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Surface protection of copper by allyl thiourea and hybrid sol–gel coatings

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ABSTRACT

A novel approach has been adopted in the surface protection of copper by combining allylthiourea (ATU) and two silanes viz., 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) forming the hybrid sol–gel coating which is designated as Hy. At first ATU was immobilized on the copper surface to introduce active tail amino groups. Subsequently, Hy sol–gel was grafted onto the ATU modified copper surface. The interaction of ATU with copper and Hy monolayers were investigated by Fourier transform infrared spectroscopy (FT-IR) which revealed the chemisorption of ATU through Cu–S bonds. Besides, it also exposed the cleavage of epoxy ring due to the reaction with free amino groups of ATU. The surface protection of these monolayers were examined by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization studies (PDS) and cyclic voltammetric (CV) techniques, while the surface morphology was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. These results indicated that combination of ATU and Hy sol–gel coatings over copper displayed excellent surface protection.

1. Introduction

Copper has a wide range of applications due to its excellent thermal, mechanical and electrical properties. However, it is easily corroded when exposed to aggressive environments [1]. Self-assembled monolayers (SAMs) can produce effective barriers to the penetration of corrosive species like water, oxygen, and aggressive ions onto the surface of reactive metals like copper [2]. SAMs bind to the substrate and they undergo spontaneous self-organization process by an aliphatic chain. SAMs have been used as primers to improve the adhesion of a second coating via physical interaction (or) chemical bonding of tail groups with head groups of second coating [3–5]. Several types of organic compounds such as alkanethiols [6–10], alkyl thiosulfate [11], aromatic thiols [12–14], Schiff bases [15,16], amino acids [17–19], phytic acid [20] and organo silanes [21] have been employed to grow SAMs on copper to protect it from corrosion.

The typical environmental hazardous chromium conversion coatings have now been substituted by the eco-friendly sol–gel coatings [22]. In general, epoxy functionalized silica sol–gel coating is widely used in the protection of aluminium [23,24], iron [25] and alloys because of its water solubility, high stability [26] and high reactivity of organic functional groups. When epoxy sol–gel coating is used on copper, adequate protection of copper could not be achieved since silanols have difficulty to form Cu–O–Si bonds needed for protection [27]. Here this difficulty was overcome by modifying the bare copper surface with ATU. It has been reported that allylthiourea (ATU) showed better inhibition than thiourea (TU) due to a stronger chemisorption with copper [28]. To the best of our knowledge, there are no reports on the use of allylthiourea in the sol–gel coatings. In the present study, an alternative approach involving in the surface modification of copper by ATU has been adopted. Subsequently, Hy monolayers were assembled onto the ATU modified copper surface through epoxy-amine reaction. FT-IR spectroscopy was used to scrutinize the interaction of ATU with copper and Hy monolayers. The anticorrosion behavior of these monolayers in 1% NaCl solution was evaluated by cyclic voltammetric (CV), potentiodynamic polarization studies (PDS) and electrochemical impedance spectroscopy (EIS) techniques. These analyses were supplemented with SEM and AFM studies.

2. Experimental

2.1. Materials and chemicals

Allylthiourea (ATU), 3-Glycidoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich (India) and used as received. All the chemicals used in this

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study were of analytical grade and the solutions were prepared with Milli-Q water.

2.2. Pretreatment of electrodes

The working electrode was made from copper (99.99%) rod embedded in a Teflon sheath with an approximate surface area of about 0.75 cm^2 was successively polished with different grades of emery papers (0–7 grit) and 0.3 μm alumina. The polished electrode was rinsed subsequently with Milli-Q water and ethanol. Finally, the electrode was treated in an ultrasonic bath to remove any existed alumina and carbon oxide produced during polishing process.

