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The corrosion performance and adhesion properties of the epoxy coating applied on the steel substrates treated by cerium-based conversion coatings

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ABSTRACT

The surface morphology and composition of the cerium-based conversion coatings (Ce) were studied for the St-37 steel substrate which was post-treated in an ambient temperature zinc phosphate chemical treatment bath (Ce–Zn). Then, the epoxy/polyamide coating was applied on the substrates treated with Ce, Zn and Ce–Zn chemical treatments. The surface characterization and electrochemical investigations were made by scanning electron microscope (SEM), energy dispersive X-ray photoelectron spectroscopy (XPS), contact angle measuring device, pull-off test and electrochemical impedance spectroscopy (EIS). Results revealed that the epoxy coating applied on the Ce–Zn treated sample showed the highest adhesion and corrosion protection properties.

1. Introduction

Epoxy coating has been widely used on the steel substrates in order to protect them against corrosive environments. Due to the high cross-linking density of this coating, it plays as a physical barrier between the metal surface and the corrosive environment [1–3]. However, this coating is osmotic to corrosive species like oxygen, water and ions. Diffusion of such components into the epoxy coating results in the coating degradation at long exposure times. The hydroxyl ions (OH^-) create at the cathode sits beneath the coating resulting in the increase of pH. This may result in the decrease of coating adhesion, and thus accelerating corrosion of the metal beneath the coating [4–7]. These mean that the coating adhesion to the steel substrate plays as an important role on its corrosion protection properties. Therefore, attempts have been made to find methods for improving the epoxy coating adhesion properties on the steel surface. In this regard, many different types of conversion coatings have been utilized. Conversion coatings can improve the epoxy coating adhesion to the steel substrate through the surface energy enhancement and/or changing the surface morphology [8,9]. Among different kinds of conversion coatings, the chromate based conversion coatings are commonly used to increase the corrosion resistance of the steel substrate and to improve the adhesion of the subsequent organic coatings. However, the chromate conversion coatings contain toxic and carcinogenic hexavalent chromium (Cr^{6+}). As a result, recent regulations have increased the restrictions on the use and handling of chromates as chemical treatment for the steel structures [10–12]. Trivalent chromium (Cr^{3+}) based conversion coatings have been also introduced as less toxic substitute for the hexavalent chromium based conversion coating. However, it has been shown that the Cr(III) based conversion coating cannot provide acceptable corrosion resistance and good adhesion of the organic coating to the steel surface like Cr(VI) [13,14]. To solve these problems, the most environmentally acceptable non-chromate corrosion resistant conversion coatings i.e. phosphate [15–19], molybdate [20], zirconium [21] and rare earth metal salts conversion coatings [22–25] are employed. Among these conversion coatings, the phosphate conversion coating has been widely used to modify the corrosion resistance of the metal substrate and to enhance the adhesion of the organic coating to the steel substrate. It has been shown that the surface treatment of the steel sample by the zinc phosphate resulted in the increase of the epoxy coating adhesion to the steel and the increase of corrosion resistance of the coating significantly [26,27]. Cerium conversion (Ce) coating is one of the most promising environmentally friendly chemical treatments to modify the metal surface properties [28–31]. However, the Ce coating did not show high corrosion resistance due to the cracks and pores presented in its structure. Attempts have been carried out to

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enhance the corrosion resistance and adhesion properties of the organic coating by different methods.

This study aims at studying the corrosion resistance of the Ce conversion films on the steel substrate without and with zinc phosphate post-treatment. The surface morphology, composition and surface energy of the Ce, Zn and Ce–Zn treated substrates were investigated by SEM, XPS and contact angle measuring device. The epoxy coating was applied on the steel surface treated by conversion coatings. The adhesion and corrosion protection properties of the epoxy coating were also studied by pull-off test and EIS.

2. Experimental

2.1. Materials

The chemical treatment baths were prepared using hydrochloric acid (37 wt.%), sodium hydroxide, cerium nitrate, phosphoric acid (85 wt.%), zinc oxide and sodium nitrite (Merck Co.). Epoxy resin (Araldite G27 7071X75) and polyamide curing agent were prepared from Saman Co. St-37 type steel specimens were prepared from Foolad Mobarakeh Co. The composition of the steel panels is given in Table 1.

2.2. Surface treatment procedure

The cerium and zinc phosphate chemical treatment baths were prepared. The composition of each bath is depicted in Table 2. The steel sheets were abraded by emery paper 800 followed by degreasing using acetone. Then, the cleaned steel sheets immersed in 100 cc of Ce chemical treatment bath. The surface treatment was done at pH = 2.5, T = 25 °C and t = 10 min. Then, the Ce treated samples were rinsed by distilled water. In the next step, the Ce treated samples were dipped in the zinc phosphate chemical treatment bath. The composition of the zinc phosphate chemical treatment bath is given in Table 2. The post-treatment was done at pH = 3.1, T = 25 °C and t = 30 min [9].

