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Preparation of Composite Polymeric Nanofilm of Triazinedithiol and Organosilane on AA5052 Surface and Anticorrosion Performance Analysis

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Poly (6-N,N-dibutylamino-1,3,5-triazine-2,4-dithiol) nanofilm (PDB) were prepared by electropolymerization of 6-N,N-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium (DBN) on an aluminum alloy (AA5052) surface. Cyclic voltammetry was used to study the electrochemical polymerization mechanism and the growth process. X-ray photoelectron spectroscopy (XPS) was utilized to identify the structure of PDB. Then, the PDB nanofilm covered surface was silanized in hydrolyzed hexadecyltrimethoxysilane (HDTMS) solution to fabricate the composite polymeric nanofilms (CPDB) by self-assembled technique. The formation mechanism of CPDB was that HDTMS reacted with AA5052 surface which was not adequately covered by PDB nanofilm. The composite polymeric nanofilms were characterized by means of XPS, scanning electron microscope (SEM), contact angle, potentiodynamic polarization and immersion test in 5% NaCl solution. The results showed that CPDB was homogenous, compact, hydrophobic and also had an excellent protection efficiency.

Keywords: Composit polymeric nanofilm, electropolymerization, silanization, corrosion inhibition

1. INTRODUCTION

Aluminum and its alloys are widely used in industrial applications especially in automobile, architecture and aerospace industries due to their low cost, low density, high mechanical intensity, easy maching and good recycling efficiency. However, their expanding application has been seriously limited because of susceptibility to corrosion. Therefore, corrosion inhibition of aluminum materials has attracted the attention of many investigators. The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. However, most of the current pre-treatments are based in chromates, which are hazardous to environment and human health [1-2]. Thus, many researches have been carried out to develop environmental-friendly system [3-5]. The inhibition action of certain organic compounds on aluminum corrosion processes has been extensively studied in recent years [6].

One important example is seen in the studies of aluminum treated with organosilane, which have currently been the subject of intensive research due to a viable and environmentally compliant alternative to the chromate technology in metal anticorrosion [7]. Another one is seen in triazinedithiols (TDTs) functional polymeric nanofilm, which also has been studied for many years [8-12]. The researches showed that the polymeric nanofilms prepared by different TDTs had basic anticorrosion property without toxicity [13-14]. Thus, during the last decade, the studies were mainly concentrated on other applications of TDTs polymeric film on various metal substrates, such as adhesion [15], lubrication property [16], dielectric property [10] and superhydrophobicity [8]. However, the anticorrosion property of TDTs has not been investigated adequately.

In this paper, we combined triazinedithiols with organosilane to prepare composite polymeric nanofilm on AA5052 surface. So far, this kind of composite polymeric nanofilm has not been reported on any metal surface. Triazinedithiol polymeric nanofilm was prepared by electropolymerization technique in the first step, and further modification with organosilane was carried out.

2. EXPERIMENTS DETAILS

2.1. Materials and Reagents

6-N, N-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium monomer was synthesized by reaction between 6-dibutylamino-1,3,5-triazine-2,4-dichloride and NaSH, according to the method described in the previous paper [17]. Hexadecyltrimethoxysilane was purchased from the Aladdin Reagent Incorporation. All of analytical reagent (AR) grade chemicals of sodium carbonate (Na_2CO_3), sodium phosphate tribasic (Na_3PO_4), sodium nitrite ($NaNO_2$), ethanol and acetone were employed without further purification. Distilled water and ethanol were used as solvent for electropolymerization and silanization, respectively. $NaNO_2$ aqueous solution was used as the supporting electrolyte for electropolymerization. The concentrations of DBN and $NaNO_2$ were kept constantly at 5 mmol/L and 0.15 mol/L, respectively. The ratio of HDTMS / high purity water / ethanol was 1/10/89 (v/v/v). The pH of HDTMS solution was adjusted to 4.5 by adding acetic acid, followed by being stirred for 1h, and aged at 35℃ for 48h to allow the sufficient hydrolysis of HDTMS [18].