2.3. Hybrid sol and allylthiourea solution preparation

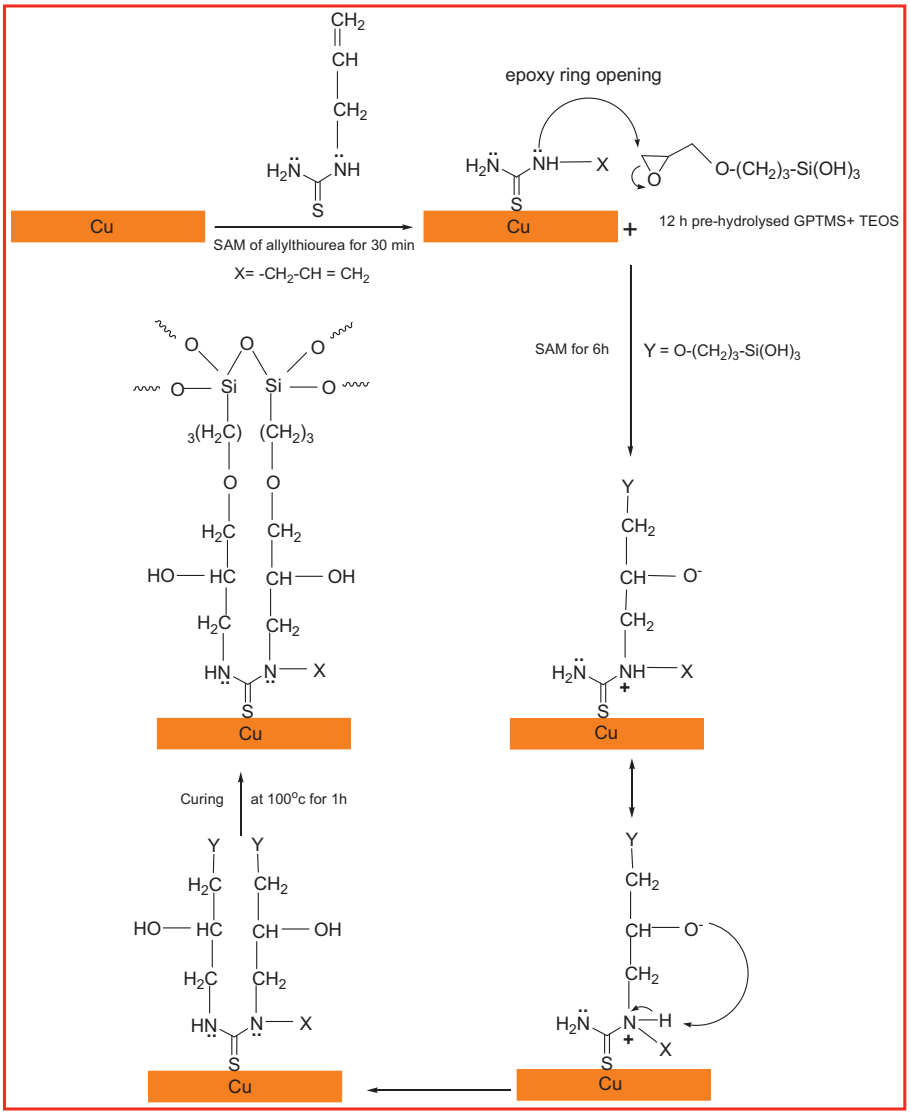
Ethanolic ATU solution (25 mM) was used as a precursor solution. Hybrid silica sol was prepared by mixing GPTMS, TEOS and H_2O in the molar ratio of 3:1:1.5. The resulting sol was subjected to hydrolysis for 12 h at room temperature and the pH was adjusted to 4 by adding 0.1 M HNO_3 [29].

2.4. Formation of self-assembled monolayers

The pretreated electrodes were immersed in ethanolic solution of ATU (25 mM) for about 30 min [28,30]. Later, the modified electrodes were washed thoroughly with ethanol to remove the physically adsorbed ATU and were marked as ATU/Cu. Afterwards, Hy silica sol was grafted onto the ATU/Cu surface by immersing the modified copper electrode into the hybrid sol for 6 h. Finally, the assembled electrodes were rinsed, first with Milli-Q water and then with methanol. It is subjected to curing at 100 °C for 1 h in an oven. The copper electrode with both ATU and Hy monolayers were designated as Hy/ATU/Cu. For comparative study, the experiment was repeated with bare copper electrode forming the self-assembled Hy layers over copper directly without pre-modification (designated as Hy/Cu). The possible self-assembly of ATU and subsequent grafting of Hy silica sol onto copper surface was displayed in (Scheme 1) [31,32].

2.5. Characterization of monolayers by FT-IR

Fourier transform infrared (FT-IR) spectra of the scratched layers of Hy/Cu, ATU/Cu and Hy/ATU/Cu electrodes have been carried out



Scheme 1. Possible self-assembly of ATU and Hy silica sol–gel onto copper surface.

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