2.3. Epoxy coating application

The epoxy coating formulation was prepared using epoxy resin based on bisphenol-A and polyamide curing agent. The solid content, epoxy value and density of the resin were 74–76%, 0.14–0.16 equivalent per 100 g and 1.08 g cm^{-3}, respectively. 100 g of the epoxy resin was mixed with 42 g polyamide curing agent. Additives including 0.2 wt.% antifoamer (Efka-2025) and 0.5 wt.% leveling agents (BYK-306) were added to the epoxy coating formulation in order to enhance the coating film formation properties. A mixture of Xylene (30 g) and butyl acetate (10 g) solvents was also added to the epoxy coating formulation to obtain appropriate viscosity. The coatings were applied on the steel sheets with and without conversion coating by a film applicator. The wet thickness of the coatings was 120 μm. Coatings were then cured at 120 °C for 20 min. The dry thickness of all coatings was about 45 ± 5 °C.

Table 1
Chemical composition of St-37 type steel substrate.

Elements	Fe	C	Si	Mn	P	S	Al
Composition (wt.%)	99.03	0.18	0.33	0.32	0.05	0.05	0.04

Table 2
The chemical composition of cerium oxide (Ce) and zinc phosphate baths (Zn).

Composition	Ce bath	Zn bath
Hydrochloric acid 37 wt.% (mL/L)	11.3	–
Cerium nitrate (mol/L)	0.0046	–
Phosphoric acid 85 wt.% (mL/L)	–	11.3
Zinc oxide (g/L)	–	5.0
Sodium nitrite (mol/L)	0.014	0.014

2.4. Techniques

2.4.1. Surface characterization

The surface morphology of the steel specimens treated by Ce, Zn and Ce–Zn conversion coatings was studied by a scanning electron microscope (SEM) model Philips XL30 (equipped with EDS). Also, the composition of the conversion coatings was studied by a Specs EA 10 Plus energy dispersive X-ray photoelectron spectroscopy (XPS) equipped with a concentric hemispherical analyzer (CHA). The radiation source (at pressure of 10^{-9} mbar) in this study was Al Kα. The shift of binding energies (BE) was calibrated with respect to reference peak of carbon at binding energy of 285 eV. Static contact angles were measured on the surface treated samples by an OCA 15 plus type contact angle measuring system.

2.4.2. Pull-off adhesion measurements

Epoxy coatings were applied on the steel substrates without and with Ce, Zn and Ce–Zn chemical treatments. The adhesion of the epoxy coating to the substrates was determined by Posi test-pull off adhesion tester (DEFELSKO) according to ASTM D 4541. The measurements were done on the samples before (dry pull-off strength) and after (recovery pull-off strength) 30 days immersion in 3.5% w/w NaCl solution. The aluminum dollies were glued on the surface of the epoxy coating using a two-part Araldite 2015 (Huntsman advanced materials, Germany) adhesive. Samples were then kept at ambient temperature for 24 h to ensure that the glue fully cured. Then, a slot was made around dollies and they were pulled at a speed of 10 mm/min normal to the coating surface until the epoxy coating was detached from the steel substrate. All tests were carried out using three replicates to ensure the measurements repeatability.

2.4.3. Corrosion protection properties evaluation

The epoxy coatings, applied on the surface treated samples, were exposed to 3.5% w/w NaCl solution for 30 days. Then, the electrochemical impedance spectroscopy (EIS) was utilized in order to investigate the corrosion protection properties of the epoxy coating on the steel substrates without and with Ce and Ce–Zn conversion coatings. The experiment was done by an AUTOLAB G1 at amplitude and frequency range of ±10 mV and 10 kHz–10 mHz, respectively. Also, the measurements were performed in a conventional three electrode cell including coated steel specimen as working electrode, Platinum as counter electrode and Ag/AgCl (KCl 3M) as reference electrode. The impedance data were obtained at open circuit potential (OCP) on 1 cm^2 area of each sample after different immersion times in 3.5% w/w NaCl solution. The measurements were done on three samples in order to calculate the standard deviations.

3. Results and discussion

3.1. Surface characterization of Ce and Ce–Zn treated samples

3.1.1. SEM and XPS analyses

The zinc phosphate coating was employed to seal the pores of the cerium conversion coating on the steel surface. The morphology of the surface of steel samples treated by Ce, Zn and Ce–Zn conversion coatings was studied by SEM. The SEM micrographs are reported in Fig. 1.