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Corrosion performance of superhydrophobic nickel stearate/nickel hydroxide thin films on aluminum alloy by a simple one-step electrodeposition process

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ABSTRACT

Superhydrophobic thin films are fabricated on chemically cleaned aluminum alloy substrates by a one-step electrodeposition process in the ethanolic solution containing Ni^{2+} ions and stearic acid (SA) under applied DC voltage. Morphological features observed by scanning electron microscopy (SEM), indicate that the thin films are composed of cauliflower-like structures with micro-nano scale particles. The chemical compositions of these films are characterized using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), which indicate that these films consist of low energy nickel stearate ($Ni(SA)_2$). A schematic model of the electrodeposition process of $Ni(SA)_2$ is also presented. Wetting analysis demonstrates that the surface of the film is superhydrophobic with a water contact angle (CA) of $160 \pm 1°$ with contact angle hysteresis (CAH) of $2.1 \pm 1°$, which is obtained under optimum electrodeposition conditions based on a 0.4 molar ratio of Ni^{2+}/SA solution. The corrosion resistance properties calculated from the Tafel curve of superhydrophobic surfaces prepared in this solution are 280 times larger than the chemically cleaned aluminum alloy substrate. Furthermore, electrochemical impedance spectroscopy (EIS) analysis demonstrates that the charge transfer resistance is $1.63 \times 10^7\ \Omega\cdot cm^2$ for superhydrophobic films ($Ni^{2+}/SA = 0.4$) compared to that of chemically cleaned aluminum alloy substrates ($1.56 \times 10^3\ \Omega\cdot cm^2$). Therefore, the superhydrophobic film of $Ni(SA)_2$ on the chemically cleaned aluminum alloy substrate improves the corrosion resistance performance of aluminum substrates in corrosive environments.

1. Introduction

A surface that has a contact angle higher than 150°, with water roll-off behavior, is deemed a superhydrophobic surface. These surfaces have seen a greater role in fundamental research and industrial applications in recent years, owing to the excellent properties of such surfaces in terms of water proofing [1], marine coating [2], corrosion resistance [3,4], anti-icing/snow [5] and self-cleaning [6]. Therefore, it has become an extremely popular field of study, attracting a multidisciplinary group of researchers [7,8,9,10]. Superhydrophobicity is governed by both the micro-nanoroughness on the surface (allowing large amount of air to be trapped in spaces between the rough features) and low surface energy coatings that reduce interactions between the surface and the water [11]. Therefore, methods that can modify the surface roughness and lower the surface energy could be utilized to fabricate superhydrophobic surfaces. Numerous methods have been used to fabricate superhydrophobic surfaces such as chemical bath deposition [12], chemical etching [13], and sol-gel processing [14]. Our group is also actively working in this field and has produced several superhydrophobic surfaces using surface functionalization [15,16], electrophoretic deposition (EPD) [17] and methylated electromodification of aluminum and copper surfaces [18,19]. Most of these methods involve complex processing, expensive materials and are time-consuming, limiting their industrial application. By contrast, electrodeposition methods can save time and are easily applied in industrial settings. Electrodeposition has been used to prepare superhydrophobic surfaces by fabricating rough structures using low surface energy materials. Chen et al. [20] fabricated a superhydrophobic $(CH_3(CH_2)_{12}COO)_2Mn$ film by electrodepositing copper plates in ethanolic solution with myristic acid. They also prepared lanthanum superhydrophobic surfaces with hierarchical micro-nanostructures on

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copper substrates using solution with lanthanum chloride, myristic acid and ethanol [21].

