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Effect of water content on corrosion inhibition behavior of self-assembled TDPA on aluminum alloy surface

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Abstract: Self assembled monolayers (SAMs) of 1-tetradecylphosphonic acids (TDPA, $CH_3(CH_2)_{13}P(O)(OH)_2$) were formed on the 2024 aluminum alloy surface in TDPA-containing ethanol-water solutions with different water content. The adsorption and corrosion protection properties of the SAMs for 2024 alloy in 0.1 mol/L H_2SO_4 solution were examined and characterized by potentiodynamic polarization, electrochemical impedance spectrum (EIS), Fourier transformed infrared spectroscopy (FTIR), Auger electron spectra (AES) and atomic force microscopy (AFM). FTIR and AES results show that the TDPA molecules were successfully adsorbed on the 2024 aluminum alloy surface, and the density of the SAMs increased with the increasing water content in the assembly solution. The results of electrochemical studies and corrosion morphologies observed by AFM show that a 4 h modification resulted in maximal inhibition efficiency, and the higher the water content in the assembly solution is, the better the inhibition performance of the SAMs can be achieved. The effect of water content in TDPA solutions on the performance of the SAMs is related to the hydration reaction of the metal surface.

Key words: 1-tetradecylphosphonic acid; self-assembled monolayer; aluminum alloys; corrosion inhibition; water content

1 Introduction

The protection against corrosion is important for aluminum alloys containing intermetallic particles, which are widely used in industry but susceptible to pitting corrosion in the media containing chloride ions [1,2]. Up to now, chromate coating is the dominant corrosion protection technology and surface pretreatment method for aluminum alloys [3,4]. The need to replace chromate coatings with environmentally friendly alternatives motivates research on new systems such as self-assembled monolayers (SAMs). SAMs form spontaneously bv chemical adsorption and self-organization on the surface of metals [5]. A highly ordered and packed monolayer can prevent a solution from transferring to the metal surface thus protecting the metal from corrosion [6,7].

Carboxylic acid, phosphonic acid and silane have been reported as the three main molecules which can form SAMs on the surface of aluminum [8,9]. The pioneering researches on the corrosion inhibition behavior of SAMs on an aluminum alloy surface were focused on the use of silane [10-12]. Although phosphonic acid molecules were reported that they have the ability to form more well-packed and more stable monolayers on the pure aluminum surface than silane and carboxylic acid [3,13], the using of self-assembled phosphonic acid as a corrosion inhibitor for aluminum alloys has been scarcely reported.

For silane, its assembly on metal surface is mainly carried out in organic solutions with a small amount of water. The added water is used to enhance the hydrolysis of silane to form more Si—OH, which can react with the metal hydroxyls to form more Si—O-metal covalent bonds [14]. In the molecule of phosphonic acid, there are two free P — OH groups, then the formation of P–O-metal covalent bonds can be accomplished in solution with or without water. To date, knowledge about the effect of water in the assembly solution on the assembling behavior and corrosion inhibition property of inhibitor molecules for the surface protection of metal appears sparse.

The aim of this work was the investigation of the

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protection of the TDPA SAMs formed in solutions with different water content for 2024 aluminum alloy against corrosion in 0.1 mol/L H_2SO_4 . The corrosion inhibition behavior of the SAMs was studied by polarization scanning, electrochemical impedance spectrum (EIS), and atomic force microscopy (AFM) observation. And the effect mechanism of water content was explored on the basis of the Fourier transformed infrared spectroscopy (FTIR) and Auger electron spectra (AES) studies.

2 Experimental

2.1 Chemical and materials

TDPA was obtained from Alfa Aesar with a purity of 98%, and was used without further purification. All other reagents were in analytical grade. Three solutions with concentration of 5 mmol/L were prepared by dissolving TDPA in absolute ethanol, in mixed solvent composed of water and absolute ethanol at a ratio of 2 to 8 in volume, and in mixed solvent composed of water and absolute ethanol at a ratio of 4 to 6 in volume, which were named solution, A, B and C, respectively. The corrosion testing electrolyte was 0.1 mol/L H₂SO₄.

