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Complex Barrier Layer of Triazinedithoil Prepared by Electrodeposition and Initiated Polymerization on Aluminum Alloy towards Corrosion Protection

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In order to improve the protection abilities of electrodeposited nanofilm of 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) on aluminum surface, cross-linked complex barrier layer was then fabricated successfully by initiated polymerization of DAN as monomer and potassium persulfate as initiator. Electrodeposited nanofilm of DAN was prepared by two-step potential electrodeposition. The formation of electrodeposited nanofilm and complex layer were confirmed by fourier transform infrared spectroscopy (FT-IR). The surface wettability was characterized by contact angle (CA). Cyclic voltammetry was applied to study the compactness of electrodeposited nanofilm and complex layer. The corrosion protection was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and saline immersion test. The surface morphologies were observed by scanning electron microscope (SEM). It was showed that cross-linked complex barrier layer on aluminum surface exhibited remarkable corrosion protection property.

Keywords: Aluminum Alloy; Electrodeposition; Initiated Polymerization; Anti-corrosion

1. INTRODUCTION

Aluminum alloy is a metal extensively used in automobile and aerospace industries because of its excellent properties (low density, easy modeling, high mechanical intensity, etc.) [1-2]. However, it is susceptible to different forms of corrosion, for example pitting, which is induced by different corrosive species such as chloride, sulfate and nitrate ions [3]. Aluminum alloys can be pretreated with various chemicals such as zirconium, chromium compounds and phosphates, but the environmental protection guidelines set strict limits for the use of them [4-5]. Therefore, many researches have been carried out to develop environmental friendly methods [6-7].

In recent years, there is a rapid upsurge of “green” technology in the field of corrosion control of metals as one of the highly ranked proposed replacements for the conventional chromating [8-10]. Among them, the surface treatment of triazinedithiols has evolved as a promising alternative for toxic chromate-based treatment. Since the electrosynthesis of polymeric nanofilm with triazinedithiols is relatively inexpensive and convenient, such compounds have been applied in the fields of metal protection [11-12]. It is known that triazinedithiol compounds have thermally stable triazine ring and two highly reactive thiol groups. Electrochemical polymerization of triazinedithiol compounds have been utilized to prepare homogeneous, oriented and packed nanofilm on the metal surface. These researches showed that the polymeric nanofilm had basic anti-corrosion property. However, the nanofilms have the propensity for containing molecule-sized defects to some extent, which lead to sufficiently high protective ability unobtainable. In order to improve the protective ability of the nanofilm, the further modification of thicker and more densely cross-linked polymer film to the electrodeposited nanofilm surface is considered to prevent the diffusion of corrosive species like O_2, OH^-. It is expected that the complex films can supplement the drawbacks of electrodeposited nanofilm mentioned above and improve the ability of anti-corrosion significantly.

In this study, the electrodeposited nanofilm of triazinedithiol with two allyl groups 6-N,N-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) was first prepared by two-step potential electrodeposition. Then the outside allyl groups of electrodeposited nanofilm were chemically modified by initiated polymerization in the solution of DAN and potassium persulfate to form cross-linked complex barrier layer. No related researches have been reported so far. The characteristics of complex layer on aluminum surface were analyzed by contact angle, scanning electron microscope (SEM), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL SECTION

2.1. Materials

AA5052 (Cu: 0.1%, Si: 0.2%, Fe: 0.4%, Mn: 0.1%, Mg:2.8%, Zn: 0.1%, Cr: 0.3%, others: 0.15%) with the dimension of 30 ×50 ×0.3 mm was prepared by cutting pieces from a sheet of aluminum alloy plate. 6-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 NaSH according to the method in the previous study [13]. All of the chemicals were employed as analytical reagents (AR) without further purification. Distilled water was used as solvent, and $NaNO_2$ was applied as supporting electrolyte in the electrodeposition. Potassium persulfate ($K_2S_2O_8$) was used as initiator for initiated polymerization. The concentrations of DAN, $NaNO_2$ and $K_2S_2O_8$ were kept at 2 mM, 0.15 M and 1 mM, respectively.

