Comparative Analysis of Triazine Self-Assembled Nanofilm with/without Fluorine Substituent on Copper Alloy Surface

Mengke Jia, Jiaolong Wang, Mingshu Shi, Fang Wang[*]

College of Science, Northwest A&F University, Xinong Road No.22, Yangling, Shaanxi, 712100, China
[*]E-mail: wangfang4070@nwsuaf.edu.cn

The self-assembled nanofilms of 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiolmonosodium (AF17N) and 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) were successfully fabricated on copper alloy surface. Surface wettability and coverage of the nanofilms were investigated by contact angle, surface free energy and cyclic voltammetry. Anticorrosion ability and surface morphology of the nanofilms were studied by potentiodynamic polarization, saline immersion test and scanning electron microscopy. The results show that the contact angle of copper surface modified by cured AF17N self-assembled film is up to 124.1° with the lowest surface free energy of 9.653 mJ/m^2. Cyclic voltammetry reveals that the cured AF17N and DAN nanofilms are more homogeneous compared with uncured samples. Also, potentiodynamic polarization and saline immersion test demonstrate that the cured AF17N self-assembled film has better anticorrosion ability, which plays a significant role in metal protection and leads a further improvement in corrosion resistance.

1. INTRODUCTION

Nowadays, copper alloy is widely applied as an important material due to its excellent properties, such as high electrical, thermal conductivity, outstanding mechanical workability and superior inactive characteristics. However, the presence of different corrosive species such as chloride, sulfate and nitrate ions make copper alloy more susceptible to localized corrosion after exposure in aggressive environments [1].

The organic compounds, azoles [2], amines [3] and amino acids [4] using as protective agent for copper alloy is well known and has been widely reported. However, with the increase of

environment conservation and safety consciousness, these corrosion inhibitors are limited to use now. In recent years, the self-assembled monolayers (SAMs) have been developed to be applied in the field of metal protection [5, 6]. Among them, triazinedithiol, which has thermally stable triazine ring and two highly reactive thiol groups, is a typical compound in metal pretreatment industries. The researchers found that the nanofilms prepared by different triazinedithiols had basic anticorrosion property. The chemistry of aromatic and heterocyclic compounds containing fluorine substituents has developed rapidly now. It has become a large division of the chemistry of intermediate products which are widely used for synthesizing pesticides, drugs, dyes and monomers for polymeric materials. Fluorinated polymers exhibit a unique combination of notable lubricity [7], chemical inertness (to acids, bases, solvents and petroleum), high dielectric [8], excellent weather ability and a good resistance to oxidation, etc. And the cladding that contains a fluorinated group can provide good hydrophobicity [9, 10].

In this study, the heterocyclic monomer containing fluorine substituent of 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium (AF17N) was chosen to prepare the nanofilm on copper alloy by self-assembled method. The self-assembled nanofilm of 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) without fluorine substituent was also fabricated to compare the difference of nanofilms with/without fluorine substituent. And the effect of curing treatment on nanofilms was studied. The characteristics of nanofilms were analyzed by means of contact angle (CA), cyclic voltammetry (CV), potentiodynamic polarization and scanning electron microscope (SEM).

2. EXPERIMENTAL

2.1 Materials and reagents

Copper alloy (Cu: 88.0~91.0%; Zn: 9.0~12.0%) with the dimension of $50 \times 20 \times 0.2$ mm was prepared by cutting a large plate into pieces.
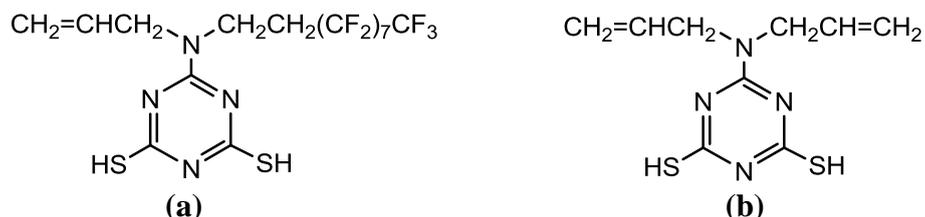

Figure 1. The molecular structures of AF17N and DAN (a) AF17N; (b) DAN

The surface of copper alloy plate was polished with 2.5 μm, 1.5 μm and 0.5 μm diamond spray polish does, followed by ultrasonic degreasing in acetone and dried in air at room temperature. 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was synthesized by the reaction between

6-N,N-diallylamino-1,3,5-triazine-2,4-dichloride and sodium hydrosulfide (NaSH) according to the method in the previous study [11]. 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium (AF17N) was prepared by reaction between 6-(N-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dichloride and NaSH [12]. The molecular structures of AF17N and DAN are shown in Figure 1. Double distilled water was used as a solvent. The concentration of DAN and AF17N self-assembled solution was 1 mmol/L.

