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A new strategy for improvement of the corrosion resistance of a green cerium conversion coating through thermal treatment procedure before and after application of epoxy coating

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ABSTRACT

The effect of post-heating of CeCC on its surface morphology and chemistry has been studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and contact angle (CA) measurements. The corrosion protection performance of the coatings was investigated by electrochemical impedance spectroscopy (EIS). The effect of thermal treatment of CeCC on the corrosion protection performance of epoxy coating was investigated by EIS. Results showed that the heat treatment of Ce film noticeably improved its corrosion resistance and adhesion properties compared to that of untreated samples. The CeCC deposited on the steel substrate at room temperature had a highly cracked structure, while the amount of micro-cracks significantly reduced after post-heating procedure. Results obtained from EIS analysis confirmed the effect of post-heating of CeCC on its corrosion protection performance enhancement. The increase of post-heating temperature and time up to 140 °C and 3 h led to better results.

1. Introduction

Due to the good mechanical properties, carbon steel has been used more and more frequently in several industrial applications. However, the low corrosion resistance of carbon steel in corrosive environments is still the big concern in many industries. Therefore, various corrosion protection methods have been proposed by a large number of researchers [1–5] to provide higher resistance for steel against corrosion. Among these, chemical treatment by conversion coatings has been introduced as a common approach for obtaining proper corrosion resistance against corrosive environments [6–9]. In addition, the surface treatment of metals i.e. steel is a promising strategy for achieving good adhesion of organic coatings [10–13]. Chromate conversion coatings have been widely used for chemical treatment of metals [14–16]. However, due to the presence of toxic and carcinogenic hexavalent chromium compounds in the coating structure, the use of this particular coating has been strongly restricted in recent years. Therefore, attempts have been made to replace chromate based conversion coatings with less toxic and environmentally safe ones [17–24].

In recent years, cerium based conversion coatings have attracted lots of attention due to theirs bold characteristic of being environmentally friendly [25,26], self-healing ability [27], and acceptable corrosion performance [3]. Furthermore it has high potential of improving the adhesion properties of the applied organic coatings [28]. Unfortunately, the cerium film has a highly cracked morphology reducing its corrosion resistance. In addition, the hydrogen peroxide, which is added to the solution bath as an accelerator, causes severe damage of coating morphology due to the fast evolution of H_2 gas [29,30]. Therefore, several researchers have focused on utilizing various methods for modification of CeCC structure. Ramezanzadeh et al. used zinc phosphate conversion coating as a sealing agent in order to improve the corrosion resistance of the CeCC sub-layer. In this way a denser and less cracked coating was formed on the surface [3]. In another study, they compared the adhesion properties of the epoxy/polyamide coating applied on the substrates treated with Zn, Ce and the Ce film post-treated by Zn. The results indicated that the lowest adhesion loss of epoxy coating was obtained on the sample treated by Ce-Zn layer. It was suggested that the Ce-Zn coating reduces the cathodic reaction rate at the coating/metal interface and prevents the cathodic detachment of the coating from the steel sub-layer [28]. Yasuyuki and Yutaka evaluated the effect of SO_4^{2-} addition to the cerium bath on the corrosion behavior of galvanized steel. The results showed that the

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Table 1
Chemical composition of steel sheet.

Elements	Fe	C	P	Mn	Si	Cr	Ni
Composition (wt%)	93.9	0.2	1.2	1.1	1	0.7	1.7

SO_4^{2-} acted as a growth inhibitor and/or grain finer and in this way enhanced the corrosion resistance of cerium layer [31].

As stated above, the cerium conversion coating performance has been widely considered in previous studies. However, to the authors' knowledge, the effect of heat-treatment on the morphological, structural and corrosion resistance of the cerium conversion coating on the steel substrate has not been reported. This study investigates the effect of thermal treatment of the cerium conversion coating applied on steel substrate on its surface morphology, chemistry, surface free energy and corrosion resistance.

2. Experimental

2.1. Materials

St-12 coupons (dimensions of 20 × 30 × 2 mm) with the composition given in Table 1, were used in this study. Chemical treatment baths were prepared using cerium nitrate and hydrogen peroxide which were purchased from Merck Co (Germany). Hydrochloric acid and sodium hydroxide were procured from Mojallali Co (Iran). Epoxy resin (Araldite GZ 7071 × 75) and polyamide hardener (CRAYAMID 115) were supplied by Saman and Arkema Co, respectively.

