Research paper

Hydrophobic polystyrene/electro-spun polyaniline coatings for corrosion protection

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ABSTRACT

Herein, bi-layer coatings were prepared through a superposition combination method, which contains polystyrene (PS) topcoat and polyaniline (PANI)/polymethyl methacrylate (PMMA) primer. PS topcoats prepared by different preparation methods show diverse microstructures, hydrophobicity, anti-medium permeability and corrosion resistance. In order to study the anti-corrosion mechanism of (PANI/PMMA primer − PS topcoat) coating system, Q235 carbon steel covered with bi-layer coatings were immersed in 3% NaCl solution for 720 h. And the anti-corrosion properties of samples were studied by open circuit potential, visual observations, electrochemical impedance spectroscopy and Tafel polarization test. Electrochemical techniques confirm that collocation of PS topcoat and PANI/PMMA primer could give full play to the shielding performance of topcoat and anodic protection performance of PANI/PMMA primer. Observed results show (PANI/PMMA primer − PS topcoat) coating system prepared by spray method has the best anti-medium permeability and outstanding corrosion protection property, which is attributed to the special microstructure.

1. Introduction

Carbon steel is widely used for constructing marine structures due to their cost-effectiveness [1]. However, steel corrosion has brought us a lot of problems, e.g. resource waste, equipment failure, and environmental pollution [2,3]. Nowadays, the most economic and effective method for restraining corrosion is applying corrosion protection coatings to metal surfaces [4–6]. During the last few years, the conducting polymers have widely been used for anticorrosion coatings [7,8]. Among the conducting polymers, polyaniline (PANI) has occupied the key position due to its good environmental stability, controllable conductivity, and good redox reversibility [9–11]. The poor mechanical stability and adhesion of PANI could be improved by combining with epoxy, polyvinyl chloride, acrylic resins and polymethyl methacrylate [12–15]. However, the formation of pores in anticorrosion coatings is almost inevitable [16]. It is well known that the pores could provide paths for corrosive ions to penetrate the coating, leading to the poor corrosion resistance [17]. So a topcoat is required to realize good barrier and protection performance. Wan et al. [4] proposed that multi-layer coatings could conquer intrinsic defects and enhance anti-corrosion performance through the synergistic effect of two or more materials. Lin et al. [18] demonstrated that the excellent anticorrosion protection of (MgRP-powder topcoat) coating system which colligated the superior barrier properties of the topcoat and favorable cathodic protection of the primer.

In our previous work, we presented that electro-spun polyaniline (PANI)/polymethyl methacrylate (PMMA) microfibers coatings could supply superior anticorrosion protection for carbon steel [19]. However, it is found that the voids between microfibers are unfavorable for anticorrosion protection. In order to make up for this defect, and further application of electro-spun anti-corrosion coatings, polystyrene (PS) topcoats were fabricated by electrospinning, traditional drop-casting and spraying methods onto the electro-spun PANI/PMMA microfibers coatings to construct a coating protection system composed of electro-spun PANI/PMMA primer and polystyrene topcoat for carbon steel. The corrosion behaviors of the bi-layer coatings with PS topcoats in 3% NaCl solution were systematically investigated by electrochemical techniques.

2. Experimental

2.1. Reagents and materials

Carbon steel sheet (Q235) was used as the working electrode, the composition (%) of which was Mn 0.45, C 0.18, Si 0.02, S 0.02, P 0.01, with the balance iron, and the working area was 1 cm^2 (1 cm × 1 cm). The stainless steel electrode was polished with 3000 grit emery paper, and then degreased in ethanol ultrasonically before coating. Ammonium persulfonate (APS), hydrochloric acid (37%), *m*-cresol, aniline, ethanol, sulfuric acid, tetrahydrofuran (THF), chloroform and xylene were purchased from National Medicine Chemicals (China). Poly (styrene) (PS, Mw350000) was obtained from Sigma-Aldrich Corporation (USA), and dodecylbenzene sulfonic acid (DBSA) was supplied by Xiya Reagent Plant (China). Polymethyl methacrylate (PMMA, Mw157200) and camphorsulfonic acid (CSA) were obtained from Heowns (China).

2.2. Preparation of PANI-PMMA primer

According to our previous report , the polymer solution prepared by mixing of soluble PANI and THF solution of PMMA [19]. Fibrous PANI/PMMA mats with PANI dosage of 15 wt% were formed on the Q235 carbon steel by electrospinning technology. The PANI-PMMA coating is measured about 40 μm in thickness by MiniTest 4100 microprocessor coating thickness gauge manufactured by ElektroPhysik.

2.3. Preparation of PANI-PMMA primer/PS topcoat systems

In this work, PS topcoats with diverse thickness (40 μm to 120 μm) were coated by electrospinning, traditional drop-casting and spraying, respectively. For the preparation of PS topcoat, the 100 g/L of PS solution in THF (or *m*-cresol, or xylene) was used. The electrospinning apparatus was equipped with a high direct voltage source (DW-P303-1ACF0, Tianjin Dongwen High Voltage Power Supply Limited Company, China) with a voltage of 12 kV. The stainless steel needle (diameter, 0.5 cm) hooked up to the end of the syringe was located 16 cm away from the Q235 carbon steel electrode. The sprayed sample was prepared using a Yingli model (Guangzhou, China) airbrush. The distance between the nozzle (diameter, 0.3 cm) and Q235 carbon steel electrode kept 16 cm. The schematic illustration of the preparation process for PANI-PMMA primer/PS topcoat systems is presented in Fig. 1.

