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

A R T I C L E   I N F O

Article history:
Received 16 January 2013
Received in revised form 12 March 2013
Accepted 13 March 2013
Available online 21 March 2013

Keywords:
Benzotriazole
Copper
Anticorrosion
Sol–gel coating
Electrochemical measurement
Salt spray test

A B S T R A C T

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.

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 environmental 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].

Benefitting 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–O–H 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).

0169-4332/5 – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.03.083
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 anticorrosion 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 N₂ gas. Tetraethoxysilane (TEOS), glycicyoxypropyltrimethoxysilane (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(GPS):n(TEOS):n(H₂O) 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(epoxy):n(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 as a counter electrode and an exposed sample (0.78 cm²) as a working electrode. The PDS were conducted in the potential range from −500 to +300 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 10⁻²–10⁻¹ 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 spectra 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 epoxy 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 bonding 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 ± 1.5° and 62 ± 0.3°, respectively. The BTA–0 sample (Seen
Fig. 2. Simplified model of possible reaction between BTA and epoxy group of ESol.

Fig. 3. Photos of water droplet on copper surfaces: (a) bare copper (42 ± 1.5°), (b) ESol-0 (62 ± 3°); (c) E-B-9 (63 ± 0.4°); (d) E-B-3 (74 ± 1.1°); (e) E-B-1 (86 ± 0.9°) and (f) BTA-0 (102 ± 2.0°) samples.

Fig. 3f shows a high CA value (102 ± 2.0°). BTA is a widely useful and important copper corrosion inhibitor [42]. Its molecule can be chemisorbed onto copper surface in deprotonated form through forming strong N–Cu bond. Kokalj et al. [43] reveal the structure of BTA-Cu polymer film using computer simulation, which is based on density functional theory. Their results demonstrate that the plane of BTA molecular is perpendicular to the copper surface with nitrogen atom closing to the copper surface and its possible structure is shown in Fig. 2h. This particular structure makes BTA-0 sample having a high CA value. Moreover, as shown in Fig. 3(c, d, e), the CA value of E-B-9, E-B-3 and E-B-1 sample are 63 ± 0.4°, 74 ± 1.1° and 86 ± 0.9°, respectively. If the CA value of sol–gel coatings covered copper surfaces are compared, one can obtain the sequence of ESol < E-B-9 < E-B-3 < E-B-1, namely the adding amount of BTA has a strong influence on the wettability properties of ESol coating. Morphology and adhesion of sol–gel coatings on copper surface Fig. 4 shows the surface and cross section morphology of the ESol coating with and without BTA on copper surface. From surface micrographs, it is found that all of those sol–gel coatings are dense and smooth. Cross section micrographs show that poor bonding performance of ESol-0 and E-B-9 coatings on copper surface. Those ESol coating obviously peeled off from the copper surface. However, the E-B-3 and E-B-1 coatings are firmly attached to the copper surface.

Cross hatch adhesion test was employed to determine the adhesion of those coatings on copper surface. The test gives a cross hatch adhesion value = 4, 4, 1 and 1 for ESol-0, E-B-9, E-B-3 and E-B-1 samples, respectively. Those results are in accordance with SEM cross section micrographs that the adhesion of E-B-3 and E-B-1 samples to copper surface is better than that of ESol-0 and E-B-9 samples. In other word, BTA can effectively improve the adhesion of ESol coating to copper surface.

3.3. Potentiodynamic scan (PDS)

Fig. 5 presents the PDS results of bare copper electrode and copper electrodes with coatings. Some parameters such as current density and corrosion potential were determined by the Tafel extrapolation method [44] and have been presented in Table 1. The
protection efficiency ($\eta$) is calculated by the following equation [45]:

$$\eta = \frac{I_{\text{corr}} - I_{\text{corr}}} {I_{\text{corr}}} \times 100\%$$

(1)

where $I_{\text{corr}}$ and $I_{\text{corr}}$ represent the corrosion current densities of bare and coatings covered copper electrodes, respectively. The value of protection efficiency ($\eta$) is also listed in Table 1.

