Synergistic effect of thiourea in epoxy functionalized silica sol–gel coating for copper protection

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ABSTRACT

In this paper, we try to employ a method of a combination of epoxy functionalized silica sol (ESol) and thiourea (TUA) to obtain a coating of excellent anticorrosion effect on copper. In order to compare the anticorrosion ability of the ESol + TUA coating with other coatings, the samples of ESol and ESol with diethylenetriamine (ESol + DETA) coatings have also been prepared. We use a variety of corresponding methods to study the properties of ESol with and without adding DETA and TUA. Aqueous contact angle analysis is used to evaluate the wetting properties of these sol–gel coatings. Scanning electron microscopy (SEM) is used to observe the surface morphology of these coatings and their cross sections. The anticorrosion ability of these coatings is evaluated by electrochemical methods and salt spray tests. The results show that ESol + TUA coating has the best anticorrosion ability. This is because adding TUA improves the physical barrier effect due to the denser coating compared to the regular ESol coating; in addition, it improves the adhesion between the coating and copper surface.

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1. Introduction

Copper is an important metal material because of its excellent thermal, mechanical, and electrical properties, and it is widely used in industry, agriculture, construction and daily use [1]. However, copper is very easy to be corroded when exposed to moist and chloride ion-rich environment [2]. If corrosion happens, copper would lose its beautiful appearance, and its excellent thermal, electrical, and mechanical properties. Therefore, in order to improve the service life of copper, surface protection of copper is needed [3].

Silica sol–gel coating is considered to be an excellent corrosion protection material of metal [4–11] because it has good adhesion on metal surface and it forms a very good physical barrier between the metal and corrosive substances [12]. The good adhesion is because of the fact that the Si-OH group in sol–gel forms a stable metal–O–Si bond on the metal surface [13–16], and the good physical barrier is because of the fact that the Si-OH group forms a hydrophobic, stable Si–O–Si three-dimensional network [17–19]. In many silica sol–gel coatings, epoxy functionalized silica sol–gel is widely used in the protection of magnesium [20], aluminum [21,22], and iron [23] alloys because of its water solubility [24], high stability [20] and reactivity of organic functional groups. In order to further enhance the protection performance, epoxy curing agents such as diethylenetriamine (DETA) [25–27], aminosilane [28], triethylenetetramine [20] and bisphenol A [29] were used to improve the crosslinking density of epoxy functionalized silica sol–gel coating. However, epoxy functionalized silica sol–gel coating does not provide a good anticorrosion performance when used on copper, because Si-OH has difficulty forming a stable Cu–O–Si bond on the copper surface [30]. In order to solve the problem, thiol functionalized silane was used alone [31–33] or as an adhesion promoter [34] to obtain a superior anticorrosion sol–gel coating on the copper surface, because this kind of silane can form a stable Cu–S bond on the copper surface [35].

Fig. 1. IR spectra of (a) pure TEOS, (b) GPTMS and (c) undiluted epoxy functionalized silica sol–gel solution on KBr pellet.
However, the use of thiol functionalized silane is limited by its poor water solubility and bad odor.

Here, we provide a new approach to modify epoxy functionalized silica sol–gel coating so that it has excellent anticorrosion ability on the copper surface. It is well known that some organic compounds with O, N, and S elements have strong interactions with copper [35–37], because they form coordination bonds or covalent bonds with copper, and some of them are used as copper corrosion inhibitor [38,39]. Based on this, we suggest that adding a corrosion inhibitor, which can crosslink the epoxy group, could greatly improve the anticorrosion ability of epoxy functionalized silica sol–gel on copper. We believe that adding this kind of corrosion inhibitors can improve the density of cross-linking of epoxy functionalized silica sol–gel coating, which causes better physical barrier; in addition, the corrosion inhibitor can also improve the adhesion of the coating on copper.

Specifically, epoxy functionalized silica sol (ESol) solution is prepared by hydrolysis of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS). Thiourea is selected to improve the corrosion resistance of the ESol coating, because it is a corrosion inhibitor [40,41] which react with the epoxy group. In addition, in order to evaluate the enhanced effect of TUA on the anticorrosion ability of the ESol coating, the samples of ESol and ESol with DETA (ESol + DETA) coatings on copper have also been prepared. Infrared spectra (IR), aqueous contact angle analysis, scanning electron microscopy (SEM), electrochemical test and salt spray test are used to evaluate the effect of TUA and DETA on the structure, wettability, morphology, and anticorrosion ability of the ESol coating.

