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Abstract

In this work, a simple approach is used to create the roughness on the aluminium surface. The aqueous hydrochloric acid (HCl) is used as a chemical etchant. Here, we studied the parameters such as wettability and corrosion of uncoated (hydrophilic), aluminium coated with silane (hydrophobic), and etched sample (superhydrophilic). Surface morphology and surface roughness were characterized by using scanning electron microscopy (SEM) and stylus profilometer, respectively. The corrosion study of uncoated, silane coated and etched samples was studied by Polarization test.

Keywords: Hydrophobic, Aluminium sheet, Chemical etching, Anti-corrosion

1. Introduction

Aluminum alloys are extensively used in industries and for applications in aerospace, building construction, marine structures, automobile windshields because of its unique properties such as low specific weight, high strength, excellent heat, and electrical conductivity [1,2]. These metals are highly proficient but due to the problems such as corrosion and low durability in the harsh environmental conditions, hinders their application [3]. Due to its limited use in industrial application, the work has been more focused to see the effect of created structured on its surface.

The wettability of the substrate is influenced by its surface roughness [4]. Recently, various methods such as plasma etching, chemical vapor deposition (CVD), anodization, and electrochemical deposition have been developed to create the roughness on the Aluminium surface [5,6]. All these processes are costly, and need rigorous operating conditions. Furthermore, the chemical etching is simple, timesaving and inexpensive process to create the roughness on the metal's surfaces. From the past studies, chemical etching is the promising method to produce the controlled surface roughness without any equipment.

2. Materials and Method**2.1 Materials**

Commercially available aluminum sheet (thickness < 1 mm) was cut with dimensions (50 mm × 20 mm) plates, and used as a substrate. The compositions of aluminium alloys are 92.48 wt% aluminium, 3.65 wt% carbon, 2.62 wt% oxygen, 0.4 wt% silicon, 0.69 wt% iron and 0.17 wt% erbium. Hexadecyltrimethoxysilane (HDTMS) was purchased from Sigma-Aldrich. Analytical reagent ethanol (99 v%), Hydrochloric acid (HCl; 37 wt%) was purchased from Merck Life Science Private Ltd., India. Sodium chloride (NaCl) was acquired from Avantor performance materials Limited, India. All chemicals were used as received.

2.2 Method

Initially, the uncoated sample was cleaned using the mixture of water and acetone in ultrasonication and dry at room temperature. The

etched sample was prepared by placing the aluminium sample in the aqueous solution of HCl at optimum time (13 min) to fabricate the microscale roughness on its surface. The hydrophobic sample was prepared by immersing the uncoated aluminium sample into the low surface energy solution for 2 h, and dry in oven at 120 °C.

2.3 Characterizations

Surface morphology of uncoated, etched and hydrophobic samples were investigated using scanning electron microscope (SEM, JEOL, JSM-6480LV) at an accelerating voltage of 5 kV.

The weight loss test of aluminium substrate was performed to measure the capability of the etching process. The weight loss (W , %) was evaluated as a difference of uncoated and treated samples using a digital laboratory analytical weighing balance (Mettler Toledo) with an accuracy 0.1 mg. The weight loss measurement was calculated by the following **equation (1)**[4].

$$W (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad [1]$$

Where, w_i and w_f are the weight of uncoated and treated samples, respectively.

Surface roughness of uncoated, etched and hydrophobic samples was performed via stylus contact profilometer (DektakXT stylus Profiler, Bruker). The measurements were performed to kept the sample in the controlled chamber at the room temperature. This is the contact mode and line type measurement. The radius of the used tips are about 2 μm . The scan line has a resolution of about 0.03342 μm with the stylus force $\approx 19.6 \times 10^{-6}$ N. The required roughness parameters were calculated three times for each sample and measured the average values.

The static water contact angle measurement of uncoated, hydrophobic and etched samples was performed using the goniometer (DSA 25, Krüss, Germany) at room temperature. The water was filled into the micro syringe, and carefully released the water droplet (3-5 μL) manually on the sample surfaces. Later, the images of the droplet were recorded using the PC software (DSA 25) to obtain the static water contact angle. The contact angle was measured at different points to measure the average water contact angles with standard deviation to attain the accuracy.

To characterize the anti-corrosion property of

the samples was evaluated by polarization test. The experiment was done at the room temperature using the three-cell system. The exposed area of the working electrode was about 1 cm². The sample was immersed in NaCl (3.5 w/v %) solution at the room temperature.

3. Results and discussion

3.1 Surface morphology

The SEM images of uncoated aluminium substrate, shows the smooth surface, as shown in **Fig. 1(a)** while the SEM image of etched sample shows the microscale roughness on its surface as shown **Fig. 1(b)**. In **Fig. 1(c)**, the hydrophobic sample, a thin layer of HDTMS was deposited on its surface which at the nano-scale. It does show the minor changes in morphology which is not visible much when compared to uncoated one.