2.2. Surface treatment process

Steel samples were abraded up to #1200 emery paper, degreased and washed before immersing in the cerium (Ce) chemical bath containing cerium nitrate (2 g/L), hydrogen peroxide (0.6 mL/L) and hydrochloric acid 37wt% (11.5 mL/L). The pH of the solution was adjusted at 3 (by addition of NaOH 5wt% solution). The chemical treatment was carried out for 5 min at ambient temperature (25 ± 5 °C). The prepared samples were washed with distilled water and dried in air. In the next step, the Ce treated samples were post-heated for different times and temperatures. The post-treatment conditions and the nomination of the samples are listed in Table 2. The final samples were kept in desiccator for further characterization.

Table 2
Thermal treatment conditions and nomination for different samples.

Heat treatment time (h)	Heat treatment temperature (°C)	Samples designation[a]
1	100	S(1 h:100 °C)
2	100	S(2 h:100 °C)
3	100	S(3 h:100 °C)
3	120	S(3 h:120 °C)
3	140	S(3 h:140 °C)

[a] S(treatment duration (h): treatment temperature (°C)), where S is the abbreviated for each sample.

2.3. Epoxy coating application

Epoxy coating was prepared through mixing the epoxy resin and polyamide curing agent with the ratio of 1.3:1 w/w. Then, the coating was applied on the bare steel and Ce treated samples (before and after post-heating) with a wet film thickness of 120 μm using a film applicator. Finally, the coated samples were kept at ambient temperature for 24 h and then post-cured at 100 °C for 1 h. The dry film thickness of the samples was 50 ± 5 μm.

2.4. Characterization

2.4.1. Surface characterization techniques

The morphology and composition of the steel samples treated by Ce film were investigated by scanning electron microscope (SEM) model Phenom ProX equipped with an energy dispersive spectroscopy (EDS) prior and after post-heating process. Static contact angles were measured on the surface of different samples by an OCA 15 plus type contact angle measuring system. Distilled water was used as probe liquid and the measurements were performed at temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively. For this purpose 1 μL distilled water was placed on the samples and then the shape of the droplets was recorded by a Canon type digital camera after 20 s.

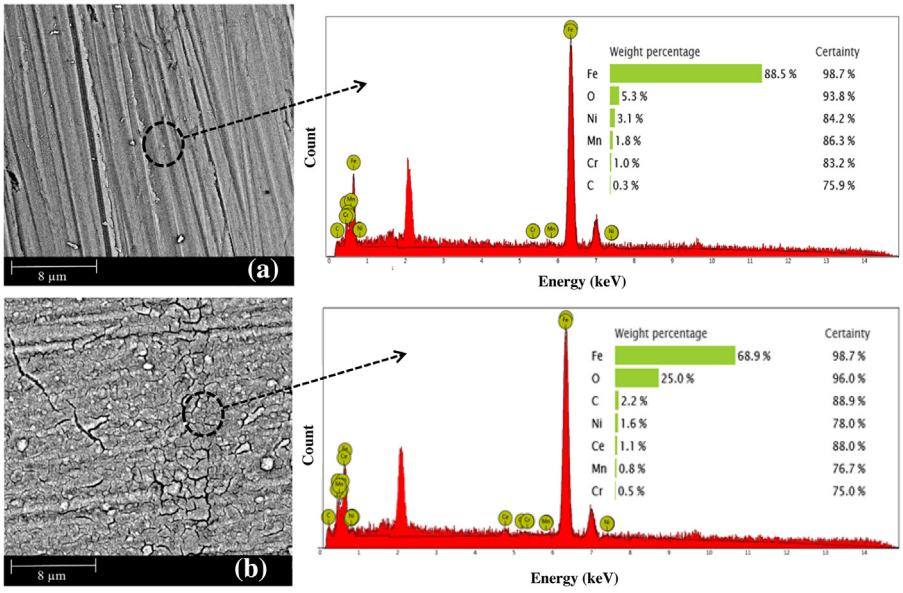

Fig. 1. SEM micrographs and EDS spectra of (a) bare steel and (b) Ce treated sample at room temperature, pH = 3 and t = 5 min.