2.2 Preparation of DAN or AF17N nanofilm on copper alloy surface

The polished copper alloys were immersed in the solution of DAN or AF17N for 60 min, followed by being rinsed with ethanol and then blow-dried in air stream. The curing treatment of copper alloy with DAN or AF17N nanofilm was conducted for 15 min in 150°C oven.

2.3 Characterization

The wettability and surface free energy of copper surface modified by DAN or AF17N self-assembled nanofilms were measured by optical contact angle instrument (SL100) at room temperature. The coverage of nanofilms was examined by CV at 20 mV/s scanning rate using electrochemical work station (CHI660C) in 0.1 mol/L sodium hydroxide (NaOH) aqueous solution. The counter electrode is stainless steel plate (SUS304) and the reference electrode is saturated calomel electrode (SCE). Potentiodynamic polarization tests were carried out to evaluate the anticorrosion property of nanofilm by CHI600C electrochemical workstation with the scanning rate of 1 mV/s. A three-electrode system was applied, in which the working electrode is copper alloy, counter electrode is graphite plate and reference electrode is SCE, and the electrolyte solution is 0.5 mol/L sodium chloride (NaCl) aqueous solution. Saline immersion test was conducted for 7 days in 0.5 mol/L NaCl aqueous solution at room temperature. The surface morphologies of coated and uncoated copper alloys were observed by SEM (JSM-6360LV) at the accelerating voltage of 20 kV.

3. RESULTS AND DISCUSSION

3.1 Wettability of coated and uncoated copper alloy

The changes of CA and surface free energy were used to characterize the wettability of copper alloy surface with different coatings. In the Figure 2, the CA of blank copper alloy was 83.7° and surface free energy was 33.43 mJ/m^2. For the DAN coated plates, the CA and surface free energy had not apparent change compared with that of blank. After the curing treatment of DAN coatings, the CA increased and the surface energy decreased slightly. It was assumed that the partial allyl groups in the DAN self-assembled nanofilm could react with each other by thermal polymerization to form the weakly cross-linked film to some extent. However, the contact angle was up to 117.6° for AF17N self-assembled nanofilm and increased to 124.1° for cured AF17N nanofilm, which suggested that the

AF17N self-assembled nanofilms on copper alloy surface exhibited better hydrophobic property. The higher CA of uncured AF17N self-assembled nanofilm attributed to the existence of many fluorine substituents in AF17N self-assembled nanofilm. The long fluorine replaced methylene group in top layer decreased the surface free energy significantly. The improvement of CA for cured AF17N nanofilm was also due to the fact that the partial allyl groups in the AF17N self-assembled nanofilm could react with each other by curing to form the weakly cross-linked film on substrate surface. Humid environment was one reason of copper alloy corrosion, and the hydrophobic surface of coated substrate was benefit for the protection of copper alloy from corrosion [13]. It was concluded that curing treated AF17N self-assembled nanofilm had excellent protective effect for copper alloy.
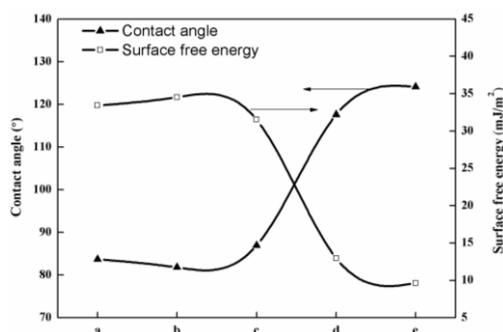

Figure 2. Contact angle and surface free energy of coated and uncoated copper alloy (a) blank; (b) uncured DAN; (c) cured DAN; (d) uncured AF17N; (e) cured AF17N

3.2 Cyclic voltammetry for evaluation of nanofilm coverage

Figure 3 displayed a comparison of the cyclic voltammograms of different self-assembled films modified copper alloy surface. It can be seen that the coated and uncoated plates have no significant influence on the general shape of the cyclic voltammograms. Two obvious activated anodic peaks (I and II) were observed for the blank copper alloy, which was due to the oxidation of copper to form Cu_2O and CuO on substrate surface [14].
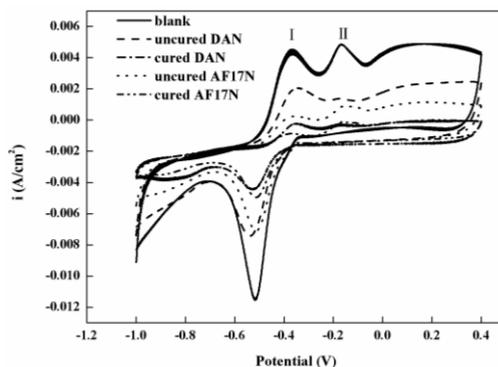