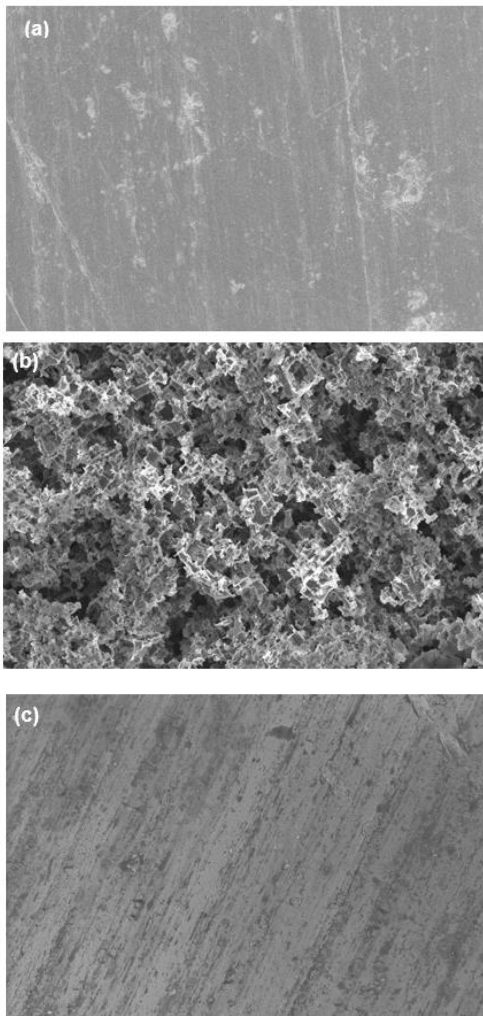


Figure 1: SEM images of (a) Uncoated aluminium sample (b) etched sample, and (c) hydrophobic sample

3.2 Wettability

The WCA of uncoated, etched sample and hydrophobic samples are shown in **Table (1)**. The uncoated aluminium substrate exhibits the (water contact angle) WCA of 72.1±0.7° with hydrophilic

nature. For aluminium sample treated with silane, the low surface energy material reacts with the (-OH) group, which are inherently present on its surface, and after modification it shows the hydrophobic nature with water contact angle about 91.3±0.8. After etching, the uncoated substrate turns into superhydrophilic from hydrophilic due to increase in the water-solid contact area, and WCA on the etched surfaces was decreased to ~0°, it follows the Wenzel theory [7].

Table 1: Static WCA of all sample with wettability nature

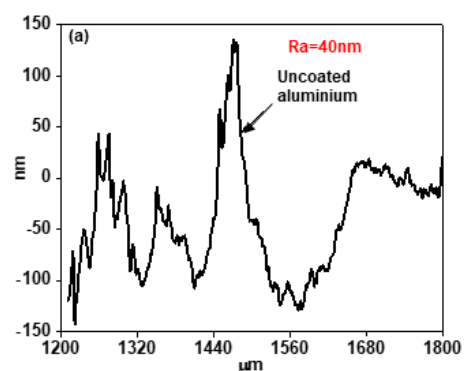
Samples	WCA (°)	Image of WCA	Wettability nature
Uncoated aluminium substrate	72.1±0.7		Hydrophilic WCA<90°
Etched aluminium substrate	0		Super-hydrophilic WCA~0°
Hydrophobic aluminium substrate	91.3±0.8		Hydrophobic WCA>90°

3.3 Weight changes

The dissolution of aluminium substrate occurred during the chemical etching process. The weight loss or gain of both treated samples was done manually. Initially, the weight of cleaned and dried uncoated sample calculated was about 1.116 gm. The weight of etched and hydrophobic samples was calculated approximately 0.9641 and 1.156 gm, respectively. The weight loss/gain (%) of the samples were calculated using the equation (1), it is decreased the 1.6% for etched sample while the weight of hydrophobic sample was increase approximate 3.6%.

3.4 Surface roughness

Fig. 2(a) shows the roughness profile of the uncoated aluminium substrate. The value of roughness for uncoated sample was observed about 40 ×10⁻⁹m. This uncoated surface exhibit the certain inherent roughness due to the rolled aluminium sheet [8]. The roughness profile of hydrophobic sample does not significantly affect the roughness value (37.8×10⁻⁹ m) because of changes at nano-scale (attachment the of silane molecules) as shown in **Fig. 2(b)**. It is observed that the average roughness is higher for etched aluminium surface about ~Ra=3447.08×10⁻⁹m as shown in **Fig. 2 (c)**. The reaction mechanism to fabricate the microscale roughness is shown in **Fig. 3**.