2. Materials and methods

2.1. Materials

The copper was polished with sandpaper, and then degreased by ultrasonication in acetone. After being rinsed by water, the copper was dried with nitrogen. Tetraethoxysilane (TEOS), 3-glycidoxypropyltrimethoxysilane (GPTMS), formic acid, acetone, diethylenetriamine (DETA) and thiourea (TUA) were purchased from Aladdin Company. All reagents were used as received.

2.2. Preparation of ESol solution and the coatings

The epoxy functionalized silica sol–gel solution was prepared in a manner analogous to a previous report [26]. GPTMS, TEOS and 0.01 mol/l formic acid solution were stirred at room temperature for 5 h. The molar ratio of n (GPTMS):n (TEOS) was 3:1, and the molar ratio of water to hydrolyzable groups of GPTMS and TEOS is 1.5. The solution was then diluted with water to 10 wt.% solid content which was calculated by the value of the GPTMS and TEOS non-hydrolyzable groups. Taking three samples of the dilute solution equally, DETA and TUA were added into two of them respectively, and stirred for 5 min. The amount of TUA and DETA was used to make n (N–H)=n (epoxy) (or n (DETA):n (GPTMS)=1:5, n (TUA):n (GPTMS)=1:4). The sample without adding epoxy crosslinking agent was marked as ESol, the sample with DETA was marked as ESol + DETA, and the sample with TUA was marked as ESol + TUA. Copper samples were immersed in ESol, ESol + DETA, and ESol + TUA for 1 min, and then were dried at 100 °C for 1 h.

2.3. Methods

Infrared spectra were recorded on a Nicolet 6700 FTIR instrument equipped with a DTGS detector. Typically, 32 scans were co-added from 4000 to 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. TEOS, GPTMS and undiluted sol–gel solution were dropped on KBr tablets for measurement. Dried ESol, ESol + DETA and ESol + TUA coatings were ground into powder, and then mixed with KBr uniformly to press into tablets (1 mg samples into 100 mg KBrt) for IR measurements. The aqueous contact angle analysis was carried out to determine the wettability of sol–gel coatings using a Dataphysics OCA20 with sessile drop method. A 2 μl drop of distilled water was put on the surface with a micro liter syringe and observed through an optical
microscope. The value of the contact angle was an average of at least three readings at different locations on the surface of each sample. The morphology of the coating surface and its cross section were observed by scanning electron microscopy (Quanta FEG 250, FEI). In order to prepare the samples easily, sol–gel coatings are coated on the copper thin film which was deposited on a silicon chip by magnetron sputtering method.

The polarization curves 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 electrode system was used, wherein the saturated calomel electrode (SCE) is the reference electrode, the platinum sheet is the counter electrode, and the sample with the exposed area of 0.78 cm² is the working electrode. The scan rate of polarization curves was 0.001 V/s. EIS was recorded in a frequency range from 10⁴ to 10⁻² Hz with a perturbation amplitude of 10 mV at the corrosion 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 and 25 g CuCl₂·H₂O were added into 9.5 l water, and then the pH value was adjusted to the range of 3.2–3.3 by acetic acid.

3. Results and discussion

3.1. IR measurements

Fig. 1 shows the IR spectra of TEOS, GPTMS and undiluted epoxy functionalized silica sol–gel solution. For the IR spectrum of TEOS [42], the peaks at 1108, 1084 and 964 cm⁻¹ are due to the asymmetrical stretching vibration of Si–OC₂H₅, and the peak at 793 cm⁻¹ is due to the asymmetrical stretching vibration of SiO₄. For the IR spectrum of GPTMS [16,25], the peaks at 1255 and 911 cm⁻¹ are related...
with the epoxy group and the peaks at 1196 and 821 cm\(^{-1}\) are associated with Si-OCH\(_3\). In the IR spectrum of undiluted epoxy functionalized silica sol–gel, three peaks at 964, 821 and 793 cm\(^{-1}\) disappear, and the peak at 911 cm\(^{-1}\) is enhanced (911 cm\(^{-1}\) is also associated with Si-OH). This shows that the Si-OC\(_2\)H\(_5\) and Si-OCH\(_3\) groups transform into the Si-OH group, namely the hydrolysis reaction has occurred. In addition, the peak at 1255 cm\(^{-1}\) shows that the epoxy group is not broken.