Figure 3. Cyclic voltammograms of blank and self-assembled film modified copper alloy

Cathodic peak was resulting from the reduction of copper oxide. While, the oxidation-reduction currents of the self-assembled nanofilm modified copper alloy surface were much less than that of blank. The differences were attributed to the formation of coordination bond between copper and thiol groups in DAN or AF17N, which led to the production of Cu-DAN or Cu-AF17N complex on the copper surface to make the oxidation of copper be depressed. In addition, the oxidation-reduction currents of cured AF17N or DAN nanofilms modified copper alloy surface were even much smaller than that of uncured nanofilms, which was owing to the formation of the weakly cross-linked film by the curing.

The previous information can be supported by the change of anodic and cathodic peak potentials, oxidative and reductive reaction current density and the area of the cyclic voltammograms as shown in table 1. By comparison of the area of CV curves for different self-assembled nanofilms modified copper alloy electrodes, it was found that the area of CV curves for cured AF17N and DAN nanofilms modified copper alloy surface was the smallest, which demonstrated that the cross-linked film was formed after the curing and made the resistance of copper alloy surface increase.

Table 1. Peak potential, oxidative and reductive current density and the area of CV for different self-assembled nanofilms modified copper alloy

Type of self-assembled nanofilms	Anodic peak I potential (V)	Anodic peak II potential (V)	Oxidative current density (mA/cm^2)	Cathodic peak potential (V)	Reductive current density (mA/cm^2)	Area of CV curves (10^{-4})
blank	-0.37	-0.17	4.86	-0.52	-11.5	63.07
uncured DAN	-0.35	-0.18	2.07	-0.54	-7.44	42.42
cured DAN	-0.35	-0.17	-0.239	-0.53	- 3.23	8.062
uncured AF17N	-0.36	-0.15	0.886	-0.51	-7.10	29.65
cured AF17N	-0.37	-0.16	-0.806	-0.51	-4.95	15.55

3.3 Potentiodynamic Polarization

To investigate the protective effect of these self-assembled nanofilms for copper alloy substrate, the potentiodynamic polarization was conducted in 0.5 mol/L NaCl aqueous solution as presented in Figure 4. Electrochemical corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and anodic/cathodic tafel slopes (β_a and β_c) by extrapolation of the tafel lines, are given in table 2. Based on the approximate linear polarization, the corrosion potential (E_{corr}), polarization resistance (R_P) and protection efficiency (PE) were calculated by the following relationships [15, 16].

$$R_P = \beta_a \beta_c / 2.3 \, I_{corr} \, (\beta_a + \beta_c) \qquad (1)$$
$$PE = (1 - I_{corr} / I_0) \times 100\% \qquad (2)$$

where I_{corr} and I_0 represent the corrosion current density of self-assembled nanofilm modified copper alloy and blank copper alloy, respectively.
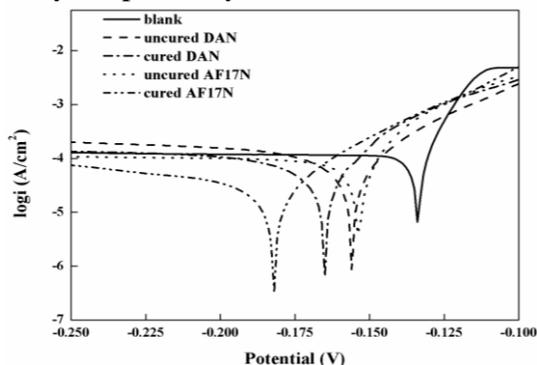

Figure 4. Potentiodynamic polarization curves of coated and uncoated copper alloy in 0.5 mol/L NaCl solution

Table 2 shows that the corrosion current density of blank copper alloy (I_0) is 2.304×10^{-3} A/cm^2, while the corrosion potential E_{corr} is -0.134 V. As for the samples with uncured DAN, cured DAN and uncured AF17N nanofilm, I_{corr} decreased one order of magnitude and E_{corr} also slightly decreased. The corrosion current density of cured AF17N nanofilm modified copper alloy decreased two orders of magnitude and E_{corr} decreased to -0.182 V, which indicated that I_{corr} was far lower than that of blank copper alloy. The negative shift of E_{corr} indicated that these self-assembled nanofilms could inhibit the cathodic reaction to some extent. At the same time, it can also be conclude that the polarization resistance and protection efficiency of cured AF17N nanofilm were higher than that of other nanofilms. All of the results demonstrated that the cured AF17N nanofilm could be served as a protective layer for copper alloy surface and exhibit excellent anticorrosion performance.