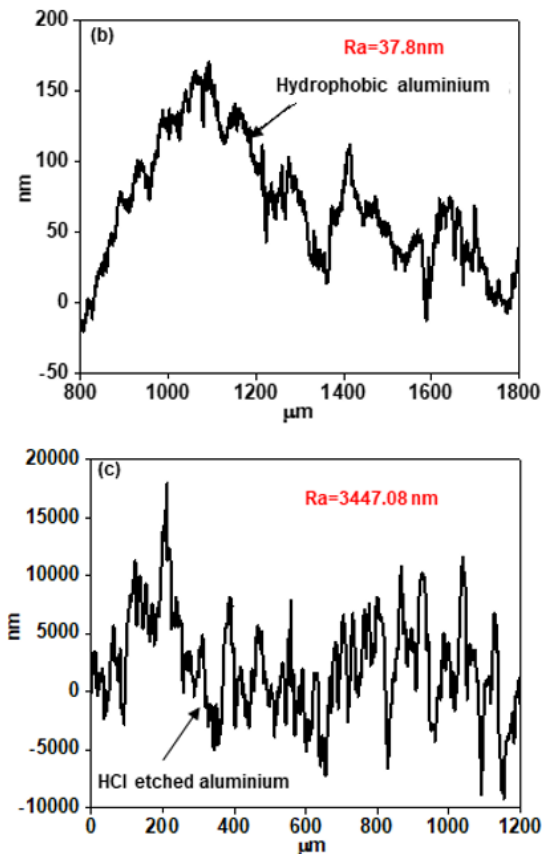


Figure 2: Average roughness of (a) Uncoated aluminium substrate (b) hydrophobic aluminium substrate, and (c) etched aluminium substrate.

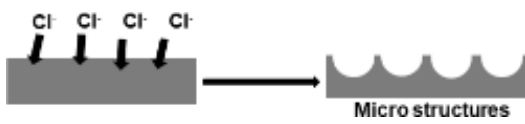


Figure 3: Reaction mechanism of etched aluminium Substrate

3.5 Anti-corrosion properties

In order to estimate the anti-corrosion properties, the Tafel plot was used for uncoated, hydrophobic and etched samples as shown in **Fig. 4**.

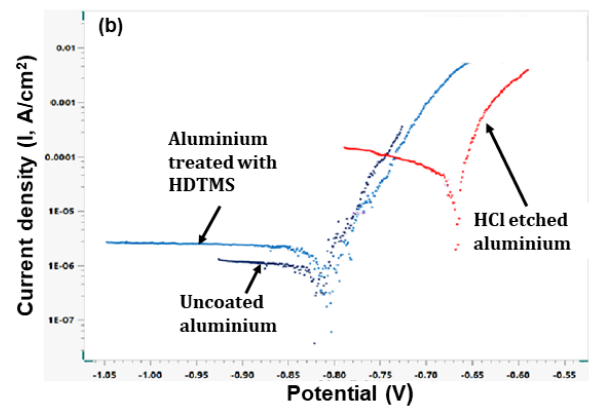


Figure 4: Polarization curve of uncoated, hydrophobic, and etched samples in NaCl solution (3.5%).

Table 2: Corrosion current density (I_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p) of all samples.

Samples	I_{corr} (A/cm ²)	E_{corr} (V)	R_p (Ω)
Uncoated aluminium	3.2949×10^{-6}	-0.80969	7908.5
Etched aluminium	2.22267×10^{-4}	-0.66514	117.02
Hydrophobic aluminium	1.8247×10^{-6}	-0.80245	14281

The value of corrosion potential, corrosion current Density and polarization resistance were summarized in **Table 2**. These parameters were calculated by drawing the tangent after plotting the Tafel graph. It has been stated that at high polarization resistance and low current density, show the best protection against the corrosion. It is generally believed that the thin on the aluminium surface shows the barrier for the electron transfer between the aluminium substrate and the NaCl electrolyte [9]. Hence, the chance of attack of electron of hydrophobic surface is low comparison to uncoated aluminium. While for the etched surface, the ion attacked more due to increase the surface area. So, it is concluded that the higher resistance was observed in hydrophobic surfaces. The corrosion mechanism is shown in **Fig 5**.

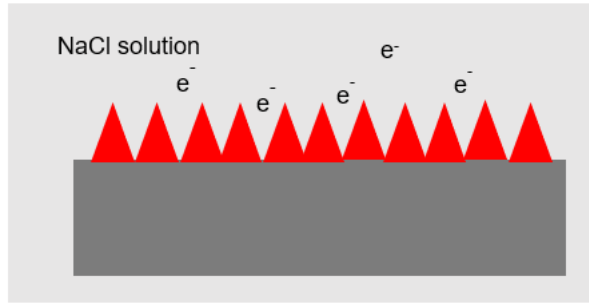


Figure 5: Corrosion mechanism

4. Conclusions

In the work, it can be analyzed that the microscale roughness on the aluminum surfaces has been successfully created using chemical etchant. The roughness effect on surface properties such as morphology, wettability and corrosion properties were studied in detail. It was concluded that the uncoated, hydrophobic and etched samples showed different WCA. Thus, the surface roughness plays and vital role to changes the surface properties with wettability. Due to increase the roughness, surface area increases so the contact of the water with solid surface was increase and change the wettability. Similarly, more electrolytes ions will interact with the superhydrophilic surface compare to other surfaces, and shows the low polarization resistance.

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