Superhydrophobic surfaces can be used as anticorrosion agents because these surfaces easily repel water. Previous literatures show that superhydrophobic surfaces on metal substrates display better anticorrosion properties compared to metal substrates analyzed by potentiodynamic polarization and electrochemical impedance spectroscopy [22,23,24]. Additionally, as nickel possesses positive properties in terms of corrosion resistance as an important engineering material, many previous reports have examined the anticorrosive behavior of nickel films [25,26]. Therefore, nickel films electrodeposited on aluminum substrates with superhydrophobic behavior can be used for anticorrosion applications involving aluminum protection. Chen et al. [27] and Liu et al. [28] have reported similar work. To date however, there have been no reports on the formation of superhydrophobic surfaces on aluminum alloy surfaces using one-step electrodeposition methods in ethanolic solutions with nickel nitrate and stearic acid. Moreover, the corrosion resistance, morphologies and water repellence properties of such surfaces have not been analyzed before and after corrosion.

In this paper, we obtain superhydrophobic film on aluminum surfaces via a one-step process by immersing chemically cleaned aluminum alloy substrates into electrolytic solutions containing nickel nitrate, stearic acid and ethanol under a DC voltage. The morphological, roughness, and water repellence properties before and after corrosion test on the superhydrophobic aluminum surfaces are also discussed. Furthermore, the corrosion properties such as corrosion current density as well as corrosion resistance on these superhydrophobic surfaces are investigated by utilizing potentiodynamic polarization and electrochemical impedance spectroscopy.

2. Experimental

Rolled AA6061 aluminum alloy plates cut to 1 in × 2 in pieces were ultrasonically cleaned in a soap solution for 15 min and then rinsed with distilled water and ethanol. In order to remove the superficial surface oxide layer, the aluminum plates were cleaned using 1 M NaOH and then 10 vol.% HNO_3, followed by washing with water and ethanol. The two chemically cleaned aluminum plates were immersed in 40 mL of an ethanoic stearic acid (SA) solution (0.005 M) containing nickel nitrate hexahydrate (0.1 M) to have different molar ratios of Ni^{2+}/SA in the electrolytic solution. A DC voltage of 20 V was applied for 10 min to obtain thin electrodeposited films on the cathodic aluminum substrates. The distance between the cathode and anode was held at 15 mm. The surface morphology of the cathodic aluminum plate was observed using a JEOL JSM-6480 scanning electron microscope (SEM), with elemental analysis capability. The modified surfaces were identified by means of X-ray diffraction (XRD) using a Bruker D8 Discover system. Infrared spectra were recorded using a Fourier transform infrared spectroscopy (FTIR, Perking Elmer Spectrum One). Images of the electrochemically modified aluminum substrates were obtained using the Clemex software (CLEMEX JS-2000, PE4.0) to calculate the diameter and number density of the cauliflower-like clusters and the distances between them. Both static and dynamic contact angles were measured using a First Ten Angstorm contact angle goniometer using 10 μL deionized water drops. The roughness of the surfaces was measured using a MicroXAM-100 HR 3D surface profilometer. Electrochemical experiments were performed using a PGZ100 potentiostat and a 300 cm^3–EG&G PAR flat cell (London Scientific, London, ON, Canada) utilizing a three-electrode system. Specifically, the corrosion cell kit consisted of an Ag/AgCl reference electrode, a platinum auxiliary electrode, and the sample surface as the working electrode. Polarization tests were carried out in a 3.5 wt% NaCl solution (pH 5.9) at room temperature by stepping the potential. The time of open circuit potential (OCP) was 45 min and the time of polarization studies was approximate 8 min. EIS experiments were conducted using 3 wt% NaCl in a frequency range between 0.01 Hz and 100 kHz with a sine-wave amplitude of 10 mV.

3. Results and discussion

3.1. Superhydrophobic surfaces prepared by electrodeposition process

Fig. 1 shows the micrographs of chemically cleaned aluminum alloy substrates and thin films electrodeposited with varying molar ratios of Ni^{2+}/SA. Fig. 1(a) and (b) show low and high magnification SEM images of chemically cleaned aluminum substrates. Fig. 1(c) and (d) show SEM images of chemically cleaned aluminum substrates electrochemically modified using only stearic acid in ethanol.