The chemical composition of AA5052 aluminum alloy is given in Table 1. Tested samples (30mm×50mm×0.3mm) were cut from a sheet of aluminum alloy plate. All test samples were degreased by ultrasonic washing in acetone for 30 min and dried in nitrogen air, followed by being immersed in a mixed solution of 1.5% Na_2CO_3 and Na_3PO_4 for 90s at 60°C and rinsed with distilled water, acetone and dried in nitrogen air. Prior to any experiment, the samples were treated as described and freshly used with no further storage.

Table 1. Chemical composition of AA5052 aluminum alloy (mass fraction, %)

Element	Cu	Si	Fe	Mn	Mg	Zn	Cr	Others	
								Each	Total
% minimum	-	-	-	-	2.2	-	0.1	-	-
% maximum	0.1	0.2	0.4	0.1	2.8	0.1	0.3	0.05	0.15

2.2. Preparation of composite polymeric nanofilm

PDB films were prepared on AA5052 surface by electrochemical polymerization of DBN as the first step, which was achieved by cyclic voltammetry with potential ranging from -0.7~3.8V at scanning rate of 10mV/s using electrochemical measurement apparatus (Hokuto Denkou Co.Ltd., HD-3000). The electrolytic cell was equipped with working electrode, Pt counter electrode and saturated calomel electrode (SCE). The whole process was conducted at 25℃ without any stirring. Then, aluminum alloy surface covered with PDB was silanized in hydrolyzed HDTMS solution for 30 min at 35℃ to form the composite polymeric nanofilm, followed by being rinsed with ethanol, dried in nitrogen air and cured for 20min at 120℃.

2.3. Characterization

The contact angle was measured by optical contact angle measuring instrument (OCA35，Dataphysics) at room temperature with lμL distilled water. XPS was performed to investigate the elemental composition of aluminum surface. Spectra were obtained by using ULVAC PHI-5600 spectrometer equipped with monochrome Al Kα radiation (1,486.6 eV). The pressure in preparation chamber was less than 10^{-7} Torr and less than 4×10^{-10} Torr in analysis chamber. Samples were examined over an area of 800 × 2,000 μm, and photoelectron spectra were recorded with a take-off angle of 45°. The corrosion property was evaluated by potentiodynamic polarization test in 3.5% NaCl aqueous solution at room temperature. The scan rate was 1mV/s and the exposed area was 1.0 cm^2. Additionally, the immersion test was carried out in 5% NaCl aqueous solution at room temperature for 15 days to study the actual anticorrosion property. The surfaces of blank, PDB and CPDB were also observed by SEM (JSM-6360LV) at accelerating voltage of 20kV.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of DBN

The conventional cyclic voltammetry is regarded as a large potential amplitude technique. Additionally, it is still a very convenient tool that provides a general view of electrochemical reaction process. Qualitative differences in the shape of CV curve may provide useful information on the impact of the changes on electrochemical response [19]. Therefore, cyclic voltammetry was carried out to understand the polymerization mechanism of DBN in $NaNO_2$ solution.

Cyclic voltammogram of AA5052 plates in 0.15 mmol/L $NaNO_2$ solution without DBN monomer is shown in Figure 1 (black dash line). A small peak was observed at 0.43 V (a), which could be explained by the production of Al_2O_3 attributed to the oxidation of aluminum alloy according to anodic reaction (1). As the potential became higher ranging from 1.2 to 3.8 V, a sharp rise of current was observed (b). At the same time, lots of bubbles could be observed on electrode surface and irritant gas could be smelt simultaneously, which indicated that the electrolysis of water and NO_2^- occurred according to reactions (2) to (6) [20-21]. No reduction peak appeared when scanning was carried out in negative direction.

