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A cost-effective method to create physically and thermally stable and storable super-hydrophobic aluminum alloy surfaces

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ABSTRACT

Physical stability and thermal stability of super-hydrophobic surfaces are some of the most significant issues for applying them in industry. A facile and cost-effective method has been developed to create thermally and physically stable and storable super-hydrophobic aluminum alloy surfaces. Chemical etching by sodium hydroxide and a solution of acetic acid and hydrochloric acid were used to create micro-nano structures over the surface and subsequently trichloro(octadecyl)silane (TCODS), trichlorododecylsilane (TCDS), and trichloro(octyl)silane (TCOS) were used to modify these roughened surfaces. The effects of different etching processes, different type of chlorosilanes, and the amount of modifiers on the resultant aluminum alloy surfaces hydrophobicity were also investigated. The resulting surface morphologies, compositions, roughness, and water contact angle were investigated by scanning electron microscopy, energy dispersive X-ray spectroscopy (EDX), 3D surface profilometer, and water contact angle (WCA) meter, respectively. Photron APX-RS high speed camera was used for imaging contact angle hysteresis (CAH) and dynamic droplet/surface interaction. The WCA and water contact angle hysteresis (CAH) of the aluminum alloy surfaces modified by TCODS reached to 165° and less than 3°, respectively; and it remained super-hydrophobic after 100 h immersing in water, 30 min ultrasonication, stored for more than 30 days under ambient condition, and heated to 375 °C for 20 min.

1. Introduction

The concept of super-hydrophobicity is borrowed from the reputed Lotus leaf effect described by Barthlott et al. in 1997 [1]. In order to achieve super-hydrophobic surfaces which exhibit high water contact angle (WCA) with values over 150° and a small hysteresis contact angle (HCA) of less than 5°, a low-surface energy coating over a micro-nano structured surface is required. For atomically flat surfaces, materials with low surface energy exhibit WCA of around 120° at best. For roughened surfaces, however, WCA can exceed 160° due to a combined effect of low surface energy, air entrapment, and other contributing factors such as surface morphology [2–6]. During the last decade, super-hydrophobic surfaces have attracted enormous attention in fundamental research as well as industrial aspects due to a variety of applications in anti-corrosion, self-cleaning, biomedical applications, anti-icing, friction drag reduction, anti-bio fouling paints, etc. [7–16]. Considering the fact that aluminum alloys are the most widely used non-ferrous materials in industry, producing super-hydrophobic surfaces based on aluminum alloys has attracted a lot of attention during recent years [17,18].

Superb heat and electrical conductivity, low weight, and high strength are some of aluminum alloys' properties which have caused wide usage of them in marine structures, building construction, airplanes, etc. [19,20]. Many methods have been used for generating super-hydrophobic aluminum surfaces which are mostly a combination of roughening and treating the surface with low surface energy materials. Layer by layer deposition [21], chemical deposition [20,22,23], plasma surface treatment [24], anodizing [18,19,25], electrospinning [26], sputtering [27], and etching aluminum surfaces followed by surface modification with low surface-energy materials [17,28,29], are some of the approaches for creating a super-hydrophobic aluminum surfaces [30].

Organosilanes such as methylsilanes, linear alkyl-silanes, aromatic-silanes, perfluorinated alkyl-silane are the most widely used materials for super-hydrophobic surface modification. Most of the silanes possess three major parts; an organo-functional group, a linker, and hydrolysable groups for chemical anchoring to the surface. During the modification process the hydrolysable groups are hydrolyzed and condensed to oligomers. Subsequently, hydrogen bond form between OH groups on the substrate and oligomers. Eventually, covalent bonds are formed during a curing or drying process [31]. The presence of aliphatic hydrocarbon substituent or fluorinated hydrocarbon substituent enables a surface to show hydrophobic properties. The linker length possesses an important role in the hydrophobicity of a surface by affecting

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reactivity restrictions and physical properties. Use of long chain silanes often leads to Self-Assembled Monolayers (SAMs) [14,28,30,32–34].

The stability, durability, and storing properties of the super-hydrophobic surfaces are three main aspects of great importance that determine their possible applications in industry. There are several articles about these properties of super-hydrophobic surfaces in literature [35–41], but just a few studies focus on super-hydrophobic aluminum surfaces stability properties [42–45].

In this paper, we described a facile, practical, and cost-effective method for creating physically and thermally stable and storable super-hydrophobic aluminum surface which is favorable for many industrial applications. Comparing to most commonly used anodizing process, our direct use of hydrochloric and acetic acids is more facile and much cheaper for creating the desirable rough surface morphology. Additionally, chlorosilane modifying agents that were used in this work to create super-hydrophobic surfaces are far cheaper than perfluoropolymers and other typical modifiers. By using the above simple and cost-effective method super-hydrophobic aluminum surfaces with water contact angle of 165° and contact angle hysteresis less than 3° were obtained which were as good as most other super-hydrophobic aluminum surfaces described in literature that mostly used more expensive methods and modifiers. The resultant super-hydrophobic aluminum surfaces showed short-term stability under water and storability for more than 6 months without remarkable changes which show their potential long-term stability, and storability. The super-hydrophobic aluminum surfaces were also thermally stable until 375 °C.