2.2. Preparation of Complex Barrier Layer

The electrodeposited nanofilm of DAN was fabricated by two-step potentiostat using electrochemical work station (CHI 660C) on AA5052 surface. The potential of 1.6 V was used in the first step, then 6V was applied for the second step. Electrodeposition time was 30 and 20 s for the two steps, respectively. A three-electrode system was applied, in which the working electrode is AA5052, counter electrodes are stainless steel plates and reference electrode is the saturated calomel electrode.

AA5052 surface covered by DAN electrodeposited nanofilm was further modified by initiated polymerization in the solution of 2 mM DAN and 1 mM $K_2S_2O_8$ for 30 minutes, followed by being rinsed with acetone, dried in nitrogen air and cured for 10 minutes at 100 °C to form the cross-linked complex barrier layer on AA5052 surface.

2.3. Characterization

FT-IR was carried out by attenuated total reflection spectroscopy (Bruker TENSOR 37). The contact angle was measured at room temperature (SL100). Corrosion tests were investigated by potentiodynamic polarization and EIS in 0.5 M NaCl aqueous solution. The exposed area was controlled at 1.0 cm^2. Potentiodynamic polarization test was conducted from -1.1 V to -0.7 V with the scanning rate of 5 mV/s. EIS was recorded after 1 hour immersion time in 0.5 M NaCl solution under open-circuit potential. The frequency of the potential perturbation was varied from 10 kHz to 10 mHz with the excitation voltage of 5 mV. The saline immersion test was carried out in 0.5 M NaCl aqueous solution for 15 days at room temperature. The morphologies of blank and AA5052 surfaces modified by electrodeposited and complex nanofilms were observed by SEM (JSM-6360LV) at accelerating voltage of 20 kV.

3. RESULTS AND DISSUSION

3.1. FT-IR spectra analysis

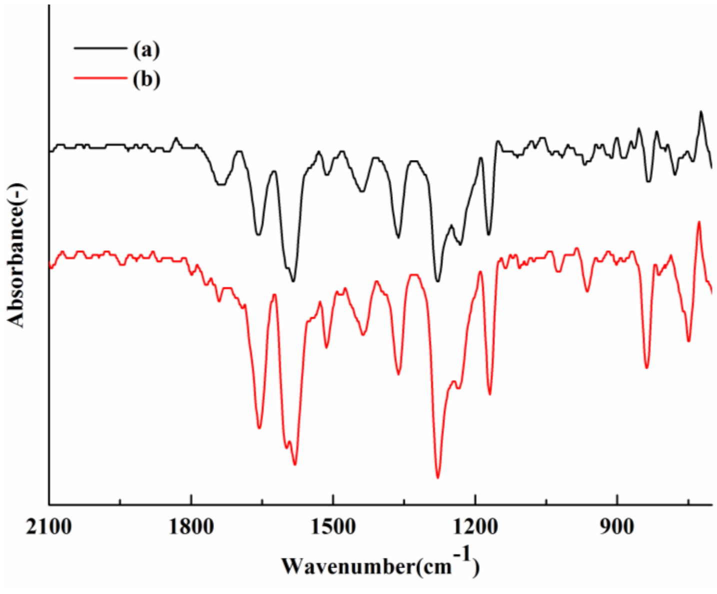

Figure 1. FT-IR spectra of AA5052 surfaces (a) electrodeposited nanofilm of DAN; (b) complex nanofilm

Figure 1 shows the structures of electrodeposited and complex nanofilms on AA5052 surface. It was noted that the presence of triazine ring was confirmed by the absorption peaks at 1650 cm^{-1}, 1596 cm^{-1} and 1566 cm^{-1} due to >C=N– bonds (Fig.1(a)). A broaden shoulder at 1275 cm^{-1} was also observed. Meanwhile a sharp peak at 1152 cm^{-1} is clearly detected, which is assigned to the stretching vibration of -C-N. The weak absorption peak of alumina at 958 cm^{-1} was also observed. It was showed that the intensity of characteristic absorption peaks for the complex nanofilm modified AA5052 is much stronger than that for only DAN electrodeposited surface. It was suggested that more compact nanofilm was formed on AA5052 surface with the further modification by initiated polymerization of DAN under the action of $K_2S_2O_8$.

