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The enhancement of benzotriazole on epoxy functionalized silica sol–gel coating for copper protection

Shusen Peng, Wenjie Zhao, He Li, Zhixiang Zeng, Qunji Xue, Xuedong Wu*

Ningbo Key Laboratory of Marine Protection Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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ABSTRACT

The influence of the amount of benzotriazole (BTA) on the wetting and anticorrosion ability of the epoxy functionalized silica sol–gel (ESol) coating was studied by various complementary methods. IR results demonstrate that BTA reacted with ESol through a 1:1 addition reaction of N–H to epoxy group. The water contact angle of the ESol coating increases with an increase in the amount of BTA. SEM and adhesion tests reveal that BTA could improve the adhesion of ESol to copper surface. Moreover, the best protection was achieved when the amount of BTA equals to the molar number of epoxy group in the ESol coating according to the results of electrochemical measurements and salt spray test.

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1. Introduction

Control of metallic corrosion is an important subject because metallic corrosion causes huge economic losses [1]. Of variety technologies for anticorrosion, organic polymeric coating is a general and economic approach to enhance corrosion resistance of metals [2]. In current industrial practices, chromium passivation is one of traditional pretreatment method to enhance the adhesion of organic polymeric coating to metal surface and provide an extra corrosion inhibition [3]. One reason of chromium coatings exhibit good corrosion resistance is due to the strong oxidation of hexavalent chromium [4,5]. However, Cr⁶⁺-containing chromium passivation technology is on the brink of being banned by environment regulation due to concerning about the adverse health and environmental effects [6,7]. Thus, scientists and engineers have dreamed of developing novel surface pretreatment to replace chromium one [8–10].

Benefiting from having good adhesion to both metallic substrates and organic polymeric top coatings, hybrid silica sol–gel coatings are considered as one of prospective metal pretreatment technologies [4,11–14]. In many hybrid silica sol–gel coating materials, epoxy functionalized silica sol–gel (ESol) coatings draw lots of interests from researchers as they possess some favorable

properties such as their mild preparation conditions, commercially available in a large scale of raw materials and their reactive epoxy group [15]. Previously, those coatings have been employed to protect various metal alloys such as steel [16], aluminum [17–19], zinc [20–22] and magnesium [23–26]. Unfortunately, the barrier effect of ESol coatings is not very well due to the inherent hydrophilic of epoxy group and the low crosslinking density of epoxy silane molecule. Besides, the adhesion of ESol coating to copper surface is poor because the difficulty of formation Si–O–Cu bonds between Si–OH and copper surface [27,28]. Thus, the protection performance of ESol coating for copper is unsatisfied. It is reported previously that incorporating organic corrosion inhibitors is a useful approach to enhance the anticorrosion performance of coatings [29–33] because those compounds can impede corrosion of metal substrate [34]. Moreover, organic corrosion inhibitors also are employed to improve the adhesion of epoxy resin to copper as those compounds can be chemisorbed onto copper surface [35,36]. Thus, we try to enhance the performance of ESol for copper protection by incorporating benzotriazole (BTA). Despite that there is report on grafting benzotriazole to glycidoxypropyltrimethoxysilane to prepare novel silane [37], to the best of our knowledge, reports on the influence of BTA on the wetting, adhesion and anticorrosion ability of ESol coating on copper surface are limited. The aim of this report is to investigate the enhancement of BTA on ESol coating for copper protection. Specifically, ESol solution was prepared from hydrolyzed tetraethoxysilane and glycidoxypropyltrimethoxysilane in an aqueous process. ESol coating with different amounts of

* Corresponding author. Tel.: +86 057487914083; fax: +86 574 86685159.
E-mail address: xdwu@nimte.ac.cn (X. Wu).

benzotriazole were deposited onto copper surface and characterized using various methods. Surface/cross section morphology and wetting of coatings were probed by scanning electron microscopy (SEM) and aqueous contact angle analysis, respectively. The anti-corrosion ability was evaluated by potentiodynamic scan (PDS), electrochemical impedance spectroscopy (EIS) and salt spray test. In addition, infrared spectroscopy (IR) was employed to study the reaction between BTA and epoxy group of ESol.

2. Experiment

2.1. Materials

Copper substrates were polished with fine emery paper and were degreased ultrasonically in acetone and then dried with N_2 gas. Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPS), ethanol, formic acid, methyl ethyl ketone (MEK), acetic acid, sodium chloride and benzotriazole (BTA) were purchased from Aladdin Company (Shanghai, China). All chemicals were used as received.

2.2. Preparation of ESol solution and coatings deposition

The epoxy functionalized silica sol–gel solution was prepared in a manner analogous to a previously report [38]. GPS, TEOS and 0.05 mol/L dilute formic acid solution were stirred at room temperature for 5 h, wherein the molar ratio of $n(\text{GPS}):n(\text{TEOS}):n(\text{H}_2\text{O})$ was 3:1:20. Water and MEK were added into as-prepared solution to adjust the solid content to 10 wt.%, which calculated based on the non-hydrolyzable group of silane.