The bare copper curve presents a reactive surface throughout most of the potential window. Moreover, an obvious anodic current peak attributed to the formation of CuCl film is observed, and a further increase of current is also found at higher potential which is resulted by the formation of Cu(II) [46]. By comparing the PDS curves of bare and coated copper electrodes (Seen Fig. 5), it is found that all of coatings suppressed the anodic and cathodic processes in the most potential window. Yet, a significantly change in $E_{\text{corr}}$ is not detected by all coatings. The protection provided by the pure ESol and BTA is limited. A discrepancy is observed on the PDS curves of BTA-0 and ESol-0 samples. The corrosion current density ($I_{\text{corr}}$) of BTA-0 sample is about $4.45 \times 10^{-8}$ A cm$^{-2}$, which is lower than that of ESol-0 ($1.99 \times 10^{-7}$ A cm$^{-2}$) and bare ($7.87 \times 10^{-6}$ A cm$^{-2}$) samples. But the cathodic current density of BTA-0 sample is obvious higher than the current density of ESol-0 at corresponding potential. In addition to this, the BTA coating

![Fig. 5. Potentiodynamic polarization curves of bare and ESol-0, E-B-9, E-B-3, E-B-1, BTA-0 samples in 3.5 wt.% NaCl solution.](image)

![Fig. 6. Bode plots representation of EIS results for bare and coatings covered copper electrodes at the beginning of immersion in 3.5 wt.% NaCl solution.](image)

![Fig. 7. Bode plots representation of EIS results for ESol coating without and with BTA covered copper electrodes after (a) 12 h and (b) 120 h immersion in 3.5 wt.% NaCl solution.](image)

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (mv) (SCE)</th>
<th>$I_{\text{corr}}$ (A cm$^{-2}$)</th>
<th>$\eta$ (%)</th>
<th>$Z_{\text{IM}}$ a ($\Omega$ cm$^{2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0 h</td>
</tr>
<tr>
<td>Bare copper</td>
<td>-201</td>
<td>7.87 × 10^{-6}</td>
<td></td>
<td>1.13 × 10^{3}</td>
</tr>
<tr>
<td>ESol-0</td>
<td>-202</td>
<td>1.99 × 10^{-7}</td>
<td>74.7</td>
<td>2.19 × 10^{4}</td>
</tr>
<tr>
<td>E-B-9</td>
<td>-198</td>
<td>4.32 × 10^{-8}</td>
<td>94.5</td>
<td>8.11 × 10^{3}</td>
</tr>
<tr>
<td>E-B-3</td>
<td>-201</td>
<td>1.40 × 10^{-8}</td>
<td>98.2</td>
<td>9.86 × 10^{3}</td>
</tr>
<tr>
<td>E-B-1</td>
<td>-203</td>
<td>1.43 × 10^{-9}</td>
<td>99.8</td>
<td>4.36 × 10^{6}</td>
</tr>
<tr>
<td>BTA-0</td>
<td>-202</td>
<td>4.45 × 10^{-8}</td>
<td>94.3</td>
<td>1.19 × 10^{4}</td>
</tr>
</tbody>
</table>

a The values of impedance modulus at 0.01 Hz which got from the Bode plots for coated and uncoated copper electrodes in 3.5 wt.% NaCl solution.
breaks down at a low potential (about \(-140\) mV) causing rapid increase in anodic current density. The \(i_{\text{corr}}\) of BTA-0 sample is even greater than that of bare copper at corresponding high potential (>40 mV). This result indicates that BTA film can protect copper, but the corrosion rate of copper would be accelerated once the BTA film is broken, which is supported by the results of salt spray test. The scarcely protection of pure ESol may be attributed to its internal hydrophilic structure resulting a bad waterproofing film. But when ESol coating is doped BTA, a remarkable enhancement could be obtained. As shown in Table 1, the \(i_{\text{corr}}\) of E-B-9, E-B-3 and E-B-1 are \(4.32 \times 10^{-8}\), \(1.40 \times 10^{-8}\) and \(1.43 \times 10^{-9}\) A cm\(^{-2}\), respectively, which is found to be significantly lower than that of ESol-0 sample. Moreover, ESol coatings with high BTA doping level (E-B-3 and E-B-1) present a very low anodic current density even at a high potential. If the protection efficiency of ESol coating with and without BTA is compared, one can obtain the sequence of E-B-1 > E-B-3 > E-B-9 > ESol-0. In other words, the anticorrosion performance of ESol coating increases with the doping amount of BTA increasing.