3.2. Contact angle

In the figure 2, it is clearly observed that the contact angle increases from 90.7° for blank AA5052 to 107.4° for AA5052 surface covered by DAN electrodeposited nanofilm. It is assumed that the dithiolate anions transfer two electrons to the anode (AA5052 surface) to change to bisthiyl radicals, which causes coupling with each other to yield DAN electrodeposited nanofilm with the ally groups outwards. And the contact angle is up to 126.5° for complex nanofilm modified surface, indicating that the hydrophobic cross-linked film is formed on AA5052 surface and the morphology is changed. Humid environment is one reason of aluminum alloy corrosion, and the hydrophobic surface of substrate is benefit for the protection of aluminum alloy [14]. It was proposed that complex cross-linked film could have excellent protective effect for AA5052.

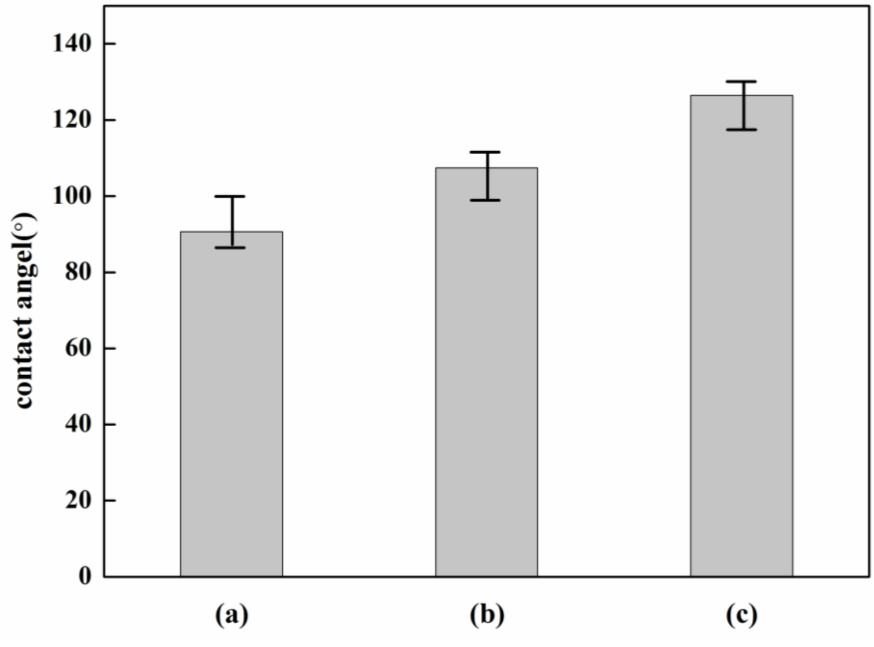

Figure 2. Contact angle of AA5052 surface (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

3.3. Surface morphologies

The surface morphologies of blank, DAN electrodeposited and complex nanofilm covered AA5052 were observed by SEM (Figure 3). As is shown in the figure 3(a), the vertical rolling direction can be seen distributed all over the surface of blank AA5052. From the figure 3(b), the original morphology of AA5052 surface becomes vague. Some white points on the surface can be speculated that the salt particles are pulled in by the experiment process. From the figure 3(c), cross-linked and dense film can be obviously seen on the AA5052 surface. It was presumed that the complex barrier layer was further prepared on electrodeposited nanofilm covered AA5052 surface with the existence of $K_2S_2O_8$. The surface is more homogenous, compact and the film coverage is high.