The metal materials were 2024 aluminum alloy with a composition: Al base, Cu 3.8-4.9%, Mg 1.2-1.8%, Mn 0.3-0.9%, Fe 0.5%, Si 0.5%, others 0.5% (mass fraction).

2.2 Preparation of SAMs

The aluminum alloy samples were wet-ground through 1200 grit SiC paper, cleaned in a sonicator, dried with a N_2 gas flow and then dipped in the TDPA solutions containing different volume fraction of water. After a certain immersion time, the samples were removed, rinsed three times with ethanol and dried under a stream of N_2 , then immediately used for electrochemical tests. In order to produce a mirror-like surface for obtaining detailed information on the alloy microstructures using atomic force microscopy (AFM), a special polishing process by diamond paste to 0.5 μ m for the sample preparation was performed after the abrading treatment by SiC papers. Then the AFM samples were cleaned in a sonicator, dried in a N_2 flow, and modified by the same process mentioned above.

2.3 Electrochemical evaluation

All electrochemical measurements were performed with an Im6e workstation (ZAHNER, Germany). The electrolyte was a 0.1 mol/L H_2SO_4 solution. Potentiodynamic scans and EIS measurements were done in a three-electrode cell with a 1 cm² exposed area of working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The potentiodynamic polarization scans were carried out from 500 below to 500 mV above the open circuit potential with a scan rate of 1 mV/s. EIS measurements were made from 100 kHz to 10 mHz with a 10 mV amplitude at open circuit potential conditions.

2.4 FTIR

Attenuated total reflectance fourier transformed infrared (ATR-FTIR) spectroscopy (VERTEX 70, Bruker) was applied to measuring the surface properties of the SAMs modified 2024 aluminum alloys. Background spectrum was obtained using the freshly bare 2024 alloy. Absorbance spectra were collected at a resolution of 0.5 cm⁻¹ (64 scans).

2.5 AES analysis

Auger electron spectra (AES) measurements on bare and modified aluminum alloy surfaces were performed using a PHI 700 scanning Auger microscope (ULVAC-PHI Corp) with field emission source and hemispherical energy analyzer. Auger point analysis was done with the primary electron beam set at 10 keV and 10 nA.

2.6 Corrosion morphology observation

Corrosion morphology was observed using atomic force microscopy (AFM, DI, NanoScope III) in contact mode. The bare and TDPA-modified 2024 alloys were placed into the solution of 0.1 mol/L H_2SO_4 solution for 6 h and then fretched out, rinsed by sonication to remove the corrosion products. The rinsed and dried surfaces were immediately used for measurement.

3 Results and discussion

3.1 Polarization scanning

Potentiodynamic polarization measurements carried out in the potential range of -500 to 500 mV versus open circuit potential to characterize the effect of TDPA SAMs formed in solutions A, B and C are shown in Figs. 1(a), (b) and (c), respectively. In all cases, TDPA SAMs shift the both anodic and cathodic curves to lower current densities. In other words, both cathodic and anodic reactions of 2024 aluminum electrode are inhibited by the SAMs. However, the presence of TDPA shifts φ_{corr} (corrosion potential) to positive, which indicates that TDPA mainly acts as an anodic-type inhibitor.

It should be noted that in anodic domain, a passivation plateau is discovered, so it is difficult to recognize the linear Tafel regions. Then the corrosion current density values were estimated from polarization curves by polarization resistance fitting. The electrochemical corrosion parameters including corrosion current densities (J_{corr}), corrosion potential



Fig. 1 Polarization curves measured in $0.1 \text{ mol/L } H_2SO_4$ for 2024 alloys assembled by TDPA for different time: (a) In solution A; (b) In solution B; (c) In solution C

 (φ_{corr}) and corrosion inhibition efficiency (*E*) are given in Table 1.