3.4. Electrochemical impedance spectroscopy (EIS)

Fig. 6 show Bode representation of EIS results for coated copper electrodes along with the bare copper electrode at the beginning immersion in 3.5 wt.% NaCl solution. It provides a good comparison of total impedance values for coated samples and uncoated sample. The values of impedance modulus (|Z|) at 0.01 Hz are listed in Table 1. According to the fact that corrosion rate is inversely proportional to the value of impedance modulus at low frequency [47], it can be concluded that all of the coated samples show lower corrosion rate than the uncoated one. Moreover, it should be noted that the EIS results show that the |Z| of ESol-0 sample is higher than that of BTA-0, however PDS results give that the \(i_{\text{corr}}\) of ESol-0 sample is higher than that of BTA-0. As previously discussed in PDS, there is also a discrepancy between the \(i_{\text{corr}}\) and anodic current density. We believe that the discrepancy is attributed to the specific character of BTA-Cu polymer film and ESol coating. According to the PDS result, it can also be known that the BTA film shows good stability at \(E_{\text{corr}}\), but is easily broken by voltage disturbance. Since a sinusoidal current signal is applied in EIS measurement the BTA film may be broken resulting a low |Z| value. However, the ESol coating is thick and hydrophilic. Thus a high \(i_{\text{corr}}\) value is obtained because that salt solution is very easy through the coating due to the effect of electric field in PDS measurement. A high |Z| value is presented because that limited salt solution is reach to the interface of Cu/coating as a result of short immersion time. Moreover, the values of |Z| give a sequence of E-B-1 > E-B-3 > E-B-9. Those results indicate that BTA can enhance the protection performance of ESol coating. With increasing the doping amount of BTA, the protection performance of ESol coating is significantly increased. Those results are in conformity with the PDS results.

Fig. 7 shows Bode representation of EIS results for E-B-9, E-B-3 and E-B-1 samples after immersion of 12 h and 120 h in 3.5 wt.% NaCl solution and the |Z| values are also listed in Table 1. The low |Z| value of ESol-0 coating after 12 h and 120 h of immersion indicates that the pure ESol coating has a poor corrosion resistance. It can be found that the |Z| value of E-B-9 sample shifts to 1.1 \times 10^5 and 1.6 \times 10^5 \Omega \text{ cm}^2 after 12 h and 120 h of immersion, respectively. Those results demonstrate that the E-B-9 coating is also easy to rot and lost its anticorrosion ability, although its anticorrosion ability is better than pure ESol coating. For E-B-3 sample, the |Z| value decreases from 9.8 \times 10^5 to 4.5 \times 10^5 \Omega \text{ cm}^2 after 12 h of immersion. This result indicates the |Z| decline of E-B-3.

Fig. 8. Photographs of salt spray test after difference exposure times: (a) bare copper, (b) BTA-0, (c) ESol-0, (d) E-B-9, (e) E-B-3 and (f) E-B-1 samples. The exposure time was remarked in the photographs.
sample is lower than that of E-B-9 sample after 12 h of immersion, namely E-B-3 coating has better corrosion resistance than E-B-9. However, after 120 h of immersion, the impedance modulus of E-B-3 sample with $E_{1001} = 2.1 \times 10^4 \Omega \cdot cm^2$ is close to that of E-B-9 sample, indicating that E-B-3 also lose its anticorrosion ability. For E-B-1 sample, the $E_{1001}$ value is $2.1 \times 10^6$ and $1.6 \times 10^6 \Omega \cdot cm^2$ after 12 and 120 h of immersion, respectively, which is significantly greater than corresponding value of E-B-9 and E-B-3 samples. Those results verify that E-B-1 coating possesses relatively good anticorrosion ability.

3.5. Salt spray test

The neutral salt spray test was used to qualitatively determine the corrosion resistance performance of bare and coated copper samples. Fig. 8 shows photographs of copper samples after different exposure time in a salt spray chamber. As seen in Fig. 8a-c, BTA-0 and ESol-0 samples show better corrosion resistance than bare copper. But the protection performances of BTA-0 and ESol-0 coatings are weak, only after 24 h, severe corrosion has occurred on those samples- surface. It can also be concluded from Fig. 8 that the anticorrosion ability of ESol coating can be enhanced by combining BTA, namely the E-B-9, E-B-3 and E-B-1 sample show better resistance to salt spray than the ESol-0 one. In those coated samples, the corrosion resistance performance of E-B-1 sample is the best one. Those results of salt spray test are in accordance with the results of electrochemical measurements (PDS and EIS).

4. Conclusions

Experimental evidence clearly demonstrates that the ESol and BTA coating can provide inhibition of corrosion for copper, but their corrosion resistance is very weak. Combining the ESol coating and BTA can achieve an enhanced corrosion protection coating for copper according to the results of electrochemical measurements and salt spray test. Moreover, the best protection is achieved when the amount of BTA equals to the molar number of epoxy group in the ESol coating. The enhancement of BTA on corrosion protection of ESol coating could be interpreted by the following possible reasons: (i) BTA can prevent corrosion on copper surface as corrosion inhibitor, (ii) BTA can improve the hydrophobic of ESol coating and improve the adhesion of ESol coating to copper surface.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Nature Science Foundation (51202263 and 51105356), the China Postdoctoral Science Foundation Funded Project (2012T50564), the “Outstanding Talent Recruiting Program” (2009A31004) dedicated to Academician Qunji Xue from Ningbo municipal government.

References