Anodic reaction:

$$Al \rightarrow Al^{3+} + 3e \tag{1}$$

$$2NO_2^- \rightarrow 2NO_2\bullet + 2e^- \rightleftharpoons N_2O_4\uparrow \rightleftharpoons NO_2\uparrow \tag{2}$$

$$2NO_2^- \rightarrow NO_3^- + NO\uparrow + e^- \tag{3}$$

$$4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e^- \tag{4}$$

Cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{5}$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \tag{6}$$

Two anodic peaks were also observed when aluminum plate was polarized in the aqueous $NaNO_2$ solution with DBN monomer (red solid line). Peak A at 0.25 V (V_A), similar to the feature in the case of blank solution, but with different potential, indicated that the thin monomer layer was formed on AA5052 plate by reaction between aluminum and thiol functional groups (-SH) in DBN accompanying with the oxidation of aluminum. The current density of peak B (2.03 mA/cm^2) sharply decreased than that of the blank solution. No bubbles could be seen on aluminum surface and no irritant gas could be smelt. These results domonstrated that the oxidation and polymerization of DBN took place [14], and the formation of PDB film inhibited direct electrolysis of OH^- and NO_2^-. No reduction peak appeared when scanning was carried out in negative direction. The absence of any reduction peak indicated that the depolymerization of polymer film on aluminum surface did not take place, since the PDB film was also insulated like Al_2O_3 film [11].

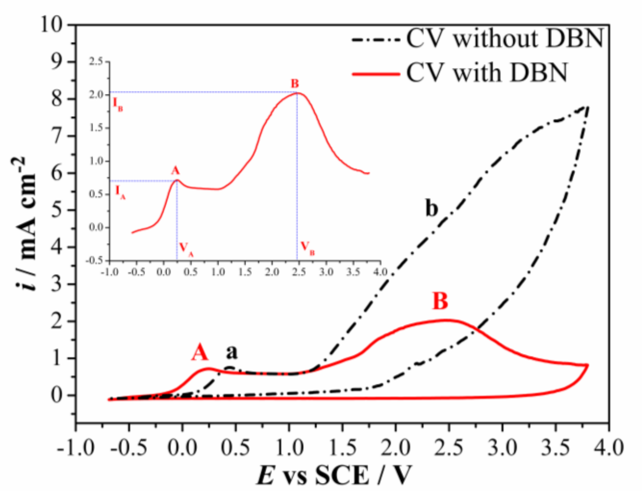

Figure 1. Cyclic voltammetry of AA5052 in 0.15 mol/L $NaNO_2$ aqueous solution with/without DBN

In order to better understand the process of electropolymerization of DBN, X-ray photoelectron spectroscopy was also used to analyze the structure of PDB film. Figure 2 depicts the fitted S2p curves in the XPS spectra of PDB film. The S2p peak is consisted of peaks assigned to C–S–Al groups at 160.49 eV, C–S–C groups at 162.53 eV, C–SS–C groups at 163.78 eV. Peak based on C–S–Al groups indicates the reaction of SH and S^- groups in DBN with aluminum during electropolymerization. The peak based on C–S–C groups suggested the reaction between SH groups and butyl groups. The peak based on C–SS–C groups revealed the electrochemical reaction of thiols. From the XPS data of S2p peak, the polymeric film formed on AA5052 plate was confirmed to consist of PDB structure. Therefore, it could be concluded that PDB film was obtained by the electropolymerization of DBN.

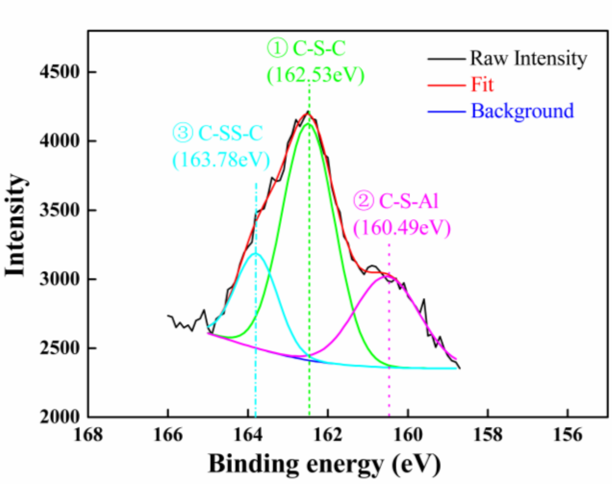

Figure 2. S2p fitted curve of high resolution XPS spectra for PDB film on AA5052 surface in 45° tilt degree (X-ray anode: Al monochromated 2 nm filament; Aperture: 800 × 2000 μm)

Based on the above analysis, the mechanism for electropolymerization of DBN is speculated as follows [17, 22, 23]. The process involved electrochemical oxidation to generate N_2O_4 species followed by chemical reaction to produce NO_2•. Free radicals which were generated by electrochemical oxidation experienced chain growth reaction of DBN polymerization, and the insoluble polymeric nanofilm was formed. Moreover, thiol group and dithiolate anion could react with aluminum, which was similar to the reaction between triazinedithiols and copper/copper alloy [24].