It is apparent that J_{corr} decreases continuously with the increasing assembly time from 0.5 to 4 h, and then reaches the minimal value accompanied with the maximum *E* value. After that the *E* value decreases conversely with the prolonged assembly time. That means that assembly time of 4 h can obtain the optimal corrosion inhibition effect for all the three kind of TDPA SAMs obtained in solutions A, B and C. The possible interpretation is that an adsorption monolayer formed by chemical Al–O–P bonds [15] has reached its maximum covering ability after 4 h assembly. Then an extended assembly may cause the growth of a second adlayer by physical adsorption [15]. This physical adsorption film is loose and contributes little to the corrosion inhibition. But these molecules of the second layer containing ionizable hydrogen atoms can desorb easily and participate in the dissolution reaction of the oxide film [16], leading to the decline of corrosion inhibition efficiency.

Table 1 Electrochemical corrosion parameters according to
potentiodynamic scans of 2024 aluminum alloys in 0.1 mol/L
H₂SO₄

Sample	Assembly time/h	$arphi_{ m corr}/$ mV	$J_{ m corr}/$ (A·cm ⁻²)	E/%
Bare	_	-608	4.67×10^{-5}	-
Assembled in solution A	0.5	-610	4.03×10^{-5}	13.70
	2	-601	2.83×10^{-5}	39.40
	4	-584	1.68×10^{-5}	64.03
	8	-597	2.03×10^{-5}	56.53
Assembled in solution B	0.5	-535	1.42×10^{-5}	69.59
	2	-511	9.74×10 ⁻⁶	79.14
	4	-479	7.22×10^{-6}	84.53
	8	-543	1.23×10^{-5}	73.66
Assembled in solution C	0.5	-530	7.69×10 ⁻⁶	83.53
	2	-524	5.39×10 ⁻⁶	88.46
	4	-509	4.01×10^{-6}	91.41
	8	-587	8.92×10^{-6}	80.90

However, compared with the same assembly time for samples obtained in solutions containing different water content, the *E* value follows the order: C>B>A. And the highest *E* was obtained as 90.09% for the SAMs formed by 4 h assembly in solution C with the highest water to ethanol volume ratio of 4 to 6. The result suggests that adding water into the TDPA/ethanol solution is beneficial for constructing a denser corrosion-inhibition SAM on the alloy surface.

The adsorption mechanism of TDPA on the aluminum alloy surface involves a condensation reaction between the anion of the deprotonated acid and the surface oxide or hydroxide groups of the alumina. This reaction results in the formation of P—O—Al bonds [17]. While in the water containing TDPA solutions, the hydration process of the alloy surface is promoted, then

higher hydroxyl concentration can be obtained to provide more chance of the formation of P—O—Al bonds, thus a denser TDPA SAM is constructed which has the more prominent corrosion inhibition performance.

3.2 EIS

The electrochemical impedance spectra were taken for bare and TDPA-assembled 2024 samples in 0.1 mol/L H_2SO_4 and the Bode plots are represented in Fig. 2. The Bode spectra demonstrate that all the modified samples have higher impedance (|Z|) values than the bare one during the whole frequency range, displaying the inhibition performance of the TDPA SAMs. However, it is obvious that the increasing amplitude of the |Z| values of the assembled samples compared with bare one followed the sequence: C>B>A. And the maximal |Z| values appear at the assembling time of 4 h for all the three kinds of samples. The results agree with those of



Fig. 2 EIS Bode plots recorded in 0.1 mol/L H_2SO_4 for 2024 alloys assembled by TDPA for different time: (a₁), (a₂) In solution A; (b₁), (b₂) In solution B; (c₁), (c₂) In solution C

potentiodynamic polarization measurements that 4 h is the optimal assembly time for TDPA SAMs and adding water into the TDPA/ethanol solution is beneficial for constructing a denser SAM on the alloy surface with more excellent corrosion inhibition performance.

