Fabrication of Mechanically Robust Superhydrophobic Coating on Aluminium Surface

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Abstract. In this research, a simple and cheap method was presented to make aluminum surface superhydrophobic. By simply spraying the mixture of hydrophobic silica nanoparticles and bonding agents, the superhydrophobic surface was obtained, which showed high water contact angle (~162°) and low sliding angle (2°). More interesting, this kind of coating exhibited excellent self-cleaning property. Furthermore, this coating retained superhydrophobicity after the damage of knife-scratch.

1. Introduction

As is known to all, aluminum and its alloys are widely used in many fields because it has many excellent properties, such as cost efficiency, excellent mechanical strength, and so on [1-3]. However, aluminum and its alloys are highly susceptible to be contaminated in damp environment. To prevent such problems, surface treatments are indispensable for preventing contamination on the surface of Al and its alloys.

Among various surface coatings of aluminum and its alloys, superhydrophobic surfaces with large contact angles (>150°) and small sliding angles (<10°) have attracted significant attention because of their comprehensive superiority and remarkable properties (e.g., self-cleaning, anti-contamination, anti-corrosion, anti-wearing, anti-icing, etc.). Water droplets are unable to stay on the superhydrophobic surfaces and simply roll off if the surfaces are tilted even slightly. Such surfaces are also defined as self-cleaning surfaces because the contamination on them will be easily removed by rolling droplets [4, 5]. The key factor constructing a superhydrophobic surface is the existence of suitable surface roughness and low surface energy [6]. So far, various methods have been successfully adopted to prepare superhydrophobic surfaces, including sol-gel [7, 8], solution immersion [9], chemical vapor deposition [10, 11], chemical etching [12] and hydrothermal synthesis [13].

Up to now, many approaches have been reported for fabricating superhydrophobic surfaces on Al and its alloys. Cho et al. produced a superhydrophobic surface on Al foil by anodic oxidation method [14]. Saleema et al. prepared a superhydrophobic aluminum alloy surface via a one-step process with the use of fluoroalkyl-silane in a base medium [15]. Yin et al. constructed a superhydrophobic coating on Al alloy through chemical etching followed by surface modification [16]. These researches have paved the way for constructing a superhydrophobic surface on Aluminum or Al alloy surface. However, the big drawback of these artificial surfaces is that they are readily abraded, sometimes with little more than brushing with a tissue [17].
In this paper, we presented a simple and cost-effective and environmental-friendly way to prepare an aluminum alloy sheet with superhydrophobicity and self-cleaning properties. Through one-step spray coating of a solution consisting of hydrophobic silica nanoparticles and bonding agents, the aluminum alloy sheet shows a contact angle of $162 \pm 1^\circ$ and a sliding angle of $2^\circ$. Furthermore, this superhydrophobic coating retained their performances after the mechanical damage of knife-scratch.

2. Experimental

2.1. The substrate preparation
Al 6061 plates with dimensions of $20\text{mm} \times 20\text{mm} \times 3\text{mm}$ were used as the substrates. Before using, Al substrates were ultrasonically cleaned in ethanol and deionized water, respectively, then dried in air for 30 min.

2.2. The fabrication of silica nanoparticle suspension (SNS)
The hydrophobic fumed silica nanoparticles (R972, Degussa) with $\sim 16$ nm diameter were used in the experiments. The commercial-grade liquid fluorosilicate resin (GK570, Daikin Chemistry), commercial-grade liquid epoxy resin (E-51 type, Kunshan Lvxun Chemicals Industry Co. Ltd., China) and reagent-grade ethyl acetate (Kemiou Chemical Co. Ltd., China) were mixed with the mass ratio of 1:1:6. Then the silica nanoparticles were added under vigorous magnetic agitation.

2.3. The synthesis of superhydrophobic coating
A spray gun was adopted to coat the Al 6061 substrate. The pressure is 0.3-0.6 MPa and the distance is 20 cm. After coating, all samples were heat-treated at 90 $^\circ$C for 1 h to remove residual solvents.