Table 2. Parameters of potentiodynamic polarization curves and protection efficiency for different self-assembled nanofilms modified copper alloy

Sample	E_{corr}(V)	I_{corr}(A/cm^2)	β_a	β_c	R_p(Ω/cm^2)	PE
blank	-0.134	2.304×10^{-3}	5.678	0.646	1.09×10^2	-
uncured DAN nanofilm	-0.156	4.280×10^{-4}	7.229	1.68	1.39×10^3	81.4%
cured DAN nanofilm	-0.165	2.538×10^{-4}	11.12	0.783	1.75×10^3	89.0%
uncured AF17N nanofilm	-0.154	5.464×10^{-4}	9.104	0.555	7.17×10^2	76.3%
cured AF17N nanofilm	-0.182	5.906×10^{-5}	21.25	1.97	1.33×10^4	97.4%

3.4 Surface morphologies

To further investigate the performance of nanofilms, the morphologies of copper alloy surface were observed by SEM. For the blank copper alloy surface (Figure 5a), the scratches introduced in rolling and polishing process could be observed distributed all over the surface. As for the surfaces covered by uncured and cured DAN nanofilms (Figure 5b and 5c), the original morphology of copper

alloy surface became gradually vague. However, some comparatively large pores and scratches could still be observed. The fringes of the copper alloy surface completely disappeared for cured AF17N nanofilm covered substrate and the surface was more homogenous (Figure 5e). It was assumed that the thiol and allyl groups in the AF17N nanofilm reacted with each other by curing which might lead to the formation of more compact nanofilm on the substrate surface. Therefore, the scratches of the copper alloy surface could not be seen after the assembling process of triazine nanofilm with fluorine substituent. It was concluded that the cured AF17N nanofilm could modify the copper alloy surface more effectively.
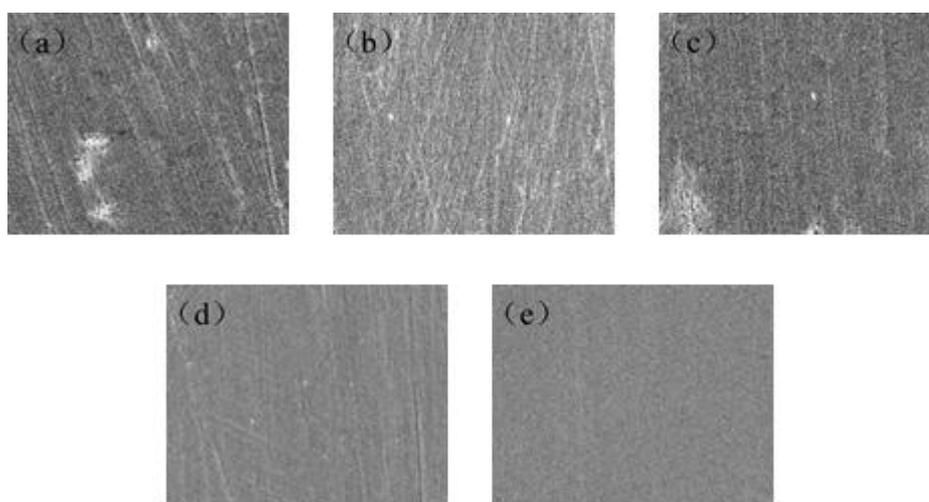