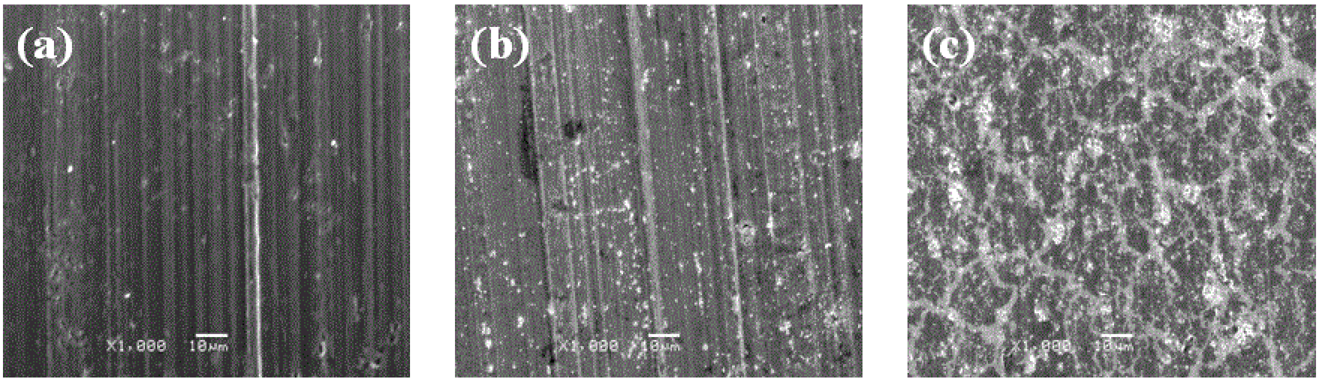

Figure 3. SEM images of AA5052 surface (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

3.4. Compactness Test

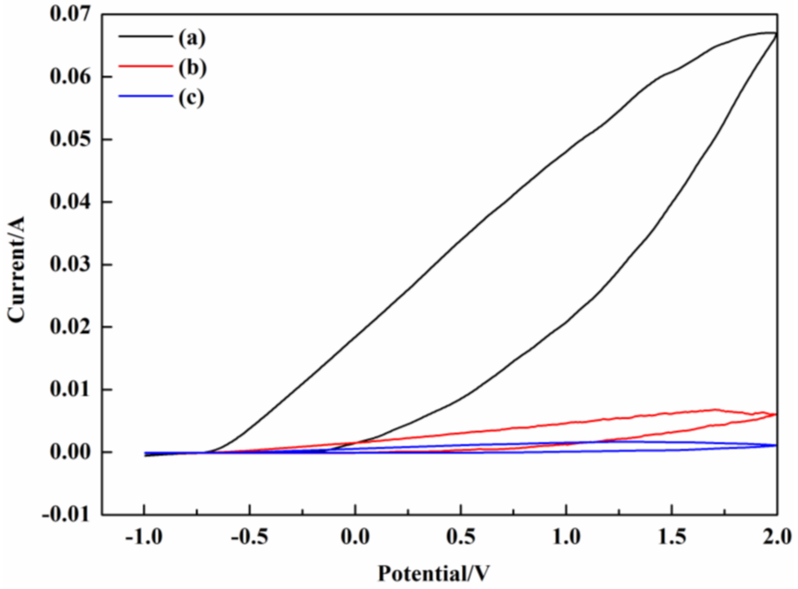

Figure 4. Cyclic voltammograms of AA5052 plates in 0.1% H_2SO_4 solution (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

Figure 4 shows a comparison of the cyclic voltammograms of blank, DAN electrodeposited and complex nanofilm covered AA5052 surfaces in 0.1% H_2SO_4 solution at a scanning rate of 10 mV/s between the potential region of -1.0~2.0 V. It was observed that the oxidation-reduction currents of electrodes modified by electrodeposited and complex nanofilm on CV curves were both much less (at least one order of magnitude) than that of the blank. Also, oxidation–reduction current of electrode modified by cross-linked complex barrier layer was little bit samller than that of DAN electrodeposited film. The cross-linked complex nanofilm is a better barrier to block charge or reactant ion transmission than only DAN electrodeposited film, suggesting the better performance of complex film in the protection of AA5052 from corrosion.