2.4. The synthesis of superhydrophobic coating
FE-SEM (Field-emission scanning electron microscope) images were obtained on a Zeiss Supra 55 instrument at 5-10 kV. Prior to FE-SEM measurements, a thin Au layer (ca. 5 nm) was deposited on the specimens by sputtering. The water contact angle and sliding angle were measured with a SL100B apparatus at ambient temperature. The volume of the individual water droplet in all measurements was 5 $\mu$L. The average contact angle and sliding angle values were obtained by measuring the same sample at least in five different positions.

3. Results and discussion
Figure 1a and b are FE-SEM top-images of spray coated Al 6061 substrate with low and high magnifications, respectively. The low-magnification FE-SEM image (Figure 1a) showed that the surface was not smooth and had macroscale roughness. We attributed this phenomenon to the aggregation state of the silica nanoparticles in the ethanol [18]. From the high magnification FE-SEM (Figure 1b), numerous void spaces among individual nanoparticles were observed and Nano scale roughness was presented. The silica nanoparticles ranged in size from dozens of nanometers to several hundreds of nanometers. Generally, superhydrophobicity tends to be formed when hydrophobic surfaces have micro- and Nano scale hierarchical structures [19].

To study the surface wettability of spray coated Al 6061 surface, the water contact angle and sliding angle were measured, as shown in Figure 2. The spray coated surface showed a high water contact angle of $162 \pm 1^\circ$ (Figure 2a). At the same time the water droplets cannot stay on the surface when the sliding angle is $2^\circ$ (Figure 2b), suggesting low adhesion between water droplet and spray coated aluminum alloy surface [20]. As is known to all, the surface wettability can be described by the Wenzel [21] and Cassie-Baxter models [22]. Both wettability models can lead to a high contact angles. However, only the Cassie-Baxter model can result in a very low sliding angle [19]. Therefore, Cassie-Baxter theory was adopted to explain the mechanism of superhydrophobic behavior on the SNS spray coated surface. On the spray coated aluminum alloy surface, the apparent solid-liquid contact is a real hybrid contact of solid-liquid-gas due to the hierarchical structures. In this hybrid contact state, air layer is trapped in the micro cavities.
and nanopores between silica nanoparticles, and then water droplets are suspended due to the “air cushion” underneath water droplets. Thus, the surface adhesion between droplets and SNS spray coated surfaces is extremely low and the water drops will slide off under low sliding angle.

![Figure 1. Top-view FE-SEM images of spray coated Al 6061 surface with low magnification (a) and high magnification (b), respectively.](image1)

![Figure 2. Water droplets on the nano silica deposited aluminum allogy substrate with (a) a contact angle of 162±1° and (b) a sliding angle of 2°.](image2)

The surface robustness is an important factor which affecting the practical application of the superhydrophobic surfaces. In this work, the knife-scratch test and sandpaper abrasion test were performed to evaluate the mechanical robustness of the spray coated superhydrophobic surface. As shown in Figure 3a and 3b, a knife was adopted to scratch the spray coated surface to examine the surface robustness. The path of knife scratch can be found in Figure 3c. As shown in Figure 3d-f, the superhydrophobic surface retained the superhydrophobic property after the knife-scratch test. Moreover, sandpaper abrasion test was reported to be an effective route to evaluate the mechanical abrasion resistance of the superhydrophobic surfaces [17, 23, 24]. In this research, SiC sandpaper (800 grit, German Warrior Co., Ltd) was adopted to evaluate the shear abrasion. The superhydrophobic surface was placed on the sandpaper with 50 g load and moved in one direction. The result shows that the as-prepared surface still maintained the CA above 150° after abrasion 550 mm.
Figure 3. Knife scratch test on the SNS spray coated Al 6061 surface: (a-b) the surface with knife scratching; (c) the surface after knife scratching; (d-f) the knife scratched surface with water drop rolling on it.

4. Conclusion
We have demonstrated a facile and effective spray-coating method to fabricate superhydrophobic surfaces on Al 6061 substrate. The resulting surface exhibited high water contact angle (162±1°) and low sliding angle (2°). Importantly, this superhydrophobic coating shows a robust resistance to knife-scratch and sandpaper abrasion. Thus, the as-prepared superhydrophobic surfaces may have a wide range of practical applications which require robust superhydrophobic aluminum surfaces.

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