Fig. 2 shows that the peaks at 1255 and 907 cm\(^{-1}\) still exist in the IR spectrum of the dried ESol, which indicates the existence of the epoxy group, but in the IR spectra of ESol + DETA and ESol + TUA, the disappearance of two peaks indicates the occurrence of epoxy crosslinking-reaction. Scheme 1 simply describes the hydrolysis reaction for TEOS and GPTMS and the crosslink reaction for the epoxy group and curing agents (TUA and DETA).

### 3.2. Surface wettability

Water static contact angle is used to characterize the wetting characteristics of copper and the coating surface. In Fig. 3a, water contact angle is 42° on the copper surface, and the contact angles are 63°, 62°, and 61° on the surfaces of the ESol, ESol + DETA, ESol + TUA coatings, respectively. That means that adding DETA and TUA does not remarkably change the wetting characteristics of epoxy functionalized silica sol–gel coating in this case.

### 3.3. Morphology of surface and cross section

We prepared three samples of each coating for SEM observation. Because the results are similar, only one image of each sample was shown in Fig. 4. In Fig. 4a, the surface of the ESol coating is very rough, and some pores can be seen on the surface. In Fig. 4b, some pores can also be seen on the surface of the ESol + DETA coating, but the surface is very smooth. In Fig. 4c, the surface of the ESol + TUA coating is very dense. These results are very similar with previous reports [43]. Adding epoxy crosslinking agent can make the epoxy functionalized sol–gel coating denser. In Fig. 4d, the image of the cross section shows the poor bonding performance of ESol and copper. The ESol coating could be obviously observed as peeled off from the copper surface. However, the ESol + DETA, and ESol + TUA coatings are firmly attached on the copper surface. This represents that adding DETA and TUA can effectively improve the bonding performance of the epoxy functionalized silica sol–gel coating and copper. In addition, a large amount of bubbles are observed in the cross section of the ESol + DETA coating, and these bubbles will weaken the corrosion resistance of the coating.

### Table 1

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(E_{\text{corr}}/\text{mV (vs SCE)})</th>
<th>(I_{\text{corr}}/\text{A cm}^{-2})</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>207</td>
<td>7.01 \times 10^{-7}</td>
<td>–</td>
</tr>
<tr>
<td>ESol</td>
<td>208</td>
<td>9.96 \times 10^{-8}</td>
<td>85.8</td>
</tr>
<tr>
<td>ESol + DETA</td>
<td>191</td>
<td>1.76 \times 10^{-8}</td>
<td>97.5</td>
</tr>
<tr>
<td>ESol + TUA</td>
<td>237</td>
<td>4.00 \times 10^{-9}</td>
<td>99.4</td>
</tr>
</tbody>
</table>

Fig. 6. EIS plots of bare copper electrode in 3.5 wt.% NaCl solution: (a) Nyquist plots and (b) Bode plots.

Fig. 7. EIS plots of ESol, ESol + DETA and ESol + TUA coating covered copper electrodes in 3.5 wt.% NaCl solution: (a) Nyquist plots and (b) Bode plots.
The polarization curves were conducted in a 3.5 wt.% NaCl solution. Fig. 5 presents the polarization curves of the bare copper electrode and copper electrode covered with a sol–gel coating. From these experiments, some parameters such as corrosion current density, and corrosion potential can be determined by the Tafel extrapolation method, and the results are listed in Table 1. In addition, the protection efficiency values were calculated according to the equation [45]

\[
\eta = \left(1 - \frac{i_{corr}}{i_{corr}^\circ}\right) \times 100\%
\]

where \(i_{corr}\) and \(i_{corr}^\circ\) are the corrosion current density of bare copper electrode and the corrosion current density of copper electrode coated with a sol–gel coating, respectively. The values of protection efficiency \(\eta\) are also listed in Table 1.

