Tribology International 119 (2018) 38–44

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Durable and regenerable superhydrophobic coatings for aluminium surfaces with excellent self-cleaning and anti-fogging properties

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ARTICLE INFO

Keywords:
Superhydrophobic
Water repellent
Chemical etching
Self-cleaning
Anti-fogging

ABSTRACT

In this work, by employing chemical etching technique with hydrochloric acid, followed by passivation with lauric acid, superhydrophobic aluminum surfaces were synthesized. The surface morphology analysis reveals the presence of rough microstructures on coated aluminium surface and contact angle increases with etching time as enhancement of surface roughness. Superhydrophobicity with water static contact angle of 172 ± 5° and sliding angle of 4 ± 0.5° is achieved. Coating exhibits the excellent self-cleaning and anti-fogging properties. Coating shows the excellent mechanical, chemical, UV, and thermal stability. Additionally coating shows the excellent regeneration capability. This approach can be applied to any size and shape of aluminium surface and hence has great industrial applications.

1. Introduction

Superhydrophobicity has been paid attention for more than one decade by numerous research groups due to its important applications ranging from self-cleaning materials to microfluidic devices. Superhydrophobicity is defined as when the contact angle of water droplet on surface is greater than 150° with a negligible hysteresis. Water droplets exhibit spherical shape, low adhesion on the superhydrophobic surface, and roll off from the surface. During rolling action, the liquid drops carry away dust particles present on the surface, indicating self-cleaning nature of the surface. Besides the self-cleaning and water repellency properties, superhydrophobic surfaces asserts anti-corrosion, anti-icing, anti-scratching, anti-fouling, anti-bacterial, and anti-aging characteristics. Water striders [1] and lotus [2] are known for excellent natural superhydrophobic surface.

Nano/micro-structures play an important role in developing artificial superhydrophobic surfaces [3,4]. Conventionally, superhydrophobic surfaces are produced by grafting low-surface energy materials on the roughened surfaces [5]. Over the past one decade, tremendous research has been carried out to develop artificial superhydrophobic coatings on different substrates such as glass [6–8], polymers [9,10], mesh [11–13], papers [14–16], textiles [17–19], metals [20–22], and wooden [23–25] for anti-scratching, self-cleaning, anti-icing, drag-reduction, oil-water separation, and anti-corrosive applications. Furthermore, expansion of superhydrophobicity research field is attracting to researcher due to its outstanding industrial applications.

Metals have tremendous applications in industries and household activities, especially aluminium due to its low weight and high mechanical properties, but these applications are limited due to corrosion or deterioration of aluminium. However, superhydrophobic coatings on aluminium substarte can slow down the process of corrosion because of their self-cleaning and water-repellent properties.

Superhydrophobic aluminium surfaces are easily produced by simple acid or alkaline treatment followed by chemical modification. The etching of aluminium in acid and alkaline solutions can simply create rough surface because of its dislocations. Several research works on creating superhydrophobic coatings on aluminium surfaces by using chemical etching technique have been reported. For instance, Fu et al. [26] created superhydrophobic aluminium surfaces by chemical etching technique using $Cu(NO_3)_2$ and HNO_3 mixed solution and silane solution. Wang et al. [27] prepared superhydrophobic aluminium surfaces by creating roughness using chemical etching with the HNO_3 and H_2O_2 mixed solution and then treatment of roughed aluminium with mixed solution of stearic acid and N, *N*-dicyclohexylcarbodiimide. Guo et al. [28] obtained superhydrophobic aluminium surfaces by roughening aluminium surface by immersing in sodium hydroxide solution and then coating with fluorinated silane. Saleema et al. [29,30] treated aluminium with fluoroalkylsilane in sodium hydroxide solution and achieved

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https://doi.org/10.1016/j.triboint.2017.10.033
Received 4 September 2017; Received in revised form 19 October 2017; Accepted 23 October 2017
Available online 27 October 2017
0301-679X/

superhydrophobicity.

Qian et al. [31] synthesized superhydrophobic aluminum surface using Beck's dislocation etchant and fluorination. Shi-heng et al. [32] generated superhydrophobicity on aluminium substrate with sodium hydroxide etchant and fluoroalkyls. Li et al. [33] created superhydrophobic aluminium surfaces by chemical etching and anodization using hydrochloric acid, sulphuric acid and boracic acid, followed by self-assembly using fluoroalkylsilane. Xie et al. [34] created first roughed aluminium surface by immersing in sodium hydroxide solution and then coating by immersion of rough aluminium in lauric acid solution. Peng et al. [35] successfully prepared a superhydrophobic aluminum surface by a simple and environmental method with hot ammonia solution etching and subsequent fluorosilane modification. Liao et al. [36] used chemical etching technique and hydrochloric acid, hexadecyltrimethoxy silane and $CuCl_2$ solution as synthesis materials to produce superhydrophobic aluminium surfaces. Zhang et al. [37] achieved water contact angle of 163°treated aluminium surfaces by immersing in hydrochloric acid and myristic acid solution. Escobar et al. [38] developed an alternative method for enhancing superhydrophobicity on aluminum surfaces with an amphiphilic reagent such as the dodecanoic acid.