3.2. CPDB analysis by XPS

Figure 3 shows the XPS spectra for blank and CPDM film covered on AA5052 surface. Only peaks of Al2p (73.6 eV) and Al2s (119.7 eV) can be observed, expect for the peaks of C1s (285.0 eV), O1s (532.0 eV) for the untreated plate. Compared with the blank plate, other five peaks of N1s (400.7eV), S2s (228.2 eV), S2p (163.6 eV), Si2p (101.9 eV) and Si2s (151.8 eV) could be clearly observed for CPDB covered plate. The peaks of Si2p (101.9 eV) and Si2s (151.8 eV) indicated that Si-OH groups in HDTMS reacted with the -OH groups during silanization process on the AA5052 surface, which were not sufficiently coated by PDB film. Hydroxy groups condensed forming Si-O-Si and Al-O-Si covalent bonds, which were fully cross-linked on PDB films surface.

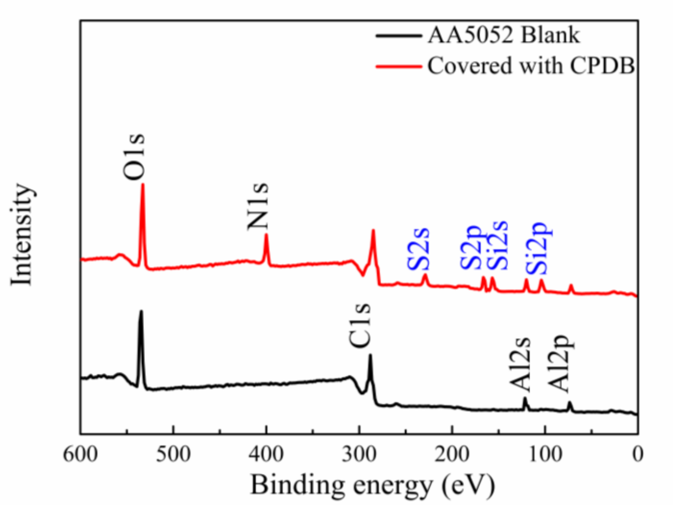

Figure 3. XPS spectra of the blank and CPDB covered aluminum surfaces in 45° tilt degree (X-ray anode: Al monochromated 2 nm filament; Aperture: 800 × 2000μm)

3.3. CPDM analysis by SEM

Figure 4 shows the SEM images of untreated and treated aluminum surface. For the untreated one (a), the rolling process has introduced scratches, kinks and folds on the material surface and a deformed layer of approximately 1μm is expected. Fine intermetallic particles which were aligned along the rolling direction were observed, distributed all over the surface. As for PDB covered surface (b), original morphology of AA5052 surface could hardly be seen. But, some pores and comparatively large fine intermetallic particles could still be observed. It was deduced that the pores were mainly caused by the hydrogen bubbling during anodic dissolution of aluminum, and the hydrolysis process may destroyed the film to some extent. Figure 5 (c) showed the image of CPDB covered surface. It was clearly seen that the surface pores and large fine intermetallic particles could not be seen. The surface was more homogenous, compact and the film coverage increased dramatically. It was concluded that the silanization treatment could modified the small defects of PDB film effectively.