2. Material and methods

2.1. Materials

Sheet of cast aluminum alloy (AA 6061) was the main material for making aluminum alloy substrates. Hexane (ACS reagent ≥ 99%), trichloro(octadecyl)silane (TCODS) (≥90%), trichlorododecylsilane (TCDS) (≥95.0%), and trichloro(octyl)silane (TCOS) (≥97%) were purchased from Sigma Aldrich, sodium hydroxide, and hydrochloric acid ACS reagent (37%) from Anachemia, and acetic acid ACS grade(≥99%) from VWR. The deionized water (D. I. water) used was of purity of >18 MΩ.

2.2. Aluminum surfaces roughening and surface modification procedure

The aluminum alloy substrates ($1 \times 1 \times 0.06$ in^3) were mechanically roughened by abrasive papers #600 and #1500, respectively until a homogeneous surface with surface micro roughness (R_{RMS}) equal to 0.5 ± 0.1 μm was obtained. The roughened aluminum alloy surfaces were ultra-sonically cleaned by acetone and D.I. water and dried for 10 min in 110 °C. The clean aluminum alloy sheets were then treated by 1 M NaOH for 10 min and ultra-sonically cleaned by D.I. water and dried for 10 min in 110 °C. Subsequently, they were immersed in a mixture of D.I. water, hydrochloric acid, and acetic acids at volume ratio of V_{H_2O}:V_{HCl}:$V_{CH_3COOH} = 20$:8:1 for different times at room temperature and rapidly washed and ultra-sonically cleaned by D.I. water and dried at 110 °C for 10 min.

The roughened and chemically-etched aluminum alloy substrates were modified from 2 to 6 mL of TCODS, TCDS, and TCOS as shown in Table 1. Surface modification was carried out by simply immersing aluminum surfaces in the solution of chlorosilane and 50 ml hexane for 2 h and rinsing with hexane. The resultant samples were then heat-treated at 200 °C for 60 min to increase their stability.

For testing the storability of the hydrophobic properties of the modified aluminum alloy surfaces, WCA was measured after 10, 20, 30, and 180 days storing the modified aluminum alloy surfaces at room temperature.

Three different methods had been used to investigate the stability of the aluminum super-hydrophobic surfaces under water. First the WCA changes of an 8 μL water droplet were measured as a function of time that water droplet connects to the surface continuously for 25 min. In the second method the S71 specimen was immersed in the D. I. water at depth of 10 cm up to 100 h and the WCA was measured after drying the specimen for 2 h in room temperature. In the third method the S71 specimen was put in ultrasonic water bath for 5 to 70 min.

For testing the thermal stability of the super-hydrophobic surfaces, WCA of the surfaces was measured after heating them to 100, 200, 300, 350, 400, and 425°C for 20 min. The samples were cooled down and rested in laboratory air for 2 h before WCA measurements.

2.3. Characterization

Scanning electron microscopic (SEM) and Energy-dispersive X-ray spectroscopy (EDX) images and spectrums were taken on a Hitachi S-4800 field emission scanning electron microscope. The SEM acceleration voltage was set to 1.0 kV at working distance from 4.00 mm to 8.7 mm. In order to avoid surface charge during SEM, the surfaces were carbon-coated 6 times (~9 nm) before SEM imaging at a vacuum of 10^{-4} mbar, using 208 CRESSINGTON carbon coater. Zeta 3D profilometer as used for measuring surfaces micro-roughness and taking surface 3D images. A Holmarc contact angle meter model

Table 1
The roughening process, surface modifier, amount of modifier, roughness, WCA, and CAH of the specimens.

Specimen	Roughening	NaOH[a]	Acid[b] (min)	Surface modifier	Modifier amount (mL)	Roughness (μm)	WCA[c]	CAH[d]
S00	N/A	N/A	N/A	N/A	N/A	0.5 ± 0.1	60° ± 1°	>10°
S01	×	×	N/A	TCODS	3	0.9 ± 0.1	133° ± 2°	>10°
S02	×	×	N/A	TCODS	6	0.9 ± 0.1	138° ± 3°	>10°
S03	×	×	N/A	TCDS	3	0.9 ± 0.1	130° ± 2°	>10°
S04	×	×	N/A	TCOS	3	0.9 ± 0.1	125° ± 2°	>10°
S51	N/A	×	5	TCODS	3	3.3 ± 0.1	154° ± 2°	<6°
S52	×	×	5	TCODS	3	3.5 ± 0.1	158° ± 2°	<5°
S53	×	×	5	TCODS	6	3.6 ± 0.1	161° ± 2°	<4°
S71	×	×	7	TCODS	3	5.4 ± 0.1	165° ± 2°	<3°
S72	×	N/A	7	TCDS	3	5.1 ± 0.1	160° ± 3°	<5°
S73	×	×	7	TCDS	3	4.9 ± 0.1	163° ± 3°	<4°
S74	×	×	7	TCOS	3	4.6 ± 0.1	159° ± 2°	<5°
S75	×	×	7	TCODS	2	5.3 ± 0.1	151° ± 5°	<6°
S75	×	×	7	TCODS	4	5.3 ± 0.1	165° ± 2°	<3°
S76	×	×	7	TCODS	5	5.4 ± 0.1	166° ± 2°	<3°
S77	×	×	7	TCODS	6	5.1 ± 0.1	166° ± 2°	<3°

[a] NaOH: 1 MNaOH treatment for 10 min.

[b] Acid: acid solution volume ratio is equal to (V_{H_2O}:V_{HCl}:$V_{CH_3COOH} = 20$:8:1).

[c] WCA: water contact angle.

[d] CAH: contact angle hysteresis.