For samples assembled in TDPA solutions of absolute ethanol, two time constants in the Bode spectra are evident, namely, a middle frequency time constant (MF, $10^{1}-10^{2}$), attributed to the capacitive behavior of the air-formed film covering the macroscopic alloy surface[18], and a low frequency time constants (LF, $10^{-2}-10^{-1}$) related to the inductive behavior accompanied with the degradation of the impedance(|Z|)with frequency lowering, corresponding to the relaxation process of adsorbed species in the oxide film covering the electrode surface [19] or re-dissolution of the oxide layer surface [20,21].

For samples assembled in TDPA solution B of water/ethanol volume ratio 2 to 8, the samples treated by 0.5 and 2 h modification show similar features as those assembled in TDPA solutions of absolute ethanol. However, a high frequency time constant (HF, $10^3 - 10^4$) appears for 4 h and 8 h-modified samples. And for those samples assembled in TDPA solution C of water/ethanol volume ratio 4 to 6, they all show three time constants in the HF, MF and LF, respectively. In the EIS studies for coating and film on the surfaces of aluminum alloy, the high frequency time constant is often defined as the capacitance of the coating layer [22,23] or the formation of inhibitor film[24,25]. So, the new time constant appearing at high frequency range can be attributed to the adsorption of the TDPA molecules and the formation of the inhibitor film. For samples assembled in TDPA solution of absolute ethanol, and assembled in TDPA solution of mixed water-ethanol of volume ratio of 2 to 8 for 0.5 and 2 h, no HF constant is observed. This means in these conditions, the TDPA SAMs are not denser, so the high frequency time constant is not distinct. This is also consistent with the results of polarization curves.

3.3 FTIR

The bare and 4 h-modified samples obtained in TDPA solutions with different water content were characterized by ATR-FTIR spectra to verify the existence and bonding modes of TDPA SAMs on the aluminum alloy surface, as shown in Fig. 3. In the methylene stretching region for the bare and all the modified surfaces the asymmetric ($v_{as}(C - H)$) and symmetric ($v_{s}(C - H)$) stretching methylene modes appear at 2935 and 2852 cm⁻¹, respectively [26]. The methylene determined on the bare surface should be due to organic contaminant. The intensity of the methylene peak increases obviously for modified samples, showing that TDPA SAMs were successfully absorbed on the

SS430 surface. At about 1455 cm⁻¹, there is a scissoring mode of $-CH_2$ group [27]. This mode is oriented perpendicular to the chain axis, indicating that the chains might be tilted at an angle to the metal surface.



Fig. 3 ATR-FTIR spectra of bare and 4 h-modified 2024 alloys obtained in different solutions

The broad absorbance peaks at 1050 and 925 cm⁻¹ can be assigned to symmetric and asymmetric valence bands of salts of alkylphosphonic groups as discussed by MAEGE et al [28]. In other hand, the two bands of the OH-stretching vibration for compounds containing P—OH groups in the wavenumber regions ranging from 2700 to 2500 cm⁻¹ and from 2300 to 2100 cm⁻¹ [29] are not discovered in the SAMs covered surface. Then these bands indicate that bonding to the aluminium oxihydroxide surface occurs via a bi-dentate bonding.

However, in comparison of these samples assembled in solutions A,B and C, it can be disclosed that the intensity of all the characteristic peaks of TDPA molecules increases gradually with the increasing of water volume from 0 to 20%, and then to 40%. The results verified the deduction from electrochemical tests that the adding water into the TDPA/ethanol solution is beneficial for the hydration process of the alloy surface, and promotes the chemical adsorption of TDPA to form more P—O—Al bonds. As a result, denser TDPA SAMs can be constructed in the higher water content containing TDPA solutions.

3.4 AES analysis

AES spectra of bare and 4 h-modified samples obtained in TDPA solutions with different water contents are illustrated in Fig. 4. As shown in Fig. 4(a), a significant phosphorous signal at about 115 eV is detected on all the modified sample surfaces compared with the blank phosphorous signal on the bare one, and the peak intensity of phosphorous increases with the increasing of the water content in the self-assembly solution. Simultaneously, the peak intensity of aluminum

peak at about 1393 eV exhibits the descent tendency with the increasing water content in the TDPA solution, as shown in Fig. 4(b). So, the conclusion being consistent with that of FTIR can be drawn that TDPA can be successfully deposited onto the surface of the 2024 alloy from all the three kinds of TDPA solutions with different water contents. However, the density of the film increases with the increasing water content in the TDPA solution.