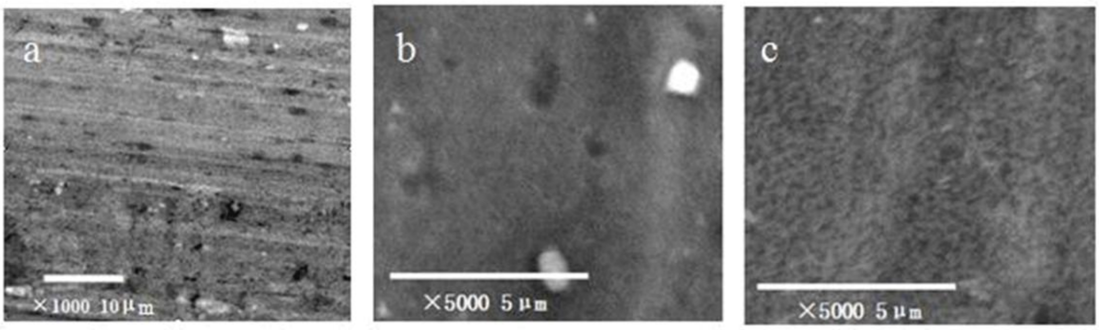

Figure 4. SEM images of AA5052 surfaces. (a) untreated AA5052; (b) PDB covered AA5052; (c) CPDB covered AA5052

3.4. Contact angle

The contact angle of blank AA5052 plate treated with/without alkaline solution, PDB and CPDB covered surface was shown in Figure 5. The contact angle of blank AA5052 is 91.9°. The contact angle of aluminum surface dramatically decreased after alkaline degreasing (13°). The decreases in contact angle indicated the morphology changes and formation of hydrophilic polar groups on aluminum surfaces, which improved the wettability of the aluminum surface and made the formation of CPBD possible. On the other hand, we observed that the contact angle increased to 115.3° after the formation of PDB on the AA5052 surface. The contact angle of CPDB was up to 137.8°, suggesting that a condensation reaction occurred between the polar groups on the AA5052 surface and the Si-OH groups in self-assembled HDTMS film. The results indicated the formation of hydrophobic CPDB nanofilm on AA5052 surface.

3.5. Corrosion test

Figure 6 displays the potentiodynamic polarization curves of AA5052 with different treatment measured in 3.5% NaCl solution. The corrosion current density (I_{corr}) decreases from 8.811×10^{-4} A/cm^2 of blank aluminum to 1.983×10^{-4} A/cm^2 for PDB covered surface. As for CPDB covered surface, the change is even more notable with the I_{corr} largely reducing to 5.060×10^{-5} A/cm^2, showing great inhibitive effect.