According to previous works in the literature [46,47], Tafel analysis for the coated metal electrode will be affected by the coating induced polarization and resistance drop effects, thus it is not suggested to analyze the polarization curves of coated electrode using the Tafel method. However, the Tafel method is often used to analyze coated electrodes to qualitatively compare the anticorrosion ability of a coating using the acquired parameters [48–50]. In Fig. 5 and Table 1, the corrosion potentials of the ESol, ESol + DETA, and ESol + TUA samples are \(-208, -191, -237\) mV, respectively. The values are not largely different from the corrosion potential of bare copper \((-207\) mV). Nevertheless, the coating significantly reduces the corrosion current density of the anode and cathode, and the corrosion current densities are \(9.96 \times 10^{-8}, 1.76 \times 10^{-8},\) and \(4 \times 10^{-9}\) A cm\(^{-2}\), respectively, and the corrosion current density of bare copper is \(7.01 \times 10^{-7}\) A cm\(^{-2}\). The reason for the decrease of corrosion current density is because the coatings impede \(O_2\) and \(Cl^{-}\) from reaching the copper surface and impede corrosion from the copper surface entering into the bulk solution. The values of protection efficiency of ESol, ESol + DETA, and ESol + TUA are calculated by Eq. (1) as 85.8%, 97.5%, and 99.4%, respectively, indicating that the ESol + TUA coating has better corrosion resistance than the ESol and ESol + DETA coatings.

### 3.5. Electrochemical impedance spectroscopy

Bare copper electrode was measured immediately after it was immersed in 3.5 wt.% NaCl solution, and the coated electrodes were measured after 30 min of immersion in the solution. As shown in Fig. 6, the Nyquist plots of bare copper electrode contain a capacitance arc and a Warburg impedance line. The result is very similar to the previous reports [33,51], so it is reasonable to use the equivalent circuit in Fig. 8a to analyze the EIS result of the bare copper. Fig. 7 presents the EIS plots of coated samples. From the Nyquist diagram of ESol (Fig. 7a), Warburg impedance is also observed. The presence of Warburg impedance means that ESol is not good in impeding the diffusion of \(O_2\) and corrosion products. This result happens to coincide with the SEM result which shows that the ESol coatings are porous. In addition, a broad peak in the phase angle diagram of the ESol sample indicates that the ESol coating results in an extra time constant. Therefore, it is reasonable to use the circuit shown in Fig. 8 to analyze the EIS result of the ESol electrode coated sample. For the samples of ESol + DETA and ESol + TUA, either the shape or size of Nyquist diagrams is different from the ESol and bare copper sample. Obviously, the Nyquist plots of ESol + DETA and ESol + TUA are composed of two indistinct capacitive loops, and the disappearance of the Warburg impedance indicates that ESol + DETA and ESol + TUA can well prevent the mass diffusion process. The EIS results of ESol + DETA and ESol + TUA can be analyzed through the circuit shown in Fig. 8c.

In the equivalent circuits presented in Fig. 8, \(R_s\) is the resistance of the solution between the working electrode and the reference electrode; \(R_t\) is the charge transfer resistance between the metal surface and the solution interface; \(W\) is Warburg resistance; \(R_{film}\) is the transfer resistance of the electrons through sol–gel coating; \(Q_{fil}\) is the capacitance of the metal surface/electrolyte interface; and \(Q_{fil}\) is the capacitance of sol–gel coating, wherein the standard capacitance is replaced by the constant phase angle element in order to describe the capacitance accurately [52]. The value of each element in the equivalent circuits was calculated by the ZSimp-Win software and the results were listed in Table 2. The value of polarization resistance is used to evaluate the anticorrosion ability of the coatings, and the equation of polarization resistance (\(R_p\)) is as:

\[
R_p = R_{film} + R_t
\]