The formation of micro-size clusters on the chemically cleaned aluminum surfaces begins at a molar ratio of 0.015 as shown in Fig. 1(e). Fig. 1(f) shows a close-up of a cauliflower-like cluster circled in (e). This cauliflower-like cluster (diameter = 4.1 ± 0.29 μm) is nucleated on the intermetallic compound belonging to the aluminum substrate. The current distribution on the chemically cleaned aluminum is uniform, but the current density is higher at the raised features due to the lower resistance to current flow at shorter anode to cathode distances, making nucleation easier at these locations. The size of these cauliflower-like clusters increases by increasing the molar ratio of Ni^{2+}/SA in solution to 0.05 as shown in Fig. 1(g). The corresponding high magnification SEM image Fig. 1(h) shows that several tiny nanoparticles (150–800 nm) assemble together to form a typical single cauliflower-like cluster. With the further increase of the molar ratio from 0.25 to 0.45, the number of the cauliflower-like clusters increases from $7.84 \times 10^2 \pm 1.49 \times 10^2$ counts/cm^2 to $1.11 \times 10^3 \pm 1.51 \times 10^2$ counts/cm^2. In contrast, the distances between the cauliflower-like clusters are shortened to 137.38 ± 7.01 μm (down from 139.70 ± 7.79 μm), as shown in Fig. 1(i) and (k). Moreover, there are new small nanoparticles (100–200 nm) electrodeposited on the former micro-size clusters as shown in Fig. 1(l). The formation of hierarchical nano-micro structures allows water to sit on the air pockets trapped [29] between the cauliflower-like clusters, which are helpful for improving the water roll-off properties of the modified surfaces.

Fig. 2 reveals the relationship between the molar ratio of Ni^{2+}/SA and the variation of average atomic percentage of C, O and Ni in the cauliflower-like micro-nano scale clusters of the thin electrodeposited films, as measured using EDS. EDS results are measured five points on each modified-substrate. According to the EDS results presented in Fig. 2(f) as well as in Table 1, all of the element variations (C, O and Ni) show upward trends. For the chemically cleaned aluminum substrate, only the Al signal appear in the EDS spectrum as shown in Fig. 2(a). Moreover, a molar ratio of 0.015 results in the appearance of C, O and Ni signals, at atomic percentages of 72.89 ± 2.82, 7.59 ± 1.90 and 1.18 ± 0.51, respectively. Under these conditions, the molecule with Ni begins to deposit on the cathodic substrate as identified by EDS and corroborated by the SEM image shown in Fig. 1(e). The molar ratio of C/Ni in the solution decreases from 600 to 45, which is more than the theoretical ratio of C/Ni in $Ni(SA)_2$ (36). Theoretically, there is enough SA^- present to form $Ni(SA)_2$ on the *as*-prepared aluminum substrates. However, the experimental molar ratio of C/Ni in the cauliflower-like micro-nano scale clusters reduces from 61.77 to 21.11 at molar ratios between 0.015 and 0.4. One possible explanation is that the films contain hydroxides at experimental C/Ni values of 26.47 and 26.11 (these value are <36). In addition, the EDS spectra in Fig. 2(a)–(e) illustrate that the Ni signal gradually increases, while the Al signal weakens. Owing to the height of the micro-nano scale cauliflower-like clusters that grow with the Ni^{2+}/SA molar ratio, stronger C, O and Ni signals are detected via EDS, whereas depth profiling with EDS obtains primarily Al signals. Of note, the atomic percentages of C, O and Ni in the cauliflower-like micro-nano scale clusters on the modified-aluminum alloy surface are significantly dependent on the molar ratio of Ni^{2+}/SA, confirmed by the SEM images shown in Fig. 1. By comparison, only the aluminum signal appears in the EDS spectra for the chemically cleaned aluminum substrate. There may be the formation of nickel stearate ($(CH_3(CH_2)_{16}COO)_2Ni$)/nickel hydroxide ($Ni(OH)_2$) after the clean