом Zn–Co легуром. Највеће вредности отпорности у порам епоксидне превлаке током целокупног испитиваног периода деловања корозионог агенса код превлаке на челику модификованом Zn–Co легуром такође указују на велику стабилност овог заштитног система.

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