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Improved performance of cerium conversion coatings on steel with zinc phosphate post-treatment

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ABSTRACT

The steel samples were pre-treated by cerium conversion layer. Then, zinc phosphate conversion coating was used as sealing agent for the cerium conversion layer to enhance its corrosion resistance. The corrosion performance and surface characteristics of the samples were characterized by electrochemical impedance spectroscopy, scanning electron microscope and X-ray photoelectron spectroscopy. Results revealed that the post-treatment of the cerium conversion coating by phosphate coating significantly increased its corrosion resistance. A denser conversion layer with less cracks were precipitated on the steel surface after post-treatment by zinc phosphate. The surface free energy was significantly increased after post-treatment by zinc phosphate.

Introduction

Steel is the most frequently used metal in various industries due to its good mechanical properties. However, it shows poor corrosion resistance in corrosive environment and because of this efforts have been carried out to enhance its corrosion resistance [1,2]. There are various methods to protect steel from corrosion. Chemical treatment of steel substrate is one effective approach to improve its corrosion resistance [3,4]. The chromate based conversion coatings have been widely used to enhance the corrosion resistance of steel substrate and adhesion properties of the subsequent organic coatings. However, the chromate conversion coatings contain toxic and carcinogenic hexavalent chromium (Cr^{6+}). As a result, using and handling of chromates as chemical treatment for the steel structures have been restricted in recent years [5–7]. Nowadays, chromate based conversion coatings are replaced with more environmental friendly alternatives [8–10]. Trivalent chromium (Cr^{3+}) based conversion coatings have been also proposed as less toxic substitute for the hexavalent chromium based conversion coating. However, the Cr(III) based conversion coating cannot provide corrosion resistance and enhance the organic coating adhesion properties like Cr(VI) [11,12]. The environmentally acceptable non-chromate based conversion coatings i.e. phosphate [13–17], molybdate [18], zirconium [19] and rare earth metal salts [20–23] have been considered in this regard.

Shin et al. [24] studied the corrosion performance of an epoxy coating on the carbon steel treated by zinc phosphate conversion layer. They revealed that applying such chemical treatment on the steel surface resulted in significant improvement of the epoxy coating corrosion resistance. Min et al. [25] studied the effect of adding potassium methyl siliconate (PMS) into silicate conversion coating as an alternative to hexavalent chromium conversion coating for corrosion protection of galvanized steels. They found that incorporation of PMS into the silicate conversion coating could significantly enhance the corrosion resistance of the galvanized steel. Ji-Eun et al. [26] studied the corrosion resistance of Ni, Mn, and Zn phosphates on car body. They revealed that as the Mn concentration increased the corrosion resistance increased, but the increase of Ni concentration resulted in the decrease of corrosion resistance. Ghanbari et al. [27] investigated the effect of surface treatment of mild steel substrates by zirconium-based conversion coating on the adhesion performance and cathodic delamination of the epoxy coating. They found that the adhesion strength of the epoxy coating was significantly increased and the cathodic delamination was decreased after surface treatment by zirconium conversion layer. In our previous study [28] the effects of adding poly(vinyl) alcohol (PVA) to the phosphate conversion coating on the anticorrosion and adhesion properties of the epoxy coating were studied. It was found that PVA could significantly enhance the epoxy coating adhesion properties and corrosion protection

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performance on the mild steel through affecting the surface free energy and the morphology of the conversion coating. The phosphate based conversion coatings have been widely used to modify the corrosion resistance of the metal substrate and provide good adhesion of the organic coating on the steel substrate. It has been shown that surface treatment of the steel sample by the zinc phosphate conversion layer can result in significant increase of the epoxy coating adhesion properties and corrosion resistance [29,30].

Cerium based conversion coating is one of the most promising environment friendly chemical treatments to modify the metal surface properties. It has been shown that chemical treatment of the steel substrate by a cerium based conversion coating can improve its corrosion resistance. However, the improvement has not been significant due to non-compact and porous structure of the coating creating the pathways for the electrolyte diffusion. Recent findings have revealed that post-treatment of the steel substrates in the chemical bathes including cerium and zinc phosphate conversion coatings could improve the surface properties and anticorrosion performances of the substrate [31–35].

In this study, a zinc phosphate post-treatment was applied on the steel substrate pre-treated by cerium conversion coating. Both cerium pre-treatment and zinc phosphate post-treatment were conducted on the steel substrate at room temperature. The surface characteristics of the samples were studied by scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Also, the corrosion protection properties of the samples were investigated by polarization test and electrochemical impedance spectroscopy (EIS) measurements.