Despite having excellent properties like self-cleaning, anti-corrosive, anti-icing, etc., aforesaid superhydrophobic surfaces are not widely industry applicable because of lack of mechanical, thermal, and chemical stability and regenerability. In current work, regenerable and durable superhydrophobic coatings on aluminium substrates were prepared by chemical etching technique using hydrochloric acid and lauric acid. Besides, the effect of etching time on wettability and surface morphologies was also studied. Additionally, wetting stability of coating under perturbation conditions were also studied by mechanical, thermal, chemical, and UV stability tests. Further, regeneration of coatings was also done. Along with, self-cleaning and anti-fogging characteristics of coatings were also examined.

2. Experimental details

2.1. Materials

Aluminium sheets (7 cm × 2 cm X 5 mm) were used for the development of superhydrophobic surface. Hydrochloric acid (35%, Emplura, Merck Specialties, Pvt. Ltd India), ethanol (Emsure, Merck KGaA, Germany) and lauric acid (99%, Loba Chemie Laboratory reagent and fine chemicals Pvt. Ltd, India), acetic acid (99.8%, Sigma-Aldrich, Chemie, GmbH), acetone (Sigma-Aldrich, Chemie, GmbH) and sodium chloride (Sigma-Aldrich, Chemie, GmbH) were the chemicals used in preparation and characterization of superhydrophobic coatings.

2.2. Synthesis of superhydrophobic surfaces

Synthesis of superhydrophobic aluminium surface was done using two-step process: producing roughness on the aluminium substrate followed by lowering the surface energy of roughed aluminum surface. The aluminium substrates were first thoroughly washed and cleaned with a solution of acetone and distilled water. First step i.e. chemical etching was carried out by immersing the aluminium substrate in a solution of hydrochloric acid (HCl) for 5 and 15 min. Then samples were washed thoroughly with acetone and distilled water and were air dried for 24 h. The second step i.e. lowering surface energy was carried out by immersing the above etched or roughed aluminum samples in ethanol solution of lauric acid of concentration 20 g/l for 30 min. Finally these samples were air dried for 24 h. All above experiments were performed under atmospheric conditions.

2.3. Characterization of superhydrophobic surfaces

Contact angle measurements were done at room temperature through sessile drop method using drop shape analyzer (25, Kruss, Germany) with droplets of distilled water having drop volume range of 7–10 μL. The experiments were repeated at five different points on each sample and their average with standard deviation was calculated. Surface morphologies of uncoated and coated samples were examined using scanning electron microscopy (SEM) (Nova Nano SEM FEI). The roughness of uncoated and coated samples was measured by atomic force microscope (AFM) (Veeco/849-012-712) using silicon nitrate tip of 10 nm radius. Noncontact mode was mainly used to obtain detailed information about surface roughness. Five scans of 10x10 μmxxμm with a pixel resolution of 512 × 512 were taken at different surface position of each sample in order to drive the corresponding roughness.

Floatation on water surface test was carried out by keeping coated sample on the water surface in a petri dish and floatation time was recorded till sample started sinking. For water jet impact test, water jet which is released from a 25 ml syringe was sprayed on uncoated and coated samples. Water jet was kept about 3 cm above the surface with angle of nearly 45° for 1 min. The jet impact speed was about 2.6 m/sec. The interaction between the water jet and surface was observed.

Mechanical durability of the superhydrophobic aluminum surface was checked by adhesive tape peeling and surface bending tests. Adhesive tape peeling test was carried out by using electrical insulation tape of adhesive strength of 100 N/m and multiple times peeling was done on coatings. Tests were continued until coating lost its superhydrophobicity. For surface bending tests, coated samples were simply bent in different directions and angles, and samples were also folded and de-folded. Water droplets were placed at different positions on bending areas to check superhydrophobicity.

A simple thermal test was carried out in a hot air oven by varying the temperature from 40 to 250 °C for 1 h period. After cooling the samples, contact angles were measured to check the superhydrophobicity. The chemical stability test was carried out by simply immersing the superhydrophobic aluminium samples in 5% acetic acid solution for 10 days and 3% by weight sodium chloride (NaCl) solution for 15 days. After regular interval of a day, contact angles were measured to check the superhydrophobicity. UV stability test was carried out by exposing coatings to an ultraviolet light of wavelength 254 nm and irradiance 6.82 mW/cm^2 for 55 h in a UV curer (UltraV-C1, Apex Instruments Co. Pvt. Ltd, India) and contact angle was measured at regular time interval of 5–10 h to check the superhydrophobicity.

In order to check regenerability of coatings, superhydrophobic aluminum surface was continuous heated at 400 °C for 24 h such that coating surface was fully damaged. To regenerate the destroyed superhydrophobic coating, substrate was again immersed in ethanol solution of lauric acid for 30 min and then air dried for 24 h. After that, contact angle of re-coated surface was measured.

The self-cleaning test was carried out by simply sprinkling small amount of graphite powder taken from a pencil led on the uncoated and coated aluminium surfaces. Water droplets were slowly dropped on the graphite powder sprinkled surfaces and flow of droplets were recorded. For anti-fogging test, uncoated and coated samples were kept in the deep freezer (−18 °C) for 5 h and then they were kept in humid atmosphere of 80% relative humidity.

3. Results and discussion

3.1. Surface morphology and wetting properties

In this paper, superhydrophobic aluminium surfaces were synthesized by chemical etching process using HCl etchant and lauric acid solution low surface energy material. Etching time of aluminium in HCl solution was also varied. The wettability and surface morphologies of coated surface were characterized using contact angle measurement technique and SEM, respectively. Fig. 1 shows the SEM images of as-received untreated and modified aluminium surfaces by chemical etching process. The static contact angle of untreated aluminium surface is about 70° and no microstructural pits are found on the surface (Fig. 1