Taking four samples of dilute solution equally, BTA was added into three of them to make the molar ratio of $n(\text{epoxy}):n(\text{BTA}) = 1:1, 3:1, 9:1$, and those solutions were denoted as E-B-1, E-B-3, and E-B-9, respectively. The sample without adding BTA was denoted as ESol-0. Copper substrates were immersed into those sol–gel solutions for 1 min at room temperature and were dried at 120°C for 2 h. The BTA treated sample was prepared by immersing copper substrate into 1 wt.% BTA ethanol solution for 5 min, then were dried at room temperature and was denoted as BTA-0.

2.3. Characterization

Infrared spectroscopy was performed on a spectrophotometer (Nicolet 6700, Thermo) in the range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . Dried sol–gel coatings were ground into powder and pressed into KBr tablets (1 mg of sample per 100 mg of KBr). The spectra were collected in absorption mode.

Aqueous contact angle analysis was employed to determine the wettability of sol–gel coatings using a Dataphysics OCA20. The value of water contact angle was an average of at least three readings at different locations on the surface of each sample. Surface and cross section morphology of sol–gel coatings was observed by scanning electron microscopy (Quanta FEG 250, FEI). The adhesion of sol–gel coating on copper surface was determined using standardized cross hatch adhesion test (GB/T 9286-1998). After the cuts were made, the cross was brushed with a soft scrubber and adhesive tape was pressed onto the cross. Afterwards, the tape was removed from the cross within 1 s in an angle of 60° . The results are presented by a rate of 5 for a poor adhering coating through 0 for a very good adhering coating.

Potentiodynamic scan (PDS) and electrochemical impedance spectroscopy (EIS) were carried out using a commercial electrochemical workstation (PGSTAT 302, Autolab) in a 3.5 wt.% NaCl solution. A three electrodes system was used, wherein a saturated calomel electrode (SCE) as the reference electrode, a platinum foil

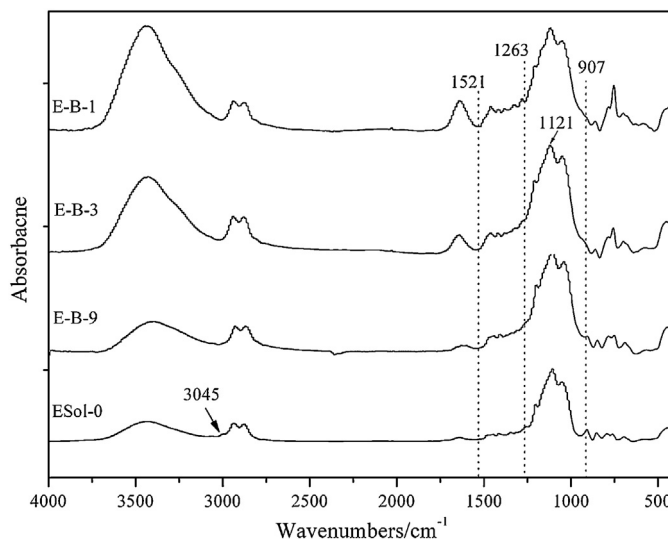


Fig. 1. IR spectra of dried ESol-0, E-B-9, E-B-3 and E-B-1 coatings.

as a counter electrode and an exposed sample (0.78 cm^2) as a working electrode. The PDS were conducted in the potential range from -500 to $+300\text{ mV}$ with a scan rate of 2 mV s^{-1} . The EIS measurements were carried out at open circuit potential applying 10 mV excitation amplitude in the 10^5 – 10^{-2} Hz frequency range. Before measurements were carried out, the electrodes were immersed in the same solution for 5 min under open circuit potential.

Salt spray test was carried out according to GB/T 10125-1997. The test was processed at 37°C and 0.1 MPa . Salt solution was prepared as follows: 500 g NaCl were added into 9.5 L water, and then the pH value was adjusted to the range of 6.5–7.2 by acetic acid.

3. Results and discussion

3.1. IR measurements

IR analysis was used to study the reaction between BTA and epoxy group of ESol. Fig. 1 shows IR spectra for the series of dried ESol coatings without and with BTA. The strong absorbance bands around 1121 cm^{-1} demonstrate that all of those sol–gels have formed the Si–O–Si network. For dried ESol-0 sample, the epoxide ring peaks at $3045, 1263$ and 907 cm^{-1} [16,39,40] are visible. Among of those peaks, the most important one is the peak at 907 cm^{-1} , which is very strong and allows monitoring the reaction of epoxy group. As shown in Fig. 1, the peak at 907 cm^{-1} absolutely disappears from the IR spectra of E-B-1 sample, but a residual peak at 907 cm^{-1} can be observed in the IR spectra of dried E-B-9 and E-B-3 samples. According to a previous report [41], it can be known that the bending peak of N–H in BTA is at 1521 cm^{-1} . Thus the absence of the peak at 1521 cm^{-1} indicate that epoxy–BTA reaction has occurred. Those results of IR analysis demonstrate that, in this case, the possible reaction between BTA and ESol is a 1:1 adduct reaction between N–H and epoxy group. Moreover, a simple schematic which is presented in Fig. 2a is used to describe the reaction between BTA and epoxy group of ESol.

3.2. Surface wettability

Water contact angle (CA) data were measured to determine the wettability properties of bare and coated copper surfaces. The images of water droplet on copper surfaces are shown in Fig. 3. As shown in Fig. 3(a, b), the CA value of bare copper and ESol-0 sample is $42 \pm 1.5^\circ$ and $62 \pm 0.3^\circ$, respectively. The BTA-0 sample (Seen

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