3.5. Potentiodynamic Polarization

The potentiodynamic polarization curves for blank, DAN electrodeposited and complex nanofilm covered AA5052 surfaces are shown in the figure 5. It was clearly observed that the E_{corr} corresponding to the modified AA5052 shifted significantly towards the higher potential from -0.683 V to -0.523 V and -0.518 V. The shift indicated that the DAN electrodeposited and complex films could suppress the cathodic reactions, and therefore inhibited the entire corrosion process in the system. It was also clearly observed that the corrosion current density (I_{corr}) reduced from 4.073×10^{-4} A/cm^2 for blank AA5052 to 7.892×10^{-5} A/cm^2 for only DAN electrodeposited modified AA5052 and 3.033×10^{-5} A /cm^2 for complex nanofilm modified AA5052. The protection efficiency (PE) was calculated by the following expression:

$$PE(\%) = 100\times[\,1-i/i_0\,]$$

Where i and i_0 are the corrosion current density of nanofilm modified and blank AA5052, respectively.

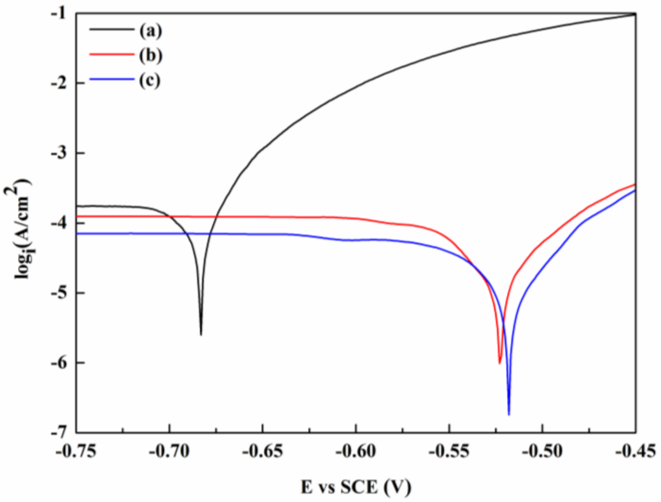

Figure 5. Polarization curves for AA5052 plates in 0.5M NaCl after 1 h exposure (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

The protection efficiencies calculated from potentiodynamic polarization data were found to be as high as 80.6% for DAN electrodeposited modified AA5052 and 92.6% for complex nanofilm modified AA5052. These results revealed that the complex nanofilm served as a protective layer on AA5052 surface and exhibited excellent anti-corrosion performance.

3.6. EIS Analysis

To further evaluate the resistance property of DAN electrodeposited and complex nanofilm, EIS was also measured (Figure 6). The EIS exhibited two components for all tested samples, one capacitive loop and one inductive loop, which meant that the blank AA5052 and the modified samples had the same anti-corrosion mechanism. The capacitive loop at high and intermediate frequencies has been attributed to the charge transfer process. Moreover, an inductive trend attributed to adsorption process is observed at lower frequencies [15]. The diameter of EIS can be equal to the charge transfer resistance value of electrode. It was seen that the diameter of blank was the smallest. However, the diameter of DAN electrodeposited and complex nanofilm modified AA5052 remarkably increased, which suggested that the ability to block the charge transfer of modified AA5052 had been improved.

