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The influence of steel surface treatment by a novel eco-friendly praseodymium oxide nanofilm on the adhesion and corrosion protection properties of a fusion-bonded epoxy powder coating

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The effect of steel surface treatment by an eco-friendly praseodymium (Pr) oxide nanofilm on the corrosion protection properties and cathodic delamination of a fusion-bonded epoxy coating (FBE) was studied. The results of AFM, FE-SEM and contact angle tests revealed that a crack free praseodymium oxide nanofilm uniformly covered the steel surface. Results of EIS and salt spray tests revealed that the steel surface treatment by Pr film significantly enhanced the FBE coating corrosion protection performance. Results of cathodic delamination test showed significant decrease in the FBE cathodic delamination rate. Results of pull-off test revealed the FBE/Steel interfacial adhesion bonds promotion.

Introduction

For decades the steel has been extensively used in construction of storage tanks (UST), underground and submerged pipelines in petroleum, oil and gas industries. Organic coatings, i.e fusion-bonded epoxy, and cathodic protection (CP) methods were simultaneously applied for corrosion control of these structures in corrosive environments. This system could provide reliable lifetime for metals [1–4]. The integrity of the coating and creation of defects or mechanical damages can affect the performance of the CP protected systems. The interfacial adhesion bonds between a coating and steel substrate can considerably affect the coating protection performance under CP. The initial adhesion can be diminished during the service life due to the coating degradation and water molecules penetration into the coating/metal interface. Water molecules diffusion to the coating/metal interface results in the polar–polar adhesion bonds degradation. The water molecules are strong hydrogen bonding agents and form stronger hydrogen bonds with hydrated oxide film of metal surface than coating. Dissolution of metal oxide and deterioration of polar–polar bonds and corrosion reactions are the reasons for the coating delamination from the substrate [5–7]. The corrosive electrolyte diffusion to the coating/metal interface intensifies the coating delamination. The hydroxyl ions create on the cathodic sites ($2H_2O + O_2 + 4e \rightarrow 4OH^-$) and interact with Na^+ cations. This results in the creation of NaOH, which is a strong alkaline agent. In this way the pH significantly increases at cathodic sites (>10), resulting in the polymer/metal interfacial adhesion bonds destruction. In the next time the hydroxyl ions can interact with dissolved Fe^{2+} and Fe^{3+} cations, forming iron hydroxide/oxide. The progress of corrosion products at the coating/metal interface results in coating delamination progress. In the case of CP protection the applied potential results in more hydroxyl ions creation and pH rise at coating/metal interface. This is the major problem of the FBE coated substrates under CP protection [8–13].

These show that the adhesion bonds between the coating/metal play an important role on the coating protection performance under CP condition. Various mechanical and chemical treatment methods have been utilized to establish stronger and more stable adhesion bonds between the organic coatings and metal substrate. It is important to know that both physic and chemistry of metal surface affect the adhesion properties of the subsequent organic coating [14]. One important strategy for adhesion improvement is increasing the number of adhesion sites with capability of chemical bonding with polar groups of epoxy. Among various methods the surface pre-treatment by chemical conversion

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coatings has been considered largely in recent researches. Chromate and zinc phosphate based conversion coatings have been largely used for decades as the most popular chemical treatments for adhesion improvement of organic coatings. However, the use of chromates has been strongly prohibited due to the toxic nature and environmental problems [15]. In addition, the phosphating approach is time and energy consuming process, producing large scale sludge with environmental problems [16–18]. So, the researchers' attention has been directed toward the use of eco-friendly chemical treatment methods. Conversion coatings based on rare earth elements are the most important alternatives for chromates. In our recent studies the cerium and lanthanum based conversion coatings have been utilized for chemical treatment of steel with the aim of improving the adhesion properties and reducing the cathodic delamination rate. It has been shown that deposition of combination of three (Ce_2O_3) and tetravalent (CeO_2) Ce oxides on the steel surface results in the increase of surface roughness, surface free energy and work of adhesion. The Ce oxide film, unlike iron oxide film, is stable in corrosive and alkaline conditions, providing strong chemical bonds with polar groups of epoxy. The Ce oxide significantly reduces the cathodic reaction rate at the coating/metal interface, inhibiting the coating/metal interfacial adhesion bonds deterioration [19–25]. It has been reported in the literature that the surface treatment of metal by praseodymium oxide enhances the metal corrosion resistance [26,27]. However, there are little works on the effect of steel surface chemical treatment by praseodymium oxide on the interfacial adhesion, cathodic delamination and corrosion protection properties.