2.4. Characterizations

The surface morphologies of bi-layer coatings were obtained using scanning electron microscopy (SEM, Hitachi TM-1000, Japan). The static water contact angle system (OCA, Dataphysics, Germany) was employed to study the hydrophobicity of coatings. The electrochemical experiments were carried out in a conventional three-electrode cell assembled with Q235 carbon steel working electrode with a Pt foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Measurements were performed in 3% NaCl aqueous solution at room temperature. For electrochemical corrosion tests, PARSTAT 4000 Potentiostat/Galvanostat (Princeton Applied Research, USA) with Versa Studio Software was used. EIS (Electrochemical impedance spectroscopy) were implemented in the frequency range of 100 kHz to 10 mHz with signal amplitude ± 10 mV about the open circuit potential (OCP). The Tafel curves were performed in the potential range of −250 mV to +250 mV with a scan rate of 1 mV s^{-1}.

3. Results and discussion

3.1. Anticorrosion performances of PANI-PMMA primer/PS topcoat systems with different PS thickness

Typical Tafel polarization curves (a), Bode magnitude plots (b) and Bode phase angle plots (c) for uncoated carbon steel, and covered carbon steel with bi-layer coatings dipped in 3% NaCl solution are presented in Fig. 2. The electrochemical parameters calculated through Tafel extrapolation technique are listed in Table 1, which including corrosion potential (E_{corr}), corrosion current density (i_{corr}) and protection efficiency (PE). The PE was calculated as follows,

$$PE\% = 100 \times (1 - i_{corr}/i_{corr}^0) \tag{1}$$

where i_{corr} and i_{corr}^0 are the corrosion current densities of coated carbon steel and bare carbon steel, respectively [20]. From the point of view of thermodynamics, the more positive the corrosion potential is, the lower the corrosion tendency will be. As can be seen from Table 1, PS topcoat could effectively resist the carbon steel from being corroded. However, when the thickness of PS topcoat is over 80 μm, the anticorrosion protection decreased on account of the uniformity of the coating.

In the Tafel plots of coated carbon steel samples (Fig. 2a), both the cathodic and anodic branches shifted to lower current densities in comparison to the bare carbon steel. This implies the corrosion reactions containing cathodic oxygen reduction and anodic dissolution of carbon steel are suppressed effectively. Moreover, the cathodic and anodic current densities of the samples with 80 μm PS are remarkably lower than those of the others. And the corrosion current density is 2.07 × 10^{-9} A cm^{-2}, which is 4 orders of magnitude lower than that of bare carbon and nearly 3 orders of magnitude lower than that of coated carbon steel by electro-spun PANI-PMMA coatings, respectively. The corresponding protection efficiency is enhanced to 99.99%. So PS topcoats are very efficient to prevent the corrosion medium from penetrating to the carbon steel surface and thus enhance the protection for carbon steel.

The corresponding Bode magnitude plots (Fig. 2b) gives measurement of modulus of impedance |Z|, and the higher impedance modulus in low frequency region represents the better barrier property of the system. The $|Z|_{0.01Hz}$ (modulus of impedance at 0.01 Hz) of 80 μm PS sample is higher than others, which suggests that 80 μm PS sample has the best anticorrosion property among these samples. The value of phase angle in low frequency region is relevant to the compactness of the coating. Fig. 2c shows the 80 μm PS sample has the lowest phase angle value, therefore it has the most compact coating. Both Tafel and Bode diagrams demonstrate the anticorrosion property of the 80 μm PS sample is the best due to its compactness.

3.2. Anticorrosion performance of PANI-PMMA primer/PS topcoat systems prepared with different solvents

Subsequently, PANI-PMMA primer/PS topcoat systems continue to be studied by fixing PS thickness of 80 μm and changing the paint solvent. Fig. 3a shows the potentiodynamic polarization plots of samples with different paint solvents. It is observed that the protection efficiency of the m-cresol sample is slightly higher than the corresponding value of the sample without topcoat, according to Table 2. The anticorrosion poverty of m-cresol sample has not been improved obviously due to the disruption of PANI-PMMA primer. It can be seen from the experiment phenomenon that PS m-cresol solution could dissolve and damage the PANI-PMMA primer when in contact with each other. Hence, the mismatches between topcoat and primer make the effection of two layers of coating can't be exploited. The i_{corr} value as 2.07 × 10^{-9}, 2.03 × 10^{-9} A cm^{-2} for the samples with xylene and THF, respectively, are obviously lower than that of the sample without topcoat, ca. 9.99 × 10^{-7} A cm^{-2}. So PS topcoat and PANI-PMMA