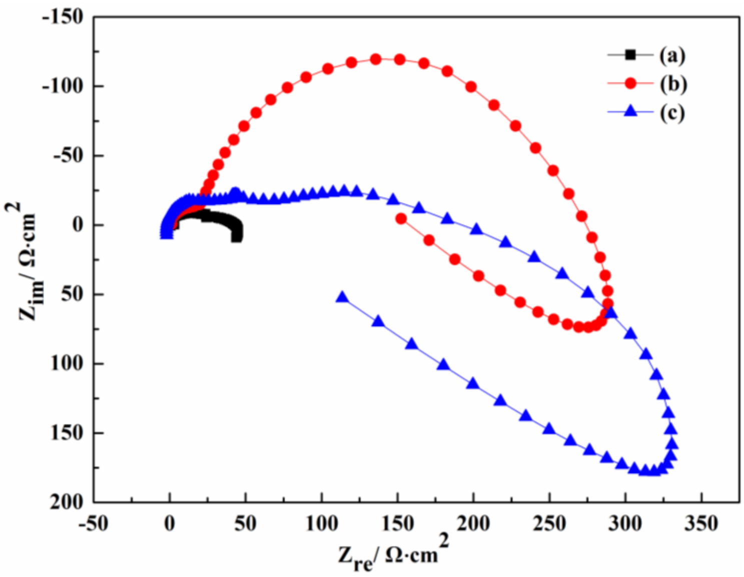

Figure 6. Nyquist plots for AA5052 plates in 0.5 M NaCl solution (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

3.6. Saline Immersion Test

Figure 7 displays the SEM images of AA5052 surface after 15 days immersion in 0.5 M NaCl solution. The figure 7(a) shows that the corrosion pits and corrosion products appear on the blank AA5052 surface. It means that the serious corrosion of AA5052 occured, namely poor protection efficiency of the blank sample. As for DAN electrodeposited film modified AA5052, only few corrosion pits are observed. While complex nanofilm modified surface has no corrosion phenomenon and corrosion sign after saline immersion, which exhibits effective corrosion protection. The good consistence of CV, potentiodynamic polarization, EIS and saline immersion test indicated the anti-corrosion performance of complex nanofilm.

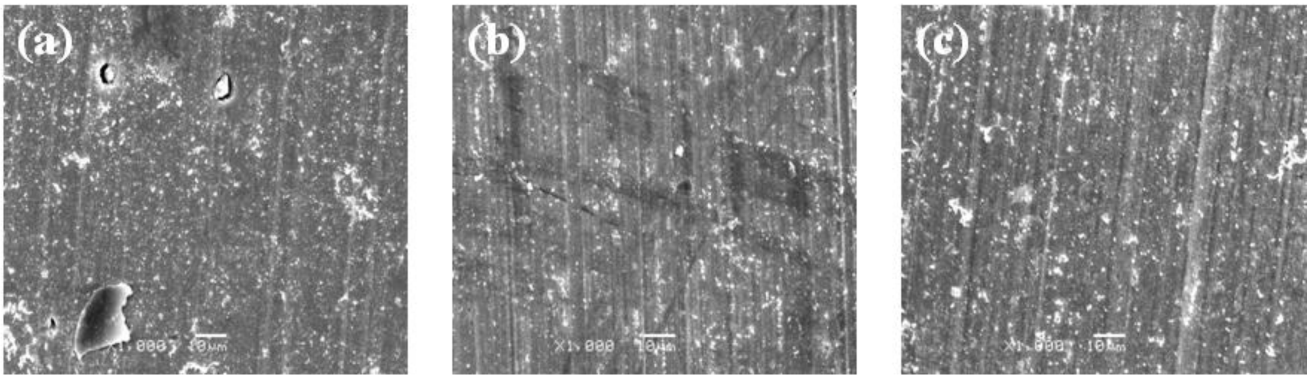

Figure 7. SEM images of AA5052 surface after 15 days immersion in 0.5 M NaCl (a) blank; (b) electrodeposited nanofilm of DAN; (c) complex nanofilm

4. CONCLUSIONS

DAN electrodeposited nanofilm and cross-linked complex barrier layer on AA5052 surface were prepared by two-step potentiostat and initiated polymerization. From the SEM, it was indicated the obtained complex film was more homogenous and compact, and the contact angle was up to 126.5°. Cyclic voltammograms, potentiodynamic polarization, EIS and saline immersion test suggested that cross-linked complex barrier layer modified AA5052 had excellent anti-corrosion performance and had a protection efficiency of 92.6%. This technique is expected to meet application requirements of the triazinedithiol complex film in the metal protection field.

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