### Table 2: Values of elements in equivalent circuit to fit EIS for bare and sol–gel coating covered copper electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Bare</th>
<th>ESol</th>
<th>ESol + DETA</th>
<th>ESol + TUA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{film}/\Omega)</td>
<td>7.17 (1.84)</td>
<td>14.62 (22.12)</td>
<td>18.26 (5.69)</td>
<td>11.34 (5.25)</td>
</tr>
<tr>
<td>(Q_{fil}/\mu F/cm^2)</td>
<td>0.80 (0.89)</td>
<td>0.57 (13.79)</td>
<td>0.74 (1.18)</td>
<td>0.79 (11.2)</td>
</tr>
<tr>
<td>(\eta/%)</td>
<td>0.80 (5.06)</td>
<td>1.88 \times 10^{-5} (25.79)</td>
<td>6.25 \times 10^{-5} (1.13)</td>
<td>3.04 \times 10^{-5} (13.21)</td>
</tr>
</tbody>
</table>

* The values in brackets correspond to the error (%) of each parameter.

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**Fig. 8.** Equivalent circuits were used to analyze the EIS plots: (a) for bare copper, (b) for ESol covered copper, and (c) for ESol + DETA and ESol + TUA covered copper.
Fig. 9. Photographs of salt spray test after different exposure times (0 h, 4 h, 20 h, 68 h and 178 h): (a) bare copper, (b) ESol, (c) ESol+DETA, and (d) ESol+TUA coated copper substrates.
where $R_{\text{film}}$ is the transfer resistance of the electrons through sol–gel coating; and $R_{c}$ is the charge transfer resistance between the metal surface and the solution interface. From Table 2, $R_{c}$ significantly increases after copper electrode covered sol–gel coating, and the $R_{c}$ value of the ESol + TUA coated sample is much greater than the values of the ESol and ESol + DETA coated samples. Also, Table 2 clearly shows that the $R_{\text{film}}$ value of the ESol + TUA coating is greater than the values of the ESol and ESol + DETA coatings. By comparing the $R_{c}$ values of the coatings, the result is ESol + TUA > ESol + DETA > ESol, indicating that the ESol + TUA coating has the best corrosion resistance, and the results coincided with the polarization curve measurement.

### 3.6. Salt spray test

Fig. 9 shows the pictures of the salt spray tests of the ESol, ESol + DETA, and ESol + TUA coatings and bare copper by timeline. Fig. 9a shows that severe corrosion occurs on bare copper after being exposed in the salt spray for 4 h. Fig. 9b shows that the ESol coated copper surface is covered with rust after 20 h, indicating the poor corrosion resistance of the ESol coating. This result coincided with the electrochemical test result. However, it was surprising that the ESol + DETA coating is very easily damaged by the salt spray and peeled off from the copper surface, even though the electrochemical measurement shows that the ESol-DETA has good anticorrosion performance. Fig. 9c (ESol + DETA 0 h) shows that the ESol + DETA coating is light blue which might be associated with copper ions. According to reports [53], DETA can promote copper dissolution by forming copper coordination compounds which lead to a large number of copper ions in the ESol + DETA coating. This might be the reason why the resistance to salt spray of the ESol + DETA coating is not good. On the other hand, the ESol + TUA coating shows a very good resistance to salt spray (Fig. 9d). After being exposed in salt spray for 178 h, the rust only appears at the edge of the copper. The results of the salt spray test also indicate that the ESol + TUA coating can protect the copper well.

The excellent anticorrosion performance of the ESol + TUA coating for copper is because of the fact that TUA plays a dual role in the enhancement of ESol corrosion resistance: (1) as a cross-linking reagent, it makes epoxy functionalized sol–gel coating denser to improve the barrier effect of coating; and (2) as an adhesion promoter, it improves the bonding between epoxy functionalized sol–gel coating and copper. Scheme 2 simply describes the different behaviors of DETA and TUA on the copper surface.

### 4. Conclusions

This study introduces a new approach to enhance the protection performance of epoxy functionalized silica sol–gel coating for copper. SEM images show that the ESol + TUA coating is very dense, and adheres well to the copper surface. The salt spray test and electrochemical test show that the ESol + TUA coating has excellent corrosion resistance performance on copper. TUA enhances corrosion resistance of the epoxy silica sol–gel coating because of two reasons: (1) TUA works as a cross-linking reagent to make the epoxy functionalized silica sol–gel coating denser, thereby improving the coating barrier effect; and (2) TUA has strong interactions with copper that tighten the epoxy functionalized silica sol–gel coating bond on the copper surface.

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