3.5 Corrosion morphology observations

The 2024 alloys were assembled in solutions A, B and C for 4 h respectively, and then were fetched out. A bare sample and all the assembled samples were immersed in the 0.1 mol/L H_2SO_4 solution for 6 h. After that they were taken out and were sonicate washed to remove the corrosion product on the surfaces. Figure 5 represents the corrosion photographs of the bare and modified 2024 aluminum alloys observed by AFM. The



Fig. 4 AES analysis of bare and 4 h-modified Al2024 surface: (a) Element P; (b) Element Al



Fig. 5 AFM images of corrosion surfaces of 2024 alloy after immersion in $0.1 \text{ mol/L H}_2\text{SO}_4$ solution for 6 h: (a) Bare; (b) Assembled in solution A; (c) Assembled in solution B; (d) Assembled in solution C

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surface of the bare 2024 suffers the most severe corrosion as shown in Fig. 5(a), while the assembled samples are not damaged so badly due to the presence of the TDPA SAMs. Obviously, the corrosion inhibition efficiency follows the order: C>B>A, which is in conformity with the electrochemical measurement data.

4 Conclusions

1) Electrochemical measurements show that the adsorption of TDPA molecules on 2024 alloy surfaces reduced the corrosion process, and 4 h modification resulted in the maximal inhibition efficiency. Extended modification caused the decrease of the corrosion inhibition efficiency. The reverse tendency might be attributed to the loosely and physically adsorbed second-layer presenting acidity by the ionizable hydrogen atoms which can dissolve the alloy surface.

2) The quantitative evaluation of the FTIR and AES datas show that a higher water content in the assembly solution was corresponding to a denser TDPA SAM detected on the modified surface. Electrochemical tests and corrosion morphology observed by AFM got the consistent results that the SAM obtained in TDPA solutions containing higher water content had more prominent corrosion inhibition performance.

3) The effect of water in TDPA-containing solutions on the performance of the SAMs was related to the hydration reaction of the metal surface. While in the water containing TDPA solutions, the hydration process of the alloy surface was promoted, then higher hydroxyl concentration could be obtained to provide more chance of the formation of P—O—Al bonds, thus a denser TDPA SAM was constructed which had the more prominent corrosion-inhibition performance.

4) In this work, the highest water content reached was 40% in volume fraction. When 50% water was applied, the solubility of TDPA in the mixed solution became smaller obviously and the 0.5 mmol/L TDPA solution became non-homogeneous. So the effect of higher water content than 40% was not involved in this study. Further work is needed to exploit the optimum water volume content of the assembly solution in the whole range from 0 to 100%.

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溶液中含水量对铝合金表面 自组装 TDPA 膜缓蚀行为的影响

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摘 要:用含水量不同的正十四烷基膦酸(TDPA)/乙醇-水混合溶液在2024 铝合金表面制备 TDPA 自组装膜。采用动电位扫描、电化学交流阻抗(EIS)、傅里叶红外(FTIR)、俄歇能谱(AES)以及原子力显微镜(AFM)等手段,研究自组装膜在0.1 mol/L 硫酸溶液中对铝合金的吸附及缓蚀性能的影响。傅里叶红外以及俄歇能谱测试结果表明: TDPA 分子成功吸附于合金表面,且吸附密度随着溶液中水含量的增加而增加。电化学测试以及腐蚀形貌观察结 果表明:4 h 的自组装能够获得最佳缓蚀效率;自组装溶液中水含量越高,得到的自组装膜缓蚀性能越好;自组 装溶液中水对自组装膜性能的影响与金属表面的水化反应有关。

关键词:正十四烷基膦酸;自组装膜;铝合金;缓蚀;水含量

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