In this study the effect of steel surface treatment by praseodymium oxide film on the adhesion, corrosion protection properties and cathodic delamination of FBE was studied. The surface morphology and chemistry of the Pr treated sample were investigated by AFM, FE-SEM, XPS and contact angle tests. EIS and salt spray tests were employed for corrosion studies. Pull-off and cathodic delamination tests were utilized for adhesion studies.

Table 1
Results obtained from contact angle measurements on the steel surface with and without Pr film.

Sample	Θ (°)	W_a (mJ/m^2)	γ_{sv} (mJ/m^2)
Untrated steel	82 ± 3	82.3 ± 1.5	34.0 ± 4
Pr treated steel	13 ± 2	137.6 ± 5	65.2 ± 3

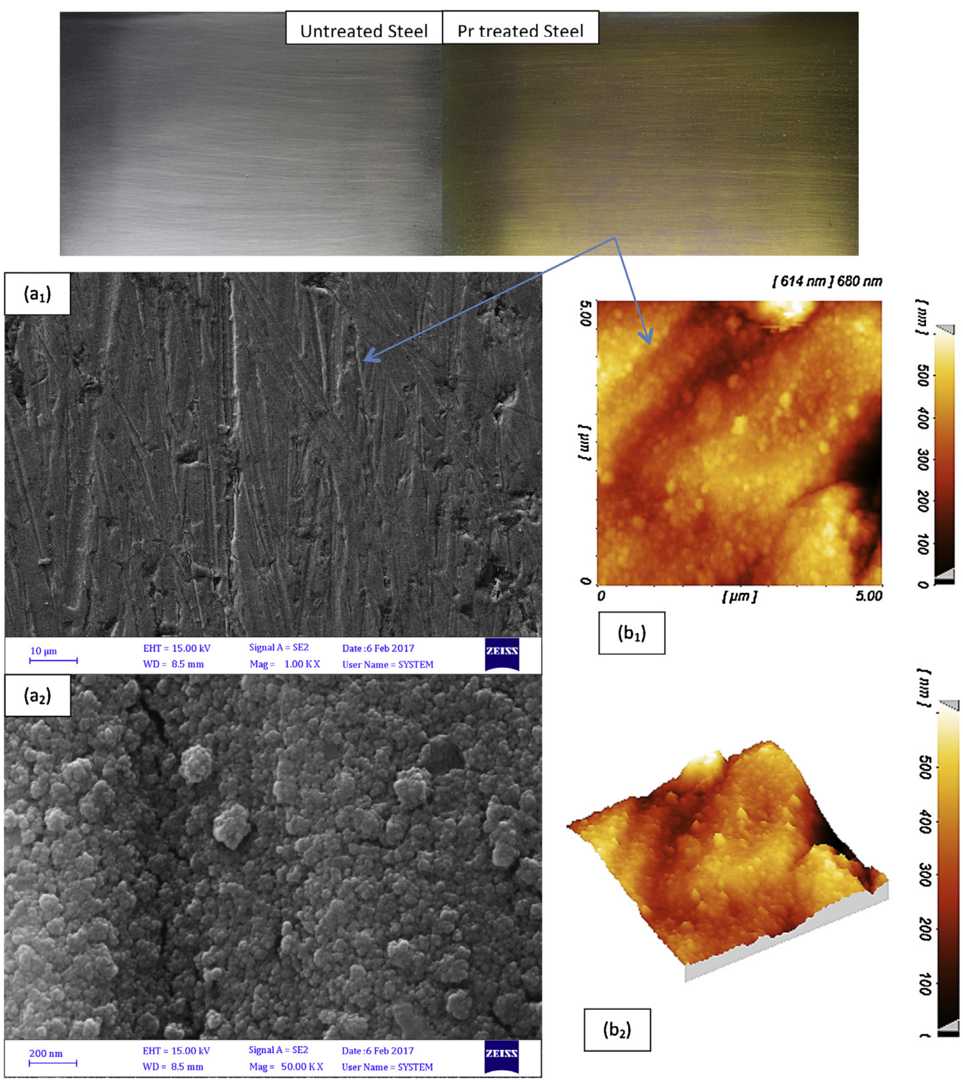

Fig. 1. (a_1 and a_2) FE-SEM micrographs at two magnifications and (b_1 and b_2) 2D and 3D AFM micrographs from the steel surface treated by Pr film.

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