Figure 5. SEM images of blank and nanofilm treated copper alloy (a) blank; (b) uncured DAN; (c) cured DAN; (d) uncured AF17N; (e) cured AF17N
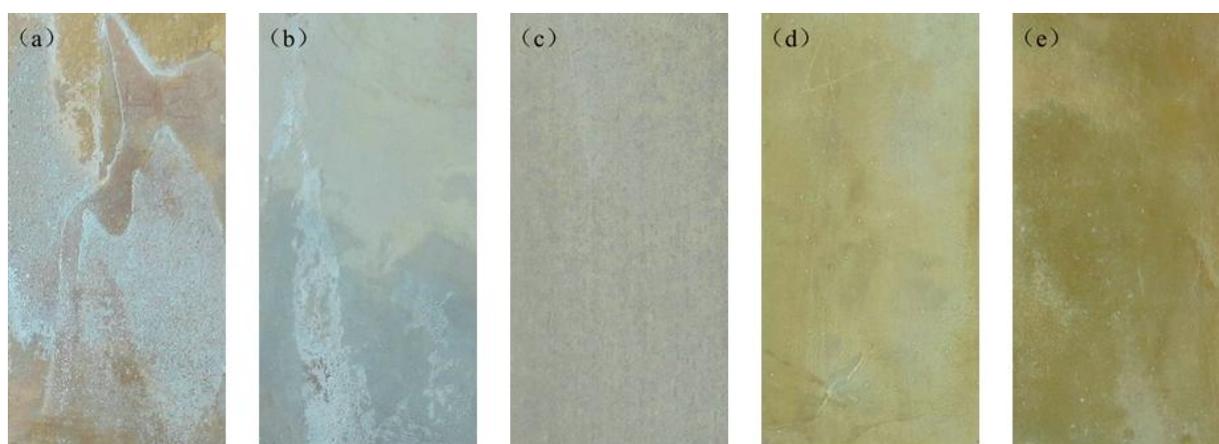
3.5 Saline Immersion Test

Figure 6. Photographs of blank and treated copper alloy in 0.5 mol/L NaCl solution (a) blank; (b) uncured DAN; (c) cured DAN; (d) uncured AF17N; (e) cured AF17N

To evaluate the property of coated and uncoated copper alloy surface, the test of saline solution immersion was carried out. The surface of blank copper alloy (Figure 6a) became green and corroded, indicating that the corrosive species had etched into the inner of substrate. In contrast, the corrosion reaction of the surface covered by DAN nanofilms (Figure 6b and 6c) became slow, especially for the surface covered by cured DAN nanofilm, which was owing to the inability of the chloride ions to penetrate through the surface of the DAN coated films. Figure 6d and 6e exhibited the surface photographs modified by AF17N nanofilms. The original color of copper alloy was maintained, which suggested that the copper alloy surface with cured AF17N nanofilm hardly suffered corrosion.

For the residuals of corrosive substance after saline immersion test, it could be examined by SEM images (Figure 7). As shown in the Figure 7a, many salt particles were observed on the blank copper alloy surface and the bigger aggregates of salt particle existed on the substrate, which demonstrated that the blank copper alloy was apt to be corroded [17]. No obvious changes were observed for the copper alloy surface (Figure 7b and 7c) with DAN nanofilms except that the salt particles and aggregates became a bit smaller. However, the surface covered by AF17N nanofilms (Figure 7d and 7e) had fewer and smaller salt particles after saline immersion and the salt particles on the surface modified by cured AF17N nanofilm was the fewest, which demonstrated that the cured film bestowed effective corrosion protection for copper alloy. The good consistence of potentiodynamic polarization, CV and saline immersion test indicated the excellent anti-corrosion performance of AF17N nanofilm.
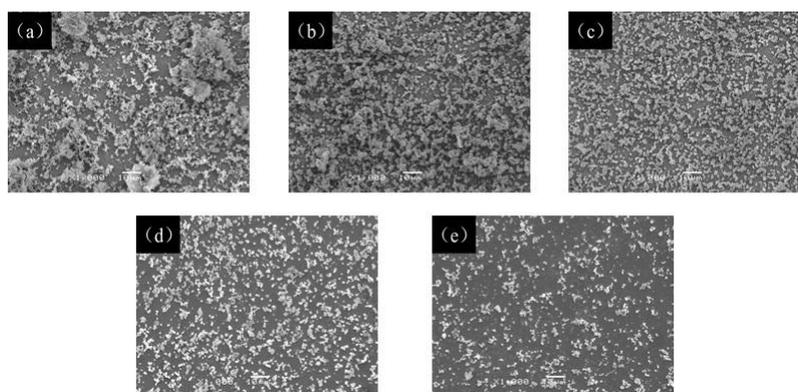

Figure 7. SEM images of blank and treated copper alloy in 0.5 mol/L NaCl solution (a) blank; (b) uncured DAN; (c) cured DAN; (d) uncured AF17N; (e) cured AF17N

4. CONCLUSIONS

Triazine nanofilms with/without fluorine substituent were easily constructed on copper alloy surface based on self-assembled method. The results indicated that the substrate surface with cured AF17N self-assembled film was more homogeneous and the contact angle was up to 124.1°, which exhibited the excellent hydrophobic property. Potentiodynamic polarization and saline immersion test demonstrated that cured AF17N self-assembled film on copper alloy surface had excellent

anticorrosion ability and the protection efficiency of cured AF17N nanofilm reached 97.4%. The cured AF17N nanofilm was expected to meet application requirements of the triazinedithiol film in the metal protection field.

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