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Full Length Article

The role of neodymium based thin film on the epoxy/steel interfacial adhesion and corrosion protection promotion

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ABSTRACT

The main aim of this study is to investigate the impact of the steel substrate Nd-based chemical modification on the corrosion protection performance, cathodic delamination and adhesion properties of epoxy coating. The morphology, chemical composition, topography and chemistry of the treated samples were studied by field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurement. The treated samples and also the epoxy coated samples corrosion resistance was examined through electrochemical impedance spectroscopy (EIS). The impact of mild steel surface modification on the epoxy coating protection efficiency, adhesion strength and cathodic disbondment (CD) resistance was surveyed by salt spray, Pull-off and CD tests. Results showed the deposition of Nd oxide/hydroxide, a surface with lower surface free energy and higher roughness compared to the untreated sample. Chemical treatment by Nd-based film remarkably improved the epoxy coating corrosion protection properties, increased the adhesion strength through chemical and hydrogen bonds, and led to an excellent CD resistance.

1. Introduction

Almost most of the metals and their alloys are vulnerable to corrosion due to their unstable electrochemical nature. This unpleasant phenomenon causes a lot of economic losses. Low carbon steels are one of the most popular kinds of steels in many industries due to being low cost, but despite having good mechanical properties, they suffer from corrosion which restricts their application in many industries [1,2]. Although there are metals and alloys with low corrosion rate (such as stainless steels and etc.), but application of low carbon steels besides using corrosion protection techniques is a very cost effective and economical way to prevent further damage. Utilization of coatings, inhibitors, anodic or cathodic protection and so on are some of the common protection strategies. Organic coatings are applied to protect steel substrates from corrosion in environments with corrosive agents. The performance of an organic coating relies on various parameters like coating chemistry, cross-linking density and adhesion to the substrate. In this case, epoxies are a wide class of polymer materials specified by the attendance of epoxy groups in their molecular composition. Epoxy coating is a widely used organic coating, due to its high density of cross-links, desirable wettability and adhesion to metallic surfaces, rapid or slow curing ability in an extensive temperature range, low shrinkage during the curing process, good mechanical strength, chemical and thermal resistance, electrical properties, toughness and etc.

The adhesion of organic coatings to metallic substrates is an important feature that influences the protection function, since in corrosive environments, the permeation of corrosive agents into metal/coating interface, leading to the adhesion loss (due to the cathodic reactions and alkalization of the cathodic sites) and metal corrosion. Furthermore, due to the differences in chemical and physical structures of the organic coatings and metallic substrate, the adhesion is almost weak [3].

Organic coatings adhere to metal surface in different ways. Among the adhesion forces, mechanical (mechanical inter-locking theory), physical (weak, secondary or van der Waals forces, dipolar interactions, hydrogen bonding and other low energy forces) and chemical bonding (covalent, ionic and metallic bonding) are the most prevalent and dominant forces between polymer coating and metallic substrate [4]. Therefore, the metal surface treatment before applying organic coating for corrosion prevention improvement and adhesion enhancement seems to be necessary. Exertion of conversion coating on the metallic surface is a technique, in order to amplify the performance of corrosion protection and adhesion to organic coating. Due to the porous nature of these coatings, the main purpose of this chemical modification is to improve the adhesion of organic coating by the related adhesion mechanisms [5–8]. One of the oldest coatings is chromate based

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conversion coatings [1,9,10]. Despite their good anti-corrosion properties, the improved adhesion of organic coating and being low-cost, due to the carcinogenicity of hexavalent chromium and environmental issues, the application of these coatings in many countries has been banned in recent years [11]. Phosphate conversion coatings are widely used in various fields, such as automotive industries and agriculture [12,13]. Low compatibility with the environment, sludge production and the high temperatures required for application are the real concerns with this type of coatings that jeopardize the human health [14,15].

Nowadays to overcome these problems, lots of investigations have been done to replace these types of coatings with more environmentally friendly coatings. It seems that the green conversion coatings may be considered as suitable alternatives for chromate and phosphate compounds replacements. Trivalent chromium [16], molybdate [17], vanadate [18], permanganate [19], titanate [20] and so on are some examples of these coatings. Attention has increased in recent years to the rare earth elements e.g. Lanthanum [21], Cerium [22], Praseodymium [23], Neodymium [24], Samarium [25], Gadolinium [26] and etc. Also application of these elements, as a new class of conversion coating, has become one of the attractive topics nowadays. Few studies about neodymium based conversion coatings are reported in literature. This element is usually employed as an isotopic reference in geology. Today, conversion coatings have widespread applications and are mainly used to protect metals against corrosion. However, due to the coating porosity, they are dominated by additional operations.