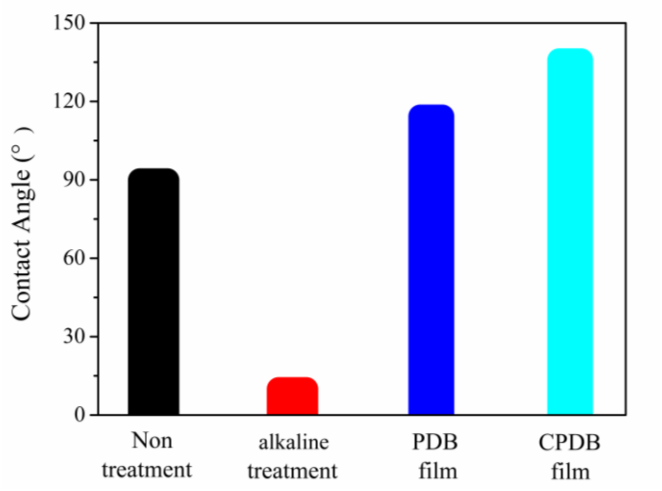

Figure 5. Contact angle of blank, PDB and CPDB covered aluminum surface

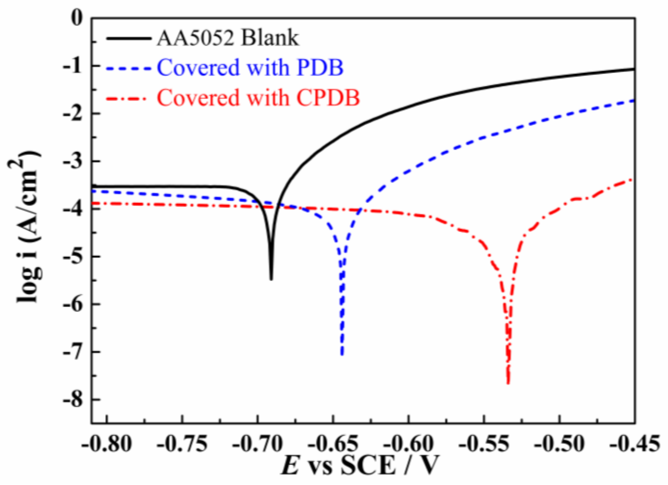

Figure 6. Polarization curves of AA5052 treated with and without silane measured in 3.5% NaCl after 1h exposure

The protection efficiency (PE) was calculated by the equation below to evaluate the performance of PDB and CPDB film [25]:

$$PE (\%) = 100 \times [1- (i / i^0)]$$

Where, i and i^0 are the corrosion current density of treated AA5052 and blank one, respectively. The protection efficiency is 77.5% for PDB covered surface, and is as high as 94.3% for CPDB covered surface. It is suggested that with the silanization in hydrolyzed HDTMS, the obtained CPDB film shows an excellent inhibitive effect to protect aluminum alloy from corrosion.

Figure 7 showed the SEM images of AA5052 surface after 15d immersion in 5% NaCl solution. For the blank (a), it could be seen that several areas were corroded heavily which were marked with cycle as A_1, A_2, B_1 and B_2. Aluminum substrate at region A_1, A_2 dissolved substantially and the regions of B_1 and B_2 showed heavily corroded areas, where the metal had been destroyed badly. As for the PDB covered one, only some small corrosive regions (C_1) were clearly observed. In the case of the CPDB covered surface, the film was still intact without visible corrosion after immersion, which showed effective corrosion protection. All the above results showed great anticorrosion performance of composite polymeric nanofilm of triazinedithiol and organosilane on AA5052 surface.

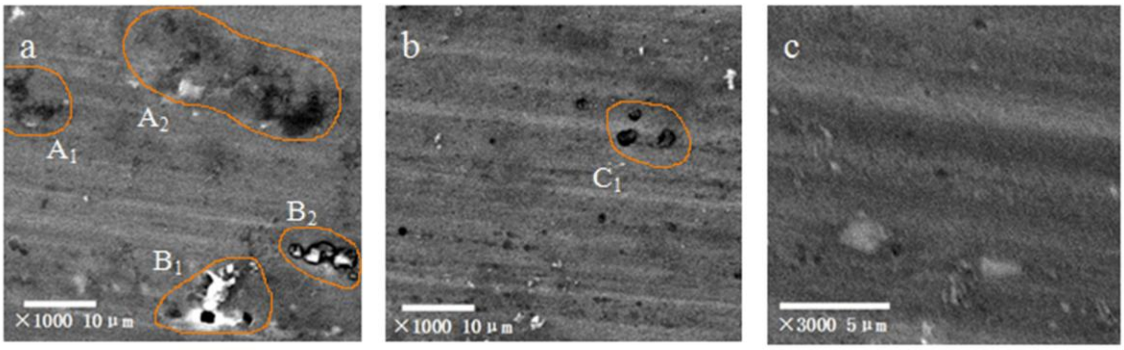

Figure 7. SEM images of AA5052 surface after 15d immersion in 5% NaCl solution, (a) untreated AA5052; (b) PDB covered AA5052; (c) CPDB covered AA5052

4. CONCLUSIONS

PDB nanofilm can be successfully prepared on AA5052 surface by cyclic voltammetry with potential ranging from -0.7~3.8 V at scanning rate of 10 mV/s. CPDB nanofilm can also be successfully obtained by silanization of PDB covered surface in hydrolyzed HDTMS solution for 30 min at 35 ℃. The CPDB nanofilm proved to be homogenous, compact and hydrophobic, which also had an excellent protection efficiency of 94.3%. It is expected that this technique, the preparation of composite polymeric nanofilm of triazinedithiol and organosilane on AA5052 surface, can be applied in fabrication of hydrophobic and anticorrosion-protective surface on aluminum materials surface.

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