Experimental

Materials

The steel substrate used in this study was St-37 (30 × 25 × 2 mm) with the composition given in Table 1.

Chemical treatment baths were prepared using cerium nitrate and sodium nitrite. Both of the chemicals were procured from Merck Co. Phosphoric acid, hydrochloric acid and sodium hydroxide were obtained from Mojallali Co. Also, the zinc oxide was supplied by Goharfam Co.

Surface treatment process

Cerium (Ce) conversion coating was deposited on the steel substrate at room temperature in the cerium chemical treatment bath. Hydrochloric acid and sodium nitrite were other chemicals which were added to the Ce bath. The pH of the solution was adjusted at 2.5 (by adding NaOH solution) and the surface treatment was carried out for 10 min. Then, the Ce treated samples were post-treated in the zinc phosphate chemical treatment bath at room temperature, pH of 3.1 for 30 min. The zinc phosphate bath consisted of zinc oxide, phosphoric acid and sodium nitrite [36]. The surface treated samples were dried in air and kept in a desiccator for further characterizations. The compositions of the cerium and zinc phosphate bathes are presented in Table 2.

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 bathes (Zn).

Composition	Ce bath	Zn bath
Hydrochloric acid 37 wt.% (mL/L)	11.3	–
Cerium nitrate (g/L)	2.0	–
Phosphoric acid 85 wt.% (mL/L)	–	11.3
Zinc oxide (g/L)	–	5.0
Sodium nitrite (g/L)	1.0	1.0

Characterization

Surface characterization techniques

The surface morphology of the samples treated by Ce and Ce–Zn was studied by scanning electron microscope (SEM) model LEO1455VP Zeiss. The compositions of the coatings were investigated by energy dispersive spectroscopy (EDS) model INCA, X-ray diffraction (XRD) model EQUINOX 3000 and X-ray photoelectron spectroscopy (XPS) model 8025-BesTec techniques. In the XPS analysis, the radiation source (at pressure of 10^{-9} mbar) was Al K_α. The shift of binding energies (BE) was calibrated with respect to the 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. For this purpose, distilled water was used as probe liquid at temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively. A small drop of

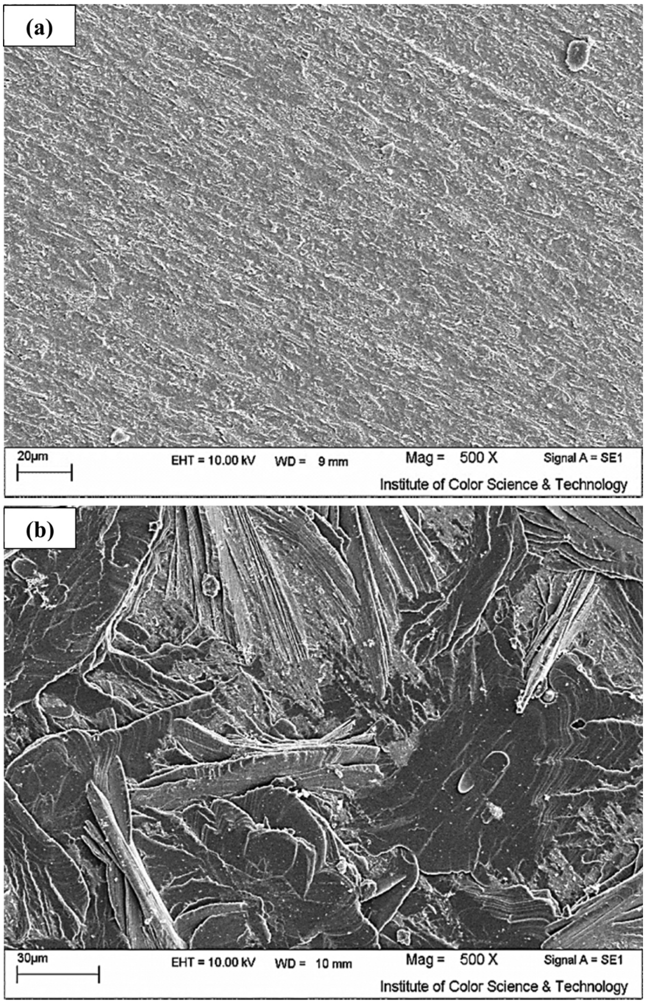

Fig. 1. SEM micrographs from the surface of steel specimens (a) treated by cerium conversion coating (Ce) and (b) Ce–Zn treated sample.