Cui et al. used Nd-based conversion coating as a reserve for noxious hexavalent chromium on AZ91D magnesium alloys. They also studied the effect of post-treatment by phytic acid. The post-treatment method improved the corrosion resistance of the surficial layer drastically [27]. Mahidashti et al. found that the post-heating process is beneficial for the improvement of cerium coating properties on St-12 surface. They asserted that the heat treatment of Ce layer could improve the corrosion resistance of the coating through sealing the cracks [28]. In another investigation they treated the steel surface by cerium-lanthanum chemical modification. Results illustrated that the post-treatment of the cerium film by a lanthanum bath led to advanced corrosion resistance. Low CD[1] rate and elevated interfacial adhesion of the epoxy coating in comparison to other coating procedures were also observed [21]. Vakili et al. surveyed the corrosion performance and adhesion strength of the epoxy applied steel substrate. The metallic surface was treated by cerium-based conversion coating with a Ce-Zn bath as post-treatment. They concluded that the epoxy applied Ce–Zn treated sample represented an excessive adhesion and corrosion protection properties [29]. Cui et al. studied the gadolinium based protective coating on die cast AZ91. They found that the formed film can ameliorate the corrosion resistance of magnesium alloy [26].

In this paper, the effect of Nd-based chemical modification on the adhesion properties, cathodic disbondment rate and protection performance of the epoxy coated steel was studied. The surficial morphology and chemical composition of the nano-structure deposited layer were investigated by FE-SEM, AFM, XPS and contact angle test. EIS and salt spray test were done for corrosion studies. Pull-off and CD test were also performed for adhesion studies.

2. Experimental

2.1. Materials

St-12 specimens (70 × 30 × 1) with given composition in Table 1 was provided from Mobarakeh Steel Co. (Iran). Chemical treatment bath consisting of Neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$), supplied from Sigma-Alderich Co. (USA), was prepared.

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

Hydrogen peroxide and hydrochloric acid were acquired from Neutron Co. (Iran) and sodium hydroxide was prepared from Mojallali Co. (Iran). Araldite GZ 7071 × 75 epoxy resin and CRAYAMID 115 hardener were provided by Saman and Arkema Co., respectively.

2.2. Surface treatment procedure

The steel samples were abraded by 220, 400, 600, 800 and 1200 grades sandpapers, degreased with a commercial acetone solvent in an ultrasonic bath and washed with deionized water. The neodymium containing solution, with the composition of: Neodymium (III) nitrate hexahydrate (1 g/L), hydrogen peroxide (0.6 mL/L) and hydrochloric acid (10 mL/L), was applied on the steel sheets cleaned with the process mentioned through air spray procedure. The pH of bath was adjusted to 3 with appropriate amount of sodium hydroxide solution (50 wt%). The whole process was carried out in different spraying times; 1, 2 and 3 min at ambient temperature. The chemically treated samples were rinsed off with deionized water and desiccated. Finally, the heat treatment process was performed on the samples at 140 °C for 3 h.

2.3. Epoxy coating application

Epoxy coatings were got ready by stirring the epoxy resin and curing agent which was polyamide with a 1.3:1 w/w ratio. After that, the bare steel and the post-heated samples (1 min of spraying) were covered with the obtained epoxy coating by a film applicator with a thickness of 120 µm. Finally, the coated specimens were retained at room temperature for 24 h and then went under a post-curing process for 1 h at 100 °C. The thickness of the final epoxy coating after curing was 50 ± 5 µm.

2.4. Characterization

2.4.1. Surface characterization techniques

The morphology and microstructure of the bare steel and Nd treated samples were examined by Nova NanoSEM 450 (FE-SEM) with an elemental analysis (EDS). Since the formed layer on the substrate is not electrically conductive, all prepared specimens were coated with a thin layer of gold coat before FE-SEM analysis to obtain images with better resolutions. Employing the X-ray photoelectron spectroscopy (XPS) technique (Specs EA 10 plus), the chemical structure of the formed layer was analyzed. Static contact angles were determined by an OCA 15 plus contact angle measuring device on different samples surface. Also by utilizing an atomic force microscopy (VEECO CP II, USA) the surface topography of the specimens was depicted in tapping mode. The roughness parameters were also extracted using AutoProbe image software (version 2.1.15). Also repeatability of data was checked on 3 samples.

2.4.2. Anticorrosion performance evaluation

Electrochemical studies were accomplished through an Autolab pgstat 302n device in a three electrode cell. The saturated Calomel electrode (SCE), platinum and steel sample with an exposing area of 1 cm^2 were used as reference, counter and working electrodes, respectively. Using a sharp blade, a 2 × 40 mm scratch was designed on the epoxy coated samples. The electrochemical evaluations were performed on the bare, Nd modified, and post-heated Nd modified samples in 300 mL 0.1 M NaCl solution at room temperature after 24 h. The epoxy coated samples without and with artificial defect were also analyzed by

[1] Cathodic disbondment.